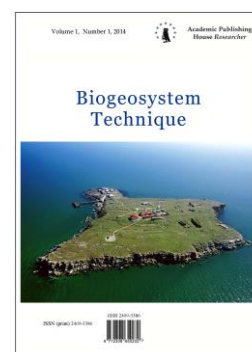


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Polycyclic Aromatic Hydrocarbons (PAHs) in Natural and Anthropogenically Modified Soils (A Review)

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Abstract

Technological progress of over than seven-billion population forces an avalanche development of industry, transport and urbanization. The unusual demographic success of the Homo sapiens species has caused very serious environmental impact on abiotic and living organisms. One of the most visible phenomenon of anthropopressure is the increase of environmental contamination of water, air and soil with various xenobiotics, in particular with Polycyclic aromatic hydrocarbons (PAHs) – organic compounds with two or more fused aromatic rings. PAHs are widespread environmental contaminants resulting from incomplete combustion of organics, but partly are of the natural biological and soil-biological origin. PAHs are low soluble in water, but highly lipophilic and easily adsorb on the air particles. PAHs are highly carcinogenic or mutagenic. The assessments of PAHs and their remediation are important. The list issued by the USEPA in 1976 with a view to use chemical analysis for assessing risks to human health, contains a set of compounds of 16 PAHs following criteria of analytical standards availability, occurrence in environment; and toxicity information. The PAHs chemical transformations via destroying double bonds by oxidants are important for safe environment. PAH content in unpolluted soils of various types is relatively low. PAHs are degradable by some microorganisms in the soil. 90 % of PAHs present in environment can be stored in soils, sediments, and sedimentary rocks. PAH content in uncontaminated soils is around 100 ppb. In the airport area, due to jet turbine exhaust, the sum of 12 PAHs ranged from 2390 ppb to 7530 ppb. PAH concentration in the town soils is up to 12390 ppb. In the soils of railway junction concentrations of 14 PAHs in 1995 was 2243 ppb, and in 2008 up to 59508 ppb. PAHs concentrations in the soils of coking plant area reach 57921 ppb. The new analytical protocol for determination of PAHs and OPAHs are elaborated. There are many classifications determining the soil pollution degree due to the level of PAH. Poland Institute of Soil Science and Plant Cultivation proposed “sum of 13 PAHs”, Poland Ministry Regulation provides “sum of nine PAHs”, Dutch List contains “sum of ten PAHs”. According every classification, under transport and industries anthropopressure, the soil PAH concentrations are dangerous to human health.

Keywords: microorganisms, hydrocarbon, soil, pollutant, transport, toxic.

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1. Introduction

Chemical xenobiotics are usually divided into inorganic and organic ones. The most important inorganic xenobiotics are sulfur and nitrogen oxides as well as heavy metals, while the most frequently studied organic xenobiotics are: polycyclic aromatic hydrocarbons (PAHs, also called polyarenes), polychlorinated biphenyls (PCBs), dioxins and some pesticides.

Technological progress of over than seven-billion population forces an avalanche development of industry, transport and urbanization. The unusual demographic success of the *Homo sapiens* species has caused very serious environmental impact on abiotic and living organisms. One of the most visible phenomenon of anthropopressure is the increase of environmental contamination of water, air and soil with various xenobiotics, in particular with PAHs – organic compounds with two or more fused aromatic rings.

Polycyclic aromatic hydrocarbons are in the first place among organic pollutants, because they have been detected in various concentrations not only in polluted industrial and urbanized environments, but also in soil, water, sediments in areas of different anthropogenic pressure.

Sources of PAHs to the environment are numerous and fundamentally well-known. PAHs are a group of compounds that come from both anthropogenic and natural sources to the environment. Generally, PAHs can be produced by the incomplete combustion of compounds containing carbon and hydrogen or during some biotransformation processes. The main anthropogenic sources of PAHs in environment include the processing of different fuels in coke plants, crude oil extraction installations and refineries, as well as combustion of liquid and solid fossils fuels (Howsam et al., 1998; Igwe et al., 2015). For this reason, the main suppliers of PAHs to the environment are industry, transport and municipal facilities. But PAHs do not originate only from anthropogenic sources. They can be formed during environmental fires of the steppes, forests and peat (Meřtrak et al., 2006; Vergnoux et al., 2011) and during volcanic eruptions (Stracquadanio et al., 2003). It was found that PAH emissions to the environment from anthropogenic sources are many times higher than natural emissions

Observation that a reasonable amount of polyarenes are present in some habitats with very little anthropogenic pollution, as well as in some sedimentary rocks led to suggestion that these compounds can be formed as a result of biochemical transformation. Many sediments of organic origin have been formed by the alteration of accumulated plant material, in which PAHs have formed. The reason is, that their biosynthetic precursors were mainly di- and triterpenoids. Hopanoids (common prokaryotic triterpenoides) and steroids may also be the precursors of polyarenes (Simoneit, 1998; Malawska et al., 2006).

It was shown that the wood of tropical forests contains naphthalene, phenanthrene, and perylene (Wilcke, 2007). Also, animal membrane components like cholesterol and steroid hormones also have structures similar to substituted phenanthrenes, which can be precursors of some PAHs, The synthesis of naphthalene and perylene can also occur in termite organisms (Wilcke, 2000).

PAHs are also found in brown coal (Bojakowska et al., 2001), hard coal (Achten et al., 2009) and crude oils (Bojakowska et al., 2012). The described ubiquity of PAHs causes that they are important environmental xenobiotics, but their presence in various types of soils is particularly important. The reason is the very high persistence of PAHs in the soil environment, which causes that these compounds can persist in it for a very long time, and their biotic and abiotic degradation is very slow. The majority of PAHs accumulate in soil (around 89.9 %), 0.3 % is contained in surface waters, 9.3 % accumulates in bottom sediments and 0.5 % remains in atmospheric air (Paterson et al., 1989). The purpose of this article is to review the basic data on PAHs, with particular emphasis on the presence of these compounds in various types of soils.

2. Discussion of the methods and results

2.1. Historical justification of the importance of PAHs

PAHs are widespread environmental contaminants suspected to be carcinogenic (Harvey, 1985). Before the carcinogenic effects of PAHs have been clearly demonstrated, many indications of this have been observed. The first one comes from the second half of the 18th century. Over 200 years ago, surgeon to St. Bartholomew's Hospital in London, Percivall Pott made the astute connection between soot and scrotal cancer, known then as the chimney sweeps cancer. Pott made the connection between the causative agent – i.e. soot, lodging in the folds of the scrotal skin – and

the disease, but left it to others to consider prevention. A weekly change of working clothes and daily washing of the private parts was the usual advice (Gordon, 1994; Herr, 2011). Of course, Pott had no idea about the chemical composition of soot.

This observation was followed a century later by von Volkmann's reports published in *Beiträge zur Chirurgie Leipzig* concerning the occupational skin cancers in workers in the coal tar industry in Germany (Harvey, 1985). The increase incidence of bladder cancer in workers employed in dye industry was first noted by Rehn in 1895 (Barile, 2003).

Although chemical induction of cancer in humans, which was described above, was noted long ago, utilizing experimental animals to examine chemical induction of cancer only began in the early 20th century when Yamagiwa and Ichikawa described for the first time induction of the skin neoplasms upon repetitive applications of coal tar to the ears of rabbits (Fujiki, 2014). Bioconcentration and bioaccumulation of PAHs in organisms occurs through various routes including ingestion, inhalation or dermal contact pathways.

Isolation of benzene and toluene, as well as some polyarenes, from coal tar in the early part of the 19th century began a period of great interest in this compound group. The number of papers dealing with PAHs rapidly grew when people realized that some polyarenes possessed highly toxic and carcinogenic activity. This meant explaining the observations of researchers combining exposure to certain organic substances with the occurrence of an increased number of cancers. PAHs are also of environmental concern not only because of their toxicity and carcinogenicity, but also because they are very resistant to decomposition. Hence, these compounds are included in a group named persistent organic pollutant (POPs). Moreover, they have possible harmful effects on soil organisms and plants (Menzie, et al., 1992). PAHs are not synthesized chemically for industrial purposes. However, there are few commercial uses of many polyarenes. They are mostly used as intermediaries in pharmaceutical, agricultural product, photographic products, thermosetting plastic, lubricating materials, and other chemical (Igwe et al., 2015).

Toxic and carcinogenic action of PAHs combined in the ubiquitous presence in the environment causes that work on this group of compounds is in the mainstream of environmental chemistry and toxicology.

2.2. Structure and properties of PAHs

PAHs are organic compounds that are mostly white, or pale yellow solids with different melting points. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. It is a relatively homogeneous group of substances in terms of physical and chemical properties. PAHs are nonpolar and lipophilic. Larger PAHs are generally insoluble in water, although some smaller PAHs are soluble to some extent, so they are known contaminants in drinking water (Feng et al., 2009).

PAHs are organic compounds containing only carbon atoms with sp^2 hybridization and hydrogen atoms. They are composed of multiple aromatic rings (organic rings in which the electrons are delocalized). Chemically the PAHs are comprised of two or more benzene rings bonded in linear, cluster, or angular arrangements. The simplest such chemicals are: naphthalene, having two aromatic rings, and the three-ring compounds anthracene and phenanthrene. PAHs with five or six-membered rings are most common. Although several hundred different polyarene structures with a large number of rings have been obtained by synthetic methods, in the environmental chemistry, hydrocarbons containing from two to six rings are the most important (Feng et al., 2009).

The chemical transformations that PAHs undergo can be divided into two groups: substitution and addition, in which double bonds are destroyed. PAHs are sensitive to oxidants, including oxygen and ozone. In the presence of oxidants, light quanta induce photochemical reactions. As a result, different types of diols, quinones and aldehydes are formed. Such transformations may be important in removing PAH from the natural environment.

Three well known lists of PAHs frequently monitored exist, i. e. the list of EU Scientific Committee for Food (SCF), the list of EU, and the list of US Environmental Protection Agency (EPA). Among them, the most frequently used in environmental research is the EPA list (Figure 1).

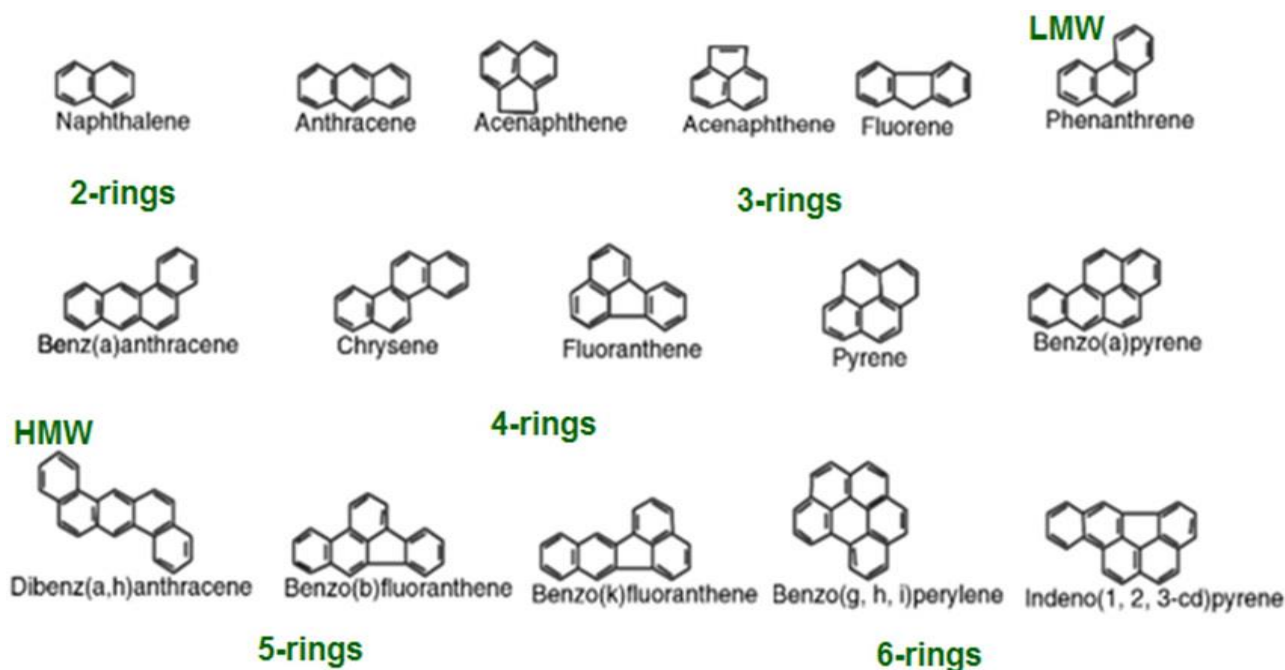


Fig. 1. Structures and nomenclatures of the 16 PAHs on the USEPA priority pollutant list (Source: https://www.researchgate.net/profile/Eman_Koshlaf/publication/313957030/figure/fig2/AS:526050025107456@1502431507235/Structures-and-nomenclatures-of-the-16-PAHs-on-the-US-EPA-priority-pollutant-list.jpg)

The list of 16 polycyclic aromatic hydrocarbons issued by the U.S. Environmental Protection Agency (EPA) in 1976 with a view to use chemical analysis for assessing risks to human health, has gained a tremendous role as a standardized set of compounds to be analysed, quite especially in environmental studies. This list of PAHs was created under time pressure with respect to the following criteria:

1. availability of analytical standards and, if available, whether they were measurable with current analytical methods (mainly GC-FID or GC-MS);
2. whether they occurred in the environment; and
3. whether they were known to be toxic.

Despite the doubts that have arisen in recent years, should this list be extended, it remains the basis for scientific research (Andersson, Achten, 2015).

PAHs generally have a low degree of acute toxicity to humans. After chronic exposure, the non-carcinogenic effects of PAHs involve primarily the: pulmonary, gastrointestinal, renal, and dermatologic systems. But the most significant endpoint of PAH toxicity is cancer. Although unmetabolized PAHs can have negative effects, a major concern is the ability of their reactive metabolites, such as epoxides and dihydrodiols, to bind to cellular proteins and DNA. Like many other carcinogens, these hydrocarbons are metabolized enzymatically to various metabolites, of which some are reactive. PAHs undergo metabolic activation to diol-epoxides, which bind covalently to DNA. The DNA binding of activated PAHs is considered to be essential for the carcinogenic effect (Rengarajan, 2015).

Several analytical methods have been usually used for determination of PAHs and their derivatives in the environment, as well as in biological or food matrices. Among chromatographic methods GC or HPLC with mass spectrometry detection are used most frequently. HPLC methods are more suitable for analysis of PAHs, as in comparison to GC, the thermally labile or low volatile compounds can be analysed easily (Kumar et al., 2014).

2.3. PAHs in different natural soils

Soil is the primary steady reservoir and sinks for PAHs in the terrestrial environment, because PAHs are readily absorbed by organic matter in soil and difficult to degrade (Yang et al., 2014). PAHs in the soil are very persistent compounds, therefore the accumulation of polyarenes in

soil may lead to contamination of food chains, which could cause a potential risk to human health (Jiang et al., 2011). Some investigation proved that about 90 % of the PAHs present in the environment can be stored in soils and sediments (Wild, Jones, 1995), which are thus the best environmental "sink" for these compounds.

PAHs occur in the natural environment as natural components of soils, water sediments and sedimentary rocks. Usually, soil rich in humic substances is characterized by a higher content of PAHs than soils with a small amount of organic substance. Polycyclic aromatic hydrocarbons form and are introduced into the natural soils also as a result of natural forest and peat fires and volcanic eruptions. These compounds may also be formed during petrogenesis, in particular at high temperatures. The formation of a whole range of aromatic hydrocarbons, including polycyclic hydrocarbons, accompanies the processes of organic matter transformation leading to the formation of crude oil (Evans et al., 1990).

The content and composition of polycyclic aromatic hydrocarbons in soils is the resultant of the processes (formation and degradation) occurring in them. The formation of hydrocarbon derivatives runs in parallel as a result of degradation of organic debris and deposition caused by anthropopressure. On the other hand, microbial degradation of these compounds occurs. Microbial degradation of PAHs depends on various environmental conditions, such as nutrients, number and kind of the microorganisms, nature as well as chemical property of the PAH being degraded (Ghosal et al., 2016).

Although much of the information available in the literature refers to the PAH content in contaminated soils in areas undergoing strong anthropogenic stress, the number of publications on the presence of PAHs in natural soils is also present in world scientific literature. A brief overview of the characteristic examples will be presented below.

An important type of relatively less contaminated soils are forest soils. In areas without industry and large cities, in soils of forests and meadows, the PAH content should not be high. Bojakowska and Sokołowska (1998) examined the PAH content in 65 soil samples from the forested areas of western Poland. The average content of 15 PAHs investigated in the soils of this area was 155 ppb. The average share of tricyclic aromatic hydrocarbons, relatively low persistent in the environment, accounted for 12 % of the total sum of PAHs. The proportion of four-ring hydrocarbons negatively affecting animal organisms was 31 %, while, the most harmful – five- and six-ring aromatic hydrocarbons – 56.6 %. The average content of polycyclic aromatic hydrocarbons with carcinogenic and mutagenic effects on animal organisms was 92 ppb in the examined soils, and their share in the total PAHs – 57.5 %.

Typical PAH concentrations in uncontaminated soils usually do not exceed 100 ppb. This has been confirmed by Trapido (1999) for Estonian soils. The typical level of total PAHs in Estonian rural soil is about 100 ppb dry weight, whereas PAH concentrations in Tallinn, Pärnu and Kohtla-Järve (big Estonian towns) soil were quite high (the mean Σ PAH concentrations were 2240, 7665 and 12390 ppb dry weight, respectively). This proves the strong impact of urbanization in terms of PAH levels. The ratio of small molecule PAHs (3–4 ring) to big molecule ones (5–6 ring) altered significantly (from 5:1 to 1.7:1).

The state of the contamination and distribution of PAH in agricultural soils (115 surface soils; 0–20 cm) in the subtropical regions was performed by Chinese scientists (Hao et al., 2007). The total PAH concentrations ranged from 22.1 to 1256.9 ppb. In general terms, the current PAH concentrations were lower than most PAH levels reported in a number of investigations from different countries and regions.

PAHs level in soils obtained from uncontaminated locations can give useful information about the influence of regional atmospheric sources, long-range atmospheric transport processes, compound retention, partitioning and fate processes in the environment. There are some evidences that background soil PAH concentrations in Europe appear most strongly affected by proximity to sources and the likelihood of enhanced deposition.

The research on PAH levels in peats is very interesting (Borgulat et al., 2018). Although, from a formal point of view, peat is not a soil, but a young sedimentary rock, it practically behaves in many aspects like soil. As locations for the biogenic accumulation of peat, which may be regarded as the youngest and least transformed sedimentary rock, mires provide records of the changing fluxes of organic compounds from both natural and anthropic sources (Berset et al., 2001).

Because peatlands in many regions of the world (also in Poland) are located in ecologically clean regions, the level of PAH in peats is a good indicator of the concentration of these xenobiotics in unpolluted soils. Very interesting and extensive research on the level and characteristics of PAHs in peats was carried out by a team of scientists from the University of Warsaw. During the many years of research, the content and characteristics of PAHs in peat profiles collected from several dozen Polish peatlands, both bogs and fens, were determined (Malawska et al., 2002a; Malawska et al., 2002b; Wilkomirski et al., 2002; Wilkomirski, Malawska, 2005; Malawska et al., 2006).

In 44 peat samples taken from different stratigraphical layers of 12 mires located in four regions of southern Poland (the Sudeten and Tatra Mountains, Silesian Lowland and Orawa Basin), the total concentration of 16 USEPA PAHs was between 39 and 384 ppb in all samples. The only exception was Lasówka, a fen in the Sudeten Mountains, where an extremely high PAH concentration (3746 ppb) was recorded.

The concentration of PAHs was also analyzed in samples of peat collected from two different peatlands (Zdory and Wołosate) located respectively in the lake district and mountains in south-eastern Poland. The total concentration in all peat samples was between 120 and 209 ppb.

The described level of PAHs in peat was also confirmed by Bojakowska et al. (2013) for samples collected from other peatlands. This investigation proved that the level of 17 USEPA PAHs in three peatland deposits selected for the study: Otałzyno near Kartuzy (northern Poland), Stoczek near Radzyń Podlaski (central Poland) and Huczwa near Tomaszów Lubelski (south-eastern Poland) was about 500 ppb.

With the content of PAHs in peat, one more interesting problem is associated. Peats are organogenic rocks formed as a result of biochemical changes in remains of dead plants under the conditions of high humidity and lack of oxygen. Various types of peat differ from each other in terms of organic and inorganic component content and these differences are a result of peats being formed under various oxygen conditions as well as various geological, hydrological, geomorphological and physical and chemical conditions, and from various plant associations (Orru, Orru, 2006). The occurrence of PAHs in peats formed in pre-industrial times can only be explained on the ground that they came from natural sources – i.e. inclusion, in peat, of compounds found in putrefying plant material, atmospheric deposition of compounds produced in fires of plant communities or by reference to the fact that these compounds were formed as a result of changes occurring during the biochemical phase in early sediment diagenesis.

As it was mentioned above PAHs, they can be formed from natural terpenoid precursors. Perylene is a good example of PAH which can form on this pathway. The peat is made up of layers that differ in their degree of decomposition, botanical composition and age; and different types of peat show different microbial activity, acidity, degree of anaerobiosis and content of humic substances. The accessibility of these properties, especially botanical composition, makes it possible to investigate the natural processes of PAH formation from precursors of aromatic compounds.

Perylene is derived from its natural precursors via post-deposition transformation during early diagenesis, and much smaller amounts of perylene than of other PAHs are produced during combustion processes (Yunker et al., 2002). Thus the abundance of perylene in some peats may reflect biochemical transformations from plant precursors. The highest concentrations of perylene occurred in woody peat. The concentration of possible chemical precursors of perylene is high in woody peat because such peat was formed mostly from higher plant residues containing greater quantities of isoprenoids than are found in moss residues.

As can be seen from the above examples, PAH content in unpolluted soils of various types is relatively low. This level can clearly increase as a result of the inflow of various types of pollutants, both natural and anthropogenic, into soils. A natural source of PAHs concentration increases in unpolluted soils is large environmental fires of forests and peat bogs. Every environmental fire is a violent phenomenon, bringing with it a series of serious consequences. In the case of environmental fires the fuel is usually living and dead vegetation (trunks, branches, leaves), but also soil humus or peat found in various peatland deposits type. Combustion of organic matter with insufficient oxygen supply must bring with it the formation and increase of PAH levels. In such processes, atoms carbon atoms are not completely oxidized and accumulate in the form of thermodynamically stable structures of aromatic rings.

The appearance of increased PAH content in the environment after forest or peat fires were repeatedly observed (Eun-Jung et al., 2003; Gabos et al., 2001; Dreyer et al., 2005). After a fire, a two-fold increase in the amount of PAHs was observed, from approximately 400 ppb to 800 ppb (Malawska et al., 2007).

The contribution of forest fires to the content of PAHs in soils was demonstrated by Vergnoux et al. (2011). Surface (0–5 cm) and subsurface (5 to 15 cm) soils from burned forest areas in South of France were analysed to determine contents of 14 priority PAHs and their distribution profile. The lowest molecular weight studied PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) appear to be the major ones produced by forest fire. Naphthalene levels are remarkably high in burned soils (more than 70 ppb, i.e. more than 20 times higher than in the control soils) and still remain important years after the last fire event.

Burning conditions (the amount of available oxygen, the duration of heating, the temperature) and the type of vegetation define the amount and composition of PAHs (Medeiros, Simoneit, 2008). A Russian-American group of scientists carried out research aimed at identifying features of PAH accumulation in podzols and histosols of drained peatlands affected by wildfires (Tsibart et al., 2014). They investigated PAHs profiles in areas occupied by drained peatland and strongly damaged by fires in 2002, 2010 and 2012.

After analysis, they came to the conclusion that: the wildfires on the drained peatlands caused the change in the morphological properties of soils; new soil horizons C_{pir}, OH_{pir}, and H_{pir} were formed with different accumulation rates of PAHs. The highest PAHs concentrations were seen in charric peat H_{pir} horizons and in post-fire incipient O horizons. Also, post-fire histosols and histic podzols differed in their PAH distribution. In both cases, the highest PAH concentrations occurred in the organogenic post-fire horizons, but in cases of histic podzols, their slight accumulation of PAHs in illuvial horizons was possible. The trends of higher PAH accumulation in soils were observed in cases of incomplete burning out of peat horizons.

Another type of research regarding the PAH content in peats was carried out by Ekonomiuk (2007). She investigated peats from whole stratigraphic profiles of three bogs; two of them are located in a non-polluted area, the third is located in a heavily polluted area, due to the vicinity of large metallurgical plants. The main objective of the research was to investigate the distribution and migration trends of PAHs in high moorland ecosystems characterized by specific physical and chemical conditions and various degrees of anthropopressure.

A different PAH content profile was observed in non-contaminated deposits and in a contaminated deposit. In the case of uncontaminated peatlands, a more even distribution of the PAHs in the stratigraphic profile is observed than in the highly contaminated deposit, in which most of these substances accumulate in the surface layer of peat. Total contents of PAHs in strongly contaminated deposit reached 6394 in 2002 and 6472 ppb in 2003, respectively. Relatively large amounts of PAHs in the subsurface peat layer of the contaminated bed probably result from the migration of some of the contaminants accumulated on the surface of the deposit. Studies have confirmed the occurrence of perylene in deeper residual peats, which probably originates from natural biochemical transformations of aromatic precursors.

A correlation was found between the PAH content in peat profiles and the level of these compounds in the leaves of selected plants growing on the peatland (Meřtrak et al., 2016).

Another important reason for the increase in PAH concentration in unpolluted agricultural soils may be alternative fertilization. Such specific fertilizers are produced mostly from municipal solid waste or sewage sludge. The compost is relatively safe in terms of PAHs concentration. Déportes et al. (1995) claim that the concentration of PAHs in municipal waste compost varies over a wide range, from 1 to 250 ppm. Such a broad range of concentrations of PAHs in municipal waste compost, results from the sources of its origin. Obviously, more PAHs were determined in municipal waste composts than in green waste compost. The one-month compost produced from municipal waste had the highest concentration of anthracene and pyrene, while the three-month compost was the richest in benzo(a)anthracene, indeno(1,2,3-cd)pyrene, and phenanthrene and the concentration of the other PAHs was the highest in the six-month compost. Fertilization of soil with municipal waste composts raised the soil content of PAHs, although in most cases the natural level of these compounds was not exceeded (Sądej, Namiołtko, 2010).

Sewage sludge (SS) is a complex organic by-product of the wastewater treatment process. Large amounts of SS are constantly produced and the disposal routes are a matter of worldwide

concern and environmental problem. This material is supposed to be potentially useful in agricultural land amendment or degraded area recovery due to its rich nutrient composition, especially in organic matter, and inorganic biogenes. However, soil fertilization with sewage sludge is much less safe, due to high level of pollutant organic compounds, such as the PAHs (Wild et al., 1991; Włóka, Smol, 2014). In all the analysed cases, an increase in the concentration of PAHs in soil was observed as a result of the introduction of sewage sludge as a fertilizer.

It is known that the addition of increasing doses of sludge into the soil resulted in a gradual increase in the amount of the polycyclic aromatic hydrocarbons contained therein. Moreover, the introduction of SS into the soil influenced the increase of the total level of some PAHs in the plants grown in this soil (Oleszczuk, Baran, 2005). Hence, the PAH concentration levels found in sewage sludge might raise potential contamination risks to the soil.

2.4. PAHs in different anthropogenically modified soils

The great ecotoxicological significance of the appearance of PAHs in the soil causes that, concentrations of PAHs in soil have been widely investigated in anthropogenically modified soil. As the examples of such environments described in this review, soil connected with transport, urbanization, mining and industry, were used.

One of the significant anthropogenic sources of PAHs is road transport. PAHs are emitted during combustion of fuels (diesel, gasoline), use of lubricative and engine oils as well as during abrasion of tyres and asphalt (Trang, Byeond-Kyu, 2009). The vicinity of roads and airports is known to be exposed to gasoline, diesel and kerosene vehicle exhausts (cars, trucks or aircrafts).

The vehicle exhausts are considered to be this source of PAH contamination, which creates a real threat to food produced on fields lying in the vicinity of transport routes. PAH contamination levels by mobile sources are studied through their profiles found in grass and soil in the vicinity of a motorway (connecting Luxembourg to the East of France and a medium size airport located in the east part of France (Crépineau-Ducoulombier, Rychen, 2003). They showed that soil can be contaminated by PAHs when they are located by a motorway or an airport. The vicinity of the motorway is almost four times more contaminated than the area around the airport.

Research carried out on soil around the International Airport in Delhi, India, showed that huge airport is really serious source of PAH contamination in peripheral soil (Ray et al., 2008). What is important, densely populated residential areas surrounding the airport come directly under both the landing and take-off flight paths. The study was undertaken to determine the level of PAH contamination due to jet turbine exhaust. Twelve priority polycyclic aromatic hydrocarbons (PAHs) were analysed in the <2 mm surface soil fraction. The sum of 12 PAHs ranged from 2390 ppb to 7530 ppb. PAH levels observed in the present study were found to be higher as compared to most of the literature data on airport contamination. Predominance of pyrene was observed in the airport soil. Factor analysis and isomer pair ratios suggest pyrogenic origin of PAHs in the study area.

Apart from roads, railways are one of the principal means of transportation. The specificity of rail transportation causes multidimensional environmental problems (Wierzbicka et al., 2015). One of them is the increase in the concentration of xenobiotics in the soil of railway areas. Among the most important railway pollutants are polycyclic aromatic hydrocarbons (Wilkomirski et al., 2012).

The classical and broadly quoted habitat research on the railway grounds, which lasted over a dozen years, has been led by a team of researchers from the University of Warsaw since the beginning of the current century. One of the threads of this research was to determine the level of PAHs in the soil of several Polish railway junctions.

Very important results were obtained for the Iława Główna railway junction (Malawska, Wilkomirski, 2001). This junction (built in 1870) is located in northern Poland about 200 km north of Warsaw on the Warsaw–Gdańsk railway route in the western part of the Mazurian Lake Region. This region covered mostly by forests and lakes is relatively clean, since no heavy industry is concentrated there. The junction having such location is the relevant place to investigate the influence of railway transportation on environmental pollution. Very heavy passenger and goods traffic is concentrated in the area of the junction because Iława Główna is situated at the crossing of a few important railway routes. The railway junction covers an area of almost 2 km² within which the different functional parts are situated.

In 1995, concentrations of 14 PAHs in soil were tested on four functional parts of this railway junction, i.e. vicinity of platforms, cleaning bay, railway siding and loading ramp. Total level of these 14 compounds was: 2243, 910, 2178 1097 ppb, respectively. 13 years later, in 2008, PAH tests were carried out in exactly the same places. During this period, no modernization works were carried out on the tested functional parts of the railway junction, which resulted in the accumulation of pollutants.

The following 17 PAHs were determined: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[123-cd]pyrene, dibenzo[ah]anthracene and benzo[ghi]perylene. The comparison of earlier findings with the results indicating the total level of the same 14 PAHs determined in the present study showed a very significant increase of PAHs content in all the functional parts of the railway junction Iława Główna. At the same time, the PAH level in the control areas did not change (Figure 2).

It was found that all the investigated areas were strongly contaminated with PAHs. The PAH contamination of the soil was the highest in the railway siding and in the platform area (59508 and 49670 ppb, respectively). In the loading ramp and cleaning bay, the PAH concentration in soil was lower but still relatively very high (17948 and 15376 ppb, respectively). The contamination in the railway siding exceeded the average control level up to about 80 times. This is one of the best examples in the scientific literature for the fact that rail transport is a serious source of PAH. The reasons for pollution of railway areas with these compounds are fuels, oils, lubricants and other petroleum products used during the operation of rolling stock, as well as creosote used to impregnate railway ties. The problem of PAHs migration from creosote-treated railway ties into ballast was described comprehensively by Brooks (2004).

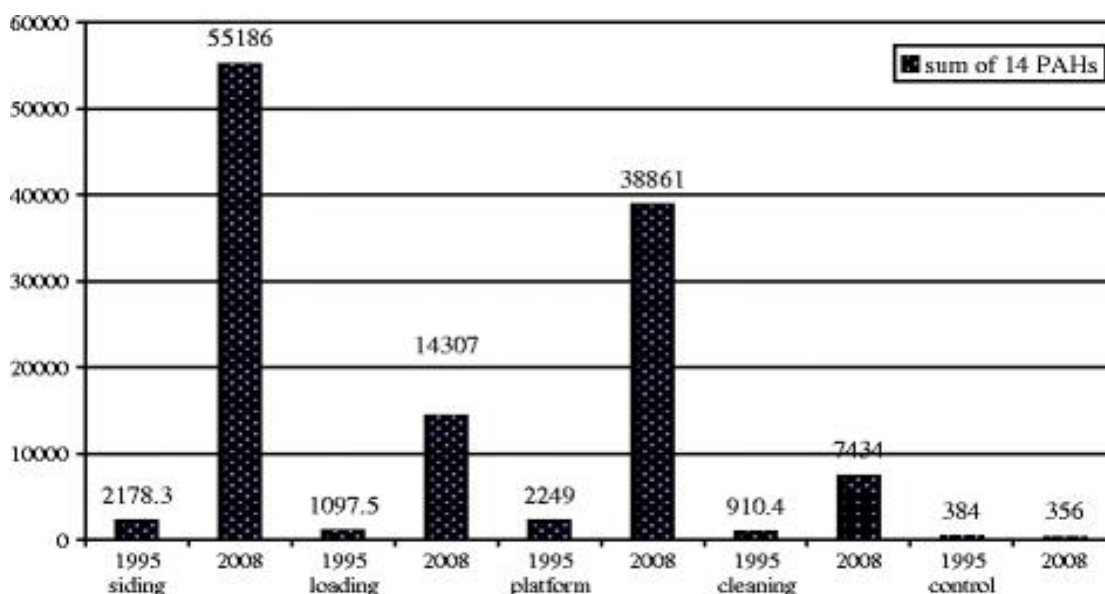


Fig. 2. The comparison of 14 PAHs content in soil in four functional parts of the railway junction Iława Główna in 1995 and 2008 years (micrograms per kilogram, ppb) (Source: [Wiłkomirski et al., 2011](#))

According to his investigations emission of creosote-derived PAHs from newly treated railway ties in supporting ballast is the biggest during the summer of the first year. Creosote-treated ties are strongly heated during the summer because the black surface of the railway ties absorbs sunlight. Specific, but serious source of PAH emissions are transport accidents.

The publication summarizing the research of the Warsaw team on the pollution of railway areas with polycyclic aromatic hydrocarbons appeared in 2015 ([Mętrak et al., 2015](#)).

Polycyclic aromatic hydrocarbons and heavy metals are the two most important groups of pollutants associated with rail transport. Both have a serious negative impact on the natural environment, including human health and degradation of sensitive ecosystems. In this study, apart from qualitative and quantitative analysis of the main PAHs associated with rail, the authors tried to assess composition of specific compounds related to functional areas of railway infrastructure

and to distinguish potential chemical markers which can be used for identification of pollution. Moreover, the authors evaluated the applicability of plants overgrowing railway infrastructure as bioindicators of rail-associated pollution. It was confirmed that high amounts of PAHs in soil are characteristic for intensively used railway infrastructure, but it was not found any typical pollution profiles for the differently used areas (i.e. platforms, sidings, cleaning bays). The major source of these contaminants is petroleum products used in conservation of railway infrastructure and rolling stock. As far as the use of plants overgrowing railway infrastructure as bioindicators of rail-associated pollution is concerned, it is rather limited, due to frequent application of herbicides for security and track stability reasons.

As already noted, the other reason for the significant increase in PAHs in the soil is urbanization. One of the most urgent environmental problems in the world is contamination of soils by a variety of chemical pollutants (including PAHs) in urban regions. In the scientific literature there are many examples of increased PAH content in soils in large urban agglomerations. It is estimated that the average PAH concentration in soils in big cities is 600–3000 ppb (Trapido, 1999). Of course, in many cases PAH levels in soils of urban agglomerations are much higher. Some examples will be discussed below.

The objective of the study carried out by Banger et al. (2010) was to determine the depth-wise distribution (0–15, 15–30, and 30–45 cm) of 16 PAHs compounds in four urban soils of different land uses (residential, public parks, public buildings, and commercial areas) in Miami, Florida, USA. Results showed that across use soils, total PAHs were significantly greater at surface (1869 ppb) than sub-surface (478–1079 ppb). Among land uses at 0–15 cm, PAHs were significantly greater in commercial areas (2364 ppb) than the residential and public parks (1508–595 ppb), but not the public buildings (2007 ppb).

Chinese researchers carried out PAH measurements in the soil of the megacity. Shanghai. 57 soil samples were collected in main urban areas of Shanghai, China (Wang et al., 2013) 26 PAHs including highly carcinogenic dibenzopyrene isomers were analysed. The total concentrations ranged from 133 to 8650 ppb for Σ_{26} PAHs and 83 to 7220 ppb for Σ_{16} PAHs (USEPA). Nearly half of the soil samples showed concentrations above the safe benzo[a]pyrene value of 600 ppb.

The last mentioned reason for increasing PAHs concentration in soils is industry and mining. We must realize that though the huge PAHs amounts are released to environment during the combustion of fossil fuels and biomass used for house heating, as well as burning of petrol by vehicles, another pool of these compounds is industrial the emission connected with coal and oil processing, mainly coking and gas plants, oil refineries, steel industry, aluminum and copper smelters.

Extensive research on the content of PAHs in soils in the industrialized areas of Poland was carried out by Bojakowska (2005). Concentrations of seventeen unsubstituted polycyclic aromatic were determined in samples of soils collected in plant and factory areas and their protective zones where raw organic-rich materials: hard coals, lignite, oils, and bituminous shales are combusted or processed. Soil samples were taken at the following localities:

- the power plant “Ostrołęka”, hard coal-fired power plant,
- power plant “Bełchatów”, the largest brown coal-fired power plant in Poland and Europe,
- coking plant “Przyjaźń” with annual average production of coke of about 2.5 mln t,
- old gasworks, where above 0.10 mln m³ of gas was produced annually,
- refinery “Glimar”, the oldest refinery in Poland producing special kind of kerosene, engine oils, industry oils, extra oils, and waxes,
- copper smelter “Legnica” in Legnica.

Analyses of the obtained results allow making an assumption that PAHs spectrum in soils, in the vicinity of industrial plant, depends to a certain degree on PAHs presence in the processed raw materials. It was noted that the WWA profile in soils in the vicinity of coking plant, gas work, and coal-fired power plant shows similarity to the spectrum of PAHs in hard coal.

In all the studied sites, PAHs contents higher than natural, occurring in unpolluted soil, were detected. Among the considered locations, the highest levels of PAHs were characterized by soils from the coking plant area, in which the maximum concentration of PAHs reached 57921 ppb, with the geometric mean 12089 ppb. Coke manufacturing based on high temperature degassing of coal without air access, creates perfect conditions for forming PAHs. The highest content was observed

in the sample taken near a tar tank. In other research locations PAH concentration in soil was also much higher than natural, occurring in unpolluted soil.

Interesting and extensive research on the increased PAH content in soils in industrialized areas has recently been carried out in China (Jiao et al., 2017). In this study, the PAH distribution and characteristics in terms of concentrations and compositions in contaminated soil at a vertical depth of 0–100 cm, and an area of 0–1500 m around a chemical plant located in Changzhi district (Shanxi, China) were determined. Samples were analysed and characterized by PAH ratios and composition. In this region coal chemical industry extracts many coal resources, producing at the same time many PAHs that are emitted as by-products of coal incomplete combustion. The concentrations of the priority control 16 PAHs in the 66 soils samples around the chemical plant varied from 3870 ppb to 116000 ppb.

All the above Estonian, Polish, American and Chinese results have shown that PAHs are present in high concentrations in the top soil of areas near the chemical industry.

One more interesting aspect related to PAH derivatives in soil is mentioned. Although PAHs have been extensively studied, the knowledge of their oxygen-containing derivatives and metabolites (OPAHs) in soils is limited (Bandowe, Wilcke, 2010). The authors elaborated new analytical protocol for determination of PAHs and OPAHs. This procedure was applied to soils from a former gasworks site, Berlin, an urban soil from Mainz, both in Germany, and a forest soil from near Manaus, Brazil. The sums of 34 PAH concentrations were 107000, 3505, and 21 ppb: those of seven carbonyl-OPAHs were 15690, 170, and 7 ppb; and for Berlin, Mainz, and Manaus soils, respectively. Several OPAHs were present at concentrations higher than or equal to their parent PAHs, demonstrating the importance of OPAH measurement for the assessment of PAH-related environmental risks. It is important in carcinogenesis, because PAHs require metabolic activation and subsequent formation of adducts with nuclear DNA.

We would like to end this review with a general remark. There are many classifications determining the soil pollution degree due to the level of PAH. In Poland, the assessment of soil quality is carried out based on different classifications, i.e. National Research Institute (Institute of Soil Science and Plant Cultivation, ISSPC) system (sum of 13 PAHs), Ministry Regulation (sum of nine PAHs) and Dutch List (sum of ten PAHs). Table 1 shows the comparison of PAHs content and soil assessment.

Table 1. Standard limiting PAH content in the soil surface layer (micrograms per kilogram) (Wilkomirski et al., 2011)

Class	1	2	3	3	4	5
ISSPC (13 PAHs)	0–200 unpolluted (natural content)	200–600 unpolluted (increased content)	600–1,000 slightly polluted	1,000–5,000 polluted	5,000–10,000 heavily polluted	up to >10,000 very heavily polluted
Ministry of Environment (9 PAHs)	<1,000 unpolluted	>1,000 polluted	>40,000			
Dutch List (10 PAHs)	<1,000 unpolluted	1,000–40,000 polluted	>40,000 Heavily polluted			

3. Conclusion

The anthropopressure, especially transport and certain industries, cause an increase in PAH concentrations in the soil to levels that can be really dangerous to human health. Soils with such PAH content are classified in all the above classifications as very heavily contaminated.

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