

ASSESSMENT OF PAH CONTENT IN SOIL AND ABOVEGROUND PARTS OF *LOLIUM PERENNE* L. NEXT TO THE COMMUNICATION ARTERIES OF THE URBAN AGGLOMERATION

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Abstract:

The research on the content of polycyclic aromatic hydrocarbons (PAHs) in soil and grass (*Lolium perenne* L.) was carried out on samples collected in the city of Białystok, in north-eastern Poland. The test samples came from green belts in the vicinity of communication routes, differentiated in terms of the surrounding buildings and infrastructure and characterized by a different car traffic intensity. The highest total concentration of all sixteen PAHs in soil and grass samples was found near a large intersection at Nicholas Copernicus Street, one of the most important communication routes connecting two parts of the city. In the aboveground parts of the studied grass samples, benzo[a]pyrene was the most abundant, its content ranging from 53.8 µg/kg DM up to 91.7 µg/kg DM. On the other hand, in soil samples, much higher benzo[a]pyrene content was found, and the dominance of this compound was observed in almost every measurement location. Based on the obtained results, it was found that car traffic is a significant source of PAH emissions to the urban soil environment and urban greenery. The squares and green belts located along communication routes and intersections are the most exposed to pollution.

Key words: PAHs, urban soil, *Lolium perenne* L., urban grasses.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants present today in all environmental components, including the atmosphere, soil, sediment, and plants (Luo *et al.*, 2004; Cheung *et al.* 2007; Kanzari *et al.*, 2014; Zhao *et al.*, 2014). Due to their carcinogenic, teratogenic and mutagenic effects, they are dangerous to humans (Xue and Warshawsky, 2004). Numerous studies indicate a relationship between exposure to PAHs contamination and the occurrence of various negative health effects (Pope

and Dockery, 2006; Clifford *et al.*, 2016). Considering the sources of polycyclic aromatic hydrocarbons in the environment, these compounds may come from natural sources as a result of volcanic eruptions, forest fires, biosynthesis, but most of all, they come from anthropogenic activities and are formed in the process of burning biomass, fossil fuels and as a result of exhaust emissions and crude oil processing (Wilcke, 2000; Kim *et al.*, 2003; Saha *et al.*, 2009; Guo *et al.*, 2013). Therefore, PAHs are ubiquitous organic pollutants derived mainly from incomplete combustion of organic materials (Wang *et al.*, 2013; Abdel-Shafy and

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Mansour, 2016). Therefore, they are strongly related to settlement, transport and industrial development (Banan *et al.*, 2018). As a result of intensive urbanization, pollution of the environment with PAH compounds increases, increasing the risk to human health (Liu *et al.*, 2016). Considering the above, urban agglomerations are exposed to the occurrence and negative impact of PAHs, including an increased risk of cancer and other undesirable health effects (Nadal, 2004; Yang *et al.*, 2002).

The presence of polycyclic aromatic hydrocarbons in the environment is largely related to air pollution. According to Duan *et al.* (2007) and Li *et al.* (2020), more than 80% of PAHs are associated with the emission of PM 2.5 and the concentration of these compounds in the particulate matter is highly dependent on the content of fine particles in the air. The development of the automotive industry is of great importance in polluting the environment with these compounds in cities. As reported by Kozielska *et al.* (2009) and Merkisz and Kozak (2002), it has contributed to an increase in the emission of toxic substances in recent years. According to Kondras and Czępińska-Kamińska (2007), exhaust gases from diesel engines contain mainly two-, three-, four-ring PAHs and the exhaust from gasoline engines may contain five- and six-ring PAHs. In places such as busy roads, car parks, tunnels and gas stations, air pollution can be 4 to 40 times higher than the average for entire urban areas. It is estimated that approximately 60–80% of air pollution in cities is of communication origin (Potarzycki and Apolinarska, 2000; Bojanowska, 2011). Air pollution is related to the pollution of other environmental components, because various types of pollutants are adsorbed on dust particles and fall onto trees, grasses, leaves and are accumulated or washed away with rainfall.

PAHs in urban areas may be emitted to the surface, groundwater and soil (Dmuchowski and Orliński, 2003). Due to their lipophilicity and persistence, PAHs tend to persist in soil (Zhang and Fan, 2016). After being deposited in the soil surface layer, they can be accumulated in fauna, flora and, along the food chain, transferred to the organisms of animals and humans (Bortey-Sam *et al.*, 2014). Moreover, in the context of the development of urban areas and the proper shaping of greenery, it is important to mow grass and collect leaves, which are often used to produce compost in municipal waste management plants. As a result, organic fertilizer is obtained, intended for fertilizing arable land, urban greenery or reclamation. Therefore, it can be assumed that PAHs from grasses or leaves may contaminate the obtained compost and can be a source of contamination of the fertilized soils. However, to understand this process, research on the migration and transformation of polycyclic aromatic hydrocarbons is necessary. However, to reduce these compounds' emissions and protect ecosystems, their concentrations and sources should be specified in detail. Therefore, in assessing the potential risk of environmental pollution with PAH compounds, research on the content of these compounds in various components of the environment, especially in the urban environment, plays a huge role.

Therefore, this study's objectives were to assess the content of PAHs in soil and grass (*Lolium perenne* L.) at selected research points located at communication nodes in the city of Białystok and to identify areas most exposed to contamination with the tested compounds.

MATERIAL AND METHODS

Description of the sampling place

The research was carried out in Białystok, a city which is located in north-eastern Poland. During the research, attention was focused on traffic junctions in Białystok with heavy traffic. Besides, they are developed with squares and extensive green belts and differ in terms of the surrounding infrastructure in terms of development and purpose. The areas adjacent to 5 large and very busy intersections were selected for the research. The area at the Towarowa Street belongs to the extreme part of the city (average traffic is 2475 vehicles per hour). On the one hand, it is characterized by a cluster of multi-family buildings, while the other part consists of undeveloped plots of land covered with grass. The area at the Czesław Miłosz Street includes vast squares and green belts, covered with grass and flower meadows, located at a large intersection in the vicinity of a shopping center, an estate of detached houses and a small Biała River (2830 vehicles per hour). At the Zwierzyniecka Street, there is a park with a municipal zoo, the largest wooded area in Białystok, surrounded by an estate, public buildings, and universities. There is a significant amount of car traffic here (3625 vehicles per hour). The next point selected for the research was two huge intersections at the Nicholas Copernicus Street (4300 vehicles per hour), connected by a tunnel and one of the most important communication routes, connecting two parts of the city, separated by a railway track. There are uninhabited warehouse areas in the immediate vicinity, car workshops, allotment gardens and the railway plant area. The Hetmańska-Zwycięstwa crossing is an area next to a shopping center and multi-family housing estates (3400 vehicles per hour).

Sampling and sample preparation

One of the grasses found on each analyzed green belt was selected to study PAH content in the plant material. The species *Lolium perenne* L. is a loose grass with a shallow and developed root system used in urban greenery. Grass samples were collected at the turn of October and November 2020, in the final period of urban greenery vegetation. Soil samples were also taken from the same sites from the surface layer (0–0.25 cm). Areas with an area of 5 m² were selected, from which, using an Egner probe, 14 primary samples were collected, which were then combined into one average sample. The samples were transported to the laboratory and stored at -5°C pending analysis.

Analytical methodology

To isolate PAHs from soil samples, the procedure proposed by the Polish Committee for Standardization was used, and the liquid-solid extraction procedure was carried out following the Polish Standard PN-ISO 18287: 2008. An aliquot of 20 g of homogenized, freshly collected material was placed in a flask with a capacity of 100 ml; an internal standard was added to control the process (deuterated PAHs such as phenanthrene- d_{10} and pyrene- d_{10} , 98%, Sigma-Aldrich, USA) and extracted with 50 ml of acetone (for liquid chromatography, LiChrosolv, Merck, Germany) and 1 hour on a magnetic stirrer at a speed of 2000 rpm. After this time, 50 ml of petroleum ether (40–60, HPLC grade, Chem-Lab, Belgium) were added, and the extraction was performed again for 1 hour. The extract was decanted, and the remaining test material was covered with a new portion of petroleum ether (50 ml) and extracted for another hour. The extracts were then filtered and combined. Acetone and the extracted polar compounds were removed by shaking twice with 300 ml of deionized water. The remaining organic phase was dried over anhydrous sodium sulfate (anhydrous, ACS reagent, $\geq 99\%$ Sigma-Aldrich, USA) and then purified using silica gel adsorption chromatography (SPE CHROMABOND SiOH columns, 500 mg, pore size 60Å, particle size 45 μm). All extracts were concentrated in a Turbo-Vap apparatus under an inert gas atmosphere (5.0 purity nitrogen) to a volume of 1 ml and analyzed by chromatography. All analyses were performed in triplicate.

A slightly different methodology was used to extract PAHs from plant samples due to the significantly different matrix composition of the tested materials. Fresh plant material was ground, 5 g was weighed, mixed with anhydrous sodium sulfate to bind the water, an internal stan-

dard was added, and an ultrasonically assisted extraction process was performed using a 2:1 (v:v) solvent mixture of dichloromethane-acetone. The dichloromethane used was liquid chromatographic grade (LiChrosolv, Merck, Germany). The process was carried out twice at 30 °C for 30 minutes. The combined extracts were filtered, dried over anhydrous sodium sulfate, and purified by silica gel adsorption chromatography analogously to the soil samples. The extract was evaporated in a Turbo-Vap apparatus under an inert gas atmosphere (5.0 purity nitrogen) to a volume of 1 ml and analyzed by chromatography (De Nicola *et al.*, 2005). All analyses were performed in triplicate.

Separation of analytes and detection were performed using a GC 7890B system coupled to a 7000C GC/MS Triple Quad mass detector (Agilent Technologies, USA) in Selected Ion Monitoring (SIM) mode. Table 1 shows the parameters of the chromatographic analysis. The compounds characteristics and the ions selected for monitoring are summarized in Table 2 (16 PAH congeners).

During the extraction, to control the analytical process and determine the recovery, the addition of an internal standard, deuterated: phenanthrene- d_{10} (m/z 188) and pyrene- d_{10} (m/z 212), was used, which determines the quantification of trace amounts of PAHs in samples of biological origin (Baumard *et al.*, 1997). In soil, the method was also controlled by simultaneously carrying out the entire analytical procedure for a sample of certified reference material – Clean Soil Reference Material EDF-5183 (CERILLIANT Analytical Reference Standards). In the studies, external calibration was used, applying calibration curves for individual compounds. Calibration solutions were prepared from a standard mixture of 16 PAHs (AccuStandard®, Inc. New Haven, USA, Z-014G). The recovery of individual PAH compounds using the method used was 91–108%.

Table 1. GC/MS analyzer operating conditions and chromatographic separation parameters.

| Parameter | Conditions |
|--|--|
| Column | HP-5MS fused silica capillary column (95% polydimethylsiloxane with 5% phenyl groups, 30 m \times 250 μm \times 0.25 μm , Agilent Technologies, USA) |
| Carrier gas | Helium, 99.9999% |
| Carrier gas flow rate | 1 ml/min |
| Injection volume | 1 μl |
| Division of the gas stream (split) | Splitless |
| Solvent delay | 6 min |
| Mass spectrometer parameters | |
| Transfer line temperature | 300°C |
| Ion source temperature | 230°C |
| Quadrupole temperature | 150°C |
| Scan mode | SIM (Selected Ion Monitoring) |
| Separation temperature program | |
| Injection temperature | 260°C |
| Initial temperature of the column oven | 60°C |
| Initial isotherm | 2 min |
| Temperature increment | 30°C/min to 120 °C |
| Temperature increment | 5°C/min to 300 °C |
| Final temperature of the column oven | 300°C |
| Final isotherm | 15 min |

Table 2. Characteristics of the tested compounds from the PAH group (16 congeners) and the ions used in the GC/MS analysis in the Selected Ion Monitoring mode (SIM).

| Compound | Symbol | The number of rings in the molecule | Molecular weight / monitored ion | Coefficient of determination R ² |
|------------------------|--------|-------------------------------------|----------------------------------|---|
| Naphthalene | NAP | 2 rings | 128 | 0.998 |
| Acenaphthylene | ACY | 3 rings | 152 | 0.999 |
| Acenaphthene | ACE | 3 rings | 154 | 0.996 |
| Fluorene | FLU | 3 rings | 166 | 0.998 |
| Phenanthrene | PHE | 3 rings | 178 | 0.992 |
| Anthracene | ANT | 3 rings | 178 | 0.992 |
| Fluoranthene | FLA | 4 rings | 202 | 0.997 |
| Pyrene | PYR | 4 rings | 202 | 0.999 |
| Benz[a]anthracene | BaA | 4 rings | 228 | 0.991 |
| Chrysene | CHR | 4 rings | 228 | 0.993 |
| Benzo[b]fluoranthene | BbF | 5 rings | 252 | 0.992 |
| Benzo[k]fluoranthene | BkF | 5 rings | 252 | 0.995 |
| Benzo[a]pyrene | BaP | 5 rings | 252 | 0.997 |
| Indeno[1,2,3-cd]pyrene | InP | 6 rings | 276 | 0.993 |
| Dibenz[ah]anthracene | DBA | 5 rings | 278 | 0.992 |
| Benzo[ghi]perylene | BgP | 6 rings | 276 | 0.993 |

For statistical data analysis, the cluster analysis according to Ward's method with Euclidean distance, a hierarchical and agglomeration approach, was used. Its purpose was to designate groups of research sites in Białystok, similar to the risk of soil and grass contamination with PAH compounds from public transport. For this purpose, the results of the total PAH content in the tested samples were used. The Statistica 13 program was used to compile the data statistically.

RESULTS AND DISCUSSION

Many reports confirm that car traffic is the main source of PAH emissions for both the urban and urban soil and green environments. The squares located along communication routes and intersections are the most exposed to pollution. PAHs released into the atmosphere in fuel combustion processes, abrasion of tires and brake blocks are adsorbed on the surface of dust and together with them are deposited on the soil and aboveground plant parts. Additionally, when they get into the soil, they can be absorbed by vegetation together with the soil solution and accumulate there (Zakrzewski, 2000).

In the analyzed samples of city grasses (Table 3), benzo[a]pyrene was the most abundant. Its content ranged from 53.80 µg/kg DM (25% of all 16 PAHs) at the Towarowa Street to 91.74 µg/kg DM (30%) at the Nicholas Copernicus Street, next to the Fieldorf-Nil tunnel. At this point, the highest total concentration of 16 PAH congeners was also recorded, which was 308.72 µg/kg DM. In all analyzed samples, acenaphthylene, acenaphthene, and anthracene were the lowest. Their content in any of the samples did not exceed 2.76 µg/kg DM. The lowest concentration of the tested substances was recorded in the grasses growing at Towarowa Street, where the total PAH content was

estimated at 214.98 µg/kg DM, which is closely related to the location and surroundings of the test point. Large amounts of PAHs are emitted during the combustion of automotive fuels and the incomplete combustion of coal and organic matter (e.g., wood, fossil fuels) in furnaces for heating the residential buildings (Dutkiewicz, 1988), which explains the lowest content of PAHs in this area, which characterizes with the lowest traffic intensity and the largest, undeveloped space of the selected experimental points. The concentration range of naphthalene (10.88–14.48 µg/kg DM), fluorene (29.70–41.38 µg/kg DM), and phenanthrene (12.92–21.158 µg/kg DM) in grasses from all sampling points were similar. A slightly smaller but significant amount of benzo[a]pyrene, considered to be the most carcinogenic, was detected in the grass samples collected at the Czesław Miłosz Street. A concentration of 72.32 µg/kg DM was recorded, which constituted 27% of the total PAH, the value of which was estimated at 266.78 µg/kg DM. The sum of 16 PAHs and the content of benzo[a]pyrene in the material from the green belt located at the Hetmańska and the Zwierzyniecka Streets were comparable. Their concentration was, respectively: 298.08 µg/kg DM and 304.82 µg/kg DM for the sum of PAHs and 67.12 µg/kg DM and 60.06 µg/kg DM for benzo[a]pyrene.

Many studies focusing on the migration of PAHs in the atmosphere indicate a close relationship, showing that the further away from the source of the emission, the lower the concentration of PAHs with higher molecular weights (Bryselbout *et al.*, 2000), which explains the behavior of PAH concentrations in grasses and soil near highways. It shows the relationship in which low-mass PAHs' dominance and the absence of high-molecular-weight PAHs were observed with increasing distance from the freeway. The results obtained in these studies are consistent with this model of PAH distribution with city aerosol. The high content of 5-ring analytes in the analyzed grasses is related

Table 3. Unit and total concentrations of 16 PAH congeners determined in plant and soil samples, expressed in $\mu\text{g}/\text{kg DM}$.

| Compound | Towarowa Street | | Czesław Miłosz Street | | Nicholas Copernicus Street | | Hetmańska Street | | Zwierzyniecka Street | |
|---------------|-----------------|--------|-----------------------|--------|----------------------------|---------|------------------|--------|----------------------|--------|
| | Grass | Soil | Grass | Soil | Grass | Soil | Grass | Soil | Grass | Soil |
| NAP | 11.50 | 9.72 | 10.88 | 11.98 | 13.38 | 12.46 | 12.24 | 2.66 | 14.48 | 11.83 |
| ACY | 0.14 | 1.54 | 0.14 | 1.66 | 1.18 | 3.84 | 1.13 | 1.65 | 1.62 | 1.59 |
| ACE | 0.54 | 0.34 | 0.45 | 0.39 | 0.56 | 9.76 | 0.71 | 0.36 | 0.46 | 10.79 |
| FLU | 31.83 | 23.63 | 29.70 | 26.29 | 37.94 | 33.21 | 34.51 | 25.35 | 41.38 | 30.54 |
| PHE | 15.81 | 27.96 | 12.93 | 34.12 | 17.91 | 113.39 | 21.16 | 30.41 | 19.16 | 73.26 |
| ANT | 2.37 | 5.96 | 1.71 | 8.59 | 2.07 | 31.10 | 2.22 | 5.68 | 2.76 | 15.10 |
| FLA | 8.05 | 65.29 | 6.32 | 84.13 | 7.29 | 352.11 | 13.73 | 75.72 | 8.13 | 145.27 |
| PYR | 7.73 | 60.90 | 6.30 | 76.90 | 6.62 | 17.55 | 10.63 | 90.83 | 6.98 | 116.06 |
| BaA | 2.84 | 30.10 | 3.12 | 41.74 | 6.16 | 207.08 | 5.26 | 41.51 | 2.43 | 76.29 |
| CHR | 6.46 | 46.72 | 7.78 | 66.89 | 11.99 | 249.11 | 11.55 | 64.21 | 6.46 | 97.39 |
| BbF | 38.45 | 91.02 | 54.30 | 159.07 | 55.49 | 290.51 | 63.21 | 169.96 | 59.24 | 113.23 |
| BkF | 24.01 | 57.44 | 34.26 | 100.38 | 37.25 | 180.17 | 39.89 | 106.59 | 37.38 | 72.53 |
| BaP | 53.80 | 65.11 | 72.32 | 199.93 | 91.74 | 268.62 | 67.12 | 83.33 | 60.06 | 110.17 |
| InP | 2.42 | 25.71 | 5.64 | 35.17 | 6.83 | 116.72 | 6.65 | 33.60 | 2.17 | 43.13 |
| DBA | 6.27 | 2.80 | 12.67 | 5.44 | 1.85 | 15.55 | 2.19 | 5.92 | 37.69 | 7.50 |
| BgP | 2.77 | 31.90 | 8.28 | 47.01 | 10.46 | 114.05 | 5.87 | 44.36 | 4.43 | 49.63 |
| Σ PAH* | 214.98 | 546.13 | 266.78 | 899.70 | 308.72 | 2015.23 | 298.08 | 782.15 | 304.82 | 974.31 |

* The permissible content of the sum of 10 PAHs (naphthalene, anthracene, chrysene, benzo[a]anthracene, dibenzo[ah]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene) for soils in built-up and urbanized areas is $1400 \mu\text{g}/\text{kg DM}$ (D.U. 1395, 2016)

to constant, direct, and, above all, close exposure to emission sources.

Global research focuses mainly on the accumulation and adsorption functions of tall plants in urban areas. Wang *et al.* (2010), Sæbø *et al.* (2012) and Liang *et al.* (2017) also drew attention to their possibilities of purifying urban air from aromatic hydrocarbon particles, e.g. in photolytic processes and soil phytoremediation. Terzaghi *et al.* (2013) report on the significant contribution of higher plants in filtering PAHs suspended in the urban ecosystem's gas phase by removing these particles from the atmosphere.

When analyzing the results of the research on the content of analytes in the soil (Table 3), it was found that the highest total concentration of 16 PAHs was recorded in the soil from the green belt located next to the complex of intersections at the Nicholas Copernicus Street, reaching the level of $2015.23 \mu\text{g}/\text{kg DM}$, which corresponds to the number of PAHs in places located near roads with heavy car traffic (Włóka and Smol, 2014). In the remaining soils, significantly lower concentrations were found, with the lowest value of their concentration reaching the level of $546.13 \mu\text{g}/\text{kg DM}$ at the Towarowa Street. According to Wydro *et al.* (2015), the average concentrations of 16 PAHs in the soils of Białystok in 2011–2012 ranged from 30 to $1000 \mu\text{g}/\text{kg DM}$ and they were dependent on the research plot location and seasonality. The values reported in the presented studies also turned out to be similar to the concentration of these pollutants in the downtown area of other Polish cities, characterized by low industrialization (Bielińska *et al.*, 2011; Maliszewska-Kordybach *et al.*, 2012). However, the content of individual PAHs differed significantly.

The content of benzo[a]pyrene in soil samples was much higher than in plants, and the dominance of this compound

was observed in almost every measurement location. In her report, Kozielska (2017) presents the dominant PAHs in soils from the adjacent areas of the city of Gliwice. According to the author, they are chrysene and fluoranthene. Their presence is associated with fuel combustion in car engines (Caricchia *et al.*, 1999). In the samples collected at the Nicholas Copernicus and the Zwierzyniecka Streets, a similar relationship was observed, respectively $249.11 \mu\text{g}/\text{kg DM}$ and $97.39 \mu\text{g}/\text{kg DM}$ for chrysene and $352.11 \mu\text{g}/\text{kg DM}$ and $145.27 \mu\text{g}/\text{kg DM}$ for fluoranthene. At the same time, increased content of 4 and 5-ring compounds from the studied group was found.

Moreover, in these locations, the compound with a significant share was benzo[b]fluoranthene, and at the Hetmańska Street, it turned out to be the dominant pollutant ($169.96 \mu\text{g}/\text{kg DM}$). The lowest concentration in the soil root layer was characteristic of the compounds with the lowest molecular weight, including acenaphthylene and acenaphthene in the lowest amounts. In most cases, at the level of $1 \mu\text{g}/\text{kg DM}$.

As Włóka and Smol (2014) report, the scale of soil contamination with organic pollutants is closely related to the location and method of land use. The highest PAH content was recorded in soils from industrial areas ($15\,227 \mu\text{g}/\text{kg DM}$) and those adjacent to routes with heavy road traffic ($1\,871\text{--}2\,092 \mu\text{g}/\text{kg DM}$).

Compared to large cities in Europe and Asia, PAH content in the studied soil from the city of Białystok is much lower. In Italian cities, the concentration value is as high as $7\,700 \mu\text{g}/\text{kg DM}$ (De Nicola *et al.*, 2014). Moreover, by comparison with the data described in the literature, the reported values were much higher for urban or industrialized areas and reached even tens of thousands of $\mu\text{g}/\text{kg DM}$ (Cachada *et al.*, 2012; Wang *et al.*, 2013).

The threshold value of the total content of 10 selected PAHs (naphthalene, anthracene, chrysene, benzo[a]anthracene, dibenzo[ah]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene) in the soil layer 0–0.25 m, defined by Polish legal regulations (Journal of Laws 1395, 2016) for soils in built-up and urbanized areas is 1 400 $\mu\text{g}/\text{kg}$ DM. The maximum concentration was exceeded at a single point only – at the Nicholas Copernicus Street. For areas of public and internal roads, areas of production facilities, warehouses, warehouses, and technical infrastructure, this value is much higher, as much as 200 000 $\mu\text{g}/\text{kg}$ DM. Thus, even at this test site, the soil does not qualify as highly contaminated.

During the test results analysis, the content of individual analytes in vegetation and soil, collected within one research area, was compared. The comparative analysis of the results presented in Table 3 shows that the concentration of naphthalene and fluorene in the grass and soil samples at all measurement points was very similar. Similar relationships of acenaphthylene, acenaphthene, and phenanthrene concentrations were also found in most locations. These compounds are characterized by water solubility at the level of 1.3–31.7 mg/L and therefore, they can be absorbed by plant roots and penetrate the aerial parts (Belykh, 2009). Due to the same properties, these compounds tend to penetrate deeper layers of the soil. Additionally, their high volatility determines transport over longer distances from the emission source, even before depositing on a solid surface.

On the other hand, the remaining PAHs with more than three condensed rings per molecule, were found in the soil in much greater amount. Due to their low mobility, it is determined by a high molecular weight, low vapor pressure and high lipophilicity (Prabhukumar and Pagilla, 2010). These compounds show low solubility in water (0.00026–0.26 mg/L) and a high affinity for solids. Therefore, unlike PAHs with two and three condensed rings, they are absorbed to a small extent by plants along with the soil solution. Thus, the PAHs adsorbed on the particles undergo dry and wet deposition on the surface of the aboveground parts of plants, which, washed by rains remain in the soil layers. They undergo very slow oxidative changes and biodegradation caused by environmental and microbiological factors (Dąbrowska *et al.*, 2002). The solubility of PAHs increases with colloidal organic fractions in soils, where occluded with surfactants are closed in micelles, showing increased hydrophilicity and affinity for the water phase (Prabhukumar and Pagilla, 2010).

Based on the cluster analysis, groups of research areas, similar due to the risk of contamination with PAHs of soils and grasses of the *Lolium perenne* L. species, were selected. On the dendrogram (Fig. 1) concerning the total PAH content in the tested grass samples, the measurement stations' groupings in Białystok are visible on the x-axis.

The conducted analysis allowed distinguishing three main groups of points. The first one is at the Hetmańska Street, the second at the Zwierzyniecka and the Nicholas

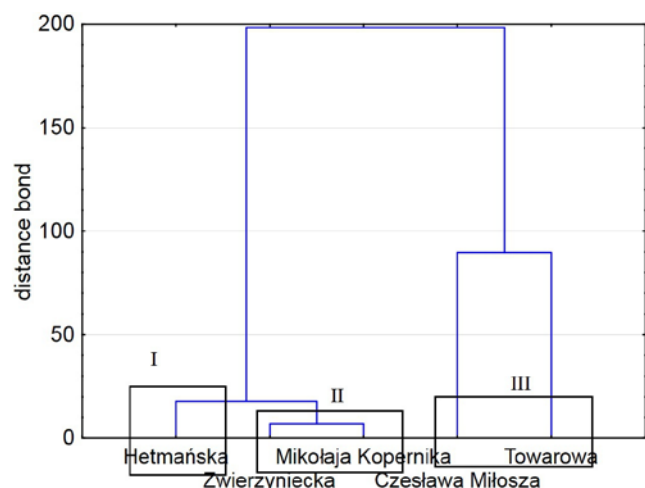


Fig. 1. Dendrogram for grouping test sites depending on the content of total PAHs in the tested samples of grasses of the *Lolium perenne* L. species (I, II, III – the numbers of the specified groups).

Copernicus Streets, and the third one is at the Czesław Miłosz and the Towarowa Streets. The applied classification allowed for identifying places in Białystok that are similar in terms of the impact of public transport and are characterized by a similar environment. The lowest total PAH content was found in grass samples collected from the vicinity of the Towarowa and the Czesław Miłosz Streets. These streets are connected by a crossroads and are characterized by a similar traffic volume, surroundings, and buildings. On the other hand, grass samples collected from the vicinity of the Zwierzyniecka and the Nicholas Copernicus Streets, i.e. the second group, separated based on cluster analysis, were characterized by the highest concentration of the total of 16 PAHs. These streets are adjacent to each other and are characterized by a similar intensity of traffic.

However, based on the cluster analysis performed for the total PAH content in the studied soils, other groups of research sites were distinguished. On the axis of the abscissa

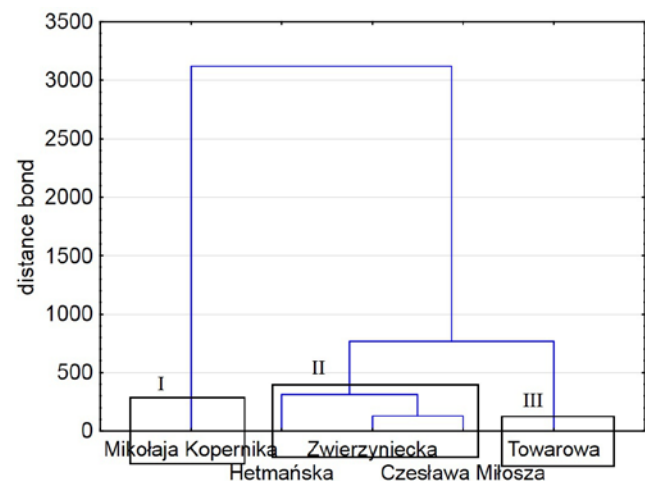


Fig. 2. Dendrogram for grouping test sites depending on the total PAH content in the tested soil samples (I, II, III – the numbers of the specified groups).

of the dendrogram (Fig. 2), groups of streets in Białystok with similar content of tested compounds are marked.

The soils near the Nicholas Copernicus Street had the highest content of the sum of 16 PAHs. The Hetmańska, Zwierzyniecka and Czesław Miłosz Streets formed the second group and were characterized by the tested compounds average content. On the other hand, the third group includes the Towarowa Street, with the lowest PAH content. The diversity of the occurrence of these compounds in grasses and soils may indicate the accumulation, mobility, and bioavailability of pollutants.

RECAPITULATION

Based on the research, it was found that car traffic can be a significant source of PAH. These compounds can be deposited in soil and aboveground parts of plants, in the analyzed case in grasses of *Lolium perenne* L. species.

Among the studied polycyclic aromatic hydrocarbons, benzo[a]pyrene, considered the most carcinogenic, was the most abundant in the analyzed grass and soil samples. Its content ranged from 53.80 to 91.74 $\mu\text{g}/\text{kg}$ DM in grasses, while from 65.11 to 268.62 $\mu\text{g}/\text{kg}$ DM in soils. The results showed that this compound is adsorbed on dust particles and can fall with them, among others, onto green areas. These observations are consistent with other authors' observations regarding the presence of benzo[a]pyrene in the urban environment and constitute an important premise for taking actions aimed at introducing restrictions and systems to prevent pollution.

Considering the spatial differentiation of PAH content in Białystok, the highest concentration of the total of 16 PAHs was observed in the samples of the tested soils and grasses near the Nicholas Copernicus Street, while the lowest at the Towarowa Street. It is because the Nicholas Copernicus Street is among the most important communication routes, connecting two parts of the city. There are uninhabited warehouse areas in the immediate vicinity, car workshops, allotments and the railway plant area. The area at the Towarowa Street belongs to the verge part of the city. On the one hand, it is characterized by a cluster of multi-family housing, while on the other hand undeveloped plots of land and meadows. Therefore, it can be concluded that the content of PAHs in soil and aboveground parts of plants in the city is related to the location, nature of the surroundings, and traffic intensity. The results obtained in these studies are consistent with the model of PAH distribution with city aerosol. The high content of 5-ring analytes is associated with constant, direct, and, above all, close exposure to emission sources.

The conducted research confirmed other authors' observations that the amount of soil and plant contamination with organic pollutants is closely related to the location and method of land use. Summing up, it can be stated that monitoring of pollution with PAHs in various components of the environment, especially in urban areas, will allow taking appropriate measures to improve the environment's quality and thus prevent its degradation.

CONCLUSIONS

Based on the research, it was found that:

1. Benzo[a]pyrene was present in the highest amount of the tested PAHs in the analyzed grass and soil samples. On the other hand, acenaphthylene, acenaphthene and anthracene were the lowest in all analyzed samples.
2. Analyzing the spatial differentiation of PAH content in the soils and grasses of Białystok, along the most important streets, it was found that the vicinity of the Mikołaja Kopernika Street was the most contaminated with the tested compounds.
3. PAHs can be deposited in soil and above-ground parts of plants, and their content in these environmental components depends, inter alia, on the location conditions, that is the environment, buildings and traffic intensity.

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