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Original Research

Concentration of Polycyclic Aromatic Hydrocarbons in Surface Horizons of Soils in Immediate Neighbourhood of Illegal Waste Dumps

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Abstract

The objective of the study was to determine the concentration of polycyclic aromatic hydrocarbons in soils in the immediate neighbourhood of illegal waste dumps and to determine the mutual relations among the particular PAHs as well as the relations between PAH and humus of a group of soils with natural and anthropogenically increased content of those compounds.

Soil samples for the determinations were taken in the immediate neighbourhood of illegal dumping grounds of municipal wastes and materials that are predominantly construction materials. The collected soil material was used to determine the grain size composition of the soils, their reaction, content of organic matter and of polycyclic aromatic hydrocarbons with the method of high-efficiency liquid chromatography with fluorescence detection.

The study revealed numerous instances of exceeding standard levels of individual PAHs as well as of their total content. Application of statistical analysis of concentrations permitted the division of the objects studied into two groups differing notably in the level of individual PAHs as well as in their total concentration. In the group of objects that were classified as non-contaminated, the existence of positive, statistically significant correlation was found between the total concentration of PAHs and the content of humus compounds, while in the group of contaminated objects the correlation was statistically non-significant.

Keywords: polycyclic aromatic hydrocarbons, pollution of soils, anthropogenic factors, dumping ground

Introduction

Polycyclic aromatic hydrocarbons (PAH) constitute a large group of compounds that contains from two to several or even over a dozen aromatic rings in the molecule. The compounds have various structural forms characterized by various positioning of benzene rings relative to one another.

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Polycylic aromatic hydrocarbons occurring in the environment originate mainly from anthropogenic sources, which is confirmed by scientific research conducted in different places of the world [1-4] and in Poland [5-7]. Amounts of PAH that originate from natural sources and constitute a "natural background" are slight compared to those introduced in the environment by man. The primary sources of PAH are the combustion of coal, wood and gas for heating, burning of wastes and refuse, forest fires, and industrial processes, such as the production of aluminium and coke. Other significant sources of PAH include hard coal mining, catalytic processing of petroleum, production of asphalt, emissions from the metallurgical industry, the wear of automobile tires, exhaust from aircraft and ship engines, and tobacco smoke. Approximately 98% of the natural and anthropogenic emission of PAHs is released directly to the atmosphere, and the remainder goes to the waters and to the soil [8-11]. Direction of PAH transformations in wastes depends on their type and composition, and the presence of add-on substances (e.g. solvents) [12, 13].

The most important processes to which PAH are subject in soil are adsorption and biodegradation [7]. Due to their low vapour pressure, low solubility and tendency to be bound by organic matter, PAHs accumulated in soil are almost wholly adsorbed by soil particles. Desorption from the soil to ground waters and to air is minimal, though limited leaching of B(a)P to ground waters may take place, especially in the presence of organic solvents. Sorption of PAH by the soil and sediments increases with increasing content of organic matter, and is also directly related to the grain size composition of the soil [2, 6, 14-18].

According to various literature reports [14, 19, 20], the half-life of PAHs in soil (time after which half of the initial PAH amount will undergo degradation) is from around a dozen to several hundred days. Other authors have reported half-lives at the level of several years [21]. It also depends on solubility in water and the number of rings [6].

Adsorption and leaching of PAHs from the soil are complex processes that depend on numerous variables, such as soil type, soil moisture, the presence of molecules of other soluble compounds, solvents, and finally pH soil. Equilibrium in the processes of PAH sorption by soils and sediments is usually attained after approximately 24 hours. Adsorption by soil particles may limit the availability of PAH for the processes of biological and chemical degradation. The presence of organic solvents may increase the bioavailability of PAH and their uptake by plants. PAH leaching together with the colloidal fraction of soil and rapid migration with water flowing through macro-pores reduces the content of those compounds in soil to only a slight degree.

The primary process that leads to reduction of the content of those compounds in soil is biodegradation. It can be performed by bacteria, fungi, plants, and even – to a lesser extent – by higher animals [22]. The rate of microbiological degradation of PAH is slow, and they can be considered to be permanent contaminants of the soil. Biodegradation of PAH may be limited in regions of occurrence of other contaminants that are toxic to micro-organisms [23-25].

Photochemical reactions leading to the degradation of PAH can take place only in the surface layer of soil, with depth of maximum 1 mm. Volatilization applies only to PAH fraction not bound with soil particles, and experiments show that the amount of PAH volatilizing from soil is negligibly small.

Regulations adopted in the world concerning the acceptable levels of PAH in soils and sediments reflect a lack of uniform views on the hazard paths and migration of the compounds in the environment. Usually, direct consumption of soil and inhalation of PAH-contaminated soil dusts is considered to be the most hazardous to man. Further down the scale is the threat to ground waters, and then to sources of drinking water. Practically all of the regulations totally neglect the threats related to potential consumption of plants uptaking PAH [15, 18, 25].

The objective of the study was to determine the concentration of polycylic aromatic hydrocarbons in soils in

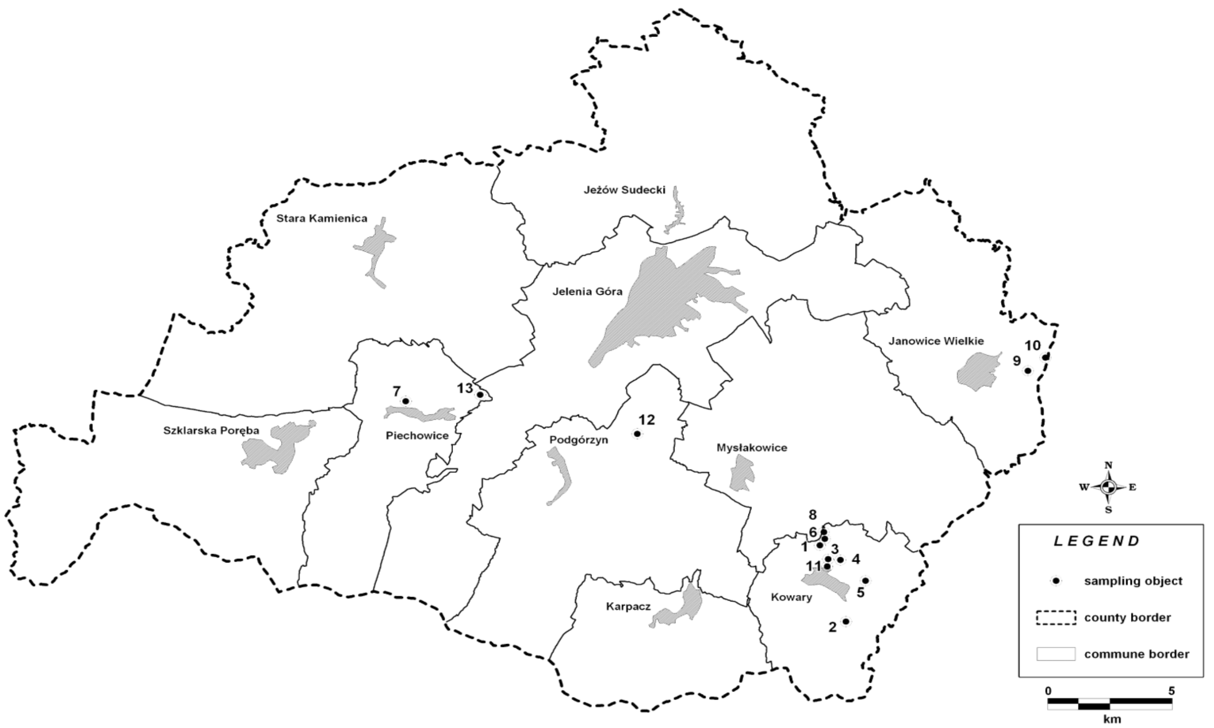

Fig. 1. Localization of analyzed objects.

the vicinity of illegal waste dumps and to identify the mutual relations among the individual PAHs as well as the relationship between PAHs and humus in a group of soils with natural and anthropogenically increased concentrations of those compounds.

Materials and Methods

The illegal waste dumps selected for the study were located in the area of the district of Jelenia Góra, in the communes of Kowary (8 objects), Janowice Wielkie (2 objects), Piechowice (2 objects) and Podgórzyn (1 object). Most of the objects were accessible from local roads or housing estate streets, which facilitated illegal dumping of municipal wastes as well as of rubble and construction site refuse (Fig. 1).

In terms of the accumulated wastes, the objects can be classified in two principal groups: dumps with dominance of household wastes, and dumps with predominance of rubble and construction materials.

Objects Nos. 2, 3, 4, 5, 6 and 13 can be classified in the first group, while those marked as Nos. 1, 7, 8, 9, 10, 11 and 12 are in the second (Table 1).

Wastes characteristic for objects classified in group I included plastic foil, PET bottles, plastic containers from food products, metal elements, metallic foils, paper, bitumic roofing paper, glass bottles, elements of light bulbs and fluorescent tubes, plastic packing from construction materials, medicine packing and wrappings.

Wastes found in objects classified in group II included ceramic construction materials, stone, roofing paper, remnants of mortar, foamed concrete, foamed polystyrene, PVC bags, fragments of concrete and asphalt – both in the form of larger lumps and of aggregate fragmented in the course of road surface milling.

Also varied were the amounts of wastes accumulated at the individual dumping grounds. The objects with clear predominance of household wastes contained a notably lower amount of waste – from 10 to 10^2 m^3, while at the dumping sites with a predominance of construction materials the amounts of wastes were in the order of 10^2-10^3 m^3. The highest amounts of construction refuse were found in objects Nos. 11 and 12.

Soil samples for analyses were taken in the immediate vicinity of illegal waste dumps, but from soil areas not covered with wastes. The samples were taken by means of a soil corer, from a depth of 0-20 cm. Depth 0 is interpreted as an upper border of mineral horizons. Averaged sample for each sampling point was obtained by mixing 5 soil cores. The soil cores were taken at points located in the centre and on the perimeter of a circle with 2 m diameter. An analogous procedure was used to collect soil samples for the determination of PAHs, the only difference being that those samples were placed in air-tight glass jars and put in a refrigerator immediately upon arrival at the laboratory. The number of samples taken from the individual objects was from 3 to 6.

The soil material collected was used for the following determinations:

- soil texture – with the areometer-sieve method acc. to standard PN-ISO 11277 [27],
- soil reaction: pH in water and in 1M KCl – with the potentiometric method acc. to PN-ISO 10390 [28],
- organic carbon content – wet oxidation method with external heating, followed by titration with ferrous ammonium sulfate,
- polycyclic aromatic hydrocarbons were assayed acc. to the "soil quality" standard. Polycyclic aromatic hydrocarbons, i.e. naphthalene, anthracene, phenanthrene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a)anthracene, benzo(g,h,i)perylene, and fluoranthene – were assayed with the method of high-efficiency liquid chromatography with fluorescence detection acc. to standard PN-ISO 13877 [29]. The analysis was made with the use of a Varian ProStar apparatus equipped with PDA detector and HPLC column RP-C18 Chromosep SS 250 mm, ϕ 4.6 mm. The volume of injection was 20 µl, the flow rate 0.8 $cm^3 \cdot min^{-1}$.
- Data evaluation has been made with the use of Statistica 8.0. The assignment of the object into subsets similar in the sense of contamination with PAH was made with the use of k-means clustering. The relations between the variables and the prediction of variables was analyzed with the use of regression analysis.

Results and Discussion

The soil formations under study, with interpretation based on PN-ISO-11277 [30], were classified in the following textural groups (Fig. 2):

- loamy sand – 1 sample,
- loamy sand (skeleton content) – 5 samples,
- sandy loam – 5 samples,
- sandy loam (skeleton content) – 16 samples,
- loam (skeleton content) – 1 sample,
- sandy silt – 10 samples,
- sandy silt (skeleton content) – 8 samples.

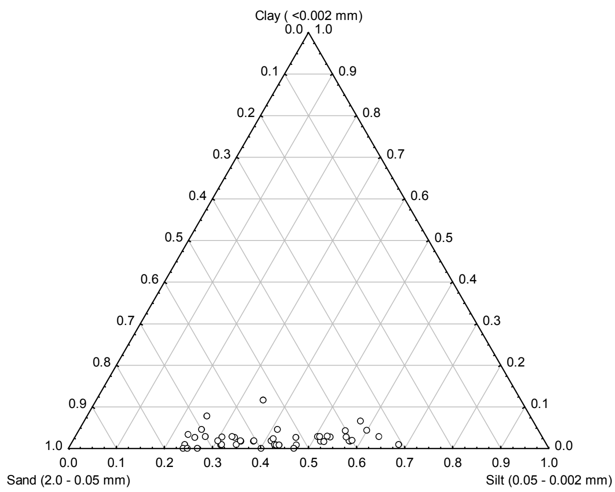

Fig. 2. Granulometric composition of examined soils according to PN –R-04033/1998.

Table 1. Concentration of PAHs in soil samples.

No.	Commune	Object	Concentration of PAH [mg·kg⁻¹] Naphtalene	Phenantrene	Antracene	Fluorantene	Benzo(a) antracene	Chrysene	Benzo(k) fluorantene	Benzo(a) pyrene	Benzo(g,h,i) perylene	Sum of 9 PAH
Intervention level for areas of group A (0-30 cm)			0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.02	0.1	1
Intervention level for areas of group B (0-30 cm)			0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.03	0.1	1
Intervention level for areas of group C (0-30 cm)			50	50	50	50	50	50	50	50	50	250
1	Kowary	Kowary – park	0.001	0.001	0.001	0.004	0.007	0.002	0.002	0.002	0.008	0.028
2			0.019	0.003	0.001	0.021	0.039	0.006	0.016	0.014	0.041	0.160
3			0.015	0.008	0.006	0.142	0.104	0.019	0.101	0.107	0.098	0.600
4		Wiejska Street (meadow)	0.001	0.007	0.001	0.039	0.021	0.022	0.064	0.047	0.149	0.351
5			0.009	0.052	0.013	0.181	0.137	0.076	0.089	0.099	0.185	0.841
6			0.006	0.008	0.001	0.031	0.039	0.012	0.020	0.016	0.057	0.190
7		Kowary – settlement (waste dump meadow)	0.001	0.011	0.004	0.036	0.077	0.033	0.029	0.029	0.100	0.320
8			0.001	0.005	0.001	0.026	0.086	0.010	0.013	0.012	0.058	0.212
9			0.001	0.007	0.001	0.072	0.225	0.029	0.115	0.134	0.313	0.897
10		Kamienno górska Street (waste dump arable lands)	0.011	0.016	0.002	0.062	0.146	0.030	0.091	0.071	0.199	0.628
11			0.001	0.017	0.003	0.077	0.130	0.035	0.105	0.079	0.197	0.644
12			0.001	0.011	0.002	0.051	0.053	0.023	0.069	0.051	0.087	0.348
13		Rejtana Street (waste dump arable lands)	0.001	0.004	0.004	0.020	0.010	0.012	0.015	0.047	0.142	0.255
14			0.004	0.009	0.002	0.060	0.552	0.037	0.114	0.106	0.367	1.251
15			0.003	0.007	0.001	0.040	0.093	0.021	0.036	0.038	0.095	0.334
16		Sanatoryjna Street (waste dump)	0.001	0.016	0.003	0.113	0.217	0.070	0.135	0.160	0.453	1.168
17			0.001	0.003	0.001	0.011	0.029	0.008	0.021	0.021	0.056	0.151
18			0.001	0.025	0.002	0.147	0.314	0.088	0.231	0.233	0.732	1.773
19	Piechowice	Piastowska Street (waste dump)	0.011	0.013	0.003	0.076	0.058	0.043	0.081	0.063	0.141	0.489
20			0.040	0.094	0.008	0.374	0.111	0.033	0.108	0.088	0.178	1.034
21			0.022	0.066	0.007	0.269	0.349	0.087	0.109	0.08	0.128	1.117
22			0.096	0.086	0.018	0.599	0.326	0.259	0.278	0.288	0.805	2.755
23	Kowary	Wojków – settlement (forest)	0.001	0.014	0.002	0.046	0.141	0.031	0.174	0.139	0.549	1.097
24			0.001	0.021	0.006	0.122	0.101	0.058	0.139	0.151	0.159	0.758
25			0.042	0.105	0.273	0.546	0.567	0.325	1.428	0.716	2.583	6.585
26			0.061	0.380	0.093	1.276	1.108	0.575	0.812	0.686	1.450	6.441
27	Janowice Wielkie	Miedzianka (meadow)	0.049	0.077	0.013	0.658	0.230	0.155	0.179	0.148	0.327	1.836
28			0.043	0.127	0.014	0.405	0.171	0.122	0.131	0.114	0.265	1.392
29			0.131	0.870	0.154	3.148	1.689	0.819	0.819	0.947	1.715	10.29
30		Janowice Wielkie – village (waste dump)	0.06	0.202	0.068	0.661	0.823	0.187	0.194	0.507	0.499	3.201
31			0.099	0.099	0.026	0.469	0.557	0.189	0.491	0.240	0.442	2.612
32			0.077	0.068	0.016	0.024	0.148	0.074	0.105	0.086	0.169	0.767
33			0.118	0.218	0.036	0.879	0.481	0.308	0.453	0.317	0.698	3.508
34			0.091	0.815	0.176	3.200	1.971	1.040	1.691	1.326	3.181	13.49
35			0.308	0.729	0.115	2.826	1.562	0.982	1.458	1.048	2.573	11.60

Table 1. Continued.

No.	Commune	Object	Concentration of PAH [mg·kg^{-1}]									
			Naphtalene	Phenantrene	Antracene	Fluorantene	Benzo(a) antracene	Chrysene	Benzo(k) fluorantene	Benzo(a) pyrene	Benzo(g,h,i) perylene	Sum of 9 PAH
36	Kowary	Supermarket Albert (lawns)	0.436	2.652	0.124	2.780	2.820	2.158	2.836	3.285	7.447	24.53
37			0.078	0.22	0.018	1.001	0.830	0.219	0.727	0.866	2.088	6.047
38			0.029	0.042	0.027	0.133	0.316	0.095	0.130	0.141	0.279	1.192
39	Podgórzyn	Staniszów (forest)	0.972	5.125	1.305	15.18	12.12	4.935	4.769	4.769	10.42	59.59
40			0.017	0.095	0.016	0.283	0.318	0.096	0.108	0.040	0.039	1.012
41			0.185	1.389	0.259	5.156	3.952	1.815	0.389	1.741	3.766	18.65
42			0.091	0.322	0.066	1.379	0.903	0.438	0.490	0.335	1.032	5.056
43	Piechowice	Pakoszów (waste dump forest)	6.770	22.01	3.697	52.22	28.86	15.83	15.67	12.04	25.59	182.6
44			0.302	1.062	0.183	5.031	2.983	1.931	2.613	2.671	5.265	22.04
45			0.110	0.531	0.118	1.991	1.230	0.659	0.869	0.884	1.965	8.357
46			2.754	2.862	1.404	14.40	11.07	6.750	10.69	10.42	17.06	77.41

The soils were characterized by varied content of skeleton fractions which, according to the Standard, contain soil particles with equivalent diameters greater than 2 mm. Among the 46 samples analyzed, 29 belonged to the group of skeletal soils – their content of skeleton fractions was greater than 5%. For all the soil samples examined, the content of those fractions fell within the range of 0 to 24%. The median of skeleton fraction content was 7%, and the value of the 3rd quartile was 9%.

The content of clay fraction (<0.002 mm) in all soil samples varied within the range 0 to 11.6%. Median of clay fraction content was 1.9%, and the value of the 3rd quartile was 2.8%.

The content of silt fractions (0.05-0.002 mm) was notably higher, and for all the samples under analysis varied within the range 23.3% to 68.3%. Median of silt fraction content was 41.3%, and the value of the 3rd quartile was 51.5%.

The highest share in the soil formations under study was that of sand fractions (2.0-0.05 mm), which fell within the range from 30.8% to 76.1%. Median of sand fraction content was 56.5 mm, and the value of the 3rd quartile was 67.5%.

The shares of the particular sand fractions were fairly uniform. The median values were 13% for very coarse sand, 10.5% for coarse sand, 10.0 for medium grained sand, 12.2 for small grained sand and 8.5% for very fine sand.

Analysis of the texture of the soil samples revealed a lack of systematic differences in grain size composition among the individual sites.

For the soil samples analyzed, soil pH values measured in 1M KCl varied within the range from pH 3.4 to pH 7.9. Median of pH values was 5.0, and the value of the 3rd quartile was 5.8. In terms of soil reaction classification, at 15 of the studied sites strongly acid reaction was found, at 17 acid reaction, at 10 – slight acid reaction, at 2 – neutral reaction, and at another 2 – alkaline reaction. The share of acid and strongly acid soils was 69.6% and thus it was somewhat lower than the average for the district Jelenia Góra of 85.6% [28].

Evaluating the individual objects, one can observe increased pH vales in the object Pakoszów, where they varied within the range from 6.8 to 7.9. The median value of pH measured in 1 M KCl for that object was 7.2, while for all the remaining sites it fell within the range 4.0 to 6.1. The higher pH values for that site should be attributed to fresh construction wastes being dumped there. Samples collected in the region of waste dump in the woods near the Wojków housing estate had acid reaction (1 sample) and slightly acid (3 samples), with median value of pH at 6.1. At the same time, soil samples collected from plot No. 148/1 near the village of Miedzianka showed strongly acid reaction (all 3 samples), while those collected from plots No. 27 and 28/1 near the locality of Janowice Wielkie – strongly acid reaction (2 samples) and acid reaction (4 samples). The acid and strongly acid soil reaction at those objects may, unfortunately, be a factor contributing to the mobilization of heavy metals.

PAH Concentration

The objects studied were characterized by highly varied PAH concentration in soils in the immediate vicinity of the illegal waste dumps. The mean levels of 4 out of 9 PAH under analysis, as well as the minimum and maximum PAH concentrations in the individual objects, are presented graphically in Figs. 3a-b. A logarithmic scale was applied on the vertical axis, due to the strong differentiation among the individual objects as well as within the objects. The objects were arranged according to increasing concentration of the particular PAH. For all PAH studied, the highest concentrations were found in the object at Pakoszów, where the mean concentration of benzo(a)pyrene was 6.5 mg·kg^{-1}, and the maximum was 12.0 mg·kg^{-1}. That object was also characterized by high concentrations of the remaining PAH (Figs. 3a-b). The highest concentration of a single PAH was 52.2 mg·kg^{-1} in the case of chrysene. The mean concentration of total PAH at the Pakoszów object was 72.6 mg·kg^{-1}. Therefore, it was higher than the "intervention level" for the sum of PAH, defined for "standard soil" (10% organic matter, 25% clay) at the "new Dutch list" which specifies the value of 40 mg·kg^{-1} for total PAH content (Fig. 4) [31]. As an example the chromatograph for sample number 43 is shown in Fig. 5.

The calculated sum of PAH contained 8 out of the 9 PAHs included in the "new Dutch list" [31]; plus anthracene instead of indeno(1,2,3-c,d)pyrene. The reason for soil contamination by PAHs in the Pakoszów object is the illegal dumping of large amounts of fragmented asphalt remaining after road surface milling during road repair/resurfacing.

The second-ranking object in terms of soil contamination with PAH was the region of the village of Staniszów, or more specifically the illegal waste dump in the woods near that village. The highest concentration of an individual PAH found in that object was 12.1 mg·kg^{-1} in the case of benzo(a)anthracene. The mean of concentration of total PAH in the Staniszów object was 21.1 mg·kg^{-1}, i.e. it did not exceed the intervention level from the "new Dutch list" [31]. However, that level was exceeded in one of the samples taken at that object, in which the total PAH concentration was 59.6 mg·kg^{-1}. As can be seen in Figs. 2a-b and 4, successively decreasing concentrations of PAH were recorded in the objects: Supermarket-Albert, Janowice Wielkie – waste dump, Janowice Wielkie – village, Piechowice, Sanatoryjna Street, Kamienngórska Str., Rejtana Str., Kowary – settlement, Wiejska Str., and Kowary – park.

Applying the method of k-means for the content of the 9 PAHs under determination, the above objects can be grouped as follows. With a division into two homogeneous clusters, the object of Pakoszów should be treated as one, while the other would include all other objects. With a division into three clusters, two single-element ones would be those of the objects Pakoszów and Staniszów, while the third would include all remaining objects. Only a division into four cluster groups permits us to obtain of a separate group of non-contaminated objects, or with a slight level of contamination, which would then include the objects of Sanatoryjna Str., Kamienngórska Str., Rejtana Str., Kowary - settlement, Wiejska Str. and Kowary - park. The mean content of 9 PAHs in that group was 0.56 mg·kg^{-1}, the maximum value was 1.77 mg·kg^{-1}, and the minimum 0.15 mg·kg^{-1}. Therefore, in that group the mean concentration of total PAHs was below the reference level. For comparison we can state that the sum of 15 PAHs at the samples collected from areas of human impact of Central Spitzbergen was lower than 0.50 mg·kg^{-1} [3].

The second group, composed of three assemblages, included the objects of Pakoszów, Staniszów, Supermarket-Albert, Janowice Wielkie – waste dump, Janowice Wielkie – village and Piechowice. Those can be considered as objects with increased PAH levels or even as objects contaminated with those substances. In that group the mean total PAH concentration was 16.98 mg·kg^{-1}, the maximum was 182.69 mg·kg^{-1}, and the minimum – 0.76 mg·kg^{-1}.

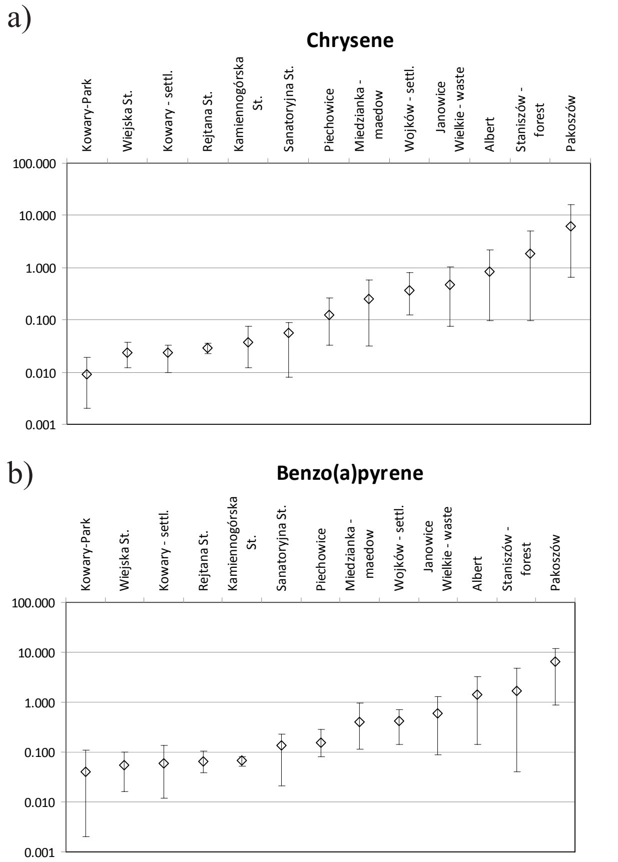

Fig. 3. The mean and range of a) chrysene, and b) benzo(a)pyrene concentration at the individual objects.

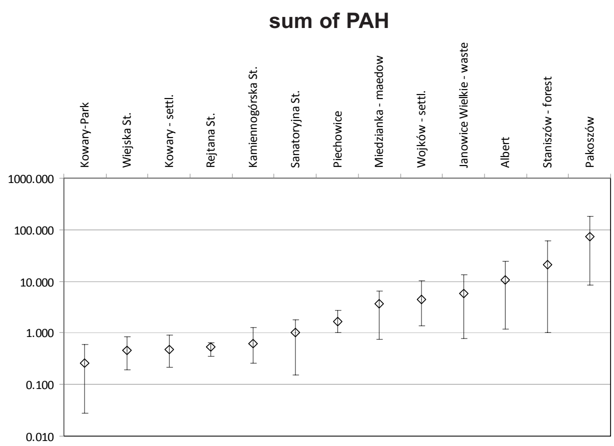

Fig. 4. The mean value and range of sum of 9 PAH concentrations at the individual objects [mg·kg^{-1}].

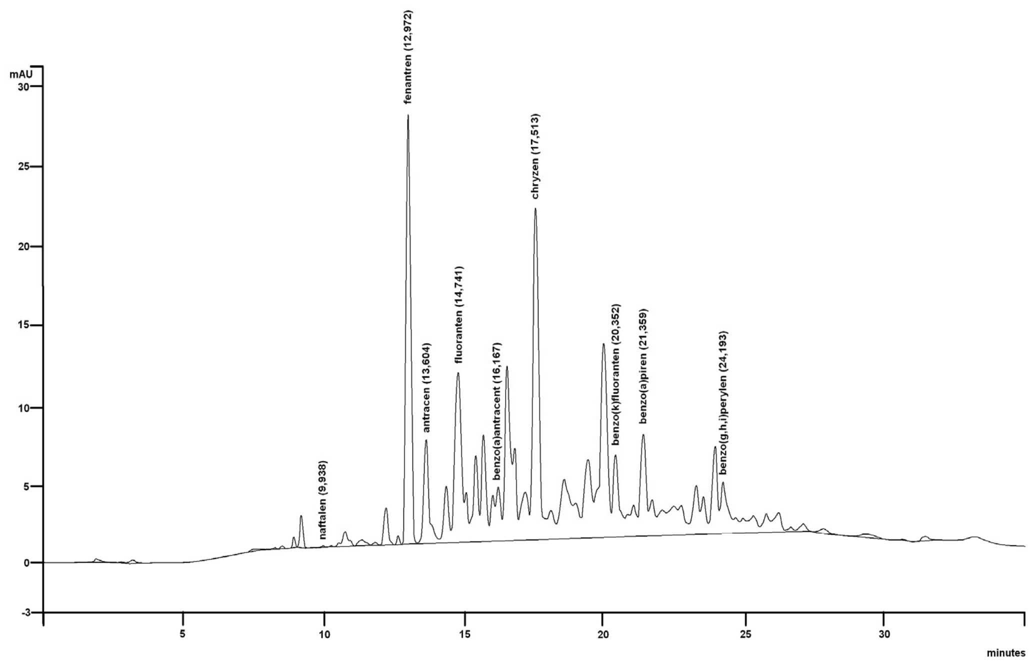

Fig. 5. The example of chromatograph for the sample most polluted with WWA (number 43 - Pakoszów).

In the first of the groups specified, more than 90% of the results did not exceed the value of 0.9 mg·kg^{-1}, while in the second group 90% of results exceeded that value.

A summative concentration of 9 measured PAHs at the most contaminated objects Pakoszów and Staniszów, was at the same level of those obtained for Poznań urban areas [7]. The similar maximum level of sum for 20 PAH concentrations was reported for 11 urban topsoils by Krauss and Wilcke [9].

A characteristic feature is the difference in the relations between the concentrations of total PAH and of organic matter in soils of the two groups under discussion. For the first group (objects not contaminated with PAH) there is a notable statistically significant positive correlation between organic matter content and total PAH concentration in the soils. The correlation coefficient for that group was 0.6893, and the correlation was significant at the level of p=0.0004 (Fig. 6a). Similar relation for grassland soils with concentration of 20 PAHs varied from 0.063 to 0.321 mg·kg^{-1} was reported by Wilcke and Amelung [2]. For the group of contaminated objects, that correlation was not statistically significant (Fig. 6b). The situation is similar if we consider the particular PAH individually. Examples of graphs for benzo(a)pyrene are given in Fig. 7a-b. This supports the natural origin of PAH, related with humus substances, in the first group, and anthropogenic origin of PAH in the second group.

The thesis of anthropogenic origin of PAH in some of the objects under study is also supported by the character of statistical distribution.

To determine the character of PAH distribution, it was analyzed using the chi-square test. Based on the chi-square test at the level of p > 0.1, it was found that there were no grounds for rejection of the hypothesis of normal distribution of values of logarithm for the concentration of 8 PAH out of the 9 under analysis. The existence of a numerous fraction of results at the level of detection threshold caused that statistically there were grounds for the rejection of that hypothesis only in the case of naphthalene.

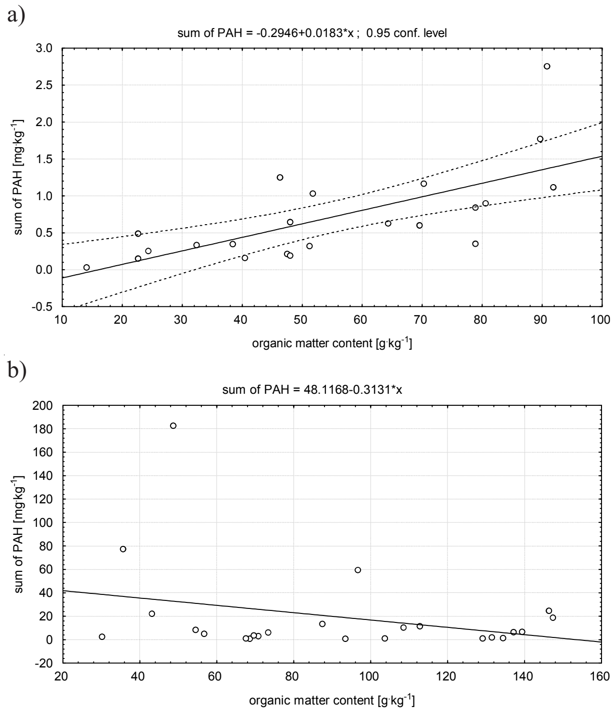

Fig. 6. a) Relation between organic matter content and the concentration of sum of PAHs in the examined soils from unpolluted sites (r = 0.6893; p = 0.0004).
b) Relation between organic matter content and the concentration of sum of PAHs in the examined soils from polluted and strongly polluted sites (r = -0.2971; p = 0.1585).

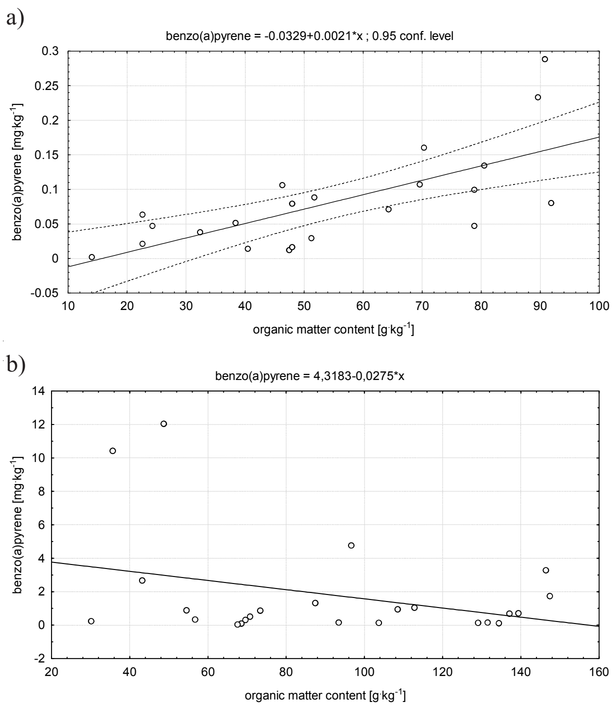

Fig. 7. a) Relation between organic matter content and the concentration of benzo(a)pyrene in the examined soils from unpolluted sites (r = 0.6984; p = 0.0003).
b) Relation between organic matter content and the concentration of benzo(a)pyrene in the examined soils from polluted and strongly polluted sites (r = -0.3288; p = 0.1167).

Associated Occurrence of PAHs

The results of our study support literature reports on the occurrence of polycyclic aromatic hydrocarbons in mixtures with specific proportions [8, 32]. The presence of one of those compounds practically guarantees the occurrence of the other ones. Benzo(a)pyrene, characterized by considerable carcinogenic properties, is considered to be the indicator of that group of compounds. The study demonstrated that although the concentration of chrysene correlates with total PAH at correlation coefficient $r = 0.9996$ (Fig. 8a), the coefficient of correlation between the concentration of benzo(a)pyrene and the sum of 9 PAH is 0.9483 (Fig. 8b). In principle, it is possible to calculate the concentration of total PAH on the basis of measurements of the concentration of e.g. chrysene with the standard error of estimation – 0.9023 (Fig. 8a), or benzo(a)pyrene with the standard error of estimation – 9.5633 (Fig. 8b). The results obtained indicate that for the main 6 PAH the error resulting from the application of such a procedure will still be at an acceptable level.

In view of the lognormal distribution of the concentration of individual PAHs and of their sum, it is justified to find the relations for logarithm from the concentration of total PAH and logarithm of chrysene (standard error 1.4196) (Fig. 9a) and logarithm of benzo(a)pyrene (standard error 1.3809) (Fig. 9b).

Such close relations between the levels of the individual PAH in soils indicate that the approach presented in the new Dutch list" [31], where the "reference value" and the "intervention value" are given for the sum of 9 PAH, is correct. It should be emphasized, however that the "intervention" value from the Dutch list is 40 times greater than the standard value for arable soils (class B soils) defined in the decree of the Ministry of Environment that has to be observed in Poland [33].

At the same time, one tends to conclude that in view of the very close correlations between the levels of the individual PAH in soils it is possible to estimate, with sufficiently good approximation, the total concentration of those compounds on the basis of determination of the concentration of one of them. The authors are aware that this will require considerable extension of the database on he basis of which such a regression equation would be formulated. Nevertheless, the results presented here indicate that such an attempt would be fully justified.

Conclusions

Based on the study and on the statistical analysis of results, it is possible to formulate the following conclusions:

1. In soils immediately adjacent to illegal waste dumps numerous instances were found for exceeding the standards for the levels of individual PAH, as well as for

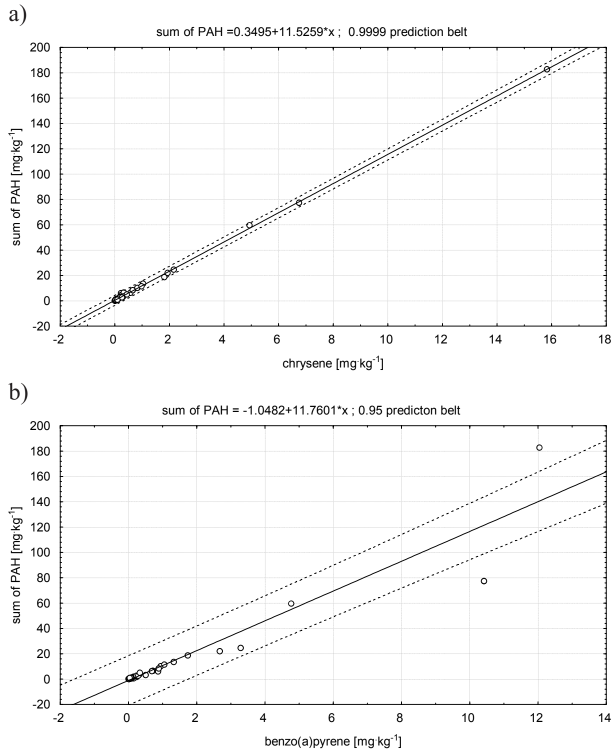

Fig. 8. a) Relation between the concentration of chrysene and the of sum of PAH in the examined soils (complete set of sites) (r = 0.9996; p < 0.0001).
b) Relation between the concentration of benzo(a)pyrene and sum of PAH in the examined soils (complete set of sites) (r = 0.9483; p < 0.0001).

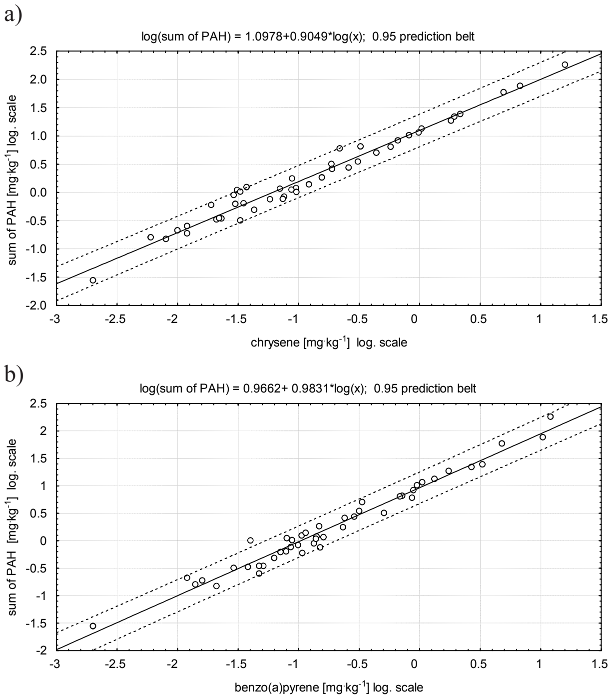

Fig. 9. a) Relation between the chrysene concentration an the sum of PAH in the examined soils (complete set of sites) ($r = 0.9846$; $p < 0.0001$). Both axis in the logarithmic scale.
b) Relation between the benzo(a)pyrene concentration and the sum of PAH in the examined soils (complete set of sites) ($r = 0.9846$; $p < 0.0001$). Both axis in the logarithmic scale.

their total concentration, as defined in the decree of the Polish Ministry of the Environment for arable soils (group B).

2. In one of the objects studied (Pakoszów), where wastes originating from the milling of road surfaces in the course of repair/resurfacing are accumulated, it was found that the PAH levels exceeded the intervention value specified in the "new Dutch list" as well as the standard defined in the decree of the Polish Ministry of Environment for industrial soil (group C).
3. The application of statistical cluster analysis permitted the classification of the objects studied into two groups differing considerably in the levels of individual PAH and of their total concentration. The first group, which can be considered as that of objects not contaminated, included 6 out of the 13 objects studied, while the group that should be considered as that of contaminated objects – 7 out of 13 objects.
4. In the group of non-contaminated objects (in which the content of total PAH remained at levels below 1 mg/kg), the existence of a positive, statistically significant correlation between the concentration of total PAH and the content of humus compounds was found, while in the group of contaminated objects (where total PAH concentration significantly exceeded the level of 1 mg/kg) the correlation was not statistically significant. This justifies the conclusion that in the case of the non-contaminated objects, where total PAH concentration is less than 1 mg/kg, we are dealing with PAH of natural origin, bound with humus compounds, while in the case of the group of contaminated objects there is a notable predominance of PAH of anthropogenic origin, not bound with the soil humus.
5. It was found that the PAH compounds under study occur in soils at almost constant proportions, and thus it is possible to estimate the total concentration of PAH on the basis of determination of one of them, using regression equations in the form of linear or power function for chrysene or for benzo(a)pyrene.

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