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Original Research

The Concentration of Polycyclic Aromatic Hydrocarbons in Sewage Sludge in Relation to the Amount and Origin of Purified Sewage

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Abstract

The present study included an evaluation of the content of 16 PAH in sewage sludge produced in 15 sewage treatment plants in southeastern Poland. Besides determining PAH content, the influence of the amount and origin of the sewage purified in the PAH content was also evaluated. Possible PAH sources in sewage were also evaluated by the calculations of the mutual relations.

The results obtained showed a clear differentiation in the content of polycyclic aromatic hydrocarbons. The content of the PAH sum ranged from 2039.9 to 36439.8 μg/kg. The predominant contribution of 3 and 4-ring PAHs was observed. A significant relation was only found in the case of properties of the sludge purified and the PAH content (-0.547, at P=0.05). Evaluating relations between individual PAHs, a statistically significant relation was observed between the sum of the PAHs determined and the content of fluoranthene, chrysene and benzo[b]fluoranthene.

Keywords: polycyclic aromatic hydrocarbons, sewage sludge, persistent organic pollutants, organic contaminants

Introduction

The commercial activities and the biological functions of human beings introduce a certain amount of waste into the natural environment. With an increase in living standards and the development of technology, their amount increases continuously [1]. One of the problem waste products resulting from humans is sewage sludge [2]. In literature, many methods for utilizing sewage sludge can be found; however, it is generally thought the most economically and ecologically justified utilization is the agricultural use of sewage sludge. Some properties of sewage sludge such as the high content of organic matter and nutrients make this waste a valuable and cheap source of fertilizer [3]. It can also be used in depleted areas for the reconstruction of damaged soil cover [4].

Sewage sludge is a mixture of broken down organic and inorganic matter which is a specific collection matrix for toxins that can be used as the basis for the evaluation of the degree of environmental pollution by harmful substances [5]. Numerous studies [6-9] have proven that sewage sludge can contain heavy metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins and furans, etc., which frequently occur at very high concentration levels. This can limit the use of sewage sludge as a fertilizer. Even though in Poland the problem of sewage sludge contamination with heavy metals was noticed some time ago, the problem of organic pollutants in sludge is at the preliminary study stage.

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Table 1. Characteristics of sewage treatment plants.

Code	Number of inhabitants	Amount of sewage treated (m^3/d)	Participial of municipal sewage (%)	Fermentation
Z-100	67500	12500	95	Yes
R-250	162000	3700	100	Yes
P-180	53100	1000	100	Yes
D-170	19666	2700	100	No
S-240	27157	2700	98	No
J-190	39000	1300	65	Yes
D-210	49000	1100	100	No
L-110	23673	300	82	No
B-40	26700	4500	97	No
K-30	20500	200	100	No
K-100	37800	6500	100	Yes
R-200	232000	4000	90	No
S-230	72100	1400	75	Yes
J-60	12100	2200	100	No
T-130	51188	500	97	Yes

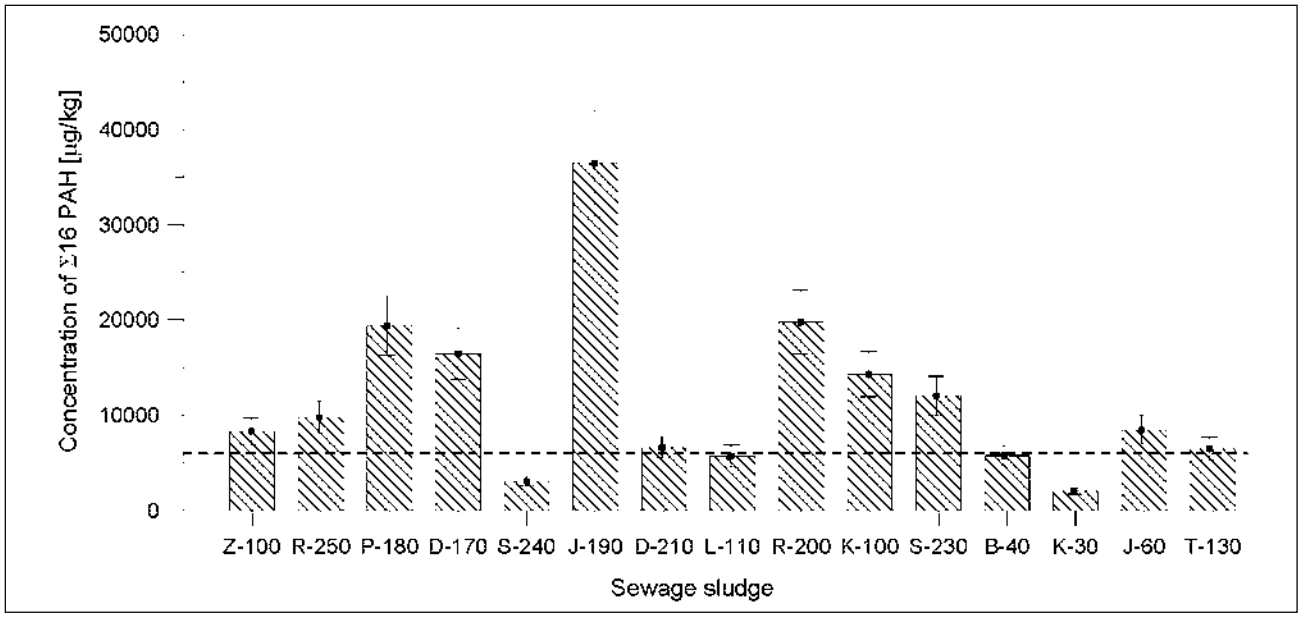

Fig. 1. The concentrations of 16 PAHs in sewage sludge studied (Dotted line presents UE norms for 16 PAHs).

Organic pollutants which are often found in sewage sludge are polycyclic aromatic hydrocarbons (PAH). The present study in addition to evaluating the degree of pollution with PAH in sewage sludge, aims also to determine the influence of the amount and genesis of purified sewage on its PAH content. Possible sources of PAH in the sludge studied were also evaluated by calculating their mutual relations.

Materials and Methods

Sample Collection and Preparation

Sewage sludge samples were collected during the summer (July/August) from 15 municipal sewage treatment plants located in southeastern Poland. The treatment plants selected were characterised by their high differentiation,

Table 2. Range of concentration and contribution of individual PAHs in sewage sludge studied.

PAH	Concentration [μg/kg]				Contribution [%]			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Na	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ace	0.0	7105.1	2132.4	1811.1	0.0	52.3	19.5	13.9
Ac	0.0	2946.5	886.6	1158.6	0.0	33.9	8.0	11.5
Fl	0.0	974.2	199.6	353.1	0.0	4.9	0.9	1.6
Phen	68.7	1149.2	526.7	361.2	2.5	9.5	4.9	2.1
Ant	17.9	425.5	165.9	123.4	0.9	3.0	1.5	0.7
Fluo	398.2	5399.9	1937.8	1401.1	4.2	31.2	18.1	6.2
Pyr	0.0	5050.5	1096.3	1439.4	0.0	22.9	8.9	8.6
B[a]A	84.8	2579.3	918.5	655.7	4.2	17.5	8.6	4.1
Ch	0.0	1869.1	577.3	488.5	0.0	13.9	4.9	3.2
B[b]F	214.5	7572.5	1857.3	2020.7	2.9	24.6	13.7	6.5
B[k]F	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B[a]P	134.7	1786.0	610.7	495.9	2.3	46.6	7.7	11.0
D[ah]A	0.0	458.9	72.3	149.8	0.0	4.7	0.7	1.3
B[ghi]P	0.0	835.1	262.6	256.5	0.0	5.4	2.2	1.5
Ind	88.2	1395.6	368.8	375.0	1.4	6.8	3.3	1.6
Sum of 16	2039.9	36034.1	11612.9	8720.4	-			

SD – standard deviation (n=3), Na – Naphthalene, Ace – Acenaphthalene, Ac – Acenaphtene, Fl – Fluorene, Phen –Phenanthrene, Ant – Anthracene, Fln – Fluoranthene, Pyr – Pyrene, BaA – Benz[a]anthracene, Ch – Chrysene, B[b]F – Benzo[b]fluoranthene, B[k]F – Benzo[k] fluoranthene, B[a]P – Benzo[a]pyrene, D[ah]A – Dibenz[a,h] anthracene, B[ghi]P – Benzo[ghi]perylene, Ind – Indeno[1,2,3-cd]pyrene

both with respect to the amount of sewage treated and the number of inhabitants served by the treatment plan, as well as the industrial character of the areas in which the treatment plant was located (quantity and variety of industrial plants) (Tab. 1). The sludge samples (about 0.5 kg) were collected at end-points of the technological line of sewage sludge digestion. The collected samples were stored in prewashed (with dichloromethane) glass bottles and immediately transported to the laboratory. All sewage sludge samples were air-dried and milled to obtain representative samples.

Determination of PAH Content

PAH was determined using the method of HPLC with UV detection UV (254 nm) after optimisation of the analytic process with respect to the amount and type of solvent used and extraction time, by means of ultrasonic method [10, 11] and optimisation of the extract purification process by the solid phase extraction method [12, 13]. The samples were extracted in an ultrasonic bath (Sonic-3, Polsonic, Poland) with two batches of dichloromethane (2 x 40 ml). The extract was centrifuged and evaporated to dryness. The residue was then dissolved in a mixture of 4 ml of acetonitrile:water (1:1 v/v) and purified by solid phase extraction (SPE) using C_{18} Octadecyl columns (JT Baker-Mallinckrodt, Germany) [12]. A Spherisorb-PAH (Schambeck SFD GmbH, Germany) was used for PAH separation. The mobile phase (acetonitrile:water, 82:18, v/v) flow was set to 1 ml/min. Detection was carried out at 254 nm. The column was installed in a thermostated oven at 31°C (LCO 101, ECOM, Czech Republic).

All reported concentration values of PAHs are expressed on a dry-wt basis of sewage sludge (determined by drying the sewage sludge for 24 h at 105°C) and are the average of triplicate extractions.

Results and Discussion

Sum of 16 PAH Contents

The content of polycyclic aromatic hydrocarbons in the sewage sludge studied was characterised by a clear differentiation. The 16 PAH content sums ranged from 2,039 to 36,440 μg/kg (Fig. 1). It should be stressed that the value of 36,440 μg/kg was noted in only one sewage sludge sample coming from a location with an operating petrochemical industry (refinery) and a considerable contribution of treated industrial sewage (Tab. 1). In the remaining samples the maximum content of the 16 PAHs

did not exceed 14,000 μg/kg (Fig. 1). Taking into consideration the standards of the European Union [14] concerning the maximum content of the 11 PAHs in sewage sludge (6 mg/kg), in only two sewage samples were the above levels not exceeded. In more than half of the sewage sludge samples studied, EU standards were markedly exceeded (for sludge sample J-190, as much as 6 times), in the case of the remaining samples, the values were close to the critical levels.

When evaluating relations between the sum of the PAH contents studied and the number of inhabitants, the amount of sewage treated, the advanced state of the fermentation process, as well as the character of the sewage treated, only in this last case was a significant negative relation (-0.547, at P=0.05) noted. To some extent this can point to the fact that with an increase in the contribution of industrial sewage in the sewage treated, the content of the polycyclic aromatic hydrocarbons increases.

Data from literature has shown [15-22] that the sewage sludge samples studied were characterised by a slightly higher or almost identical content of the PAHs sum to the values quoted by various authors and they were close to the levels given for sludge produced in the countries of the European Union [5, 16-18, 23]. Considerably higher PAH concentration levels were determined in the sewage sludge from industrialised regions of the USA and Canada [19, 22].

However, it is difficult to relate the data obtained in this study to other studies by Polish researchers as the number of publications on the 16 PAHs is very scarce [7, 8, 23]. Most of the studies published are limited to a few compounds from this group only [24-26]. Czekała et al. [8] determined rather lower levels of the 16 PAH contents in sewage sludge from the Wielkopolska (Greater Poland) region than the values quoted in this study. On the other hand, in studies by Janoszka et al. [23] - data obtained on the 17 PAHs in the sewage sludge from the area of Upper Silesia - was very close or clearly higher (as much as up to 270 mg/kg).

PAH Profiles

Figure 2 presents the percentage contribution of PAH with respect to the number of rings. In most of the sewage sludge samples studied, 3- and 4-ring PAHs had the highest contribution level. Only in one sewage sludge sample was there more than a 50% contribution of the 5-ring PAHs determined (Fig. 2). In the case of the remaining PAHs, the share of especially carcinogenic and mutagenic 5- and 6-ring forms did not exceed 20% and 10%, respectively.

The highest content in most of the sewage sludge studied was observed for acenaphthalene, fluoranthene and benzo[b]fluoranthene. In a few samples there were also pyrene, acenaphtene and benzo[a]pyrene. The share of acenaphthalene in almost all of the studied sludge samples (except for Z-100, B-40 and K-30) was higher than 10% (on average - 20%). Also, the content of fluoranthene was at a similar high level (except for R-250) (on average - 19%).

Taking into account the data presented above, it seems more plausible to take into consideration some chosen (mutagenic and carcinogenic) compounds from the PAH group when evaluating the possibility of the natural utilisation of sewage sludge since the standards implemented in the countries of the European Union determine the maximum concentration of 3 PAH, i.e. fluoranthene (5 mg/kg), benzo[a]pyrene (2.5 mg/kg) and benzo[b]fluoranthene (2 mg/kg). Similar standards concerning a higher num-

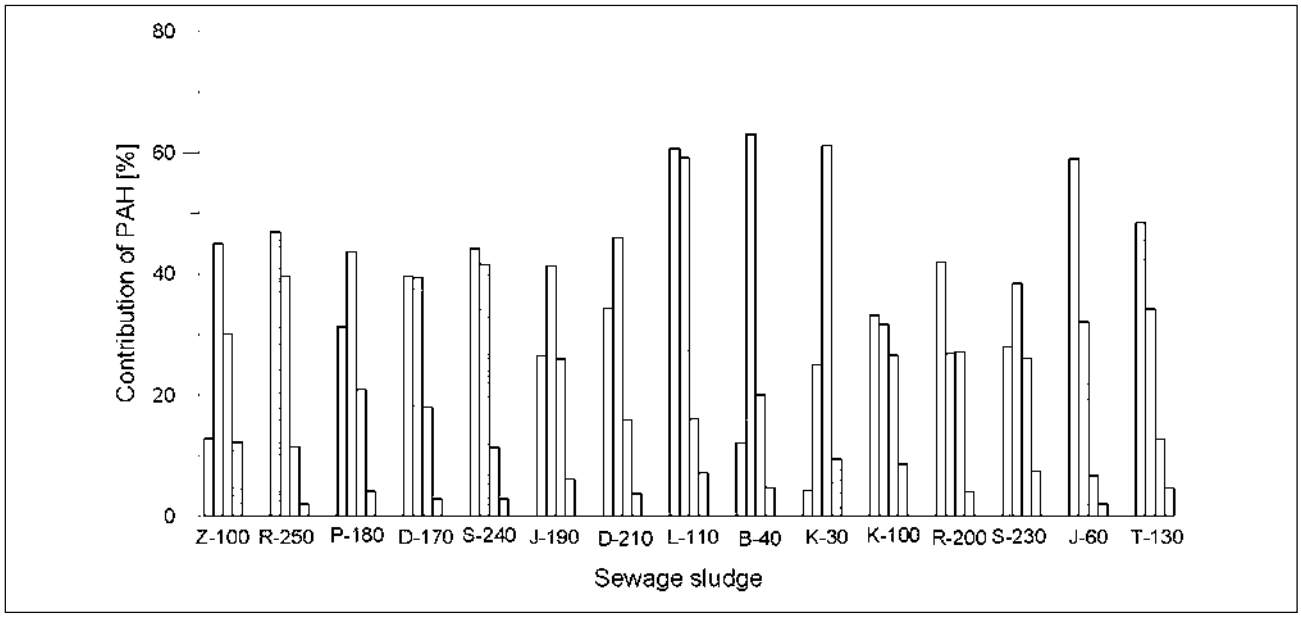

Fig. 2. Contribution of PAHs with respect to the number of rings in sewage sludge studied (Bars in the series reply 3, 4, 5 and 6-ring PAHs respectively) .

ber of PAHs are also valid in Austria [27]. According to the Austrian standards, the maximum concentration of the 6 PAHs (fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) in sewage sludge utilised for agricultural purposes cannot exceed 9.6 mg/kg. Taking into account the European Union standards, only in the case of fluoranthene were slightly exceeded levels observed in the sludge with the highest total content of PAH (J-190). This last sludge did not fulfil the requirements of the Austrian standard either. In the remaining sewage sludge samples, the content of the three individual PAHs and the sum of the six PAHs met the standards required.

When evaluating the relation between the content of individual PAHs and the number of inhabitants, the amount of sewage treated, the occurrence of the fermentation stage, as well as the character of the sewage treated, similarly as in the case of the PAH sum, only very few relations existed within the character of sewage treated. A negative correlation (statistically significant at P=0.05) was noted only in the case of acenaphthalene (-0.693), and also (at P=0.01) for fluoranthene (-0.540), benzo[a]anthracene (-0.578), chrysene (-0.624), benzo[b]fluoranthene (-0.632), benzo[ghi]perylene (-0.573) and indeno[1,2,3-cd]pyrene (-0.569).

PAH Sources and Correlations Between Individual PAHs

Some authors attempt to identify the source of PAH in order to determine the origin based on the presence of individual compounds from this group or determining relations between individual PAHs. The above method is used mainly for soils [28, 29] and sediments [30-32]. In the case of sewage sludge, the most representative seems to be the method proposed by Budzinski et al. [30]. Further to this method, it is assumed that the value of the coefficient phenantrene/anthracene (Fen/Ant) > 10 indicates that the source of the origin of PAHs are the processes to which crude oil is subjected, whereas the value of the phenantrene/anthracene coefficient lower than 10, points to the predominance of pyrolytic processes. In the case of the fluoranthene/pyrene coefficient, it is assumed that values higher than 1 are related to pyrolytic processes, mainly coal burning.

Figure 3 presents the values of coefficients: phenantrene/anthracene and fluoranthene /pyrene in the sewage sludge samples studied. They showed that the main share of PAHs in most sewage sludge samples was related to pyrolytic processes. Only in the case of two sewage sludge samples (Z-100 and R-250) was the value of the fluoranthene/pyrene coefficient above 1. At the same time, the highest value of the phenanthrene/anthracene coefficient was found in these samples. On the basis of the above data, it can be assumed that discharges from the fuel industry could have contributed to the pollution of sewage sludge with PAHs. It would also confirm the high contribution of benzo[ghi]perylene when compared to other sludges studied as suggested by Perez et al. [18].

Evaluating relations between the content of the PAHs sum and the content of individual compounds from this group, it was found that in almost all cases there occurs an almost identical and statistically significant relation, with the exception of acenaphthene and dibenz[ah]anthracene. In the case of the remaining compounds, the calculated values of the correlation coefficient were higher than 0.740 (at P=0.05), whereas for fluoranthene, chrysene and benzo[b]fluoranthene these values ranged from 0.941 to 0.958 (Fig. 4).

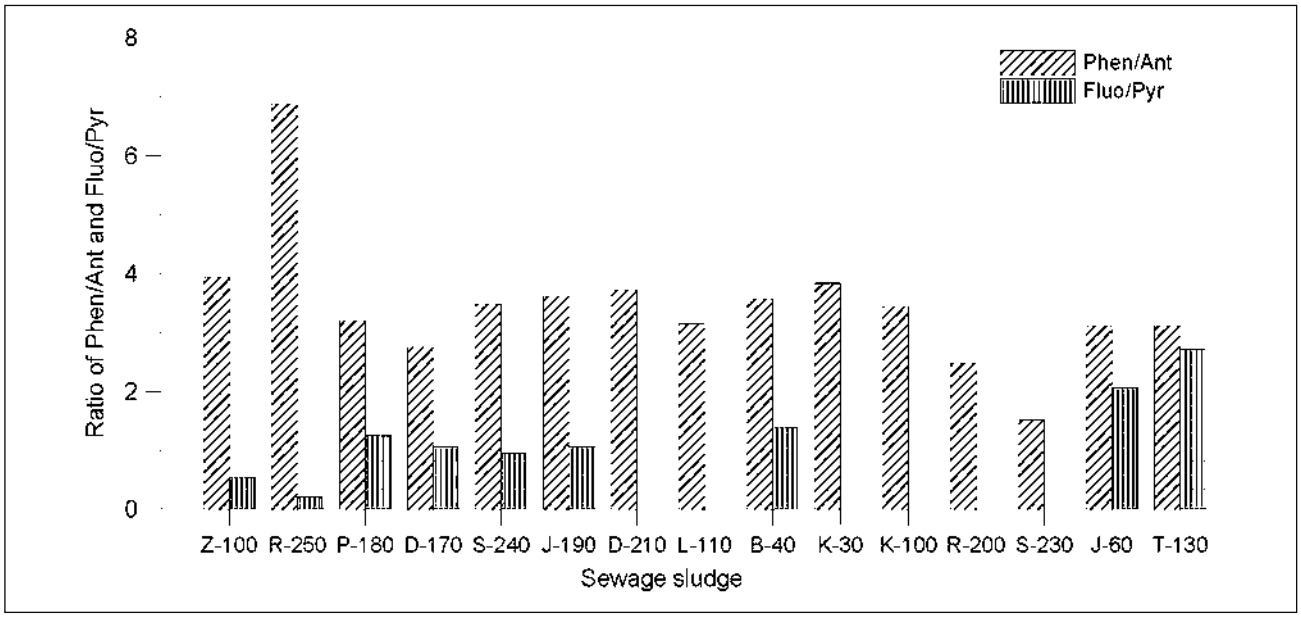

Fig. 3. The values of ratio phenanthrene/anthracene (Phen/Ant) and fluoranthene/pyrene (Fluo/Pyr) in the sewage sludge studied.

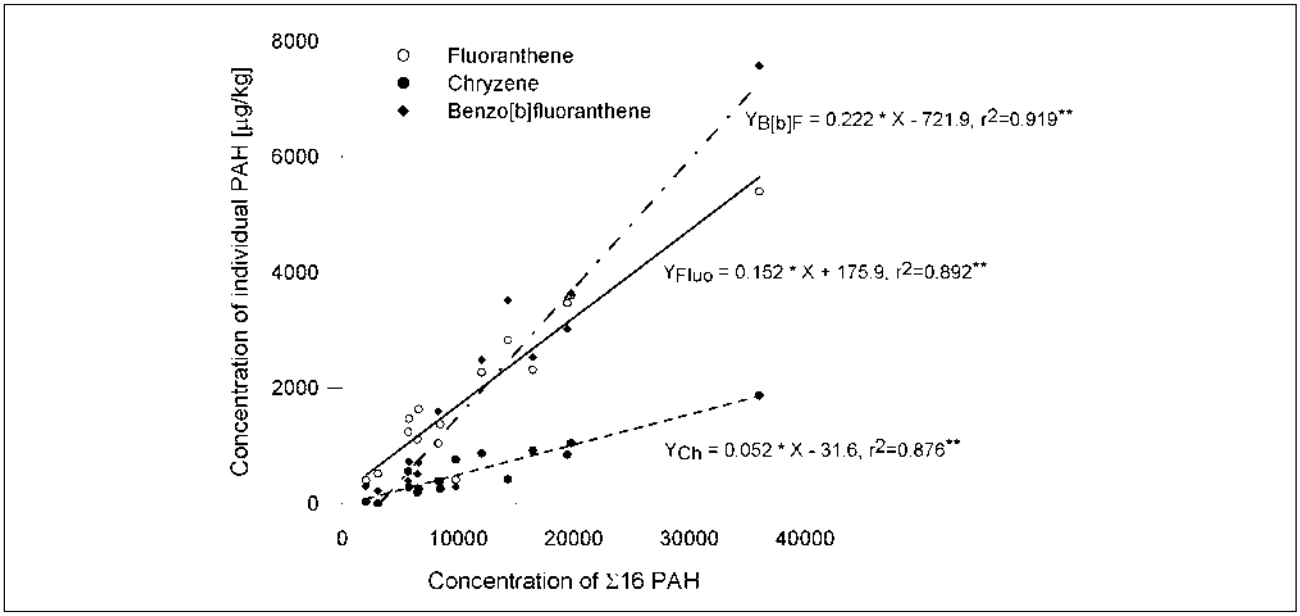

Fig. 4. The linear relationship between 16 PAH concentrations and concentrations of fluoranthene, chrysene and benzo[a]pyrene (n=15, **- P = 0.001).

The highest frequency of the occurrence of positive and high (>0.800, at *P*=0.01) relations between the individual PAHs was noted in the case of fluoranthene and benzo[b]fluoranthene. The above compounds showed a relation to over one half of the PAHs determined.

Conclusion

The results obtained showed a high divergence in the amount of polycyclic aromatic hydrocarbons in sewage sludge from the south-eastern part of Poland. The lack of relation between the amount of sewage sludge treated and the PAH content as well as the clear influence of the origin of the sewage sludge treated (a positive correlation) showed that it is the type of sewage treated that influences the PAH content in sludge (the increase in the share of industrial sewage is closely related to the increase in the PAH concentration PAH) more than their quantity.

The fact that permissible levels according to the standards of the European Union were exceeded (as far as the sum of the 16 PAHs is concerned) makes the agricultural use of most sewage sludge studied questionable.

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