

Original Research

Trace Metals and Polycyclic Aromatic Hydrocarbons in Surface Sediment Samples from the Narew River (Poland)

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Abstract

Polycyclic aromatic hydrocarbons and trace metals were analysed in surface sediments of the Narew River (north-eastern Poland). Sediment samples originated from sites with a differentiated human influence starting with the unpolluted areas (the Biatowieza Forest / Puszcza Białowieska, the so-called "green lungs of Poland") to the areas in the neighbourhood of small towns in northeastern Poland. Marked differences in pollution levels of the above areas were observed. The PAH contents range from 21-600 µg/kg, with a dominant share of low molecular PAHs. The sediment pollution level with trace metals was relatively low. None of the metals determined (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) occurred in an amount that could have created a risk to water organisms.

Keywords: sediments, environmental analysis, PAH, trace metals, Narew River

Introduction

Surface sediments are specific elements of the natural environment. They are a "natural sponge" that adsorb all kinds of pollutants occurring in water. The structure of sediments together with their developed surface, makes them a natural sorbent in which the accumulation of all sorts of harmful substances takes place.

Substances and elements including trace metals [1-3], polycyclic aromatic hydrocarbons (PAHs) [4, 5], phenols [6, 7], pesticides [7], and other compounds [3] were determined in sediments. The main sources of trace metals and PAHs in the water environment (rivers and lakes) mentioned in literature are precipitation and urban runoff. The PAH source in the water environment may also be biological synthesis [8] with biogenic precursors like terpenes, pigments, and steroids [9, 10].

The transportation of organic contaminants in a water environment depends on their solubility in water. Most contaminants (e.g. PAHs, PCB) are characterised by low solubilities, and their transportation over considerable distances can be significantly limited if they are adsorbed on the sediments. Pollutants adsorbed on an immovable matrix result in the contamination of a given area and do not pose any threats to water organisms. Once deposited in sediments, these compounds are less subject to photochemical and biological oxidation and thus tend to persist for longer periods and to accumulate in high concentrations [11].

Besides, contaminants may be sorbed on the surface of small particles suspended in water and are thus subject to possible sedimentation [12].

In some cases, the adsorbed contaminants can be remobilised and a secondary water pollution may occur.

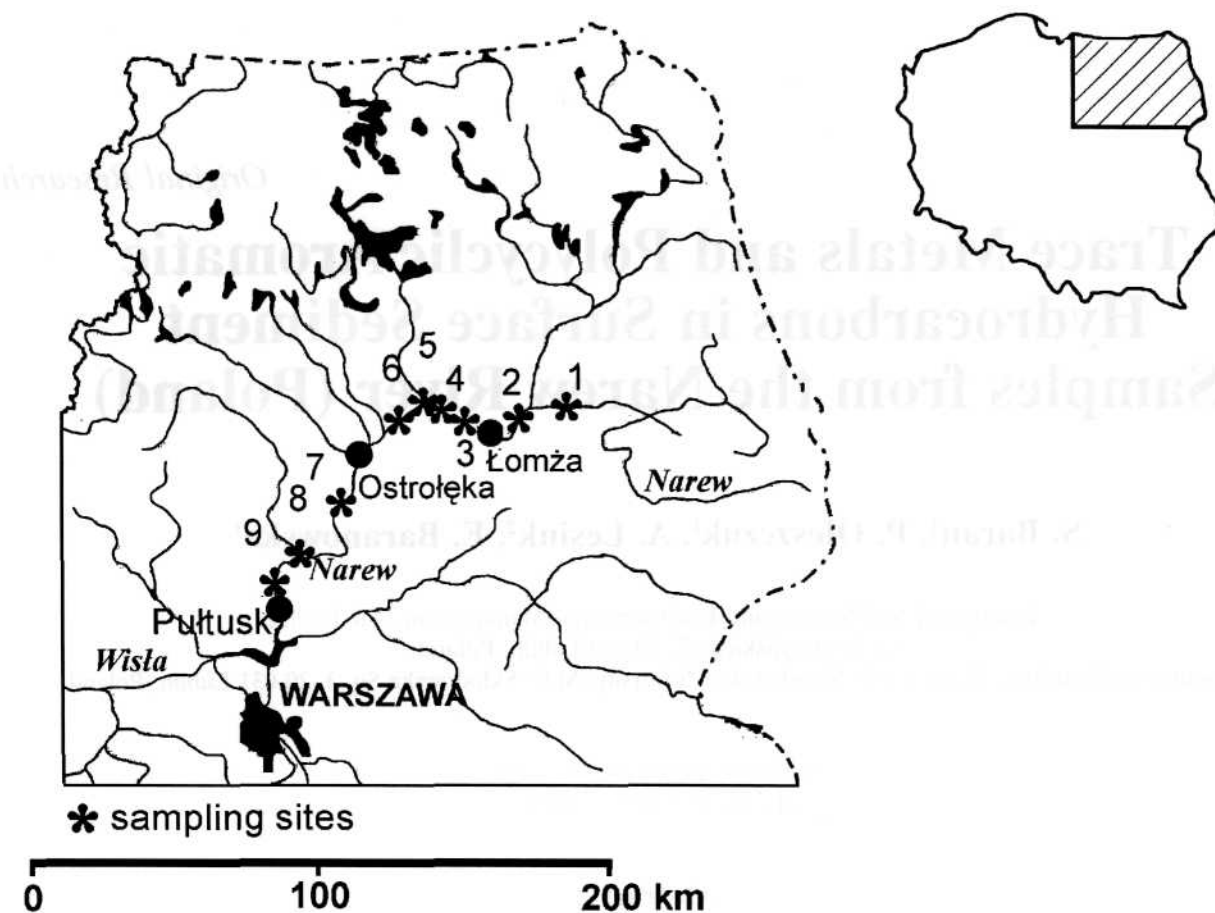


Fig. 1. Map showing sampling sites in the study area.

This takes place when the solubility of contaminants is increased (e.g. by the presence of surfactants) [13], or when the particles of contaminants undergo desorption from an immovable matrix and undergo a secondary sorption on particles with a sorption ability higher than that of the sediments, and which are carried by water currents (in general only the finer fractions ($< 63 \mu\text{m}$) are transported by river currents) [12].

A considerable part of the information available is related to the PAH content in sediments from industrial zones with considerable pollution and is rare in areas where pollution is low. Hence, in the present study samples of surface deposits from areas with a medium influence of anthropogenic pollutants were examined.

Materials and Methods

Site Characteristics

The Narew is a river in the eastern part of Poland (Fig. 1) with a length of 484 km (448.1 km with in Poland) and a surface basin area of 75.1 thousand km^2 (53.8 thousand km^2 with in Poland). Its sources are located in the Białowieża Forest (in Polish - Puszcza Białowieńska)

in Byelorussia. It runs through the Biebrza Bite Region, the Kurpie Forest and discharges into the River Vistula. The Narew Valley is wide and boggy, and its flume forms numerous branches. The river passes through the following towns: Łomża (furniture industry, a brewery, cotton processing industries, metal processing, and silk industries), Ostrołęka (paper industry, and industries associated with wood, meat, construction materials, and heat generating, plus a power plant with a power of 720 MW), and Pultusk (electro-technical industry, metal processing, construction materials, textile, leather, and food industries).

The Narew runs partly through the Białowieża Forest with an area of 125 thousand ha, of which 58 thousand ha are in Poland. Various types of forest stands have been preserved in the Białowieża Forest in pristine condition. They represent various types of forest communities. Both ground cover and thatch are varied. A bison reserve has been established, and rare animals such as elk and beaver, lynx, wolf, ermine, otter, eagle, and black stork live there. Part of the forest was taken under the strict protection of the Białowieża National Park (it occupies an area of 5348 ha, of which 4747 ha are under strict protection). The Białowieża National Park has been recognised by UNESCO (United Nations Educational, Scientific and Cultural Organisation) as a Biosphere Reserve.

Sample Collection

Sediment samples were collected in July 2000. Three surface samples of sediments (0-10 cm) were collected per site and mixed surface samples were obtained for analysis in order to ensure representation of particular sites. The sampling locations are shown in Fig. 1. All sediments were air-dried and sieved (< 1 mm) (content of potassium available and phosphorus, pH, total carbon content were analysed), (< 2 mm) (PAHs was analysed). For trace metals, air-dried and sieved samples (< 2 mm) were milled in agate mortar. Next, sediment samples were kept in plastic bags until extraction. Foils were cleaned by rinsing with acetonitrile.

Determination of PAH Content

A sediment sample (25 g) was 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 4 ml of acetonitrile and purified by solid phase extraction (SPE) using C₁₈ Octadecyl columns (JT Baker-Mallinckrodt), according to JT Baker-Mallinckrodt application nr. Env. 105 [14]. A qualitative and quantitative analysis of PAHs was carried out on a liquid chromatograph with UV detection (TermoSeparation Products) [14].

Determination of Trace Metals

Each sediment sample (3g) was mineralised in a PROLABO microwave oven (Microdigest 3.6, France), using a wet method in a mixture of nitric acid (8 ml) and perchloric acid (8 ml) at the ratio of 1:1. The temperature of mineralisation did not exceed 200°C. In the final stage of mineralization a 30% of hydrogen peroxide solution was added (1 x 5 ml, 1 x 6 ml). Details of the mineralisation are described in Table 1. An analysis for the content of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was carried out using emission spectrometry on the Leeman Labs (PS 950) apparatus with ICP induction in argon. Analytic lines according to the apparatus catalogue were used. Evaluation of the accuracy and precision of analytical procedures used reference materials (Heavy Clay Soil, RTH 953, Promochem).

The following parameters were also determined in the sediment samples: reaction - by a potentiometric method in 1 mol/dm³ KCl; the content of potassium available and phosphorus forms followed the method by Egner-Rhiem, and total carbon content by the Tiurin's method as modified by Simakow [15].

Statistical analysis was performed using MS Excel 2000 (Microsoft). Standard deviation (SD), relative standard deviation (RSD) (%) and Pearson correlation coefficient were calculated. Significance was set at P < 0.05.

Results and Discussion

Characteristics of Surface Sediments

The characteristics of the basic physical and chemical properties of the sediments are presented in Table 2. The sediments were characterised by a neutral reaction (pH values 6.8-7.7). The content of available phosphorus

Table 1. Mineralisation stage of the sediment samples.

Time	Power*	Reagents
10.00 min	-	8 ml HNO ₃ (65%) + 8 ml HClO ₄ (70%)
10.00 min	10 %	
10.00 min	30 %	
5.00 min	40 %	
0.15 min	-	5 ml H ₂ O ₂ (30%)
0.30 min	100 %	
0.15 min		6 ml H ₂ O ₂ (30%)
6.00 min	100 %	

* - maximum microwave power - 250 W

Table 2. The physicochemical properties of sediments from the Narew River.

Sampling location	pH _{KCl}	K* [mg/100 g]	P* [mg/100 g]	C _{org} [%]
S1	7.7	1.7	14.3	3.18
S2	7.6	1.5	7.1	3.48
S3	6.8	10.8	42.7	15.60
S4	7.5	2.7	12.7	3.15
S5	7.7	1.7	3.7	3.57
S6	7.5	2.8	18.4	3.45
S7	7.0	2.4	11.9	3.51
S8	7.5	2.2	9.8	3.78
S9	7.5	1.4	5.3	3.21

* - available forms

forms was low or medium; only in the case of S6 and S3 was it high and very high, respectively (Table 2). All the sediment samples studied (except S3) were characterised by a low content of available potassium, which proved the low content of this element in the samples studied. A high dependency of available potassium forms and trace metal concentrations was observed, especially in the case of Cr (0.996*), Cu (0.993*) and Zn (0.996*). Whereas in the case of phosphorus, this relation was not so clear; however, it was still significant in the majority of samples (> 0.919*).

Contents of Trace Metals in the Surface Sediments

Trace metals are omnipresent in the environment. Such an omnipresence results mainly from the numerous

Table 3. The concentration of the trace metals in sediments from the Narew River [mg/kg]

Sampling location	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S1	0.04 ± 6	0.78 ± 3	1.70 ± 4	0.39 ± 3	2550 ± 4	176 ± 3	1.26 ± 4	1.59 ± 8	7.0 ± 5
S2	0.09 ± 3	0.87 ± 5	2.36 ± 4	0.79 ± 4	3040 ± 6	68 ± 6	1.46 ± 4	1.73 ± 3	9.1 ± 7
S3	1.07 ± 5	2.58 ± 3	40.50 ± 5	25.20 ± 4	16000 ± 3	932 ± 4	7.81 ± 6	17.00 ± 8	166 ± 4
S4	0.17 ± 3	1.02 ± 8	3.89 ± 3	1.66 ± 3	4310 ± 5	199 ± 3	2.43 ± 6	2.54 ± 5	15.5 ± 5
S5	0.16 ± 3	1.66 ± 3	2.20 ± 6	1.33 ± 2	3590 ± 5	136 ± 5	2.56 ± 5	4.12 ± 7	9.5 ± 6
S6	0.37 ± 4	1.28 ± 4	7.36 ± 7	4.51 ± 7	7660 ± 7	308 ± 4	3.81 ± 4	7.13 ± 5	28.6 ± 6
S7	0.12 ± 7	0.65 ± 4	3.99 ± 7	3.75 ± 3	3090 ± 4	117 ± 8	1.66 ± 7	1.64 ± 4	15.6 ± 9
S8	0.10 ± 4	0.94 ± 7	3.02 ± 8	2.74 ± 5	3320 ± 3	175 ± 6	2.05 ± 5	1.94 ± 6	11.6 ± 7
S9	0.07 ± 5	0.58 ± 3	2.39 ± 3	1.17 ± 5	3070 ± 5	135 ± 3	0.97 ± 4	0.71 ± 3	8.5 ± 3
min	0.04	0.58	1.70	0.39	16000	68	1.26	0.71	7.0
max	1.07	1.28	40.50	4.51	2550	932	7.81	7.13	166
mean-1*	0.1	0.97	3.36	2.04	3828	164	2.03	2.67	13.7
mean-2**	0.2	1.15	7.49	4.61	5181	250	2.67	4.27	30.2

* - mean without S3, ** - mean with S3, ± - relative standard deviation — RSD [%] (n = 2)

sources of their origin, as well as from their ability for self sorption on various particles that are transferred over considerable distances by air currents (atmosphere) and/or water currents (rivers, lakes, etc.) Hence, it is possible to find them in distant places where the influence of anthropogenic processes is limited. In water, trace metals do not last long in dissolved form as they undergo precipitation due to the processes of oxygenation, the formation of all sorts of chemical compounds, the influence of micro-organisms, and sorption onto the mineral and organic sediment fraction.

Studies carried out on the content of trace metals in the sediments aimed at determining their origin, their distribution rate and routes, and were the basis for establishing the possibilities of the secondary pollution of a given water reservoir [16].

The concentration of trace metals in the samples from the Narew are listed in Table 3. It should be stated that the pollution level of the sediments with trace metals studied was very low, and only in the case of the S3 sample were the contents of the metals determined as being several times higher (mainly Cd, Cr and Zn) than other samples (Fig. 2 a-c). The above amounts, however, are considerably lower than in the case of data presented by other authors [1, 3, 17, 18], and in the majority of cases below the geo-chemical background of the main Polish rivers [19] and European rivers [20].

The somewhat higher content of trace metals in the S3 sample (sediment from the neighbourhood of Lomza) is attributable first of all to the properties of this sediment (muddy), as characterised by a high content of organic matter (Table 2), which plays an important role in the sorption of organic and inorganic xenobiotics [21]. This pollutant may result in part from urban contamination originating from Lomza.

The lowest content of the above metals was observed at the initial sites of sample collection (S1 and S2) in the

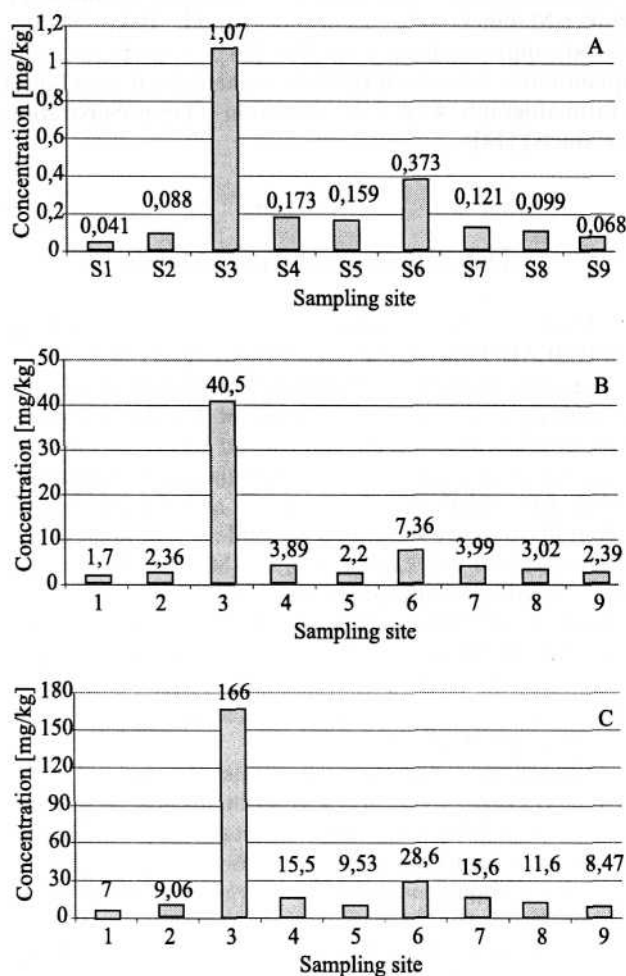


Fig. 2. Trace metals contents (Cd (A), Cr (B) and Zn (C)) in sediments from the Narew River [mg/kg].

area of the Bialowieza National Park (see characteristics of the area studied).

In the case of the remaining samples, the levels of their contamination were very similar and no significant differences between them were observed. Only the S6 sample was, to a certain degree, different from the others; however, the differences were not as significant as in the case of the S3 sample. These differences are especially significant in the case of Cr and Cd, that is those metals whose occurrence in the environment is strictly related to human activity.

PAH Content in Surface Sediments

PAH properties exert a significant influence on the amount of PAHs in the sediments. Poor water-solubility and a rather limited ability to self-adsorb on the soil which is mainly limited, favours accumulation in the sediments [22]. Contamination of sediments with PAHs covered a broad range, i.e. 9.1-20 000 $\mu\text{g}/\text{kg}$ [4, 5, 23, 24]. The factors that mainly influence their content are: type of sediments (e.g. slimy, rocky), percentage of total

organic carbon, depth of sediment collection, and season [2, 11].

Table 4 presents determinations of the 16 PAH concentration levels in the sediments studied. Total PAH concentration in the surface sediments in this study ranged from 21.0 to 598.8 $\mu\text{g}/\text{kg}$ with an average of 192.8 $\mu\text{g}/\text{kg}$. Similarly as in the case of trace metals, clear differences were observed in the content of PAHs originating from various sampling sites. The content of individual PAHs depended on the sample collection site. At sites where human influence was limited it was very low (S1, S2), whereas at the sites where this influence was higher and able to be compared to data presented by other authors from the areas with a certain level of urbanisation and industrialisation, it was also higher. The highest concentration of PAHs was observed at site S3 (598.8 $\mu\text{g}/\text{kg}$), similar to the case of trace metals, and the lowest at sites S1 and S2 - 21.0 i 31.2 $\mu\text{g}/\text{kg}$, respectively. When compared to other levels of pollution, the pollution level in the sediment from the S3 site was found to be high and probably resulted from urban pollutants (domestic waters from the city of Lomza), similarly as in the case of trace metals. Without any doubt, the type of sediments

Table 4. The concentration of 16 PAHs in sediments from the Narew River [$\mu\text{g}/\text{kg}$]

Sampling location	S1	S2	S3	S4	S5	S6	S7	S8	S9
Naph	5.1 ± 7	8.6 ± 6	222.3 ± 8	39.5 ± 8	66.6 ± 16	141.8 ± 13	63.9 ± 20	45.5 ± 19	44.4 ± 17
Aceny	0.00	0.0	49.4 ± 16	3.9 ± 11	0.0	26.1 ± 15	11.7 ± 21	15.13 ± 16	30.1 ± 12
Acen	0.00	0.0	103.4 ± 19	10.1 ± 17	0.0	44.2 ± 24	19.9 ± 19	0.00	22.4 ± 16
Fluo	1.6 ± 11	3.9 ± 9	53.1 ± 11	8.6 ± 9	11.7 ± 9	24.7 ± 12	11.1 ± 17	13.3 ± 15	7.7 ± 16
Phen	1.1 ± 6	1.7 ± 9	81.9 ± 8	35.2 ± 6	29.4 ± 7	35.0 ± 9	15.8 ± 6	21.7 ± 7	10.7 ± 7
Anth	0.1 ± 9	0.2 ± 7	5.3 ± 7	2.4 ± 9	2.9 ± 8	3.8 ± 16	1.7 ± 12	2.1 ± 11	1.9 ± 8
Flua	3.3 ± 9	2.7 ± 4	13.7 ± 7	20.5 ± 7	15.9 ± 4	13.1 ± 11	5.9 ± 8	5.6 ± 8	6.7 ± 4
Pyr	1.3 ± 3	1.0 ± 5	18.1 ± 4	24.7 ± 7	3.8 ± 5	11.8 ± 9	5.3 ± 9	4.5 ± 7	8.3 ± 7
B(a)A	0.5 ± 4	0.7 ± 5	1.4 ± 4	0.0	0.0	1.9 ± 7	0.9 ± 11	0.0	2.2 ± 5
Chry	0.6 ± 7	1.5 ± 4	18.6 ± 6	4.7 ± 5	7.8 ± 7	11.9 ± 7	5.0 ± 8	7.3 ± 9	8.5 ± 4
B(b)F	3.0 ± 2	3.0 ± 3	6.1 ± 2	1.7 ± 4	4.7 ± 3	3.7 ± 11	1.7 ± 17	5.5 ± 14	4.2 ± 5
B(k)F	1.4 ± 7	2.0 ± 7	4.4 ± 6	3.1 ± 8	2.8 ± 9	2.2 ± 14	1.0 ± 9	3.3 ± 11	2.6 ± 6
B(a)P	1.0 ± 8	1.7 ± 11	7.9 ± 12	2.4 ± 9	6.2 ± 11	5.6 ± 9	2.5 ± 13	4.0 ± 10	3.7 ± 12
D(ah)A	0.0	2.5 ± 14	8.7 ± 11	3.3 ± 9	8.4 ± 12	3.7 ± 11	1.7 ± 9	10.0 ± 9	8.5 ± 10
B(ghi)P	0.0	0.0	2.4 ± 7	0.6 ± 8	0.7 ± 9	1.6 ± 7	0.7 ± 11	0.9 ± 9	0.7 ± 5
IP	1.9 ± 2	1.7 ± 4	2.3 ± 2	0.7 ± 4	1.5 ± 3	1.3 ± 3	0.6 ± 4	1.8 ± 6	1.1 ± 3
Phen/Anth	10	12	16	15	10	9	9	10	6
Flua/Pyr	2.62	2.72	0.76	0.83	4.22	1.11	1.11	1.25	0.80
Sum LPAH	13.6	20.3	567.1	124.9	138.1	313.5	141.2	115.1	142.7
Sum HPAH	7.4	10.9	31.7	11.9	24.2	18.2	8.2	25.5	20.7
Sum PAH	21.0 ± 4	31.2 ± 7	598.8 ± 6	136.8 ± 7	162.3 ± 5	331.7 ± 9	149.4 ± 9	140.6 ± 10	163.5 ± 6

Naph - Naphthalene, Aceny - Acenaphthalene, Acen - Acenaphthene, Fluo - Fluorene, Phen - Phenanthrene, Anth - Anthracene, Flua - Fluoranthene, Pyr - Pyrene, B(a)A - Benz[a]anthracene, Chry - 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, IP - Indeno[1,2,3-cd]pyrene S1-S9 - sampling location; LPAH - low molecular PAHs; HPAH - high molecular PAHs; ± - relative standard deviation - RSD (%); n = 2

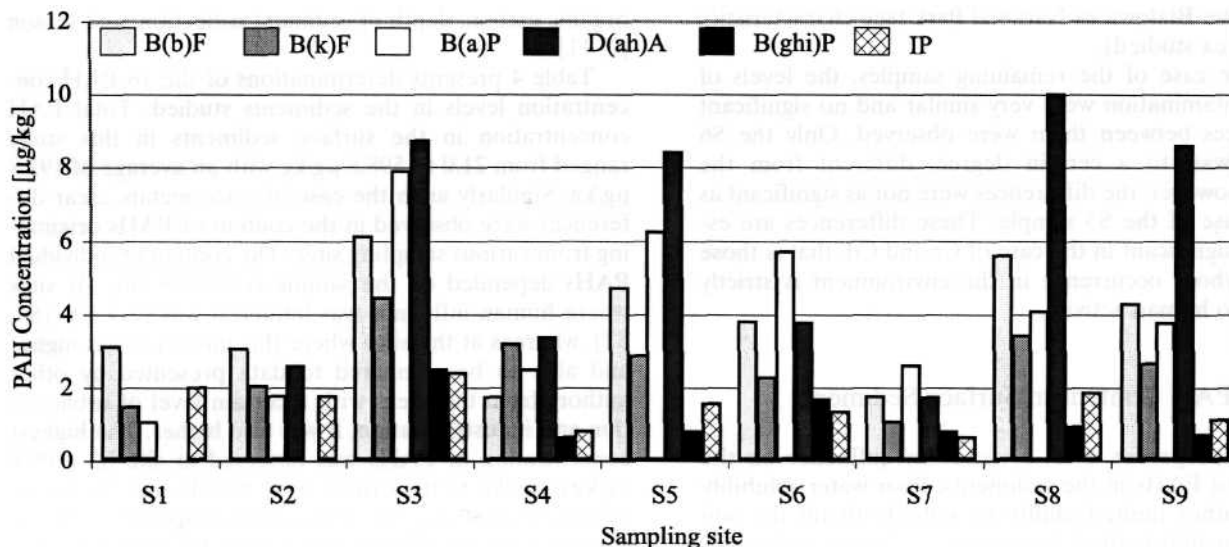


Fig. 3. The concentration of high molecular PAHs in sediments from the Narew River [µg/kg].

influenced the degree of PAH concentration (muddy sediment). Also Budzynski et al. [25] reported similarly higher concentrations in muddy sediments than in sandy sediments.

The low concentrations obtained in sand showed a weak adsorption of PAHs to this type of material. The PAH appeared to be preferentially associated with fine particles [25].

Lower molecular PAHs (LPAH) (< 4 rings) were the dominant hydrocarbons. They usually constituted more than 65% of the total amount of PAHs determined, and in the case of the S3, S6 and S7 samples constituted as much as 95%. The contribution of high molecular PAHs (HPAH) (5-6 rings) was low. Benzo[b]fluoranten, benzo[a]piren and dibenz[ah]antracen (Fig. 3) were dominant. Based on the rule proposed by Fernandes et al. [26], which says that PAHs with high molecular weight are generated mainly by high temperature combustion whereas PAHs with lower molecular weight may be derived from fossil fuel combustion, it should be assumed that the main source of PAHs in the sediments studied are processes related to fossil fuel combustion.

In order to determine the source of PAH origin some authors [25, 27, 28] have relied on the concentration ratios of phenanthrene/anthracene (Phen/Anth) and fluoranthene/pyrene (Fluo/Pyr).

Generally speaking, it can be assumed that in the case of Phen/Anth coefficient values > 10, the source of PAH origin are petrogenic processes, whereas Phen/Anth < 10 points to the dominance of pyrolytic sources [25]. The same considerations can be applied to the Fluo/Pyr ratio. Values greater than 1 are classically related to pyrolytic origins, namely coal combustion [29].

The Fluo/Pyr coefficient for most of the samples ranged from 0.76 to 1.25. It is difficult to determine the source of PAH origin on the basis of such a small variation. Most probably both pyrolytic processes and also to some extent, oil contamination played a part in it. It is also difficult to determine PAH origin using the

Phen/Anth coefficient. The rule assumed is that the coefficient values below 15 point to the origin of PAH from the incomplete combustion of, for example, carbon. Considering the above assumption, it can be expected that in all the samples studied (except for S3), PAHs originated from this type of process.

However, in the case of S1 and S2 samples it is difficult to establish unequivocally the origin of the PAHs occurring in them on the basis of the coefficients analysed. The values of the Phen/Anth coefficient pointed to the pyrolytic origin of PAH, whereas the Fluo/Pyr coefficient clearly showed oil contamination.

Hence, coefficient values can only be treated as indicative and can be used only occasionally as an aid in determining potential PAH sources.

Conclusions

The above studies show that the pollution level of the sediments studied was low and close to the data obtained from areas with a similar level of urbanisation and industrialisation. Samples originating from the park area are slightly polluted both with trace metals and PAHs. The higher levels of concentration at some sites of sample collection were caused by human presence as well as by the properties of the sediments studied. The studies carried out permit the formulation of the following generalisations:

- Pollution levels of the surface sediments in the section studied with trace metals and PAHs is only low, and the differentiation in the concentration levels is closely related to the intensity of urban processes.
- Low molecular PAHs were dominant among PAH pollutants.
- The origin of PAH can be determined on the basis of coefficients; the present studies show that these can serve as an indication / guide only.

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