

Distribution of polynuclear aromatic hydrocarbons (PAHs) in sediments of the southern Baltic Sea

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Abstract

Polynuclear aromatic hydrocarbons (PAHs) were determined by a diode-array HPLC method in recent (0–10 cm) sediments collected from the southern Baltic Sea in 1994–1996. The sum of the concentrations of 12 unsubstituted PAHs were from 10 to 7000 ng g⁻¹ (d.w.) (av. 1830 ng g⁻¹). It is proposed that, besides the most abundant individual PAHs and ‘total PAH’ values, which cannot be compared owing to the different sampling and analytical methods used, a marker of pyrogenic pollution such as benzo(a)pyrene should be regarded as obligatory by all the laboratories dealing with environmental PAHs. The concentration of benzo(a)pyrene in the sediments examined ranged from 0.3 to 418 ng g⁻¹ (d.w.) (av. 98 ng g⁻¹). Comparison of the correlation coefficients for PAH concentrations with phytoplankton pigments and organic carbon in Baltic sediments indicates that phytoplankton is the factor principally responsible for the transport of PAHs from the water to the southern Baltic sediments.

1. Introduction

The concept of ‘polynuclear aromatic hydrocarbons’ (PAHs) covers a wide range of compounds characterised by the presence of two or more condensed aromatic rings in their structure, and may be the parent, unsubstituted compounds or their alkyl derivatives.

PAHs are ubiquitous constituents of the natural environment, and thus also of the sea. As several PAHs are known to have toxic and carcinogenic properties, they are classified as priority environmental pollutants (Schuster, 1994; Fitzmaurice, 1992; Andruliewicz and Rhode, 1987). These compounds have therefore been subjected to intensive study, primarily as markers of anthropogenic input into the sea, since the occurrence of PAHs in the environment is due mainly to the combustion and pyrolysis of fossil fuels or wood, and to the release into the environment of petroleum products (Law and Nicholson, 1995). PAHs originating from combustion are dominated by non-alkylated compounds, those from petroleum – by the alkyl derivatives.

PAHs occurring in the marine environment can also be formed in diagenetic processes in coastal sediments or on land (Bouloubassi and Saliot, 1993). Numerous authors have suggested, moreover, that at least some PAHs can be synthesised by unicellular algae, higher plants or bacteria, but at the same time others have concluded that organisms accumulate PAHs rather than synthesise them (Cripps and Priddle, 1991; Cripps, 1992). Despite these controversies, one thing is certain: PAH production resulting from natural processes is generally very low compared to PAHs originating from anthropogenic sources.

Once released into the environment, all PAHs are subject to a variety of changes as a result of microbial degradation, photo-oxidation and chemical oxidation (Readman *et al.*, 1982); even so, most PAHs are persistent both in the aqueous phase and in sediments.

Elucidation of already complex environmental processes is made more difficult because analysis of the complex mixtures occurring in low concentrations (10^{-5} – 10^{-10} g g⁻¹) in a rich organic matrix still causes a lot of problems, even when the latest chromatographic techniques (GC/MS and HPLC) are applied. Some authors claim to have determined as many as 80 different compounds; in most cases, however, these were from 6 to 16 different unsubstituted PAHs. For example, a group of 10 unsubstituted PAHs was selected for studies performed under the auspices of the International Council for the Exploration of the Sea (ICES) (Law and Nicholson, 1995). The first stage of the intercalibrations organised within the framework of the Quality Assurance of Information for Marine Monitoring in Europe (QUASIMEME) programme in 1994 included the intercalibration of these PAHs in solution (Law and Klungsöyr, 1996). Furthermore, some authors determine PAH content only in the finest-grain sediment fraction (< 63 μ m). Under such circumstances any attempt to compare ‘total PAH’ values, determined moreover by different analytical procedures, can be very misleading. A much more reasonable approach would be to compare the con-

centration of individual PAHs with at least one commonly agreed 'pyrogenic PAH' marker (Tab. 2).

At present, few publications have dealt with PAHs in Baltic sediments, and fewer still with the southern Baltic area (Tab. 2). The aim of the present work was therefore to obtain a consistent set of concentration levels of 12 unsubstituted PAHs, thereby enabling the sources and distribution of pyrogenic PAHs in recent sediments in different regions of the southern Baltic to be determined. In order to follow the paths of PAH transport in the environment, the organic carbon and plankton pigments were also determined in these sediments.

2. Experimental

2.1. Sampling area

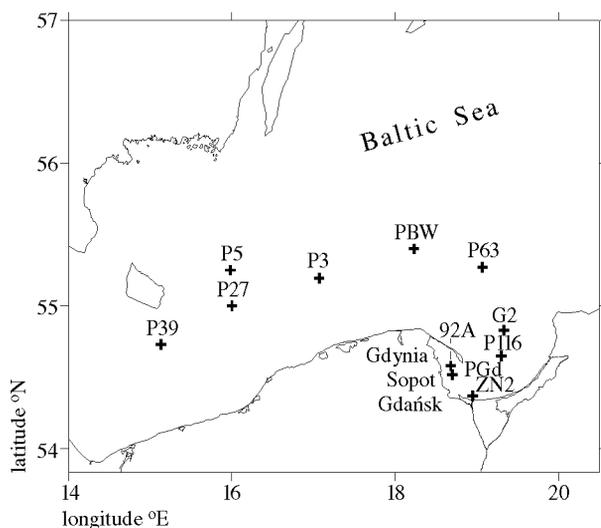


Fig. 1. Locations of the sampling stations

The locations and characteristics of the sampling stations are given in Fig. 1 and Tab. 1. In 1995–1996 recent sediments (0–10 cm) were collected with a Niemistö core sampler during cruises of r/v 'Oceania'; in 1994, samples were taken with a box corer during cruises of r/v 'Baltica'. After collection, the samples were divided into 0–1 cm, 1–5 cm and 5–10 cm layers and frozen immediately at -20°C on board. Of the 1994 samples only the surface layers (0–3 cm) were analysed. The sampling stations were selected so as to cover different types of sediments and locations, and can be divided into three groups: 1 – coastal stations: near the mouth of the river Vistula (ZN2), in the vicinity of the port of Gdynia (PGd), and in Puck Bay (92A),

Table 1. Characteristics of the sampling stations

Station	Date of sampling	Coordinates	Depth [m]	O ₂ * [ml l ⁻¹]	% C _{org.} (0–10 cm)	Description of sediment
open sea						
P63	April 1994	55°21'N 19°04'E	85	3.5	1.2**	silt
PBW	October 1995	55°21'N 18°14'E	80	< 2	3.3–3.85	silt
P3	March 1995	55°13'N 17°04'E	91	3	0.2–0.75	sand
	October 1995			< 2	0.4–1.0	
P39	October 1995	54°44'N 15°08'E	63	3	5.6–5.8	silt/clay
the Deeps						
P5	April 1994	55°15'N 15°59'E	89	2.7	4.6**	clay
P27	March 1995	55°00'N 16°00'E	78	< 2	5.0–5.4	clay
G-2	April 1994	54°50'N 19°20'E	108	2.4	6.0**	clay
	November 1995			-1	5.8–6.8	
	May 1996			112	< 1	
P116	April 1994	54°39'N 19°18'E	88	3	5.2**	clay
	March 1995			89	< 4	
coastal stations						
92A	March 1995	54°35'N 18°41'E	40	8.5	3.3–4.5	silt/clay
PGd	May 1996	54°31'N 18°41'E	28	11	2.8–3.4	silt
ZN2	October 1995	54°22'N 18°57'E	17	6.5	0.26–0.5	sand

* Łysiak-Pastuszak, 1995; Trzosińska, 1996; *Environmental ...*, (in preparation)

** 0–3 cm

a shallow, eutrophic, brackish-water bay; 2 – open-sea stations (P39, P3, PBW, P63) with different water depths and sediment types; 3 – the Bornholm Deep and the Gdańsk Deep (P5, P27, G–2, P116), the deepest regions of the Polish economic zone. The Gdańsk Deep acts as a sink for organic matter transported by the Vistula. At some stations samples were collected twice and at station G–2 even three times in 1994–1996.

2.2. Analytical methods

PAHs (12 unsubstituted compounds from phenanthrene to benzo(g,h,i)perylene) were determined according to a procedure elaborated earlier (Kowalewska and Toma, 1996) using an HPLC system (Knauer, Germany) with a Chrom-a-Scope diode-array detector in the UV range. The mixture of PAHs (Supelco, mix 610–M) and benzo(a)pyrene (Labor. Dr. Ehrenstorfer) were used as standards. Additionally, the method was calibrated on EPA-certified reference material (RTC, CRM 104–100) – sediment from Chesapeake Bay not ‘spiked or fortified’ with PAHs.

The detailed pigment analysis is described in Kowalewska (1994) and Kowalewska *et al.* (1996).

Organic carbon was determined by the chromic acid titration method (Goudette *et al.*, 1974).

3. Results and discussion

3.1. Results of PAH analysis of the RTC reference material

The results of this calibration are presented in Fig. 2: 1 – the mean, maximum and minimum values obtained from 4 independent analyses using the HPLC method worked out by Kowalewska and Toma (1996); 2 – the mean concentration, 95% confidence interval (CI) and 95% prediction interval (PI) quoted in the certificate attached to the reference material: these values were obtained by a GC/MS method with Soxhlet extraction. According to the certificate, laboratories analysing this sediment should obtain results within the 95% probability PI window, and when the same analytical procedures are applied, the results should lie within the 95% probability CI window. Almost all the individual PAHs means obtained by the HPLC method used fall within the PI range; only the values for phenanthrene lie beyond the upper limit of this range. The means for pyrene and benzo(a)pyrene are within the CI range, while those for anthracene, fluoranthene, indeno(1,2,3,-c,d)pyrene and benzo(g,h,i)perylene are close to that range. The sum of benzo(a)anthracene and chrysene also fits in the CI range and the non-agreement of the means of these individual hydrocarbons arises from the integration of their peaks, the retention times of which are very similar.

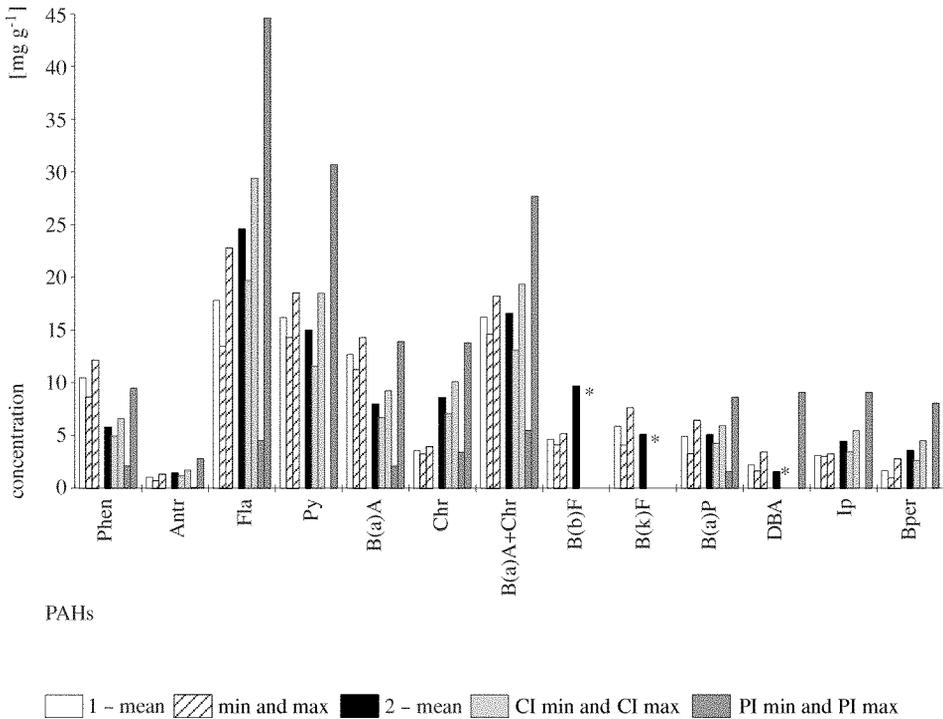


Fig. 2. Results of calibration with RTC reference material (abbreviations of PAH names – see Tab. 4): 1 – mean value of 4 analyses by the HPLC method; min – minimum, max – maximum values, 2 – RTC reference value; CI – 95% confidence interval, PI – 95% prediction interval, * – results not validated

3.2. PAH concentrations in Baltic sediments

The two principal mechanisms of PAH transport from the terrestrial to the marine environment – the fluvial and the aeolian – are usually taken into consideration (Lipiatou and Salot, 1991). Hydrocarbon distributions at remote sites, though low in concentration compared to those at coastal sites, confirm the long-range transport of hydrocarbons from natural and urban/industrial sources to remote depositional environments (Cripps, 1992). In coastal areas, direct deposition of atmospheric PAHs may be relatively minor compared to fluvial inputs, but in open ocean areas it can be dominant.

The solubility of PAHs in water is low and decreases with increasing molecular mass. Thus in the water column, PAHs are assumed to adsorb to particles and deposit with them to the underlying sediments, where degradation is generally slow, especially that of the higher-molecular-mass PAHs.

The depositional areas in deep waters are regarded as a PAH sink (Lipiatou *et al.*, 1993). In shallower and more dynamic environments, significant remobilisation of sediment PAHs can occur. On the other hand, aerosols are assumed to be strongly depleted in lower-molecular-mass PAHs and enriched in higher-molecular-mass compounds in relation to the gaseous phase (Lipiatou and Albaiges, 1994). This, and the loss of the more soluble, low-molecular-mass PAHs during transport through the water column would lead to sedimentation in deep water of particles depleted of low-molecular-mass components.

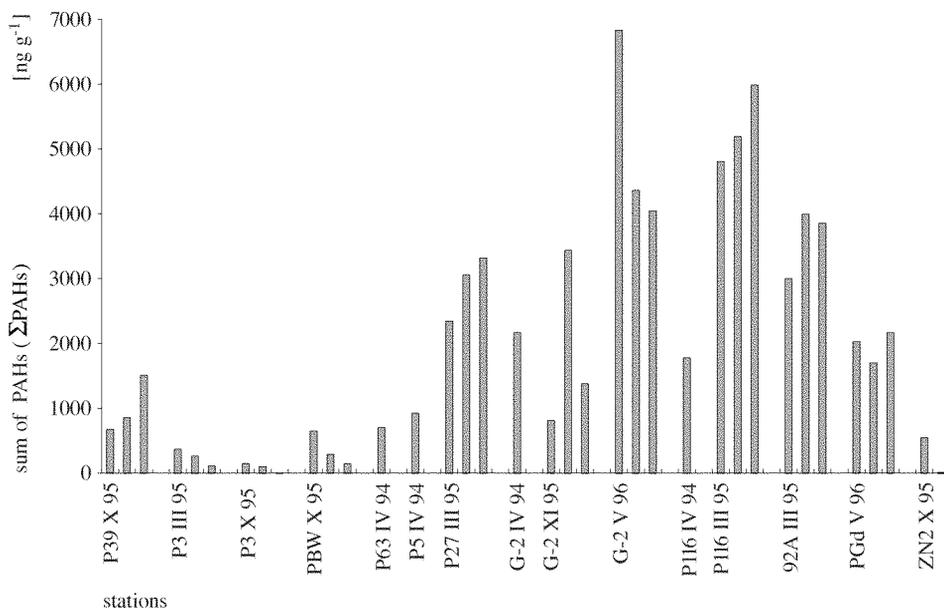


Fig. 3. Total concentrations of 12 unsubstituted PAHs (Σ PAHs) in the investigated sediments of the Baltic Sea (1994–1996) [ng g^{-1} d.w.]

The sum of PAH concentrations (Σ PAH) in our samples reached 7000 ng g^{-1} (Fig. 3), which is consistent with Poutanen's results (1988) though higher than the results obtained for the Baltic by other authors (Głód *et al.*, 1993; Lamparczyk *et al.*, 1990; Maliński *et al.*, 1993; Witt, 1995). Such discrepancies are readily explained, as none of these data sets are comparable. To begin with, all these samples were collected using a variety of samplers at different stations and from different sediment layers. Next, a fact of crucial importance, the extractive and analytical procedures employed were different, and as a consequence, different PAHs were determined (Tab. 2).

Table 2. Examples of PAH concentration levels [ng g^{-1}] in sediments – literature data

Area PAHs*	No. of PAHs	Σ PAHs min-max (mean)	Phen	Antr	Py	B(k)F	B(a)P	No. of stations	Date of sampling	Sampler	References
Tamar Estuary (Atlantic)	10	4900	1042	497	1597	382	741	7	September, 1980	gravity Butler corer	Readman <i>et al.</i> , 1982
Nap-B(a)P										0–5 cm	
Lagoon of Venice	11	900	47	42	94	–	0	1	July, 1982	box corer	Pavoni <i>et al.</i> , 1987
Phen-B(a)P									0–4 cm		
Adriatic Sea	10	27–527 (128)	–	–	25–150	1–50	< 1–38	32	March, 1990	Petersen grab	Guzzella and de Paolis, 1994
Fla-Py										0–20 cm	
Mediterranean Sea	15	182–1798 (808)	20–200	1.8–3.4	12–174	8–81	9.5–117	6	1987/1988	box corer	Lipiatou and Saliot, 1991
Phen-Bper	33	325–3182 (1524)								0–1 cm	
Black Sea	28	160–240 (788)	4–56	0.2–7	8–220	17–275	1–9	13	1988/1990	grab sampler,	Wakeham, 1996
Ace-Cor		470–1200 (789)	3–33	0.2–4	40–105	8–180	2–34			box corer	
										0–2 cm	

Table 2. (continued)

Area PAHs*	No. of PAHs	Σ PAHs min-max (mean)	Phen	Antr	Py	B(k)F	B(a)P	No. of stations	Date of sampling	Sampler	References
Baltic Sea	?	4000-14000 (8000)	3.9-180	0.3-12	1.7-150	-	-	9	1978/1982	Van Veen grab sampler 0-1 cm	Law and Andruliewicz, 1983
- Gotland Deep	22	4400	294	30	480	814	158	1	August, 1987	Niemistö corer 0-2 cm	Malinski <i>et al.</i> , 1993
Nap-BFs	?	500-7000	-	-	-	-	-	?	?	Niemistö corer	Poutanen, 1988
- Gulf of Gdańsk	10	580-2321 (1470)	155-466	26-93	102-547	-	-	5	January, May, June, 1992	Niemistö corer 0-2 cm	Głód <i>et al.</i> , 1993
Nap-Py	15	10-1870 (1180)	1.4-81	0.3-84	0.4-108	0.3-157	0.4-210	14	1992/1994	Van Veen grab sampler 0-1 cm	Witt, 1995
- Belt Sea	11	447-3354 (1730)	5-132	3-89	69-1340	2-49	42-360	20 (14 coastal)	1983	?	Lamparczyk <i>et al.</i> , 1990
Arkona Basin	12	10-7000 (1830)	0.7-2110	0.4-309	2-968	3-920	0.3-418	11	1994/1996	Niemistö corer 0-10 cm	own results
Nap-Bper											
- southern Baltic											
Phen-Bper											
- southern Baltic											
Phen-Bper											

* Nap - naphthalene, B(a)P - benzo(a)pyrene, Phen - phenanthrene, Fla - fluoranthene, Ace - acenaphthene, Cor - coronene, Py - pyrene, Bper - benzo(g,h,i)perylene, BFs - benzophenanthrenes, Antr - anthracene, B(k)F - benzo(k)fluoranthene

Generally, the highest Σ PAH levels were found in the Bornholm and Gdańsk Deeps (up to 7000 ng g^{-1} , av. 2900 ng g^{-1}), those in the coastal region were somewhat lower (up to 4000 ng g^{-1} , av. 2300 ng g^{-1}), while the open-sea levels were very distinctly lower (up to 1500 ng g^{-1} , av. 500 ng g^{-1}) (Fig. 3 and Tab. 3). Evidently, the Σ PAH concentration depends more on the sediment type than on distance from the shore. Muddy sediments contained higher levels of PAHs than sandy ones, *e.g.* PAHs levels were lowest in the sediment at the station (ZN2) nearest to the shore, but highest at the Puck Bay station. A sink for the Vistula inputs, the Gdańsk Deep contained more PAHs than did the Bornholm Deep. These results are consistent with the conclusions of some authors that the PAH content correlates with the fine-particle content (Readman *et al.*, 1982; Pavoni *et al.*, 1987) and the organic carbon content (Witt, 1995).

Table 3. Ratio of mean of Σ PAHs [ng g^{-1}] and content of 3-, 4-, 5- and 6-ring PAHs [in %], in 0–1 cm/0–10 cm layers

Stations	Mean Σ PAHs	3-ring	4-ring	5-ring	6-ring
all	1789/1878	23/18	29/31	23/25	20/20
open sea	521/495	19/18	8/7	22/24	48/48
the Deeps	2753/2868	25/17	25/24	28/29	22/30
coastal area	2092/2271	23/19	39/46	17/29	9/2

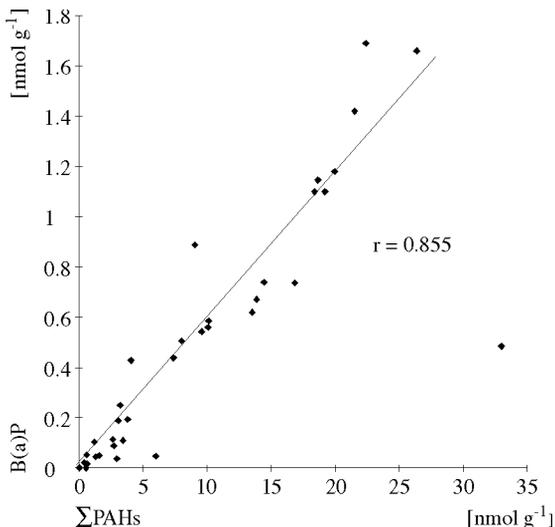


Fig. 4. Correlation between benzo(a)pyrene (B(a)P) and Σ PAHs

In the study of PAH pollutants the most reasonable approach, besides determining the so-called 'total PAH' level and the most abundant compounds, would be to choose an obligatory marker. This could be benzo(a)pyrene, which is formed during every process of pyrolysis and, compared to other PAHs, is relatively easy to determine. The correlation between benzo(a)pyrene and Σ PAHs is presented in Fig. 4.

However, detailed analysis of the correlation coefficients for individual PAHs and Σ PAHs reveals differences depending on the location of the sampling stations (Fig. 5). The most abundant of the individual PAHs studied in the open-sea sediments were phenanthrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene and benzo(b)fluoranthene (Tab. 4). In the Deeps, the generally most abundant compounds were benzo(b,k)fluoranthenes, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene and phenanthrene, particularly in the 0–1 cm layer. The concentrations of the lower-mass PAHs were broadly differentiated. The most common compounds in the coastal sediments were the lower-mass PAHs – pyrene, fluoranthene and phenanthrene; only at the mouth of the Vistula was phenanthrene significantly the most abundant. This was due to the different sources of the particular

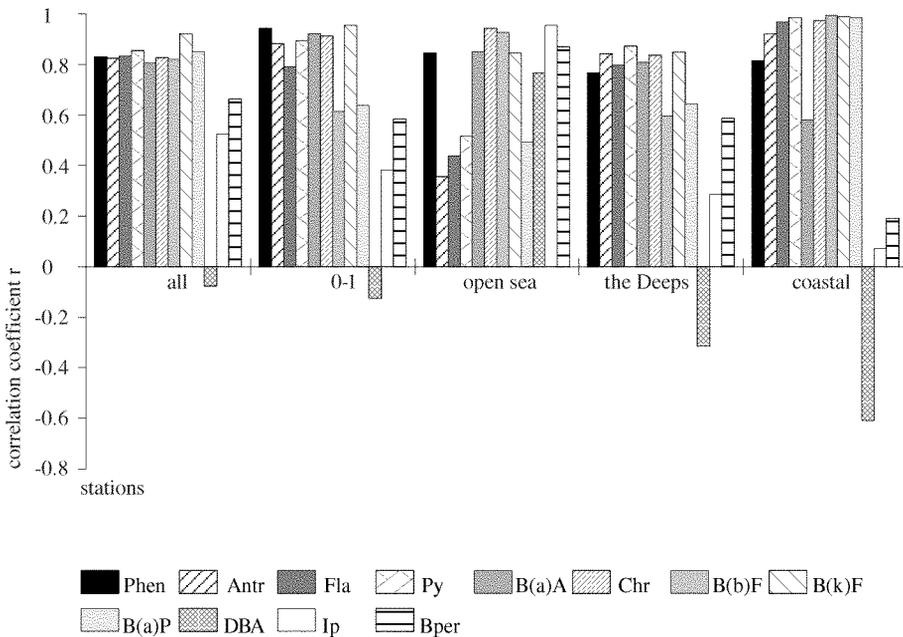


Fig. 5. Correlation coefficients between Σ PAHs and individual PAHs

Table 4. PAH concentration levels [ng g^{-1} d.w.] in recent Baltic sediments

Stations	Phen*	Antr	Fla	Py	B(a)A	Chr	B(b)F	B(k)F	B(a)P	DBA	Ip	Bper
open sea												
P39, October 1995												
0-1 cm	84	0	31	11	5	7	111	15	22	11	160	216
1-5 cm	70	9	10	28	15	15	150	64	28	17	284	166
5-10 cm	174	6	21	16	19	20	165	92	12	221	571	190
P3, March 1995												
0-1 cm	65	9	46	26	9	4	26	13	13	57	44	55
1-5 cm	66	11	0	29	10	5	39	19	12	0	63	42
5-10 cm	49	4	0	6	0	0	4	3	0	0	7	38
P3, October 1995												
0-1 cm	17	2	1	0	4	5	21	21	13	0	46	16
1-5 cm	8	3	7	5	2	2	14	7	5	14	24	10
5-10 cm	0.7	0	0	0	0	0	0.2	0.2	0.3	0	0.3	0.6
PBW, October 1995												
0-1 cm	94	21	0	0	7	9	93	13	29	4	221	158
1-5 cm	36	3	11	0	3	9	73	41	26	11	-**	75
5-10 cm	52	1.5	0	0	0.4	0.4	21	3	4	0	45	18
P 63, March 1994												
0-3 cm	185	9	14	10	8	12	76	71	47	0	134	136

Table 4. (continued)

Stations	Phen*	Antr	Fla	Py	B(a)A	Chr	B(b)F	B(k)F	B(a)P	DBA	Ip	Bper
the Deeps												
P5, April 1994												
0-3 cm	144	9	19	0	30	24	184	217	108	6	12	170
P27, March 1995												
0-1 cm	334	-	-	276	128	61	327	234	142	0	489	352
1-5 cm	374	94	477	341	107	49	376	222	158	0	502	355
5-10 cm	392	88	508	300	134	64	456	231	187	0	586	372
G-2, April 1994												
0-3 cm	355	17	20	22	39	50	352	341	224	53	493	203
G-2, November 1995												
0-1 cm	122	6	29	12	15	18	128	142	63	0	276	811
1-5 cm	252	21	45	20	40	39	293	311	186	0	428	1797
5-10 cm	265	9	64	0	63	56	134	57	49	0	618	63
G-2, May 1996												
0-1 cm	2110	190	1130	640	970	140	217	920	122	0	585	230
1-5 cm	1170	74	300	360	500	55	380	290	297	0	548	388
5-10 cm	980	79	370	440	580	65	373	260	288	0	720	190
P116, April 1994												
0-3 cm	286	18	35	18	20	37	266	270	111	109	465	142

Table 4. (continued)

Stations	Phen*	Antr	Fla	Py	B(a)A	Chr	B(b)F	B(k)F	B(a)P	DBA	Ip	Bper
P116, March 1995												
0-1 cm	903	247	-	666	293	131	500	575	357	0	680	453
1-5 cm	357	168	765	689	226	97	561	381	342	0.2	798	608
5-10 cm	523	206	980	738	282	133	767	520	418	0	805	611
coastal												
92A, March 1995												
0-1 cm	390	112	560	546	165	106	221	199	168	0	238	292
1-5 cm	617	309	686	968	278	203	325	324	282	0	-	-
5-10 cm	547	247	862	837	281	179	311	300	286	0	-	-
PGd, May 1996												
0-1 cm	401	68	271	339	322	105	156	169	137	0	-	50
1-5 cm	322	50	226	291	326	50	119	146	128	0	-	42
5-10 cm	319	62	321	406	407	68	174	180	147	0	-	84
ZN2, October 1995												
0-1 cm	435	13	25	22	6	6	13	18	9	0	0	0
1-5 cm	4	0.4	1	2	0.7	0.3	0.4	0.8	0.4	0.7	0.3	0

*Phen - phenanthrene, Antr - anthracene, Fla - fluoranthene, Py - pyrene,
 B(a)A - benzo(a)anthracene, Chr - chrysene, B(b)F, B(k)F - benzo(b,k)fluoranthene,
 B(a)P - benzo(a)pyrene, DBA - dibenzo(a,h)anthracene

** not determined

compounds and their fates in the environment, resulting from their physico-chemical properties, *e.g.* solubility in water or volatility. While in coastal sediments it was the four-ring PAHs that generally prevailed and in the open-sea sediments the six-ring PAHs that were dominant, PAHs were more evenly distributed in the Deeps. The surface layer of sediments (0–1 cm) were rich in three-ring PAHs but contained smaller amounts of five-ring PAHs. Four-ring PAHs were more abundant in the surface layer (0–1 cm) in the Deeps and in the open-sea regions. The percentage of six-ring compounds is higher in the surface layer of coastal sediments (0–1 cm) and in the deeper layers of the sediments in the Deeps (1–10 cm) (Tab. 3).

The distinct differences in the geochemistry of PAHs may be due to the fact that PAHs enter the southern Baltic Sea from the land through both aeolian and fluvial input. More soluble in seawater, the lower-molecular-mass PAHs, are less readily scavenged from the water column to the sediments, but are later more easily remobilised. Conversely, the higher-molecular-mass PAHs from such input are scavenged to the sediments more easily, but not so readily remobilised.

3.3. Correlation with pigments and organic carbon

The correlation between PAHs in sediments and the fine particulate fraction (Readman *et al.*, 1982; Pavoni *et al.*, 1987) or the organic carbon content (Witt, 1995) has been noted by various authors, though not by all (Wakeham, 1996). This discrepancy can be explained by the fact that PAHs are derived from a variety of sources and are transported in different ways in the environment.

The correlation coefficients of PAHs for organic carbon and the phytoplankton pigments are presented in Fig. 6. When Σ PAHs and all the samples studied were taken into consideration, the correlation coefficient for phaeophytin *a* was found to be the highest ($r = 0.68$), while that for organic carbon was slightly lower ($r = 0.64$) (Fig. 6a). For all the individual lower-mass PAHs from phenanthrene to benzo(k)fluoranthene, the correlation with phaeophytin *a* is distinctly higher than with organic carbon. Benzo(b)fluoranthene and benzo(a)pyrene display a different correlation coefficient pattern, the highest being for organic carbon ($r = 0.57$ – 0.68), and the next-highest for phaeophytin *a* ($r = 0.49$ – 0.51). For the six-ring PAHs the correlation is similar, only much more significant with chlorophyll *a*.

In the 0–1 cm layer of sediments (Fig. 6b) the correlation coefficient for organic carbon ($r = 0.58$) is slightly lower than that for the other samples. For Σ PAHs the highest correlation coefficient is obviously that for phaeophytin *a* ($r = 0.9$), and is followed by the corresponding coefficients for

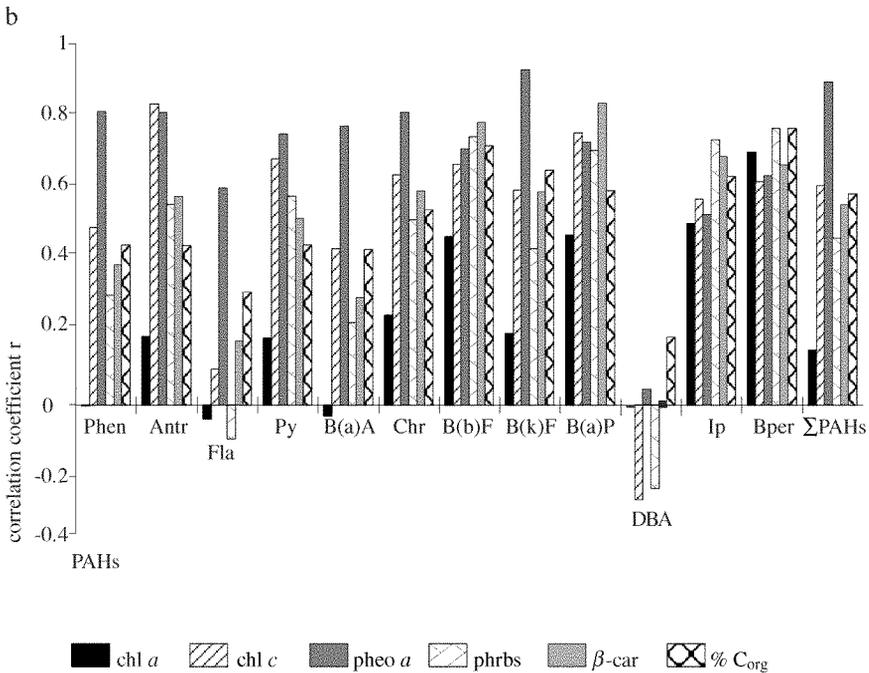
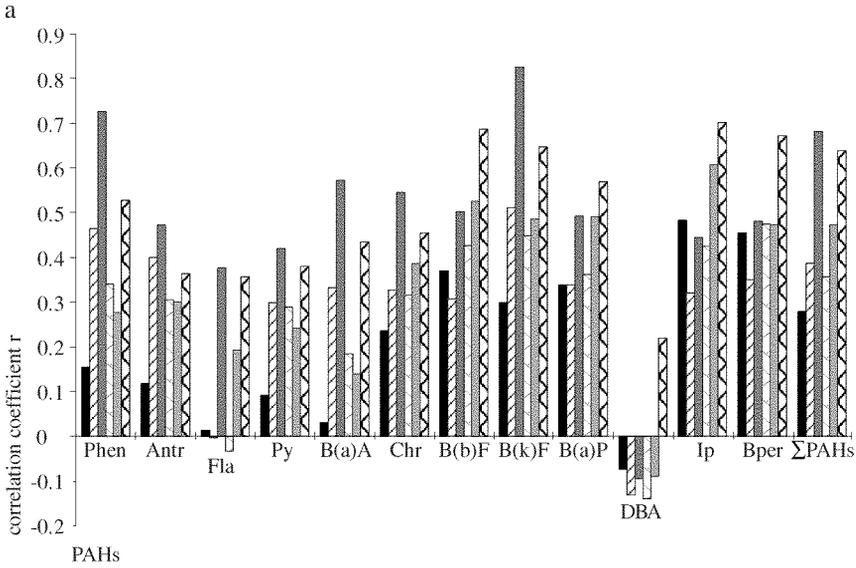
chlorophylls *c* ($r = 0.61$), organic carbon ($r = 0.58$) and β -carotene ($r = 0.56$). For the several PAHs from phenanthrene to benzo(k)fluoranthene, the most significant correlation is clearly the one with phaeophytin *a* ($r = 0.6$ – 0.93). For anthracene, pyrene and chrysene the next most significant correlation is the one with chlorophylls *c*; the one with organic carbon takes third place in this ranking order. For benzo(b,k)fluoranthenes and benzo(a)pyrene the correlation with β -carotene is higher than that with chlorophylls *c*. The correlation phaeophorbides is distinctly higher, especially for the six-ring PAHs.

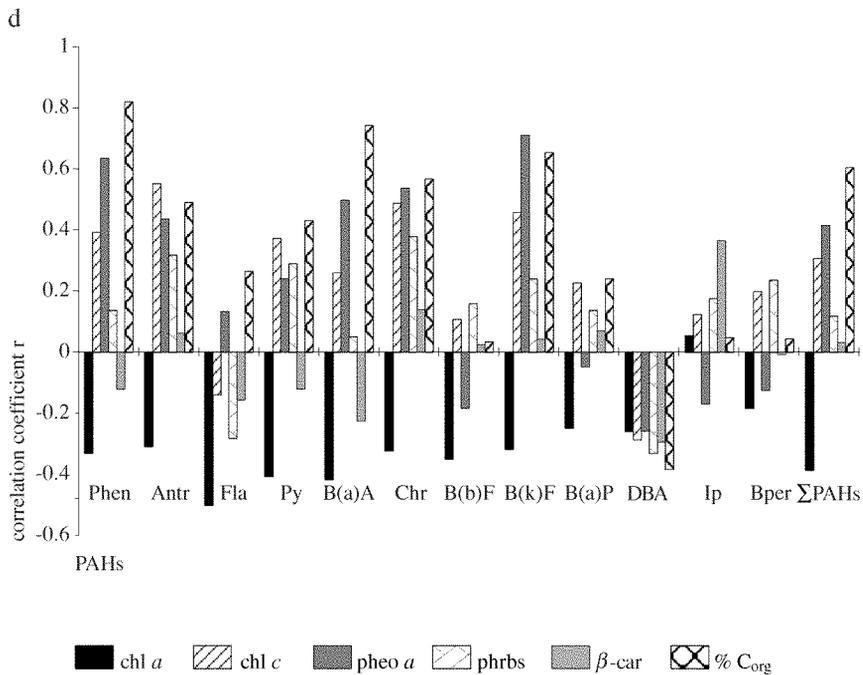
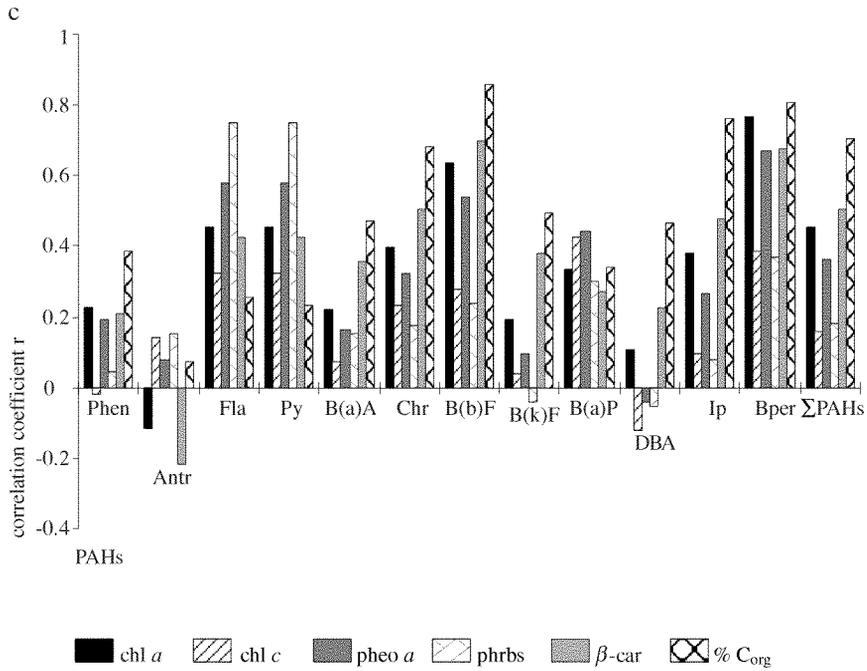
In the open-sea sediments (Fig. 6c) the most significant correlation in the case of Σ PAHs is that with organic carbon ($r = 0.7$); that with phaeophorbides is very much lower ($r = 0.18$). The order of the correlation with pigments is similar for both low- and high-molecular-mass PAHs with the exception of anthracene, benzo(a)pyrene and dibenzoanthracene. For fluoranthene and pyrene the highest correlation is with phaeophorbides.

The most varied are the correlation coefficients for the sediments of the Deeps (Fig. 6d). Here, as at the other open-sea stations, correlation with organic carbon is the highest ($r = 0.6$ – 0.8), that with phaeophytin *a* and chlorophylls *c* being only slightly lower. The correlation with phaeophorbides and β -carotene, with the exception of indeno(1,2,3-cd)pyrene, is very much lower, however. Correlation with chlorophyll *a* is negative.

In the coastal samples (Fig. 6e) the correlation with organic carbon ($r = ca\ 0.9$) is the highest, higher than that for the other sediments. This order of correlation coefficients is surprisingly similar for most of the the PAHs studied, from phenanthrene to benzo(a)pyrene, with the exception of benzo(a)anthracene, dibenzoanthracene and indeno(1,2,3-cd)pyrene. In the case of indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene the correlation with organic carbon is much lower than with chlorophyll *a*, phaeophytin *a* or β -carotene.

During sedimentation, collection, storage and analysis, chlorophyll *a* decomposes first to phaeophytin *a*, and then to phaeophorbides. This could explain the higher correlation with phaeophytin *a* than with chlorophyll *a*. Like chlorophyll *a*, β -carotene is best preserved when sedimentation occurs under anoxic conditions at high rates of primary production. Hence, the recent large variations in the oxygen content of the Deeps (Łysiak-Pastuszak, 1995; Trzosińska, 1996; *Environmental ...*, (in preparation)) have much altered the pigment and PAH composition in the sediments in these areas. This explains why the correlations with β -carotene and chlorophyll *a* were higher in the 0–1 cm layer and at the seashore than in the deeper layers and open-sea sediments.





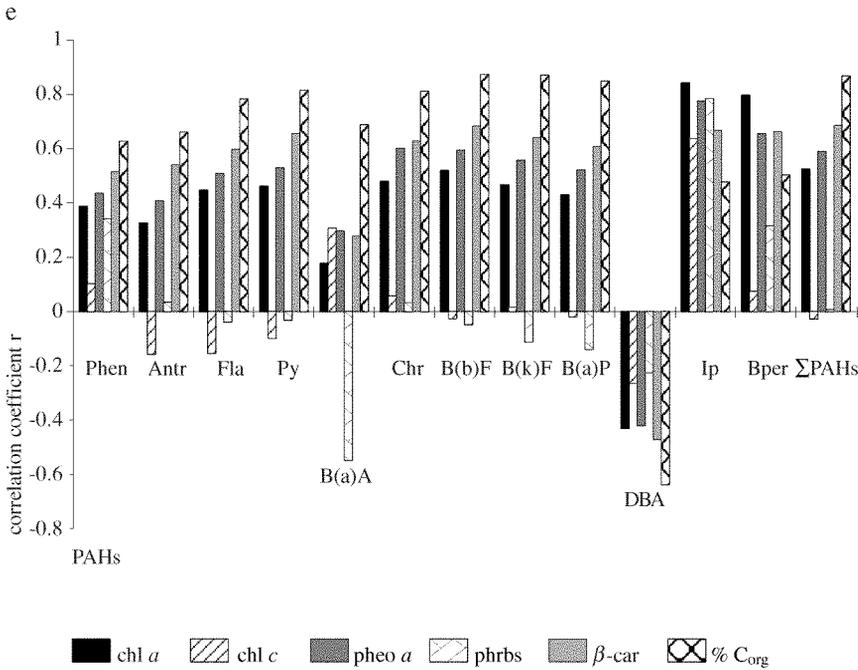


Fig. 6. Correlation coefficients between PAH content [nmol g^{-1}] and pigment content [nmol g^{-1}] in sediments in all the samples studied (a), the 0–1 cm layer (b), open-sea samples (c), samples from the Deeps (d), coastal samples (e)

The phaeophorbides in the water column and sediments are mostly products of zooplankton grazing. The high correlation coefficients for individual high-molecular PAHs at all the stations and for Σ PAHs at the open-sea stations implies that in these cases either straightforward adsorption of PAHs on the phytoplanktonic detritus is occurring or that these compounds are products of zooplankton digestion.

The observed relationships with pigments lead one to the conclusion that the correlation with organic carbon is a secondary phenomenon, not a primary one. This means that PAHs are removed from the water either by absorption or adsorption by phytoplankton cells. Such conclusion is confirmed by the fact that the PAH content in sediments was so varied, especially in the 0–1 cm layer. After a phytoplankton bloom, the water is purified of dissolved and particulate PAHs, which are later transported to the sediments together with the phytoplankton detritus.

4. Conclusions

- The sum of the concentrations of 12 unsubstituted PAHs from phenanthrene to benzo(g,h,i)perylene in recent sediments in the southern

Baltic Sea ranges from 10 to 7000 ng g⁻¹ (d.w.) (av. 1830 ng g⁻¹), which is in agreement with the results of the work of other authors done on Baltic sediments, despite the differences in the sampling and analytical procedures employed.

- Benzo(a)pyrene is proposed as a marker of environmental pollution with pyrolytic PAHs; its concentration varied from 0.3 to 418 ng g⁻¹ (d.w.) (av. 98 ng g⁻¹).
- The land is the main source in the Baltic Sea sediments of the unsubstituted three- to six-ring PAHs, which reach the sea by both fluvial and aeolian way.
- PAHs are scavenged from the water column mainly by absorption or adsorption by phytoplankton cells, after which they are carried to the sediments along with the phytoplankton detritus.
- Deep-sea sediments rich in organic matter may act as a sink for PAHs, especially under anoxic conditions.

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