Polynuclear aromatic hydrocarbons (PAHs) in the sediments of the Oder Estuary (Szczecin Lagoon) before the flood of 1997

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Abstract

Concentrations of 12 unsubstituted PAHs were determined in sediments of the Oder Estuary (Szczecin Lagoon), an exceptional aquatic basin on the Baltic coast, collected in 1996, *i.e.* before the flood of 1997. Four-ring PAHs (fluoranthene and pyrene) were the most abundant, six-ring PAHs the least abundant group of PAHs, as is the case in the coastal southern Baltic sediments. The PAH concentration levels were higher than those recorded in the southern Baltic Sea (av. ΣPAHs – 1830 ng g^{-1}, benzo(a)pyrene (B(a)P) – 98 ng g^{-1}), and higher in samples collected in August (av. ΣPAHs – 4960 ng g^{-1}, B(a)P – 319 ng g^{-1}) than in October (av. ΣPAHs – 4581 ng g^{-1}, B(a)P – 281 ng g^{-1}). This result is consistent with the fact that the coastal area is mainly responsible for PAH pollution of the Baltic Sea, and that unsubstituted PAHs are of pyrogenic origin. Their concentration should therefore decrease after summer, since their residence time in the Oder Estuary is very short. PAHs are scavenged from the water column by phytoplankton, mainly by living phytoplankton cells. This conclusion confirms the previous results obtained for sediments from the southern Baltic Sea. The sorption of unsubstituted PAHs by phytoplankton cells varies, depending not only on the concentration and physico-chemical properties of the PAH in question but also on the symmetry of its molecule.

1. Introduction

The greatest concern has been expressed in marine ecological studies about the possible impact of pollutants on coastal ecosystems. Aromatic hydrocarbons, particularly polynuclear aromatic hydrocarbons (PAHs), are of priority interest here because of their persistence in the environment, high bioaccumulation and toxic potential, including their mutagenic and carcinogenic properties (GESAMP, 1993). Unsubstituted polynuclear aromatic hydrocarbons, compounds mainly of pyrogenic origin, are transported to the sea principally by rivers or the atmosphere (Lipiatou and Albaiges, 1994). Once there, most of them remain stable, but some may undergo microbial degradation, photo-oxidation or chemical oxidation (Readman *et al.*, 1982).

Our previous results with regard to PAHs in the sediments of the southern Baltic (Kowalewska and Konat, 1997) proved that these compounds are accumulated mainly in sediments containing a considerable admixture of fine organic particles; moreover, it was evident that PAHs are better preserved under anoxic conditions. A high positive correlation with pigments, especially with phaeophytin *a*, indicated further that it is the phytoplankton that is principally responsible for transporting PAHs from the water column to the sediments.

There are no papers in the literature on PAHs in the sediments of the Oder Estuary (Szczecin Lagoon), and this is an exceptional area for studying PAH transport mechanisms in a natural aquatic environment. The Oder Estuary (Szczecin Lagoon) is a coastal, brackish-water basin polluted by petroleum products, where primary production is high but the oxygen conditions better than in the Deeps of the southern Baltic. The aim of this work was to determine PAH concentration levels in the sediments of the Oder Estuary (Szczecin Lagoon) and to assess their correlation with phytoplankton pigments and organic carbon.

2. Materials and methods

2.1. Sampling area

Collecting waters from 122 712 km^2 of urban areas, the river Oder transports large quantities of domestic and industrial wastes, as well as a variety of organic and inorganic pollutants both in dissolved and in particulate form, which are deposited in the Oder Estuary (Poleszczuk *et al.*, 1995; Grelowski and Pastuszak, 1996). The sedimentation rate there has been estimated at 0.4–0.6 mm a^{-1} for sands and 0.8–1.1 mm a^{-1} for silts (Müller *et al.*, 1996). The sedimentation rate is difficult to determine owing to the unique hydrological conditions in the Oder Estuary (Fig. 1), a shallow coastal basin (usual depth 2–6 m, with a maximum of *ca* 10 m in the shipping channel), supplied to a substantial degree by freshwater from the Oder (15 km^3 a^{-1}, 464 m s^{-1}), but periodically also by Baltic seawater (0.5–1.5 km^3 $month^{-1}$). The basic factor affecting water movements in this basin, however, is the riverine water inflow, which is highest in spring with a maximum in March (Majewski, 1980; Robakiewicz, 1993; Poleszczuk *et al.*, 1995).

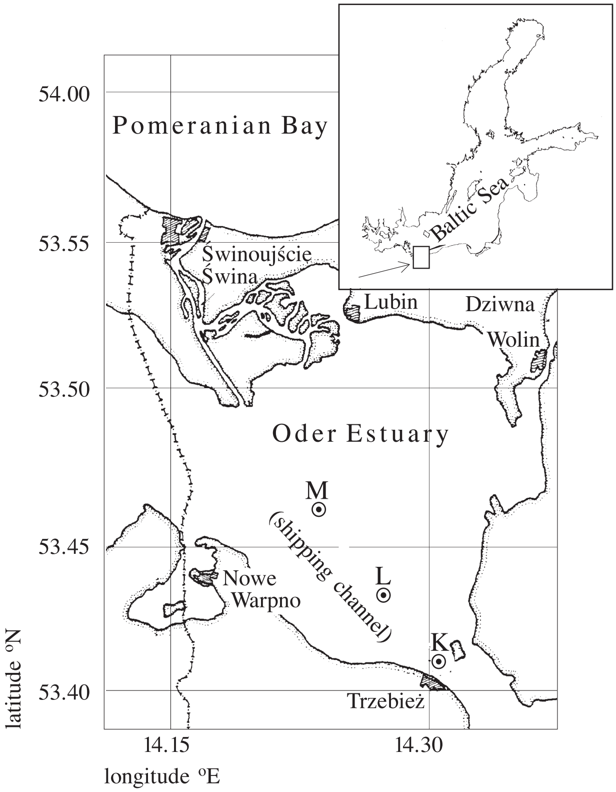


Fig. 1. Location of the sampling stations in the Oder Estuary; samples collected on 6 August and 17 October 1996

The seawater inflow depends not only on the riverine freshwater input but also on such factors as wind direction and atmospheric pressure. Inflows of seawater are weaker in spring and summer (February–August), stronger in autumn and winter (September–January). Exchange of water with the

Baltic Sea through the Świna, Dziwna and Piana Straits can occur in parallel. Such inflows of seawater may cause areas of stratified water to form. However, this stratification is not permanent: the currents may change very rapidly in a few minutes. As a consequence of these complex and unstable hydrological conditions, redeposition and resuspension of sediments occurs constantly in this basin (Majewski, 1980; Robakiewicz, 1993; Poleszczuk *et al.*, 1995).

The large quantities of nutrient ions discharged into the Estuary provide good conditions for phytoplankton blooms. These can be intensive, especially in summer, and are often dominated by blue-green algae of the class *Microcystis*, which are potentially dangerous for other species in the area.

The locations of the sampling stations are shown in Fig. 1, their characteristics in Tab. 1. Sediments were collected at three stations in the vicinity of the shipping channel: station K is influenced predominantly by riverine waters, station M mainly by Baltic waters, while station L is situated between them. Station K was affected by municipal and industrial sewage from the city of Szczecin, station M by sewage from Świnoujście, Międzyzdroje and Wolin. Samples were collected in August and October 1996 with a core sampler. After collection, the cores were divided into 0–1, 1–5 and 5–10 cm sections and frozen at –20°C until analysis.

Table 1. Characteristics of the sampling stations in the Oder Estuary

Station	Coordinates	Time of sampling	% stn O_2*	chl a* [μg l^{-1}]	pheo a* [μg l^{-1}]	% C_{org} in layers		
						0–1	1–5 [cm]	5–10
K	53°40′38″N	August 1996	59.5	40.7	17.9	6.27	7.32	6.20
	14°30′42″E	October 1996	71.9	7.9	11.1	7.14	8.24	8.17
L	53°43′44″N	August 1996	50.4	29.9	7.8	6.56	7.58	3.82
	14°26′33″E	October 1996	51.7	13.2	9.9	6.15	6.75	7.90
M	53°46′46″N	August 1996	55.0	32.9	10.0	4.90	2.97	3.62
	14°22′23″E	October 1996	86.8	10.7	6.9	3.20	2.00	3.46

* water depth 11 m, values measured 1 m above bottom (PIOŚ, 1996)

2.2. Analytical methods

The analytical procedure for PAHs was described by Kowalewska and Toma (1996). Sediments were extracted fivefold with acetonitrile. The acetonitrile extract was then re-extracted with benzene in the 10:1:10 (v/v/v) acetonitrile-benzene-water system and evaporated to dryness. The residue was dissolved in acetonitrile and fractionated by TLC on Merck Kieselgel 60 plates in the 20:35 (v/v) acetone-hexane system. The silica gel with PAHs fluorising at $R_f = 0.7$ was scratched off the plate and extracted with acetonitrile, after which the solution was transferred to a vial and evaporated to dryness under a stream of argon. After being dissolved in a small amount of acetonitrile (200–1000 μl), the sample was analysed using a chromatograph system (Knauer, Germany) with a Chrom-a-Scope diode-array detector. Very low PAH concentrations were determined using a fluorescence detector (Shimadzu, type RF–551) at constant excitation/emission wavelengths 238–400 nm. The column was a Merck Superspher 100 RP18 (250 × 4 mm, 4 μm) with a Merck Lichrospher 100 RP18e precolumn (4 × 4 mm, 4 μm). The mobile phase was acetonitrile – water in a 95:5 (v/v) isocratic system at a 0.4 ml min^{-1} elution rate.

The pigment analysis has been described in detail elsewhere (Kowalewska, 1994, 1995; Kowalewska *et al.*, 1996). Sediments were extracted threefold with acetone. The pigments were then re-extracted from acetone to benzene in the 30:3:27 (v/v/v) acetone-benzene-water system. The benzene layer was transferred to a vial and evaporated to dryness in a stream of argon. The residue was dissolved in a small amount of acetone (200–2000 μl) immediately prior to HPLC analysis. The analyses were performed with the same HPLC set as that used for PAHs. The fluorescence detector was used for determining chlorophylls *b*, *c* and phaeophytin *b*, the diode-array detector for other pigments. The column used was a Merck Lichrospher 100 RP18e (250 × 4, 4 μm) with the same precolumn (4 mm, 4 μm). The mobile phase was acetone – water in the gradient system (0 min, 80:20; 10 min, 85:15; 20 min, 95:5; 40–55 min 100% acetone, at elution rates of 1 ml min^{-1} and 0.5 ml min^{-1}).

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

3. Results and discussion

The sum of the concentrations of 12 unsubstituted PAHs ($\sum$PAHs) is presented in Fig. 2. The August values were lower than the October ones. It becomes clear why this was so when one takes into account the fact that the unsubstituted PAHs are mainly of pyrogenic origin, so their concentration should decrease after summer. The respective $\sum$PAH levels for August and October, *i.e.* 2925–7969, av. 4960 ng g^{-1}, and 1693–7080, av. 4581 ng g^{-1}, are higher than those for sediments in the southern Baltic, higher even than those in the Gdańsk Deep (10–7000, av. 1830 ng g^{-1}) (Kowalewska and

Konat, 1997). Furthermore, it is evident that the ∑PAH concentrations fall with the decreasing percentage of the fine sediment fraction from station K to M.

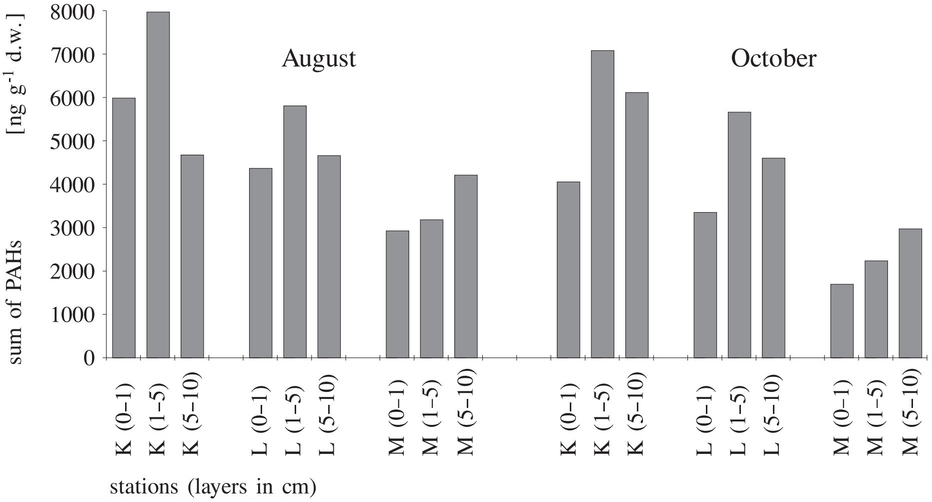


Fig. 2. ∑PAH concentrations of 12 unsubstituted compounds in the Oder Estuary sediments, 1996

The separate PAH concentrations are given in Tab. 2. Fluoranthene and pyrene were the most abundant in summer and in autumn. Benzo(a)pyrene concentrations ranged from 171 to 540, (av. 319 ng g^{-1}) in August and from 75 to 504, (av. 281 ng g^{-1}) in October; in both cases these values were higher than those for the southern Baltic (0.3–418, av. 98 ng g^{-1}). Generally, the four-ring PAHs were the most abundant group of PAHs (for the percentages of three-, four-, five- and six-ring PAHs – see Tab. 3). Such a result is consistent with the results for the southern Baltic, where in the coastal sediments the four-ring compounds were also the most abundant group and the six-ring ones the least abundant (Kowalewska and Konat, 1997).

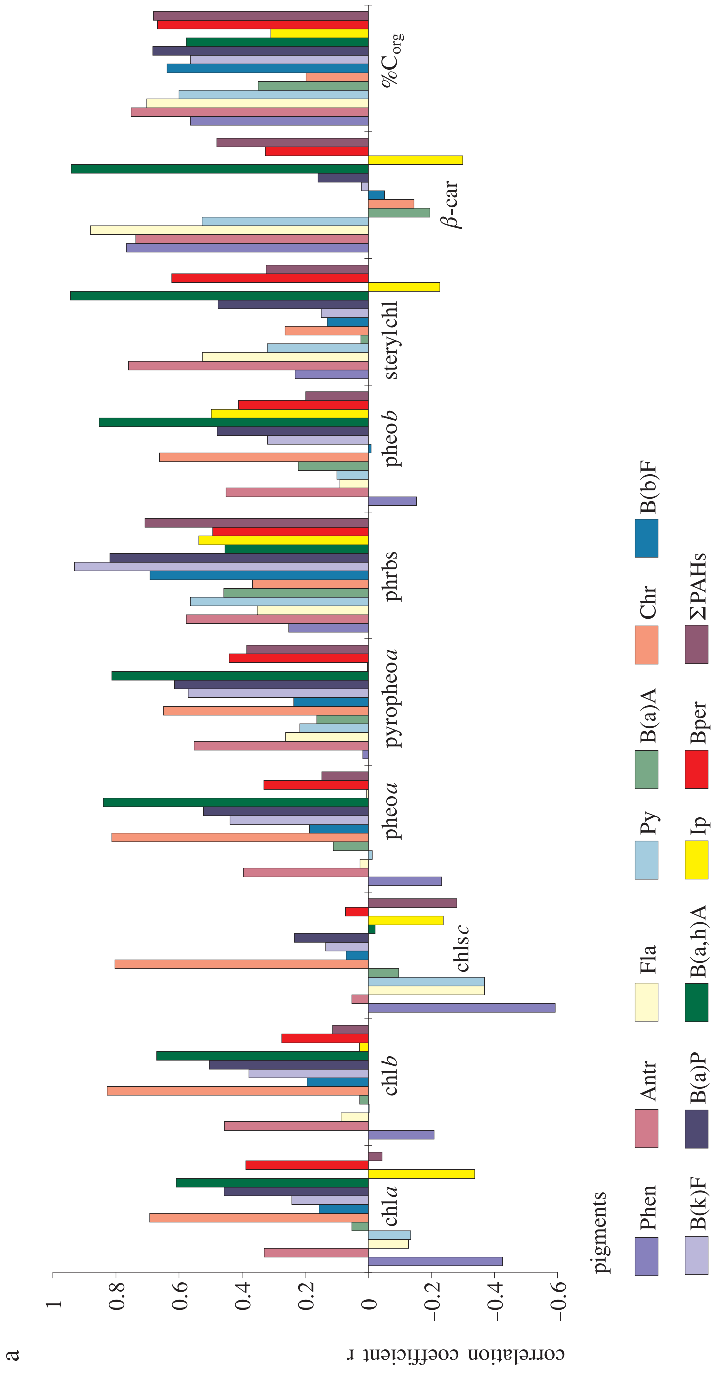
The correlations with pigments and organic carbon are shown in Figs. 3a and 3b. There is a distinct difference in the correlation pattern between August and October. In August the correlation with pigments is insignificant for all the PAHs except anthracene, chrysene and dibenzo(a,h)anthracene. Generally, the best correlation in August was with phaeophorbides (for ∑PAHs $r = 0.71$), even slightly better than with organic carbon (for ∑PAHs $r = 0.68$). The October results show that the correlation coefficients are much more uniform; the best correlation of PAHs is with chlorophyll *a* (for ∑PAHs $r = 0.84$) and is almost equal to that with organic

Table 2. PAH levels in sediments of the Oder Estuary [μg g^{-1} d.w.]

Time of sampling	Station	Layers [cm]	Phen*	Antr	Fla	Py	B(a)A	Chr	B(b)F	B(k)F	B(a)P	B(a,h)A	Ip	Bper
August 1996	K	0–1	486	232	1170	1230	362	261	402	560	407	499	143	222
		1–5	594	270	1241	1773	886	98	623	730	540	413	430	370
		5–10	438	164	933	960	487	54	325	273	288	432	25	294
	L	0–1	105	223	599	883	523	370	383	478	468	nd**	nd	335
		1–5	631	314	1586	1480	249	131	351	337	401	nd	nd	326
		5–10	350	201	887	1000	279	207	209	276	271	559	209	218
	M	0–1	356	148	778	725	24	291	179	201	171	nd	nd	52
		1–5	292	174	664	984	70	65	245	319	262	105	nd	nd
		5–10	248	145	648	1009	742	70	367	302	334	132	nd	212
October 1996	K	0–1	423	215	753	1090	295	231	283	285	262	17	nd	201
		1–5	713	355	1143	1576	411	370	465	430	504	nd	271	503
		5–10	727	323	1432	1498	369	310	350	336	321	339	205	242
	L	0–1	268	134	588	785	486	147	224	190	272	71	75	109
		1–5	464	251	1081	1180	nd	nd	475	335	387	398	298	254
		5–10	451	240	522	1129	nd	nd	277	341	300	382	165	177
	M	0–1	314	208	627	207	nd	nd	31	18	75	18	71	nd
		1–5	179	97	464	666	209	124	125	129	170	nd	nd	nd
		5–10	194	127	530	794	224	162	201	194	239	92	nd	77

* Phen – phenanthrene, Antr – anthracene, Fla – fluoranthene, Py – pyrene, B(a)A – benzo(a)anthracene, Chr – chrysene, B(b)F – benzo(b)fluoranthene, B(k)F – benzo(k)fluoranthene, B(a)P – benzo(a)pyrene, B(a,h) – benzo(a,h)anthracene, Ip – indeno(1,2,3-c,d)pyrene, Bper – benzo(g,h,i)perylene

** nd – not determined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correlation coefficient r
1
0.8
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chl*a*
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pheo*a*
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Phen
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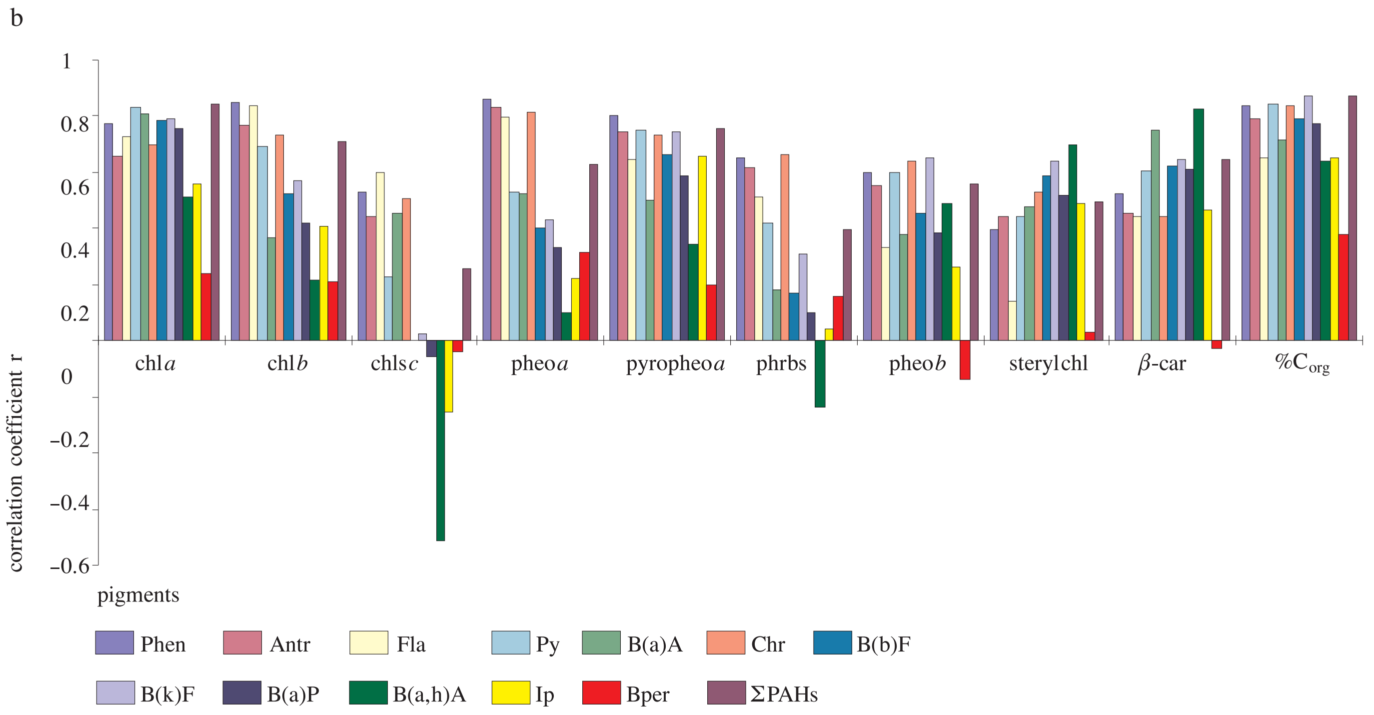

Fig. 3. Correlation coefficients between PAHs and phytoplankton pigments in sediments of the Oder Estuary, 1996: samples collected in August (a), samples collected in October (b); chl *a* – chlorophyll *a*, chl *b* – chlorophyll *b*, chls *c* – chlorophylls *c*, pheo *a* – phaeophytin *a*, pyropheo *a* – pyrophaeophytin *a*, pheo *b* – phaeophytin *b*, phrbs – phaeophorbides, sterylchl – steryl chlorins, β-car – β-carotene, C$_{org}$ – organic carbon

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

Time of sampling	Station	Mean ∑PAHs	3-ring	4-ring	5-ring	6-ring
August 1996	K	5986/6123	15/15	54/54	27/25	5/6
	L	4367/5089	9/15	57/58	27/21	6/6
	M	2925/3669	20/15	63/63	16/20	1/3
October 1996	K	4055/6294	19/19	60/57	18/17	4/6
	L	3349/4900	15/16	62/60	19/22	4/6
	M	1693/2548	35/21	59/62	7/14	3/4

carbon (for ∑PAHs r = 0.87). This may be explained by the fact that a blue-green algae bloom occurred in summer and PAHs were transported from the water column to the sediments together with the detritus formed after the bloom. However, the fact that the highest correlation with ∑PAHs among the pigments present in the sediments collected in October is with chlorophyll *a* suggests that PAHs are absorbed to a considerable degree by living phytoplankton cells. Spring was late in 1996 and the Oder Estuary was icebound until the end of April, so it was not until June or July, depending on the station, that the algal bloom began, the blue-green algae bloom reaching its maximum in August. Consequently, there was no intensive deposition of phytoplankton debris at the beginning of August when the samples were collected. Thus, the correlation with chlorophyll transformation products was higher at the beginning of August for the samples collected at that time, the highest correlation being with phaeophorbides, the products of chlorophyll decomposition. The next highest correlation coefficient was with steryl chlorin esters, and this was followed in decreasing order by pyrophaeophytin *a*, phaeophytin *a* and chlorophyll *a*. This order is the reverse of that of chlorophyll *a* transformation in the environment. Similarly, the correlation with phaeophytin *b* was higher than with chlorophyll *b*.

Variations in the correlation coefficients of different PAHs with a pigment may be explained by the fact that PAHs react differently with phytoplankton cells depending on the physico-chemical properties and molecular structure of the PAHs. Some compounds with a linear symmetry, like anthracene, chrysene or dibenzo(a,h)anthracene, are absorbed into the cell and form more stable complexes than PAHs of a lower symmetry, which may only be adsorbed on the surface of living cells and/or detritus particles.

4. Conclusions

- ΣPAH concentration levels in the Oder Estuary sediments were higher in August (2925–7969, av. 4960 ng g^{-1}) than in October (1693–7080, av. 4581 ng g^{-1}) and higher than those in the Baltic (10–7000 ng g^{-1}). The respective average benzo(a)pyrene concentrations in August and October were 319 and 281 ng g^{-1} for Estuary sediments and 98 ng g^{-1} for the Baltic. This is consistent with the general opinion that the coastal area is mainly responsible for PAH pollution of the Baltic Sea, and that unsubstituted PAHs are of pyrogenic origin; hence their concentration should decrease after summer.
- The four-ring PAHs were most abundant in the sediments collected both in summer and in autumn, while the six-ring PAHs were least abundant, as was the case in the coastal Baltic sediments.
- PAHs are absorbed to a considerable extent by living phytoplankton cells. This process depends not only on the physico-chemical properties of a PAH, such as solubility, but also on its symmetry. Compounds with a linear symmetry, like anthracene, chrysene or dibenzo(a,h)anthracene, form stable complexes, whereas those of a lower symmetry may only be adsorbed at the surface of phytoplankton cells and/or on detritus particles.

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