The role of phytoplankton in the transport and distribution of polynuclear aromatic hydrocarbons (PAHs) in the southern Baltic environment

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Abstract

PAHs (12 compounds from phenanthrene to benzo(g,h,i)perylene) were determined in plankton samples collected from the southern Baltic Sea and the Oder Estuary (Szczecin Lagoon) in 1996. The maximum ΣPAH (sum of 12 PAHs) concentrations were 16 000 ng g^{-1}, *i.e.* values about twice as high as the maximum levels in sediments of the southern Baltic and the Oder Estuary. PAHs are selectively sorbed from water by phytoplankton, depending not only on their physico-chemical properties like solubility, but also on their molecular structure. The results obtained indicate that phytoplankton plays a decisive role in the transport and distribution of PAHs in the southern Baltic environment.

1. Introduction

The effects of polynuclear aromatic hydrocarbons (PAHs) on marine species have been studied intensively for a number of years (GESAMP, 1993). Environmental investigations have dealt principally with the animal species; in the Baltic Sea, for example, these were mainly mussels, fish and birds (HELCOM, 1987, 1990, 1996). The influence of aromatic hydrocarbons on unicellular algae has been studied predominantly under laboratory conditions (Siron *et al.*, 1991). PAH concentration data relating to marine phytoplankton are much scarcer, except in the Antarctic, where PAHs have been investigated rather more carefully than elsewhere in the World Ocean (Cripps, 1990; Cripps and Priddle, 1991).

Different hypotheses concerning the occurrence of PAHs in phytoplankton have been put forward. Some authors have advanced theories that some unsubstituted (parent) aromatic hydrocarbons are produced by algae, bacteria and fungi (Hase and Hites, 1976; Cripps, 1992) or are derived from biogenic precursors during early diagenesis (Wakeham, 1980); others are shifting towards the view that the parent PAHs are merely absorbed by algal cells. Our previous results (Kowalewska and Konat, 1997) pointed to phytoplankton as being the factor mainly responsible for PAH transport from water column to sediments in the southern Baltic Sea. This transfer may proceed *via* absorption or/and adsorption of PAHs by living or dead phytoplankton cells, or phytoplankton detritus, followed by sedimentation of the organic debris carrying the bonded PAHs.

The aim of this work was to estimate the distribution of PAHs and their concentration levels in phytoplankton from various areas of the southern Baltic environment. Phytoplankton pigment analyses were also carried out to determine the quantitative species composition and the state of plankton decomposition in the samples studied.

2. Materials and methods

2.1. Samples

Two sets of samples were collected: one at the end of the spring diatom bloom at six stations in the southern Baltic during a cruise of r/v 'Oceania' in May 1996 (spring was late that year), the other at the time of the expected blue-green algae bloom in the Oder Estuary (Szczecin Lagoon) in August 1996. The location of the sampling stations is shown in Fig. 1. The stations in the Baltic were chosen in such a way as to include as many different areas as possible: first and foremost, the most polluted coastal ones – near the port of Gdynia and near the mouth of the Vistula, the largest Polish river discharging into the Baltic, but also the open sea areas over the Gdańsk and Bornholm Deeps, the deepest areas in the Polish economic zone. Besides these, there are two stations in the Gulf of Gdańsk. There were three stations in the Oder Estuary (Szczecin Lagoon), an area polluted *i.a.* with hydrocarbons, where algal blooms occur, especially of the toxic blue-green algae of the class *Microcystis*. The phytoplankton samples included two of the most abundant groups of algae in the southern Baltic – diatoms and blue-green algae.

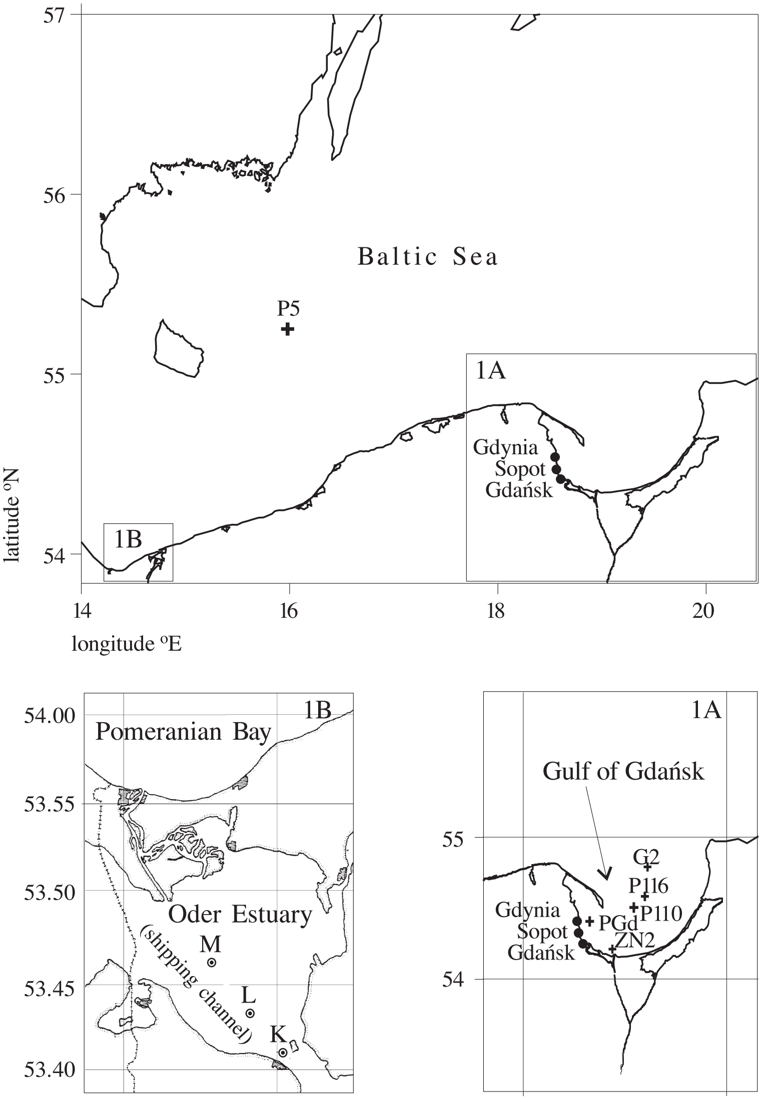

Fig. 1. Location of the sampling stations in the Baltic Sea, May 1996 and in the Oder Estuary (Szczecin Lagoon), August 1996

The samples from the Baltic were collected with a Copenhagen type (60 μm) phytoplankton net towed horizontally behind the ship. Samples from the Oder Estuary were filtered through a phytoplankton net (50–55 μm) (30–150 l of water). The phytoplankton samples were frozen immediately after collection and stored frozen at –20°C until further analysis.

2.2. Analytical procedures

The extraction of PAHs and pigments from plankton samples is similar to their extraction from sediments, which has already been described (Kowalewska, 1995; Kowalewska and Toma, 1996). The extracted material from the Baltic Sea was dried at 60°C, PAHs and pigment concentrations were calculated per dry weight, and the relevant concentrations for the Oder Estuary samples were calculated per litre of water filtered.

The procedure of HPLC measurements of PAHs and pigments is described in detail elsewhere (Kowalewska, 1993, 1994; Kowalewska and Toma, 1996; Kowalewska and Konat, 1997). Twelve unsubstituted polynuclear aromatic hydrocarbons (PAHs) were determined, *i.e.* phenanthrene (Phen), anthracene (Antr), fluoranthene (Fla), pyrene (Py), benzo(a)anthracene (B(a)A), chrysene (Chr), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (DBA), indeno(1,2,3-c,d)pyrene (Ip) and benzo(g,h,i)perylene (Bper). The following phytoplankton pigments were determined: chlorophylls *a*, *b* and *c* (chl *a*, *b* and *c*), phaeophytin *a* (pheo *a*), pyrophaeophytin *a* (pyropheo *a*), phaeophorbides (phrbs) and β-carotene (β-car).

3. Results and discussion

The pigment composition of the plankton samples collected in the Baltic Sea is shown in Tab. 1. The samples collected at the mouth of the Vistula (No. 2) and near the port of Gdynia (No. 6) consisted almost entirely of phytoplankton, the majority being diatom cells, especially of *Skeletonema costatum.* Sample No. 3, collected in the Gulf of Gdańsk, was composed almost exclusively of zooplankton; the samples collected

Table 1. The pigment content in plankton from the southern Baltic, May 1996; $\sum$Pig (sum of pigments) [nmol g^{-1} d.w.], chl *a* to β-car/$\sum$Pig [(nmol g^{-1}/nmol g^{-1}) $\times$ 100%]

Station	$\sum$Pig	chl *a*	chl *b*	chls *c*	pheo *a*	pyropheo *a*	phrbs	β-car
1 P5	599	0	0	11.2	78.5	0.1	1.3	20.1
2 ZN2	4828	0.2	0	10.3	55.5	0.5	39.0	4.7
3 P110	690	0	0	0	51.6	0.3	0	48.0
4 P116	1710	0	0	3.5	75.1	0.4	0.7	23.8
5 P1	1868	0	0	1	72.4	0.4	0	27.2
6 PGd	402	0	0	0	62.4	0.4	8.2	28.9

Table 2. PAH content in plankton from the southern Baltic [ng g^{-1} d.w.], May 1996 ($\sum$PAH – sum of 12 PAHs)

Station	$\sum$PAHs	Phen	Atr	Fla	Py	B(a)A	Chr	B(b)F	B(k)F	B(a)P	DBA	Ip	Bper
1 P5	9783	7260	102	802	308	557	87	<10	<10	136	350	<10	151
2 ZN2	15740	9710	340	2960	790	1370	201	82	168	92	<10	<10	<10
3 P110	<100	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
4 P116	15123	14498	309	<10	<10	<10	226	<10	<10	<10	<10	<10	<10
5 P1	9763	9597	66	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
6 PGd	16343	16082	161	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

in the Bornholm Deep (No. 1) and in the Gulf of Gdańsk (Nos. 4 and 5) contained less zooplankton than sample No. 3.

The PAH concentration levels in the plankton samples collected in the Baltic are set out in Tab. 2. The highest $\sum$PAH levels were found in samples 2 and 6 (about 16 000 ng g^{-1}); they were roughly twice as high as those recorded in the Baltic and Oder Estuary sediments (Kowalewska and Konat, 1997; Kowalewska *et al.*, 1997) and about ten times higher than those in phytoplankton from the Antarctic (1280 ng g^{-1}, average of six samples) (Cripps and Priddle, 1991). Samples 2 and 6 in the present study were almost purely phytoplankton samples but at the same time were collected on the coast; the coastal area is generally regarded as the main source of PAH pollution in the Baltic Sea. One feature was common to all these samples: each contained the highest content of phenanthrene. Furthermore, the concentration pattern of particular PAHs was different: a fact reflecting this differentiation is that the correlation coefficients of $\sum$PAHs with particular PAHs were higher for the low molecular weight compound (Fig. 2). In addition, the correlation coefficients of $\sum$PAHs, phenanthrene and anthracene with pigments were different, that for anthracene being the highest (Fig. 3).

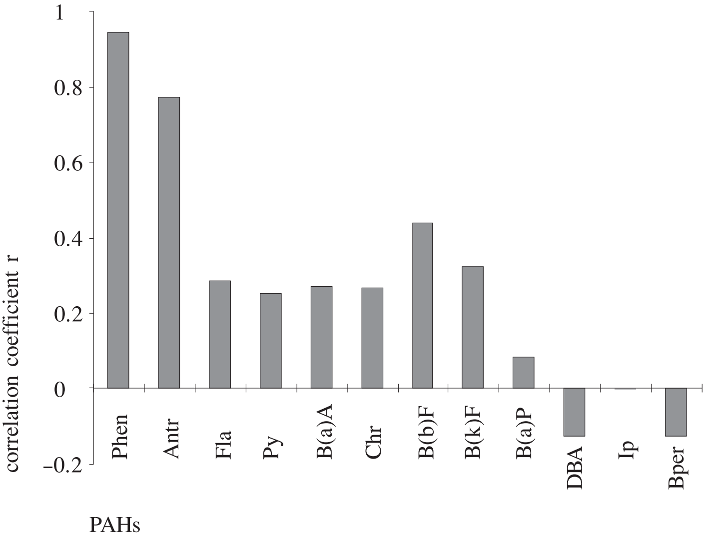

Fig. 2. Correlation coefficients of $\sum$PAHs with particular PAHs in plankton samples from the Baltic Sea, May 1996

Though collected on the same day, the plankton samples from the Oder Estuary included algae at three different stages of decomposition, as can

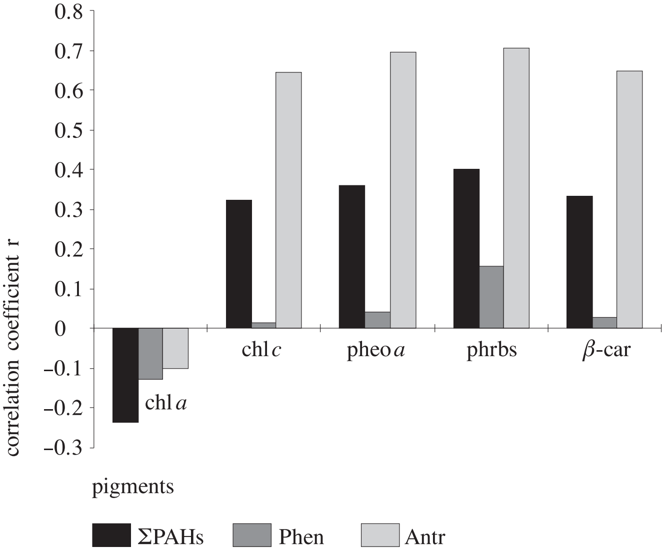

Fig. 3. Correlation coefficients of PAHs with pigments in plankton samples from the southern Baltic Sea, May 1996

be judged from the pigment content (Tab. 3). At station L a bloom of blue-green algae occurred (the maximum chlorophyll *a* content), at station K there were freshly decomposed cells (highest phaeophytin *a* content) and at station M there was highly decomposed material, containing a large amount of phaeophorbides.

Table 3. Pigment content in the plankton from the Oder Estuary (Szczecin Lagoon), August 1996; ΣPig (sum of pigments) [nmol l^{-1}], chl *a* to *β*-car/ΣPig [(nmol l^{-1}/nmol l^{-1}) × 100%]

Station	ΣPig	chl *a*	chls *c*	pheo *a*	pyropheo *a*	phrbs	*β*-car
K	2.7	0.3	1	59.5	0.7	20.0	20
L	80.5	47.4	0	35.6	0	1.9	15
M	1.8	1.1	0	1.6	2.2	48	47

The total PAHs (ΣPAHs) determined for the Oder Estuary samples (1–30 ng l^{-1}) (Tab. 4) is surprisingly low, and is comparable with the concentration level in Antarctic areas (4.9–57.5 ng l^{-1}) (Cripps, 1992). One explanation for this is that the phytoplankton concentrations in the Oder Estuary were much higher than in the Antarctic, the other that the methods of collection of the samples are not comparable.

Table 4. PAH content in the plankton from the Oder Estuary (Szczecin Lagoon) [ng l^{-1}], August 1996

Station	∑PAHs	Phen	Atr	Fla	Py	B(a)A + Chr	B(b)F	B(k)F	B(a)P	DBA	Ip	Bper
K	1.086	0.886	0.016	0.106	0.037	0.078	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
L	29.156	17.950	0.131	2.589	0.441	8.045	< 0.01	<0.01	<0.01	<0.01	<0.01	<0.01
M	5.662	0.039	1.252	0.062	0.935	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

The Oder Estuary samples contained the highest quantities of low molecular weight PAHs, *i.e.* the three- and four-ring compounds from phenanthrene to chrysene, phenanthrene being predominant, as was the case in the Baltic samples (Kowalewska *et al.*, 1997) and in the phytoplankton from the Southern Ocean (Cripps and Priddle, 1991). This led us to the conclusion that phytoplankton organisms first absorb PAHs of lower mass, *i.e* the three- and four-ring PAHs. This is in agreement with our results for sediments, both those of the Oder Estuary and of the coastal Baltic Sea, where the four-ring PAHs and phenanthrene make up the highest proportion in $\sum$PAHs. Hence phytoplankton cells absorb PAHs from water differently, depending on their physico-chemical properties like their solubility in water, but also on their molecular structure. Anthracene, which has a linear structure, evidently forms complexes with living cells. Though much more soluble in water than anthracene (Whitehouse, 1984), despite occurring in the highest concentration in the plankton samples both from the Oder Estuary and the Baltic, phenanthrene does not correlate as well with chlorins (chlorophyll *a* and its derivatives). This implies that this compound may be only adsorbed on the surface of cells or detritus particles and that such bonds may be broken more easily as a result of changes in *e.g.* temperature, salinity or oxygen content.

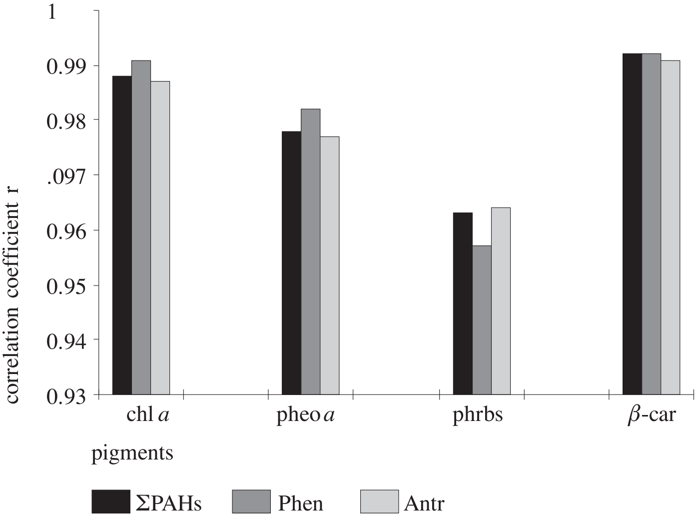

Fig. 4. Correlation coefficients of PAHs with pigments in plankton samples from the Oder Estuary (Szczecin Lagoon), August 1996

The correlation coefficients of $\sum$PAHs, phenanthrene and anthracene with chlorins in the Oder Estuary samples were very high (Fig. 4). This is consistent with the results for sediments of the Oder Estuary (Kowalewska *et al.*, 1997) where anthracene, though present in low concentrations, also correlated best with chlorins, and much better than phenanthrene, which is evidently released much more easily from its associates than anthracene.

4. Conclusions

- PAHs are sorbed by phytoplankton cells from water to a considerable degree ($\sum$PAHs up to 16 000 ng g^{-1}), to levels about twice as high as the highest values determined for the Baltic and Oder Estuary sediments.
- The sorption of particular PAHs by phytoplankton varies: it depends not only on their concentration in water, and hence on their solubility but also on their molecular structure.
- PAHs fixed to phytoplankton cells are transferred with the detritus formed after the death of the cells to the sediments where, depending on the type of associate and the environmental conditions, PAHs may be either fixed or released.
- Phytoplankton plays a decisive role in the transport and distribution of PAHs in the southern Baltic Sea environment.

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