

**Distribution and fate
of polycyclic aromatic
hydrocarbons (PAHs) in
recent sediments from
the Gulf of Gdańsk
(SE Baltic)***

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) were determined in recent (0–10 cm) sediments from the Gulf of Gdańsk during 2003–07 and correlated with environmental parameters. Located in the south-eastern part of the Baltic and receiving the waters of the River Wisła (Vistula), this area of negligible tides and strong anthropogenic stress, highly eutrophic as a consequence, is an exceptional model basin for studying the fate of hydrophobic organic contaminants introduced to the sea. Environmental conditions determine the distribution and composition patterns of parent PAHs in Gulf of Gdańsk sediments. PAHs were associated mainly with fine particle sediments, rich in organic carbon, with hypoxia/anoxia

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near the bottom. The highest PAH contents were found in the Gdańsk Deep (ca 110 m), where the mean concentration of $\sum 12\text{PAHs}$ was $\sim 3600 \text{ ng g}^{-1}$, and no distinct temporal trend was observed. Lighter PAHs were found to be depleted in deeper regions. It was estimated that the Wisła discharges $\sim 50\%$ of the total PAH load deposited in recent Gulf sediments.

1. Introduction

Polynuclear (polycyclic) aromatic hydrocarbons (PAHs) contain at least two fused aromatic rings. These compounds are of great concern because of their persistence, toxicity and widespread occurrence in different compartments of the environment, including marine areas (Nikolaou et al. 2009). Certain PAHs, mainly those of high molecular weight (HMW PAHs), pose a carcinogenic and mutagenic threat to human and animal organisms; they also exhibit embryotoxic, teratogenic, immunotoxic, cytotoxic and phototoxic effects (ATSDR 1995). Selected PAHs have been recognized as hazardous substances in many conventions and other environmental legislation, e.g. the Helsinki Convention (HELCOM 2008), the Water Framework Directive (EU 2000). Major long-term monitoring programmes focus on PAHs in marine sediments as a tool for assessing environmental quality (Roose & Brinkman 2005). In the marine environment, the hydrophobic properties of PAHs cause them to accumulate in sediments and organisms. An expert AMPS (Analysis and Monitoring of Priority Substances) subgroup on sediment monitoring recommends that PAHs be determined preferably in the sediments of aquatic environments (AMPS 2004).

PAHs occur in environmental matrices as complex multicomponent mixtures, which are both natural and anthropogenic (Baumard et al. 1998, Page et al. 1999, Soclo et al. 2000, Stout et al. 2001). Natural sources include volcanic eruptions, forest, grass and bush fires, natural spills of petroleum, and the erosion of bituminous rocks. Some natural PAHs (e.g. perylene) are formed as a result of the transformation of organic material in recent sediments and in soils. However, most PAHs that enter the environment are linked to human activities; they are derived mainly from incomplete combustion (its unintentional by-products) and from oil spills. Commercial production is regarded as a negligible source of PAHs. Pyrogenic hydrocarbons predominate in many industrialized areas and enter the environment during the burning of wood, coal, garbage and petrogenic products (Saha et al. 2009).

PAHs make up a numerous group of organic pollutants (ATSDR 1995). The fate of these pollutants in the environment is determined by their physicochemical properties, as well as biotic and abiotic environmental

factors (Palm et al. 2004). With the increasing number of aromatic rings, the solubility of these compounds in water decreases and their affinity for particulate matter increases. The behaviour of PAHs in the environment is also source-dependent, because those derived from petroleum display greater bioavailability compared to those originating from combustion processes, which are strongly associated with soot particles (Benlahcen et al. 1997).

The aim of this work was to determine the distribution and fate of polynuclear aromatic hydrocarbons (PAHs) in recent bottom sediments of the Gulf of Gdańsk, SE Baltic Sea. Despite the large number of papers dealing with PAHs in many worldwide marine regions, data on this subject for this particular area are surprisingly scarce. Up to now, only a few papers have reported the occurrence of PAHs in sediments from the Gulf of Gdańsk (e.g. Law & Andrulowicz 1983, Falandysz et al. 2006), even though this area is extremely important both for Poland and the whole Baltic community, and is also an interesting model area for studying the fate of hydrophobic organic contaminants introduced into a brackish marine environment.

2. Material and methods

2.1. Sampling site

The Gulf of Gdańsk (area 4940 km²) is a part of the southern Baltic Sea (Majewski 1990); as the Gdańsk conurbation lies adjacent (>1.2 million inhabitants), the Gulf suffers from considerable human pressure. In addition, the River Wisła (Vistula) flows into the Gulf, annually discharging into it some 39 km³ of freshwater, which corresponds to ~13% of its total water volume; the extent to which this freshwater disperses is strongly dependent on the weather conditions, however. The catchment area of the Wisła covers about 54% of the territory of Poland, which is inhabited by almost 60% of the country's population (~27% of the Baltic catchment area's population), and the river itself accumulates pollutants from industrial and municipal, and agricultural effluents. The salinity of Gulf surface waters varies from ~4.5 near the Wisła mouth to ~8 in the northern part of the basin. In deeper regions, vertical stratification of the water is distinct. The halocline, located at a depth of 60–80 m, separates the more saline deep water (~12.5) from the surface water. As vertical water exchange is limited, the bottom water in the deepest areas suffers seasonally from hypoxia/anoxia and hydrogen sulphide is produced. The oxygen conditions improve during intermittent inflow events of cold and well-oxygenated seawater from the North Sea through the Danish Straits. The hydrological

Table 1. Characteristics of the sampling stations in the Gulf of Gdańsk

Station	Coordinates	Survey year	Water depth [m]	Parameters of near-bottom water			Sediment characteristics	
				Salinity	Temperature [°C]	O ₂ [mg dm ⁻³]	Organic carbon [%]	Sediment type
Mch	54°36'N 18°34'E	2007	13	7.5	10.7	8.4	0.17–0.39	fine sand
P101	54°31'N 18°36'E	2003–2006–2007	13	6.9–7.6	5.6–15	7.7–9.1	0.22–0.59	fine sand
NP	54°27'N 18°39'E	2003–2006–2007	14	7.0–7.6	7.7–15.3	5.4–10.9	0.05–0.88	medium sand
K	54°24'N 19°26'E	2007	21	7.5	8.4	7.7	0.19–0.30	fine sand
92A	54°35'N 18°40'E	2006–2007	40	7.5–8.1	5.3–7.7	6.9–8.2	2.43–3.76	sandy mud
BMPK10	54°33'N 18°40'E	2003–2004–2006–2007	33	7.4–7.8	4.15–9.5	8.6–11.3	0.79–1.87	sandy mud
PGd	54°30'N 18°40'E	2003–2004–2006–2007	29	7.3–7.6	4.4–9.4	7.5–11.3	0.73–2.48	sandy mud
P110d	54°30'N 18°47'E	2003–2004–2006	30	7.3–7.5	3.2–10	7.7–11.3	0.03–0.19	medium sand
P115b	54°26'N 19°11'E	2003–2006–2007	63	7.7–9.3	3.2–5.5	4.9–9.6	0.86–2.17	sandy mud
P104	54°34'N 18°47'E	2003–2004–2006–2007	59	7.4–9.2	3–7.8	6–9.3	0.84–3.23	fine sand
ZN2	54°23'N 18°57'E	2003–2004–2006	18	7.1–7.4	4–13.7	8.2–11.6	0.16–1.02	fine sand
P114	54°24'N 19°00'E	2003–2006–2007	33	7.3–7.6	3.8–9.7	7.8–11.6	0.22–0.52	fine sand
P115	54°26'N 19°01'E	2003–2004–2006–2007	56	7.5–8.4	3–8.3	6.6–10.2	0.54–1.06	fine sand
P110	54°29'N 19°06'E	2003–2004–2006–2007	74	10.3–10.5	4.6–6.1	2.7–7.7	4.34–6.04	clay/mud
P104b	54°34'N 19°14'E	2003–2004–2006–2007	85	10.5–11.6	4.6–7.7	1.9–5.8	5.35–7.32	clay/mud
P116	54°38'N 19°17'E	2003–2004–2006–2007	93	11.7–12.4	4.5–7.8	0.8–5.8	4.74–8.53	clay/mud
M1	54°44'N 19°17'E	2003–2004–2006–2007	107	12.2–13.5	4.3–8	0.8–6.6	5.34–7.28	clay/mud
P1	54°49'N 19°19'E	2003–2004–2006–2007	113	12.3–14	4.9–8.3	1.2–6.7	3.78–7.68	clay/mud

conditions and bottom topography strongly differentiate this shallow basin (depth: average – 59 m; max – 118 m) as far as sediment characteristics are concerned. The sediments in the Gulf vary from coarse sands to silty clay. All this and the lack of tides make the Gulf an exceptional natural model basin for studying the fate of pollutants in a marine environment strongly impacted by freshwater input.

Table 1 shows the location and characteristics of the sampling sites, and Figure 1 shows the location of stations. The stations were selected in such a way as to cover a wide range of environmental conditions in the study area, i.e. different water depth, salinity, dissolved oxygen, sediment type and distance from the coastline. Recent sediments were collected during four cruises of r/v 'Oceania' in May 2003, October 2004, October 2006 and May 2007. Sediments were taken with a Niemistö corer. The sediment cores were divided into 0–1 cm, 1–5 cm, 5–10 cm thick sections, which were frozen onboard immediately after collection. Altogether 165 sediment samples were collected for PAH determination.

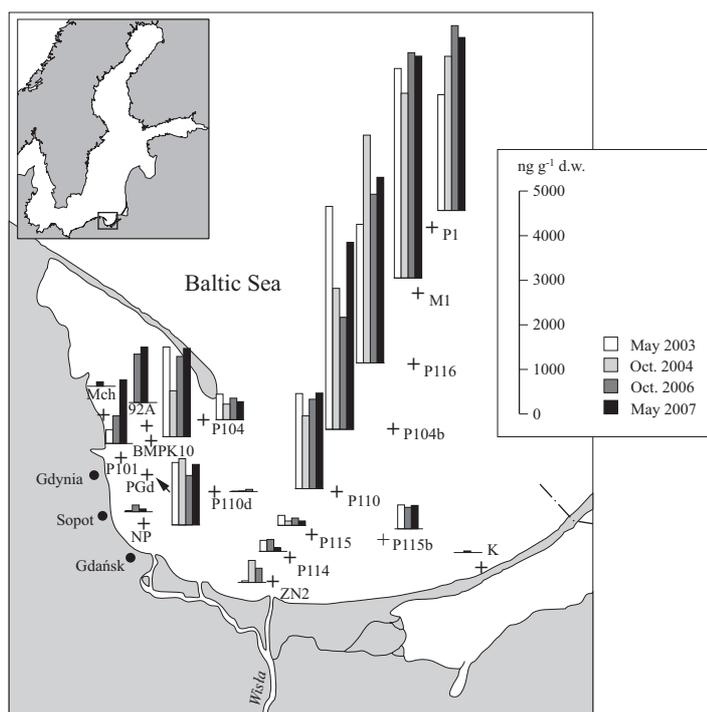


Figure 1. Location of the sampling stations. Concentrations of $\sum 12\text{PAHs}$ averaged for the 0–10 cm layer in recent sediments collected from the Gulf of Gdańsk [$\text{ng g}^{-1} \text{d.w.}$]

2.2. Extraction and chromatographic (GC/MS) analysis of PAHs

PAHs were extracted and analysed using GC/MS; the analytical procedure is described in detail elsewhere (Filipkowska et al. 2005). After thawing out, a frozen sediment sample was sonication-extracted with acetonitrile (5×20 ml). The acetonitrile fractions were combined and re-extracted in the acetonitrile extract/water/benzene (10:10:1 v/v/v) liquid-liquid extraction system. The benzene extract was evaporated in a rotary evaporator and cleaned up by thin layer chromatography (TLC). The TLC chromatogram was developed in the acetone:hexane (4:7 v/v) system. The fraction of PAHs detected under UV light was extracted with acetonitrile and purified of sulphur on a copper bed column. The sample dissolved in isooctane was injected into a gas chromatographic system coupled with an ion trap mass spectrometer detector (Varian GC/MS, Saturn 2100T). A fused silica capillary column with a 5% phenyl-substituted dimethylpolysiloxane phase, 0.25 mm ID \times 60 m, 0.25 μ m film thickness (Varian, CP-Sil 8 CB Low Bleed/MS or VF-5 ms), was used. The following 12 parent PAH compounds were determined: phenanthrene (Phen), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benzo(a)anthracene (B(a)A), chrysene (Chry), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), indeno(1,2,3-cd)pyrene (Ip), dibenzo(a,h)anthracene (DBA), benzo(ghi)perylene (Bper). The method was validated on the basis of certified reference material IAEA-159 supplied by the Marine Environment Laboratory in Monaco, and the results were satisfactory for almost all the PAH compounds (except Ant) in terms of the Z-score. PAHs were quantified by an external standard method. Concentrations of PAHs were blank- and recovery-corrected. Recovery yields of the individual PAHs were determined: with the exception of anthracene (44%), they varied from 64 to 96%. Standard PAH solutions were purchased from LGC Promochem and Chiron.

2.3. Other analyses and measurements

The organic carbon concentration in the sediments was determined by wet chromic acid titration according to the modified Walkley-Black method (Gaudette et al. 1974). Data on chloropigment content were provided by Dr. Szymczak-Żyła (IO PAS). Dr. Wawrzyniak-Wydrowska (Szczecin University) supplied the granulometric characteristics of the sediment samples taken in May 2003 and October 2004, which were obtained by wet sieve analysis according to the procedure given in Folk & Ward (1957). Seawater parameters (depth, temperature, salinity and dissolved

oxygen content) were measured with a CTD probe (SBE 911+, Sea-Bird Electronics, INC., USA) and a mobile device for multiparametric measurements (Multi 197i, WTW, Germany) during sampling.

2.4. Statistical analysis

The results were statistically processed using Microsoft Office Excel and STATISTICA 6.0 software. The following methods were applied: correlation analysis, Kolmogorov-Smirnov test, analysis of variance (ANOVA) and principal component analysis (PCA). Non-parametric methods were mostly used because in the majority of cases the data were not normally distributed (Shapiro-Wilk test) and/or the required condition of equality of variance (Brown-Forsyth and Levene tests) was not satisfied. The calculated R-Spearman (non-parametric) correlation coefficient was a measure of the strength of the linear relationship between variables, and a correlation with $p < 0.05$ was considered significant. Differences between the arithmetic means of various groups of variables were regarded as significant for $p < 0.05$. The relationship between all the target compounds and environmental parameters was also derived from PCA analysis.

3. Results and discussion

3.1. Concentrations of PAHs in sediments

Figure 1 shows the concentrations of $\sum 12\text{PAHs}$ for a 0–10 cm sediment layer, calculated as the weighted means for particular layers (i.e. 0–1, 1–5, 5–10 cm). In 2003–07 the sum of 12 PAHs was found to vary from 9 (P110d – May 2003) to $\sim 5100 \text{ ng g}^{-1}$ (P116 – Oct. 2004). The highest concentrations were recorded at stations located in the Gdańsk Deep, in the northern part of the Gulf. Elevated PAH concentrations were found in sediments collected at stations PGd, BMPK10 and 92A in the western part of the basin. The temporal variability at certain stations was high. For example, the $\sum 12\text{PAHs}$ content in the 0–10 cm sediment layer at station P104b in the Gdańsk Deep was highest in May 2003 (5000 ng g^{-1}) and May 2007 (4200 ng g^{-1}), but distinctly lower in October 2004 (3290 ng g^{-1}) and October 2006 (2510 ng g^{-1}).

Table 2 lists the concentrations of the 12 parent PAHs in particular sediment layers (i.e. 0–1, 1–5, 5–10 cm) for the four sampling campaigns. A high temporal variability in PAH levels was reported at certain stations. For example, at site P104b the concentration of $\sum 12\text{PAHs}$ was 4630 ng g^{-1} in the 1–5 cm layer in May 2003, but only 1320 ng g^{-1} in October 2006. Considerable variations were also observed at station P101, where the $\sum 12\text{PAHs}$ content in the 1–5 cm layer varied from 360 to 2890 ng g^{-1} .

Table 2. Concentrations of PAHs in recent sediments in the Gulf of Gdańsk (SE Baltic Sea), 2003–2007 [ng g⁻¹ d.w.]

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	∑12PAHs
Mch	May 2007	0–1	2.3	1.5	14	12	6.4	6.2	13	4.9	7.3	13	7.7	11	100
		1–5	1.1	1.2	7.0	5.9	3.0	2.8	9.7	3.5	4.8	11	9.9	8.9	69
		5–10	2.9	1.2	19	16	10	8.2	12	6.9	9.8	12	5.5	10	114
P101	May 2003	0–1	<1.1	0.7	18	17	nd ^a	12	10	4.4	4.6	4.4	2.9	5.7	79
		1–5	13	14	53	47	27	18	41	17	38	42	16	35	360
	Oct. 2006	0–1	22	7.7	58	46	31	26	27	15	27	28	7.5	23	320
		1–5	138	43	177	154	86	71	64	37	81	45	17	42	950
		5–10	23	13	68	63	35	28	42	22	41	33	16	34	420
	May 2007	0–1	12.5	40	148	112	89	69	59	31	72	42	19	32	730
1–5		379	125	508	393	310	243	250	112	265	144	47.1	111	2890	
5–10		36	11	58	51	29	22	40	15	37	37	32	33	400	
NP	May 2003	0–1	12	1.1	1.9	1.5	0.7	0.6	0.8	0.5	0.5	1.0	1.6	1.3	24
		1–5	<3.6	1.0	3.0	2.5	<0.5	<0.6	2.7	0.8	0.9	2.3	2.8	2.6	19
		5–10	<2.2	0.7	3.5	2.1	<0.2	<0.2	0.9	0.6	0.9	0.8	0.5	0.9	11
	Oct. 2006	0–1	6.6	<0.4	6.3	5.0	3.3	3.2	4.2	2.6	3.8	5.4	2.8	4.7	48
		1–5	21	2.8	9.8	7.7	5.9	5.5	10.4	6.7	11	15	6.9	13	115
		5–10	12	5.1	27	22	15	13	25	12	18	19	7.2	19	194
May 2007	0–1	3.7	0.6	2.8	2.4	<0.3	<0.3	4.0	1.2	1.5	3.7	3.0	2.2	25	
	1–5	2.2	<0.3	11	10	5.1	4.5	7.6	2.9	4.7	7.2	5.7	6.2	67	
K	May 2007	0–1	2.0	0.9	4.2	3.5	<0.3	<0.3	5.4	2.0	2.3	4.9	3.4	3.2	32
		1–5	<2.8	<0.4	2.8	2.4	<0.3	<0.3	5.3	1.5	1.5	5.6	5.7	3.9	29

Table 2. (continued)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
92A	Oct. 2006	0–1	111	37	246	198	147	125	213	125	207	226	100	186	1920
		1–5	81	43	195	160	114	89	207	105	204	237	89	187	1710
		5–10	39	7.1	36	31	18	12	68	29	35	57	26	63	420
	May 2007	0–1	152	49	275	222	128	107	174	90	150	132	48	123	1650
		1–5	61	47	205	170	117	79	175	77	138	155	63	125	1410
		5–10	43	28	149	123	74	56	130	64	101	116	44	102	1030
BMPK10	May 2003	0–1	72	13.5	66	54	33	26	44	22	40	35	18	34	460
		1–5	36	29	155	126	44	39	103	37	102	79	20	70	840
		5–10	116	198	1016	747	251	89	220	109	248	110	21	137	3260
	Oct. 2004	0–1	<5.9	3.7	47	36	25	25	39	20	30	37	15	35	310
		1–5	33	19	141	120	60	39	72	30	56	46	10	42	670
		5–10	52	66	443	314	108	60	119	47	105	63	18	71	1470
Oct. 2006	0–1	115	50	266	210	118	97	157	73	134	103	41	89	1450	
	1–5	76	73	243	239	99	64	158	87	159	128	65	126	1520	
	5–10	96	60	356	301	157	118	250	104	202	193	70	187	2090	
May 2007	0–1	44	27	148	123	75	65	94	54	89	74	44	73	910	
	1–5	90	59	343	274	126	88	141	92	158	115	81	116	1680	
	5–10	78	82	674	509	180	97	198	106	188	132	61	135	2440	
PGd	May 2003	0–1	97	57	218	176	nd	87	139	74	143	114	48	115	1270
		1–5	87	56	240	188	42	38	170	81	179	151	47	121	1400
		5–10	98	70	253	194	132	81	143	60	160	107	24	106	1430
	Oct. 2004	0–1	35	17	139	106	66	60	127	52	87	110	22	84	900
		1–5	123	35	246	186	108	86	147	57	99	111	23	94	1320
		5–10	85	46	254	194	118	81	239	95	165	235	46	189	1750

Table 2. (continued)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
PGd	Oct. 2006	0–1	43	17	106	81	56	47	87	38	75	69	30	58	710
		1–5	90	26	150	114	77	58	91	40	87	81	33	66	910
		5–10	87	48	225	186	100	72	159	70	130	118	42	110	1350
	May 2007	0–1	86	195	324	260	191	198	195	98	196	136	49	128	2060
		1–5	91	42	189	154	116	91	134	88	172	130	80	119	1410
		5–10	138	60	218	166	86	68	92	53	90	77	42	75	1170
P110d	May 2003	0–1	<0.8	0.7	1.0	1.0	1.1	1.0	1.4	1.2	1.4	1.9	2.3	2.2	15
		1–5	<3.6	0.5	0.6	0.5	<0.5	<0.6	2.4	0.5	0.5	3.1	2.8	2.2	13
		5–10	<2.1	0.5	<0.1	<0.1	<0.2	0.2	0.4	0.9	0.5	0.7	0.5	0.7	4
	Oct. 2004	0–1	<2.3	<0.3	<0.2	<0.2	<0.5	<0.5	0.3	0.2	0.3	2.2	<0.4	1.9	5
		1–5	<2.4	0.4	1.0	0.8	<0.5	<0.5	0.9	0.7	0.5	1.2	0.4	0.9	7
		5–10	7.8	0.8	2.0	1.5	<0.6	<0.6	1.6	1.0	0.8	2.3	1.0	1.8	21
	Oct. 2006	0–5	19	<0.4	4.0	3.1	2.4	2.3	3.1	1.7	2.5	3.1	2.3	3.2	47
	May 2003	0–1	67	21	82	64	53	46	59	30	58	45	22	42	590
		1–5	57	29	160	114	102	69	106	47	94	95	30	62	960
5–10		9.9	4.1	24	17	12	5.5	29	12	16	26	6.6	22	185	
P115b	Oct. 2006	0–1	47	18	80	61	47	40	63	34	60	73	32	59	610
		1–5	37	17	72	61	57	47	74	49	86	90	44	69	700
		5–10	12	2.9	27	23	15	10	54	16	24	51	9.3	39	280
	May 2007	0–1	49	29	119	93	81	74	90	46	71	65	30	53	800
		1–5	37	25	83	66	59	49	72	47	82	75	46	64	710
		5–10	<5.5	4.7	36	28	27	20	43	18	36	47	28	36	320

Table 2. (*continued*)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
P104	May 2003	0–1	25	3.3	12	7.4	4.9	5.3	8.3	4.3	8.4	7.2	4.1	5.7	96
		1–5	41	11	90	63	43	41	64	29	51	67	25	50	570
		5–10	77	26	114	83	48	49	69	33	59	50	15	48	670
	Oct. 2004	0–1	18	4.0	32	20	13	14	17	12	14	16	5.7	14	180
		1–5	43	11	94	65	36	36	59	24	31	44	8.9	36	490
		5–10	19	4.1	50	35	20	18	39	15	20	28	7.8	23	280
	Oct. 2006	0–1	31	7.3	37	28	16	17	24	12	21	32	6.1	25	260
		1–5	30	8.1	40	28	23	20	28	19	32	35	17	27	310
		5–10	41	15	99	77	55	53	83	41	61	61	26	62	670
	May 2007	0–1	32	10	71	49	29	31	49	22	39	46	19	40	440
		1–5	14	5.2	37	33	33	22	32	14	30	30	18	23	290
		5–10	31	20	80	58	34	31	53	28	47	46	18	39	485
ZN2	May 2003	0–1	12	1.7	3.0	2.5	1.9	1.8	2.7	1.6	3.3	2.6	1.6	2.4	37
	Oct. 2004	0–1	<2.4	1.9	12	9.8	4.7	4.8	7.8	4.4	8.8	13	8.5	12	87
		1–5	19	11	86	64	36	26	48	22	39	32	6.2	30	420
		5–10	53	22	119	91	50	35	80	29	58	50	12	42	640
	Oct. 2006	0–1	11	3.1	19	17	11	10	12	7.5	15	14	5.8	13	140
		1–5	36	9.1	44	37	22	22	37	21	43	40	18	34	360
P114	May 2003	0–1	14	4.7	15	12	10	8.2	11	6.8	15	11	5.2	8.6	120
		1–5	14	9.3	55	43	4.1	4.1	48	24	48	43	17	34	340
		5–10	10	2.9	31	25	12	9.9	23	11	17	21	6.5	19	190

Table 2. (continued)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
P114	Oct. 2006	0–1	16	11	38	30	25	26	30	16	28	33	7.9	27	290
		1–5	4.0	2.8	17	14	11	7.6	8.6	5.5	13	14	8.1	11	120
		5–10	22	8.7	53	43	28	21	46	24	38	40	16	35	370
	May 2007	0–1	5.0	1.7	16	13	7.3	8.3	15	4.9	12	14	7.1	12	120
		1–5	<3.2	0.6	5.8	4.4	3.3	2.9	12	3.0	4.1	14	13.0	8.9	72
	P115	May 2003	0–1	22	4.5	25	19	nd	16	19	11	15	17	9.4	17
1–5			15	6.5	54	43	22	21	63	28	45	75	16	55	440
5–10			2.7	1.4	6.3	5.9	5.1	4.4	6.2	4.1	5.1	4.8	2.5	4.8	53
Oct. 2004		0–1	<5.0	2.0	12	9.0	5.7	6.6	11	5.9	7.5	13.5	6.3	12	92
		1–5	10	1.8	15.5	12	7.8	6.7	14	6.1	7.1	12	2.6	10	110
		5–10	3.6	0.9	9.0	8.6	4.9	4.2	16	5.9	7.1	16	3.9	12	93
Oct. 2006		0–1	19	5.4	59	50	38	36	58	28	55	58	18	47	470
		1–5	24	8.4	29	25	15	12	29	12	21	26	8.9	22	230
		5–10	6.1	<0.4	<0.3	<0.3	<0.5	<0.5	14	3.9	4.0	6.7	7.4	7.6	50
May 2007		0–1	14	3.5	31	24	15	15	23	9.1	17	20	8.9	16	200
		1–5	<3.3	1.8	19	15.5	16	11	23	11	20	25	12	20	170
		5–10	<3.2	<0.4	<0.3	0.7	<0.3	<0.3	1.4	1.1	0.8	4.3	3.5	3.1	15
P110	May 2003	0–1	217	39	216	164	96	85	201	100	145	198	71	178	1710
		1–5	159	48	284	209	138	131	285	157	206	363	135	300	2420
		5–10	76	46	292	208	137	90	296	103	220	266	37	221	1990

Table 2. (continued)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
P110	Oct. 2004	0–1	82	23	214	149	91	85	194	91	115	191	51	172	1460
		1–5	54	19	190	128	82	81	180	75	90	160	33	132	1220
		5–10	179	39	265	183	113	90	317	112	156	257	60	222	1990
	Oct. 2006	0–1	60	33	176	131	95	81	194	95	155	226	96	185	1530
		1–5	74	38	204	159	124	106	253	147	233	335	137	248	2060
		5–10	69	41	260	206	126	94	390	139	184	274	53	226	2060
	May 2007	0–1	86	32	207	156	115	111	221	113	162	219	87	188	1700
		1–5	92	28	204	152	121	100	223	131	211	254	114	201	1830
		5–10	103	45	333	247	165	122	354	174	251	320	108	269	2490
P104b	May 2003	0–1	463	77	317	231	149	120	341	159	302	387	142	350	3040
		1–5	163	92	529	409	258	199	646	323	512	714	172	618	4630
		5–10	182	125	566	442	293	224	836	358	595	966	321	774	5680
	Oct. 2004	0–1	138	54	386	274	210	150	620	305	432	1002	239	746	4560
		1–5	140	52	372	273	168	144	417	187	246	394	78	341	2810
		5–10	140	46	417	292	178	157	565	185	262	593	132	456	3420
	Oct. 2006	0–1	162	67	332	255	188	157	483	230	363	601	203	490	3530
		1–5	24	22	132	100	100	52	201	92	134	227	83	151	1320
		5–10	123	69	360	285	189	157	550	223	313	486	108	403	3270
	May 2007	0–1	223	46	344	279	197	169	418	218	315	472	174	411	3270
		1–5	205	53	446	345	243	188	617	293	429	643	234	517	4210
		5–10	142	89	542	433	262	197	600	299	460	662	159	523	4370
P116	May 2003	0–1	409	95	436	322	217	155	564	256	447	635	168	512	4210
		1–5	228	41	306	215	147	101	496	200	273	654	119	533	3310
		5–10	133	34	235	180	121	79	439	154	226	557	126	444	2730

Distribution and fate of polycyclic aromatic hydrocarbons (PAHs) . . .

Table 2. (continued)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
P116	Oct. 2004	0–1	228	46	364	266	187	164	510	297	275	901	216	717	4170
		1–5	182	63	555	413	250	181	651	329	377	706	121	595	4420
		5–10	174	75	622	466	279	206	1095	336	507	1085	200	806	5850
	Oct. 2006	0–1	171	71	419	343	226	172	669	309	444	878	241	671	4620
		1–5	127	65	391	309	214	142	463	232	374	597	148	453	3510
		5–10	118	68	395	325	220	128	604	266	387	671	144	512	3840
	May 2007	0–1	190	43	453	361	245	206	633	305	433	760	217	641	4490
		1–5	238	56	377	303	231	176	537	291	448	596	279	516	4050
		5–10	136	77	465	384	231	177	551	306	438	699	175	548	4190
M1	May 2003	0–1	401	93	348	287	192	161	507	248	438	613	323	597	4210
		1–5	365	115	494	376	261	205	557	306	468	912	244	635	4940
		5–10	173	84	524	412	264	173	678	294	503	738	127	635	4600
	Oct. 2004	0–1	197	32	442	350	177	153	638	262	319	640	130	570	3910
		1–5	117	35	397	290	159	136	526	186	194	517	87	422	3060
		5–10	170	67	520	421	237	180	836	300	436	960	171	754	5050
	Oct. 2006	0–1	203	59	402	338	255	212	696	338	522	971	341	764	5100
		1–5	136	66	432	367	248	159	631	304	467	767	178	594	4350
		5–10	202	67	488	424	266	217	857	419	541	1059	259	810	5610
May 2007	0–1	150	62	356	304	204	273	554	252	387	669	188	549	3950	
	1–5	281	63	432	358	290	224	715	363	572	930	339	732	5300	
	5–10	126	49	489	401	250	192	736	359	452	922	207	735	4920	
P1	May 2003	0–1	140	80	363	280	191	139	556	262	459	736	191	598	3990
		1–5	83	35	275	195	104	97	369	166	247	484	114	407	2570
		5–10	50	27	197	172	108	58	405	159	202	496	72	392	2340

Table 2. (continued)

Station	Date of sampling	Sediment layer [cm]	Phen	Ant	Fla	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	\sum 12PAHs
P1	Oct. 2004	0–1	180	26	408	321	81	55	550	224	276	655.0	118	568	3460
		1–5	153	53	385	303	183	143	507	211	263	583	98	469	3350
		5–10	93	29	283	224	138	95	628	218	264	833	139	601	3550
	Oct. 2006	0–1	188	88	332	296	215	162	603	310	455	900	314	702	4570
		1–5	113	51	317	267	204	127	577	267	355	724	181	546	3730
		5–10	162	46	348	294	207	161	622	321	422	903	226	683	4390
	May 2007	0–1	163	49	334	284	193	154	591	248	360	738	181	594	3890
		1–5	221	60	370	317	251	180	697	336	489	902	309	708	4840
		5–10	63	36	267	237	158	113	444	232	299	618	147	496	3110

a – not detected.

Abbreviations of PAH compounds: Phen – phenanthrene, Ant – anthracene, Fla – fluoranthene, Py – pyrene, B(a)A – benzo(a)anthracene, Chry – chrysene, B(b)F – benzo(b)fluoranthene, B(k)F – benzo(k)fluoranthene, B(a)P – benzo(a)pyrene, Ip – indeno(1,2,3-cd)pyrene, DBA – dibenzo(a,h)anthracene, Bper – benzo(ghi)perylene.

The sediments most polluted with PAHs in the study area were obtained from the Gdańsk Deep, whereas the lowest concentrations were generally recorded in sandy sediments collected from coastal areas (e.g. Mch, NP, ZN2, K).

On the basis of PAH pollution levels, the stations from the Gulf of Gdańsk can be divided into two distinctly different groups. One includes the Gdańsk Deep stations, the other covers the shallower stations, which is consistent with the classification of bottom sediments given by Pieczka (1980). The statistical analysis confirmed that the differences between the mean $\sum 12\text{PAHs}$ concentrations in the sediments of these two groups were statistically significant (Kolmogorov-Smirnov test – $p < 0.05$).

The highest PAH concentrations were recorded at the Gdańsk Deep stations, where the sediments consist mainly of clay and mud. In this study there were five stations in the Gdańsk Deep where the halocline was present: P1, M1, P116, P104b, P110. Mean $\sum 12\text{PAHs}$ concentrations in the Gdańsk Deep sediments for the period 2003–07 were as follows: $\sim 3570 \text{ ng g}^{-1}$ in the 0–1 cm layer, $\sim 3400 \text{ ng g}^{-1}$ in the 1–5 cm layer, and $\sim 3770 \text{ ng g}^{-1}$ in the 5–10 cm layer; the weighted mean for the 0–10 cm layer was $\sim 3600 \text{ ng g}^{-1}$. According to the classification given by Notar et al. (2001), all the sediments from the Deep can be regarded as relatively highly polluted with PAHs ($\sum \text{PAHs} > 500 \text{ ng g}^{-1}$). For this area, the differences between the mean $\sum 12\text{PAHs}$ contents calculated for each sampling campaign (i.e. May 2003, October 2004, October 2006, May 2007) for the 0–1 cm sediment layer were not statistically significant (ANOVA – $p > 0.05$); the same applied to the other layers. This implies that there were no pronounced seasonal variations in the pollution level in the sediments. The sediment trap deployed in the water column appears to be more suitable for detecting seasonal fluctuations in PAH input (Bouloubassi et al. 2006), but sediments are a good indicator of long-term changes in the state of the marine environment.

The mean concentrations of $\sum 12\text{PAHs}$ calculated for sediment layers (i.e. 0–1, 1–5, 5–10 cm) from the Gdańsk Deep stations were not statistically different (ANOVA – $p > 0.05$) in each year. The homogeneity of recent sediment cores in terms of PAH pollution may probably be due to their partial mixing. Staniszewski's (2005) investigations based on Pb-210 measurements suggest that the mixing zone may extend to a depth of 7 cm in the core in this area. Bradshaw et al. (2006) also observed sediment strata disturbances in the NW Baltic Proper, which were probably brought about by physical processes rather than bioturbation.

Several environmental factors distinguish the Gdańsk Deep from the other parts of the Gulf. Seafloor topography, sedimentation and hydrodynamic conditions make the Deep the main accumulation area (sink) for

particulate matter in this part of the Baltic Sea (Kannen et al. 2004). Suspended particulate matter with adsorbed pollutants may be introduced into the Gulf mainly with Wisła waters, surface runoff and from the atmosphere. The high fluvial input leads to the formation of a distinct salinity gradient in the water column, which may enhance flocculation and sedimentation processes, though perhaps not as intensive as in oceanic estuarine areas like those of the River Ob (Dahle et al. 2003) or Montevideo Bay (Muniz et al. 2004). Phytoplanktonic organisms are also a source of large amounts of particulates and hence play an important role in the transfer of PAHs from the water column to bottom sediments in this area (Kowalewska 1999). The occurrence of gyre-like structures in the water circulation favours deposition of suspended matter in the Deep and restricts its transport to other Baltic basins (Jankowski 1996). Favourable hydrological conditions cause the clay/mud fraction to settle, and the percentage of the < 0.063 mm grain-size fraction was at least 95% in all the sediment layers analysed in 2003 and 2004. However, this rule is not as clear-cut as it appears to be. For example, the quantities of PAHs contained in the sediments collected at station P110 were almost half those at other stations from the Deep, although they had similar finest-fraction and organic carbon contents. This discrepancy may probably be due to differences in grain size distribution within the < 0.063 mm particle fraction, the diverse chemical composition of the material deposited, or its resuspension and transport towards deeper regions. The sediments from the Gdańsk Deep had the highest organic matter content in the study area. Dissolved oxygen depletion in deep bottom waters is one of the key factors enhancing the persistence of pollutants in sediments and limiting the development of benthic organisms. The highest oxygen concentrations were recorded in the near-bottom layer in May 2003, which was associated with the ventilation of the basin resulting from the intensive input of cold Atlantic waters through the Danish Straits in the January of that year (Meier et al. 2006). This episodic event interrupted the period of stagnation, but because of the lack of further inflows, oxygen conditions again deteriorated in subsequent years.

As mentioned earlier, many factors create favourable conditions for the long residence times of organic matter in recent sediments from the Deep; this is corroborated by the high concentrations of chlorophyll *a*, which is an unstable compound (Szymczak-Żyła & Kowalewska 2007). It is worth noting that sunlight does not penetrate into this deep, so the organic matter deposited there is protected from photodegradation.

Distinct variations in concentrations of PAHs, organic carbon and grain size composition were recorded in sediments from stations located in the shallower parts of the Gulf. PAH contents were lowest in sandy sediments,

Table 3. Concentrations of PAHs in recent sediments in the Baltic Sea – literature data

Area	Survey year	Sediment layer [cm]	Number of PAHs analysed	\sum PAHs range [ng g ⁻¹]	References
Gulf of Finland, Baltic Proper, Arkona Basin, Kattegat	2001–2002	0–4 (5)	13	125–3624	Pikkarainen 2004
Baltic Proper, NW to Gotland	1996	0–1	15	1560–2190	Pettersen et al. 1999
Gotland Deep Arkona Basin	–	4–4.5 0–5	35	7813 4586	Ricking & Schulz 2002
SW Baltic	1993	0–1	15	9.5–1871.4	Witt 1995
Odra Estuary and Peenestrom	–	0–1	15	3450–8146	Witt 1999
Arkona Basin and Pomeranian Bay	1995–1997	0–1	–	9–1116	Schulz & Emeis 2000
Mecklenburg Bay	2001	0~2	>18	500 (mean) 2000 (max)	Leipe et al. 2005
Kiel Warnemünde Pomeranian Bay Odra Estuary	1995–1996	0–5	18	474–30100 4.6–1640 3.16–273 30–17000	Baumard et al. 1999
Gulf of Gdańsk, harbour and coastal sites	2002–2003	0–10	16	200–52000 170000 (max)	Falandysz et al. 2006
Southern Baltic	1994–1996	0–10	12	10–7000	Kowalewska & Konat 1997
Gulf of Gdańsk	2003–2007	0–10	12	9–5100	this study

which were poor in fine particles (< 0.063 mm) and organic matter. Coarse fractions (sand, gravel) predominate in areas where the movements of the water masses are intense. Strong wave motion and currents may cause intensive erosion and transport of seabed material, which prevents the accumulation of fine sediment particles with sorbed pollutants. On the other hand, elevated concentrations of both PAHs and organic carbon were found at stations with higher contents of < 0.063 mm particles (92A, BMPK10, PGd). There may also be PAH pollution due to the proximity of sites where spoil dredged from harbours is dumped. However, high contents of organic matter relative to PAHs were recorded at station P104, located at the bottom of the steep slope off the Hel Peninsula.

Few papers have been written on PAHs in the Gulf of Gdańsk. The results of the present work for stations P1, P116 and PGd are generally comparable with those obtained by Kowalewska & Konat (1997). But it is difficult to draw comparisons with the results of other authors because they investigated only sediments collected from harbours and sites near the coastline (Falandysz et al. 2006) or analysed a very limited set of parent PAH compounds (Law & Andruliewicz 1983).

The highest PAH concentrations in the Gdańsk Deep sediments were similar to those reported for other areas of the Baltic Sea, including the deeps (Gotland Deep, Arkona Basin) and the Szczecin Lagoon (Table 3).

3.2. Percentages of n-ring PAHs

Figure 2 sets out the percentages of 3-, 4-, 5- and 6-ring PAHs in the sum of 12 PAHs in recent sediments (0–10 cm layer). A distinct variation in the relative concentrations of low and high molecular weight compounds was observed along the transect from the station near the Wisła mouth (ZN2) to station P1 (Gdańsk Deep). The average percentage of 4-ring PAHs decreased gradually from station ZN2 ($\sim 36\%$) to station P1 ($\sim 24\%$), and simultaneously the percentage of 6-ring PAHs increased from $\sim 16\%$ (ZN2) to $\sim 36\%$ (P1). The relative concentrations of 3-ring compounds remained almost constant along the transect ($\sim 5\text{--}\sim 7\%$), with the exception of station ZN2 ($\sim 20\%$). The percentages of PAHs with 5 rings at stations on the ZN2-P1 transect amounted to $\sim 34\text{--}37\%$, and lower percentages were reported at station ZN2 ($\sim 28\%$). In sediments from other stations 4-ring PAHs generally predominated, e.g. at site BMPK10 they ranged between 44% and 60% of $\sum 12\text{PAHs}$. Along the ZN2-P1 transect the trends in relative concentrations of 3,4,5,6-ring PAHs were similar in all the layers and measurement series in the different years, as in the case of the mean weighted for the 0–10 cm layer.

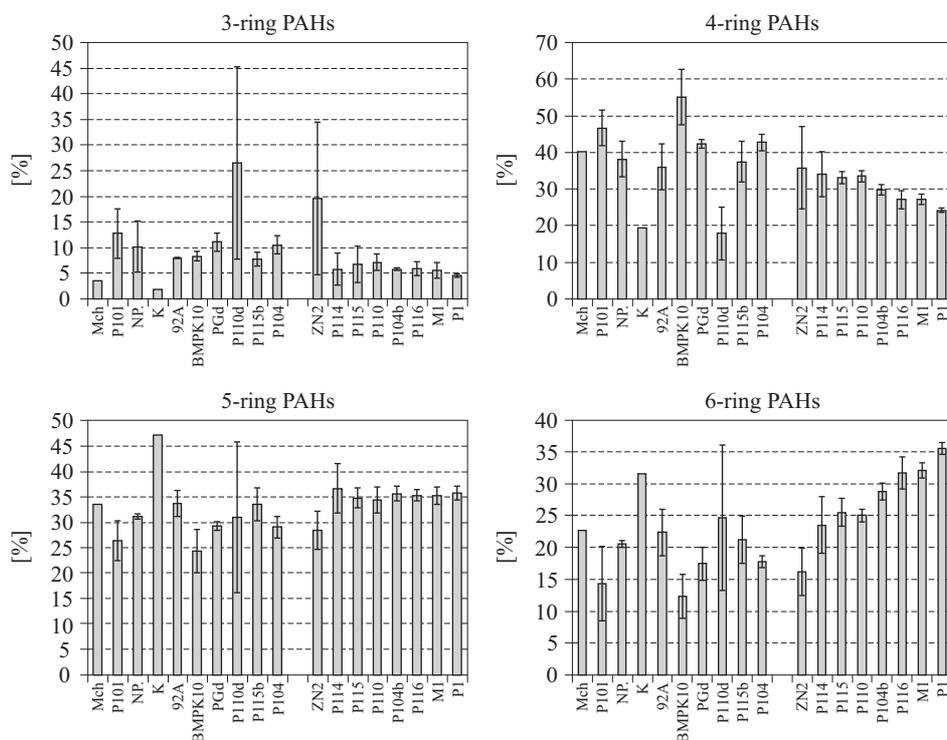


Figure 2. Percentages of 3-,4-,5- and 6-ring PAHs in $\sum 12\text{PAHs}$ in recent sediments, averaged for the 0–10 cm layer from the Gulf of Gdańsk

Changes in the physicochemical parameters of the near-bottom water (depth, salinity, dissolved oxygen) in the transect from the Wisła mouth to the Gdańsk Deep involved an increase in the proportions of HMW PAHs in $\sum 12\text{PAHs}$. A similar trend was observed by Baumard et al. (1999) in surface (0–5 cm) sediments along a transect from Kiel harbour to the open sea (SW Baltic), but the total PAH content decreased with increasing distance from the harbour. Witt (1999) also recorded a similar tendency on a transect from the Szczecin Lagoon to the open sea (SW Baltic).

The changes in the PAH composition on transect ZN2-P1 may have resulted from a relatively higher input of airborne soot, which contains large amounts of HMW PAHs and ultimately reaches the deepest region of the Gulf. A higher proportion of HMW PAHs is considered to be an indicator of pyrogenic origin. However, the main cause of these changes seems to be the sorting of pyrogenic and petrogenic compounds during transport in the water column. PAHs strongly associated with soot particles are more resistant to biodegradation and other decomposition processes than petrogenic PAHs, which contain higher percentages of lighter compounds.

LMW PAHs dissolve more easily in water and are more easily biodegraded, which leads to the relatively faster loss of these compounds from particulate matter. Gogou et al. (2000) gave a similar explanation for the elevated proportions of heavier PAHs in recent sediments in deep areas of the Cretan Sea in comparison with shallow water regions. Interestingly, contradictory trends were observed in the Yangtze estuary, where the percentage of LMW PAHs in sediments surprisingly increased towards the open sea, which the authors explained by a probable dilution effect or the degradation of pyrogenic material introduced with the river waters (Liu et al. 2008).

The main feature distinguishing the PAH distribution in sediments from the Gdańsk Deep and other areas is the ratio of low to high molecular weight compounds. Sediments from the western part of the Gulf generally contained a lower proportion of 6-ring and a higher percentage of 4-ring PAHs in comparison with the Deep. The depth of the water column at stations in this western part ranged from over a dozen to 60 m (P104), and no strong vertical stratification was recorded. The oxygen conditions in the whole water body are therefore not the limiting factor for benthos in this area, although seasonal oxygen deficiency may occur (Janas et al. 2004). Seabed dwelling organisms are able to take up PAHs, preferentially lighter compounds, an observation confirmed by the results of studies performed on mussels *Mytilus trossulus* collected from the Gulf (Pazdro 2007). The inference to be drawn here is that biological activity should lead to an increase in the proportions of heavier PAHs in the bottom sediments from the western part of the Gulf. But the observed PAH patterns indicate that bioaccumulation by benthos is of minor importance as regards the fractionation of these pollutants. Most probably, higher loads of petrogenic products from industrial and municipal sources account for the greater abundance of LMW PAHs.

It has been shown that during the transport of material in surface runoff to river waters, the sandy fraction is selectively enriched in lighter PAHs compared to muddy sediments (Krein & Schorer 2000). Coarse particles of sand, which are moved more slowly in the aquatic environment, release relatively smaller amounts of LMW compounds. The silt/clay fraction of suspended particulate matter has a lower sedimentation rate and is more easily resuspended, which increases the likelihood of LMW PAH conversion into a dissolved form. This mechanism seems to explain the more effective enrichment of fine particles in less water-soluble pollutants, relative to coarse particles in the Gulf. Furthermore, some authors maintain that the degradation rate of petrogenic hydrocarbons from oil spills is higher in muddy sediments than in sands as a result of greater microbial activity

(Tam et al. 2001). In addition, hydrological conditions in shallow waters impede the deposition of fine soot particles with adsorbed pyrogenic PAHs.

3.3. Correlation of PAHs with environmental parameters

Table 4 sets out R-Spearman correlation coefficients between concentrations of PAHs in the 0–1 cm sediment layer and selected environmental parameters of sediments and near-bottom water. Correlations between PAH contents and concentrations of organic carbon and chlorophylls were statistically significant ($p < 0.05$) and mostly above 0.8 except for phaeophorbides and chlorophylls *c*. High positive, statistically significant values of R-Spearman correlation coefficients were also obtained for particular PAH compounds and the percentage of the finest grain size fraction (< 0.063 mm). There was a high positive, statistically significant ($p < 0.05$) relationship between all PAH compounds, and water depth and salinity, but for the dissolved oxygen content this relationship was negative. Correlation coefficients with temperature were low and for most PAHs not statistically significant.

Organic matter concentration is a crucial parameter governing the distribution of hydrophobic pollutants in bottom sediments (King et al. 2004). The quantity of organic matter deposited is a consequence of the primary production yield, sedimentation rate and mineralization in the sediments and water column. Some researchers, presupposing a strong relationship between PAH contents and organic matter, express PAH concentrations per amount of organic carbon (e.g. Pettersen et al. 1999, Oros & Ross 2004), but this approach cannot be applied uncritically to all areas (Tam et al. 2001, Sprovieri et al. 2007). Simpson et al. (1996) found a high correlation of PAHs vs C_{org} only for the most polluted sites in Kitimat Fjord (Canada). High, statistically significant correlations between PAH concentrations and organic carbon in the Gulf of Gdańsk ($r = 0.94$ for $\sum 12\text{PAHs}$ and C_{org} , $p < 0.05$) demonstrate that these pollutants have a strong affinity for organic matter in this area. Similar relationships were observed in other coastal areas of the Baltic Sea, e.g. in the vicinity of Warnemünde and the Szczecin Lagoon (Baumard et al. 1999, Kowalewska et al. 2003), and also in the Belt Sea and Arkona Basin (Witt 1995, Schulz & Emeis 2000).

The high correlations between PAHs and chlorophylls indicate that phytoplankton plays an important role in the transport of these compounds from the water column to the bottom sediments. All the taxonomic pigments analysed (i.e. chl *a*, chl *b*, chls *c*) were positively correlated with particular hydrocarbons. Chlorophylls *c* are present mainly in diatoms and

Table 4. R-Spearman correlation coefficients of concentrations of particular PAHs in the 0–1 cm sediment layer with environmental parameters of near-bottom seawater, contents of organic carbon (C_{org}) and chloropigments in sediments and the finest-grain (< 0.063 mm) sediment fraction, for samples collected in the Gulf of Gdańsk in 2003–07

	Water depth [m]	S^b	O_2 [mg dm ⁻³]	t [°C]	C_{org} [%]	allo chl a	chl a	phaeo a	phrbs	pyro-phrbs	chl b	phaeo b	chls c	< 0.063 mm [%]
Phen	0.80 ^a	0.79 ^a	-0.58 ^a	-0.30 ^a	0.94 ^a	0.84 ^a	0.93 ^a	0.90 ^a	0.56 ^a	0.86 ^a	0.80 ^a	0.85 ^a	0.86 ^a	0.89 ^a
Ant	0.66 ^a	0.72 ^a	-0.52 ^a	-0.12	0.86 ^a	0.77 ^a	0.83 ^a	0.76 ^a	0.43 ^a	0.73 ^a	0.78 ^a	0.82 ^a	0.66 ^a	0.89 ^a
Fla	0.76 ^a	0.80 ^a	-0.66 ^a	-0.10	0.92 ^a	0.81 ^a	0.88 ^a	0.85 ^a	0.42 ^a	0.85 ^a	0.85 ^a	0.92 ^a	0.74 ^a	0.89 ^a
Py	0.77 ^a	0.80 ^a	-0.66 ^a	-0.09	0.91 ^a	0.81 ^a	0.88 ^a	0.84 ^a	0.42 ^a	0.84 ^a	0.85 ^a	0.93 ^a	0.74 ^a	0.90 ^a
B(a)A	0.75 ^a	0.81 ^a	-0.70 ^a	-0.10	0.89 ^a	0.80 ^a	0.85 ^a	0.79 ^a	0.42 ^a	0.78 ^a	0.86 ^a	0.89 ^a	0.70 ^a	0.92 ^a
Chry	0.71 ^a	0.77 ^a	-0.67 ^a	-0.04	0.89 ^a	0.80 ^a	0.85 ^a	0.78 ^a	0.40 ^a	0.78 ^a	0.86 ^a	0.89 ^a	0.68 ^a	0.88 ^a
B(b)F	0.81 ^a	0.83 ^a	-0.69 ^a	-0.15	0.94 ^a	0.84 ^a	0.90 ^a	0.87 ^a	0.46 ^a	0.86 ^a	0.89 ^a	0.95 ^a	0.76 ^a	0.91 ^a
B(k)F	0.80 ^a	0.82 ^a	-0.67 ^a	-0.15	0.94 ^a	0.84 ^a	0.90 ^a	0.87 ^a	0.47 ^a	0.87 ^a	0.90 ^a	0.95 ^a	0.76 ^a	0.92 ^a
B(a)P	0.79 ^a	0.82 ^a	-0.65 ^a	-0.17	0.93 ^a	0.84 ^a	0.90 ^a	0.86 ^a	0.48 ^a	0.84 ^a	0.90 ^a	0.94 ^a	0.75 ^a	0.92 ^a
Ip	0.81 ^a	0.83 ^a	-0.69 ^a	-0.13	0.94 ^a	0.84 ^a	0.90 ^a	0.87 ^a	0.46 ^a	0.87 ^a	0.91 ^a	0.96 ^a	0.75 ^a	0.92 ^a
DBA	0.80 ^a	0.83 ^a	-0.66 ^a	-0.12	0.94 ^a	0.84 ^a	0.90 ^a	0.84 ^a	0.44 ^a	0.86 ^a	0.89 ^a	0.94 ^a	0.74 ^a	0.92 ^a
Bper	0.82 ^a	0.83 ^a	-0.68 ^a	-0.16	0.95 ^a	0.84 ^a	0.91 ^a	0.88 ^a	0.48 ^a	0.88 ^a	0.91 ^a	0.96 ^a	0.77 ^a	0.93 ^a
$\sum 12\text{PAHs}$	0.79 ^a	0.82 ^a	-0.66 ^a	-0.16	0.94 ^a	0.84 ^a	0.90 ^a	0.87 ^a	0.47 ^a	0.85 ^a	0.89 ^a	0.93 ^a	0.76 ^a	0.93 ^a

a – statistically significant at $p < 0.05$;

b – S – salinity; O_2 – dissolved oxygen content; t – temperature; C_{org} – organic carbon; allo chl a – chlorophyll a allomers; chl a – chlorophyll a ; phaeo a – phaeophytin a ; phrbs – phaeophorbides; pyrophrbs – pyropheophorbides; chl b – chlorophyll b ; phaeo b – phaeophytin b ; chls c – chlorophylls c . Abbreviations of PAH compounds – see section 2.2.

dinoflagellates, which may be treated as markers of seawater, as opposed to freshwater, input to the Gulf (Kowalewska et al. 1996). The lower correlation of PAHs with chlorophylls *c* may be due to the predominant load of PAHs associated with the biogenic particulate matter derived from terrestrial freshwater sources and/or the higher degradation rate of these pigments compared to chlorophylls *a* and *b*. The high correlation between PAH contents and decomposed chlorophyll products in both relatively fresh (e.g. phaeophytin *a*, chlorophyll *a* allomers) and more decomposed (e.g. pyropheophorbides) plant material, endorses the previously observed (Szymczak-Żyła & Kowalewska 2007) significant role of detritus in the migration of these pollutants in this marine environment.

The high positive, statistically significant R-Spearman correlation coefficients between PAH contents and the percentage of the < 0.063 mm fraction ($r=0.93$ for $\sum 12\text{PAHs}$ and % fr. < 0.063 mm, $p < 0.05$) show that these hydrocarbons in the Gulf sediments are associated mainly with mud and clay particles. The high correlation observed for 5- and 6-ring compounds supports the fractionation mechanism of PAHs adsorbed on fine particulate matter, which was described earlier. Many authors have reported higher PAH concentrations in sediments abundant in fine particles with diameters < 0.063 mm in other marine areas (e.g. Dahle et al. 2003, Oros & Ross 2004), and some scientists have analysed these pollutants only in this fraction (e.g. Viganò et al. 2003, Bodnár et al. 2005) or have excluded samples depleted of fine particles from further investigations (e.g. Lauenstein & Kimbrough 2007). It should be borne in mind that in some regions no strong correlation of PAHs vs. percentage of < 0.063 mm fraction was observed (Medeiros & Bicego 2004, Cortazar et al. 2008). Wang et al. (2001) found the highest PAH concentrations in Boston harbour in coarser particles (with diameter > 0.25 mm), which they attributed to the fact that detritus and faecal pellets have a higher sorption capacity than clay particles. In contrast, in Irish Sea sediments the correlation with the < 0.015 mm fraction was better than for the < 0.063 mm fraction (Charlesworth et al. 2002).

The content of oxygen dissolved in water significantly influences the extent and rate of postdepositional processes in sediments and determines the redox potential in pore waters (Muniz et al. 2004). Moreover, the oxygen content is an important factor for the development of benthic communities and affects the intensity of bioturbation. Literature data indicate that hypoxic/anoxic conditions enhance the persistence of PAHs deposited in sediments (Boyd et al. 2005). The negative correlation coefficients between PAH contents and dissolved oxygen ($r = -0.66$ for $\sum 12\text{PAHs}$, $p < 0.05$) confirm this observation. As mentioned earlier, the frequency and magnitude of inflows of well-oxygenated waters from the

North Sea influence the oxygen conditions in the deeper parts of this basin. During periods of oxygen deficiency, growth of aerobic organisms is suppressed and oxidation of organic matter slows down. Under anoxic conditions certain microorganisms (e.g. nitrate-reducing, sulphidogenic, methanogenic bacteria) are capable of biodegrading PAHs, but the extent of this process is restricted (Genthner et al. 1997).

A high correlation between PAHs and near-bottom water salinity ($r = 0.82$ for $\sum 12\text{PAHs}$, $p < 0.05$) was noted, but it is difficult to judge whether this is a primary or secondary effect. The salinity in the bottom waters of the Gulf correlates well with both water depth and oxygen content. The salting-out effect due to the increase in salinity over a narrow range recorded in the Gulf seems to be slight. On the basis of Setschenov's formula (according to Schlautman et al. 2004) one can calculate that changes in salinity from 7 to 14 lead to a reduction in average PAH solubility in pure water by $\sim 7\%$, but this value may be underestimated in real environmental conditions because of the simultaneous salting-out of organic matter with its associated pollutants (Means 1995).

There was no distinct relationship between PAH concentrations and near-bottom seawater temperature in the Gulf ($r = -0.16$ for $\sum 12\text{PAHs}$, $p > 0.05$), possibly due to the narrow range of recorded temperatures. Some authors suggest that in certain areas this parameter plays a surprisingly minor role in the biodegradation of aromatic hydrocarbons (e.g. Rantamäki 1997, Boyd et al. 2005). Although this observation was confirmed by results from this work, it is worth remembering that temperature is a key factor controlling PAH solubility in the aqueous phase (Whitehouse 1984).

The results of the analysis of correlations between PAHs and environmental parameters and pigments were confirmed by principal component analysis (Figure 3). This statistical method was applied to reduce the large number of variables investigated. Factor 1, which accounts for $\sim 71\%$ of the observed variance, allows one to distinguish a single large group containing all the PAHs together with such parameters like water depth and salinity of the near-bottom layer. This means that the correlation coefficients between these variables should be high and positive. A high value of the factor loading, but of opposite sign, for dissolved oxygen shows that with increasing oxygen concentration we can expect lower contents of pollutants and organic matter in the Gulf. Additionally, PCA results confirm the weaker dependence of PAH distribution on temperature in the environment under study. Factor 2, explaining only $\sim 11\%$ of the total variance, distinguishes LMW and HMW PAHs, which is consistent with the higher percentage of LMW PAHs in sediments deposited in shallower and well oxygenated areas.

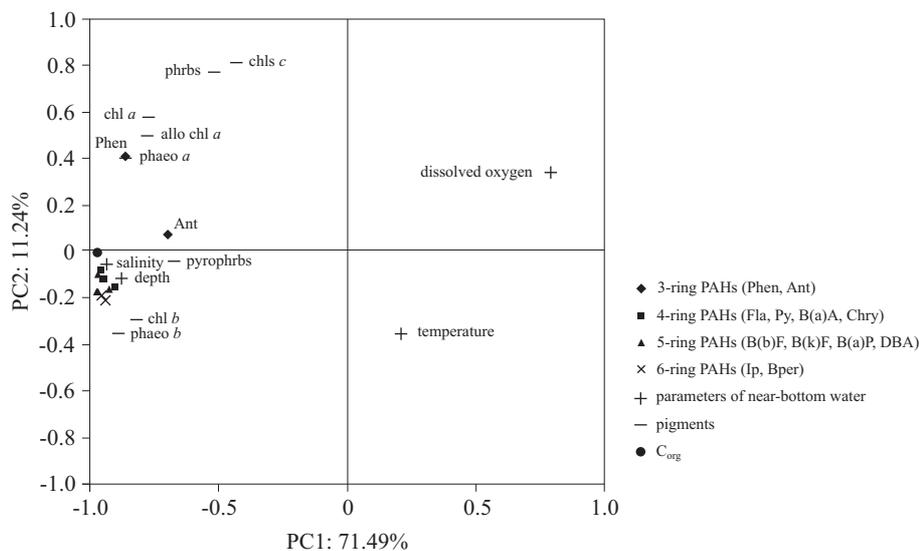


Figure 3. PCA results – factor loadings obtained from the chemical and environmental variables. Abbreviations – see footnote to Table 4

3.4. Ecotoxicological risk evaluation

Solely on the basis of the chemical composition and concentration of pollutants, it is not really possible to predict the adverse effects of organisms exposed to PAHs; other site-specific physical and biological factors also have to be taken into consideration (Fernández et al. 2008). Because of the lack of ecotoxicological criteria established for most marine coastal regions, as in the case of the Baltic Sea, many authors have assessed ecotoxicological status using pollution thresholds set up for other areas (e.g. Viguri et al. 2002, Pikkarainen 2004, Tolosa et al. 2004, Cardellicchio et al. 2007). For this reason, the concentrations of the 12 PAH compounds presented in this work were referred to the non-regulatory sediment quality guidelines (SQGs) issued by NOAA (NOAA 1999) and OSPAR (OSPAR 1997).

Sediments from the Deep stations (i.e. P1, M1, P116, P104b, P110) contained the highest number of hydrocarbons exceeding NOAA (1999) threshold values, below which adverse effects are rarely observed (i.e. ERL – effects range low, TEL – threshold effect level). The background reference concentrations (BRC) set up by OSPAR (1997) for the northern part of the North Sea and Skagerrak were not exceeded only in typical sandy samples (i.e. Mch, NP, K, P110d, P114, P115), so these sediments can be classified as not strongly impacted by human activity.

In recent sediments from the Gdańsk Deep the concentrations of only one compound (dibenzo(a,h)anthracene) were above the PEL (probable effect

level) threshold (NOAA 1999), which implies a relatively high probability of the incidence of negative effects in exposed benthic organisms. However, the less restrictive ERM (effects range median; NOAA 1999) and EAC (environmental assessment criteria; OSPAR 1997) thresholds were not exceeded at any of the sampling sites in the Gulf, which leads to the conclusion that reports of adverse effects in biota exposed to PAHs should not be frequent.

For assessing the potential synergic effects of all the PAHs determined in the Gulf sediments, two approaches, based on mean ERM quotients (mERMq) or mean PEL quotients (mPELq), were applied (NOAA 1999, Cardellicchio et al. 2007). These indices were derived by dividing the concentration of each compound by its respective ERM and PEL values, after which the mean of the quotients for all compounds was calculated. Following the classification used by Cardellicchio et al. (2007), based on the mERMq index, the pollution level was generally medium-low ($0.1 < \text{mERMq} < 0.5$) at the stations from the Deep and low ($\text{mERMq} < 0.1$) at the other stations, except for one sediment sample (BMPK10, V 2007). The mPELq values for sediments taken from the Deep and certain sites in the western part of the Gulf (P101 – but only the samples collected in May 2007, 92A, BMPK10, PGd) lay in the medium-low range ($0.1 < \text{mPELq} < 1.5$), whereas samples from other stations fell into the ‘low’ category in terms of PAH pollution ($\text{mPELq} < 0.1$).

PAH concentrations in all the samples were below those stated in the relevant regulations issued by the Polish Ministry of the Environment (Dz.U. 2002) concerning the quality of spoil dredged from marine and harbour areas and dumped into the sea.

3.5. PAH budget for the Gulf of Gdańsk

The total PAH content in recent bottom sediments of the Gulf was assessed on the assumption that the sampling sites were representative of the study area. The mean PAH concentrations in the Gulf sediments in all the layers analysed were calculated for the period 2003–07 on the basis of data from 18 stations (Table 5). Amounts of $\sum 12\text{PAHs}$ and benzo(a)pyrene deposited and their annual fluxes to sediments were estimated on the assumption that the following parameters held true: area of the Gulf – 4940 km² (Majewski 1994), sediment density – 2.55 g cm⁻³ (Kepińska & Wypych 1990), sedimentation rate – 1.47 mm yr⁻¹ (Szczepańska & Uścińowicz 1994), determined moisture content of sediments – from ~30% to ~90%. The annual flux to the sediments averaged over the whole area

Table 5. Mean concentrations and amounts of PAHs deposited and their mean annual flux to recent sediments in the Gulf of Gdańsk

$\sum 12\text{PAHs}^a$	0–1 cm	1–5 cm	5–10 cm	0–10 cm
mean concentration [ng g ⁻¹ d.w.]	202	296	329	303
amounts in sediments [10 ³ kg]	25.5	149.3	207.3	382.0
mean annual inflow [kg yr ⁻¹]	3743			
[kg km ⁻² yr ⁻¹]	0.76			
B(a)P ^b	0–1 cm	1–5 cm	5–10 cm	0–10 cm
mean concentration [ng g ⁻¹ d.w.]	19.3	29.4	30.0	28.7
amounts in sediments [10 ³ kg]	2.4	14.8	18.9	36.1
mean annual inflow [kg yr ⁻¹]	358			
[kg km ⁻² yr ⁻¹]	0.072			

a – sum of 12 PAH compounds, b – benzo(a)pyrene.

of the Gulf was 0.76 kg km⁻² yr⁻¹ for $\sum 12\text{PAHs}$ and 0.072 kg km⁻² yr⁻¹ for benzo(a)pyrene, but these values may differ significantly from those at particular sites.

The PAH load carried by suspended particulate matter in Wisła river waters was also calculated. It was assumed that the Wisła annually discharges about 39 km³ of freshwater with $\sim 0.54 \times 10^6$ tonnes of particulates (IMGW 2000), which have the same PAH concentration as that averaged for the 0–1 cm layer sediments from the Deep stations (i.e. $\sum 12\text{PAHs} - \sim 3570$ ng g⁻¹, B(a)P – ~ 340 ng g⁻¹). On the basis of these assumptions, the annual influxes of $\sum 12\text{PAHs}$ and benzo(a)pyrene entering the Gulf with Wisła waters were estimated at ~ 1930 kg and ~ 180 kg, respectively, which in both cases accounts for $\sim 50\%$ of the total annual amount of PAHs deposited in sediments. The remaining PAH load may enter the Gulf through dry and wet deposition of airborne PAHs, inputs from other watercourses, storm-water drains, sewage, ballast and bilge water dumps, and oil spills from ships.

4. Conclusions

- Environmental conditions determine the distribution and composition patterns of parent PAHs in Gulf of Gdańsk sediments. These pollutants tend to be associated mainly with organic matter and fine-grained particles, and are well preserved under anoxic conditions. Compared to sediments from other Gulf areas, those from the Gdańsk Deep act as a sink for PAHs and are particularly rich in the high molecular weight fraction.
- Sediments from the Gdańsk Deep can be classified as relatively highly polluted with PAHs ($\sum\text{PAHs} > 500 \text{ ng g}^{-1}$). The mean $\sum 12\text{PAHs}$ concentration averaged for the 0–10 cm sediment layer was $\sim 3600 \text{ ng g}^{-1}$ for the period 2003–07; no distinct temporal trend in PAH pollution was observed.
- Based on non-regulatory NOAA and OSPAR guidelines, sediments from the Gulf should not exert statistically frequent adverse effects on benthic organisms in relation to the pollution caused by the 12 PAHs investigated in this study; the PAH pollution level was generally medium-low at the stations from the Deep and low at the majority of the other stations.
- Amounts of $\sum 12\text{PAHs}$ deposited in recent sediments from the Gulf were calculated: e.g. for the 0–10 cm layer this quantity was equal to ~ 380 tonnes, and the mean annual input was $0.76 \text{ kg km}^{-2} \text{ yr}^{-1}$. Wisła river discharges made up $\sim 50\%$ of the total PAH load.

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