

Methylphenanthrenes in the southern Baltic as markers of petrogenic pollution

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LUDWIK LUBECKI
MAŁGORZATA SZYMCZAK-ŻYŁA
GRAŻYNA KOWALEWSKA*

Institute of Oceanology,
Polish Academy of Sciences,
Powstańców Warszawy 55, PL-81-712 Sopot, Poland;

e-mail: Kowalewska@iopan.gda.pl

*corresponding author

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Abstract

Mono- and dimethylphenanthrenes were determined in recent (0–10 cm) sediments collected at about 30 stations in the southern Baltic Sea from 1995 to 2001. The stations were located in the Szczecin Lagoon, the Pomeranian Bay, the Bornholm Deep, the open sea (without the Bornholm and Gdańsk Deeps), the Gdańsk Deep, and the Gulf of Gdańsk including the Wisła (Vistula) Lagoon. The results were related to the unsubstituted PAH content. The annual load of methylphenanthrenes in relation to unsubstituted PAHs in the Rivers Odra and Wisła was estimated. Methylphenanthrenes are more abundant in the Odra estuary than in the Wisła estuary, and more abundant in the coastal sediments than in the open sea sediments. The results indicate that methylphenanthrenes related to the lower molecular, unsubstituted PAHs are a good measure of petrogenic pollution in the southern Baltic.

1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) in marine sediments make up a broad group of compounds, both unsubstituted and substituted; in

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either case they are mainly anthropogenic (Pereira et al. 1999). Their distribution patterns in this environment depend primarily on their sources. Thus, the parent (unsubstituted) PAHs originate largely from the incomplete combustion of different fuels, although the lower-molecular PAHs (3,4-ring) may also be petrogenic (e.g. Reddy & Quinn 2001). Alkyl derivatives of naphthalene, phenanthrene, anthracene, fluoranthene and pyrene have been proposed as markers of petrogenic PAHs (Page et al. 1999, Yunker et al. 2002a, Beg et al. 2003, Fang et al. 2003, Medeiros & Bicego 2004). Each of these groups of PAH derivatives contains numerous compounds, differing both in the number of substituents and in their position in the molecule. Methylphenanthrenes are investigated the most often (Benner et al. 1995, Mazeas & Budzinski 2002). In the Baltic environment they have been determined in recent sediments on the German coast (Baumard et al. 1999), in cores from the Arkona and Gotland Deeps (Ricking & Schulz 2002), and at the dumping site in the Mecklenburg Bay (Leipe et al. 2005), although the last-mentioned work gives only the sum of PAHs. The proportions of particular methylphenanthrenes have been used to determine the maturity of petroleum (Yunker et al. 2002a) and different pollution sources (Benner et al. 1995, Notar et al. 2001, Muniz et al. 2004). The best way to distinguish pyrogenic and petrogenic sources for a marine coastal zone is to use the ratios of selected parent and alkylated PAHs (Budzinski et al. 1997, Baumard et al. 1998, Soclo et al. 2000, Yunker et al. 2002b, Wetzel & van Vleet 2003, Zhou & Maskaoui 2003, King et al. 2004). However, one should bear in mind that environmental analysts use different PAH ratios, worked out for specific sites, which are not necessarily applicable to other areas. In the present study, methylphenanthrenes were determined and traced in relation to the parent compound (phenanthrene) and other unsubstituted PAHs as markers of petroleum pollution in the southern Baltic Sea.

2. Experimental

Sample collection

The location of the sampling stations is shown in Fig. 1. At some of them, samples were collected more than once (e.g. G2, K, L, M). The study area was the southern Baltic Sea, principally the Polish economic zone. Stations of different water depth, sediment type and distance from the coast were selected. The study area was divided into six main zones: the Szczecin Lagoon, the Pomeranian Bay, the Bornholm Deep, the open sea (without the Bornholm and Gdańsk Deeps), the Gdańsk Deep, and the Gulf of Gdańsk together with the Wisła (Vistula) Lagoon. The Szczecin Lagoon

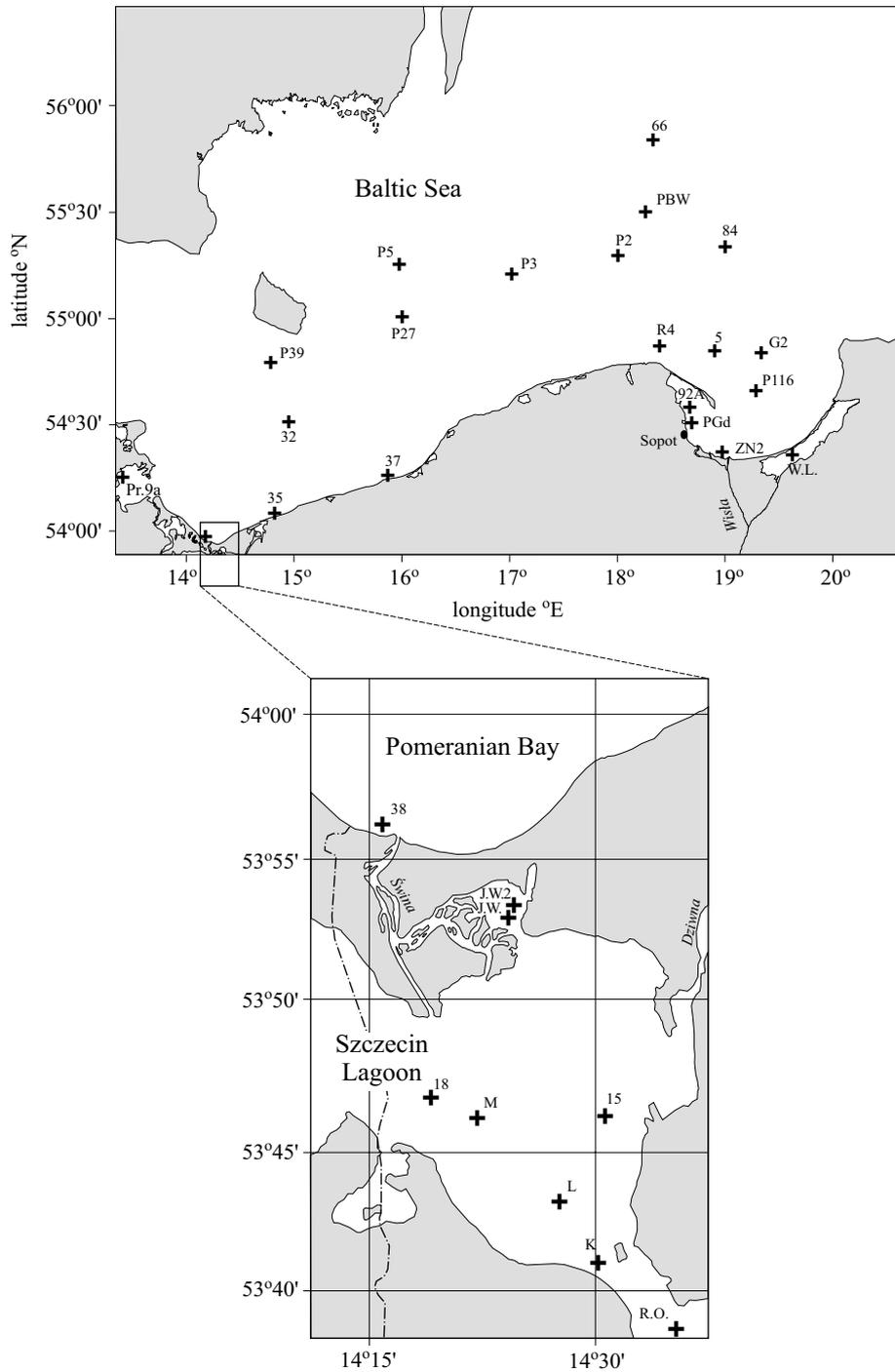


Fig. 1. Location of the sampling stations

and the Gulf of Gdańsk are examples of sites subject to fluvial impact. The Szczecin Lagoon is the first depositional zone for organic matter and contaminants transported by the River Odra (Oder). Similarly, the Gulf of Gdańsk collects the particulates with sorbed contaminants transported by the Wisła. The Bornholm and Gdańsk Deeps are sinks for fluvial particulate matter, carried out to sea by the Odra and Wisła respectively. Samples were collected during the cruises of r/v 'Oceania' of the Institute of Oceanology, Polish Academy of Sciences (IO PAS), those from the Szczecin Lagoon were collected from a boat belonging to Szczecin University, and sample Pr.9a was collected within the framework of the PROSA project during a cruise of r/v 'Professor Albrecht Penck' of the Institut für Ostseeforschung Warnemünde (IOW), Germany. A Niemistö core sampler was used to collect all the samples except the sandy sediments, which were sampled with a box corer. After collection, a sediment sample was divided into 0–1 (exceptionally 0–2), 1–5 (exceptionally 2–5) and 5–10 cm-thick layers and frozen immediately at -20°C aboard.

PAH analysis

The detailed analytical procedure has been described (Kowalewska et al. 2003, Filipkowska et al. 2005). After thawing, a sediment sample was centrifuged to separate water and then extracted five times with 20 cm^3 portions of acetonitrile. The combined acetonitrile extracts were transferred to benzene in the following system: acetonitrile extract-water-benzene (10:10:1 v/v/v). Next, the benzene layer was separated and evaporated to dryness under vacuum. The residue was dissolved again in acetonitrile and cleaned-up by thin layer chromatography (TLC). The silica gel containing PAHs was scratched off the TLC plate and then extracted with acetonitrile. The purified sample dissolved in a small amount of acetonitrile was injected into an HPLC system (Knauer, Germany) with a diode-array detector registering absorption in the UV range (DAD, Chrom-a-Scope). Separations were performed on a Merck Superspher 100 RP-18 column. The mobile phase was acetonitrile:water (95:5 v/v or 85:15 v/v), at a flow rate of 0.4 or $0.6\text{ cm}^3\text{ min}^{-1}$. During the analysis, the spectrum was scanned in the 220–360 nm range. All the PAHs were determined at $\lambda = 254\text{ nm}$. The PAH standard for unsubstituted PAHs was a TCL PAH mix (mixture of 16 EPA Priority PAHs – Supelco) and for methylphenanthrenes single PAHs (1-methylphenanthrene, 2-methylphenanthrene, 3,6-dimethylphenanthrene, 9,10-dimethylphenanthrene – Dr. Ehrenstorfer GmbH). 1-, 2-methylphenanthrenes were selected as the most often investigated isomers and 3,6- and 9,10-dimethylphenanthrenes as those with

Table 1. Methylphenanthrene content in sediments of the southern Baltic Sea, averaged for a 0–10 cm thick layer [$\mu\text{g g}^{-1}$]

Area	Date	Monometphens	Dimetphens	Σ Metphens
Gulf of Gdańsk				
92A	March 1995	98.6	179.9	278.5
PGd	May 1996	39.9	59.0	98.9
ZN2	October 1995	2.8	1.3	4.1
ZN2	October 1997	50.0	99.1	149.1
W.L.	May 2000	19.4	68.1	87.5
Mean		42.1	81.5	123.6
Gdańsk Deep				
G2	November 1995	0.0	33.0	33.0
G2	May 1996	175.4	176.7	352.1
G2	September 1998	75.1	190.0	265.1
G2	November 2000	65.3	169.1	234.4
P116	March 1995	94.8	237.4	332.3
5	May 2001	45.2	88.2	133.4
Mean		76.0	149.1	225.1
Baltic-open sea				
P3	March 1995	7.2	3.7	10.9
P3	October 1995	1.9	4.5	6.4
P3	May 2001	0.7	0.4	1.1
PBW	October 1995	0.0	0.2	0.2
66	May 2001	11.8	32.7	44.4
84	May 2001	3.3	6.8	10.1
P2	May 2001	1.1	1.0	2.0
R4	May 2001	0.5	0.0	0.5
Mean		3.3	6.1	9.5
Bornholm Deep				
P5	September 1998	79.5	105.1	185.0
P5	November 2000	22.1	65.0	87.1
P27	March 1995	62.1	102.6	164.7
Mean		54.6	90.9	145.6
Szczecin Lagoon				
K	August 1996	238.5	265.2	503.6
K	October 1996	289.3	321.4	610.7
K	October 1997	232.6	329.7	563.1
K	October 1999	204.6	360.6	564.8
K	October 2000	184.2	376.3	560.4
L	August 1996	222.1	263.8	485.9
L	October 1996	209.1	171.3	380.4
L	October 1997	228.4	419.2	647.6
L	October 1999	304.8	463.3	767.8
L	October 2000	196.0	407.0	602.9
M	August 1996	119.5	148.5	268.0

Table 1. (*continued*)

Area	Date	Monometphens	Dimetphens	Σ Metphens
Szczecin Lagoon				
M	October 1996	111.8	131.2	243.1
M	October 1997	107.7	216.3	323.5
M	October 1999	145.7	233.4	379.1
M	October 2000	96.4	198.3	294.7
15	October 1999	64.0	92.3	156.8
15	October 2000	86.4	175.5	261.9
18	October 1999	189.5	265.5	454.1
18	October 2000	90.3	174.4	265.2
R.O.	October 1999	188.5	369.8	557.8
R.O.	October 2000	201.5	462.4	663.4
J.W.	October 1999	5.4	2.1	7.5
J.W.	October 2000	130.2	224.1	354.8
J.W.2	October 2000	103.6	215.8	319.4
Mean		164.6	262.0	426.5
Pomeranian Bay				
P39	October 1995	0.0	27.5	27.5
38	May 1997	16.1	16.8	32.9
38	October 1997	18.0	40.4	58.4
38	October 1999	65.8	72.6	137.8
38	October 2000	7.5	11.8	19.3
Pr.9a	July 1997	37.5	56.8	94.6
Pr.9a	September 1997	53.8	58.8	111.9
37	June 2001	0.6	0.0	0.6
35	June 2001	0.6	0.0	0.6
32	June 2001	1.1	0.8	1.6
Mean		20.1	28.6	48.5

the most different retention times in GC/MS. Because of their co-elution in HPLC chromatograms, dimethylphenanthrenes were quantified together. This was done by the external standard method using 3,6-dimethylphenanthrene on the assumption that the absorption coefficient of all dimethylphenanthrenes is equal to that of 3,6-dimethylphenanthrene. The selected samples were analysed by GC/MS. The details of the analysis are given elsewhere (Filipkowska et al. 2005). The extract for GC/MS was additionally purified of sulphur by being passed through a micro-column packed with copper powder (Merck, particle size < 63 μm). The purified PAH fraction was dissolved in i-octane and analysed using a gas chromatograph (Varian 3900 GC, USA) with a mass spectrometer detector (Saturn 2100T GC/MS, Varian). A fused capillary column (Varian CP-Sil 8 CB Low Bleed/MS – 0.25 mm ID \times 60 m, 0.25 μm film thickness)

with a 5% phenyl, 95% dimethylpolysiloxane stationary phase was used. The carrier gas was helium and the sample was injected in splitless mode; after 2 min the split mode was switched on. PAHs were detected by a mass spectrometer equipped with an ion-trap using a SIS (Selected Ion Storage) acquisition programme under electron impact ionisation. Quantification was performed by an external standard procedure.

The concentration of each analyte was corrected by the relevant mean recovery from spiked pre-extracted sediment. PAH recovery depended on the compound and ranged from 80 to 96%; anthracene (50%) was the exception. The analytical methods were validated against the certified reference material – a sediment sample from the Venice lagoon (CRM –IAEA-417).

3. Results and discussion

The results for the methylated phenanthrenes are shown in Table 1. The highest contents of both mono- (sum of 1- and 2-methylphenanthrene) and dimethylphenanthrenes were in the Szczecin Lagoon. The muddy sediments of the Gdańsk and Bornholm Deeps, rich in the fine-grain fraction, also contained elevated levels of methylated PAHs. The lowest concentrations were at the open sea stations.

Tables 2 and 3 present the respective results of comparing the HPLC method with GC/MS for CRM IAEA-417 and for the field samples.

Table 2. Results of the analysis of certified reference material IAEA-417 [$\mu\text{g g}^{-1}$ d.w.]

PAHs	Phen	Antr	Fla	Pyr	B(a)A+Chr	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	1-Metphen	2-Metphen
HPLC													
(n = 4)													
Mean	1538	331	5464	4635	3851	1948	1138	1583	3021	577	1613	411	438
SD	122	53	398	219	373	279	144	80	426	94	156	68	27
GC/MS													
(n = 4)													
Mean	1054	445	4742	3461	4842	1884	1572	1984	2190	586	1751	180	383
SD	146	62	554	398	624	319	191	271	357	49	270	20	43
Certified value													
Mean	3900	630	7700	6000	6800	4100	2000	2800	2700	1100	2300	320	580
SD	1500	240	3000	2200	2900	2000	300	1200	370	1100	1300	150	230

Table 3. Comparison of analytical results by HPLC and GC/MS [ng g^{-1} d.w.]

Station	Method	Phen	Antr	Fla	Pyr	B(a)A+Chr	B(b)F	B(k)F	B(a)P	Ip	DBA	Bper	Σ 12PAHs	1-Metphen	2-Metphen	Monometphens	Dimetphens
K 1–5 cm	HPLC	713	355	1143	1576	781	465	430	504	271	–	503	6740	114	176	290	360
	GC/MS	153	247	954	731	1213	838	333	543	525	130	519	6187	52	111	162	335
October 1996																	
K 5–10 cm	HPLC	364	146	636	655	445	302	179	328	–	128	565	3748	48	70	118	228
	GC/MS	218	185	394	308	391	488	143	267	385	50	256	3086	24	57	81	114
October 1999																	
L 0–1 cm	HPLC	1431	445	1769	1810	1302	872	397	104	–	395	459	8983	277	267	544	622
	GC/MS	930	396	976	760	1062	757	333	494	512	119	564	6902	125	248	373	518
October 1999																	
P5 5–10 cm	HPLC	52	2	94	125	95	175	92	55	–	76	184	951	13	11	24	75
	GC/MS	45	15	72	78	88	189	72	53	215	39	190	1055	8	15	23	20
November 2000																	
R.O. 5–10 cm	HPLC	1020	451	1322	2165	1465	759	310	633	–	443	244	8812	92	164	256	555
	GC/MS	505	493	724	642	894	912	247	495	489	85	379	5864	61	132	193	342
October 2000																	
G2 1–5 cm	HPLC	129	36	545	373	291	595	279	276	603	457	467	4050	36	38	74	225
	GC/MS	126	59	323	264	275	208	200	231	497	92	444	2719	20	36	56	78
November 2000																	

The concentrations of parent PAHs (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, Ip – indeno(1,2,3-cd)pyrene, DBA – dibenzo(a,h)-anthracene, Bper – benzo(g,h,i)perylene) for 1995–2000 were taken from the Marine Pollution Laboratory IO PAS data base. These data have already been published (Kowalewska & Konat 1997, Kowalewska et al. 1997, 2003). The distribution of parent PAHs with respect to the percentage of n-ring molecules in the sum of 12 PAHs was comparable for most of the areas studied with the exception of the Gulf of Gdańsk and Szczecin Lagoon (Table 4). These areas, strongly affected by riverine input and industrial activities, demonstrate a distinct predominance of 4-ring PAHs and a relatively low content of 6-ring PAHs. This, according to the literature data (Baumard et al. 1998, Wetzel & van Vleet 2003), indicates higher ratios of petrogenic PAHs to pyrogenic ones at coastal sites than at the offshore stations. In other words, on the coast of the area in question there were mainly pyrogenic PAHs with a substantial input of products of incomplete petroleum combustion.

Table 4. Content of n-ring PAHs in the sum of PAHs (unsubstituted, $(\text{ng ng}^{-1}) \times 100\%$), averaged for a 0–10 cm layer

Area	3-ring	4-ring	5-ring	6-ring
Gulf of Gdańsk	19.9	54.1	23.9	2.1
Gdańsk Deep	14.1	31.3	28.2	26.4
Baltic-open sea	15.0	24.9	34.0	26.3
Szczecin Lagoon	15.1	53.3	24.9	6.7
Pomeranian Bay	14.4	33.9	24.4	27.3
Bornholm Deep	14.5	32.2	29.5	23.8

Literature data on the distribution of methylphenanthrenes in sediments in other areas are scarce and difficult to compare; results are therefore given for variable numbers of compounds and in different sediment layers (Table 5). Moreover, samples were collected with different devices. However, the methylphenanthrene concentrations determined in this work are in general comparable with the available data for the southern Baltic (Baumard et al. 1999) and the estuarine areas of average petrogenic pollution in the world (Baumard et al. 1998, Pereira et al. 1999, Notar et al. 2001, Beg et al. 2003, Wetzel & van Vleet 2003, Muniz et al. 2004). The percentages of phenanthrene, methylphenanthrenes and dimethylphenanthrenes in the sum of all phenanthrenes differ distinctly (Table 6). The relative contribution of unsubstituted phenanthrene exceeded that of the methylated compounds

Table 5. Selected literature data on methylphenanthrene concentration in marine sediments

Area	Sediment layer [cm]	Analytes	Range [ng g ⁻¹]	Reference
Baltic Sea, 1995–1996	0–5	Σ Monometphens		Baumard
– Kiel		(1-, 2-, 3-, 4-, 9-	5.93–994	et al. 1999
– Warnemünde		Metphens)	0.14–63.9	
– Peenemünde			0.21–15.8	
– Odra areas			2.05–923	
Baltic Sea		Σ Monometphens		Ricking
– Arkona Basin	0–5	(1-, 2-, 3-, 4-, 9-	147	et al. 2002
	5–10	Metphens)	252	
– Gotland Basin	4–4.5		333	
	9.5–10		274	
Gironde estuary, France, 1993	0–2	1-Metphen	0.8–25.4	Budzinski
		2-Metphen	1.1–27.3	et al. 1997
		3-Metphen	1.0–19.1	
		4/9-Metphen	1.4–36.2	
Western Mediterranean Sea (French, Spanish and Balearic coasts), 1996	0–2	Σ Monometphens (1-, 2-, 3-, 4-, 9- Metphens)	0.24–310	Baumard et al. 1998
Gulf of Trieste, northern Adriatic Sea, 1996	0–2	1-Metphen	1.59–14.06	Notar
		2-Metphen	2.17–18.17	et al. 2001
Shuaiba industrial area, Kuwait		Σ Monometphens	0–46.82	Beg et al. 2003
		Σ Dimetphens	2.35–107.5	
Xiamen Harbour and Yuan Dan Lake, China, 2002	0–8(10)	1-Metphen	4.2–152.9	Ou et al. 2004
San Francisco Bay, USA	0–10			Pereira
– Richardson Bay		1-Metphen	27	et al. 1999
		2-Metphen	35	
– San Pablo Bay		1-Metphen	5.7	
		2-Metphen	10	
Montevideo Harbour, Uruguay, 1998		Σ Monometphens	170–6590	Muniz
		Σ Dimetphens	300–5270	et al. 2004
Southern Baltic Sea	0–10	Σ Monometphens (1-, 2-Metphens)	0.0–304.8	this study
		Σ Dimetphens	0.0–463.3	

considerably, which indicates the dominance of pyrogenic PAHs (Page et al. 1999). The respective contents of alkylated homologues for mono- and dimethylphenanthrenes ranged from ~11 to 19% and from ~21 to 30%. In general, the proportion of methylated PAHs was slightly higher

Table 6. Content of phenanthrene, monomethyl- and dimethylphenanthrenes in the sum of phenanthrenes (unsubstituted and substituted, $(\text{ng ng}^{-1}) \times 100\%$) in 0–10 cm layer

Area	% in ΣPhens		
	Phen	Monometphens	Dimetphens
Gulf of Gdańsk	65.4	11.8	22.8
Gdańsk Deep	64.4	12.0	23.6
Baltic – open sea	68.2	11.1	20.7
Szczecin Lagoon	51.7	18.6	29.7
Pomeranian Bay	53.2	19.3	27.5
Bornholm Deep	59.3	15.3	25.4

in areas affected by Odra waters. This suggests that PAHs originating from petrogenic sources are more abundant in the total PAH load carried to sea by the Odra than in that transported by the Wisła. The average phenanthrene loads carried by the Wisła and Odra were estimated on the assumption that both the surface sediments (0–1 cm layer) and the suspended matter contain the same amounts of PAHs per dry weight (Table 7), as was done for the parent PAHs and the River Odra (Kowalewska et al. 2003). The calculations of PAH concentration were based on data from sites considered to be primary sinks for both rivers, i.e. the Szczecin Lagoon (all the stations except for J.W., 0–1 cm layer) and the Gdańsk Deep (0–1 cm layer) for the Odra and Wisła respectively. The annual inflows from the Wisła and Odra were ~ 39 and 20 km^3 , and suspended matter input 0.54 and $0.39 \times 10^6 \text{ t year}^{-1}$ a respectively (IMGW 2000). As these estimates show, the Wisła discharges larger quantities of phenanthrene and its alkylated homologues than the Odra. On the other hand, taking into account the mean

Table 7. Estimations of PAH input by the Rivers Wisła (Vistula) and Odra (Oder) (in suspended matter)

	Mean concentration in 0–1 cm sediment layer [ng g^{-1}]	Annual input [kg year^{-1}]	Annual input related to riverine water inflow [$(\text{kg year}^{-1}) \times \text{km}^{-3}$]
Wisła (Vistula)			
Phen	688	372	9.53
Σ Metphens	459	248	6.36
Σ 12 PAHs	3738	2019	51.76
Odra (Oder)			
Phen	476	186	9.28
Σ Metphens	429	167	8.37
Σ 12 PAHs	4185	1632	81.61

water flow and suspended particulate matter content, the Odra appears to be more polluted with PAHs, also with the methylated compounds, i.e. petrogenic PAHs.

4. Conclusions

- The percentage of phenanthrene, monomethylphenanthrenes and dimethylphenanthrenes in the sum of phenanthrenes in sediments is a sensitive measure of petrogenic pollution in the southern Baltic environment.
- Sediments affected by the River Odra are characterised by a greater petrogenic input than those affected by the River Wisła.

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