

**Content and pattern of
organic pollutants (PAHs,
PCBs and DDT) in blue
mussels (*Mytilus trossulus*)
from the southern Baltic
Sea***

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Abstract

The objective of this work was to assess the contents and patterns of selected organic pollutants (polycyclic aromatic hydrocarbons – PAHs, polychlorinated biphenyls – PCBs, and chlorinated pesticides – DDT) in the southern part of the Baltic Sea proper, using blue mussels, *Mytilus trossulus*, as sentinel organisms. The mussels were collected from the Baltic Sea off Poland. The sampling programme focused on the mouths of the rivers Odra and Vistula, located respectively in the Pomeranian Bay and the Gulf of Gdańsk, both known to be under anthropogenic pressure.

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The analyses of PCBs and DDT were performed by GC-ECD, that of PAHs by GC-MS. Mussels from both the Vistula and Odra estuaries were found to contain higher levels of organic contaminants (PAHs, PCBs, DDT; 29.7 ng g⁻¹ w.w. (wet weight), 22.3 ng g⁻¹ w.w., 11.2 ng g⁻¹ w.w. respectively) as compared to the reference point (PAHs – 8.6 ng g⁻¹ w.w., PCBs – 1.9 ng g⁻¹ w.w., DDT – 1.3 ng g⁻¹ w.w.). These results confirm the direct influence of land-based pollution sources on the content of organic pollutants (PAHs, PCBs, and DDT) in the southern Baltic Sea, and point to the Gulf of Gdańsk as the area most under threat.

P/A and Fluo/Py ratios indicate that in all the mussels analysed, the contaminants were derived mainly from pyrolytic combustion. The mussels collected along the Polish coast of the Baltic contain mostly tetra-aromatic isomers (fluoranthene, pyrene, benzo(*a*)anthracene and chrysene), penta-aromatic isomers (benzo(*b*)fluoranthene, benzo(*e*)fluorene, benzo(*a*)pyrene and dibenzo(*a,h*)-anthracene) and hexa-aromatics (indeno(1,2,3-*cd*)pyrene and benzo(*ghi*)perylene) rather than di- and tri-aromatics (naphthalene, fluorene, phenanthrene and anthracene). As regards PCBs, the Baltic mussels contain mostly the more highly chlorinated congeners (penta- and hexachlorobiphenyls). The PCB/*pp'*DDE and PAH/*pp'*DDE ratios indicate the predominance of PCBs and PAHs over agriculturally derived DDE in both the Pomeranian Bay and the Gulf of Gdańsk.

1. Introduction

Environmental protection and the prevention of pollution became one of the main scientific, social and economic activities towards the end of the 20th century. However, the increasing concentrations of toxic substances in biota and their accumulation along food chains reported in many coastal areas is a sign that degradation of the natural environment is still in progress (Porte & Albaigès 1993, Baumard et al. 1998). Contamination of the environment is apparent not only in areas of direct anthropogenic influence, e.g. in estuaries, owing to the pollutant load in the river run-off and huge conurbations usually located close to river mouths, but also in remote areas, such as open sea waters, as a result of long range atmospheric transport and deposition of pollutants (Sánchez et al. 1993). This applies predominately to persistent organic pollutants (POPs) (Neff 1979, Lipiatou & Saliot 1991, Barrie et al. 1992, Strandberg et al. 1998, Escartin & Porte 1999a, b, Sole et al. 2000).

Polycyclic aromatic hydrocarbons (PAHs), one of the most widespread POPs in the environment, are ubiquitous contaminants in aquatic environments, including estuaries (Means 1998). They are mainly of anthropogenic origin, including the combustion of oil, wood, fossil fuels or recent organic matter, and the release of hydrocarbons in connection with crude-oil prospecting (Wakeham et al. 1980). PAHs can also be produced in nature as a result of forest fires or natural seepage of petroleum, or be derived from biogenic precursors (Baumard et al. 1999).

Chlorinated organic compounds such as polychlorinated biphenyls (PCBs) and chlorinated pesticides (DDTs) are known to be exclusively anthropogenic POPs (Sánchez et al. 1993). PCBs are used in many industrial processes, for example, in dielectric fluids for transformers and capacitors. River run-off is thought to be one of the major sources of PCBs to the marine environment. Organochlorines can be present in the environment for a long time owing to their slow biodegradation (Zakrzewski 1995).

PAHs, PCBs, and DDT and its derivatives have been subjected to intensive study world-wide in the last ten years because of their high rates of production and consumption, their considerable environmental persistence, toxic potential, high levels of bioaccumulation and harmful biological effects, including their mutagenic and carcinogenic properties (Lee et al. 1996, Baumard et al. 1998). Because of their hydrophobicity and resistance to degradation, they are widely distributed in the various components of the environment. The majority of persistent PAHs and organochlorines and their by-products are released from primary sources to marginal seas and the ocean, where they are accumulated by biota and become biomagnified (Evans et al. 1991, Porte & Albaigès 1993).

As a result of its limited and slow water exchange with the ocean, large freshwater input from rivers and precipitation, and the high level of industrialisation of its catchment area, the Baltic Sea is an area very much under threat from environmental pollution. Contaminants enter the Baltic Sea primarily through atmospheric transport and riverine input (Broman et al. 1991, Falandysz et al. 1994). The occurrence of PAHs and organochlorines in the Baltic Sea has been the subject of several studies (Broman et al. 1990, Witt 1995, Falandysz et al. 1998, Strandberg et al. 1998, Falandysz et al. 2001). Baumard et al. (1999) measured PAH residues in surface sediments and mussels *Mytilus edulis* collected from the western Baltic Sea and reported total PAH concentrations in sediments from 3 to about 30 000 ng g⁻¹, while total PAH concentrations in mussels ranged from 90 to 3900 ng g⁻¹ d.w. (dry weight) The concentrations of organochlorines (PCBs, DDT) determined in mussels *M. edulis* from the south-western Baltic Sea reported by Lee et al. (1996) ranged from 38 to 487 µg kg⁻¹ d.w. (total PCB content) and from 6.6 – 88.3 µg kg⁻¹ d.w. (total DDT content). Blue mussels sampled from the Gulf of Gdańsk in 1992 contained PCBs and DDTs in concentrations of 910 ng g⁻¹ lipid and 14 ng g⁻¹ w.w. (wet weight) respectively (Falandysz et al. 1999, Dembowska 2000). Strandberg et al. (1998) reported on the content of organochlorine compounds in a pelagic food web in the northern Baltic Sea. Total concentrations of PCBs were in the range from 100 to 250 ng g⁻¹ lipid in zooplankton, from 230 to 300

ng g⁻¹ lipid in mysis (*Mysis* sp.), and from 690 to 1600 ng g⁻¹ lipid in the Baltic herring (*Clupea harengus*). DDT concentrations ranged from 17 to 100 ng g⁻¹ lipid in zooplankton samples and from 170 to 580 ng g⁻¹ lipid in the herring. The total DDT content in mysis was at the level of 100 ng g⁻¹ lipid (Strandberg et al. 1998). Kowalewska & Konat (1997) reported concentrations of PAHs from 10 to 7000 ng g⁻¹ d.w. in sediments collected from the southern Baltic Sea, a range well within that reported by Baumard et al. (1999).

Mussels, particularly *Mytilus* sp., have several advantages as a bioindicator, such as a wide distribution, abundance, sedentary behaviour, and a pronounced ability to accumulate organic compounds. Filter-feeding mussels process large volumes of sea water (approximately 2 dm³ per hour), thereby accumulating organic compounds in concentrations two to five orders of magnitude greater than those in the ambient sea water. In comparison to high trophic levels such as fish and marine mammals, the enzyme systems metabolising organic contaminants in mussels exhibit rather a low activity (Boon et al. 1989, Stegeman & Lech 1991). The pattern of organic pollutant concentrations detected in mussels could therefore resemble their pattern in the ambient water to a good approximation.

The object of the present work was thus to provide information on the occurrence, geographical distribution and pattern of persistent organic pollutants, such as PAHs, PCBs and DDT, in the southern part of the Baltic off Poland, especially near the mouths of the Odra and Vistula, since both rivers discharge substantial loads of POPs to the sea. The concentrations of these compounds in the soft tissue of the mussel *M. trossulus* was used as an indicator of contamination. The sampling stations were chosen along the expected pollution gradients. Several sampling sites were located close to the mouths of two large rivers – the Vistula and the Odra, which drain much of Poland. The Vistula discharges into the Gulf of Gdańsk, the Odra into the Pomeranian Bay. The Gdańsk and Szczecin conurbations extend along the shores of the Gulf of Gdańsk and Pomeranian Bay respectively. Mussels collected far from the coast were used as a reference.

2. Materials and methods

Sample collection and preparation

The tested organisms – blue mussels (*M. trossulus*) – were collected with a drag net during a cruise of r/v 'Oceania' in September 1997. The location of sampling stations is shown in Fig. 1. Two stations – Z1 and Z2 – were located in the Pomeranian Bay, near the urban area and port of Świnoujście. Two more stations – G2 and G3 – were located in the Gulf of Gdańsk,

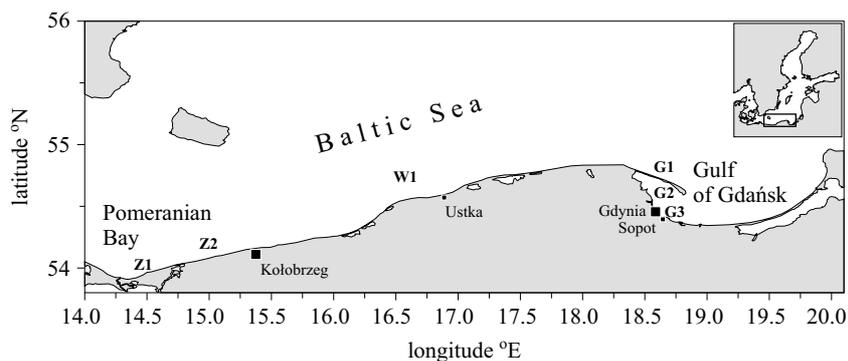


Fig. 1. Location of sampling stations in the southern Baltic Sea

station G2 near the port of Gdynia and station G3 near the port of Gdańsk. Stations G1 and W1 were located on the open sea, G1 on the seaward side of the Hel Peninsula, W1 near Ustka. The latter was used as a reference site.

Once on board, mussels 35–45 mm in length were selected, cleaned, then immediately frozen and stored at -20°C until analysis.

Analyses

The analyses were based on procedures described by Porte & Albaigès (1993) and Albaigès et al. (1987). In brief, some 30 specimens from each station were defrosted and the soft tissue separated from the shell. About 5 g of homogenised wet tissue were saponified with 20 ml 6N NaOH (18 h, 40°C) and extracted with hexane:dichloromethane (4:1) solvent. The solvent extract was evaporated under vacuum to 1 ml and then separated by liquid chromatography (5% water deactivated silica:alumina column) into three fractions containing alkanes + alkenes (*n*-hexane), monocyclic and polycyclic aromatics (10% and 20% methylene chloride in *n*-hexane, respectively). The second fraction contained the PCBs, as well as the *pp*'DDE (the original *pp*'DDE and *pp*'DDT converted to *pp*'DDE after saponification with NaOH).

These fractions were evaporated under vacuum to approximately 1 ml and then to dryness under a gentle stream of nitrogen. Prior to analysis, they were redissolved in 1 ml of isooctane.

The second fraction was injected into a gas chromatograph (Hewlett-Packard 5890) equipped with an ECD detector at 300°C . The capillary column (50 m \times 0.25 mm, CP-Sil 5 CB fused silica, Chrompack, Middelburg, NL) was programmed from 80°C (5 min) to 290°C (15 min) at a rate of $6^{\circ}\text{C min}^{-1}$. The carrier gas was helium at a linear flow-rate of 50 cm s^{-1} . The injector port temperature was 280°C . Quantification was performed

using an external standard calibration mixture (recovery better than 90%) containing 20–30 ng l⁻¹ of selected ‘indicative’ chlorobiphenyl congeners (IUPAC Nos: 28, 52, 101, 118, 153, 138, and 180). The detection limit for PCB and DDT congeners in mussel tissue was 0.01–0.07 ng g⁻¹.

The third fraction was analysed by capillary GC-MS-EI using a Fisons GC 8000 Series chromatograph interfaced to a Fisons MD mass spectrometer. A capillary column (30 m × 0.25 mm, HP-5MS cross-linked 5% PH ME siloxane, Hewlett-Packard) was programmed from 80°C (5 min) to 120°C (10 min) at a rate of 15°C min⁻¹, and from 120°C to 300°C (15 min) a rate of 6°C min⁻¹. The carrier gas was helium at 80 kPa. The injector temperature was 250°C, and the ion source and the analysis were maintained at 200 and 250°C respectively. The mass spectra were obtained at 70 eV in the selected ion register (SIR) mode. 2,6-dibromophenol and hexamethylbenzene were used as surrogate standard and GC internal standard respectively. Polycyclic aromatic hydrocarbons were identified and quantified by comparison of retention times and spectra of reference compounds (their recoveries were better than 95%). Fourteen unsubstituted PAHs were determined: naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*e*)fluorene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, dibenzo(*ah*)-anthracene, benzo(*ghi*)perylene. The detection limit of the GC-MS-EI technique – calculated as signal to noise ratio 3:1 – was at the level of 0.04–0.09 ng g⁻¹ for mussel tissue.

The methods reported above included the processing of blanks, duplicates and standard mixtures between each group of samples. The protocol for the determination of organochlorine compounds was validated through participation in an intercalibration exercise (UNEP-IOC-IAEA).

3. Results and discussion

The PAH, PCB and DDT concentrations in the soft tissue of the mussel *M. trossulus* collected from the southern Baltic Sea are presented in Table 1. The results are expressed in ng g⁻¹ wet weight.

There was an increase in the total PAH concentrations (Σ PAHs; Table 1) as compared to the reference point (W1 – 8.6 ng g⁻¹ w.w.) in the samples from the Pomeranian Bay and the Gulf of Gdańsk (Z2 – 29.7 ng g⁻¹ w.w. and G3 – 29.2 ng g⁻¹ w.w. respectively). This is evidence for the influence of local pollution sources, such as river input (the Odra to the Pomeranian Bay and the Vistula to the Gulf of Gdańsk), and the important ports and shipyards located there.

Table 1. The concentrations of organic contaminants (PAHs, PCBs, DDT) in the soft tissue of mussels *Mytilus trossulus* collected from the southern Baltic (ng g⁻¹ w.w.)

Contaminant	Sampling station					
	Z1	Z2	W1	G1	G2	G3
Polycyclic aromatic hydrocarbons (PAHs)						
– low molecular weight PAHs						
naphthalene	0.41	0.20	–	–	–	0.32
fluorene	0.04	0.02	–	0.14	0.12	0.56
phenanthrene (P)	0.44	0.38	0.23	0.79	1.33	1.29
anthracene (A)	0.06	0.06	–	0.06	0.57	0.87
fluoranthene (Fluo)	1.76	5.40	0.87	4.25	6.21	5.34
pyrene (Py)	1.00	2.07	0.27	1.80	3.00	2.32
benzo(<i>a</i>)anthracene	2.41	2.83	1.87	1.63	1.80	2.30
chrysene	1.71	3.06	2.14	2.46	2.14	3.51
Σlow	7.83	14.02	5.38	11.14	15.17	16.51
– high molecular weight PAHs						
benzo(<i>b</i>)fluoranthene	0.98	3.14	0.77	2.19	1.91	2.86
benzo(<i>e</i>)fluorene	0.89	2.67	0.70	2.48	2.23	2.91
benzo(<i>a</i>)pyrene	0.51	2.38	0.28	0.86	1.00	1.86
indeno(1,2,3- <i>cd</i>)pyrene	0.84	3.90	0.56	1.27	1.21	1.91
dibenzo(<i>ah</i>)anthracene	0.89	1.82	0.80	1.74	1.48	2.27
benzo(<i>ghi</i>)perylene	0.25	1.79	0.15	0.22	0.37	0.89
Σhigh	4.36	15.70	3.26	8.77	8.19	12.70
ΣPAHs	12.19	29.72	8.64	19.91	23.36	29.21

Table 1. (continued)

Contaminant	Sampling station					
	Z1	Z2	W1	G1	G2	G3
$\Sigma\text{low}/\Sigma\text{high}$	1.79	0.89	1.65	1.27	1.85	1.30
P/A	7.33	6.33	–	13.17	2.33	1.48
Fluo/Py	1.76	2.61	3.27	2.36	2.07	2.30
Polychlorinated biphenyls (PCBs)						
2,4,4'-trichlorobiphenyl (CB-28)	–	–	–	0.13	0.30	0.10
2,2',5,5'-tetrachlorobiphenyl (CB-52)	0.07	0.26	0.14	0.33	0.66	0.22
2,2',4,5,5'-pentachlorobiphenyl (CB-101)	0.34	0.89	0.32	1.04	3.41	3.79
2,3',4,4',5-pentachlorobiphenyl (CB-118)	0.30	0.74	0.26	0.83	3.30	3.89
2,2',4,4',5,5'-hexachlorobiphenyl (CB-153)	1.49	2.07	0.61	1.18	6.38	6.52
2,2',3,4,4',5'-hexachlorobiphenyl (CB-138)	1.02	1.57	0.53	1.14	6.49	5.43
2,2',3,4,4',5,5'-heptachlorobiphenyl (CB-180)	0.20	0.26	0.07	0.20	1.78	2.36
ΣPCBs	3.42	5.79	1.93	4.85	22.32	22.31
<i>pp'</i> dichlorodiphenylethylene (<i>pp'</i> DDE)	1.24	3.62	1.25	3.05	11.23	4.91

A land-locked sea surrounded by countries with differing ranges of human activities, the Baltic Sea receives significant amounts of persistent organic pollutants (POP) via air transport and deposition (HELCOM 1997). Because the water exchange between the Baltic and the North Sea is limited, atmospheric processes may play an important role as regards the occurrence of POPs in the former (HELCOM 1997). The two principal mechanisms of PAH transport from the terrestrial to the marine environment – the fluvial and the atmospheric – are usually taken into consideration (Lipiatou & Saliot 1991). Hydrocarbon distributions at site W1, remote from pollution sources, though low in concentration compared to those at coastal sites, confirm the long-range transport of hydrocarbons from natural and urban/industrial sources to depositional environments (Cripps 1992). In coastal areas, direct deposition of atmospheric PAHs may be relatively minor compared to fluvial inputs, but in open ocean areas it can dominate (HELCOM 1997, Kowalewska & Konat 1997). Thus, at the Pomeranian Bay stations (Z1 and Z2) the mussel PAH concentrations are higher in comparison with the PAH contamination level at the reference point (W1). However, there was an increase in the PAH content in mussels from site Z1, situated closer to the Odra mouth, to site Z2, located farther from the mouth (from 12.2 ng g⁻¹ w.w. to 29.7 ng g⁻¹ w.w.). This situation may be related to the strong influence of atmospheric transport, since Z2 lies to the east of Z1. The prevailing winds in this area are westerlies (HELCOM 1997, Baumard et al. 1999). Direct transport of pollution from the Odra mouth is thus less likely.

Three main processes can generate PAHs: (1) combustion of organic matter at a very high temperature, (2) release of petroleum, or (3) diagenetic processes such as degradation of organic matter (Neff 1979). The molecular PAH patterns generated by each source are like fingerprints and it is possible when studying PAH distributions to determine the processes that generate PAHs. Pyrolytic aromatic hydrocarbons are characterised by the occurrence of PAHs of a wide range of molecular weights, while petroleum hydrocarbons are dominated by the lowest molecular weight PAHs (Neff 1979). To characterise PAH sources, molecular indices based on the thermodynamic stability of various isomeric compounds have been developed (Baumard et al. 1999). Among the tri-aromatic isomers, phenanthrene (P) is thermodynamically more stable than anthracene (A). Pyrolysis of organic matter at a very high temperature generates PAHs with a low P/A ratio (<10), whereas the slow maturation of petroleum at lower temperatures leads to much higher P/A ratios (>25) (Raoux & Garrigues 1993). The Fluo/Py index is applied in the same way. Fluoranthene (Fluo) is thermodynamically less stable than pyrene (Py) and a predominance

of fluoranthene over pyrene is characteristic of pyrolytic products, while in petroleum-derived PAHs, pyrene is more abundant than fluoranthene (Budzinski et al. 1997). P/A and Fluo/Py ratios (Table 1) indicate that with respect to all the mussels analysed in the present work, the contaminants originated mainly from pyrolytic combustion. The pyrolytic PAHs in the southern part of the Baltic Sea (Polish coast) are derived from industry, traffic and fuel combustion (in Poland coal and lignite are frequently used for heating during winter). The percentage distribution of the PAHs (Σ PAHs = 100%) in the soft tissue of mussels, *M. trossulus*, is presented in Fig. 2a, b. In samples from the reference point (W1) di-aromatic (naphthalene) and tri-aromatic isomers (fluorene and anthracene) were below the detection limit. The other PAHs (except chrysene and benzo(*a*)anthracene) were in the range from 2% (benzo(*ghi*)perylene) to 10% (fluoranthene) of the total amount. Tetra-aromatics (chrysene and benzo(*a*)anthracene) were dominant in mussels from the reference point W1 (25% and 22% of the total amount respectively), but remained at the same low level of approximately 2 ng g⁻¹ w.w., as in the mussels from the other sampling stations (Table 1). In mussels from the Pomeranian Bay (Z2) and the Gulf of Gdańsk (G1, G2, and G3), the content of fluoranthene (tetra-aromatic isomer) was the highest of all the PAHs analysed (mean – 21% of the total amount, in comparison to 10% of the total amount of PAHs at the reference point W1). The predominance of low-molecular weight PAHs (tri- and tetra-aromatics) is characteristic of petroleum contamination and indicates an additional, local source (Neff 1979, Garrigues et al. 1995, Baumard et al. 1999).

The mussels collected from the Polish coast of the southern Baltic contain mainly tetra-aromatic isomers (fluoranthene, pyrene, benzo(*a*)anthracene and chrysene), penta-aromatic isomers (benzo(*b*)fluoranthene, benzo(*e*)fluorene, benzo(*a*)pyrene and dibenzo(*a,h*)anthracene) and hexa-aromatics (indeno(1,2,3-*cd*)pyrene and benzo(*ghi*)perylene) rather than di- and tri-aromatics (naphthalene, fluorene, phenanthrene and anthracene). Several recent papers have shown that bivalves preferentially bioaccumulate 4-, 5- and 6-ringed PAHs rather than 2- and 3-ringed PAHs (Porte & Albaigès 1993, Hickey et al. 1995, Baumard et al. 1998).

The concentrations of PAHs in the soft tissue of mussels collected from the southern Baltic in this work are comparable to the findings of Baumard et al. (1999). In the latter work the concentration of PAHs in the soft tissue of mussels collected from the Pomeranian Bay was in the range from 99 to 374 ng g⁻¹ d.w. In our study the PAH concentration in mussels collected from the same region ranged from 12.2 ng g⁻¹ w.w. (Z1) to 29.7 ng g⁻¹ w.w. (Z2). Assuming a moisture content of 90%,

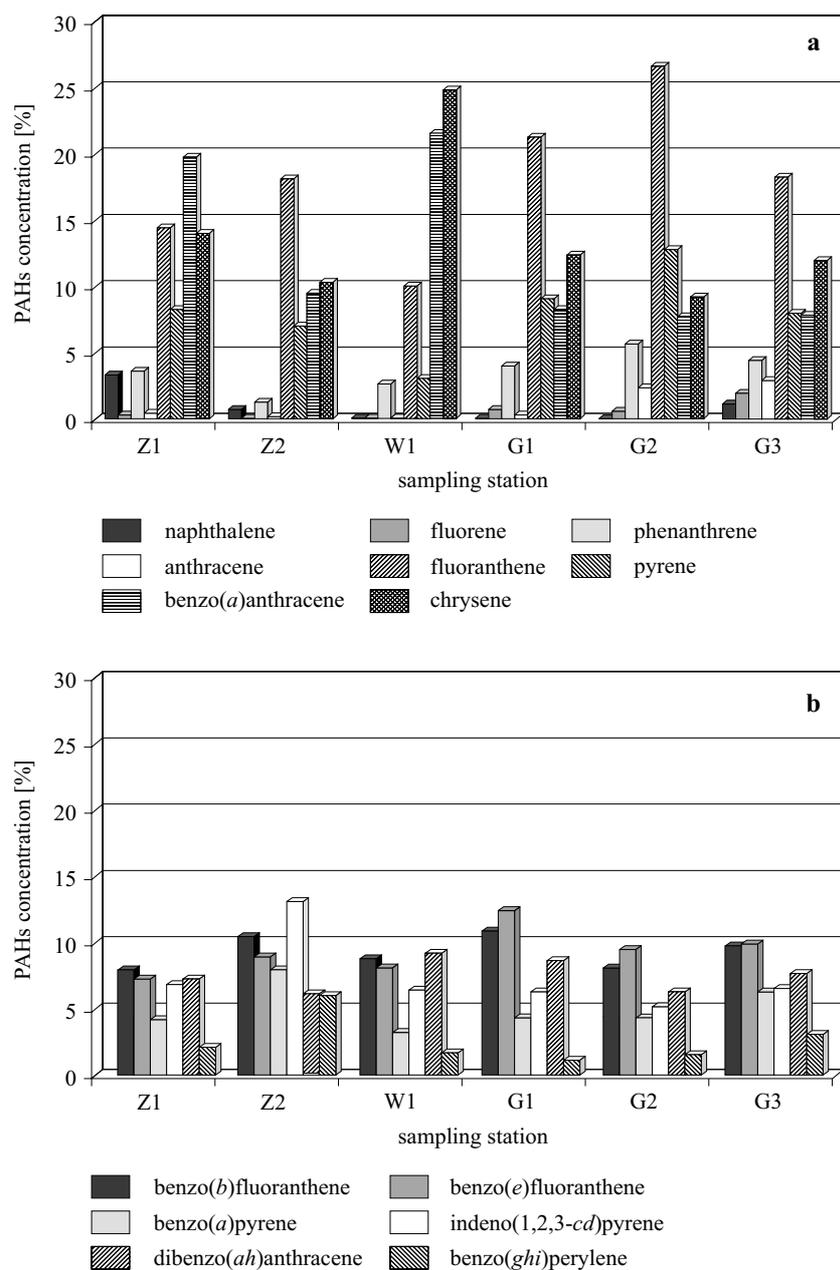


Fig. 2. Concentrations [%] of polycyclic aromatic hydrocarbons (Σ PAHs = 100%) in the soft tissue of mussels *Mytilus trossulus* from different areas of the southern Baltic Sea (a, b)

this is approximately equivalent to $124.7 \text{ ng g}^{-1} \text{ d.w.}$ for Z1 and $297.1 \text{ ng g}^{-1} \text{ d.w.}$ for Z2 – values well within the range reported by Baumard et al. (1999).

The PAH concentrations in mussels from the southern Baltic are relatively low in comparison to the mean concentrations of PAHs in the surface sediments of the southern Baltic (1830 ng g⁻¹ d.w.) obtained by Kowalewska & Konat (1997). This may indicate the effective removal of PAHs from the water to the sediments, protecting filter-feeding benthic organisms from even greater loads of PAHs.

The total concentrations of PCBs (Σ PCBs) in the soft tissue of *M. trossulus* are shown in Table 1. Mussels from the Gulf of Gdańsk, especially those collected close to the shore (G2 and G3) contain the highest contents of PCBs (22.3 ng g⁻¹ w.w.) in comparison to mussels from the reference point (W1 = 1.9 ng g⁻¹ w.w.), and to mussels from other sampling stations (G1 = 4.9 ng g⁻¹ w.w., Z1 = 3.4 ng g⁻¹ w.w. and Z2 = 5.8 ng g⁻¹ w.w.). As is the case with PAHs, atmospheric transport and deposition are important pathways for organochlorine contaminants, and atmospheric fluxes have been shown to be an important factor with regard to the occurrence of these organic contaminants in aquatic ecosystems both far away from and near source areas (Barrie et al. 1992). The relative contribution of atmospheric deposition to the total PCB load in the North Sea was calculated. It was found that more than 90% of the PCB input was due to atmospheric deposition (HELCOM 1997). The obtained pattern of PCB distribution indicates that local pollution sources are responsible for the contaminant pattern in the southern Baltic Sea. In the Gulf of Gdańsk, the input from the Vistula and the large industries of Gdańsk and Gdynia could be the most important sources of PCB pollution. Major industrial activities in this area include shipbuilding, chemicals (fertilisers, oil refinery, paints), food processing and fisheries. The high PCB contamination within the Gulf of Gdańsk could be caused by shipping, shipyards, and by discharges from sewage treatment plants. Falandysz (1999) obtained a similar pattern of PCB content in fish from the southern Baltic, especially from the Gulf of Gdańsk.

The percentage distribution of PCBs (Σ PCBs = 100%) in the soft tissue of mussels, *M. trossulus*, from different regions of the southern Baltic is presented in Fig. 3. It appears that Baltic mussels largely contain the more highly chlorinated congeners (penta- and hexachlorobiphenyls). The selective accumulation of penta- and hexachlorinated isomers was also observed in mussels *M. galloprovincialis* collected from the Catalan Mediterranean coast (Porte & Albaigès 1993). Among the PCB congeners in Baltic mussels, hexachlorobiphenyls (PCB-153 and 138) were found at the highest level in all the tested mussels and represented over 50% of the total PCB content (the respective mean contributions of PCB-153 and 138 were

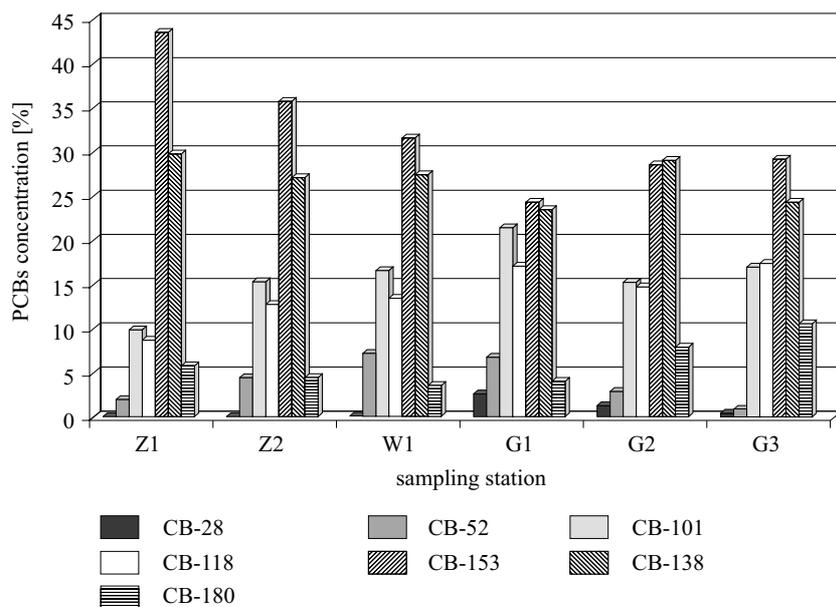


Fig. 3. Concentrations [%] of polychlorinated biphenyls (Σ PCBs = 100%) in the soft tissue of mussels *Mytilus trossulus* from different areas of the southern Baltic Sea

28% and 23%), while trichlorobiphenyl PCB-28 was found only in mussels from the Gulf of Gdańsk, and represented less than 3% of the total PCBs.

Many authors have suggested that direct equilibrium partitioning is responsible for the accumulation of lipophilic organic compounds like PCBs in gill-breathing organisms (Borislavskyj et al. 1987, Tanabe et al. 1987). The uptake and release of these pollutants is a function of their exchange through the gills and across the body surface to balance their levels between the ambient water and body lipids. The body load of lipophilic compounds in these organisms depends primarily on the level of contamination in the water and on the physico-chemical properties of individual compounds. Fewer lipophilic PCBs, such as those with less than seven chlorine atoms, which occur predominantly in water, are readily accumulated by *Mytilus* spp. (Metcalf & Charlton 1990). The much higher concentrations of penta- and hexa-chlorinated PCBs obtained in mussels collected near the coast of the Gulf of Gdańsk (G2 and G3) in comparison to mussels from other sampling sites could have been due to the relatively high concentrations of these isomers in the environment close to the sources. This again indicates that local pollution sources are responsible for the presence of these contaminants in the Gulf of Gdańsk. Tanabe et al. (1987) observed that low-chlorinated PCBs were both taken up and

excreted by the green-lipped mussel *Perna viridis* more rapidly than the more lipophilic, highly chlorinated PCBs. The selective accumulation of penta- and hexachlorinated PCBs in mussels could be explained by their high persistence, i.e. by their low rate of decomposition.

Expressed as the concentrations of its metabolite *pp'*DDE, DDT concentrations in the soft tissue of Baltic mussels following saponification of the homogenates (Porte & Albaigès 1993, Strandberg et al. 1998) are presented in Table 1. Among the different organochlorine compounds, *pp'*dichlorodiphenylethylene (*pp'*DDE) is the most abundant. It is a degradation product of *pp'*dichlorodiphenyltrichloroethane (*pp'*DDT), which can be formed either by UV-irradiation in the atmosphere or by the metabolism of organisms (Sánchez et al. 1993). The metabolism of DDT in organisms is generally accomplished through dehydrodechlorination to DDE (Schmitt et al. 1990). The content of *pp'*DDE reported in the soft tissue of Baltic mussels is rather low (1.2 – 11.2 ng g⁻¹ w.w.). The highest concentrations of *pp'*DDE were found in mussels from the Gulf of Gdańsk, especially in the molluscs collected from the sampling point G2, located near the shipyard and port in Gdynia (11.2 ng g⁻¹ w.w.). Like the concentrations of PAHs and PCBs, those of *pp'*DDE in the soft tissue of mussels *M. trossulus* confirm the influence of local pollution sources on the distribution of *pp'*DDE in the southern Baltic. It is known that the main pathway of global distribution of organochlorine pesticides is through atmospheric transport. Their high solubility in water promotes enrichment in the aquatic environment through atmospheric washout by rain (Sánchez et al. 1993). The fluvial transport of organochlorine pesticides from the terrestrial to the marine environment is also important. The elevated concentrations of these pollutants in mussels from Gulf of Gdańsk seem to have been a consequence of the high input of the contaminants with the Vistula river run-off, because of the heavy use of DDT in Poland in the period from the 1950s to the 1970s (Falandysz et al. 1994). Brown et al. (1986) suggest that the high level of DDE residues in abiotic and biotic matter are due to micro-organisms. DDT can be metabolised by micro-organisms to DDE under aerobic conditions. It seems that the high concentration of DDE in mussels from the Gulf of Gdańsk could be due to the oxygen content in the ambient water, which promotes the conversion of DDT to DDE.

The PCB/*pp'*DDE ratio is shown in Fig. 4a. In comparison to the reference point (W1 = 1.81) it is double the value for mussels collected from the Pomeranian Bay near the port of Świnoujście and the Odra mouth (Z1 = 3.28), and more than twice as high for organisms from the Gulf of Gdańsk collected near the port of Gdańsk and the Vistula mouth (G3 = 5.32). This indicates the predominance of industrial over agricultural

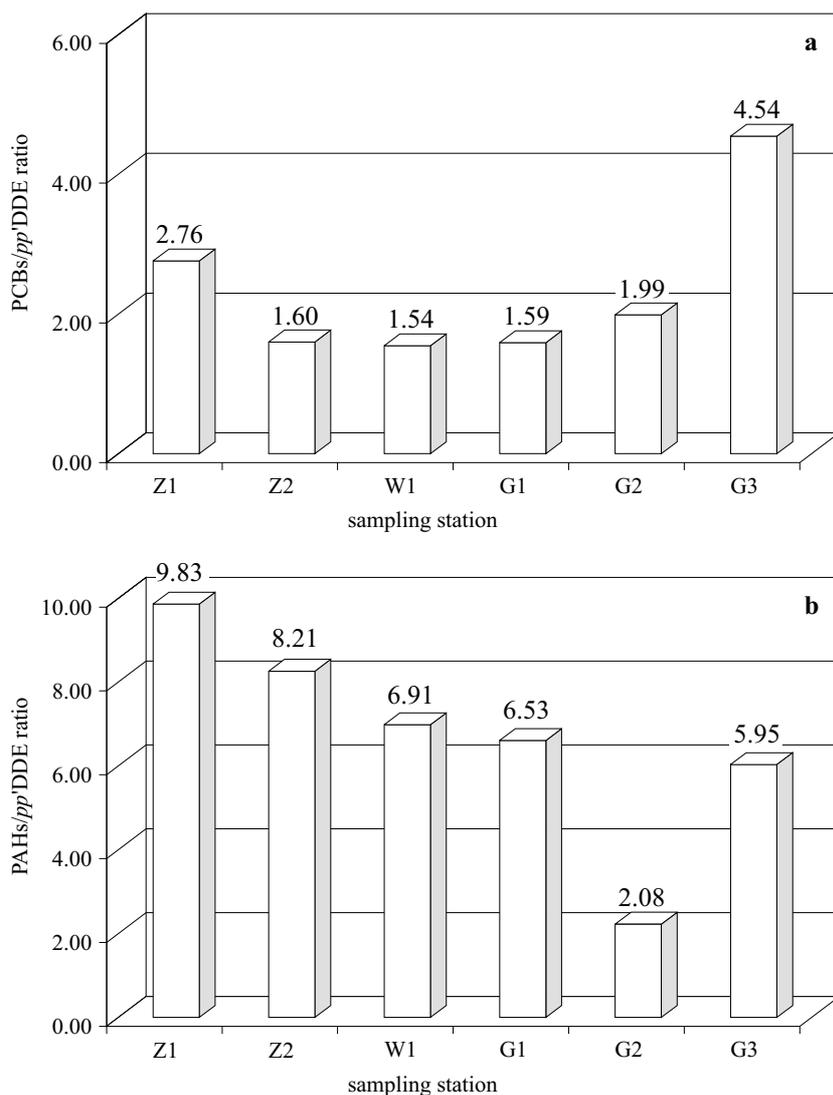


Fig. 4. PCBs/pp'DDE (a) and PAHs/pp'DDE (b) ratios in the soft tissue of mussels *Mytilus trossulus* from different areas of the southern Baltic Sea

activities as sources of contaminants in the Pomeranian Bay and the Gulf of Gdańsk.

The PAH/pp'DDE ratio presented in Fig. 4b also reflects the predominance of industrial over agricultural activities along the Polish coast. The low value (2.08) of this ratio for mussels collected from sampling station G2 (near the shore of the Gulf of Gdańsk) confirms the higher input of organochlorine pesticides to this area from the Vistula.

4. Conclusions

The content of persistent organic pollutants in the soft tissue of Baltic mussels, *M. trossulus*, followed the order PAHs > PCBs > DDT.

Elevated PAH, PCB and DDT concentrations in soft tissues, as compared to the reference point, were recorded in the mussels collected from areas close to river mouths and municipal sources, like the Gulf of Gdańsk and the Pomeranian Bay.

Influenced as it is by the River Vistula and the Gdańsk, Gdynia and Sopot municipal area, the Gulf of Gdańsk is especially threatened by the occurrence of persistent organic pollutants. This is because of the limited water exchange with the open Baltic.

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