7

# Persistent Organic Pollutants in Plankton from the Gulf of Gdańsk

Ksenia Pazdro, Maria Łotocka Institute of Oceanology, Polish Academy of Sciences, Sopot

#### **1. Introduction**

Persistent organic pollutants (POPs) are widespread, ubiquitous compounds, which can be found in all types of environmental compartments [7, 15]. They include a wide range of compounds like dioxins, polychlorinated biphenvls (PCBs), and several organochlorine pesticides [32]. PCBs and organochlorine pesticides like lindane, HCB, DDT and its derivatives have been produced and used for several decades. Despite a ban in many countries, on their use, these compounds persist in various abiotic and biotic compartments resulting in bioaccumulation and biomagnification in the food chain [20]. Polycyclic aromatic hydrocarbons are a group of common environmental contaminants, originating from anthropogenic sources as well as from natural processes [22]. They exhibit properties similar to those of persistent chlorooorganic pollutants. Occurence of PAHs in the environment is of great interest due to their carcinogenic properties [33, 34]. A large variety of POPs are transported into estuarine environments through different input pathways, such as riverine and municipal sewage discharges, run-off from nonpoint sources and atmospheric deposition [10, 16]. It is well established that organic contaminants present in water, air and sediments migrate into organisms such as invertebrates, fish, plants, mammals and birds and may then undergo subsequent transport from organism to organism in food [28]. Thus, POPs are the group of contaminants remaining a cause for concern.

Gulf of Gdańsk, due to the geographical layout and as a catchment area of an industrialized region, is obviously exposed to large and changing loads of environmental pollutants. At the same time this area is characterized by high biomass of organisms from different trophic levels. Existing papers on POPs concentrations in the food web in the Baltic Sea deal mainly with animal organisms from higher trophic levels (fish, mollucs and birds) [12, 14, 25]. Relatively few data on the POPs levels in plankton organisms are available [18, 27]. Except the paper of Falandysz et al. [13], no published data on organochlorine contaminants and PAHs concentrations in plankton from the Gulf of Gdańsk ecosystem are available. However, phytoplankton plays a central role in the biogeochemical cycles of POPs in aquatic environments [8]. Several potential pathways exist for the introduction of POPs into food webs, but since phytoplankton is the first step of the food web, plankton uptake is thought to be a key process in the transfer of pollutants from the water to fish. Second, plankton uptake of pollutants influences the transport, occurrence and distribution of POPs in aquatic environments. POPs associated with phytoplankton may be transfer to successively higher trophic levels through interactions between predators and their preys [26].

#### 2. Aim of the study

The aim of this work was to establish the level of pollution by persistent organic contaminants in plankton communities from the Gulf of Gdańsk. Concentrations of 12 polycyclic aromatic hydrocarbons (PAHs), 7 polychlorinated biphenyls (PCBs) and selected organochlorine pesticides (HCB, lindane) were determined in plankton collected from 4 stations. The sampling stations were chosen along the expected pollution gradient. The POPs distribution has been correlated with lipid content in organisms.

#### 3. Materials and methods

#### 3.1. Samples collection

Samples of plankton were collected using a plankton net (60  $\mu$ m mesh) during r/v "Oceania" cruises in 2004 and 2005. The distribution of sampling stations is shown in Fig.1, while characteristics of sampling stations and collected material are given in Table 1. The plankton samples were retrieved, frozen (-18°C) in precleaned glass jars and transported to the laboratory. The subsamples were preserved for plankton species identification.

a:	Date of	Coord	linates	Depth		Lipid
Station	sampling	Latitude	Longitude	(m)	Predominant species	(% d.w.)
UW 1	Aug. 2004	54°22,3' N	19°00,6' E	16	Rotatoria (Keratella cruciformis) Cladocera (Bosmina coregoni maritima)	1.36
UW 2	May 2005	54°22,3' N	19°00,6' E	17	Rotatoria (Synchaeta sp.) Cladocera (Bosmina coregoni maritima) Copepoda (nauplius, copepodit)	5.59
UW 3	May 2005	54°22,3' N	19°00,6' E	17	Bacillariophyceae (Cyclotella me- neghiniana) Dinophyceae (Perid- iniella catenata)	5.15
MECH 1	Aug. 2004	54°39,6' N	18°32,3' E	11	Rotatoria (Keratella cruciformis; Keratella quadrata)	3.23
MECH 2	May 2005	54°39,6' N	18°32,0' E	11	Rotatoria ( <i>Synchaeta</i> sp.) Copepoda (nauplius)	5.42
OKS 1	Aug. 2004	54°33,5' N	18°36,2' E	20	Cyanobacteria (Aphanizomenon flos- aque; Nodularia spumigena)	4.54
OKS 2	Aug. 2004	54°33,5' N	18°36,2' E	20	Rotatoria (Keratella cruciformis; Keratella quadrata)	10.61
OKS 3	May 2005	54°33,5' N	18°36,2' E	20	Rotatoria (Synchaeta sp.)	9.25
GG	Aug. 2004	54°39,1' N	19°10,2' E	89	Copepoda ( <i>Acartia</i> sp., nauplius, copepodit)	6.96

**Table 1.** Location of sampling stations and material characteristics**Tabela 1.** Lokalizacja punktów pobierania próbek i charakterystyka próbek planktonu



**Fig. 1.** Location of sampling stations **Rys. 1.** Lokalizacja punktów pobierania próbek

#### 3.2. Sample preparation

The analyses were based on procedures described by Deshpande [9], Mazeas and Budziński [19], Behar 1989. In brief, a frozen sample was freezedried in the laboratory and then 10-15 g of dry material was subjected to extraction with methylene chloride (3 x 30 cm<sup>3</sup>) in an ultrasonic bath. The internal standards were added to all samples in order to establish the recoveries. After filtration, the solvent was partly evaporated under vacuum. Further concentration was carried out under gentle nitrogen stream. The extracts were concentrated and subjected to clean-up procedures. Silica/alumina columns and solvent mixtures increasing in polarity were used (F1: 100% hexane, extracting HCB and PCBs, F2: 90% hexane: 10% methylene chloride extracting PAHs and F3: 75% hexane:25% methylene chloride, extracting HCHs). Elemental sulphur and sulphur containing compounds were removed from fraction 1 using powdered elemental cooper. The fractions were evaporated and prior to final analysis, dissolved in isooctane.

#### 3.3. Quantitative and qualitative determination

Extracts were analysed by gas capillary chromatography. A Shimadzu 17A GC equipped with a split/splitless injector at a 280°C and DB 5 column (60m x 0,25 mm inner diameter x 0,25  $\mu$ m film thickness) were used. FID de-

tector, helium as a carrier gas and following oven temperature were used for PAH analyses: 50°C held for 1 min, followed by 15°C/min increase to 150°C, followed by 30°C/min increase to 310°C, hold for 10 min. PCBs and organochlorine hydrocarbons (HCB and lindane) were analyzed applying ECD detector, helium as carrier gas and the following oven temperature program: 100°C - 1 min; 60C/min do 140°C; 10°C/min do 310°C, hold for 20 min. Identification and quantification were performed by means of internal and external standards. Recoveries in the range of 70-99% and relative standard deviation in the range of 10÷20% characterized the method in respect to individual compounds. The limit of detection of organochlorines using the method was 10 - 60 pg g<sup>-1</sup> dry weight, and of PAHs – 5÷50 ng g<sup>-1</sup> dry weight. The laboratory blanks were analysed in parallel with the samples. Procedural blanks were at least 5 times below measured concentrations.

#### 3.4. Supporting sample characterization

Lipid content in each of analysed samples was determined gravimetrically. Major groups of phyto- and zoo-plankton were determined by using the inverted microscope (Axiovert M40) and Utermöhl's sedimentation technique [11].

### 3. Results and discussion

The PAHs concentrations in the analyzed plankton samples are presented in Table 2. The results are expressed in ng  $g^{-1}$  wet weight. The concentrations of individual PAHs ranged from 0.19 to 5.98 ng  $g^{-1}$  w.w. The highest contents of PAHs were observed, irrespectively of season and identified plankton species, at the station located in the neighbourhood of Navy harbour in Gdynia and shipping channel. These findings are in good agreement with data obtained for sediment, identifying this area as the most polluted one inside the Gulf of Gdańsk [23]. Relatively high concentrations were found in spring 2005 at station UW, situated in the coastal area at the Vistula mouth.

The group of PCBs consists of 209 different possible congeners. Since different PCB congeners have been determined in a number of studies, often data are not comparable. In recent papers standard monitoring mixture of 7 congeners have been used, e.g. PCBs nos. 28, 52, 101, 118, 138, 153 and 180 were selected as the most abundant in the environment and covering a wide degree of biphenyl molecule chlorination [17]. Individual concentrations and the sum of concentrations levels of 7 congeners in the studied sediments are presented in Table 3. The concentrations of individual chlorobiphenyls ranged between 0.033 to 0.597 ng g<sup>-1</sup> w.w. The lowest values were observed at the station situated in the open sea, at the Gdańsk Deep. Highest concentrations were detected in the plankton samples collected at the Oksywie station. High values were also

found in plankton collected at the station situated close to the Vistula river mouth (UW). The obtained data are in good agreement with results obtained by Falandysz et al. [13]. However the detailed comparison of individual compounds concentration obtained in this study with published data is impeded, due to differences in sampling techniques, extractive and analytical procedures, and finally - different compounds sets normalisation, reported in the literature. As a consequence, different proportions of individual compound could be determined and reported.

 Table 2. The concentrations of polycyclic aromatic hydrocarbons in the plankton samples (ng g<sup>-1</sup> w.w.)

	Sampling station									
Compound	UW 1	UW 2	UW 3	Mech 1	Mech 2	OKS 1	OKS 2	OKS 3	GG	
Fluorene (F)	1.66	2.08	1.11	_*	0.62	4.55	1.24	3.05	0.36	
Phenathrene (P)	4.32	3.93	3.75	_*	3.05	5.91	1.66	6.85	1.59	
Anthracene (A)	0.19	0.94	0.26	_*	0.15	0.63	0.10	0.52	0.09	
Fluoranthene (Fl)	2.34	5.98	1.31	_*	1.99	4.52	4.79	4.39	1.69	
Pyrene (Py)	0.62	2.41	0.96	_*	1.10	1.06	4.53	1.89	0.60	
Benzo(a)anthracene (BaA)	0.37	1.48	0.41	_*	0.23	1.90	0.94	2.16	0.40	
Chrysene (Ch)	1.16	1.84	0.96	_*	0.91	2.18	2.06	0.69	1.17	
Benzo(k)fluoranthene (BkFl)	0.41	1.40	0.75	_*	1.26	2.22	1.68	1.42	1.90	
Benzo(a)pyrene (BaPy)	1.42	1.10	0.99	_*	1.13	1.05	5.24	1.95	1.97	
Dibenzo(ah)anthracene (DBA)	0.15	1.18	0.82	_*	2.06	0.99	1.42	0.66	1.50	
Benzo(ghi)perylene (Bper)	0.09	0.92	0.19	_*	0.00	1.44	1.09	0.12	1.87	
Indeno(1.2.3 – cd)pyrene IPy	0.17	2.26	1.46	_*	2.06	0.15	0.21	0.61	3.24	
ΣPAHs	12.92	25.52	12.97	_*	14.56	26.60	24.96	24.32	16.34	

**Tabela 2.** Stężenia wielopierścieniowych weglowodorów aromatycznych w próbkach planktonu (ng g $^{-1}$ w.w.)

\* not determined

**Table 3.** The concentrations of organochlorine contaminants in the plankton<br/>samples (ng  $g^{-1}$  w.w.)

Tabela 3. Stężenia	związków	chloroorganie	cznych w	próbkach	planktonu	(ng g <sup>-1</sup>	w.w)
--------------------	----------	---------------	----------	----------	-----------	---------------------	------

	Sampling station								
Compound	UW	UW	UW	Mech	Mec	OKS	OKS	OKS	GG
	1	2	3	1	h 2	1	2	3	00
2.4.4'-									
trichlorobiphenyl	0.393	0.076	0.121	0.172	0.064	0.074	0.115	0.597	0.033
(CB 28)									
2.2'.5.5'-									
tetrachlorobiphenyl	0.059	0.040	0.047	0.112	_*	0.156	0.274	0.116	0.018
(CB 52)									
2.2'.4.5.5'-									
pentachlorobiphenyl	0.039	0.023	0.057	0.104	0.027	0.139	0.329	0.125	0.020
(CB 101)									
2.3'.4.4'.5-									
pentachlorobiphenyl	_*	0.004	0.007	0.026	0.017	0.061	0.152	0.024	_*
(CB 118)									
2.2'.4.4'.5.5'-									
hexachlorobiphenyl	0.030	0.050	0.055	0.086	0.031	0.183	0.355	0.079	0.034
(CB 153)									
2.2'.3.4.4'.5'-									
hexachlorobiphenyl	0.018	0.000	0.048	0.082	0.031	0.135	0.309	0.079	0.044
(CB 138)									
2.2'.3.4.4'.5.5'-							0.0.10		
heptachlorobiphenyl	_*	_*	0.020	0.001	0.000	0.029	0.069	0.018	_*
(CB 180)									
$\Sigma PCB$	0.538	0.193	0.355	0.583	0.170	0.777	1.605	1.038	0.149
(7 congeners)									
lindane (γ- HCH)	0.015	0.018	0.014	_**	0,121	_**	_**	0.117	_**
HCB	0.038	_*	0.489	0.053	0.016	0.070	0.031	0.041	0.007

\* – below the detection limit,

\*\* – not determined

The presence of HCB and lindane was detected in the analyzed samples. Concentrations of heksachlorobenzene were found to be within a range between 0.007 ng g<sup>-1</sup> w.w in the open sea to 0.489 ng g<sup>-1</sup> w.w. near Oksywie. Concentrations of  $\gamma$ -HCH (lindane) were low as compared to other POPs. They ranged from 0.015 ng g<sup>-1</sup> w.w. in plankton organisms living in open sea waters (GG) to about 0.121 ng g<sup>-1</sup> w.w. in plankton collected near Mechelinki (Mech).

The percentage distribution of individual PAHs in the analysed sediment samples is presented in Fig. 2. It follows from the results that the low molecular PAHs (tri- and tetra-aromatics) prevailed over high molecular ones at all stations in the inner part of the Gulf of Gdańsk (Table 4). The opposite trend was noted at deep water station (GG). Among the low molecular compounds triaromatic compound – phenanthrene was dominant in all samples (up to 32% at the UW station). The other low molecular PAHs were in the range from 4% (benzo(a)anthracene) to 19% (fluoranthene) of the total content. Among the high molecular weight PAHs, hexa-aromatics benzo(ghi)perylene (Bper) and indeno(1,2,3,-c,d)perylene (IP) were the dominant ones in the samples from the Gdańsk Deep (GG). The other plankton samples were characterized by pentaaromatics dominance.

**Table 4.** Selected ratios of POPs determined in the plankton samples from the Gulf of Gdańsk

	Sampling station								
Ratio	UW	UW	UW	Mech	Mech	OKS	OKS	OKS	GG
	1	2	3	1	2	1	2	3	00
low molecularPAHs/	82.05	73 12	67 56	*	55 28	78.00	61 36	80.43	42 11
total PAHs [%]	62.93	13.12	07.50		55.28	78.00	01.50	80.43	42.11
high molecular-									
PAHs/ total PAHs	17.05	26.88	32.44	_*	44.72	22.00	38.64	19.57	57.89
[%]									
Phenanthrene/	22 30	1 18	14 66	*	20.32	0.38	16 58	13 17	17 18
Anthracene	22.30	4.10	14.00		20.52	9.50	10.58	15.17	17.10
Fluoranthene/Pyrene	2.54	2.48	1.37	_*	1.80	4.27	1.06	2.32	2.83
Low chlorinated									
PCBs(3+4 Cl atoms/	84.02	49.45	47.16	48.66	37.57	29.68	24.29	68.71	34.23
total PCBs [%])									
Higher chlorinated									
PCBs(5+6+7Cl	15.98	50.55	52.84	51.34	62.43	70.32	75.71	31.29	65.77
atoms/ total PCBs [%]									
Total PAH/	25	167	37	*	86	34	16	23	110
Total PCBs content	25	107	57		80	54	10	23	110
*									

 Tabela 4. Wybrane stosunki związków z grupy TZO wyznaczone w próbkach planktonu z Zatoki Gdańskiej

\* - not determined



- **Fig. 2A.** Polycyclic aromatic hydrocarbons content [% of Σ PAHs] in the plankton samples from the Gulf of Gdańsk; low molecular PAHs fraction; F fluorene, P phenathrene, A–anthracene, Fl fluoranthene, Py pyrene, BaA anthracene, Ch–chrysene
- **Rys. 2A.** Zawartość wielopierścieniowych węglowodorów aromatycznych w próbkach planktonu z Zatoki Gdańskiej [% Σ WWA]; frakcja WWA niskocząsteczkowych; F fluoren, P fenantren, A –antracen, Fl fluoranten, Py piren, BAA antracen, Ch chryzen



- Fig. 2B. Polycyclic aromatic hydrocarbons content [%of Σ PAHs] in the plankton samples from the Gulf of Gdańsk; high molecular PAHs fraction; BkF benzo(k)fluoranthene, BaPy benzo(a)pyrene, DBA dibenzo(ah)anthracene, Bper benzo(ghi)perylene, Ipy indeno(1,2,3-c,d)pyrene
- Rys. 2B. Zawartość wielopierścieniowych węglowodorów aromatycznych w próbkach planktonu z Zatoki Gdańskiej [% Σ WWA]; frakcja WWA wysokocząsteczkowych; BkF – benzo(k)fluoranten, BaPy – benzo(a)piren, DBA – dibenzo(ah)antracen, Bper – benzo(ghi)perylen, Ipy – indeno(1,2,3-c,d)piren.



**Fig. 3.** PCBs content [% of Σ PCBs] in the plankton samples from the Gulf of Gdańsk **Rys. 3.** Zawartość polichlorowanych bifenyli [% Σ PCBs] w próbkach planktonu z Zatoki Gdańskiej

The differences in PAHs pattern could be related to different sources of the particular compounds and their fate in the environment, resulting from their physico-chemical properties (Kowalewska and Konat, 1997). The occurrence of PAHs in the environment is mainly due to combustion and pyrolysis of fossil fuels and to release into the environment of petroleum products (Law and Andrulewicz, 1983). PAH production resulting from natural processes is generally very low compared to PAHs originating from anthropogenic sources (Readman et al., 1982). Some indicators based on molecular ratios of specific hydrocarbons were developed to distinguish between PAHs originating from various origins [3]. Phenanthrene is the most thermodynamically stable triaromatic isomer. As shown by thermodynamical calculations, the ratio of phenanthrene concentration to anthracene concentration (P/A) is temperature dependent [2]. Thus, high temperature processes such as combustion of organic matter generate PAHs characterized by a low P/A ratio (<10), whereas the slow maturation of organic matter during catagenesis leads to much higher P/A values (>25). The same considerations can be applied to the isomeric ratio of 4 rings compounds- fluoranthene to pyrene concentrations (Fluo/Py). Values greater than 1 are characteristic of pyrolitic origin [29], whereas values lower than 1 are related to petroleum hydrocarbons. P/A and FL/Py ratios, calculated for the analysed plankton samples (Table 4) indicate that situated near the shipping channel, the contaminants originated rather from pyrolitic sources. They can be derived mainly from industry and fuel combustion [25].

The percentage distribution of individual PCBs in the sediment from the Gulf of Gdańsk is shown in Fig. 3. Among the detected PCB congeners low chlorinated CB 28 was the dominant one in almost all investigated plankton samples. Input of the most hydrophobic congener (CB 180) seems to be low. Most reasonably, it seems that better solubility of lower chlorinated in water are responsible for the observed PCB distribution [4, 26].

The distributions of organic contaminants in biota tissue are related to their physico-chemical properties (mainly hydrophobicity) and therefore to the lipid content in organism [21, 22]. However, in the course of this study no statistically significant correlation was observed between analyzed POPs contents in plankton samples and the lipid content. Similar findings were reported by Quental et al. [26] studying the distribution of PCBs and DDTs in seston and plankton along the Portuguese coast and Skoglund and Swackhamer 1999, discussing bioaccumulation factors normalisation.

The interspecies differences have been also investigated. Samples composed predominantly of zooplankton (Rotatoria, nauplial stages of Copepoda and/or Cladocera). Only two samples composed predominantly of phytoplankton species (UW 3 collected in May 2005 and OKS 1 collected in August 2004). No clear trend in distribution of POPs was observed among the species. It could be related to phenomena that in coastal waters the composition of contaminants in plankton biomass may vary with several factors, namely surface/volume ratio of cells, physiological and biochemical status of plankton, composition of suspended matter and diet [1, 4, 21].

Uptake of hydrophobic organic contaminants in algal and small zooplankton organisms occurs by passive diffusion [30, 31]. Thus, the correlation between PAH, PCB and organochlorine pesticides content in plankton and water concentrations was investigated. Generally, the analyzed data set yielded a positive correlation between POPs levels in plankton and those dissolved in water (r>0.65). It seems that the differences in individual compounds distribution in plankton are driven rather by water concentrations than the interspecies differences. These findings could be confirmed by comparison of two data sets from heavily contaminated station Oksywie. The individual contaminants percentage distribution seems to be uniform both for phytoplankton (OKS 1) and zooplankton (OKS 2) samples. Concentration in both communities correlates with water concentration (r = 0.78).

### 5. Conclusions

The content of persistent organic pollutants in the analyzed plankton samples collected from the Gulf of Gdańsk followed the order PAHs>PCBs>HCB ≈lindane.

Dominance of lower chlorinated polychlorinated biphenyls and lower aromatic PAH was stated in plankton from the Gulf of Gdańsk.

Accordingly to the obtained results the most polluted station in the Gulf of Gdansk located near Navy harbour in Gdynia and in the vicinity of the shipping channel could be distinguish from the other locations. These findings coincide well with the results for sediment samples collected at the same stations as plankton samples.

No statistically significant correlation between POPs concentrations and lipid content in plankton organisms was observed.

The observed differences in POPs contents and pattern could be attributed rather to levels of contaminants in surrounding water than to inter-species and inter-seasonal differences. It makes natural plankton communities useful tool for monitoring contamination levels in ecosystem.

## References

- 1. Axelman J., Broman D., Naf C.: Field measurements of PCB partitioning between water and planktonic organisms: influence of growth, particle size and solute-solvent interactions. Environ.Sci.Technol., 1997. 665÷669.
- Baumard P., Budziński H., P.Garrigues: Polycyclic Aromatic Hydrocarbons in Sediments and Mussels of the Western Mediterranean Sea. Environ. Toxicol.Chemistry, 17(5), 1998. 765÷776.

- 3. Baumard P., Budziński H., Garrigues P., Dizer H., Hansen P.D.: Polycyclic Aromatic Hydrocarbons in Recent Sediments and Mussels (Mytilus edulis) from Western Baltic Sea: Occurrence, Bioavailability and Seasonal variations. Mar. Environ.Res., 47, 1999. 17:47.
- 4. Borga K., Fisk A., Hargrave B., Hoekstra P., Swackhamer D., Muir D.: *Bioaccumulation factor for PCBs revisited*. Environ.Sci.Technol., 39, 2005. 4523÷4532.
- 5. Behar F., Leblond C., Saint-Paul C.: Analyse quantitative des effluents de pyrolyse en milieu ouvert et ferme. Revue de l'Institut Français du Petrole, 44, 1989. 387÷411.
- 6. Borga K., Gabrielsen G.W., Skaare J.U., Differences in contamination load between pelagic and sympagic inverterbrates in the Arctic marginal ice zone: influence of habit, diet and geography, Mar.Ecol.Prog.ser., 235. 157÷169.
- 7. Dachs J., Bayona J.M., Albaiges J.: Spatial distribution, vertical profiles and budget of organochlorine compounds in Western Mediterranean seawater. Mar.Chem., 57, 1997. 313÷324.
- 8. Del Vento S., Dachs J.: Prediction of uptake dynamics of persistent organic pollutants by bacteria and phytoplankton. Environ. Toxicol. Chem., 21(10), 2002. 2099÷2107.
- 9. Deshpande A., Draxler A., Zdanowicz V., Schrock M., Paulsen A.J.: Contaminant levels in the muscle of four species of fish important to the recreational fishery of the New York Bight Apex. Mar. Poll. Bull., 44, 2002. 162÷177.
- Doong R-A., Peng C., Sun Y., Liao P.: Composition and Distribution of Organochlorine Pesticide Residues in Surface Sediments from the WU-Shi River Estuary, Taiwan. Mar.Poll.Bull., 45, 2002. 246÷253.
- 11. Dybern B.I., Ackefors H., Elmgren R.: *Recommendations on methods for marine biological studies in the Baltic Sea*. Baltic Mar.Biol.Publ., 1, 1976. 11÷98.
- 12. Falandysz J.: Polichlorowane bifenyle (PCBs) w środowisku: chemia, analiza, toksyczność, stężenia i ocena ryzyka. Fundacja Rozwoju Uniwersytetu Gdańskiego. Gdańsk, 5-143, 1999. 173÷221.
- Falandysz J., Wyrzykowska B., Puzyn T., Strandberg B., Rappe C.: Pelagic multivariate analysis of the bioaccunulation of polychlorinated biphenyls (PCBs) in the food marine web from the southern part of Baltic Sea, Poland. J.Environ.Monit., 4, 2002. 929:941.
- 14. HELCOM: Environment of the Baltic Sea Area 1994-1998. Balt. Sea Environ. Proc. No 82B, 2002. 119÷140.
- 15. Iwata H., Tanabe S., Sakal N., Tatsukawa R.: Distribution for persistent organochlorine in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ.Sci.Technol., 27, 1993. 1080÷1098.
- Jeffrey T.F.A., Baker J.E.: Hydrophobic Organic Contaminants in Surficial Sediments of Baltimore Harbor: Inventories and Sources. Environ. Toxicol. Chem., 18, 1999. 838÷849.
- 17. Konat J., Kowalewska G.: Polychlorinated Biphenyls(PCBs) in Sediments of the Southern Baltic Sea. Sci.Tot.Environ., 280, 2001. 1÷15.
- 18. Konat-Stepowicz J, Kowalewska G.: *PCBs in phytoplankton in the Odra Estuary*. Oceanologia, 45(3), 2003. 491÷506.

- Mazeas L., Budziński H.: Improved accuracy of GC-MS quantification of aliphatic and aromatic hydrocarbons in marine sediments and petroleums validation on reference matrices and application to the Erika oil spill. Intern. J. Environ. Anal. Chem., 82, 2002. 157÷173.
- 20. Meador J.P., Adams N.G., Cassilas E., Bolton J.: Comparative Bioaccumulation of Chlorinated hydrocarbons from sediment by Two Infaunal Invertebrates. Arch.Environ.Toxicol., 33, 1999. 388:400.
- 21. Muir D., Savinova T., Savinov V., Alexeeva L., Potelov V., Svetochev V.: Bioaccumulation of PCBs and chlorinated pesticides in seals, fish and invertebrates from the White Sea, Russia. Sci. Total Environ., 306, 2003. 111÷131.
- 22. **Neff J.M.:** *Bioaccumulation in marine organisms.* Effect of contaminants from oil well produces water, Elsevier, Amsterdam, 37-53, 2004. 241÷314.
- 23. **Pazdro K.:** *Persistent organic pollutants in the Gulf of Gdańsk.* Ann. Set The Environ.Prot, 6, 2004. 63÷76.
- 24. Peters L.D., Porte C., Livingstone D.R.: Variation of antioxidant enzyme activities of sprat (sprattus sprattus) larvae and organic contaminant levels in mixed zoop-lankton from the southern North Sea. Mar.Poll.Bull., 42, 2001. 1087÷1091.
- 25. Potrykus J., Albalat A., Pempkowiak J., Porte C.: Content and pattern of organic pollutants (PAHs, PCBs and DDT) in blue mussels (Mytilus trossulus) from the southern Baltic Sea. Oceanologia, 45(2), 2003. 337÷355.
- 26. Quental T., Ferreira A., Vale C.: The distribution of PCBs and DDTs in seston and plankton along the Portuguese coast. Acta Oecologica, 24, 2003. 33÷339.
- Schulz-Bull D.E., Petrick G., Kannan N., Duinker J.C.: Distribution of individual chlorobiphenyls (PCB) in solution ans suspension in the Baltic Sea. Mar.Chem., 48, 1995. 245÷270.
- 28. Sharpe S., MacKay D.: A framework for evaluating bioaccumulation in food webs. Environ.Sci.Technol., 34, 2000. 2373÷2379.
- Sicre M.A., Marty J., Saliot A.: Aliphatic and Aromatic Hydrocarbons in Different Sized Aerosols over the Mediterranean Sea: Occurence and Origin. Atmos.Environ. 21, 1987. 2247÷2259.
- 30. Skoglund R., Stange K., Swackhamer D.: A kinetics model for predicting the accumulation of PCBs in phytoplankton. Environ.Sci.Technol., 30, 1996. 2113÷2121.
- 31. Swackhamer D.L., Skoglund R.S.: *Bioaccumulation of PCBs by alga: kinetics versus equilibrium.* Environ, Toxiciol. Chem., 12, 1993. 831÷838.
- 32. UNEP (United Nations Environment Program): Final act of the conference of plenipotentiares on the Stockholm Convention on persistent organic pollutants. UNEP, Geneva 2001. 44 p.
- 33. Vethaak A., Jol J., Meijboom A., Eggens M., Rheinalt T., Wester P., Van de Zande, Bergman A., Dankers N., Ariese F., Baan R., Everts J., Opperhuizen A., Marquenie J.: Skin and liver diseases induced in flounder (Platichthys flesus) after long-term exposure to contaminated sediments in large-scale mesocosms. Environ. Health Perspect., 104, 1996. 1218÷1229.
- 34. White K.L.: An overview of immunotoxicology and carcinogenic polycyclic aromatic hydrocarbons. Environ. Carcinogen Res., 2, 1986. 163÷202.

## Trwałe zanieczyszczenia organiczne w planktonie Zatoki Gdańskiej

#### Streszczenie

Zanieczyszczenia antropogeniczne, w tym trwałe zanieczyszczenia organiczne (TZO) wnoszone są do środowiska morskiego z wodami rzek i ścieków oraz w wyniku procesów transportu atmosferycznego. W środowisku morskim podlegają procesom transportu i transformacji w biotopie i w biocenozie, zależnym od warunków panujących w danym ekosystemie oraz właściwości fizykochemicznych samych związków. Pomimo wielu badań, cykl biogeochemiczny związków z grupy TZO w strefach przybrzeżnych pozostaje rozpoznany w niewystarczającym stopniu. W szczególności określenie ekologicznych i ekotoksykologicznych zagrożeń, jakie niesie dla środowiska morskiego wprowadzanie doń hydrofobowych mikrozanieczyszczeń organicznych wymaga rekonstrukcji dróg ich migracji oraz rozpoznania zależności determinujących ich rozmieszczenie w środowisku. Jedną z właściwości związków pochodzenia antropogenicznego jest ich zdolność do kumulacji w tkankach organizmów żywych. Podstawowym zagadnieniem jest zatem określenie stopnia kumulacji badanych związków w poszczególnych ogniwach łańcucha troficznego, którego końcowymi elementami są ryby i człowiek. Organizmy planktonowe stanowią początkowe ogniwa łańcucha troficznego i odgrywają istotną rolę w przenoszeniu zanieczyszczeń pomiędzy składowymi abiotycznymi i biotycznymi ekosystemu.

Celem prezentowanej pracy było określenie stężeń związków z grupy wielopierścieniowych węglowodorów aromatycznych (WWA), polichlorowanych bifenyli (PCB) oraz wybranych pestycydów chloroorganicznych (lindan, heksachlorobenzen -HCB) w naturalnych zespołach planktonowych ekosystemu Zatoki Gdańskiej. Próbki planktonu pobierano przy użyciu siatki planktonowej o średnicy oczek 60 µm. W próbkach wykonano oznaczenia składu gatunkowego. Analizowane zanieczyszczenia izolowano z liofilizowanych próbek planktonu stosując ekstrakcję chlorkiem metylenu. Po zastosowaniu procedur oczyszczania ekstraktów, WWA oznaczano stosując kapilarną chromatografię gazową z detektorem płomieniowo-jonizacyjnym FID. Zanieczyszczenia chloroorganiczne oznaczano stosując detektor wychwytu elektronów ECD.

W wyniku przeprowadzonych analiz stwierdzono, że organizmy planktonowe są najbardziej zanieczyszczone związkami z grupy wielopierścieniowych węglowodorów aromatycznych (WWA > PCB > HCB  $\Box$   $\Box$ -HCH). Najwyższe stężenia analizowanych związków obserwowano w materiale pobieranym na stacji zlokalizowanej w pobliżu Portu Wojennego w Gdyni i toru wodnego. W wyniku przeprowadzonych badań nie stwierdzono istnienia korelacji pomiędzy zawartością trwałych zanieczyszczeń organicznych a zawartością lipidów w organizmach planktonowych. Analiza zbioru wyników nie wykazała zmienności międzygatunkowej i sezonowej. Stwierdzono natomiast istnienie statystycznie istotnej korelacji pomiędzy poziomem TZO w planktonie i TZO rozpuszczonych w wodzie w miejscu pobierania próbek. Wskazuje to na możliwość wykorzystania planktonu do monitorowania poziomu zanieczyszczeń organicznych w danym akwenie.