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Persistent Organic Pollutants in Sediments from the Gulf of Gdańsk

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1. Introduction

Persistent organic pollutants (POPs) are widespread, ubiquitous compounds, which can be found in all types of environmental compartments (Neff, 1979). They include a wide range of compounds like polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and several organochlorine pesticides (e.g DDT, lindane). These compounds vary in their potential to bioaccumulate and to produce the adverse effects in biota (Meador et al., 1999).

PAHs are a group of common environmental contaminants. They originate from anthropogenic sources as well as from natural processes (Neff, 1979). Occurrence of PAHs in the environment is of great concern due to their carcinogenic properties (Mastrangelo et al., 1996). PCBs and organochlorine pesticides (e.g. lindane, 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 environmental compartments and biota. These chemicals are suspected to cause a variety of adverse effects including compromised reproductive fitness and abnormal reproductive system development (Tyler et al. 1996). Thus, POPs are the group of contaminants remaining a cause for concern. A large variety of POPs are transported into estuarine environments through different input pathways, such as riverine and municipal sewage discharges, runoff from nonpoint sources and atmospheric deposition (Doong et al., 2002, Jeffrey and Baker, 1999). Coastal sediments in urban environments are known to be contaminated or even polluted by high concentrations of persistent organic pollutants (Wakeham et al, 1980; Baumard and Budziński, 1999; Pavoni et al., 1997).

Relatively a few data on sediment contamination in the Gulf of Gdańsk are available. These include PAHs levels in a few sediment samples from the Gulf of Gdańsk were reported by Kowalewska and Konat (1997), while organochlorine compounds levels were studied by Sapota (1997) and Konat and Kowalewska (2001). However, the 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. Therefore gradients of POPs concentration could be expected and should be better documented.

2. Aim of the study

The aim of this work was to establish the level of pollution by persistent organic contaminants in sediments from the Gulf of Gdańsk. Concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and selected organochlorine pesticides (DDTs, lindane) were determined in the surface sediments (0÷5 cm depth) from 7 stations. The sampling stations were chosen along the expected pollution gradient. The station localised in the open sea, off Hel Peninsula, served as a reference site. The POPs distribution has been correlated with organic carbon and fine-grained fraction content.

3. Materials and methods

3.1. Samples collection

Surface sediment samples (Baltic Sea) were collected during r/v Oceania cruises in 2002 using a Reineck corer or Niemistő corer. The distribution of sampling stations is shown in Fig. 1, while characteristics of sampling stations are given in Table 1. The 0÷5 cm layer was retrieved, frozen (-18^{0}C) in pre-cleaned glass jars and transported to the laboratory.

3.2. Sample preparation

The analyses were based on procedures described by Khim et al. (2001). In brief, a frozen sample was freeze-dried in the laboratory and then 5÷10 g of dry material w as subjected to extraction with methylene chloride (3 x 30 cm^3) in an ultrasonic bath. The internal standards were added to all samples in order to establish the recoveries. Elemental sulphur and sulphur containing compounds were removed using activated powdered elemental cooper. After filtration, the solvent was partly evaporated under vacuum. Further concentration was carried out under gentle nitrogen stream. The concentrated extract was subjected to clean up procedures on alumina/silica gel colums. The compounds were eluted with solvent mixtures, increasing in polarity (F1 – 100% hexane; F2 – 90% hexane:10%methylene chloride; F3 – 75% hexane:

25% methylene chloride). F1 contained PCBs, F2 PAHs and F3 – lindane. The fractions were evaporated and prior to analysis, dissolved in isooctane.

Table 1. Location of sampling stations and sediment samples characteristics
Tabela 1. Położenie punktów poboru prób i charakterystyka próbek osadów

Station name	Date of sampling	Coordinates		Depth (m)	Organic matter content (%)	Fine grained fraction content (<63 μm) (%)
		Latitude	Longitude			
UW	October '02	54°22.3' N	19°00.6' E	16	4.58	27
SO	November '02	54°28.7' N	18°38.6' E	14	0.15	0.33
MECH	November '02	54°36.2' N	18°33.5' E	11	0.86	0.77
TW	November '02	54°30.0' N	18°50.0' E	33	0.24	0.62
REF	November '02	54°50.2' N	18°40.2' E	45	0.95	0.20
GG 2	November '02	54°39.1' N	19°10.2' E	89	21.23	95.00
GG 1	November '02	54°49.9' N	19°18.6' E	110	19.80	97.00

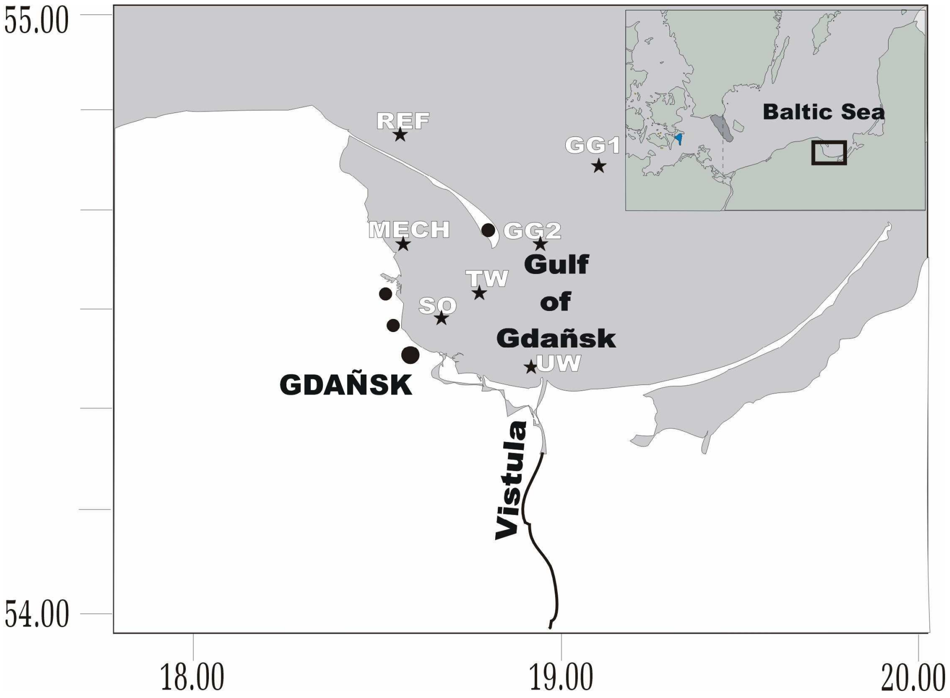

Fig. 1. Location of sampling stations
Rys. 1. Położenie punktów poboru prób

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 280ºC and DB 5 column (60m x 0,25 mm inner diameter x 0,25 μm film thickness) were used. FID detector, helium as a carrier gas and following oven temperature were used for PAH analyses: 50ºC held for 1 min, followed by 15ºC/min increase to 150ºC, followed by 30ºC/min increase to 310ºC, hold for 10 min. PCBs and organochlorine hydrocarbons (DDT and lindane) were analyzed applying ECD detector, helium as carrier gas and the following oven temperature program: 100^0C – 1 min; 6^0C/min do 140^0C; 10^0C/min do 310^0C, 310^0C – 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 pg $g-^1$ dry weight, and of PAHs – 100 pg g^{-1} dry weight. The details were described earlier by Tronczyński at al., 1999). Recoveries were calculated for each of the added deuterated PAHs. The recoveries were in the range of and 81÷101% for both mussels and SPMDs The laboratory blanks, were analysed in parallel with the samples. Procedural blanks were at least 10 times below measured concentrations, except for few analytes.

3.4. Supporting sample characterization

Organic matter content in sediment samples was measured as loss on ignition (450ºC, 8 h). Fine-grained fraction was separated by sieving with a 63 μm mesh stainless steel sieve.

4. Results and discussion

The PAHs concentrations in the analyzed sediment samples are presented in Table 2. The results are expressed in ng g^{-1} dry weight. The concentrations of individual PAHs ranged from 1.6 to 400 ng g^{-1} d.w. The highest content of PAHs was observed in the areas of intensive sediment accumulation (GG1 and GG2). Relatively high concentrations were found at station TW, situated near the shipping channel and at the station UW, located close to Vistula mouth. Total PAHs concentrations of 14 analysed compounds coincide well with those reported by Kowalewska and Konat (1997) for the same area. Baumard et al. (1998) reported values higher by 1.5÷7 times for PAH total concentrations in sediments of Western Mediterranean Sea.

Table 2. Concentrations of polycyclic aromatic hydrocarbons in the sediment samples (ng g^{-1} d.w.)

Tabela 2. Stężenia wielopierścieniowych węglowodorów aromatycznych w próbkach osadów (ng g^{-1} s.m.)

Compound	Sampling station						
	UW	SO	MECH	TW	REF	GG2	GG1
Phenathrene (P)	1248.1	44.6	71.5	344.4	61.1	344.2	400.6
Anthracene (A)	75.6	7.4	31.3	15.8	6.8	34.8	153.0
Fluoranthene (Fl)	115.4	34.7	84.9	109.1	7.3	57.6	86.4
Pyrene (Py)	92.7	39.7	76.0	177.9	3.3	23.0	58.4
Benzo(a)anthracene (BaA)	43.5	34.7	31.7	74.6	16.2	26.9	65.5
Chrysene (Ch)	24.6	16.9	22.3	33.0	13.6	53.4	128.9
Benzo(b)fluoranthene (BbFl)	46.3	20.3	35.7	153.5	23.0	286.2	275.8
Benzo(k)fluoranthene (BkFl)	69.4	22.3	37.5	130.6	20.4	303.6	240.4
Benzo(a)pyrene (BaPy)	53.3	14.9	31.3	91.8	22.6	125.7	134.4
Dibenzo(ah)anthracene (DBA)	33.1	2.2	7.1	12.9	1.6	152.8	163.7
Benzo(ghi)perylene (Bper)	31.8	3.0	4.4	186.6	35.2	367.4	315.4
Indeno(1,2,3 – cd)pyrene (Ipy)	10.2	6.4	13.4	114.7	23.5	154.5	183.0
Σ PAHs	1891.0	247.3	447.3	1444.9	235.0	1933.6	2205.0

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 (Wells, 1993; Konat and Kowalewska, 2001). 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 0.30 to 12.21 ng g^{-1} d.w. Generally, the lowest values were observed at the station situated in the vicinity of shipping channel (TW), Sopot (SO) and at the reference site (REF). Highest concentrations were detected in the sediment accumulation area – Gdańsk Deep (GG1 and GG2). High values were also found at the station situated close to the Vistula river mouth (UW). The obtained data are in good agreement with results obtained by Konat and Kowalewska (2001) and Sapota (1997). They studied PCBs levels in sediments in the same area. Van Bavel et al.(1996) estimated that PCB concentrations (sum of 12 congeners) in the surface sediments in the coastal zone of the Gulf of Bothnia ranged from 0.9 to 3.5 ng g^{-1} d.w. in the northern Gulf of Bothnia and from 4.1 to 6.5 ng g^{-1} d.w. in the southern Gulf of Bothnia. Higher PCBs levels, up to 11 ng g^{-1} d.w. were measured in surface sediments of the Baltic

Proper (Nylund, 1992). Dannenberger (1996) reported concentrations in the range from 8.4 to 200 ng g-1 d.w. (sum of 23 congeners) from the Western Baltic Sea (Pomeranian Bight and Greifswald Boden). Van Zoest and Van Eck (1993) observed in Scheldt estuary (North Sea) PCB concentrations up to 200 ng g^{-1} d.w.

The presence of p,p' DDT together with p,p'DDE and p,p'DDD, which are the primary decomposition products of p,p'DDT, was detected in all samples. Concentrations of individual compounds were found to be within a range between 1.50 ng g^{-1} d.w at reference site to about 6 ng g^{-1} d.w. in the Gdańsk Deep. Concentrations of γ-HCH (lindane) were low as compared to other POPs. They ranged from 0.50 ng g^{-1} d.w. at the reference site to about 4 ng g^{-1} d.w. in the Gdańsk Deep.

Table 3. Concentrations of organochlorine contaminants in the sediment samples (ng g^{-1} d.w.)

Tabela 3. Stężenia związków chloroorganicznych w próbkach osadów (ng g^{-1} s.m.)

Compound	Sampling station						
	UW	SO	MECH	TW	REF	GG2	GG1
2.4.4'-trichlorobiphenyl (CB 28)	3.37	0.65	0.93	0.61	0.30	9.05	12.32
2.2'.5.5'-tetrachlorobiphenyl (CB 52)	4.07	0.48	1.41	0.59	0.47	10.12	13.36
2.2'.4.5.5'-pentachlorobiphenyl (CB 101)	2.92	0.36	0.78	0.32	0.22	6.98	12.02
2.3'.4.4'.5-pentachlorobiphenyl (CB 118)	2.09	0.42	0.52	0.49	0.31	7.56	10.67
2.2'.4.4'.5.5'-hexachlorobiphenyl (CB 153)	4.02	0.43	0.71	0.39	0.26	10.19	12.12
2.2'.3.4.4'.5'-hexachlorobiphenyl (CB 138)	4.01	0.47	0.58	0.48	0.33	7.65	10.56
2.2'.3.4.4'.5.5'-heptachlorobiphenyl (CB 180)	4.52	0.17	0.36	0.21	0.05	6.75	7.08
Σ PCB (7 congeners)	25.00	2.98	5.29	3.09	1.94	58.30	78.13
lindane (γ- HCH)	nd**	0.73	0.99	1.09	0.50	3.93	3.46
DDT***	3.81	1.77	3.06	1.57	1.54	5.04	6.17

*** – not determined*

*DDT*** – includes DDT. its isomers and metabolites*

The percentage distribution of individual PAHs in the analysed sediment samples is presented in Fig. 2. The low molecular PAHs (tri- and tetra-aromatics) prevailed over high molecular ones (Table 4) at three stations in the inner part of the Gulf of Gdańsk: UW, SO and MECH, while the opposite trend was noted at deep water stations (GG1 and GG2) and at the reference site (REF). Among the low molecular compounds tri-aromatic compound – phenanthrene was dominant in all samples (up to 55% at the UW station). The other low molecular PAHs were in the range from 0.5% (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. The other sediments were characterized by penta-aromatics dominance.

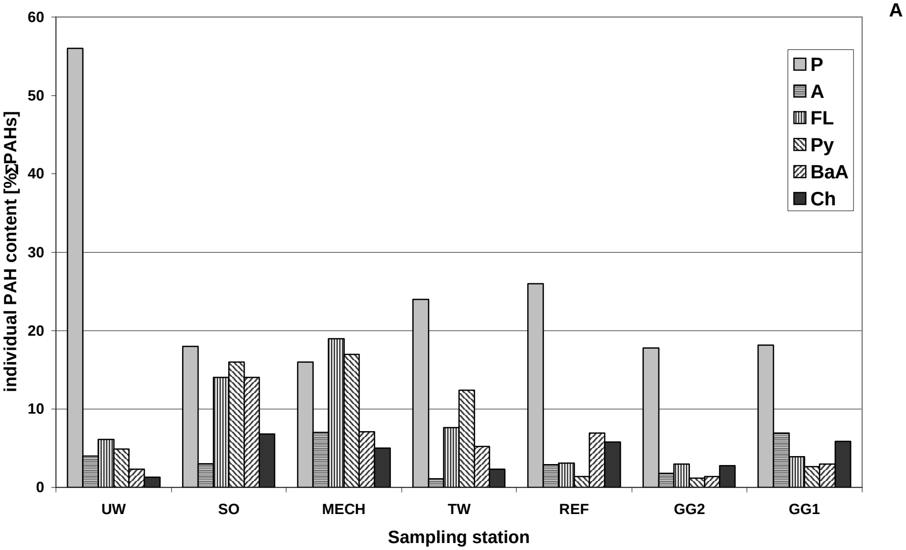

Fig. 2A. Polycyclic aromatic hydrocarbons content [% of Σ PAHs] in the sediment samples from the Gulf of Gdańsk; low molecular PAHs fraction;
P – phenanthrene, A – anthracene, Fl – fluoranthene, Py – pyrene, BaA – anthracene, Ch – chrysene

Rys. 2A. Zawartość wielopierścieniowych węglowodorów aromatycznych w próbkach osadów z Zatoki Gdańskiej; frakcja WWA małocząsteczkowych;
P – fenantren, A – antracen, Fl – fluoranten, Py – piren, BaA – antracen, Ch – chryzen

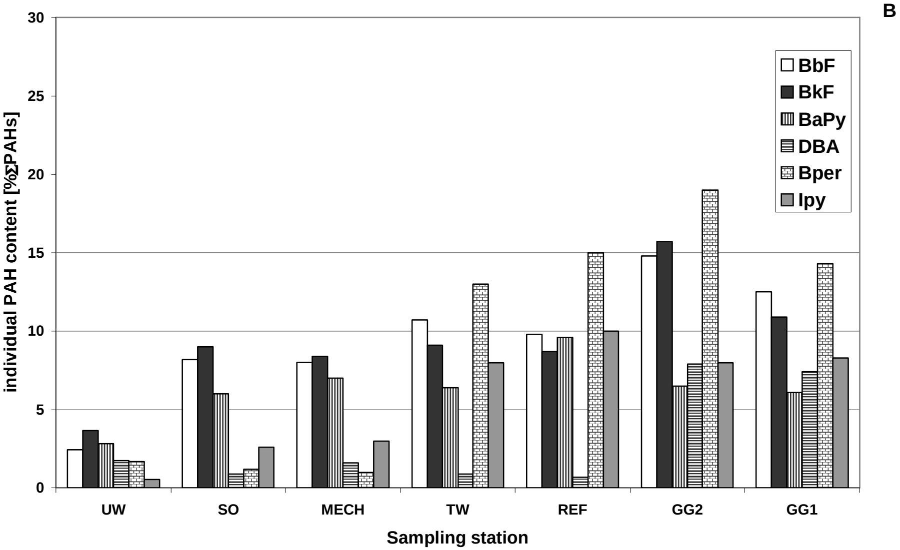

Fig. 2B. Polycyclic aromatic hydrocarbons content [% of Σ PAHs] in the sediment samples from the Gulf of Gdańsk; high molecular PAHs fraction;
BbF – benzo(b)fluoranthene, BkF – benzo(k)fluoranthene,
BaPy – benzo(a)pyrene; DBA – dibenzo(ah)anthracene,
Bper – benzo(ghi)perylene, IPy – indeno(1,2,3-c,d)pyrene

Rys. 2B. Zawartość wielopierścieniowych węglowodorów aromatycznych w próbkach osadów z Zatoki Gdańskiej; frakcja WWA wielkocząsteczkowych;
BbF – benzo(b)fluoranten, BkF – benzo(k)fluoranten,
BaPy – benzo(a)piren; DBA – dibenzo(ah)antracen,
Bper – benzo(ghi)perylen, IPy – indeno(1,2,3-c,d)piren

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 detailed comparison of individual PAHs distribution obtained in this study with literature data is impeded, due to differences in sampling techniques, extractive and analytical procedures, and finally – different compounds sets reported in the literature. As a consequence, different proportions of individual compound could be determined and reported.

Table 4. Selected ratios of POPs determined in the sediment samples from the Gulf of Gdańsk
Tabela 4. Wybrane stosunki TZO wyznaczone w próbkach osadów z Zatoki Gdańskej

Ratio	Sampling station						
	UW	SO	MECH	TW	REF	GG2	GG1
low molecularPAHs/ total PAHs [%]	74.60	71.80	71.04	52.60	46.10	27.92	40.49
high molecular PAHs/total PAHs [%]	25.40	27.90	28.96	48.09	53.80	71.89	59.53
Phenanthrene/Anthracen	14.00	6.00	2.29	21.82	8.97	9.89	2.62
Fluoranthene/Pyrene	1.24	0.88	1.10	0.61	2.21	2.50	1.47
Low chlorinated PCBs(3+4Cl atoms/total PCBs [%])	29.76	37.92	44.23	38.83	39.60	33.30	32.45
Higher chlorinated PCBs (5+6+7Cl atoms)/total PCBs [%])	70.24	62.04	55.77	61.17	60.31	66.66	67.55
Total PAH/Total PCBs content	76	83	84	467	121	32	28

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 (Baumard et al., 1999). 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 (Baumard et al., 1998). 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 (>15). The same considerations can be applied to the isomeric ratio of 4 rings compounds- fluoranthene to pyrene concentrations (Fl/Py). Values greater than 1 are characteristic of pyrolitic origin (Sicre et al., 1987), whereas values lower than 1 are related to petroleum hydrocarbons. P/A and FL/Py ratios, calculated for the analysed sediment samples (Table 4) indicate that contaminants in sediment samples collected at deeper stations in the outer part of the Gulf of Gdańsk GG1, GG2 and REF originated mainly from pyrolitic combustion. Sediments at the station TW, situated near the shipping channel were characterized by contaminants derived mainly from petroleum pollution. In the case of shallow water stations UW, So and Mech, located in the inner part of the Gulf of Gdańsk, close to the coast a superimposition of both pyrolitic and petrogenic origins of PAH should be noted.

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 and CB 52 were the dominant ones in shallow sandy sediments (stations SO, Mech, TW and REF). At deeper stations (GG1 and GG2) and close to the Vistula mouth (UW) the congeners were more uniformly distributed. The significant input of the most hydrophobic congener (CB 180) should be noted at these stations. Most reasonably, it seems that its better solubility in water or decomposition of higher chlorinated congeners by microbial attack (Brownawell and Farrington,1986) are responsible for the observed PCB distribution.

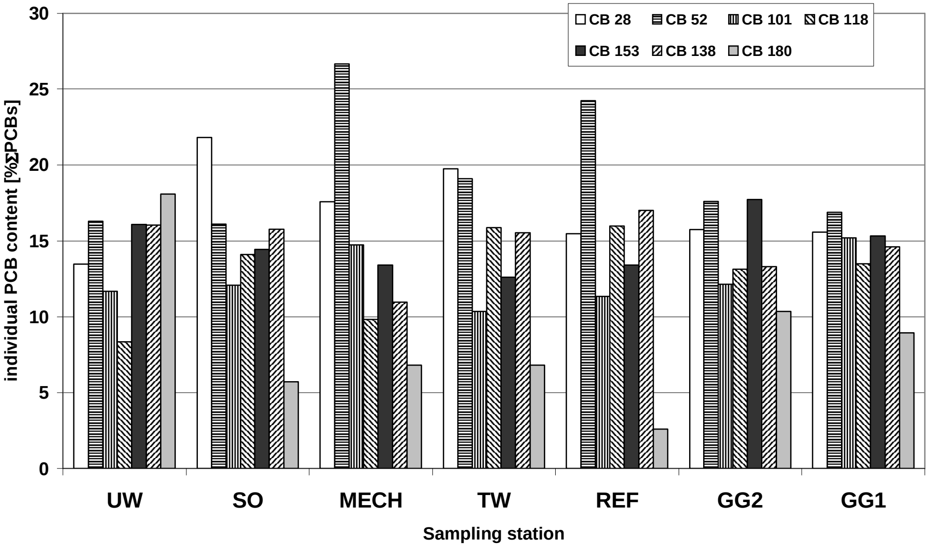

Fig. 3. PCBs content [% of Σ PCBs] in the sediment samples from the Gulf of Gdańsk
Rys. 3. Zawartość PCB [% sumy PCB] w próbkach osadów z Zatoki Gdańskiej

The distributions of organic contaminants in sediments are strongly related to their physico-chemical properties (mainly hydrophobicity). However, sediment properties play also an important role (Leppanen and Kukkonen (2000). Sediment organic carbon content and grain-size distribution are main parameters influencing contaminants pattern and bioavailability (Harkey et al., 1995, Witt, 1995). Organic contaminants tend to adsorb mainly on fine-grained material, thus often the analyses are performed on a sieved fraction of sedimentary material. However, in terms of potential contaminants bioavalability, bulk sediment analysis is more appropriate. The analysed sediments characteristics are listed in Table 1. Generally, the coastal stations were characterized by both, low organic matter and small fine grained fraction proportions. Only sediment sampled close to the Vistula mouth exhibits different properties. This is, possibly, due to specific riverine/marine waters mixing in this area resulting in intensive flocculation of suspended particles and organic matter enrichment in sediments. Samples from deep areas were characterized by high organic matter content and consisted exclusively of fine grained particles. Generally, the analyzed data set yielded a positive correlation between total and individual POPs levels and organic matter content (r>0.65). Organic matter – poor, sandy sediments were less contaminated then organic matter rich muddy sediments.

5. Conclusions

The content of persistent organic pollutants in the analyzed sediment samples collected from the Gulf of Gdańsk followed the order PAHs>PCBs>DDT>lindane

Persistent organic pollutants in the investigated area occured in low concentrations when compared to other marine, coastal areas in the industrialized regions (Mediterrean Sea, Adriatic Sea, North Sea) (Boulloubassi and Saliot, 1991; Fava et al., 2003; Van Zoest i Van Eck, 1993).

A positive correlation between sediment POPs concentrations and sediment organic matter concentrations as well as fine-grained fraction content were observed.

The highest content of POPs were observed not in the vicinity of the most probable sources of pollution, but in the areas of intensive net sediment accumulation. The obtained results indicate the importance of transport processes of POPs. Both, atmospheric fluxes and near bottom fluxes should be taken into account.

Samples taken from so called reference site situated in the open sea were characterized by the lowest concentrations of the studied contaminants.

Molecular indices were shown to be useful to differentiate between pyrolytic/petroleum PAH contamination sources. In the studied samples, PAH were mainly of pyrolytic origin, with some evidence of super-imposed petrogenic hydrocarbons close to Gdańsk harbour and in the vicinity of the fairway.

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Trwałe zanieczyszczenia organiczne w osadach Zatoki Gdańskiej

Streszczenie

Trwałe zanieczyszczenia organiczne (TZA) są rozpowszechnionymi, wszechobecnymi związkami chemicznymi, które można znaleźć we wszystkich typach nisz środowiskowych (Neff, 1979). Do tej grupy należy szeroki zakres związków chemicznych, takich jak polichlorowane bifenyle (PCB), wielopierścieniowe węglowodory aromatyczne (WWA) oraz szereg chloro-organicznych pestycydów (np. DDT, lindan). Związki te różnią się między sobą potencjałem bioakumulacyjnym oraz potencjałem do wywoływania niekorzystnych zjawisk w faunie i florze (Meador et al., 1999).

Jednym z głównych problemów dotyczących losu trwałych zanieczyszczeń organicznych wprowadzanych do środowiska przyrodniczego przez człowieka, jest określenie ich potencjalnej przyswajalności przez organizmy żywe. Hydrofobowe zanieczyszczenia organiczne zdeponowane w morskich powierzchniowych osadach dennych mogą być kumulowane przez organizmy wodne, bezpośrednio z osadów, lub pośrednio po desorpcji do fazy wodnej.

Przedmiotem prezentowanej pracy było określenie poziomu zanieczyszczenia osadów Zatoki Gdańskiej związkami z grupy wielo-pierścieniowych węglowodorów aromatycznych (WWA), polichlorowanych bifenyli (PCB) oraz wybranych pestycydów chloro-organicznych (DDT, lindan). Stacje pobierania osadu wyznaczono na podstawie spodziewanego gradientu zanieczyszczeń. Próbki osadu pobierano przy użyciu sondy skrzynkowej typu Reineck lub sondy rdzeniowej Niemisto. Analizowane zanieczyszczenia izolowano z próbek osadów 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.

Analizowane próbki charakteryzowały się zawartością pojedynczych WWA w zakresie od 1,6 do 400 ng g $^{-1}$ s.m., PCB w zakresie od 0,3 do 12 ng g $^{-1}$ s.m. W wyniku przeprowadzonych analiz stwierdzono, że osady powierzchniowe Zatoki Gdańskiej są najbardziej zanieczyszczone związkami z grupy wielopierścieniowych węglowodorów aromatycznych (WWA>PCB>DDT>lindan). Najwyższe stężenia analizowanych związków stwierdzono w rejonie akumulacji osadów – na Głębi Gdańskiej, co wskazuje na znaczenie procesów transportu w obiegu trwałych zanieczyszczeń organicznych w ekosystemie morskim. W wyniku przeprowadzonych badań stwierdzono istnienie korelacji pomiędzy zawartością trwałych zanieczyszczeń organicznych a zawartością materii organicznej oraz zawartością frakcji drobnoziarnistej (<63 μm).