Pol. J. Environ. Stud. Vol. 21, No. 2 (2012), 297-306

Original Research

Determination of PAHs and PCBs in the Polish Area of Shipwreck Exploration

Marzena Bogdaniuk*, Grażyna Sapota, Grażyna Dembska, Barbara Aftanas

Department of Environmental Protection, Maritime Institute in Gdańsk,
Długi Targ 41/42, 80-830 Gdańsk, Poland

Received: 14 February 2011
Accepted: 29 September 2011

Abstract

Wrecks are a serious danger to marine ecosystems. This danger includes the possibility of a single spill of toxic substances from a wreck, or may result from slow seepage of the substances. The investigations of organic pollutants in water and bottom sediment samples were taken in Pomeranian Bay, Puck Bay, and the Gulf of Gdańsk from sites where the wrecks of the ships Neuwerk, Orion, Schlessien, and a fishing vessel were lifted. In the present work are shown results of analysis of 16 polycyclic aromatic hydrocarbons – PAHs (naphthalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene), and 7 polychlorinated biphenyls – PCBs (CB 28, CB 52, CB 101, CB 118, CB 138, CB 153, CB 180) in water and sediment samples. Samples were taken at sites from which wrecks had been lifted and in reference areas. Organic pollutants were analyzed using the gas chromatography-mass spectrometry (GC-MS) technique. Levels of pollutants of PAHs were analyzed in water samples contained from below detection limit 1.0 $ng \cdot dm^{-3}$ to 31.0±0.6 $ng \cdot dm^{-3}$. The concentrations of PCB congeners in water samples were below detection limit 1.0 $ng \cdot dm^{-3}$. The sum of PAHs in sediment samples ranged from 0.091±0.004 $mg \cdot kg^{-1}$ d.w. to 6.57±0.32 $mg \cdot kg^{-1}$ d.w. and the sum of PCBs oscillated from 0.001 $mg \cdot kg^{-1}$ d.w. to 0.42±0.02 $mg \cdot kg^{-1}$ d.w.

Keywords: water, sediment, PAHs, PCBs, Baltic Sea

Introduction

The First and Second World Wars were periods when large numbers of vessels were sunk in a short time. During World War II actions on seas and oceans played a crucial role. One of the after-effects of these naval operations was the great number of merchant vessels and warships that ended up on the sea bed. Many of these wrecks still have considerable quantities of fuel, ammunition, and chemical weapons in their holds. Their on-going corrosion in sea water means that it is only a matter of time before such a wreck gives rise to an environmental disaster. The largest concentrations of wrecks are thought to be in the southern Asian Pacific, the northwestern Atlantic, and northwestern Pacific [1-6]. The problem is particularly serious in small, enclosed seas like the Baltic, which was the scene of intense naval action. Indeed, the Baltic, one of the largest semi-enclosed brackish water regions in the world (415,000 km^2), is considered to be an especially sensitive and endangered marine ecosystem [7, 8]. The ports of Gdańsk (Poland), Gdynia (Poland), Pillau (since 1946 Baltiysk, Russia), Kronstadt (Russia), and Liepaja (Latvia) were strategic naval bases. In consequence, large numbers of warships and auxiliary vessels were lost as a result of naval and aerial bombardment. Some of these vessels were sunk in fairways or near port entrances. In order to restore safe

*e-mail: Marzena.Bogdaniuk@im.gda.pl

navigation in areas with a high intensity of shipping traffic after the war, these wrecks began to be systematically removed. Vessels were raised from the bed and refitted, but if they were too badly damaged or if lifting them to the surface was too costly, they were removed by means of high explosives. The pyrotechnic method enabled only part of the wreck to be raised, and frequently led to leakage of fuel and other harmful substances into the sea [9].

Due to low accessibility and problems with accurate positioning, practically no investigations of the influence of these wrecks on the species composition, biology, and ecology of organisms living in the wrecks and within close vicinity of this area have been conducted. A wreck can be a non-typical ecological niche for some benthos species and fish [10, 11]. At the same time, if the wreck releases toxic compounds, such as phenol, PAHs or oil hydrocarbons, it can cause significant changes in fauna and flora. This may result in species selection and finally lead to impoverishment of the environment [12], even up to complete disappearance of life near the wreck. The fauna and flora are highly endangered by the mutagenic and pathogenic influences of the above-mentioned toxic compounds, remaining on the bottom of the wreck and in its neighborhood. These toxic substances cause impoverishment of the environment, cancerous changes, and genetic damaging of organisms living in the wreck and its neighborhood [13-15]. Many of the toxic substances accumulate in animals and become directly dangerous to humans.

Because of this, in order to assess the degree of danger to the environment, it is necessary to collect accurate data on contamination of water and bottom sediments in direct vicinity of the wrecks with substances seeping from them, and to determine the degree of contamination of sediments within a possibly wide area around the wrecks. In the case of oil spills, physical and chemical characteristics of the oil and the shape of the seabed and geology of the sea bottom are important for the environment and organisms living in it. A large role is played by bathymetry, hydrodynamic conditions (predominant directions and speed of currents), and type of bottom sediment (grain size, direction, and speed of sediment transport). These factors determine the direction and speed of propagation of the contaminants.

According to HELCOM recommendations, which were also adopted by Poland, not only endangered species are protected within the Baltic Sea Area (BSA), but also whole biotopes, which are under risk due to anthropogenic influences. According to HELCOM classification, to such biotope complexes along the Polish coast belong: sandy and moraine-type coasts, lagoons, and sandy barriers limiting water exchange with the open sea and river mouths [16].

Protection of the Baltic Sea against pollution is one of the key tasks facing the BSA states. This problem is extremely important both from the environmental point of view and because it is highly significant for recreation, aesthetics, and tourism.

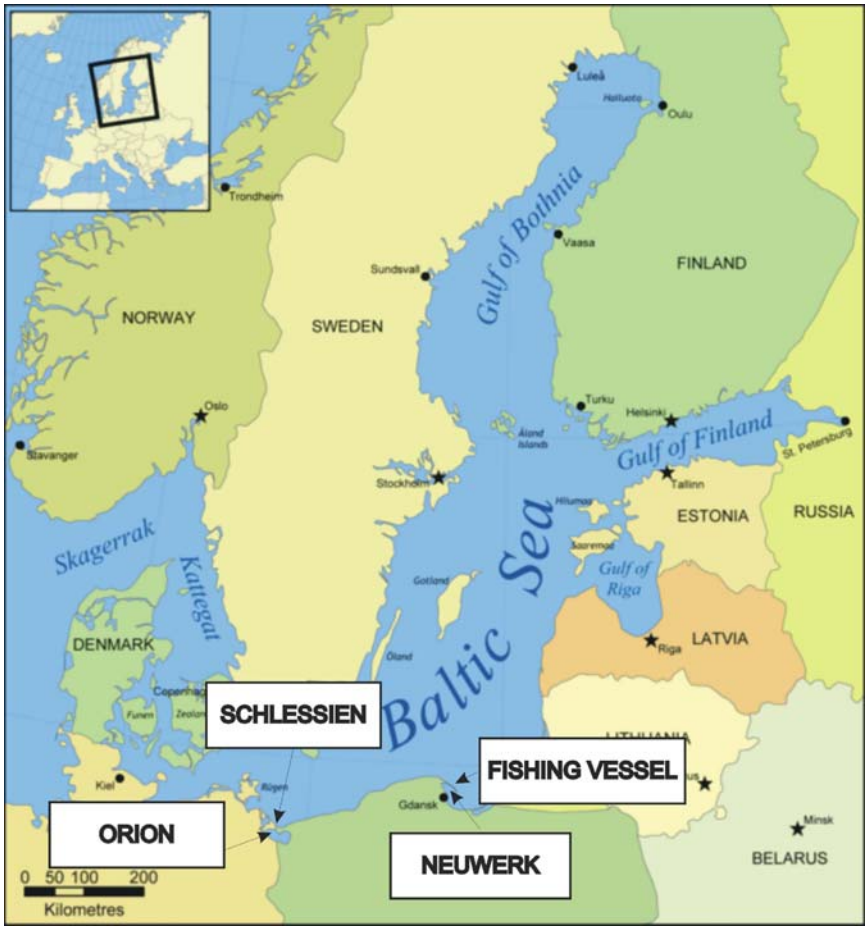

Fig. 1. Shipwreck sites.

Experimental Procedures

Sampling

Thirteen samples of sea water and bottom sediments were taken from the sites, from which four wrecks had been removed (Gulf of Gdańsk, Puck Bay, and Pomeranian Bay), we took 8 samples of sea water and bottom sediments in the reference sites about 1 km from shipwreck exploration. The samples were collected from r/v IMOR multipurpose oceanographic research laboratory in 2008.

The sites of shipwreck exploration were determined by an acoustical technique – multibeam echo sounder SeaBat 8101 (Reson) and digital side sonar DF 1000 (EdgeTech). Bathymetry surveys, using both single-beam and multibeam echo sounders, can characterize the seafloor over large areas. They are used to locate bottom features such as sediment ridges, bedrock outcrops, sunken ships, and underwater cables. They help identify areas that should be avoided by vessels and fishing gear. These techniques have improved seafloor mapping and the management of these benthic habitats. Side-scan sonar is an acoustical technique that provides high resolution, almost photographic – quality imagery of the seafloor. These systems send and receive pulses of sonar signals across the seabed. The side-scan sonar system can identify different seafloor cover types such as mud, smooth sand, and rippled sand, and they can distinguish bottom features such as rock outcrops and canyons.

The surface sediments were sampled using a Van Veen grab, whereas the cores were obtained with a vibro corer. The sea water samples were taken with a bathometer about 1 m above the sea bed. Fig. 1 shows the positions of the sampling sites, and Table 1 sets out the details of each site.

The cores were taken from the following sediment layers 0-100 cm. The sediment samples were deep frozen as soon as possible at approximately -20ºC, then lyophilized at -48ºC and at a pressure of 0.030 MPa (Martin Christ, Germany).

Determination of PAHs and PCBs

Solid-phase extraction (SPE) was used for determining PAHs and PCBs in water [17]. It was performed by passing 1 dm^3 volume of a water sample through C_{18} extraction cartridge (J.T. Baker) at a rate of ca. 10 cm^3 per minute. The cartridges were conditioned prior to use by washing them twice with 5 cm^3 of methanol (high purity grade) and twice with 2 cm^3 of "zero" water. The trapped compounds were extracted from the sorbent cartridge with 2 portions (2.5 cm^3 each) of a mixture of n-pentane and dichloromethane (1:1 v/v). Both portions of extract were combined and evaporated to a volume of 0.5 cm^3 [18-20].

Sediment samples were prepared in accordance with the diagram [10, 21-24]:

- Lyophilization
- Wetting (acetone) of dry sediment (1 g), drying (app. 24 h)
- Extracting dry sediment (1 g) in shaker (5 cm^3 of dichloromethane, 24 h)

Table 1. Geographic position of sites from which wrecks were lifted.

Name of wreck	Geographic position	
Orion	φ= 53º56'42"	λ= 14º17'24"
Schlessien	φ= 54º00'28"	λ= 14º17'38"
Fishing vessel	φ= 54º47'33"	λ= 18º38'30"
Neuwerk	φ= 54º34'06"	λ= 18º37'24"

- Decantation
- Extract evaporation to 1 cm^3 (N_2 stream)
- Cleaning of extract using SPE columns (SiO_2) and activated copper (HCl/water 1:1, neutralization – water, drying – acetone)
- Elution of 8 cm^3 dichloromethane
- Extract evaporation to 1 cm^3 (N_2 stream)
- GC-MS analysis of PAHs
- Evaporation of extract to dryness
- Extraction of dry residue (3×100 mm^3 of pentane)
- Fractioning of combined extracts, elution with pentane, and evaporation to dry state
- Dissolving of dry residue in 50 mm^3 of n-hexane
- GC-MS analysis of PCBs

The final extracts were analyzed using gas chromatography-mass spectrometry (GC-MS) with an HP 6890 gas chromatograph equipped with 60 m×0.32 mm I.D. fused-silica capillary column, coated with bonded 0.5 µm nonpolar DB-5 phase (JW), and model MSD 5973 detector operated in the selected-ion monitoring (SIM) mode. The temperature program was: from 50ºC to 120ºC at 40ºC·min^{-1} gradient, followed by 5ºC·min^{-1} gradient up to 280ºC, and a 15 min isothermal run. The detection limit of this method was 0.001 µg·dm^{-3} for PAHs in water samples, 0.001 mg·kg^{-1} for PAHs, and 0.0001 mg·kg^{-1} for PCBs in bottom sediment samples.

Standard mixture contained all 16 PAH analytes, as recommended by the US EPA, in dichloromethane (2,000 µg·cm^{-3} for each compound; Restek Corporation, USA) and 7 PCB congeners in isooctane (10 µg·cm^{-3} for each compound; LGC Standards).

Calibration of the GC-MS system was performed for all 16 PAH and 7 PCB compounds. Standard samples of 2 mm^3 containing known amounts of the analytes were injected onto the chromatographic column. Four standard mixtures of 51, 83, 133, and 333 ng·dm^{-3} were used for calibration.

The background was checked using tap water. Three samples of the tap water containing 120 ng·dm^{-3} standard mixture (1 dm^3 of the tap water with the mixture of standards added) were passed through the extraction cartridges. The same procedure was performed with 3 samples of the tap water without standards (1 dm^3 of the tap water).

Correctness of analytical method for determining PAHs and PCBs in bottom sediment samples has been tested for reference material LGC6188 (River Sediment – PAHs) and in the International Sediment Exchange for

Table 2. Concentrations of PAHs in reference water samples.

[ng·dm^{-3}]	Fishing vessel	Neuwerk	Orion	Schlessien
Naphtalene	11.0±0.2	29.0±0.6	12.0±0.2	8.0±0.1
Acenaphtylene	6.0±0.1	11.0±0.2	2.0±0.1	2.0±0.1
Acenaphtene	4.0±0.2	8.0±0.1	2.0±0.1	2.0±0.1
Fluorene	2.0±0.1	6.0±0.1	3.0±0.1	3.0±0.1
Phenanthrene	4.0±0.2	25.0±0.5	4.0±0.2	8.0±0.1
Anthracene	3.0±0.1	23.0±0.4	6.0±0.1	5.0±0.1
Fluoranthene	n.d.	n.d.	n.d.	n.d.
Pyrene	n.d.	n.d.	n.d.	n.d.
Benzo(a)anthracene	n.d.	n.d.	n.d.	n.d.
Chrysene	n.d.	n.d.	n.d.	n.d.
Benzo(b)fluoranthene	n.d.	n.d.	n.d.	n.d.
Benzo(k)fluoranthene	n.d.	n.d.	n.d.	n.d.
Benzo(a)pyrene	n.d.	n.d.	n.d.	n.d.
Dibenz(ah)anthracene	n.d.	n.d.	n.d.	n.d.
Benzo(ghi)perylene	n.d.	n.d.	n.d.	n.d.
Indeno(1,2,3-cd)pyrene	n.d.	n.d.	n.d.	n.d.

n.d. – not detected (< 1.0 ng·dm^{-3})

Tests on organic contaminants – WEPAL programs organized by Wageningen University Environmental Science). Recoveries in the utilized technique were determined as follows: from 74% for naphthalene in water samples and 82% to 106% for other analytes in water and sediment samples.

Solvent extracts obtained from the bottom sediments contained many groups of organic compounds with varying levels of concentration. Determination of PAHs and PCBs in the same extract was difficult due to high concentrations of PAHs and relatively low concentrations of PCB compounds. In order to solve this problem, fractionation of solvent extracts [24] was included in the analytic procedure of sample preparation.

Water and sediment samples were prepared in accordance with procedures recommended by HELCOM. These procedures are used by all Baltic countries within COMBINE – the program for monitoring the sea and coastal zone areas of the Baltic Sea [25].

Results and Discussion

The present work shows results of analyzing 16 PAHs (naphthalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene), and 7 PCBs (CB 28, CB 52, CB 101, CB 118, CB 138, CB 153, and CB 180) in water and sediment samples taken at sites from which wrecks had been lifted and in reference areas. Such investigations are both of cognitive and utilitarian value, especially for the investigated areas (the Gulf of Gdańsk, Puck Bay, and Pomeranian Bay).

Table 2 presents concentrations of PAHs in reference water samples. In all reference samples concentrations of pollutants were at a comparable level of n.d. (not detected, below 1.0 ng·dm^{-3}) to 29.0±0.5 ng·dm^{-3} for naphthalene (Neuwerk). The sum of PAHs in reference water samples were 30.0±0.6 µg·dm^{-3} for the fishing vessel, 102±2 ng·dm^{-3} for the Neuwerk, 29.0±0.05 ng·dm^{-3} for the Orion, and 28.0±0.5 ng·dm^{-3} for the Schlessien.

In all reference samples, concentrations of pollutants were below 1.0 ng·dm^{-3} (limit of detection).

In Baltic Sea waters PAHs are present at ng·dm^{-3} levels [26]. The background PAH concentrations in Baltic Sea range from 5.4 to 17.6 ng·dm^{-3} for bottom water and from 2.5 to 21.3 ng·dm^{-3} for surface water [12]. Generally, PAH concentrations described in the literature after different oil spills were µg·dm^{-3} level [9, 27].

The concentrations of PCB congeners in water samples were below the limit of detection of 1.0 ng·dm^{-3}.

In marine water, PCBs can either be dissolved in the water phase or be adsorbed to particles suspended in the water column. PCB concentrations in the Baltic waters range from a few pg·dm^{-3} to a few ng·dm^{-3} [28, 29].

PAHs and PCBs are not very soluble in water and display a strong tendency to be sorbed on solid particles. In an aquatic environment, according to Wolska in 2003 and

Table 3. Concentrations of PAHs and PCBs in reference sediment samples.

[mg·kg^{-1}]	Fishing vessel	Neuwerk	Orion	Schlessien
Naphtalene	0.110±0.002	0.170±0.008	n.d.	n.d.
Acenaphtylene	0.0140±0.0007	0.040±0.002	n.d.	n.d.
Acenaphtene	0.058±0.003	0.042±0.002	n.d.	n.d.
Fluorene	0.066±0.003	0.076±0.004	n.d.	n.d.
Phenanthrene	0.027±0.001	0.036±0.002	n.d.	n.d.
Anthracene	n.d.	0.0110±0.0005	n.d.	n.d.
Fluoranthene	0.0150±0.0007	0.073±0.004	n.d.	0.080±0.004
Pyrene	0.0110±0.0005	0.058±0.003	n.d.	0.0070±0.0003
Benzo(a)anthracene	0.097±0.005	0.034±0.002	0.039±0.002	0.0040±0.0002
Chrysene	0.080±0.004	0.027±0.001	0.025±0.001	0.0010±0.001
Benzo(b)fluoranthene	0.098±0.005	0.092±0.005	0.090±0.004	0.0010±0.001
Benzo(k)fluoranthene	0.028±0.001	0.055±0.003	0.082±0.004	0.0030±0.001
Benzo(a)pyrene	n.d.	n.d.	n.d.	n.d.
Dibenz(ah)anthracene	n.d.	n.d.	n.d.	n.d.
Benzo(ghi)perylene	n.d.	n.d.	n.d.	n.d.
Indeno(1,2,3-cd)pyrene	n.d.	n.d.	n.d.	n.d.
PCB 28	n.d.	n.d.	n.d.	n.d.
PCB 52	n.d.	n.d.	n.d.	n.d.
PCB 101	n.d.	n.d.	n.d.	n.d.
PCB 118	n.d.	n.d.	n.d.	n.d.
PCB 138	0.00050±0.00005	0.0100±0.0005	0.0020±0.0001	n.d.
PCB 153	0.00050±0.00005	0.060±0.003	0.0100±0.0005	n.d.
PCB 180	n.d.	0.0100±0.0005	0.0040±0.0002	n.d.

n.d. – not detected (PAHs<0.001 mg·kg^{-1}; PCBs<0.0001 mg·kg^{-1})

2008 [30, 31], the ratio of the concentration of these compounds in the sediment to their levels in water is high: 10^6 for PAHs and 10^3 for PCBs. It appears that at such low concentrations, PAHs and PCBs are not the reason for the disappearance of the fauna and flora in the vicinity of the wreck [9].

Table 3 presents concentrations of PAHs and PCBs in reference sediment samples. The sum of PAHs were 0.604±0.030 mg·kg^{-1} d.w. for the fishing vessel, 0.714±0.035 mg·kg^{-1} d.w. for the Neuwerk, 0.236±0.012 mg·kg^{-1} d.w. for the Orion and 0.096±0.004 mg·kg^{-1} d.w. for the Schlessien. The sum of PCBs were 0.00100±0.00005 mg·kg^{-1} d.w. for the fishing vessel, 0.080±0.004 mg·kg^{-1} d.w. for the Neuwerk, 0.0160±0.0008 mg·kg^{-1} d.w. for the Orion and below 0.0001 mg·kg^{-1} for the Schlessien. The content of 7 PCBs sum in water from the Gulf of Gdańsk reported by Sapota [32] ranged from 0.3 to 1.8 ng·dm^{-3} in surface water and from 0.2 to 2.1 ng·dm^{-3} in near bottom water.

Fig. 2 shows concentrations of PAHs in water samples taken at the wreck sites. In all analyzed samples, the level of pollutants was comparable with levels of PAHs in reference samples, and ranged from below limit of detection 0.001 µg·dm^{-3} for fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene,

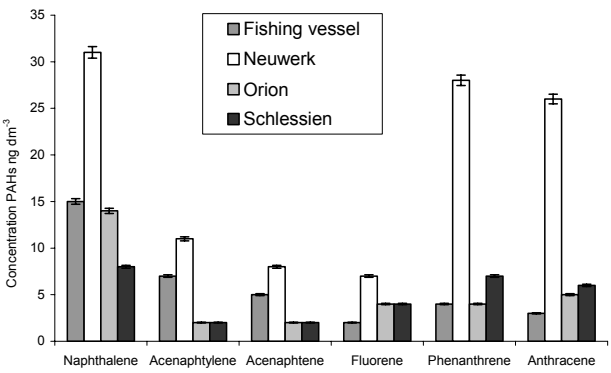

Fig. 2. Concentrations of PAHs in water samples.

Table 4. Macroscopic description of sediment samples.

Name of sample	Layer [m]	Type of sediment	Color	Remarks
Fishing vessel 1	0.0-1.0	fine sand	grey	shells and clay
Fishing vessel 2	0.0-1.0	fine sand	grey	shells
Fishing vessel 3	0.0-1.0	fine sand	grey	
Fishing vessel 4	0.0-0.96	fine sand	grey	
Fishing vessel – reference sample	0.0-1.0	fine sand	grey	shells
Orion 1	0.0-0.55/0.85-1.0	fine sand	grey	shells
Orion 2	0.0-1.0	fine sand	brown and grey	addition of small shells and clay
Orion – reference sample	0.0-1.0	fine sand	grey	addition of small shells and plastic clay
Schlessien 1	0.0-1.0	fine sand	grey	
Schlessien 2	0.0-1.0	fine sand	grey	
Schlessien – reference sample	0.0-1.0	fine sand	grey	
Neuwerk	0.0-0.86	mud	black	
Neuwerk – reference sample	0.0-0.86	mud	black	

and indeno(1,2,3-cd)pyrene to 0.031±0.0006 $\mu g \cdot dm^{-3}$ for naphthalene, 0.028±0.0005 $\mu g \cdot dm^{-3}$ for phenanthrene, and 0.026±0.0005 $\mu g \cdot dm^{-3}$ for anthracene in water samples from the Neuwerk site.

Table 4 presents a macroscopic description of the sediments taken from the wreck sites. The most common sediment was fine sand; only samples taken at the Neuwerk wreck site were made up of mud.

Fig. 3 shows concentrations of PAHs and PCBs in sediment samples from the fishing vessel site. The sum of PAHs in samples was from 1.711±0.085 $mg \cdot kg^{-1}$ d.w. to 3.180±0.159 $mg \cdot kg^{-1}$ d.w. Sum of PCBs ranged from 0.00100±0.00005 $mg \cdot kg^{-1}$ d.w. to 0.0090±0.0004 $mg \cdot kg^{-1}$ d.w. The highest concentration was for naphthalene 0.71±0.035 $mg \cdot kg^{-1}$ d.w., fluorene, and phenanthrene 0.69±0.034 $mg \cdot kg^{-1}$ d.w., PCB 118 and PCB 180 – 0.0090±0.0004 $mg \cdot kg^{-1}$ d.w.

Fig. 4 shows concentrations of PAHs and PCBs in sediment samples from the Neuwerk site. The sum of PAHs in samples was 6.57±0.328 $mg \cdot kg^{-1}$ d.w. and the sum of PCBs was 0.42±0.021 $mg \cdot kg^{-1}$ d.w. The concentration of PAHs contained from 0.0110±0.0005 $mg \cdot kg^{-1}$ d.w. for benzo(ghi)perylene and indeno(1,2,3-cd)pyrene to 0.940±0.047 $mg \cdot kg^{-1}$ d.w. for chrysene, 0.903±0.045 $mg \cdot kg^{-1}$ d.w. for pyrene, and 0.851±0.042 $mg \cdot kg^{-1}$ d.w. for benzo(a)anthracene. The concentration of PCBs contained from 0.021±0.001 $mg \cdot kg^{-1}$ d.w. for CB 118 to 0.152±0.007 $mg \cdot kg^{-1}$ d.w. for CB 153.

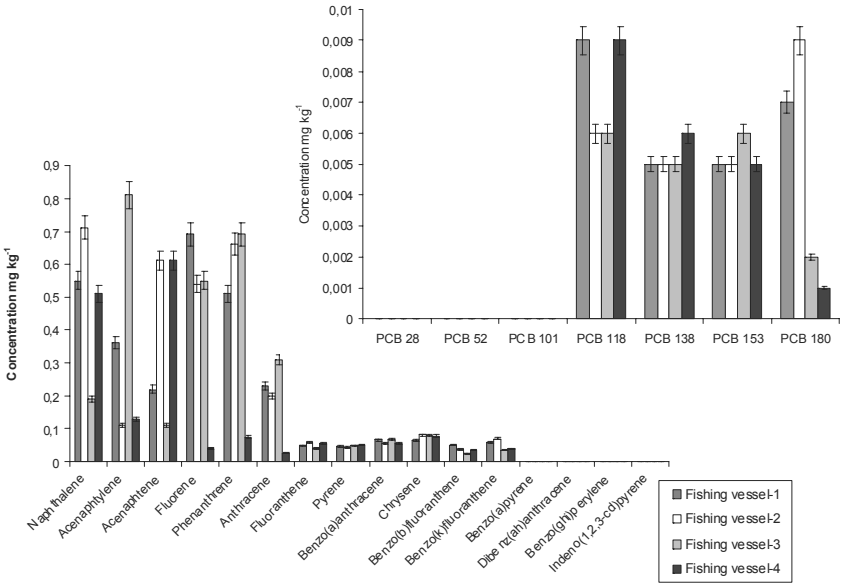

Fig. 3. Concentrations of PAHs and PCBs in bottom sediment samples from the fishing vessel site.

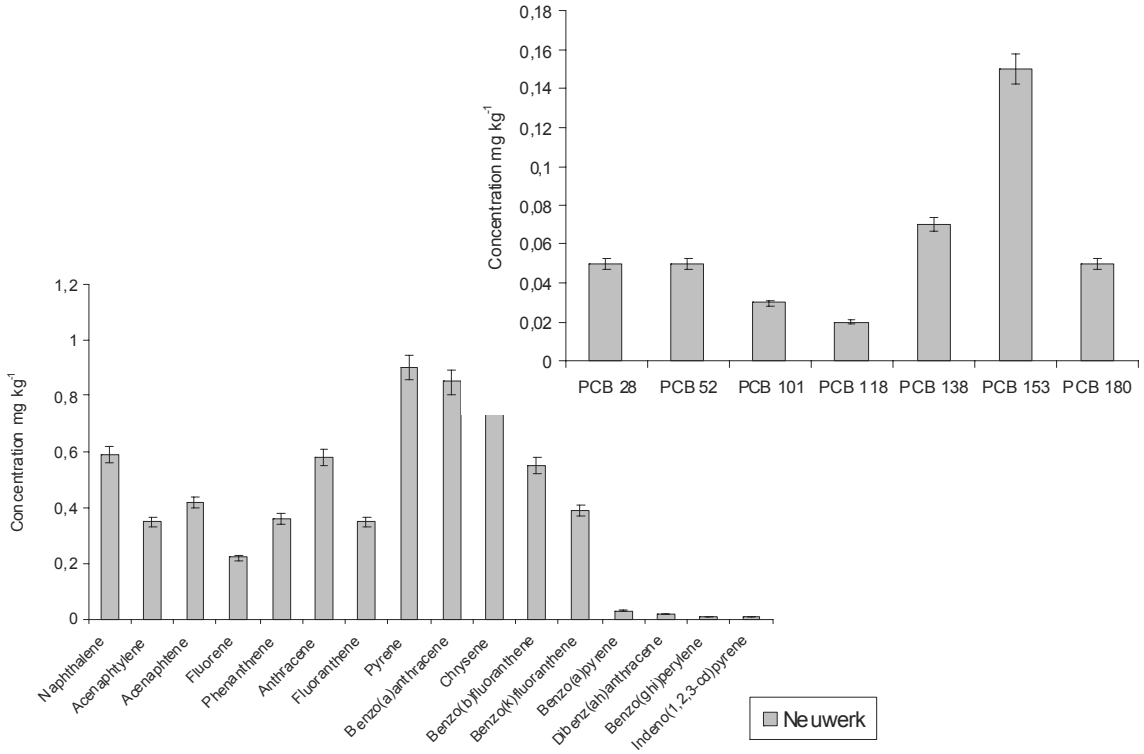

Fig. 4. Concentrations of PCBs and PCBs in bottom sediment samples from the Neuwerk site.

Fig. 5 shows concentrations of PAHs and PCBs in sediment samples from the Orion site. The sum of PAHs in samples ranged from 3.34±0.16 mg·kg^{-1} d.w. and 3.44±0.172 mg·kg^{-1} d.w. The sum of PCBs was 0.117±0.005 mg·kg^{-1} d.w. and 0.148±0.007 mg·kg^{-1} d.w. The highest concentrations were for naphthalene 0.85±0.04 mg·kg^{-1} d.w., phenanthrene 0.81±0.04 mg·kg^{-1} d.w., acenaphtene 0.74±0.03 mg·kg^{-1} d.w., PCB 138 0.07±0.003 mg·kg^{-1} d.w., and PCB 180 0.034±0.001 mg·kg^{-1} d.w.

Fig. 6 shows concentrations of PAHs and PCBs in sediment samples from the Schlessien site. The sum of PAHs in samples was 0.091±0.004 mg·kg^{-1} d.w. and 0.104±0.005 mg·kg^{-1} d.w. Individual compounds of PCBs were not detected, meaning that concentrations were below 0.0001 mg·kg^{-1}. Concentration of PAHs contained from below 0.001 mg·kg^{-1} (naphthalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene) to 0.074±0.003 mg·kg^{-1} d.w. for fluoranthene.

Only in samples taken at the Schlessien site PAH were concentrations at the same level as in reference samples (below the limit of determination, i.e. below 0.0001 mg·dm^{-3}). In the rest of the analyzed samples from wreck sites, PAH concentrations were higher. The highest concentrations were detected for the Neuwerk site, which could be connected with the problem of general environmental pollution of Puck Bay, where the wreck was located. The Hel Peninsula impedes free water exchange between Puck Bay and the open Baltic Sea, and the system of currents in the region facilitates transport of pollutants to the northwest, i.e. into Puck Bay. Depending on porosity, grain size, and organic matter content, bottom sediments form a substratum, binding in varying degree the pollutants, especially organic pollutants, and the site of the wreck was characterized by sandy and clayey mud, i.e. sediments facilitating absorption of pollutants.

Comparison of PAH concentrations in sediments taken at the Orion and Schlessien sites and in reference samples shows a point pollution of the Pomeranian Bay bottom, which probably was caused by the Orion wreck.

Sediment samples from analyzed sites contained PAH and PCB concentrations lower than the value of the limit of Polish regulations, i.e. 1.0 mg·kg^{-1} for benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, 1.5 mg·kg^{-1} for benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and 0.3 mg·kg^{-1} for the sum of PCBs (CB 28, CB 52, CB 101, CB 118, CB 138, CB 153, CB 180).

The sum of the concentrations of 12 PAHs in the southern Baltic sediments reported by Kowalewska and Konat in 1997 and 2001 [33, 34] ranged from 0.010 to 0.70 mg·kg^{-1} (av. 1.830 mg·kg^{-1}), while PAH concentrations in the Gulf of Gdańsk sediments in the study by Pazdro [35] were 0.235-2.205 mg·kg^{-1}. The dry weigh sediment content of the 12 PCBs ranged from 0.0017 mg·kg^{-1} to 0.517 mg·kg^{-1} with a mean of 0.0065 mg·kg for sediments of the North Sea – Baltic Sea transition zone [36]. The content of sum of 7 PCBs in sediments from the Gulf of Gdańsk in 2002 reported by Sapota [37] ranged from 0.0017 mg·kg^{-1} near Hel Peninsula to 0.0048 mg·kg^{-1} in Gdańsk Deep. The background level of the individual PAHs in Baltic Sea sediments ranged between 1 and 3 ng·kg^{-1} [38].

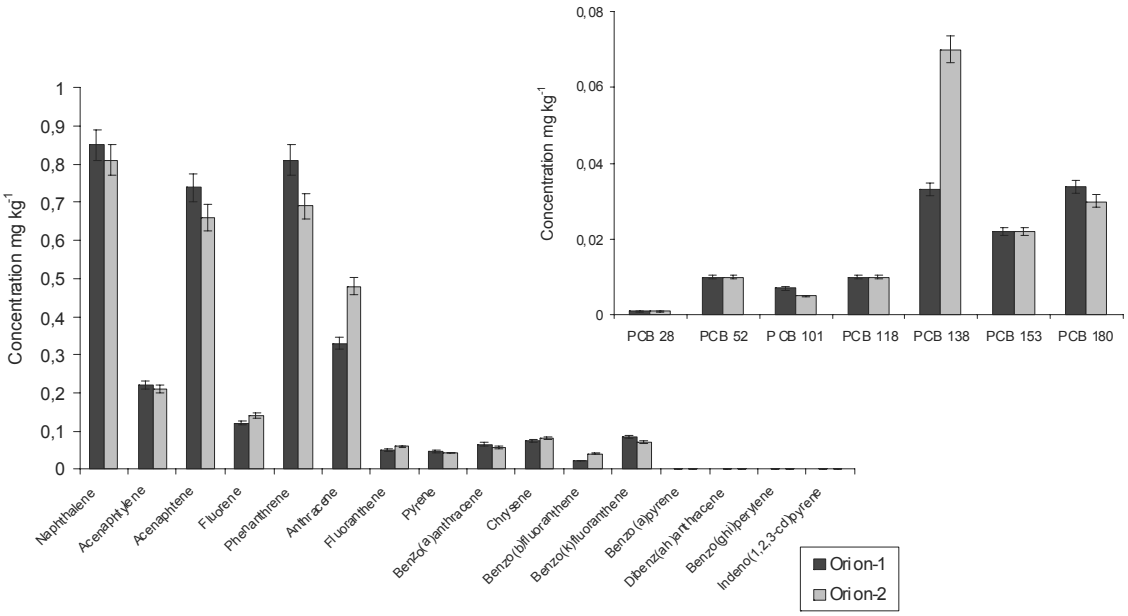

Fig. 5. Concentrations of PCBs and PCBs in bottom sediment samples from Orion site.

Conclusions

Level of pollutants of PAHs analyzed in water samples contained from below the limit of detection 1.0 ng·dm^{-3}, the highest concentrations were found in samples from the Gulf of Gdańsk (Neuwerk shipwreck) 31.0±0.1 ng·dm^{-3}. the content of PCB congeners was below the limit of detection 1.0 ng·dm^{-3}.

The distribution of PAHs and PCBs was investigated in water and bottom sediments along the Baltic Sea coast. The highest concentrations of organic pollutants were found in Puck Bay (Neuwerk shipwreck). Water and sediment samples were characterized by high levels of concentration of the investigated groups of compounds, both in samples taken at the wreck site and at a significant distance from the site.

The Neuwerk wreck could have strengthened the negative effects. However, it is highly probable that the pollution comes from other sources, e.g. discharge from land, especially from the catchments of the Reda and Kacza rivers, and from industrial waste discharges from shipbuilding and ship repair yards, the fish processing industry, and from the big seaport in Gdynia.

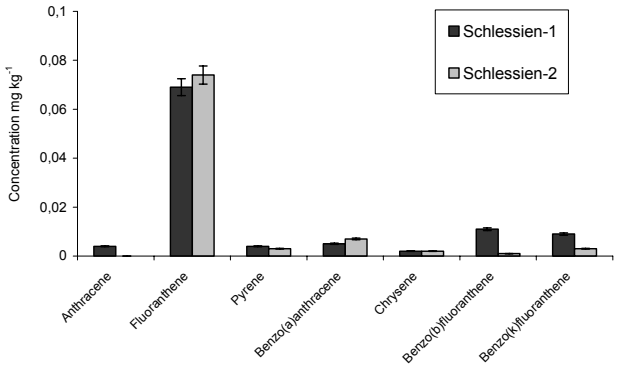

Fig. 6. Concentrations of PCBs and PCBs in bottom sediment samples from Schlessien site.

Based on investigations of sediment and water samples taken in Pomeranian Bay at the sites from which the Orion and Schlessien wrecks have been lifted, it may be stated that the Schlessien wreck did not pollute the marine environment. However, point accumulation of pollution was found in samples taken at the Orion site, with an especially high concentration of PAH compounds in the bottom sediment samples.

In samples taken at the fishing vessel site, no influence of the wreck on the state of water and sediments of the Gulf of Gdańsk was observed. The wreck site was located in the open part of the Gulf, and this could have facilitated propagation of pollution over large distances.

The investigations of organic pollutants in water and bottom sediment samples taken in Pomeranian Bay, Puck Bay, and the Gulf of Gdańsk, carried out by the Department of Environmental Protection of the Maritime Institute in Gdańsk, are part of the program of monitoring the movements of pollutants in the coastal zone of the southern Baltic. Obtained results are especially valuable for the investigated areas, i.e. Pomeranian Bay – Świnoujście, Miedzyzdroje, and Puck Bay – Gdynia, Puck, Hel, both in the aspect of environmental protection and due to the aesthetic, recreational, and touristic values of the regions.

References

1. ROGOWSKA J., NAMIEŚNIK J. The assessment of the marine environment risk due to the presence of substances of ship wrecks origin – analytical problems. Analityka **3**, 52, **2009**.

2. MICHAEL J., GILBERT T., WALDORN J., BLOCK-SIDGE CH.T., SCHMIDT ETKIN D., URBAN R. Potentially polluting wrecks in marine waters. An Issue Paper Prepared for the 2005 International Oil Spill Conference **2005**.
3. FRANCO M.A., VINAS L., SORIANO J.A., de ARMAS D., GONZALEZ J.J., BEIRAS R., SALAS R., BAYONA J.M., ALBAIGES J. Spatial distribution and ecotoxicity of petroleum hydrocarbons in sediment from the Galicia continental shelf (NW Spain) after the Prestige oil spill. Mar. Pollut. Bull. **53**, 260, **2006**.
4. HO K., PATTON L., LATIMER J.S., PRUELL R.J., PELLETIER M., MCKINNEY R., JAYARAMAN S. The chemistry and toxicity of sediment affected by oil from the North Cape spilled into Rhode Island Sound. Mar. Pollut. Bull. **4**, 314, **1999**.
5. XU J., YU Y., WANG P., GUO W., DAI SH., SUN H. Polycyclic aromatic hydrocarbons in the surface sediments from Yellow River, China. Chemosphere **67**, 1408, **2007**.
6. BIHARI N., FAFANDEL M., HAMER B., KRALJ-BILEN B. PAH content, toxicity and genotoxicity of coastal marine sediments from the Rovinj area, Northern Adriatic, Croatia. Sci. Total Environ. **366**, 602, **2006**.
7. WITT G., LIEHR G.A., BORCK D., MAYER P. Matrix solid-phase microextraction for measuring freely dissolved concentrations and chemical activities of PAHs in sediment cores from western Baltic Sea. Chemosphere **74**, 522, **2009**.
8. LOZAN J.L., LAMPE R., MATTHAUS W., RACHOR E., RUMOHR H., WESTERNHAGEN V.H. (Eds.) Warning signals from the Baltic Sea, Paul Parey Verlag, Berlin, Germany, pp. 384, **1996**.
9. ROGOWSKA J., WOLSKA L., NAMIEŚNIK J. Impact of pollution derived from ship wrecks on the marine environment on the basis of s/s Stuttgart (Polish coast, Europe). Sci. Total Environ. **408**, 5775, **2010**.
10. GREGORY D. Experiments into deteriorating characteristics of materials on the Duart Point wreck site: an interim report. Int. J. Naut. Archaeol. **24**, 61, **1995**.
11. WHEELER A.J. Environmental controls on shipwreck preservation: the Irish context. J. Archaeol. Sci. **29**, 1149, **2002**.
12. WITT G., Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. Mar. Pollut. Bull. **31**, 237, **1995**.
13. NAMIEŚNIK J., GÓRECKI T., WARDENCKI W., ZYGMUNT B., TORRES L. Secondary effects and pollutants of the environment, pp. 134-142, **1993**.
14. SZAREJKO A., NAMIEŚNIK J. The Baltic Sea as a dumping site of chemical munitions and chemical warfare agents. Chem. Ecol. **25**, 13, **2009**.
15. ZIETZ B. P., NORDHOLT G., KETSERIDIS G., PFEIFFER E.H. Mutagenicity of Baltic seawater and the relation to certain chemical and microbiological parameters. Mar. Pollut. Bull. **42**, 845, **2001**.
16. HELCOM, Baltic Sea Environmental Proceedings, **64B**, 252, **1996**.
17. ISO 17993: water quality – determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction **2002**.
18. WOLSKA L., RAWA-ADKONIS M., NAMIEŚNIK J. Determining PAH and PCB in aqueous samples: finding and evaluating sources of error. Anal. Bioanal. Chem. **382**, 1389, **2005**.
19. MA J., XIAO R., LI J., YU J., ZHANG Y., CHEN L. Determination of 16 polycyclic aromatic hydrocarbons in environmental water samples by solid-phase extraction using multi-walled carbon nanotubes as adsorbent coupled with gas chromatography-mass spectrometry. J. Chromatogr. A **1217**, 5462, **2010**.
20. KUCZYŃSKA A., WOLSKA L., NAMIEŚNIK J. An attempt to identify volatile and semi-volatile organic compounds present in the Odra river waters. Chromatographia **60**, S279, **2004**.
21. GALER K., WOLSKA L., NAMIEŚNIK J., Evaluation of a new procedure for PCB determination in sediments, Materials of Fifth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe, 12-14.09.2000, Prague, Czech Rep. p. 76, **2000**.
22. GASPARE L., MACHIWA J.F., MDACHI S.J.M., STRECK G., BRACK W. Polycyclic aromatic hydrocarbon (PAH) contamination of surface sediments and oysters from the inter-tidal areas of Dar es Salaam, Tanzania. Environ. Pollut. **157**, 24, **2009**.
23. SMITH J.N., LEE K., GOBEIL C., MACDONALD R.W. Natural rates of sediment containment of PAH, PCB and metal inventories in Sydney Harbour, Nova Scotia. Sci. Tot. Environ. **407**, 4858, **2009**.
24. WOLSKA L. Miniaturised analytical procedure of determining polycyclic aromatic hydrocarbons and polychlorinated biphenyls in bottom sediments. J. Chromatogr A **959**, 173, **2002**.
25. Third periodic assessment of the state of the marine environment of the Baltic Sea, 1989-93; Background document, Helsinki Commission, Baltic Marine Environment Protection Commission **1996**.
26. KOT-WASIK A., DĘBSKA J., NAMIEŚNIK J. Monitoring of organic pollutants in coastal waters of Gulf of Gdańsk, Southern Baltic. Mar. Pollut. Bull. **49**, 264, **2004**.
27. BOEHM P.D., NEFF J.M., PEGE D.S. Assessment of polycyclic aromatic hydrocarbons exposure in the waters of Prince William Sound after the Exxon Valdez oil spill: 1989-2005. Mar. Pollut. Bull. **54**, 339, **2007**.
28. SCHULZ-BULL D.E., PETRICK G., KANNAN N., DUINKER J.C. Distribution of individual chlorobiphenyls (PCB) in solution and suspension in the Baltic Sea. Mar. Chem. **48**, 245, **1995**.
29. SZLINDER RICHERT J., BARSKA I., MZAERSKI J., USYDUS Z. PCBs in fish from the southern Baltic Sea: levels, bioaccumulation features, and temporal trends during the period from 1997 to 2006. Mar. Pollut. Bull. **58**, 85, **2009**.
30. WOLSKA L. Determination (monitoring) of in surface waters: why an operationally defined procedure is needed. Anal. Bioanal. Chem. **391**, 2647, **2008**.
31. WOLSKA L., GALER K., NAMIEŚNIK J. Transport and speciation of PAH and PCB in a river ecosystem. Anal. Bioanal. Chem. **382**, 1389, **2005**.
32. SAPOTA G. Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in seawater of the southern Baltic Sea. Desalination **162**, 153, **2004**.
33. KONAT J., KOWALEWSKA G. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea – trends and fate. Sci. Total Environ. **280**, 1, **2001**.
34. KOWALEWSKA G., KONAT J. Distribution of polynuclear aromatic hydrocarbons (PAH) in sediments of the southern Baltic Sea. Oceanologia **1**, 83, **1997**.
35. PAZDRO K. Persistent organic pollutants in sediments from the Gulf of Gdańsk. Ann. Set. Environ. Prot. **6**, 63, **2004**.

36. CHRISTIANSEN CH., LEIPE T., WITT G., CHRISTOFFERSEN P.L., LUND-HANSEN L.C. Select elements, PCBs, and PAHs in sediments of the North Sea – Baltic Sea transition zone: sources and transport as derived from the distribution pattern. Geografisk Tidsskrift – Danish Journal of Geography **109**, 81, **2009**.
37. SAPOTA G. Persistent organic pollutants (POPs) in bottom sediments from the Baltic Sea. Oceanol. And Hydrobiol. Studies **4**, 295, **2006**.
38. WITT G., TROST E. Polycyclic aromatic hydrocarbons (PAHs) in sediments of the Baltic Sea and of the German costal waters. Chemosphere **38**, 1603, **1999**.