

Migration of pentachlorophenol in artificial and natural sediments of Puck Bay

by

Joanna Maciak,
Krzysztof Lewandowski,
Elżbieta Niemirycz*

DOI: **10.1515/ohs-2016-0033**

Category: **Original research paper**

Received: **October 1, 2015**

Accepted: **November 30, 2015**

*Department of Marine Chemistry and
Environmental Protection,
Institute of Oceanography, University of
Gdańsk, Al. M. Piłsudskiego 46, 81-378 Gdynia,
Poland*

Abstract

Pentachlorophenol (PCP) is an anthropogenic substance, toxic to humans. The major source of this compound in the environment are wastes from factories producing PCP and materials (textiles, wood) treated with PCP. In 2008, a dossier was prepared to support the inclusion of PCP in Annex I to the Protocol of the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants. The draft decision to add PCP along with its salts (NaPCP) and esters (PCPL) in Annex A of the Stockholm Convention was adopted during the seventh meeting of the Conference of the Parties to the Stockholm Convention in 2015. The aim of present study was to assess the status of contamination in Puck Bay with this harmful substance. The surface bottom sediments of Puck Bay were contaminated with pentachlorophenol to varying degrees, ranging from $17.4 \pm 5.6 \text{ ng g}^{-1} \text{ d.w.}$ to $230.1 \pm 20.8 \text{ ng g}^{-1} \text{ d.w.}$ The majority of samples collected from deepwater areas of Puck Bay were contaminated with PCP above $25 \text{ ng g}^{-1} \text{ d.w.}$ (value of Predicted No Effect Concentration). It has been assessed that bottom currents occurring in Puck Bay can affect sediments deposited at the Gdynia dumping site.

Key words: organochlorine contaminants, toxicity, total organic carbon, bottom sediments, dumping site

* Corresponding author: oceen@ug.edu.pl

Introduction

The outer part of Puck Bay is a shallow reservoir (average depth of 20.5 m) covering the western part of the Gulf of Gdańsk described as a region of exceptional natural beauty (Nowacki 1993a). It is located between the Hel Peninsula and the line connecting Hel with Gdynia as well as stretching further to the south – *Cypel Orłowski* (Orłowo Spit; Kruk-Dowgiałło et al. 2008). The environmental quality status of the Gulf of Gdansk is determined by the outflow of pollutants with the Vistula waters, direct point sources and atmospheric transport (Niemirycz 2008; 2011). Puck Bay is mainly under the influence of the last two factors. The nearest point sources affecting the conditions in the Bay are the Port of Gdynia and its dumping site. The research on bottom sediments of Puck Bay has been undertaken to assess their contamination with pentachlorophenol (PCP), an extremely toxic substance, recently discussed at the Conference of the Parties to the Stockholm Convention in 2015, Geneva (United Nations Environment Programme 2015). In 1991, Europe banned the production and the use of pentachlorophenol (PCP) in e.g. pest control (insects or fungi). In Asia and the USA, however, it is still used in protection of cotton or wood despite clearly harmful effects on the liver, kidneys and the central nervous system (Borysiewicz 2008; Krupanek 2011).

The bottom of Puck Bay is characterized by areas of up to 55 m deep where favorable conditions for the accumulation of PCP can be expected, especially in the fine fraction of silt-clay sediments (Uścińowicz 2011). Similar processes have shaped places of the Bay characterized by a high content of terrigenous components such as iron (Fe_2O_3). Another factor in the migration of PCP are benthic sea currents, causing the movement of sedimentary material.

The main objectives of this study was to assess the PCP contamination in the surface bottom sediments in Puck Bay and to determine factors that are significant for the migration of PCP in the marine environment of the Puck Bay area.

Materials and methods

Study area

The study area included 7 sites located in the outer part of Puck Bay, one site located in the shallowest place of Puck Lagoon (ZP 1) and one located outside the Bay (ZP 7) (Fig. 1). The selection of marine sediment sampling sites in Puck Bay was based on the organic carbon content data (Uścińowicz 2011) as well as

characteristics of the Bay bottom. The study also included samples of bottom sediments collected near the quays of the Port of Gdynia.

Collection and preservation of samples

Samples of bottom sediments were collected using a Van Veen grab during the cruises on board r/v "Oceanograf 2" in 2012 (November) – the Port of Gdynia and in 2013 (June) – Puck Bay. Prior to the analysis, sediment samples were stored in a freezer at a temperature of -21°C , and then air-dried (Wang et al. 2003; Ganeshjeevan et al. 2007; Padilla – Sánchez et al. 2010), sieved (particles larger than 2 mm were removed) and homogenized in a porcelain mortar.

Granulometric analysis

The analysis of sediment grain composition in samples from Puck Bay and the Port of Gdynia was conducted using a sieve analysis (Myślińska 2001; Pempkowiak et al. 2005). Characteristics of bottom sediments were described with the GRADISTAT 5.11 beta program.

Analysis of pentachlorophenol

All the bottom sediment samples were prepared for PCP analysis by 24 h extraction in a Soxhlet apparatus or 40 minutes in an ultrasonic bath of 10 g to 20 g dry sediment (fraction $\phi < 2.00$ mm) with the solution of methanol: Milli-Q water (4:1) and addition of 10% triethylamine. The extracts were cleaned by solid phase extraction (SPE) using Clean-Up C-18 CUC18 ($6\text{ cm}^3\ 500\text{ mg}^{-1}$) columns as described (with minor changes) in Lewandowski et al. (2014). The HPLC analysis was performed using a DIONEX apparatus and the chromatographic conditions were as follows: the thermostat temperature 25°C , the UV-VIS detector (wavelength $\lambda = 254\text{ nm}$), the chromatography column Hypersil GOLD ($250\text{ mm} \times 4.6\text{ mm} \times 5\text{ }\mu\text{m}$), mobile phases: eluent (B) acetonitrile and eluent (A) Milli-Q water, the flow rate $1.0\text{ cm}^3\text{ min}^{-1}$, gradient elution: 5% B for one and a half minute, then B was gradually increased to a maximum of 95% at the nineteenth and a half minute, this gradient was maintained for one and a half minute and returned to the 5% B gradient within the last minutes of the analysis.

Validation and quality parameters of pentachlorophenol analysis

Methanol, Milli-Q water, triethylamine, acetonitrile were of HPLC grade purchased from Avantor

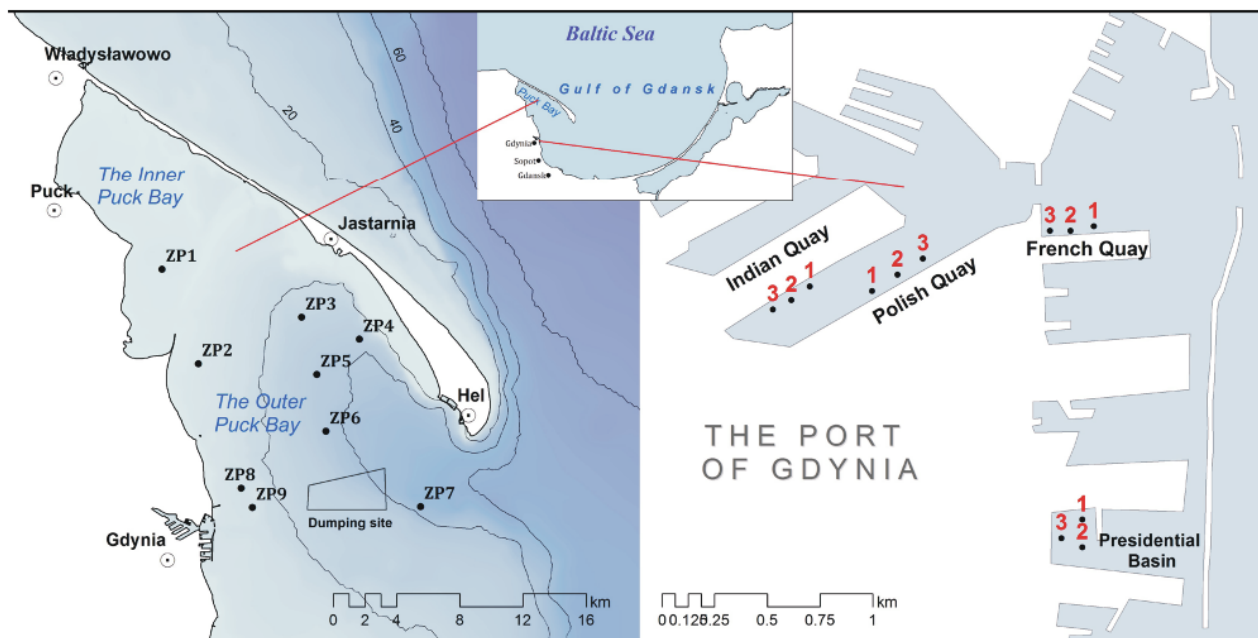


Figure 1

Location of the sampling sites of marine bottom sediments collected from Puck Bay and quays of the Port of Gdynia

Performance Materials (POCH). The linearity of the applied analytical method, based on 6 points, was calculated by Pearson's correlation analysis (correlation coefficient $r = 0.995$). The recovery of each extraction method was determined by adding a defined amount of PCPaq standard (Supelco). The obtained recovery value for extraction in an ultrasonic bath was 75% and 92% for extraction in a Soxhlet apparatus. The limit of quantification (LOQ) for pentachlorophenol analysis was $2.9 \text{ ng g}^{-1} \text{ d.w.}$ and the limit of detection (LOD) was $1.0 \text{ ng g}^{-1} \text{ d.w.}$

Test Microtox® – toxicity assessment

Sediment (fraction $\varphi < 2.00 \text{ mm}$) toxicity was investigated using the Basic Solid Phase Test in accordance with the procedure provided by the producer Azur Environmental Ltd. (Azur Environmental 1998, ASTM 2004). The determined toxicity can be expressed as 30 min EC_{50} values (%) which correspond to the effective concentration of a xenobiotic (solid or liquid) causing a 50% decrease in light emission. Another parameters to express the toxicity are toxicity units (TU), which are an inverse of EC_{50} to facilitate the interpretation of the obtained results, where a higher value of TU means higher toxicity, contrary to EC_{50} values which decrease as toxicity increases (Salizzato et al. 1998; Coxa et al. 2000; Mamindy-Pajany et al. 2012; Witt et al. 2014; Lewandowski et al. 2014; Kobusińska et al. 2014).

Total Organic Carbon (TOC)

The content of organic carbon (TOC) was determined in sediment samples using a Vario TOC analyzer at the Department of Marine Chemistry and Environmental Protection, in accordance with the recommended methodology (Parsons et al. 1985). Details of the analysis (with minor changes), validation and quality parameters are described in Lewandowski et al. (2014). The TOC value in samples is given in % of sediment dry weight (equals $\text{mg g}^{-1} \text{ d.w.}$). Additionally, the content of organic matter expressed as a loss on ignition (LOI) was analyzed (Ciborowski 2010).

Results and discussion

Description of physicochemical parameters of sediments from the study areas

Based on the grain size composition, the sediment type (Table 1) and the percentage content of selected fractions were determined. For the purpose of this publication, only the fraction with a diameter below 0.0625 mm is presented in Table 2 a) and b) as the most important in terms of PCP sorption. The bottom sediments from Puck Bay ZP: 3, 4, 5, 6 and 7 are characterized by a high percentage (ranging from 67.0 to 74.3%) of the silt-clay fraction. In other samples (ZP: 1, 2, 8 and 9) collected near the shore,

Table 1

Description of marine bottom sediment sampling sites in Puck Bay and the Port of Gdynia during the cruise in 2012 and 2013

Station		Latitude	Longitude	The depth of sampled sediment (m)	macroscopic description	Salinity (PSU)	Water temperature (°C)
Puck Bay	ZP1	54°41'30"N	18°30'17"E	3.7	fine-grained sand, gray, silty, shells	6.8	17.5
	ZP2	54°38'12"N	18°32'50"E	5.3	fine-grained sand, small shells	6.8	16.4
	ZP3	54°39'42"N	18°38'49"E	28.1	gray, very coarse silt,	6.8	15.0
	ZP4	54°39'14"N	18°42'32"E	36.3	very coarse silt, black,	6.8	15.2
	ZP5	54°37'49"N	18°39'48"E	40.0	very coarse silt, gray, the smell of hydrogen sulfide	6.8	15.0
	ZP6	54°35'57"N	18°40'14"E	41.1	very coarse silt, gray, the smell of hydrogen sulfide	6.8	15.4
	ZP7	54°33'10"N	18°46'23"E	54.1	very coarse silt, gray, smell of hydrogen sulfide	6.7	16.0
	ZP8	54°33'53"N	18°35'27"E	11.2	fine-grained sand, shells	6.4	15.9
	ZP9	54°33'28"N	18°36'36"E	12.2	fine-grained sand, shells	6.4	16.0
Port of Gdynia	French Quay	54°32'03"N	18°33'04"E	13.0	medium-grained sand, gray, smell of oil, shells	6.0	7.8
	Indian Quay	54°31'53"N	18°31'56"E	11.0	medium-grained sand, black, smell of oil, lots of shells, coal	6.0	7.5
	Polish Quay	54°31'51"N	18°32'11"E	13.0	medium-grained sand, black, smell of oil, a lot of shells	6.0	7.5
	Presidential Basin	54°31'14"N	18°33'10"E	10.0	fine-grained sand, black, smell of oil	6.0	7.5

Table 2

Physicochemical parameters and toxicity (*Microtox*[®] test) expressed in toxicity units (TU) of the bottom sediment samples collected from Puck Bay and the Port of Gdynia

a)

Puck Bay									
Sample name	ZP1	ZP2	ZP3	ZP4	ZP5	ZP6	ZP7	ZP8	ZP9
LOI [%]	1.96	0.37	16.25	15.75	14.55	11.47	8.09	1.15	1.11
TOC [%]	0.52	0.09	5.46	5.30	4.87	3.55	3.58	0.52	0.35
TU	0.4	0.1	77.3	105.2	81.1	40.9	26.8	4.0	2.4
Fraction $\phi < 0.0625$ mm [%]	9.4	0.3	74.3	74.3	70.3	67.4	67.0	9.2	9.4

b)

Port of Gdynia												
Sample name	I 1	I 2	I 3	P 1	P 2	P 3	F 1	F 2	F 3	PB 1	PB 2	PB 3
LOI [%]	1.23	5.00	6.80	6.97	6.42	3.88	2.08	1.86	4.64	7.15	13.26	13.34
¹ TOC [%]	0.31	2.16	3.29	3.41	3.04	1.52	0.65	0.56	1.95	3.53	6.81	7.41
TU	0.5	22.5	20.2	21.0	n.a.	n.a.	1.3	1.3	0.7	n.a.	165.5	310.0
Fraction $\phi < 0.0625$ mm [%]	1.0	5.8	4.4	6.8	6.0	1.4	0.8	1.1	2.0	4.6	10.6	8.2

Names of quays: I – Indian; P – Polish; F – French; PB – Presidential Basin

LOI – loss on ignition, TOC – Total organic carbon, ¹TOC in sediments from the Indian, Polish and French Quays was calculated according to the equation $y = 0.237x^{1.373}$; $r = 0.8844$ for correlation between values of LOI and TOC for the Port of Gdansk (Lewandowski et al. 2014; unpublished observations), n.a. – not analyzed

a similar percentage content of this fraction (0.3-9.4%) was determined as in the harbor sediments. Based on the interpretation of statistical analysis (GRADISTAT 5.11 beta program) of the grain size distribution in sediments from the Port of Gdynia, the following was determined: all the collected material was poorly sorted, the main fraction was sand (89-98%) and the silt-clay fraction represented a small admixture (1-11%) (Table 2 b). On the one hand, these values are similar to the data presented in the SMOCS project report (Sapota et al. 2012), but on the other hand, they are much lower than those presented by Radke et al. (2012). The differences show how strongly the environment of harbor sediments can be disturbed.

The TOC concentrations in the sediments from Puck Bay and the Port of Gdynia varied in a wide range (Table 2 a and b). Lower values (0.09-0.52 and 0.31-1.52, respectively) were obtained for sandy sediments collected from shallow coastal areas (samples ZP 1, 2, 8 and 9) or those located in the vicinity of the main harbor canal (French Quay 1, 2; Indian Quay 1 and Polish Quay 3) (Fig. 1). Significant amounts of TOC (3.55-5.46 and 3.04-7.01, respectively) were determined for sediments collected from greater depths (samples ZP 3, 4, 5, 6 and 7) or further off the main harbor canal (Presidential Basin, Indian Quay 2, 3 and Polish Quay 1, 2) in the Port of Gdynia. The highest value of total organic carbon (7.41%) was determined in sediments

from the Presidential Basin of the Port of Gdynia, which is probably related to the contamination with oil compounds (Uścińowicz 2011).

The low organic carbon content in sandy coastal sediments is not the effect of low intensity of carbon release into the bottom sediments but the result of rapid circulation of matter (Huettel et al. 1998). A regional and seasonal difference in organic carbon content occurs alike in areas of shallow and deepwater sediments (Uścińowicz 2011). In Puck Bay, there are areas with a relatively high TOC content (Table 3). The process of pre-sedimentation of the carbon-rich organic matter occurs there through its transportation by rivers and production in the basin as a result of intensive supply of biogenic salts. The distribution of TOC concentration depends on the seabed topography and the related circulation of currents (Uścińowicz 2011). A positive correlation was determined for Puck Bay and the Port of Gdynia between the content of total organic matter expressed as LOI and TOC content ($r = 0.98$). According to the above data, the increased accumulation of PCP can be expected in sediment collected from sites ZP 3, 4, 5, 6, 7, and part of the quays located further away from the main channel of the Port of Gdynia.

Toxicity assessment

The overall toxicity was an additional parameter measured and used in the assessment of the analyzed sediments. The influence of bottom sediment samples

(NaCl extracts) on vital functions of *Vibrio fischeri* bacteria expressed as values of toxicity units (TU) is presented in Table 2 a and b. The toxic effect (values above 25 TU, according to Sawicki et al. 2007) was determined for sediment samples from Puck Bay, in which the content of the silt-clay fraction (>70%) and TOC (>3.5%) was significant. Sandy sediments of Puck Bay showed no acute toxicity. Bottom sediments collected close to the quays of the Port of Gdynia (at which regular dredging works are carried out) and analyzed for the content of PCBs, PAHs and metals did not show strong toxicity either ($TU < 25$). Nonetheless, the analysis of samples from Indian 2, 3 and Polish 1 quays revealed a low-toxic (between 10 and 25 TU) effect on bacteria. Reference samples from the Presidential Basin (not tested regularly), which contained the largest amounts of TOC and the fine fraction (<0.0625 mm) were described as strongly toxic ($TU > 100$). In some publications (Łukawska-Matuszewska et al. 2009), a strong correlation between high values of TU and the content of fine fraction (<0.0625 mm) was explained by adsorption of *Vibrio fischeri* on sediment grains. This thesis is confirmed or disproved after the correlation between the toxicity and the content of total carbon (TC) is determined. The low value of the correlation coefficient means that the sediment granulation affects the toxicity value. In this study, the effect of organic contaminants was observed for sediment samples collected in the Port of Gdynia and Puck Bay, because values of toxicity were strongly correlated ($r = 0.90$ and $r = 0.94$, respectively).

Table 3

The minimum and maximum levels of total organic carbon (TOC) in marine sediments and selected waters of the Baltic Sea and other regions of the world

Region	TOC (%)	Layer of sediment (cm)	Literature
The Gulf of Riga	0.53-6.32	0-1	Carman et al. 1996
Curonian Lagoon	0.40-6.64	0-5	Emelyanov Eds. 2002
Vistula Lagoon	0.50-10.20	0-10	Uścińowicz & Zachowicz 1996; Emelyanov Eds. 2002; Chechko & Blazhchishin 2002
Puck Lagoon	0.23-8.18	0-2	Uścińowicz 2008
Puck Bay	0.10-7.98	0-2	Uścińowicz 2008
Puck Bay	0.24-6.21	0-5	Witt et al. 2014
Puck Bay	0.09-5.46	0-5	Own study
Lagoon of Szczecin	0.41-13.10	0-1	Miltner & Emeis 2001; Emeis et al. 2002
Gulf of Gdańsk	3.62-6.20	0-5	Niemirycz 2011; Witt et al. 2014
Gulf of Gdańsk	0.03-8.53	0-5	Lubecki et al. 2010
Zhifu Bay, China	0.35-0.91	0-2	Wang et al. 2015
Jiaozhou Bay, China	0.07-0.45	0-2	Dai et al. 2007
Zhelin Bay, China	0.38-1.28	0-2	Wang et al. 2013
Chesapeake Bay, the USA	0.75-3.46	0-5	Zimmerman & Canuel 2000; Bratton et al. 2003
Port of Gdańsk	0.80-8.26	0-5	Lewandowski et al. 2014
Port of Gdynia	0.31-7.41	0-5	Own study

with TOC content, which is 80-90% of the TC mass (Niemirycz 2007).

Distribution of PCP concentrations in bottom sediments of Puck Bay and the Port of Gdynia

PCP was determined in the surface bottom sediments of Puck Bay and the Port of Gdynia in varying concentration (Table 4). These are the first data on the concentration of the researched compound in these areas. The values of PCP concentration in sediment samples from Puck Bay ranged from <LOD to $230.1 \pm 20.8 \text{ ng g}^{-1}$ expressed in sediment dry weight. The highest concentration of PCP was determined in the sediments collected from the deeper area of Puck Bay (Table 1). An exception was the sample of sediment collected at site ZP 3, the value of which was below the limit of detection, even though it was collected from a considerable depth and contained a significant amount of TOC and the fraction <0.0625 mm. Sample ZP 7 (collected out of Puck Bay) was characterized by the highest degree of contamination with PCP ($230.1 \pm 20.8 \text{ ng g}^{-1}$ d.w.) and a lower value of TOC. The PCP concentration in this region is significantly above the accepted limit for the Baltic Sea, i.e. 25 ng g^{-1} d.w. recognized as Predicted No Effect Concentration (PNEC) (Muir & Deluge 1999). Compared to the other study sites of Puck Bay, site ZP 7 is located (about 2 km to the east) within the closest proximity to the Gdynia dumping site – a storage place for dredged spoil coming from port channels and basins.

The range of PCP concentrations determined in bottom sediments of the Port of Gdynia – from <LOD

to $25.0 \pm 3.6 \text{ ng g}^{-1}$ d.w. – is similar to that determined in the Port of Gdańsk, i.e. from <LOD to 12.4 ng g^{-1} d.w. (Lewandowski et al. 2014). This indicates a similar contribution of PCP sources in these areas. It should be pointed out that the Port of Gdańsk is located in the estuary of the Dead Vistula, i.e. an arm of the Vistula, which can transport PCP to harbor waters. Dmitruk et al. (2008) analyzed samples of bottom sediments collected at the 800th km (Cracov), the 405th km (Warsaw) and the 13th km (Gdańsk) of the Vistula. The average concentration of PCP was 1.2 ng g^{-1} d.w. It appears from the above data that the Vistula River (through the Dead Vistula) has a minor impact on PCP concentration in the Port of Gdańsk. Despite low concentrations of PCP in sediments of the harbor, which represents a dynamic environment strongly affecting the surface layer of bottom sediments, it should be kept in mind that this material is removed to the sea as dredged spoil. This operation may result in higher availability of PCP in the marine environment. Dredged spoil is analyzed for a number of substances considered as toxic, but not PCP, even though some characteristics of POPs were confirmed for this compound (Borysiewicz 2008; Subramanian 2010; United Nations Environment Programme 2015). The content of fine fraction (<0.0625 mm), total organic carbon and mechanical mixing of sediments close to the studied quays had a major impact on the differences in PCP concentrations in bottom sediments of Puck Bay (natural environment) and the Port of Gdynia (anthropogenic environment). The obtained range of PCP concentration in Puck Bay was similar to that presented in the above-mentioned publications and other papers on the content of PCP in sediments of other regions of the Baltic Sea, Europe ($15\text{--}200 \text{ ng g}^{-1}$ d.w. Muir & Eduljee 1999) or the nearby North Sea ($26.5\text{--}200 \text{ ng g}^{-1}$ d.w. Eurochlor 1999).

Due to the coastline structure in Puck Bay and Puck Lagoon, the authors of this paper assume that the value of PCP concentrations may be affected by the Vistula and the bottom currents. These two areas are separated by the Rybitwia Shoal which causes the formation of different circulation systems in each of them. In Puck Bay, vectors of currents also induce the formation of circulation dominated by currents moving in a clockwise direction. The average currents flow within its coastal waters in the northern directions near Gdynia and Rybitwia Shoal and to the east, near the Hel Peninsula.

Long-term observations of bottom currents in Puck Bay gave rise to the conclusion that there is a current (upwelling type) opposite to the surface current with an average speed of 4 cm s^{-1} flowing into the Rybitwia Shoal (Nowacki 1993b). The speed of bottom currents

Table 4

The concentration of PCP in surface sediments of Puck Bay and the Port of Gdynia (fraction $\phi < 2.00 \text{ mm}$)

Name of samples n = 28	ng g ⁻¹ d.w. ± standard deviation
ZP1	<LOD
ZP2	<LOD
ZP3	<LOD
ZP4	131.3 ± 10.7
ZP5	139.1 ± 15.4
ZP6	86.4 ± 11.8
ZP7	230.1 ± 20.8
ZP8	17.4 ± 5.6
ZP9	<LOD
Indian 3	<LOD
Polish 2	10.6 ± 2.2
Polish 3	10.5 ± 2.8
French 3	<LOD
Presidential Basin 2	25.0 ± 3.6

n – number of results

increases with increasing salinity and decreasing depth. The coastline structure in Puck Bay and its exposure to the wind result in a varying speed of the currents and the associated flows, depending on the wind direction (south, south-east). The vectors of currents in Puck Lagoon indicate the existence of two systems of circulation, resulting from the existence of the two major morphological forms. The average vectors of currents in Puck Bay prove the dominance of the inflow and transport of waters in the direction of Puck Bay (Nowacki 1993b). The incoming waters from the Gulf of Gdańsk into Puck Bay are characterized mainly by higher salinity. Sometimes, however, these waters are a mixture of seawater and the Vistula waters, which results in the reduced salinity (Nowacki 1993c).

The highest concentration of PCP in bottom sediments of the Gdańsk Basin was obtained for site ZP 7, which is located to the east of the Gdynia dumping site. Based on the conducted studies, it seems that the material stored at the dumping site may be spread by the bottom currents into areas where accumulation processes occur. Interdisciplinary research, including hydrodynamic modeling, will confirm the hypothesis. Based on the maps of surface currents (Fig. 2) and salinity, generated by the Ecohydrodynamic Model of the Gulf of Gdańsk (<http://model.ocean.univ.gda.pl/>, University of Gdańsk), it can be concluded that the waters of the Vistula in certain months (June – September) have a strong impact on the outer part (north-eastern) of Puck Bay and a weaker effect on its inner part. Consequently, the freshwater mixes with saltwater, which can lead to faster sedimentation of matter.

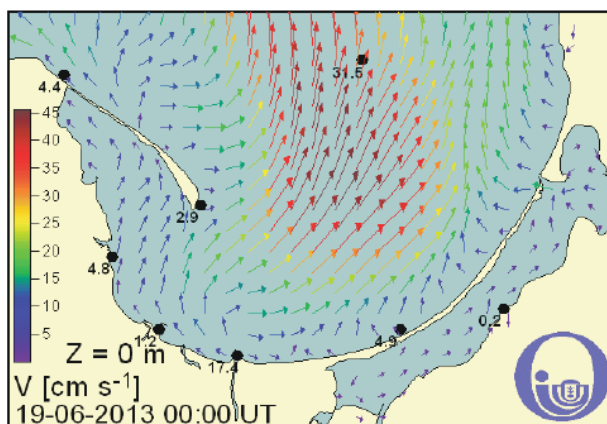


Figure 2

Map of surface currents occurring in the Gulf of Gdańsk on 19th of September 2013 generated by the Ecohydrodynamic Model (<http://model.ocean.univ.gda.pl/>, University of Gdańsk)

Conclusions

- It was determined that PCP occurs in the surface bottom sediments of Puck Bay in varying concentration, ranging from $17.4 \pm 5.6 \text{ ng g}^{-1} \text{ d.w.}$ to $230.1 \pm 20.8 \text{ ng g}^{-1} \text{ d.w.}$ The material collected from the deeper parts of Puck Bay was characterized by PCP concentrations significantly higher than the PNEC value of $25.0 \text{ ng g}^{-1} \text{ d.w.}$, which is considered as not causing adverse effects.
- PCP was identified in the bottom sediments of the Port of Gdynia but its concentration did not exceed the PNEC value.
- On the basis of the conducted toxicity studies (test *Microtox*®), it was found that deepwater sediments of Puck Bay were toxic. In the case of the studied sediments from the Port of Gdynia, a significant harmful effect on bacteria *Vibrio fischeri* was determined only for samples from the Presidential Basin. The toxicity of sediments from both study areas, expressed as TU values, was significantly correlated with the content of total organic carbon and the fraction $<0.0625 \text{ mm}$.
- Bottom currents occurring in Puck Bay can induce migration of sediments from the Gdynia dumping site to the deepest areas of Puck Bay. The high concentration of PCP in sediments collected from the deepwater areas of Puck Bay (Table 1) probably confirms this hypothesis.

Acknowledgements

This research was funded from the resources of the project financed by the National Science Center, no. 0604/B/P01/2011/40 under the supervision of Prof. Elżbieta Niemirycz and within the framework of the Research project for Ph.D. students and young scientists (project no. 538–G235–B552–14 and 538–G235–B879–15). The authors would like to thank Prof. Jan Jędrasik and Ph.D. Katarzyna Łukawska-Matuszewska from the Institute of Oceanography at the University of Gdańsk for providing very valuable help and Ph.D. student Maria Witt for the time spent on preparing maps of the study area.

References

- ASTM (American Society for Testing and Materials) (2004). Standard Test Method for Assessing

- the Microbial Detoxification of Chemically Contaminated Water and Soil Using a Toxicity Test with a Luminescent Marine Bacterium. ASTM D5660-96, USA.
- Azur Environmental (1998). Microtox Basic Solid-phase Test (Basic SPT). Carlsbad, CA, USA.
- Borysiewicz, M. (2008). *Pentachlorophenol, Dossier prepared in support of a proposal of pentachlorophenol to be considered as a candidate for inclusion in the Annex I to the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants (LRTAP Protocol on POPs)*. Institute of Environmental Protection, Warsaw, Poland.
- Bratton, J.F., Colman, S.M. & Seal, II R.-R. (2003). Eutrophication and carbon sources in Chesapeake Bay over the last 2700 yr: human impacts in context. *Geochim. Cosmochim. Acta* 67: 3385-3402.
- Carman, R., Aigars, J. & Larsen, B. (1996). Carbon and nutrient geochemistry of surface sediments of the Gulf of Riga, Baltic Sea. *Mar. Geol.* 134: 57-76.
- Chechko, V.A. & Blazhchishin, A.I. (2002). Bottom sediment of the Vistula Lagoon of the Baltic Sea. *Baltica* 15: 13-22.
- Ciborowski, T. (2010). Substancja organiczna. In J. Bolałek (Ed.), *Fizyczne, biologiczne i chemiczne badania morskich osadów dennych* (pp. 287-289). Wyd. Uniwersytetu Gdańskiego.
- Coya, B., Marañón, E. & Sastre, H. (2000). Ecotoxicity assessment of slag generated in the process of recycling lead from waste batteries. *Resources Conservation and Recycling* 29: 291-300. ISSN: 0921-3449. DOI: 10.1016/S0921-3449(00)00054-9.
- Dai, J., Song, J., Li, X., Yuan, H., Li, N. et al. (2007). Environmental changes reflected by sedimentary geochemistry in recent hundred years of Jiaozhou Bay, North China. *Environ. Pollut.* 145: 656-667.
- Dmitruk, U., Piascik, M., Taboryska, B. & Dojlido, J. (2008). Persistent Organic Pollutants (POPs) in Bottom Sediments of the Vistula River, Poland. *Clean* 36(2): 222-229. DOI: 10.1002/clen.200700107.
- Emeis, K., Christiansen, C., Edelvang, K., Jahmlich, S., Kozuch, J. et al. (2002). Material transport from the near shore to the basinal environment in the southern Baltic Sea. II: Synthesis of data on origin and properties of material. *J. Mar. Syst.* 35: 151-168.
- Emelyanov, E.M. (2002). *Geology of the Gdańsk Basin, Baltic Sea*. Yantarny Skaz.
- Euro Chlor Risk Assessment for the Marine Environment (1999). Pentachlorophenol. OSPARCOM Region - North Sea. Draft.
- Ganeshjeevan, R., Chandrasekar, R., Kadigachalam, P. & Radhakrishnan, G. (2007). Rapis, one-pot derivatization and distillation of chlorophenols from solid samples with their on-line enrichment. *J. Chromatogr. A* 1140: 168-173.
- Huettel, M., Ziebis, W., Forster, S. & Luther III, G.W. (1998). Advective transport affecting metal and nutrient distributions and interfacial fluxes in permeable sediments. *Geochim. Cosmochim. Acta* 62: 613-631.
- Kobusińska, M., Skauradszun, M. & Niemirycz, E. (2014). Factors determining the accumulation of pentachlorophenol - a precursor of dioxins in bottom sediments of the Gulf of Gdańsk (Baltic Sea). *Oceanological and Hydrobiological Studies* 43(2): 154-164. DOI:10.2478/S13545-014-0128-9.
- Kruk-Dowgiałło, L. & Szaniawska, A. (2008). Gulf of Gdansk and Puck Bay. In U. Schiewer (Ed.), *Ecology of Baltic Coastal Waters* (pp. 139-162). Ecological Studies, vol. 197.
- Krupanek, J., Krzysztofik, E., Zielonka, U., Piasecka, J., Pilch, A. et al. (2011). *Summary report POLAND - Work package 4: Identification of sources and estimation of inputs/impacts on the Baltic Sea*, Institute for Ecology of Industrial Areas.
- Lewandowski, K., Witt, M., Kobusińska, M. & Niemirycz, E. (2014). Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and pentachlorophenol (PCP) in bottom sediments of the Port of Gdańsk. *Oceanological and Hydrobiological Studies* (43)3: 312-323. DOI:10.2478/s13545-014-0146-7.
- Lubecki, L. & Kowalewska, G. (2010). Distribution and fate of polycyclic aromatic hydrocarbons (PAH) in recent sediments from the Gulf of Gdańsk (SE Baltic). *Oceanologia* 52(4): 669-703.
- Łukawska-Matuszewska, K., Burska, D. & Niemirycz, E. (2009). Toxicity Assessment by Microtox® in sediments, pore waters and sediment saline elutriates in the Gulf of Gdańsk (Baltic Sea). *Clean* 37(7): 592-598. DOI: 10.1002/clen.200900021.
- Mamindy-Pajany, Y., Geret, F., Roméo, M., Hurel, Ch. & Marmier, N. (2012). Ex situ remediation of contaminated sediments using mineral additives: Assessment of pollutant bioavailability with the Microtox solid phase test. *Chemosphere* 86: 1112-1116. DOI: 10.1016/j.chemosphere.2011.12.001.
- Miltner, A., & Emeis, K.-C. (2001). Terrestrial organic matter in surface sediments of the Baltic Sea, Northwest Europe, as determined by CuO oxidation. *Geochim. Cosmochim. Acta* 65(8): 1285-1299.
- Muir, J. & Eduljee, G. (1999). PCP in freshwater and marine environment of the European Union. *The Science of the Total Environment* 236: 41-56. ISSN: 0048-9697.
- Myślińska, E. (2001). *Laboratoryjne badanie gruntów*. Warszawa: Wydawnictwo Naukowe PWN. 277s.
- Niemirycz, E. & Jankowska, D. (2011). Concentrations and profiles of PCDD/Fs in sediments of major Polish rivers and the Gdansk Basin – Baltic Sea. *Chemosphere* 85: 525-532. DOI:10.1016/j.chemosphere.2011.08.014.
- Niemirycz, E. (2008). *Halogenated organic compounds in the environment in relation to climate change*, Bibl. Ochrony Środowiska, Warszawa. ISBN-978-83 61227-00-7.
- Niemirycz, E., Nitchthausen, J., Staniszevska, M., Nałęczy-Jawacki, G. & Bolałek, J. (2007). The Microtox® biological test: Application in toxicity evaluation of surface waters and sediments in Poland. *Oceanological and Hydrobiological*

- Studies* 36(4): 151-163. DOI:10.2478/v10009-007-0030-5.
- Nowacki, J. (1993a). Morfometria zatoki. In K. Korzeniewski (Ed.), *Zatoka Pucka* (pp. 71-78). Instytut Oceanografii UG, Gdańsk.
- Nowacki, J. (1993b). *Cyrkulacja i wymiana wód*. In K. Korzeniewski (Ed.), *Zatoka Pucka* (pp. 181-206). Instytut Oceanografii UG, Gdańsk.
- Nowacki, J. (1993c). *Termika, zasolenie i gęstość wody*. In K. Korzeniewski (Ed.), *Zatoka Pucka* (pp. 71-78). Instytut Oceanografii UG, Gdańsk.
- Padilla-Sanchez, J.A., Plaza-Bolanos, P., Romero-Gonzalez, R., Garrido-Frenich, A. & Martinez, V. (2010). Application of a quick, easy, cheap, effective, rugged and safe-based method for the simultaneous extraction of chlorophenols, alkylphenols, nitrophenols and cresols in agricultural soils, analyzed by using gas chromatography-triple quadrupole-mass spect. *J. Chromatogr A*. 1217: 5724-31.
- Parsons, T.R., Maaita, Y. & Lalli, C.M. (1985). A Manual of Chemical and Biological Methods for Seawater Analysis, Pergamon Press, Oxford.
- Pempkowiak, J., Świdarska, R., Piaskowski, K. & Wojnicz, M. (2005). *Chemia morza: przewodnik do ćwiczeń laboratoryjnych*. Koszalin: Wydawnictwo Uczelniane Politechniki Koszalińskiej. 128.
- Radke, B., Wasik, A., Jewell, L.-L., Piketh, S., Pączek, U. et al. (2012). Seasonal changes in organotin compounds in water and sediment samples from the semi-closed Port of Gdynia. *Science of the Total Environment* (441): 57-66. DOI: 10.1016/j.scitotenv.2012.09.006.
- Salizzato, M., Pavoni, B., Ghirardini, A.V. & Ghetti, P.F. (1998). Sediment toxicity measured using *Vibrio fischeri* related to the concentrations of organic (PCBs, PAHs) and inorganic (metals, sulphur) pollutants. *Chemosphere* 36: 2949-2968. DOI: 10.1016/S0045-6535(98)00001-0.
- Sapota, G., Dembska, G. & Bogdaniuk, M. (2012). *Contamination in sediments from the Baltic Sea region - situation and methods*. Project - Sustainable Management of Contaminated Sediments.
- Sawicki, J., Nałęcz-Jarecki, G., Mankiewicz-Boczek, J., Izydorczyk, K., Sumorok, B. et al. (2007). *Kompleksowa analiza ekotoksykologiczna wód powierzchniowych*. ZBŚAM, Project of MNiI nr 2 P05F 056 28, 2005-2007. Warszawa. (In Polish).
- Subramanian, B., Namboodiri, V., Khodadoust, A.-P. & Dionysiou, D.-D. (2010). Extraction of pentachlorophenol from soils using environmentally benign lactic acid solutions. *Journal of Hazardous Materials* 174: 263-269. DOI: 10.1016/j.jhazmat.2009.09.046.
- United Nations Environment Programme (2015). Report of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants on the work of its seventh meeting, 4-15 May 2015 Geneva, Switzerland.
- Uścińowicz, S. (2011). *Geochemia osadów powierzchniowych Morza Bałtyckiego*. Państwowy Instytut Geologiczny-Państwowy Instytut Badawczy. Warszawa.
- Uścińowicz, S. (2008). *Rozpoznanie i wizualizacja budowy geologicznej Zatoki Gdańskiej dla potrzeb gospodarowania zasobami naturalnymi*. Centr. Arch. Geol. Państw. Inst. Geol., Oddz. Geologii Morza, Gdańsk.
- Uścińowicz, S. & Zachowicz, J. (1996). Atlas geochemiczny Zalewu Wiślanego. Państw. Inst. Geol., Warszawa.
- Wang, L., Huang, W., Shao, X. & Lu, X. (2003). An organic solvent-free microwave-assisted extraction of some priority pollutants of phenols in lake sediments. *Anal. Sci.* 19: 1487-90.
- Wang, Z.-H., Feng, J. & Nie, X.-P. (2015). Recent environmental changes reflected by metals and biogenic elements in sediments from the Guishan Island, the Pearl River Estuary, China. *Estuarine, Coastal and Shelf Science* 164: 493-505.
- Wang, Z.-H., Feng, J., Jiang, T. & Gu, Y.-G. (2013). Assessment of metal contamination in surface sediments from Zhelin Bay, the South China Sea. *Marine Pollution Bulletin*, 76: 383-388.
- Witt, M., Kobusińska, M., Maciak, J. & Niemirycz, E. (2014). Geostatistical methods for estimation of toxicity of marine bottom sediments based on the Gdańsk Basin area. *Oceanological and Hydrobiological Studies* 43(3): 247-256. DOI: 10.2478/s13545-014-0139-6.
- Zimmerman, A.R. & Canuel, E.A. (2000). A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. *Mar. Chem.* 69: 117-137.