

Polychlorinated Biphenyls (PCBs) in Blue Mussels (*Mytilus edulis* L.) in the Danish Straits and Southeastern Baltic Sea

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Received: 6 July 2009

Accepted: 30 November 2009

Abstract

The aim of our study was to estimate the concentrations of polychlorinated biphenyls (PCBs) in blue mussels (*Mytilus edulis*) originating from the Danish Straits and southeastern parts of the Baltic Sea, collected between 2003 and 2004. The samples taken from the ferry harbour of Gedser contained the highest amount of PCBs among all places analyzed ($289 \pm 61.6 \text{ ng g}^{-1}$ wet weight), while in case of the Polish coast the highest concentration of these compounds was detected in samples coming from Gdynia Orłowo ($117 \pm 25.3 \text{ ng g}^{-1}$). PCBs were not detected in the samples taken from Copenhagen (municipal beach), while the lowest concentration of these compounds on the Polish side was discovered in samples coming from Kuźnica ($8 \pm 5.06 \text{ ng g}^{-1}$). It was also proven that blue mussels from the area of the Danish Straits, except for the ferry harbour of Gedser, are less contaminated with PCBs than those coming from the southeastern Baltic. In the samples taken from Gdańsk Bay ($59 \pm 53.0 \text{ ng g}^{-1}$) PCBs were detected, while in the samples coming from the open sea the PCB level was $23 \pm 10.7 \text{ ng g}^{-1}$. The obtained results indicate that the vicinity of ports and cities influences concentrations of PCBs in blue mussels. The results confirm usability of blue mussel in the research concerning levels of PCB pollution of the Baltic Sea environment.

Keywords: Baltic Sea, polychlorinated biphenyls (PCBs), blue mussel

Introduction

Polychlorinated biphenyls (PCBs) are synthetic, aromatic compounds belonging to the category of persistent organic pollutants causing serious damage to the environment. In 2001 in the Convention on Persistent Organic Pollutants they were classified as one of the most toxic xenobiotics. The features of PCBs, including lipophilicity, chemical stability and resistance to degradation cause them to be subject to bioaccumulation in organisms and biomagnification in food chains [1]. That is why, in spite of the prohibition of production and limitations in the use of these compounds in

many countries – including Poland and all other Baltic countries – they are still present in ecosystems and can constitute a real danger.

They are transported to the Baltic Sea by air, via river tributaries, by superficial draining, and due to penetration from local sources [2-5]. The Baltic Sea is particularly exposed to pervasion of pollution from land. The danger is related to the shape and the inland position of the Baltic surrounded by nine highly industrialized countries. This water reservoir is characterized by a relatively small surface area as compared to the surface of the drainage basin area, inhabited by population of almost 150 millions. Moreover, there are about 60 highly industrialized cities situated on its coasts [3, 6]. The Baltic is a closed reservoir separated from

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the Ocean by narrow, shallow and meandering straits that hinder water flow. It is estimated that total Baltic water exchange is slow and takes place every 25-30 years. Another limitation for the oceanic water inflow to the Baltic is significant shallowing of the Danish Straits (where average depth is only 19 meters) and a big difference between the salinity levels of the North and Baltic seas. All these factors cause the pollutants – including PCBs – arriving to the Baltic from surrounding land areas to be deposited there and included in food chains of this ecosystem.

The toxic effect of PCBs was demonstrated in three species of seals living in the Baltic: Ringed Seal (*Pusa hispida*), Common Seal (*Phoca vitulina*), and Grey Seal (*Halichoerus grypus*). The results of the contamination are some pathological changes in the uterus that include knitting of the walls and closing of the uterine cervix, which in extreme cases can cause infertility [7]. PCBs also have toxic effects on many species of sea invertebrates such as sea stars, polychaetes [8], amphipods [9], shrimp, or crabs [10-12]. Aroclor 1242 and 1254 given to blue mussel (*Mytilus edulis* L.) slows down the byssus filaments formation process [13] and also causes limitation in consumption and an increase in the respiration rate [14]. Blue mussels, being hard-bottom filter-feeders significantly modify the flow of polychlorinated biphenyls in the marine ecosystem, especially by increasing the net deposition of PCBs to the bottoms and by constituting a significant source of contaminants to fish and other species that feed on blue mussels [15, 16]. Bivalves, including blue mussels, due to the ability of filtering large amounts of water, are organisms that relatively quickly react to the changes of PCB concentrations in the environment, and the concentration of the xenobiotic in their bodies reflects the level of local water pollution. Therefore, they are considered useful bioindicators [17-20].

The aim of the following paper was to estimate the current level of pollution with polychlorinated biphenyls of the blue mussel in different areas of the Baltic Sea, in particular along Polish and Danish Coasts, as well as to estimate pollution changes in the Baltic waters by comparing obtained results with those from previous years.

Study Areas, Materials, Methods

The samples were collected between July and August in 2003-04 at four points along the Danish coast (positions 1-4) and nine points along the middle and eastern part of the Polish coast (positions 5-13) (Fig. 1). Blue mussels were dug out from a depth of 5-30 meters and various distances from land. The collected samples were kept at -20°C until analysis. Each sample was the extract from one specimen of blue mussel. The levels of PCBs in the samples were calculated in reference to wet weight. The total number of collected mussels (samples) was 136 (Table 1).

The extraction of PCBs from the analyzed material was done using methods suggested by the National Institute of Hygiene (Państwowy Zakład Higieny – PZH) [21-23].

Hexane extracts from blue mussels were treated with KOH + C₂H₅OH, temp. 80-90°C and then with C₂H₅OH: H₂O (1:1, - v/v). Obtained solution was extracted with 3 ml. volumes of n-hexane three times. The mixed n-hexane volumes were treated with H₂O + H₂SO₄ + K₂Cr₂O₇ and heated for 30 min., temp. >90°C. After cooling, the sample volume was set to 1 ml., and 9 ml. of distilled water was added. The obtained extract was injected into the GC. Marking the remains of PCBs in the analyzed material was done with the use of GC – ECD Unicam series 610 with capillary column BPX – 5 (non polar), length 30 m., film thickness 0.25



Fig. 1. Sample locations: 1 – Skagerrak, 2 – Gilleleje (Kattegat), 3 – Copenhagen, 4 – Gedser, 5 – Gdańsk Bay, 6 – Gdynia Orłowo – coast, 7 – Gdynia Orłowo, 8 – Jastarnia, 9 – Kuźnica, 10 – Jastrzębia Góra, 11 – Łeba, 12 – Czołpino, 13 – Jarosławiec.

Table 1. Mean level of concentration of PCBs in blue mussels (wet weight), distance between the places where the samples were taken and cities and ports.

Position (number of samples)	Distance from ports and cities (km)	PCBs $\text{ng g}^{-1} \pm \text{S.D.}$ range $x - y$
1. Skagerrak (20)	65	6 ± 6.1 0 – 18
2. Kattegat (Gilleleje) (20)	30	9 ± 8.3 0 – 20
3. Copenhagen (8)	0	n.d.
4. Gedser (8)	0	289 ± 61.6 228 – 412
5. Gdańsk Bay (10)	18	45 ± 48.8 12 – 140
6. Gdynia Orłowo – coast (5)	5	117 ± 25.3 88 – 162
7. Gdynia Orłowo (10)	9	16 ± 3.6 12 – 22
8. Jastarnia (10)	18	15 ± 4.5 10 – 24
9. Kuźnica (10)	20	8 ± 5.06 0 – 16
10. Jastrzębia Góra (5)	8	36 ± 8.8 22 – 46
11. Łeba (10)	13	29 ± 5.6 22 – 42
12. Czołpino (10)	24	27 ± 5.1 22 – 40
13. Jarosławiec (10)	21	15 ± 7.8 10 – 30

n.d. – not detected

micron, I.D. 0.22 mm., O.D. 0.33 mm. The quantitative analysis was done with the use of RPCM – 200 standard [24–29]. RPCM – 200 [produced by Ultra Scientific (USA)] content PCBs: 28, 52, 101, 118, 138, 153, and 180.

GC control method: detector oven: 320°C , injector oven: 220°C , column oven: 80°C .

Temperature column oven programme:

Ramp	Rate $^{\circ}\text{C}/\text{min.}$	Upper temp. $^{\circ}\text{C}$	Upper time (minutes)
1	30.00	190	1.00
2	6.00	280	1.00
3	6.00	310	10.00

For statistical analyses the variation analysis (ANOVA), Tukey's test and variation analysis for correlation (ANOVA) were applied.

Results

The highest level of concentration of the PCBs in blue mussels from the area of Danish Straits was detected in the samples from the ferry harbour of Gedser ($289 \pm 61.6 \text{ ng g}^{-1}$ wet weight) (Table 1). In the Polish area, the highest level of PCBs ($117 \pm 25.3 \text{ ng g}^{-1}$) was detected in the samples from the Gdynia Orłowo coast. The lowest PCB concentrations were detected in the samples taken in the Kattegat area (Gilleleje) and Skagerrak Strait, as well as in the samples from Copenhagen municipal beach, where the presence of these compounds was not detected (Table 1).

PCB concentrations in blue mussels depended significantly on the place where the samples were taken (ANOVA $F=118.761$, $p<0.0001$). Blue mussels from the area of ferry harbour of Gedser had significantly higher PCB concentrations than those from all other areas (Tukey test: $p<0.05$).

Similarly, blue mussels from Gdynia Orłowo, which had $117 \pm 25.3 \text{ ng g}^{-1}$, were different from the groups coming from all other areas (Tukey test: $p<0.05$). The concentration of PCBs in the remaining areas was also differentiated. The concentration in the Gdańsk Bay ($45 \pm 48.8 \text{ ng g}^{-1}$) was significantly higher than in Kuźnica, Gilleleje, and Skagerrak (Tukey test: $p<0.05$).

The mean concentration of the analyzed compounds in the samples taken from the entire area of Gdańsk Bay was $59 \pm 53.0 \text{ ng g}^{-1}$, while in the samples taken from the open sea side it was $23 \pm 10.7 \text{ ng g}^{-1}$. The concentration levels were significantly different (ANOVA $F = 28.154$, $p < 0.0001$). It was also discovered that the concentration of PCBs is the highest in the samples collected in the vicinity of big cities and ports (Table 1). It was discovered that the distance between places where the samples were collected and the area of cities and ports is a statistically significant factor regarding the concentration of PCBs in blue mussels ($r = -0.448$, ANOVA: $F = 32.852$, $p < 0.0001$) (Fig. 2).

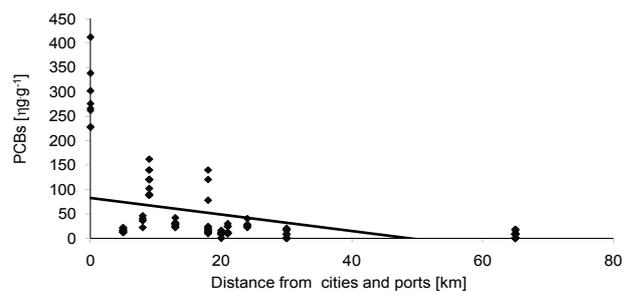


Fig. 2. Relation between the level of PCB concentrations in blue mussels and the distance of the places where they were collected from cities and ports.

Discussion

It is estimated that the emission of PCBs to the Baltic Sea was the most intensive in the 1960s and 1970s, and these compounds are still present (in most places in a lower range of concentration). However, recent monitoring data have shown fairly stable, sometimes even increasing concentrations in some places [30, 31]. Among all the places where samples have been taken, the highest concentration of PCBs was found in the samples coming from the area of the ferry harbour of Gedser. The higher concentration of PCBs in mussels from harbour areas in comparison to mussels taken from beach areas was also described elsewhere [e.g. 32]. The concentrations of PCBs in samples from Gedser ferry harbour showed significantly higher levels compared to the results concerning other places of this region of the Baltic Sea, that is Skagerrak and Copenhagen and the rest of Polish territory (Table 1). The higher concentrations of PCBs in blue mussels from Baltic Sea waters as compared to Skagerrak were also detected by other authors [31]. It seems that the samples from Gedser are the most contaminated with PCBs, due to the penetration of these compounds into the water mainly coming from oil paints, hydraulic oils, etc. from ships and ferry boats. Comparing the samples collected in the vicinity of port canals in Szczecin (which contained about 38 ng g⁻¹ PCBs), the sediments from the area of the Odra River's estuary to Szczecin Bay contained slightly over 8 ng g⁻¹ [33]. Some interesting results were obtained in research concerning contamination by PCBs in the canals of Nagasaki Bay in the 1980s. The bottom sediments from this region contained over 10,000 ng g⁻¹ of PCBs. It was discovered that the content of these compounds in the samples was caused mainly by the penetration of PCBs coming from oil paint on ships [34]. An increased concentration of PCBs in blue mussels collected in the port area also was detected by research carried out in Korea [35].

Blue mussels collected in the area of the city beach in Copenhagen did not contain any remains of PCBs. This can be caused by the fact that the place where the samples were collected was exposed and distant from the routes of ferry boats and ships, and for the reason that emission of these compounds has been significantly limited in Denmark in the latest ten years [36]. Except for the samples collected in Gedser, from the Danish part of the Baltic Sea, it has been discovered that the level of concentration of PCBs in blue mussel is much lower there than it is at Polish coastal sites (Table 1). Only in the samples collected in Kuźnica were the PCB concentrations similar to the one discovered in Skagerrak and Kattegat from the Danish side. In the samples from Gdynia Orłowo coast the highest level of contamination was found on the Polish coast side, yet it was significantly lower than the one observed in the samples from Gedser (Table 1). Excluding the samples from Copenhagen, the coefficient of correlation between the distance from big cities and ports and the level of PCB concentrations equals -0.448 (ANOVA F=32.850, p<0.0001). This means that the bigger the distance from big cities and ports, the lower the level of concentration of PCBs in blue mussels.

Analyzing the results obtained from the samples taken in the southeastern part of the Baltic, it was discovered that mussels coming from Gdańsk Bay are more contaminated than those coming from the open sea area (Table 1). This could be connected with the absence of PCBs in the samples from some rivers near the sea (Łeba, Łupawa, Słupia); research carried out within the national monitoring of the environment between 1993 and 1994 discovered the absence of PCBs in these rivers [37]. In blue mussels taken from the Świnoujście area 36.2 ng g⁻¹ (wet weight) PCBs was detected [38], while in the same species taken from Gdańsk Bay area 22 ng g⁻¹ (wet weight) was detected [39].

The obtained results confirm the usability of blue mussels as indicator species in research concerning the pollution of the marine environment with PCBs. Thanks to their capacity of filtration of large amounts of water, these organisms react relatively quickly to the changes in PCB presence in water [17]. The detected levels of these compounds in blue mussels reflect local contamination in the harbours, but offshore it is caused by widespread loads in seawater and sediments. Despite many administrative measures aimed at eliminating the fresh inputs of PCBs into the environment, these compounds are still present in the Baltic Sea and their increased levels are detected mostly in the vicinity of ports. The obtained results show that the Baltic is still highly contaminated with PCBs. However, the results presented in this paper indicate that the level of contamination of different regions of the Baltic Sea with PCBs might be highly differentiated.

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