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Polychlorinated Biphenyls in the Sediments of the Odra River and Its Tributaries

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Abstract

This paper presents the results of polychlorinated biphenyls (PCBs) determination in sediments from different sites of the Odra River and its tributaries, collected in 1998-2002. It was found that concentrations of PCBs varied significantly. The results of individual congeners show that contents of PCBs 180 and 138 were the highest in the sediments investigated. For better identification of places most polluted by PCBs, PCB contents on TOC (total organic carbon) basis in surface sediments are presented.

Keywords: PCBs, TOC, sediments, the Odra River

Introduction

Polychlorinated biphenyls (PCBs) are persistent organic compounds of anthropogenic origin, which have been produced on an industrial scale since 1929. They were commonly used in the period 1950-1980. PCBs have low or no flammability, good thermal stability, low rates of evaporation and high electrical resistivity. For all these reasons, they have been used in many industrial branches as heat transfer fluids, dielectric for transformers and capacitors, additives in hydraulic fluids in vacuum and turbine pumps, and plasticizers. They have been incorporated into formulations for printing inks, pesticides, paints, flame-retardants, waterproofing agents and adhesives. PCBs enter the environment mainly during accidents, not controlled or not properly controlled disposal of products containing the substances, chlorination of drinking water and wastewater and as a by-product in the chlorine bleaching of wood-pulp [1 - 8].

PCBs are stable compounds, resistant to decomposition by physical, chemical and biological factors. It is estimated that the half-life of PCBs in the environment is between 10 and 15 years [9, 10]. PCBs can be removed from the natural environment by reaction with active forms of metals and alkali, hydrogenation as well as by photolysis, thermochemical reactions and microbiological degradation [1]. The number and position of the chlorine atom in the molecule determine PCBs rate of degradation. Mono and dichloro biphenyls are more easily decomposed than polychlorinated biphenyls. The congeners containing the chlorine atoms in one benzene ring are more easily degraded than the ones with chlorine atoms in two rings. PCBs containing a chlorine atom in orto position (in one or two benzene rings) degrade with great difficulty [2].

PCBs are present in almost every element of the environment because of their resistance to degradation, low rates of evaporation, lipophilicity and usage on a large scale for over 60 years (Table 1). High concentrations of PCBs occur in cold and moderate climates in the northern hemisphere. These substances can be transported over large distances, and therefore they are found in distant regions of Africa and Antarctica [1, 8, 11].

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Table 1. Polychlorinated biphenyls in the natural environment [2, 9, 12].

Medium	Concentration
Air	0.1 – 20 ng/m^3
Water	0.001 - 908 ng/l
Sediment	1.1 – 6000 µg/kg (dry wt.)
Plankton	0.01 - 20 mg/kg
Invertebrates	0.01 - 10 mg/kg
Fish	0.01 - 25 mg/kg
Bird eggs	0.1 - 500 mg/kg
Human beeing	0.1 - 10 mg/kg

Despite the relatively low concentrations of PCBs in the natural environment, they have a negative influence on living organisms. PCBs undergo accumulation in consecutive links of the food chain. Plants, crustaceans and fish easily absorb them. This results in a decrease of photosynthesis, plant and fish growth and reproductive capacity of aquatic organisms, and also in increase of larvae mortality [13]. In the case of mammals, PCBs could cause pathologic changes in spleen and skin. They also can damage immune, digestive, nervous and reproductive systems, and promote the generation of tumours [11, 14, 15, 16].

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Table 2. Determined PCB congeners.

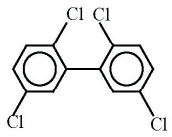
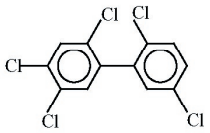
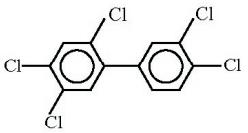
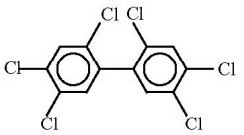
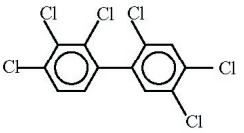
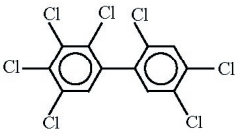
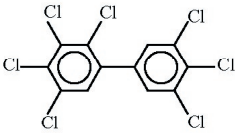
No	Number of PCBs acc. to IUPAC	TEF - Toxic Equivalency Factor	Structural formula
1.	52	-	
2.	101	-	
3.	118	0.0001	
4.	153	-	
5.	138	-	
6.	180	-	
7.	189	0.0001	

Table 3. Parameters of chromatographic determination of PCBs.

	System 1	System 2
Chromatograph type and model	GC Hewlett Packard 6890	GC 8000 Fisons
Column	HP 5.30 m x 0.25 mm x 0.25 μm	HP Ultra 2.25 m x 0.2 mm x 0.33 μm
Detector	HP 5973 MSD in SIM mode	ECD
Injection temperature	300 °C	280 °C
Temperature program	60 °C, step 15 °C/min to 150 °C, step 3 °C/min to 300 °C	80 °C, step 4 °C/min, to 280 °C
Carrier gas flow rate	Helium 0.9 ml/min	Helium 1 ml/min
Make-up gas	-	Nitrogen
Volume of injected sample	1μl	1 μl

Branch of the Institute of Meteorology and Water Management carried out studies on especially toxic organic substances in the river environment. This paper presents the results of PCB contents in sediments collected from the Odra River and its tributaries in 1998-2002 [17, 18, 20].

Materials and Methods

Sediment samples were collected during five campaigns: in May and November 1998, June 1999, May/ June 2000 and June 2002. The location of sampling sites in the Odra basin is presented in Figure 1 [17-18].

PCB congeners determined in collected sediment samples are shown in Table 2.

Sample Preparation

Samples of surface sediments (0-5 cm) were collected with a stainless steel bucket, transferred to glass vessels, subsequently frozen, and stored at -20 °C. After being defrosted, the samples were lyophilized, then sieved manually (sieve mesh – 2 mm) and ground in a ball-grinder. The internal standard (9-chloroanthracene) was added to a 2 g sample of dry sediment and extracted with dichloromethane in Soxhlet apparatus for 15 h. The extract was condensed by evaporation of the excess solvent in evaporator under reduced pressure. After sulphur removal, achieved by adding copper powder, the extract was purified on the micro-column filled with silica gel. A 9: 1 (v/v) mixture of hexane and dichloromethane was used for elution. The eluate was condensed by evaporation of the excess solvent in a stream of nitrogen and analyzed chromatographically [17 - 18].

Chromatographic Analysis

The chromatographic analyses were performed on two gas chromatographs. The chromatographic run conditions in analysis of PCBs are shown in Table 3.

Discussion of Results

The concentrations of 7 PCBs in sediment samples collected at different sites along the Odra River and its tributaries in May 1998 ranged from 1.3 μg/kg (dry wt.) in the Odra at Krosno Odrzańskie to 13.6 μg/kg (dry wt.) in the Warta near confluence. In November 1998, the sum of 7 PCBs in all studied sediments varied from 1.3 to 28.0 μg/kg (dry wt.). The lowest concentration was measured in the Odra for Widuchowa while the highest was in the Odra Braid.

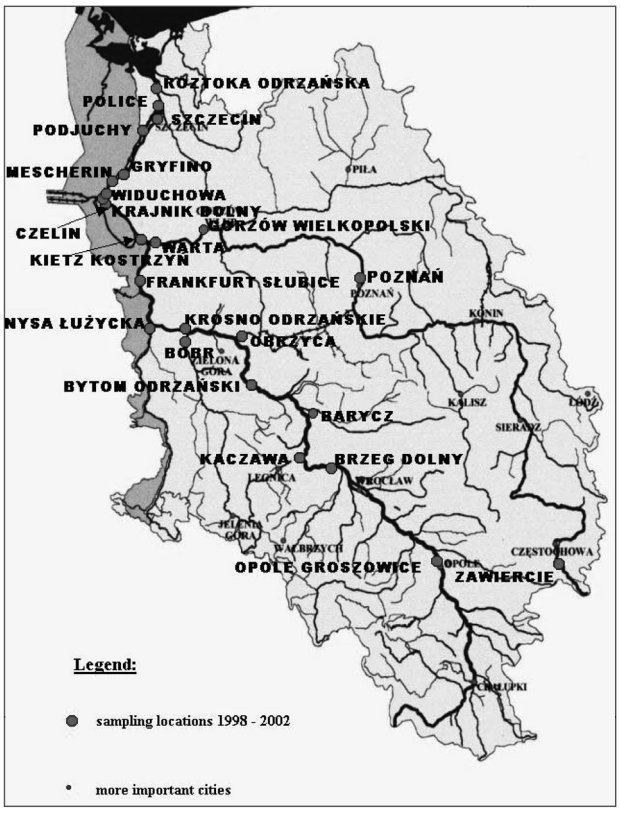


Fig. 1. Sediment sampling sites in the Odra River and its tributaries, 1998-2002 [17-18].

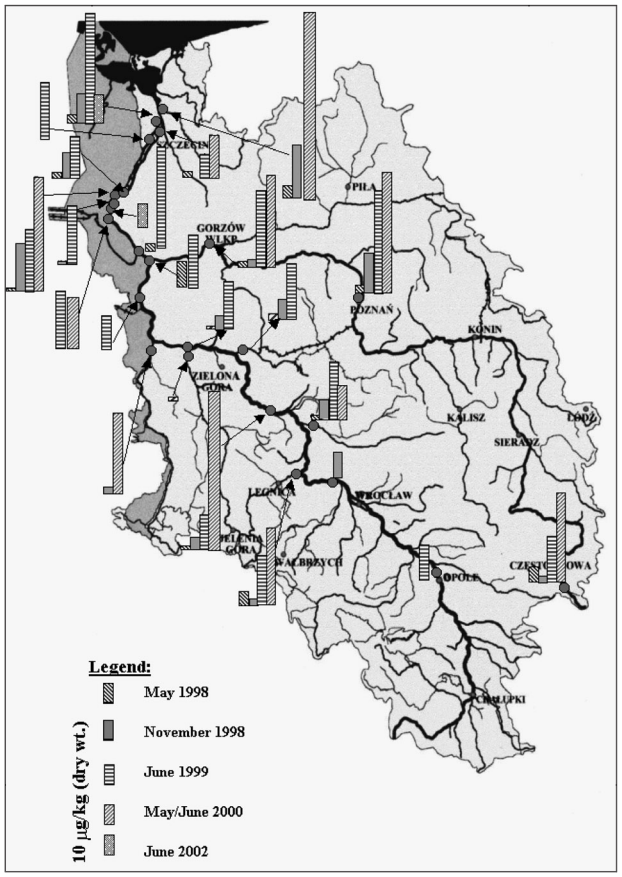


Fig. 2. Contents of PCBs in sediments from the Odra River and its tributaries, 1998 – 2002.

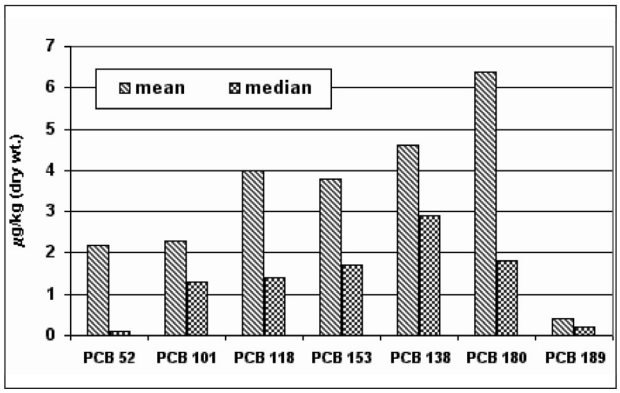


Fig. 3. Average concentrations of PCB congeners in sediments from the Odra River and its tributaries, 1998 – 2002.

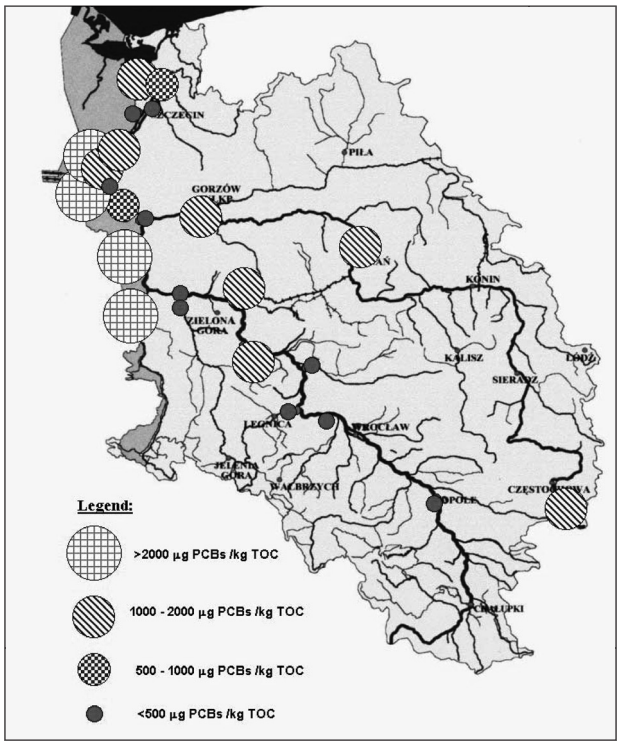


Fig. 4. Average concentrations of PCBs on TOC basis in sediments from the Odra river and its tributaries, 1998 – 2002.

Sediments from the Odra basin taken in 1999 and 2000 had higher contents of PCBs than in 1998. In June 1999, the concentration of PCBs ranged from 12.6 (Szczecin) to 58.2 µg/kg (dry wt.) (Police), and in May/June 2000 from 17.9 (Barycz) to 81.2 µg/kg (dry wt.) (the Odra Braid). In 2002 sediment samples were collected from the Odra River at Police and Krajnik Dolny. At these sites the contents of 7 PCBs were 12.8 µg/kg (dry wt.) and 14.2 µg/kg (dry wt.), respectively (Fig.2). Generally, by PCBs most polluted the sediment was taken near the Odra mouth, while the least polluted was from the Barycz where the river joins the Odra.

The decree of the Minister of the Environment in September 2002 on quality standards for soil and ground determines maximum allowable concentrations of the sum of 7 PCB congeners (No: 28, 52, 101, 118, 138, 153, 180) in the surface layer of sediments accumulated or originating from the reservoirs of flowing or stagnant waters [19]. The permissible value of PCBs for protected, agricultural, forest, urban and recreation-rest areas is 20 µg/kg (dry wt.) and for industrial and traffic areas 2000 µg/kg (dry wt.). The investigation of the PCB contents in sediments indicates that permissible concentration levels of PCBs in surface sediments of protected areas (non-polluted) has been exceeded in 13% of samples from November 1998, in 79% of samples from June 1999 and in 90% of samples from May/June 2000 [20-21]. In the case of sediments from 1998 and 2002, PCB concentrations were below permissible value.

PCBs 180 and 138 were found in the highest concentrations in the studied sediments (Fig. 3).

Data for sediments polluted with PCBs in the Odra basin after the flood in the summer of 1997 are available in literature. The concentration of 7 PCBs (No: 28, 52, 101, 118, 138, 153, 180) in sediment samples taken at different sites in the upper and middle Odra in August 1997 varied from below detection limit 0.05 µg/kg (dry wt.) to 420 µg/kg (dry wt.). The allowable concentration of PCBs in surface sediments of protected areas (non-polluted),

i.e. 20 μg/kg (dry wt.) was exceeded in 24% of examined sediment samples [22].

As found by Konat and Kowalewska, the sum of concentrations of 7 PCBs in sediments collected from the Szczecin Lagoon before the 1997 flood was not higher than 20 μg/kg (dry wt.); only at one station did 7 PCBs reach a rather high value of ca. 55 μg/kg (dry wt.) [23]. The highest concentration of PCBs was observed not in the vicinity of the most probable sources of pollution, but in areas of intensive sedimentation. One month after the flood of 1997, the concentrations of 7 PCBs were about 1.5 - 3.7 times higher than before this disaster. Even 2 years after the flood, PCB pollution was still at a high level. These facts confirm the conclusion drawn from our investigation, that an increase of PCB concentration level occurred in sediment samples taken from the Odra and its tributaries after the 1997 flood, up to the year 2000 [23].

In many publications, for better identification of places most polluted by PCBs, PCB concentrations on TOC basis in surface sediments are presented (Fig. 4). The high concentration of PCBs on TOC basis in surface sediments (>2000 ng PCBs/g TOC) were noted between the site where the Nysa Łużycka joins Odra and Mescherin at the Odra River. These values were much higher than presented in the earlier publication concerning the Szczecin Lagoon [24].

Summary

- The studies on the PCB contents in sediments from the Odra basin conducted in the 5-year period after a disastrous flood in 1997 indicate that PCB compounds occurred in variable concentrations. Most of the samples exceeded the permissible value of sum PCBs for non-polluted areas (20 μg/kg dry wt.) [19].
  The highest contents of PCBs were found at Bytom Odrzański, Mescherin, Szczecin and Roztoka Odrzańska; this could indicate the discharge of PCBs from industrial plants and rubbish.
- Sediments from the Odra River in the region between the Nysa Łużycka confluence and Mescherin can be regarded as most polluted with PCBs (PCBs on TOC basis). The PCB concentrations were significantly higher than in sediments from the German zone of the Szczecin Lagoon.
- After the 1997 flood, up to the year 2000, an increase of PCB concentrations in the studied sediments of the Odra and its tributaries was observed. The similar phenomenon was noted in the case of sediments from the southern Baltic Sea.

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