The role of a lowland reservoir in the transport of micropollutants, nutrients and the suspended particulate matter along the river continuum

Magdalena Urbaniak, Edyta Kiedrzyńska and Maciej Zalewski

ABSTRACT

The water and sediment samples from the Sulejow Reservoir and Pilica River (Central Poland) were analysed for nutrients: total phosphorus (TP), total nitrogen (TN) and the suspended particulate matter (SPM) and dioxin-like PCBs (dl-PCBs) concentration. Dl-PCBs were detected in sediments from all seven sampling locations with mean concentrations of 14.29 ng kg^{-1} dry weight (d.w.). The lowest concentration was recorded in the sediment collected below the Sulejow Reservoir (PR5; 2.92 ng kg^{-1} d.w.) and the highest in the sample collected from the mouth section of the Pilica River (PR7; 26.30 ng kg^{-1} d.w.). The 29% reduction of the total dl-PCBs concentration – from 9.21 ng kg^{-1} d.w. in the middle section to 6.54 ng kg^{-1} d.w. in the dam section of the Sulejow Reservoir – demonstrated the hydraulic transport and deposition of measured pollutants in the reservoir's sediments. The results obtained also revealed the reduction of nutrients and the SPM concentrations. A 45% reduction of SPM, 28% reduction of TP and 34% of TN was observed between the water inflow and outflow from the Sulejow Reservoir.

Key words | ecohydrology, nutrients, polychlorinated biphenyls, reservoir, river continuum

Magdalena Urbaniak (corresponding author)
Edyta Kiedrzyńska
Maciej Zalewski
Department of Applied Ecology,
European Regional Centre for Ecohydrology u/a
    UNESCO,
International Institute of the Polish Academy of
    Sciences,
Tylna 3,
90-364 Lodz,
Poland
E-mail: *m.urbaniak@unesco.lodz.pl*

Magdalena Urbaniak
Maciej Zalewski
Department of Applied Ecology,
University of Lodz,
Banacha 12/16,
90-237 Lodz,
Poland

INTRODUCTION

According to the River Continuum Concept, various ecological processes and patterns of river ecosystems are changing continuously along a river (Vannote et al. 1980; Bowes et al. 2003). Therefore, large reservoirs are considered as constructions with negative effects on the structure and functioning of river ecosystems. According to Miller (2005), one of the main negative impacts of large dams on the environment was expressed as degradation of the river continuity, which influences the hydrological regime below the dam. Nevertheless, in the face of the global climate changes, large reservoirs may also play an increasingly important role in protecting the water resources, contributing to human development by providing reliable sources of drinking water and irrigation, hydropower, recreation, navigation, income and other important benefits (WCD 2000).

Moreover, they are considered as an efficient trap for sediments and consequently, for the associated chemical toxicants, including nutrients and PCBs (Devault et al. 2009). The decrease in the flow velocity and the increase of flocculent settling in constructed reservoirs create perfect conditions for sedimentation and deposition of pollutants. It was estimated that 97% of the released PCB in a water column was retained in sediments (DiPinto et al. 1993), which serve as storage compartments for micropollutants (Knezovich et al. 1987). Thus, reservoirs act as a sink for contaminants and therefore are important for pollution studies and monitoring of ecosystem stress. Therefore, according to the I principle of Ecohydrology (Zalewski et al. 1997) the main objectives of this study are: (1) quantification of suspended sediment matter, nutrients and dioxin-like PCBs

(dl-PCB) transfer along the Pilica River continuum, and (2) evaluation of the role played by the Sulejow Reservoir in their deposition and retention.

Study area

The Pilica River watershed (Figure 1) is located in central Poland (length: 342 km, catchment area: 9,258 km^2). In 2006, its average and maximum discharges (Q) were 33.4 m^3 s^{-1} and 178.7 m^3 s^{-1}, respectively (the town of the Sulejow gauge) (Kiedrzyńska *et al.* 2008a, b). Agriculture is present in over 60% of the Pilica catchment area and results in an increased supply of nutrients, micropollutants, humic substances and other pollutants from non-point sources into the river and the Sulejow Reservoir (Ambrożewski 1996).
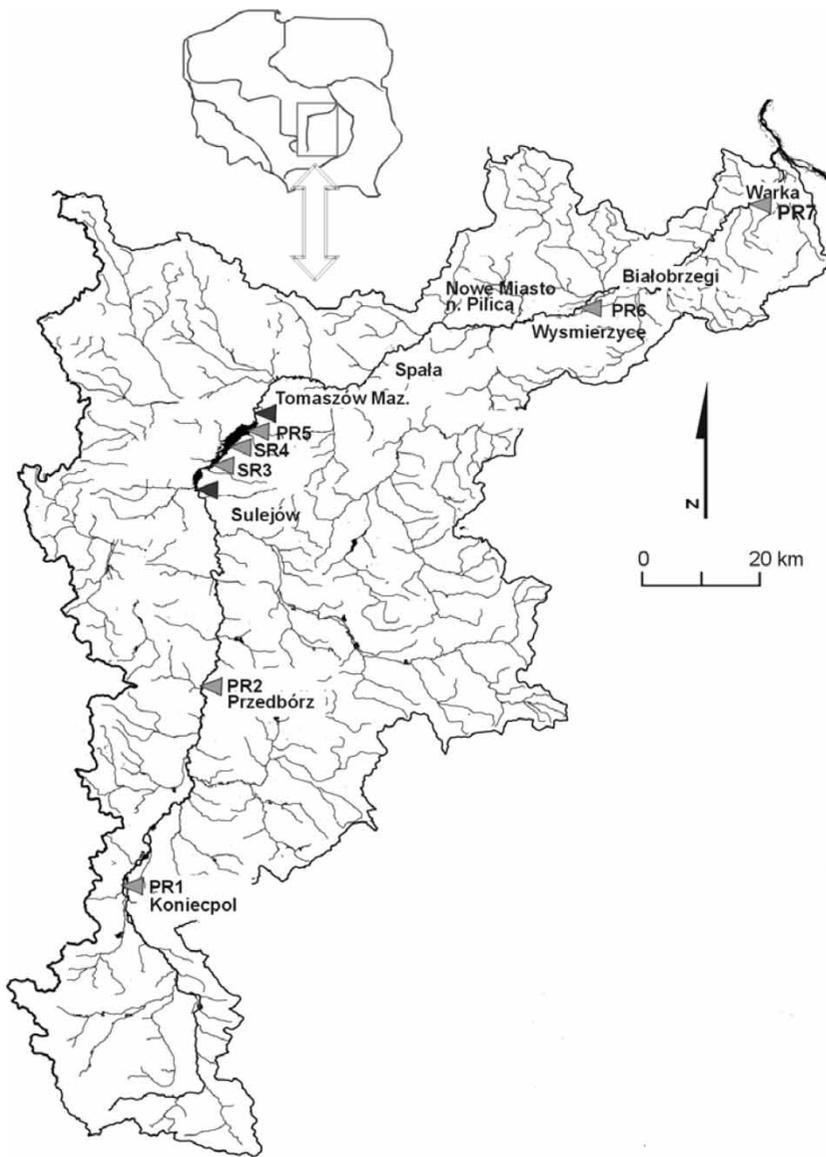

Figure 1 │ Location of sediment sampling points (grey arrows: PR1, PR2, SR3, SR4, PR5, PR6 and PR7) and water samples (black arrows: below and above the reservoir) on the Pilica River and the Sulejow Reservoir.

The Sulejow Reservoir is a shallow, lowland reservoir situated in the middle course of the Pilica River. The maximum length of the reservoir is 15.5 km, and the maximum width is 2.1 km. At the maximum capacity (75×10^6 m^3), the reservoir covers 22 km^2, with average and maximum depths of 3.3 and 11 m, respectively. It was constructed in 1973 as a drinking water supply reservoir for about 1 m inhabitants. Two water utilities supply the cities of Lodz and Tomaszow with drinking water from the Sulejow Reservoir. The reservoir has also been used as a recreational area for sport activities, such as swimming, sailing or canoeing (Ambrożewski 1996).

Disturbances of reservoir ecosystems are occurring due to high contaminant loads transported by the Pilica, Luciaza and Strawa Rivers, and by surface flow from the direct reservoir catchment area. The recreational use of the reservoir also contributes to the contaminant loading. Another important contribution to the environmental pollution of the Sulejow Reservoir originates from domestic and municipal sources. Some contaminants, such as PCBs are being released as untreated sewage from cities situated along the Pilica River (Galicka 1996).

MATERIAL AND METHODS

Water sampling for nutrients and SPM analysis

During the hydrological year 2006, water samples for analyses of nutrients and the suspended particulate matter (SPM) were collected every 4 to 10 days from two stations located in the middle course of the Pilica River: (1) above the Sulejow Reservoir (43 water samples); and (2) below the Sulejow Reservoir (63 water samples) (Figure 1). The concentrations of the SPM in the water were measured with a PIHM bathometer. Daily discharges of the Pilica River and outflows from the reservoir's dam were used in the research.

Analysis of nutrients and SPM

Total forms of nutrients were analysed in the unfiltered water. Total phosphorus (TP) was analysed with the addition of Oxisolve Merck reagent with Merck MV 500 Microwave Digestion System and determined by the ascorbic acid method (Greenberg *et al.* 1992). Total nitrogen (TN) was analysed using the persulphate digestion method (HACH 1997). Water samples for analyses of soluble forms of nutrients were immediately filtered through Whatman GF/F (0.45 μm) filters and measured with the Ion Chromatography System (DIONEX, ICS 1000).

The SPM was estimated by drying Whatman GF/F filters at 105 °C and weighing them on a laboratory scale. The particulate inorganic matter (PIM) was estimated by loss on ignition at 550 °C (Ostrowska *et al.* 1991). The particulate organic matter (POM) was estimated as the difference between SPM and PIM.

Sediment sampling for PCBs

The sediment samples for dl-PCB analyses were collected by using a sediment core sampler once during the autumn period of 2006 from seven stations situated along the Pilica River (PR1, PR2, SR3, SR4, PR5, PR6, PR7), including two stations situated on the Sulejow Reservoir (SR3 and SR4) (Figure 1). The samples from each sampling point were collected in triplicate.

The collected sediments were freeze-dried (-40 °C, 1 mba, 72 h; Edwards Freeze Dryer), sieved through a 2 mm mesh sieve and mixed in proportion 1:1:1 in order to obtain one representative sample (Urbaniak *et al.* 2008, 2009a, b, c).

PCBs extraction and clean-up

The method of sample pretreatment was according to PN-EN 1948-3, 2002; U.S. EPA Method 1668, 1999 (PN-EN 1948-3 2002; U.S. EPA METHOD 1668 1999). Samples were spiked with isotopically labelled standards (Cambridge Isotopes Laboratories, USA) and extracted by ASE (Accelerated Solvent Extraction) 200 Dionex at 150 atm (11 Mpa) with toluene. The extracts were purified with multilayer silica columns using 200 ml of hexane. The hexane extracts were further concentrated to 5 ml by rotary evaporation and concentrated to 100 μl under a gentle stream of nitrogen, replacing the *n*-hexane to *n*-nonane.

PCBs identification and quantification

Identification and quantification of PCBs were performed by HRGC/HRMS: HP 6890N Agilent Technologies coupled with a high resolution mass spectrometer (AutoSpec Ultima). The HRMS was operated in the splitless injection mode with perfluorokerosene (PFK) as a calibration reference. Separation of PCBs congeners was achieved using a DB5-MS column (60 m × 0.25 mm i.d., film thickness 0.25 μm) (U.S. EPA Method 1668 1999; PN-EN 1948-3 2002).

PCBs WHO-TEQ concentration

WHO-TEQ is an acronym for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) equivalents. It is a means of expressing the net toxicity of a complex mixture of different PCDD, PCDF and dl-PCB. In the present study, this term was used to evaluate the toxicity of a sediment sample polluted by dl-PCB. Each of the individual dl-PCB congeners has been assigned a toxic equivalency factor (TEF), based on its toxicity relative to that of 2,3,7,8-TCDD, which is universally assigned a TEF of 1. Multiplication of the concentration of dl-PCBs by its assigned TEF gives the concentration in terms of Toxic Equivalent (TEQ) calculated for all dl-PCB congeners (Van den Berg *et al.* 2006).

PCBs quality assurance/quality control

The analytical method used for dl-PCBs analysis was properly validated on the basis of internal reference materials and the analytical laboratory involved in 2005 successfully passed the accreditation procedure. Each analytical batch contained a method blank, a matrix spike and duplicate samples. A reagent blank was used to assess artefacts and the precision was verified by replicate analyses. Spiked samples were used as an additional accuracy check. Analyte recoveries were determined by analysing the samples spiked with PCB standards. The recovery coefficient was taken into account for calculating the final concentrations of analytes. Additionally, in order to assess the method's correctness, the Standard Reference Material: 1939a Polychlorinated Biphenyls in River Sediment A (Certificate of Analysis 1990) was used. The PCBs method detection limit (MDL),

the relative standard deviation (RSD) and recoveries were presented in the previous publications (Urbaniak *et al.* 2008, 2009a, b, c).

RESULTS

Transport and reduction of nutrients and SPM concentration in the Sulejow Reservoir

In 2006, the total inflow of the Pilica River into the Sulejow Reservoir amounted to 1,070 million m^3 (Table 1), and the total outflow from the dam of the reservoir was 678 million m^3 (including 592 million m^3 as outflow from the hydroelectric power station and 86 million m^3 as barren outflow from the dam), and evapotranspiration and filtration was 50.7 million m^3. The remaining water volume was retained in the reservoir.

The research results showed the following mean concentrations of phosphorus in the water inflow and outflow from the Sulejow Reservoir: inflow 220.1 μg TP dm^{-3}, outflow 159.2 μg TP dm^{-3}; inflow 96.2 μg P-PO_4 dm^{-3}, outflow 85.9 μg P-PO_4 dm^{-3}. Furthermore, a decrease in the concentrations of the following nitrogen forms was observed: TN – inflow 3,864.7 μg dm^{-3}, outflow 2,539.5 μg dm^{-3}; organic nitrogen (N-org.) – inflow 1,896.2 μg dm^{-3}, outflow 158.6 dm^{-3}; N-$NO_{2/3}$ – inflow 1,952 μg dm^{-3}, outflow (2,352 μg dm^{-3}); N-NH_4 – inflow 20.6 μg dm^{-3}, outflow 28.8 μg dm^{-3}. The mean inflow SPM concentration was 13.56 mg SPM dm^{-3} and the mean outflow concentration 7.48 mg SPM dm^{-3}. The research showed a significant reduction of nutrients and SPM concentrations and retention in the reservoir, which amounted to: 28% of TP, 34% of TN and 45% of SPM.

Retention of nutrients loads in the reservoir was: TP – 100.3 ton day^{-1}; TN – 2,700.8 ton day^{-1}, and SPM – 7,744.5 ton day^{-1} (Table 1).

Transport of PCBs along the Pilica River continuum

Total dl-PCB concentrations, as well as the total WHO-TEQ concentrations are presented in Table 2 and Figures 2 and 3, and show that samples were heterogeneous with values

Table 1 | Summary of nutrients and SPM concentrations and loads transported by the Pilica River at the inflow to the Sulejów Reservoir and the outflow from the reservoir

Concentrations ($\mu g\ dm^{-3}$):	TP	PO_4	TN	$NO_{2/3}$	$N\text{-}NH_4$	N-org	Particulate inorganic matter (PIM)	Particulate organic matter (POM)	Suspended particulate matter (SPM)
Inflow to the reservoir ($\mu g\ dm^{-3}$)	220.1	96.2	3,864.7	1,951.8	20.6	1,896.2	6.02	7.54	13.56
Outflow from the reservoir ($\mu g\ dm^{-3}$)	159.2	85.9	2,539.5	2,352.1	28.8	158.6	5.32	2.16	7.48
Reduction ($\mu g\ dm^{-3}$)	60.9	10.3	1,325.2	−400.3	−8.3	1,737.6	0.7	5.4	6.1
Reduction (%)	28	11	34	−21	−40	92	12	71	45

Loads	Flow (mln m³)	TP (ton day⁻¹)	PO_4 (ton day⁻¹)	TN (ton day⁻¹)	$NO_{2/3}$ (ton day⁻¹)	$N\text{-}NH_4$ (ton day⁻¹)	N-org (ton day⁻¹)	Particulate inorganic matter (PIM) (ton day⁻¹)	Particulate organic matter (POM) (ton day⁻¹)	Suspended particulate matter (SPM) (ton day⁻¹)
Inflow to the reservoir	1,069.8	206	96.1	4,512.9	2,329.7	21.3	2,166.8	6,033.51	6,987.5	13,021.02
Outflow from the reservoir	677.7	105.7	54.1	1,812.1	1,691.7	17.2	103.2	3,611.19	1,665.36	5,276.55
Evapotranspiration	50.7	–	–	–	–	–	–	–	–	–
Retention in the reservoir	341.3	100.3	42.0	2,700.8	638.0	4.1	2,063.6	2,422.3	5,322.1	7,744.5

ranging from 2.92 to 26.30 ng kg⁻¹ of dry weight (d.w.). The differences between the respective pollution levels at the sampling points were confirmed by the Kruskal–Wallis ANOVA by Ranks test ($p > 0.05$). The maximum concentration of total dl-PCBs was observed at the last, the PR7 site (26.30 ng kg⁻¹ d.w.) with dominant congeners: PCB-81 (5.88 ng kg⁻¹ d.w.), PCB-105 (5.83 ng kg⁻¹ d.w.) and PCB-118 (8.79 ng kg⁻¹ d.w.) (Table 2).

The analysed dl-PCBs were divided into two categories: the first category (called coplanar or non-ortho congeners which possess more toxic properties than non-coplanar congeners) consisted of four PCB congeners: PCB-77, PCB-81, PCB-126 and PCB-169; whereas the second (mono-ortho) included: PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167 and PCB-189 (Van den Berg *et al.* 2006).

The lowest percentage of non-ortho PCBs was observed at the SR4 site (16%), whereas at the other sampling points this value was higher and ranged from 20% for PR5 to 26% for PR2 (Table 3). Concentrations of PCB-77 and PCB-81 were the highest in samples collected from the PR2 site (0.19 and 3.30 ng kg⁻¹ d.w., respectively), whereas at the other sites, these values were up to nine and 21 times lower (for PCB-77 and PCB-81, respectively). Congener PCB-169 was not observed among the three following samples: PR2, PR6 and PR7; with very low concentrations observed at the other sampling points (ranging from 0.02 to 0.09 ng kg⁻¹ d.w.) (Table 2).

Congener PCB-118 had the highest frequency of occurrence in all the samples with the value ranging from 31% for the PR1 site to 44% for SR3 (Table 3). Also congener PCB-105 possessed high percentage of occurrence, especially at the PR1 (25%) and PR5 sites (25%). In other points its values were within the ranges from 17 and 18% for reservoir samples (SR3 and SR4, respectively), to 21 and 22% for samples from the last two sampling points (PR6 and PR7, respectively). The compositions of other congeners were several times lower and ranged from 0 to 9% of the total amount of dl-PCBs. In consequence, mono-ortho pentachlorobiphenyls were the dominant homologues in all sediments samples (Table 3).

The presented results showed that in the Pilica River and the Sulejow Reservoir, non-ortho PCBs were present with a lower concentration as compared to mono-ortho

Table 2 | Changes in concentrations of individual dl-PCB congeners along the Pilica River and the Sulejow Reservoir

Congener	PR1	PR2	SR3	SR4	PR5	PR6	PR7
PCB-77	0.06	0.19	0.12	0.06	0.01	0.24	0.27
PCB-81	2.01	3.30	1.51	0.84	0.53	5.06	5.88
PCB-126	0.09	0.05	0.17	0.10	0.02	0.13	0.15
PCB-169	0.01	0.00	0.09	0.04	0.02	0.00	0.00
Sum of non-ortho PCB [ng kg^{-1}]	**2.17**	**3.55**	**1.89**	**1.04**	**0.58**	**5.44**	**6.30**
PCB-105	2.57	2.59	1.59	1.16	0.72	4.88	5.83
PCB-114	0.25	0.36	0.16	0.10	0.07	0.72	0.70
PCB-118	3.27	5.27	4.04	2.40	1.08	9.46	8.79
PCB-123	0.65	1.19	0.76	0.46	0.17	0.00	1.90
PCB-156	0.89	0.45	0.04	0.73	0.14	1.48	1.60
PCB-157	0.25	0.10	0.02	0.17	0.05	0.37	0.38
PCB-167	0.31	0.20	0.65	0.37	0.07	0.56	0.63
PCB-189	0.09	0.05	0.06	0.10	0.04	0.06	0.16
Sum of mono-ortho PCB [ng kg^{-1}]	**8.29**	**10.21**	**7.32**	**5.50**	**2.34**	**17.54**	**20.00**
Total concentration [ng kg^{-1}]	**10.45**	**13.76**	**9.21**	**6.54**	**2.92**	**22.97**	**26.30**
WHO-TEQ concentration [ng TEQ kg^{-1}]	**0.34**	**0.53**	**0.42**	**0.25**	**0.11**	**0.96**	**0.90**

PCBs and are comparable with the results presented world-wide (e.g. Gardinali *et al.* 1996; Hong *et al.* 2005).

Reduction of PCBs concentration along the Sulejow Reservoir

A decrease was observed in the concentration of all dl-PCB congeners between the sites SR3 and SR4, with the exception of three congeners: PCB-156, PCB-157 and PCB-189, which showed an increase of their value along the Sulejow

Reservoir (Table 4). The decrease was also observed in the percentage composition of dl-PCB congeners between these two sampling points. Moreover, 5% decrease of highly toxic non-ortho PCBs was recorded along the reservoir (from 21% in SR3 to 16% in SR4) in favour of the increasing mono-ortho congeners (from 79% in SR3 to 84% in SR4) (Table 3).

The 29% reduction of the total dl-PCBs concentration, 45% reduction of non-ortho PCBs, 25% of mono-ortho PCBs and 40% of WHO-TEQ concentration observed along the Sulejow Reservoir (Table 4) demonstrates the
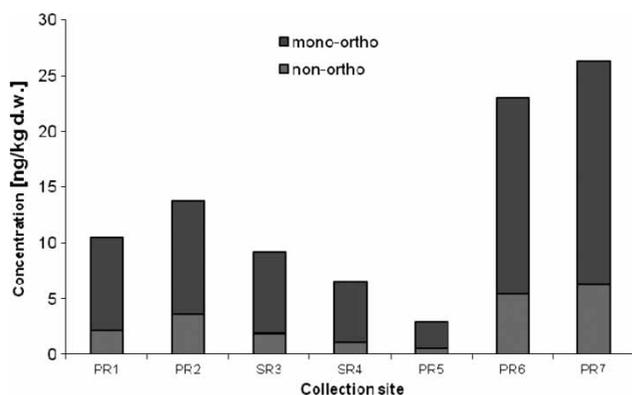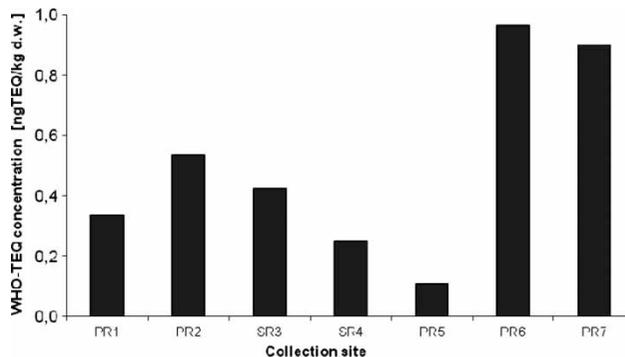

Figure 2 | Changes in concentrations of non-ortho and mono-ortho PCB congeners in sediment samples along the Pilica River (PR) and the Sulejow Reservoir (SR).

Figure 3 | Changes in WHO-TEQ concentration of dl-PCBs in sediment samples along the Pilica River (PR) and the Sulejow Reservoir (SR).

Table 3 | Changes in percentage composition (%) of individual dl-PCBs in sediment samples along the Pilica River (PR) and the Sulejow Reservoir (SR)

Congener	PR1	PR2	SR3	SR4	PR5	PR6	PR7
PCB-77	1	1	1	1	0	1	1
PCB-81	19	24	16	13	18	22	22
PCB-126	1	0.4	2	2	1	1	1
PCB-169	0.1	0	1	1	1	0	0
Sum of non-ortho PCB	**21**	**26**	**21**	**16**	**20**	**24**	**24**
PCB-105	25	19	17	18	25	21	22
PCB-114	2	3	2	2	3	3	3
PCB-118	31	38	44	37	37	41	33
PCB-123	6	9	8	7	6	0	7
PCB-156	9	3	0.4	11	5	6	6
PCB-157	2	1	0.2	3	2	2	1
PCB-167	3	1	7	6	2	2	2
PCB-189	1	0.4	1	2	1	0.3	1
Sum of mono-ortho PCB	**79**	**74**	**79**	**84**	**80**	**76**	**76**

role of a lowland reservoir in the deposition and accumulation of pollutants transported along the river continuum.

DISCUSSION

The role of a lowland reservoir in the transport and reduction of nutrients concentration along the river continuum

Flood pulses shape the water body quality in the reservoir and along the river continuum because they trigger physical erosion and influence the sediment deposition (Junk *et al.* 1989; Heiler *et al.* 1995; Kiedrzyńska *et al.* 2008a). Water quality analysis of the major tributaries provided the background of the reservoir's hydrologic pattern (Wagner & Zalewski 2000; Kiedrzyńska *et al.* 2008b) and allowed the identification of the SPM and nutrient transport into the reservoir (Kiedrzyńska *et al.* 2010, Zalewski & Kiedrzyńska 2010). In summer, this usually occurred during rising water stages of medium floods and at the very initial stages of floods (Kiedrzyńska *et al.* 2008a, b). These results show a possible application of the river's discharge regulation for downstream SPM and nutrient transport control. The

Table 4 | Summary of dl-PCBs reduction along the Sulejow Reservoir

Concentration (ng kg^{-1}):	PCB-77	PCB-81	PCB-126	PCB-169	Non-ortho PCB	PCB-105	PCB-114	PCB-118	PCB-123	PCB-156	PCB-157	PCB-167	PCB-189	Mono-ortho PCB	Total	WHO-TEQ
SR3	0.12	1.51	0.17	0.09	1.89	1.59	0.16	4.04	0.76	0.04	0.02	0.65	0.06	7.32	9.21	0.42
SR4	0.06	0.84	0.1	0.04	1.04	1.16	0.1	2.4	0.46	0.73	0.17	0.37	0.1	5.5	6.54	0.25
Reduction (ng kg^{-1})	0.06	0.67	0.07	0.05	0.85	0.43	0.06	1.64	0.3	−0.69	−0.15	0.28	−0.04	1.82	2.67	0.17
Reduction (%)	50	44	41	56	45	27	38	41	39	−1,725	−750	43	−67	25	29	40

Percentage composition (%)	PCB-77	PCB-81	PCB-126	PCB-169	Non-ortho PCB	PCB-105	PCB-114	PCB-118	PCB-123	PCB-156	PCB-157	PCB-167	PCB-189	Mono-ortho PCB
SR3	1.34	16.41	1.81	0.98	20.54	17.28	1.73	43.86	8.24	0.44	0.23	7.03	0.66	79.48
SR4	0.89	12.9	1.5	0.66	15.95	17.73	1.52	36.66	7.03	11.21	2.64	5.73	1.52	84.04
Reduction (%)	0.5	3.5	0.3	0.3	4.6	−0.4	0.2	7.2	1.2	−10.8	−2.4	1.3	−0.9	−4.6

present study supplements the previous research on the hydrological pattern and nutrient transport in the Pilica River–Sulejow Reservoir system. Another study monitored phosphorus concentrations along the River Swale and shows considerable changes in the phosphorus dynamics along the river continuum (Bowes *et al.* 2003). The authors presented that phosphorus in the lowland part of the river was transported predominantly in the particulate form and the seasonality of phosphorus export increased down the river continuum. They observed that 85% of the TP exported from the River Swale was generated within the lowland zone and the lowest rates of phosphorus export usually occurred in the summer months (Bowes *et al.* 2003).

In 2006, we also observed a large mean concentration of N-org in inflow to the reservoir and a small mean concentration in outflow, and bigger concentration of $NO_{2/3}$ in the outflow than inflow (Table 1). These results show the dynamic of the nitrogen cycle in the reservoir which appears in a number of oxidation states. Various nitrogen transformations permanently occur in the littoral zone of reservoirs and involve several microbiological processes. These results point at nitrogen mineralization that converts organically bound nitrogen to ammonium nitrogen as the organic matter is being decomposed and degraded. This pathway occurs under both anaerobic and aerobic conditions and is often referred to as ammonification (Mitsch & Gosselink 2007). Once the ammonium ion (NH_4^+) is formed, it can take several possible pathways. It can be absorbed by plants through their root system in the littoral zone of the reservoir or by anaerobic microorganisms and converted back to organic matter. Another possible nitrogen transformation that occurs in an aerobic environment is nitrification, where ammonium nitrogen can be oxidized in two steps by *Nitrosomonas* sp. and by *Nitrobacter* sp. (Mitsch & Gosselink 2007). Nitrification can also occur in the oxidized rhizosphere of littoral plants, where adequate oxygen is often available to convert the ammonium nitrogen to nitrate nitrogen.

The role of a lowland reservoir in the transport and reduction of dl-PCBs concentration along the river continuum

The obtained results, in comparison with other data on dl-PCBs contamination, show a very low pollution level.

Data presented previously by Urbaniak *et al.* (2008) for the Jeziorsko and Barycz Reservoir demonstrated that the dl-PCBs concentrations in these two dam reservoirs were much higher and amounted to 121.36 ng kg^{-1} d.w and 350.06 ng kg^{-1} d.w., respectively. Results presented by Niemirycz *et al.* (2003) for sediments of the Wloclawek Reservoir reported the PCBs concentration as 164 ng kg^{-1} d.w. In comparison, the PCBs contamination of sediments collected from the Rhine Delta (The Netherlands) were up to 200,000.00 ng kg^{-1} d.w. (Camusso *et al.* 2000).

In this study, the highest potential for dl-PCBs accumulation was recorded at the sampling point situated at the end of the river continuum (PR7). This situation can be linked to: (1) the input of the highest amount of PCBs from the surface and groundwater runoff from the urbanized and agricultural catchment, and (2) to the hydraulic transport of PCBs along the river continuum and their deposition at the end of the river system and/or in the dam reservoir.

The input of PCBs from surface and groundwater runoff

The atmosphere is the conduit through which PCBs, as well as other persistent organic pollutants (POPs) can move from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems (Urbaniak 2007). In consequence, atmospheric burdens and fluxes can greatly influence the total amount of PCBs in the environment, and they are considered as a major input of PCBs to bodies of water. As reported by Urbaniak (2007), the atmospheric deposition process occurs in two ways, as dry and wet deposition. Thus, rainfall can be reported as one of the PCBs transport steps to bodies of water. Moreover, rainfall-induced high runoff from landscape scours the deposited substances, of which the most important are those connected with agriculture (fertilizers and pesticides) (Mullis *et al.* 1996). Thus, deposition of PCBs containing particulates on the catchment surface and then their flush during the rain may be reported as one of the main PCB sources in the river catchment.

Additionally, higher PCB concentration in the samples collected from the downstream section of the Pilica River (PR6 and PR7) can be related to a larger drainage area and consequently the higher PCB pollution level of this part of the river. Similar results were reported by Sapozhnikova *et al.* (2005) on the basis of the Dniestr River research. The

authors demonstrated that downstream sampling sites had significantly higher concentration of total PCBs as compared with the upstream samples. Moreover, the research conducted at six sites on the Hyeongsan River (Korea) demonstrated an increase in the total concentrations of non-ortho and mono-ortho PCB congeners from 12 to 4,500 ng kg^{-1} d.w. along the river flow (Qi *et al.* 1999). The same situation was reported by Koh *et al.* (2004). Additionally, Sapozhnikova *et al.* (2005) observed an increase in the concentration of PCB-81 and PEL (Probable Effects Level, suggesting potential adverse effects on benthic organisms) from upstream to downstream samples. This is in accordance with our studies, in which concentration of congener PCB-81 increased along the river. The exception was samples collected from the Sulejow Reservoir where a decrease in PCB-81 concentration was observed.

Additional pollution sources in the Pilica watershed, which consequently influence the concentration and pattern of dl-PCBs in the river and reservoir sediments, are the input of domestic and/or industrial wastewater discharges from the surrounding cities, as well as touristic and recreational places situated along the river (Figure 1). The research conducted by Pham & Prolux (1997) demonstrated that the concentration of PCB in sewage in Montreal (Canada) was close to 4.3 ng l^{-1}. The study of Blanchard *et al.* (2004) reported the PCB contamination of sewage from the Paris area varied from 70,000 to 650,000 ng kg^{-1} d.w., with the highest input delivered from the most urbanized catchment (up to 3.5 kg year^{-1}). Other researches demonstrated high PCB discharges, either from domestic and industrial sewage (Chevreuil *et al.* 1989; Loganathan *et al.* 1997).

Some values of dl-PCBs might also be connected with the usage of technical products containing PCBs (Aroclors products) derived mainly from those imported and used in Poland for several decades of the 20th century. As reported by Falandysz (1999), this kind of human activity is recognized as one of the possible sources of PCBs in the environment. This thesis was confirmed by Zieliński *et al.* (2007), who reported that the percentage composition of Aroclors No. 1232 and 1016 was similar to that found in the Polish river sediment samples. Our study also suggested that PCBs composition with the predominance of PCB-118 and PCB-105 – similar to their content in the Aroclor products – can be related to their usage in the past. Moreover,

within Poland, two technical PCB products, called Chlorofen and Tarnol, containing 63.6 and 40% of Cl, respectively, were produced and handled (Holoubek 2000; Falandysz & Szymczyk 2001). Nevertheless, there is no comparative analysis of their composition with relation to the current PCB concentration in the environment.

The hydraulic transport of PCBs along the river continuum

The year of 2006 can be characterized by very rapid meteorological changes with periods of intensive storm events (January–February; April–May) and droughts (July–October). This could have a great influence on the PCBs fate and distribution in the river. The occurrence of rapid and intensive precipitation led to a rinsing off of the sediments down the river continuum, and activated matter from floodplains. Furthermore, during such high flows, deeper layers of sediments can be suspended, thus mobilizing the PCBs deposited in the past. Whereas periods of lower flow, observed during the summer/autumn season, led to intensification of sedimentation processes in the river channel and the dam reservoir (Mullis *et al.* 1996). Therefore, sediments mobilized during high flow events and then deposited at the end of the river system during low flows can be the dominant source of SPM and nutrients (mainly phosphorus and nitrogen) (Altinakar *et al.* 2006), and consequently associated with PCBs (Urbaniak *et al.* 2010). Moreover, a high input of sediments with smaller grain size increases the surface area, which may account for higher concentrations of PCBs. Transport of the suspended sediment load by the Pilica River was reported by Kiedrzyńska (2007). The author showed that between 2002 and 2004, the total outflow of the Pilica River amounted to 3,500 mln m^3, and the total suspended sediment load transported by the river was 33,054 t (ton), where the mineral fraction (T_{Min}) was 49% (16,192 t) and the organic fraction (T_{Org}) was 51% (16,861 t). In this period, flood water discharges $Q > 40$ m^3 s^{-1} (water level $H > 180$ cm) of the Pilica River were observed during 38% of the study time and low water discharges $Q < 40$ m^3 s^{-1} ($H < 180$ cm) occurred for 62% of the study time. Furthermore, the Pilica River transported 42 and 58% of the suspended sediment load during floods and low water discharges, respectively. Therefore, dams

constructed on running waters, where a decrease in flow velocity and an increase in suspended particulates occur, create the perfect conditions for the deposition of organic and mineral matter and, by association, dl-PCB. This, in consequence, diminishes the dl-PCB in the outflow water resulting in their reduced concentration below the dam.

CONCLUSIONS

The HELCOM climatic scenarios of the South Baltic Sea catchment, including Pilica River catchment, predict a decrease of the summer river flow up to 50%; whereas in winter it may increase up to 70% (Helcom 2007). If such dramatic changes occur, extreme floods and droughts will constitute a severe threat to sustainable development.

Therefore the traditional view of the role of dams in shaping basin-scale ecological processes (e.g. Ward & Stanford 1979; Lillehammer & Saltveit 1984; Petts 1984; Power *et al.* 1996) has to be reconsidered. This is especially important because, with climate change, dams may also play an increasingly important role in protecting water resources and thus contributing to human development by providing reliable sources of drinking water and irrigation, hydropower, recreation, navigation, income and other important benefits (WCD 2000). The other important role of dams is the reduction of the transfer of micropollutants, such as nutrients and PCBs, from land to mouth sections of the river. The study results presented here indicate that the concentration and the transfer of the nutrients and pollutants along the river continuum might be diminished by anthropogenic retention through construction of reservoirs, in which the reduction of concentration of SPM, TP, TN and PCBs in sediments have been observed and suggested as an important purging mechanism.

ACKNOWLEDGEMENTS

REFERENCES

Altinakar, M., Kiedrzyńska, E. & Magnuszewski, A. 2006 Modelling of inundation patterns on the Pilica River floodplain, Poland. In: *The Fifth FRIEND Conference*, November 2006, Havana, Cuba.

Ambrożewski, Z. 1996 Ecological and flooding problems of the Sulejow Reservoir. *Aura* **7**, 19–21. [In Polish].

Blanchard, M., Teil, M. J., Ollivon, D., Legenti, L. & Chevreuil, M. 2004 Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France). *Environ. Res.* **95**, 184–197.

Bowes, M. J., House, W. A. & Hodgkinson, R. A. 2003 Phosphorus dynamics along a river continuum. *Sci. Total Environ.* **313**, 199–212.

Camusso, M., Vignati, D. & Van De Guchte, C. 2000 Ecotoxicological assessment in the rivers Rhine (The Netherlands) and Po (Italy). *Aquat. Ecosys. Health Manag.* **3**, 335–345.

Certificate of Analysis, Standard Reference Material (SRM) 1939 1990 *Polychlorinated Biphenyls (Congeners) in River Sediment A*. National Institute of Standards and Technology, Gaithersburg, MD, October 22.

Chevreuil, M., Chesterikoff, A., Letolle, R. & Granier, L. 1989 Atmospheric pollution and fallout by PCBs and organochlorine pesticides (Iles-de-France). *Water Soil Pollut.* **43**, 73–78.

Devault, D. A., Gerino, M., Laplanche, Ch., Julien, F., Winterton, P., Merlina, G., Delams, F., Sanches-Perez, J. M. & Pinelli, E. 2009 Herbicide accumulation and evolution in reservoir sediments. *Sci. Total Environ.* **407**, 2659–2665.

DiPinto, L. M., Coull, B. C. & Chandler, G. 1993 Lethal and sublethal effects of a sediment-associated PCB Aroclor 1254 on a meiobenthic copepod. *Environ. Toxicol. Chem.* **12**, 1909–1918.

Falandysz, J. 1999 *Polychlorinated Biphenyls in the Environment: Chemistry, Analysis, Toxicity, Concentration and Risk Assessment*. Gdansk University Development Foundation, Gdańsk [in Polish].

Falandysz, J. & Szymczyk, K. 2001 Data on manufacture, use, inventory and disposal of polychlorinated biphenyls (PCBs) in Poland. *Pol. J. Environ. Stud.* **10**, 189–193.

Galicka, W. 1996 Limnological characteristic of the lowland dam reservoir on the Pilica River in the years 1981–1993.

University of Lodz Publisher, Lodz, Vol. 1, pp. 1–146 [in Polish].

Gardinali, P. R., Wade, T. L., Chambers, L. & Brooks, J. K. 1996 A complete method for the quantitative analysis of planar, mono, and diortho PCB's, polychlorinated dibenzodioxins and furans in environmental samples. *Chemosphere* **32**, 1–11.

Greenberg, A. E., Clesceri, L. S. & Eaton, A. D. 1992 *Standard Methods for the Examination of Water and Wastewater.* American Public Health Association, Washington, DC.

HACH 1997 *Water Analysis Handbook.* Hach Company, Loveland, CO, pp. 1309.

Heiler, G., Hein, T., Schiemer, F. & Bornette, G. 1995 Hydrological connectivity and flood pulses as the central aspects for the integrity of a river floodplain-system. *Regulated Rivers: Res. Manage.* **11**, 351–361.

Helcom (Helsinki Commission) 2007 Climate change in the Baltic Sea Area. In: *Baltic Sea Environment Proceedings No. 111.* Helcom, Helsinki.

Holoubek, I. 2000 Polychlorinated biphenyls (PCBs) worldwide contaminated sites. TOCOEN Reports No. 173. Available from: http://www.recetox.muni.cz/reports/TR173/p2.htm

Hong, S. H., Yim, U. H., Shim, W. J. & Oh, J. R. 2005 Congener specific survey for polychlorinated biphenyls in sediments of industrialized bays in Korea: regional characteristics and pollution sources. *Environ. Sci. Technol.* **39**, 7380–7388.

Junk, W. J., Bayley, P. B. & Sparks, R. R. 1989 The flood pulse concept in river-floodplain systems. Proceedings of the International Large River Symposium. *Canad. J. Fish. Aquat. Sci.* **106**, 110–127.

Kiedrzyńska, E. 2007 Nutrients retention and flood sediments deposition in the Pilica River valley for the reduction of eutrophication of the Sulejów Reservoir. PhD Thesis. Department of Applied Ecology University of Lodz, Poland.

Kiedrzyńska, E., Kiedrzyński, M. & Zalewski, M. 2008a Flood sediment deposition and phosphorus retention in a lowland river floodplain: impact on water quality of a reservoir, Sulejów, Poland. *Ecohydrol. Hydrobiol.* **8**, 2–4.

Kiedrzyńska, E., Wagner-Łotkowska, I. & Zalewski, M. 2008b Quantification of phosphorus retention efficiency by floodplain vegetation and a management strategy for a eutrophic reservoir restoration. *Ecological Eng.* **33**, 15–25.

Kiedrzyńska, E., Macherzyński, A., Skłodowski, M., Kiedrzyński, M. & Zalewski, M. 2010 Analysis of point sources of pollution with biogenic compounds in the catchment area of the Pilica River, as well as the application of the ecohydrological approach for their reduction. In: *Hydrology for Protection and Shaping of the Environment* (A. Magnuszewski, ed.). Monographs on Environmental Engineering Committee, Vol. 69, pp. 285–295 [in Polish].

Knezovich, J. P., Harrison, F. L. & Wilhelm, R. G. 1987 The bioavailability of sediment sorbed organic chemicals: a review. *Water Air Soil Pollut.* **32**, 233–245.

Koh, C. H., Khim, J. S., Kannan, K., Villeneuve, D. L., Senthilkumar, K. & Giesy, J. P. 2004 Polychlorinated dibenzop-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) and 2,3,7,8-TCDD equivalents (TEQs) in sediments from the Hyeongsan River, Korea. *Environ. Pollut.* **123**, 489–501.

Lillehammer, A. & Saltveit, S. J. 1984 *Regulated Rivers.* Unversiteitsforlaget, Oslo.

Loganathan, B. G., Irine, K. N., Kannan, K., Pragatheswaran, V. & Sajwan, K. S. 1997 Distribution of selected PCB congeners in the Babcock Street sewer district: a multimedia approach to identify PCB sources in combined sewer overflows (CSOs) discharging the Bufallo River, New York. *Arch. Environ. Contam. Toxicol.* **15**, 133–140.

Miller Jr., G. T. 2005 *Environmental Science*, 5th edition. Belmont, Wadsworth, UK.

Mitsch, W. J. & Gosselink, J. G. 2007 *Wetlands*, 4th edition. Wiley and Sons, Inc., New York.

Mullis, R. M. D., Revitt, M. & Shutes, R. B. 1996 The impacts of urban discharges on the hydrology and water quality of urban watercourses. *Sci. Total Environ.* **189/190**, 385–390.

Niemirycz, E., Gozdek, J., Kaczmarczyk, A. & Tyszkiewicz, H. 2003 Antropogenic organic substances: origin, distribution and influence in the sediments of Wloclawek Reservoir. IMGW, Project report GF/POL/INV/R.22. [In Polish].

Ostrowska, A., Gawliński, S. & Szczubiałka, Z. 1991 *Analysis and Estimation Methods of Soil and Plants Properties.* Catalogue of the Institute of Environment Protection, Warsaw, pp. 334 [in Polish].

Petts, G. E. (ed.) 1984 *Impounded Rivers. Perspectives for Ecological Management.* Wiley, Chichester.

Pham, T. & Prolux, S. 1997 PCBs and PAHs in the Montreal urban community (Quebec, Canada) wastewater treatment plant and in the effluent plume in the St Lawrence river. *Water Res.* **31**, 1887–1896.

PN-EN 1948-3 2002 Emission from the stationary sources. Estimation of the PCBs mass concentration. Part 3: Identification and quantitative estimation. [In Polish].

Power, M. E., Dietrich, W. E. & Finlay, J. C. 1996 Dams and downstream aquatic biodiversity: potential food web consequences of hydrologic and geomorphic change. *Environ. Management* **20**, 887–895.

Qi, M., Blunt, J., Chen, J. & Gao, X. 1999 Determination of polychlorinated biphenyl congeners in sediment samples of twelve rivers in eastern China. *Toxicol. Environ. Chem.* **71**, 497–508.

Sapozhnikova, Y., Zubcov, E., Zubcov, N. & Schlenk, D. 2005 Occurrence of pesticides, polychlorinated biphenyls (PCBs), and heavy metals in sediments from the Dniestr River, Moldova. *Arch. Environ. Contamin. Toxicol.* **49**, 439–488.

Urbaniak, M. 2007 Polychlorinated biphenyls (PCBs): sources, distribution and transformation in environment – literature review. *Acta Toxicol.* **15**, 83–93.

Urbaniak, M., Zieliński, M., Wesołowski, W. & Zalewski, M. 2008 PCBs and heavy metals contamination in bottom sediments

from three reservoirs of different catchment characteristics. *Pol. J. Environ. Stud.* **17**, 941–949.

Urbaniak, M., Zieliński, M., Wesołowski, W., Dąbrowska, H. & Zalewski, M. 2009a Spatial heterogeneity of the PCDD and PCDF content in the dam reservoirs of Włocławek and Sulejówek. *Monograph Dioxins in Industry and Environment* **10**, pp. 64–68. [in Polish].

Urbaniak, M., Zieliński, M., Wesołowski, W. & Zalewski, M. 2009b Sources and distribution of polychlorinated dibenzo-para-dioxins and dibenzofurans in sediments of urban cascade reservoirs, Central Poland. *Environ. Protect. Eng.* **35**, 93–103.

Urbaniak, M., Zieliński, M., Wesołowski, W. & Zalewski, M. 2009c Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) compounds in sediments of two shallow reservoirs in Central Poland. *Arch. Environ. Protect.* **35**, 125–132.

Urbaniak, M., Skowron, A., Frątczak, W., Zieliński, M. & Wesołowski, W. 2010 Transport of polychlorinated biphenyls in urban cascade reservoirs: levels, sources and correlation to the environmental conditions. *Polish J. Environ. Stud.* **19**, 201–211.

U.S. EPA METHOD 1668 1999 *Revision A: Chlorinated Biphenyls Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS*. Washington DC, USA.

Van den Berg, M., Birnbaum, L., Denison, M. & Farland, W. 2006 The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. *Toxicol. Sci.* **93**, 223–241.

Vannote, R. L., Minshall, G. W., Cummings, K. W., Sedell, J. R. & Cushing, C. E. 1980 The River Continuum Concept. *Can. J. Fish. Aquati. Sci.* **37**, 130–137.

Wagner, I. & Zalewski, M. 2000 Effect of hydrological patterns of tributaries on biotic processes in a lowland reservoir – consequences for restoration. Special Issue. *Ecological Engineering* **16**, 79–90.

Ward, J. V. & Stanford, J. A. (eds.). 1979 *The Ecology of Regulated Streams*. Plenum, New York.

WCD World Commission on Dams 2000 *Dams and Development, A New Framework for Decision-Making*. Earthscan, London.

Zalewski, M., Janauer, G. S. & Jolankai, G. 1997 Ecohydrology – a new paradigm for the sustainable use of Aquatic resources. UNESCO IHP-V. Technical Documents in Hydrology, no 7.

Zalewski, M. & Kiedrzyńska, E. 2010 System approach to sustainable management of inland floodplains declaration on sustainable floodplain management. *CAB Reviews: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources* **5** (056), 1–8.

Zieliński, M., Wesołowski, W. & Kucharska, M. 2007 HRGC/HRMS technique in Estimation of Non-ortho and Mono-ortho PCB in Industrial Products of Aroclor. In: *Conference: Application of Chromatographic Techniques in Environmental and Clinical Analysis*. 16.IV. Technical University in Lodz, Poland [in Polish].