Original Research

Transport of Polychlorinated Biphenyls in Urban Cascade Reservoirs: Levels, Sources and Correlation to Environmental Conditions

Magdalena Urbaniak[1,2]*, Aleksandra Skowron[1], Wojciech Frątczak[1,2], Marek Zieliński[3], Wiktor Wesołowski[3]

[1]Department of Applied Ecology, University of Łódź, Banacha 12/16, 90-237 Łódź, Poland
[2]International Institute of the Polish Academy of Sciences,
European Regional Centre for Ecohydrology under the auspices of UNESCO, Tylna 3, 90-364 Łódź, Poland
[3]Nofer Institute of Occupational Medicine, Teresy 8, 91-348 Łódź, Poland

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Abstract

Intensified human impact in urban catchments is reflected through degradation of hydrological cycles and acceleration of matter, energy and pollutants flows. In this study the comparative analysis of occurrence, concentrations and transfer of twelve dioxin-like PCBs in the bottom sediment collected from five cascade reservoirs located on the Sokołówka River (in the northwestern part of the city of Łódź, central Poland) were determined using isotopically labelled internal standards and HRGC/HRMS. The total concentration of analyzed PCBs ranged from 79.75 to 3,741.34 ng/kg d.w. with maximum concentrations in the last two reservoirs (3,741.34 and 2,594.36 ng/kg d.w., respectively). Reservoirs situated at the beginning of the cascade system showed concentrations several times lower: 694.32 in the first, 292.15 in the second and 79.75 ng/kg d.w. in the third reservoir. The obtained data showed moderate or strong correlations between PCB concentration in sediments and environmental conditions of the water column: pH (-0.81), conductivity (0.94), mineral suspended solids (0.82), total and organic suspended solids (0.61), total phosphorus (-0.83) and total nitrogen (0.67). Furthermore, these parameters could have played an indirect role in PCB reduction through the stimulation of phytoplankton production. This in consequence might have influenced PCB pathways in reservoirs through changes in their sedimentation, transport and degradation processes as significant relations between PCBs and chlorophyll *a* content was found (0.64).

Keywords: PCBs, sediments, reservoirs

Introduction

The urbanization processes led to changes in stream hydrology and geomorphology that result in accelerated fluxes of matter, nutrient and organic pollutants. The contamination from traffic (exhaust, oil spills, wear and tear of tires, vehicles), buildings (weathering, renovation, demolition, paint, plaster) and industry may be the most frequent causes of pollution within the urban drainage area [1-3]. Additionally, this kind of human activity leads to accelerated sewage and waste production.

Urban-induced increases in stream fluxes of organic matter and pollutants may be diminished by anthropogenic retention through the construction of reservoirs, which

*e-mail: m.urbaniak@unesco.lodz.pl

Table 1. Characteristics of studied reservoirs [12].

	UP	LP	ZR	TR	PR
Max surface area (m^2)	16,400	11,000	18,600	4,000	15,000
Capacity (m^3)	22,500	11,100	24,000	4,100	20,000
Retention time (days)	8.70	3.90	7.70	1.20	3.40
Age (years)	~100	~100	4	4	~100
Input flow (m^3/s):					
Min	0.006	0.006	0.007	0.008	0.014
Average	0.030	0.033	0.036	0.039	0.068
Max	0.680	0.750	0.810	0.920	1.480
Macrophyte presence	absent	absent	present	absent	absent

create an efficient trap for sediments, nutrients and pollutants, especially when interlinked in a cascade. Deposition and burial in sediments, as the final sink for organochlorine pollutants, have been suggested as an important purging mechanism. The decrease in the flow velocity and increase of flocculent settling in reservoirs situated at the end of a watercourse or reservoir cascade create perfect conditions for sedimentation and deposition of pollutants [4]. However, urban shallow interconnected reservoirs located along an urban stream continuum are exposed to high hydrological instability due to storm water flush events. During such events, reservoirs may act as sources of pollutants through resuspension and redistribution of the deposited compounds to the water column [5-7]. The floating matter, with organic compounds like PCB bound to the finest fraction of sediments, can be transported along the urban reservoir continuum. Additionally, internal processes and interactions in water ecosystems may impose great influence on the fate of organochlorine pollutants and their redistribution between water, biota and sediments. Berglund et al. [7] and Roessink et al. [8] suggested that concentrations of organochlorine compounds in aquatic organisms decreased with the trophic status of lakes, measured as total phosphorus concentration or plankton biomass. Pollutants associated with the phytoplankton may undergo sedimentation purging the water column. Due to greater amounts of settling algae, the microbial degradation in shallow eutrophic lakes is insufficient to mineralize the entire pool of settling organic carbon. Thus pollutants bounded to settling algae may not be released back to the water and accumulate in the sediment [5, 9-11].

This paper provides data demonstrating:

1) the concentration of PCBs in urban cascade reservoirs,
2) identification of sources affecting the obtained levels, and
3) transfer of analyzed contaminants along the river with respect to different environmental conditions like average annual water temperature, pH, oxygen content, conductivity, total suspended solids (TSS), organic suspended solids (OSS), mineral suspended solids (MSS) total phosphorus (TP), total nitrogen (TN) and chlorophyll *a* content.

Materials and Methods

Study Site

The Sokołówka River (drainage area 45.40 km^2) situated in the northwestern part of the city of Łódź, central Poland, represents a highly urbanized and industrialized catchment contaminated with organic compounds due to sewer and stormwater overflows. The main channel was channelized to straighten the course and deepen the bed for the purpose of detention of storm waters. To reduce of storm water flow peaks along river length several reservoirs were constructed. As an element of the "green belt" of the Sokołówka Valley, reservoirs are also used for recreation [12-15].

The five reservoirs located along the Sokołówka River selected for analysis (Fig. 1) differ from each other in age, size, theoretical water residence time, light intensity and input flow. All can be regarded as small, with riverine character and short water retention time (Table 1).

The first and second ponds (UP and LP) are situated in an old park in the vicinity of a large housing development. The following two (ZR and TR) are newly constructed ones, located in an estate area, and the last one (PR) is placed on the outskirts of the city, in the middle section of a river valley that has maintained a semi natural character [12-15]. Additionally, the last reservoir (PR) is a recipient for waters from Sokołówkas's tributary – the Brzoza River (Fig. 1), which is also a storm water receiver.

Sampling

The reservoir sediment samples (10-25 cm thickness) were collected once during spring 2007 using a gravity core sampler and stored in an icebox at 4°C in black glass jars (to avoid sunlight). The glass jars were previously cleaned with detergent and rinsed with ultra-pure water, followed by heating to 450°C overnight. Before being used in the field they were rinsed with acetone and hexane. The jars' teflon caps were also cleaned with detergent, rinsed with ultra-pure water, and before being used rinsed with acetone and hexane.

Samples were collected from three stations (inlet, medium part and dam) in each reservoir, resulting in 15 samples. After collection, sediment samples were transported to the laboratory, where they were directly freeze dried (-40°C, 1mba, 72 h; Edwards Freeze Dryer) and sieved trough 2 mm mesh sieve. Then each of three samples from one reservoir were mixed in proportion 1:1:1 to obtain one representative sample.

Samples of water were collected 2-4 times a month from May to October 2006 to measure total phosphorus (TP), total nitrogen (TN), total suspended solids (TSS), organic suspended solids (OSS), mineral suspended solids (MSS) and chlorophyll *a* content. During the sampling, water temperature, pH, oxygen content and conductivity were measured.

The flow velocity was measured by the use of on-line monitoring stations located above and beneath the cascade of the first three reservoirs (Fig. 1).

PCB Analysis

PCBs Extraction and Clean-Up

The method of sample pretreatment was according to PN-EN 1948-3 [16], 2002; EPA Method 1668, 1994) [17]. For each sediment sample, 2 g were spiked with isotopically labelled standards (Cambridge Isotopes Laboratories, USA) and extracted by automatic system extraction (ASE) 200 Dionex at 150 atm (11 Mpa) and the oven was heated to 175ºC with toluene. The extracts were purified with multilayer silica columns packed with neutral, acidic and basic silica gel and eluted with 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.

PCB Identification and Quantification

Identification and quantification of PCBs were performed by HRGC/HRMS: HP 6890N Agilent Technologies coupled to 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 PCB congeners was achieved using a DB5-MS column (60 m x 0.25 mm i.d., film thickness 0.25 µm).

The oven temperature program was 150ºC for 2 min. 20ºC/min. to 200ºC (0 min.), 1ºC/min. to 220ºC for 16 min. and 3ºC/min. to 320ºC for 3 min. The injector temperature was 270°C. The MS was operated under positive EI conditions: 34.8 eV electron energy at a resolving power of 10,000 with an ion source temperature of 250°C. Helium was used as a carrier gas at a flow rate 1.60 mL/min. Samples were quantified with an isotope dilution method [16, 17].

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 (dioxin-like PCB).

In our study we used this term to evaluate the toxicity of sediment sample polluted by dl-PCB. Each of individual dl-PCB congeners have been assigned a toxic equivalency factor (TEFs) 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 its concentration in terms of TEQ calculated for all dl-PCB congeners [18].

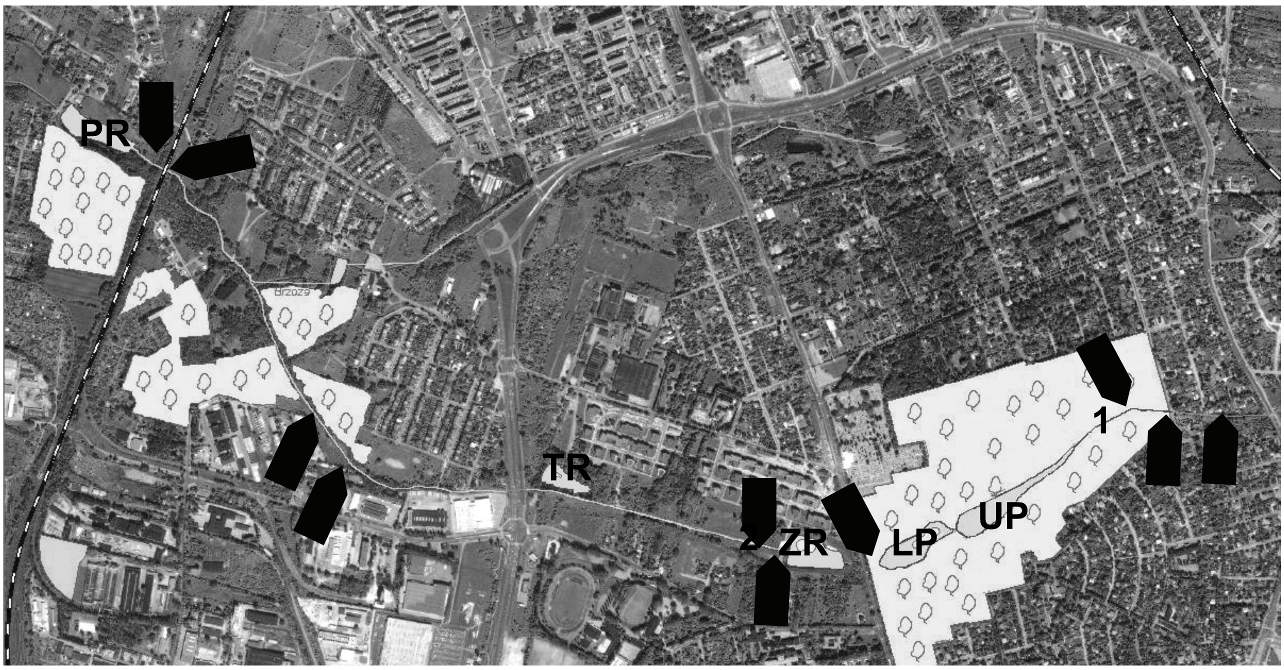

Fig. 1. Sediment sample collection sites (UP, LP, ZR, TR and PR) and most important stormwater outlets (black arrows) situated along the Sokołówka River [13]. 1, 2 – location of on-line flow velocity monitoring stations (scale 1:125000).

Table 2. PCB congener's method detection limit [(MDL), pg/kg. d.w.], relative standard deviation [(RSD), %] and recoveries [%].

Congener PCB	Method Detection Limit	RSD	Recovery
77	0.12	3.01	105
81	0.35	4.49	94
126	0.15	1.76	102
169	0.13	2.35	102
105	0.48	6.96	101
118	0.25	3.85	93
123	0.37	4.20	102
156	0.21	2.87	96
157	0.22	2.40	98
167	0.21	3.64	93
189	0.37	6.96	104
114	0.13	2.37	101

Chemicals

The hexane, nonane and toluene used for extraction and clean up of sediments samples were purchased from Bujno Chemicals (Warsaw, Poland). The Na_2SO_4, H_2SO_4 and silica gel were purchased from Sigma-Aldrich Co (Poznań, Poland). The silica gel was heated overnight at 450ºC to reduce background levels of PCBs. All solvents were pesticide residue analysis grade. The PCB standards were all obtained from LGC Promochem, CIL Cambridge (Łomianki, Poland).

The numbering system of PCB congeners adopted by the International Union of Pure and Applied Chemistry (IUPAC) was followed by confirmation and discussion of the results.

PCB Quality Assurance/Quality Control

The analytical method used for PCB analysis was properly validated on the basis of internal reference materials and the analytical laboratory involved in 2005 successfully passed the accreditation procedure.

All glassware and bottles used in field and laboratory were cleaned with detergent, rinsed with ultra-pure water followed by heating at 450°C overnight. Glassware was rinsed with acetone and hexane before use.

Each analytical batch contained a method blank, a matrix spike, and duplicate samples. A reagent blank was used to assess artifacts and precision was verified by duplicate analyses. Samples spikes were used as an additional check of accuracy. Analyte recoveries were determined by analyzing samples spiked with PCB standards. The recovery coefficient was taken into account for calculating the final concentrations of analytes.

Additionally, to assess method correctness the Standard Reference Material: 1939a Polichlorinated Biphenyls in River Sediment A was used.

The PCB method detection limit (MDL), relative standard deviation (RSD), and recoveries were presented in Table 2.

Other Environmental Parameters Analysis

Organic Matter Analysis

Measurement of the carbon content in the sediment samples was determined using the gravimetrical method according to the method described by Ostrowska et al. [19] with accuracy of 5%.

10 g of sediment samples were placed in crucibles in a drying oven at 105ºC overnight. After that, sediments were weighed and dried in a muffle furnace at 500ºC overnight. The determination of organic matter content was calculated as:

$$M_{om}=(M_{105}-M_{500})/M_0$$

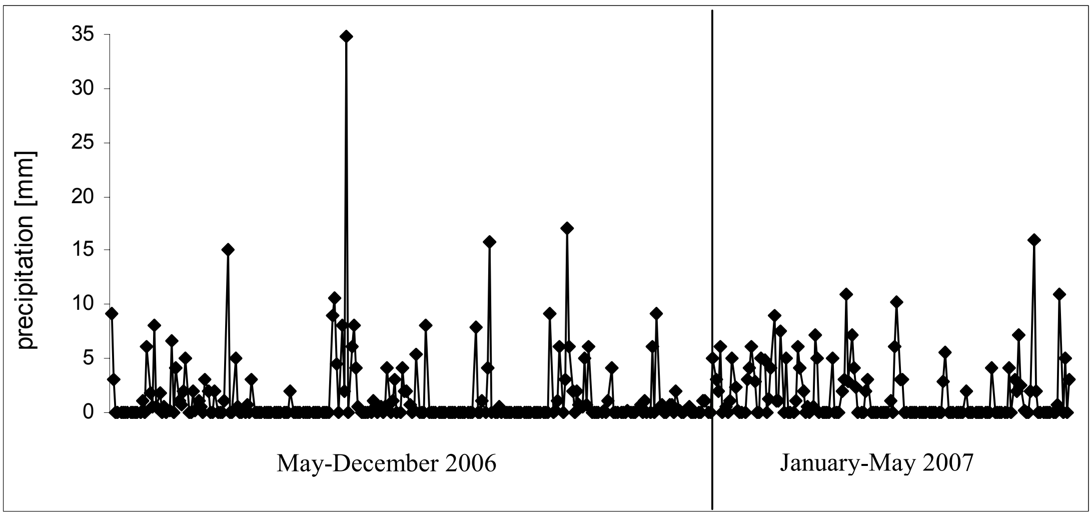

Fig. 2. Precipitation in the Sokołówka River catchment in the monitoring season of 2006-07.

Table 3. Concentration of 12 PCB congeners [ng/kg d.w.] (recommended by EPA 1668 Method) in sediment samples collected from Sokołówka River reservoirs during spring 2007.

Congener	UP	LP	ZR	TR	PR
PCB-77	20.57	2.43	2.15	49.26	85.99
PCB-81	4.06	9.67	3.46	110.51	187.65
PCB-126	13.91	2.70	0.54	8.45	21.94
PCB-169	0.07	n.d.	n.d.	n.d.	n.d.
Sum of non-ortho PCBs	38.62	14.80	6.14	168.22	295.58
PCB-105	162.69	11.34	2.79	57.46	165.37
PCB-114	26.23	9.51	2.72	154.89	n.d.
PCB-118	327.34	168.25	57.47	2,834.50	787.70
PCB-123	57.18	26.63	8.00	118.00	143.08
PCB-156	1.80	n.d.	1.40	5.46	20.60
PCB-157	17.35	n.d.	0.70	2.73	10.30
PCB-167	60.72	56.34	n.d.	399.71	1,171.72
PCB-189	2.40	5.29	0.53	0.36	n.d.
Sum of mono-ortho PCBs	655.70	277.35	73.61	3,573.12	2,298.78

n.d. – not detected: measured concentration was below detection limit.

Total Phosphorus and Total Nitrogen Analysis

Water samples were collected and transported at 4°C to the laboratory, where they were immediately analyzed or frozen for later analysis. Total forms of nutrients were measured in unfiltered water. Total phosphorus was measured according to the ascorbic method with accuracy of 5% [20]. Total nitrogen was analyzed using the persulfate digestion method with accuracy of 3% [21].

Chlorophyll *a* Analysis

For chlorophyll *a* analysis the water sample of known volume was filtered through GF/C glass fibre filters (Whatmann). The filters were frozen and then analyzed according to acetone extraction method and determined by spectrophotometry [22] with 0.05 μg chlorophyll *a*/L precision.

Suspended Solids Analysis

Total Suspended Solids (TSS) content was determined in two replicates for each sample by filtering the water through 0.45 μm filters of known weight and drying at 105°C (12 h). Mineral solids content was determined by next burning the filters at 500°C (4 h). Organic suspended solids content was calculated as a difference between total and mineral solids content [23].

Meteorological Data

Meteorological data were obtained from the publicly available meteorological database, from weather station No. 124650 (http://www.tutiempo.net/en/Climate/LODZ/124650.htm).

Flow Velocity

The flow velocity was measured using on-line monitoring stations equipped with 2150 Flow Module (ISCO). The stations were placed above and beneath the cascade of the first three reservoirs (Fig. 1). The 2150 Flow Module uses continuous wave Doppler technology to measure mean velocity. The sensor transmits a continuous ultrasonic wave, then measures the frequency shift of returned echoes reflected by air bubbles or particles in the flow. Data show preliminary results collected in the period between 9 June and 15 December 2008.

Statistics

All data were subjected to statistical analyses using "Statistica" software for Windows. A Kruskal-Wallis ANOVA by Ranks test was used to compare treatment levels. The Pearson linear correlation coefficient was used to assume the correlation between concentration of PCBs and the measured conditions. The statements of significance were based on a probability level of $P \leq 0.05$.

Results

PCB Levels

Individual PCB congener concentrations, as well as total WHO-TEQ concentrations and sediment organic matter content, are given in Tables 3 and 4, and showed that reservoirs were heterogeneous with values ranging from n.d. (below detection limit) to 2,834.50 ng/kg of dry weight (d.w.). The differences between the reservoirs' respective pollution levels were confirmed by the Kruskal-Wallis ANOVA by Ranks test ($H = 10.41$; $p = 0.03$).

The maximum concentration of total PCBs was observed at TR site (3,741.34 ng/kg) with dominant congeners: PCB-118 (2,834.50 ng/kg dry weight), PCB-167 (399.71 ng/kg dry weight), PCB-114 (154.89 ng/kg dry weight) and PCB-123 (118.00 ng/kg dry weight) (Table 2). Additionally, congener PCB-118 had the highest frequency of occurrence in all the samples with value ranging from 75.76% for TR site, 72.07% for ZR, 57.59% for LP 47.15% for UP to 30.36% for PR. Either congener PCB-105 possessed high percentage of occurrence, especially in the first reservoir (UP) 23.43%. In other reservoirs this value ranged from 1.54% (TR) to 6.37% (PR). In consequence, pentachlorobiphenyls were the dominant homologues in all sediments samples.

From all congeners recommended by WHO, homologues PCB-77, 81, 126 and 169, called as coplanar or non-

Table 4. Total PCB concentration, WHO-TEQ concentration and organic matter content in sediment samples collected from Sokołówka River reservoirs during spring 2007.

	UP	LP	ZR	TR	PR
Total PCBs [ng/kg d.w.]	694.32	292.15	79.75	3,741.34	2,594.36
WHO-TEQ [ng TEQ/kg d.w.]	1.42	0.28	0.06	0.99	2.33
Sediment Organic Matter [%]	20.25	32.98	2.10	3.23	13.07

ortho, possess more toxic properties than non-coplanar congeners (Table 3) [18]. In this study, the lowest percentage of non-ortho PCBs was observed in the second and the fourth reservoir, whereas in the first, third and fifth this value was higher (Fig. 3). Concentration of PCB-77, PCB-81 and PCB-126 were the highest in samples collected from the PR reservoir (85.99 ng/kg, 187.65 ng/kg and 21.94 ng/kg dry weight, respectively), whereas at the other sites these value were about 50 to 2 times lower. Congener PCB-169 was not observed among all analyzed samples, with the exception of first reservoir, where its concentration was 0.07 ng/kg d.w. (Table 3).

PCBs WHO-TEQ Concentration

The WHO-TEQ concentration decrease from the first to third reservoir with the lowest TEQ concentration in the central - ZR site (0.06 ng TEQ/kg d.w.), and then increased in the last two reservoirs. Thus the highest WHO-TEQ concentration was noted in the first (UP) and last (PR) sites (1.42 and 2.33 ng TEQ/kg d.w., respectively). This high toxicity was mostly generated by PCB-126 congener concentrations (13.91 and 21.94 ng/kg in UP and PR, respectively) that posses the highest TEF value (0.10) (Table 4).

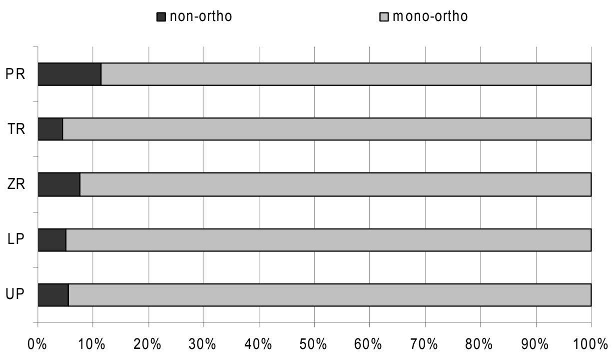

Fig. 3. Composition (%) of non-ortho and mono-ortho PCB in sediments collected from urban cascade reservoirs situated along the Sokołówka River.

Sediment Organic Matter Content

The content of organic matter in sediments ranged from 2.10% in the ZR to 32.98% in the LP site. The highest percentage participation of organic matter in sediments was observed in the first and second ponds (20.25% and 32.98%, respectively) (Table 4). This confirms that old reservoirs possess a higher content of organic matter than newly built ones. However, this situation could also be linked to the location of the above-mentioned ponds in the old park and, in consequence, the relatively higher contribution of organic matter from surrounding trees and other green areas. Additionally, these reservoirs received sewage sludge from the surrounding housing estate, which can increase the OC content in water and, in consequence, sediments.

Physical, Chemical and Biological Conditions of the Reservoirs

The physical, chemical and biological parameters of the reservoirs are given in Table 4.

The lowest average temperature due to its location in an old park had the LP reservoir while ZR as mostly insolated was the warmest one. Oxygen content was the highest at the UP and PR (10.60 and 11.87 mg/L), respectively, whereas the lowest concentration was noted in the second reservoir (8.09 mg/L). Because water temperature and Dissolved Oxygen are factors influencing physical, chemical and biological processes in waterbodies, they define self-purification processes and maintenance of aquatic organisms, which in turn affect concentrations of other pollutants in the water ecosystem. This was confirmed by the positive correlation between PCB concentrations and oxygen content (R=0.34). pH value was more or less stable and ranged from 8.10 to 8.64. Conductivity qualitatively reflects the status of inorganic pollution and is a measure of total dissolved solids and ionic species in the waters. It varies from 0.05 for pure water to about 225 mS/cm for concentrated brine [24]. In our study the lowest concentration was observed for the UP site (598 µS/cm), while in the other reservoirs this value ranged from 676 to 843 µS/cm (Table 5).

The nutrient concentrations varied between reservoirs with the maximum TP and TN concentrations in the second (LP) and last (PR) and first (UP) and the last reservoir (PR), respectively, and exceed the critical values for eutrophication (0.10 mg P/L and 1.50 mg N/L; [25]. Analysis of chlorophyll *a* concentrations confirmed the hypertrophic (> 25.00 mg/m^3) character of the reservoirs with maximum concentration in the last site (Table 5).

The content of TSS decreased from the first to third reservoirs from 24.39 to 11.21 mg/L, and then increased in the third and fourth reservoirs to 27.16. The same pattern was observed for the OSS and MSS (Table 4). The reduction in the first three reservoirs can be related to a decrease in the flow velocity and increase of flocculent settling creating perfect conditions for sedimentation and deposition of suspended solids in the cascade [4]. The increase in third reservoir might be a result of blooming, and in the last of the additional water supply from the Brzoza River.

Table 5. Average (A) and standarized deviation (D) values of measured parameters in UP, LP, ZR, TR and PR reservoirs.

		May-October 2006				
		UP	LP	ZR	TR	PR
Chlorophyll *a* [mg/m³]	A	54.33	39.49	22.75	41.52	54.22
	D	36.75	29.92	10.76	64.70	39.89
TP [mg/L]	A	0.30	0.46	0.35	0.25	0.32
	D	0.15	0.23	0.41	0.12	0.18
TN [mg/L]	A	2.00	1.80	1.60	1.90	2.20
	D	0.90	1.00	1.04	1.27	1.26
TSS [mg/L]	A	24.39	20.82	11.21	21.05	27.16
	D	29.20	11.54	4.75	19.45	10.65
OSS [mg/L]	A	24.39	18.72	9.24	15.54	19.55
	D	29.21	10.95	4.88	16.67	10.59
MSS [mg/L]	A	9.65	2.10	1.31	4.27	6.02
	D	26.55	1.01	0.67	3.84	3.79
Oxygen content [mg/L]	A	10.6	8.09	9.45	8.89	11.87
	D	5.4	4.32	2.98	2.21	4.14
pH	A	8.3	8.20	8.40	8.10	8.10
	D	0.4	0.50	0.60	0.50	0.40
Conductivity [µS/cm]	A	598	676	702	843	751
	D	112	150	191	206	152
Water temperature [°C]	A	19.2	18.82	20.38	19.98	19.59
	D	4.3	4.59	4.47	4.64	4.85

A – average; D – standard deviation; TSS – total suspended solids; OSS – organic suspended solids; MSS – mineral suspended solids; TP – total phosphorus; TN – total nitrogen.

The preliminarily obtained data of flow (Q), flow velocity (V), water level (H) on the first monitoring station was in the scope of 0.00-3.12 m/s and on the second station 0.00-1.27 m/s and the flow 0.00-2.92 (1) 0.00-2.12 (2). Water level, flow velocity and flow measured at the first station corresponded with meteorological data from the database (Pearson coefficients 0.94, 087, and 096, respectively, $p<0.05$).

Discussion

PCBs Levels

The results indicate low to moderate PCB contamination levels of analyzed sediments. Obtained data corresponded with results presented previously by Urbaniak et al. [26] for the sediments from reservoirs situated in mixed agricultural and urban areas (121.36, 350.06 and 694.31 ng/kg d.w, respectively). In the same study the WHO-TEQ concentration was 1.42 for the urban reservoir, 0.27 for the mixed and 0.40 ng TEQ/kg d.w. for the agricultural reservoir.

Loganathan et al. [27] reported that concentrations of PCB in Kentucky Lake (USA) were between 580.00-1,300.00 ng/kg d.w. Research of Niemirycz et al. [28] accounted for the PCB concentrations in the Włocławek Reservoir for 164.00 ng/kg d.w. In comparison, the PCB contamination of sediments collected from the highly urbanized Rhine Delta (The Netherlands) were up to 200,000 ng/kg d.w. [29]. Data obtained from the other regions of the world also indicate a wide range of pollution levels. As an example, we can list the study of Marvin et al. [30] conducted on Lake Ontario and Lake Erie, Ontario, Canada. Authors showed the mean concentrations were of about 728.60 and 2,712.00 ng/kg d.w. for Indian Point and Port Dalhousie in Lake Ontario, and 778.80 ng/kg d.w. for Fort Erie in Lake Erie. The toxicity equivalent were in the order: 0.51, 2.10 and 0.46 ng TEQ/kg d.w. for Indian Point, Port Dalhousie and Fort Erie, respectively. It could be stated that the above-mentioned authors used I-TEQ with higher values of I-TEF for PCB Nos. 105, 114, 118, 123, 156, 157, 167, and 189, thus TEQ presented in their study was higher than that obtained using WHO-TEF values.

PCB Sources

In our study the highest potential for PCB accumulation was in the reservoirs situated at the end of the river system. This situation can be linked to the input of PCBs from the past (textile industry and Aroclor usage) and present sources (input of sewage and stormwater), as well as hydraulic transport of PCBs along reservoirs cascades and their deposition at the end of a river system.

Historical Sources of PCBs

The textile industry, which was developed in Łódź from the 1830s to the end of the 1980s, may have discharged some amounts of PCBs from pigments to the sewer system, and subsequently to the river. As reported by Allock and Jones [31] and Bostian et al. [32], pigments like chloranil, or dyes produced on the basis of chloranil may contain from 300.00 to 2,900.00 and from 2.00 to 200.00 μg TEQ/kg of PCDD, PCDF and dl-PCB, respectively. From this reason the rapid development of the textile industry can be listed as one of the PCB sources within the city of Łódź. This thesis may be confirmed by the simulations presented by Ghir et al. [33] and Lexen et al. [34].

Moreover, in Poland some values of PCB (mainly as Aroclors products) were derived from import. Information about exact imported amounts of organochlorine compounds are not known [35]. Nevertheless, Zieliński et al. [36] reported that the percentage composition of Aroclors Nos. 1232 and 1016 were similar to those found in the polish river sediment samples. Our study also suggested that PCB compositions with a predominance of PCB-118 and PCB-105 may be related to the usage of Aroclor in the past.

Furthermore in Poland, two technical PCB products with trade names Chlorofen and Tarnol containing 63.6% and 40% of Cl, respectively, were produced. The total produced amount of these chemicals were assessed to 1,700 tones [37, 38]. Nevertheless, no comparative analyses of their composition with the relation to the current PCB concentration in the environment were conducted.

Present Sources of PCBs

Input of Sewage Sludge

The presence of un-permitted domestic and industrial wastewater discharges into the Sokołówka River by stormwater outlets situated along the river (Fig. 1) can influence the concentration and pattern of PCBs in the reservoir sediments. Additionally, higher PCB concentrations in the last reservoirs can be related to the input of contaminants with the Brzoza River, which transports untreated domestic sewage from Radogoszcz housing estate (Fig. 1). In consequence, a higher drainage area of PR reservoir resulted in higher PCB pollution levels. Similar results were reported by Sapozhnikova et al. [39] on the basis on the Dniestr River research. The authors demonstrated that downstream sampling sites had significantly higher concentrations of total PCBs compared to the upstream samples. Moreover, research conducted in six sites on the Hyeongsan River (Korea) demonstrated an increase in total concentrations of non-ortho and mono-ortho PCB congeners from 12 to 4,500 ng/kg along the river [40]. The same situation was reported by Koh et al. [41]. Additionally, Sapozhnikova et al. [39] observed an increase in the concentration of PCB-81 and PEL (probable effects level, suggesting potentially adverse effects to benthic organisms) from upstream to downstream located samples. This is in accordance with our studies in which the concentration of congener PCB-81 raised along the reservoir cascade with the exception of the third pond (ZR).

Atmospheric Deposition and Urban Run-Off

The atmosphere is the conduit through which PCBs as well as other POPs can move from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems [31]. In consequence, atmospheric burdens and fluxes can greatly influence total PCB amounts in the environment and they are considered a major input of PCBs to waterbodies. As reported by Urbaniak [42], the atmospheric deposition process occurs in two ways: as dry and wet deposition. Thus rainfall can be reported as one PCB transport step to the waterbodies. Moreover, rainfall induced high runoff from streets scouring the deposited substances, from which the most important are those connected with road transport [43]. As reported by Polkowska et al. [44], a dynamic increase in the number of motor vehicles creates a serious problem due to exhaust gases and usual wear and tear of car parts involving PCBs. Thus deposition of PCBs containing particulates on the catchment surface and then their flush during rain may be reported as a main PCB source in an urban area.

Hydraulic Transport of PCB in Urban Cascade Reservoirs

Urban water systems are very sensitive and dependent on weather conditions, mostly precipitation. The total annual precipitation in large industrialized cities is generally 5-10% higher than in the surrounding areas, and for individual storms, this increase in precipitation can be as high as 30% [45].

The year 2006 can be characterized as having very rapid meteorological changes with periods of drought (July, September and October) disturbed by intensive storms (e.g. up to 34.80 mm/day precipitation in August) (Fig. 2). This could have great influence on PCB fate and distribution in the cascade due to changes of reservoir character from lotic to lentic and vice versa. Periods of lower flow intensified deposition processes in the river channel and disconnected it from the stormwater system. The occurrence of rapid and intensive precipitation after the drought period led to flushing of sediment down the cascade and activated matter from surface water outlets and combined sewage overflows [43]. Violent weather phenomena observed in Łódź directly influence the quality and volume resources of the

Table 6. Ln correlation of total PCB with chlorophyll *a*, TP, TN TSS, OSS, MSS, pH and conductivity.

	Ln correlation
Chlorophyll *a*	0.64
TP	-0.83
TN	0.67
TSS	0.61
OSS	0.61
MSS	0.82
pH	-0.81
Conductivity	0.94

Sokołówka River. These extreme phenomena and the high river water level caused high discrepancies in river hydrology and might confirm the above-mentioned trends.

Furthermore, during such high flows deeper layers of sediment can be suspended, mobilizing the PCBs deposited in the past. Therefore, sediments mobilized during high flow events and then deposited at the end of a river system can be the dominant source of PCBs. Moreover, high input of sediments of lower grain size increase surface area, which may account for higher concentrations of PCBs.

PCB Release from Plastic Material

As an additional explanation of the increasing PCB concentrations in reservoirs, the strengthening of the reservoir bed by a plastic material net may be reported. This kind of material may release small amounts of PCBs to the bottom sediments. The same material was used for construction of ZR and TR reservoirs. Nevertheless, the highest concentrations were noted in the last two reservoirs, thus this operation can be related to the transport of contaminated sediments into the lower section of a reservoir system during high flow events and their deposition in the last reservoir.

Correlation to Environmental Conditions

The highest positive correlation was found between PCBs and conductivity and mineral suspended solids. Conductivity is defined as ionic content in a solution, and in many cases is linked directly to the total dissolved solids. Thus deposition of solids from the atmosphere on catchment area and then surface run-off can confirm scouring of atmospherically and transport originated deposits from streets.

Urban runoff also leads to the overloading of reservoirs with nutrients, which are, with toxicants, the major environmental stressors in aquatic ecosystems [8]. The interaction between them may magnify their impact on biota. On the other hand, the chemical and physical processes are often regulated by biotic factors or strongly depend on them [46].

Moreover, the distribution of PCBs is associated with the cycle of growth, sinking and remineralization of phytoplankton [7, 8, 47, 48]. Algae can accumulate the micropollutants from water, which highly depends on their lipid content, influenced by nutrient status of the water [7, 49, 50]. Lipid storage in phytoplankton cells increases with nutrient limitations [49, 50]. This is probably why the negative correlation between PCBs and TP was found (Table 6), as there was no phosphorus restriction (Table 5). On the other hand, the positive correlation that was found with TN content may suggest adsorption to the peptide cell walls [39, 40].

Four complex interactions between organic micro-pollutants and biota, that influence fate of both of them are described: type I - dilution by biomass, type II - impact on transport and cycling of pollutants, type III and IV - direct and indirect toxicity-nutrient status interaction [8]. In our studies, mechanism types I and II played a significant role in PCB fate. The type III and IV mechanisms were not directly investigated. However, they could not be excluded, as phytoplankton play a significant role in all types of mechanisms [7, 8, 47] and a positive correlation was found (0.64) between chlorophyll *a* and PCBs (Table 5). This can be especially important in reservoirs in a turbid state [51]. The opposite equilibrium of reservoirs is more resistant and resilient to the impact of toxic PCBs due to macrophytes direct and indirect interaction with phytoplankton, nutrients and PCBs [8], which was also observed in our investigations in the ZR site (Tables 1, 4).

After the vegetation season, phytoplankton undergoes sedimentation and accumulation in sediment from where it may be washed out during storm events. This is consistent with the data presented by other researchers worldwide [5, 9, 10, 11]. In Poland, Kowalewska [47] and Kowalewska et al. [48] showed correlation between PAHs and phytoplankton in the water column, as well as the correlation of PCBs with total phosphorus content. Additionally, the mentioned authors suggested that during enhanced algae growth and, in consequence, oxygen production, sediments may release some amounts of PAHs that can be bonded by phytoplankton and suspended matter and in this form transferred along the river. Our investigations also showed the negative interaction with pH, which might be caused indirectly by phytoplankton in the photosynthesis processes.

Conclusions

Urban catchments are frequently contaminated with PCBs. Major current sources to urban rivers include sewage input and combined sanitary overflows, although direct urban runoff and re-suspension of contaminated bed sediments may also be key sources. In shallow, turbid, hypertrophic reservoirs located on such rivers the fate of PCBs is mostly dependant on the allohtonic mineral matter, dissolved carbon dioxide and phytoplankton that are transported down the cascade during intensive storm events. Phytoremediation (based on aquatic macrophytes planting) can prevent PCB transport and increase their degradation.

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References

1. WALKER W.J., MCNUTT R.P., MASLANKA C.K. The potential contribution of urban runoff to surface sediments of the Passaic River: sources and chemical characteristics. Chemosphere **38**, (2), 363, **1999**.
2. FOSTER G.D., ROBERTS E.C., GRUESSNER B., VELINSKY D. Hydrogeochemistry and transport of organic contaminants in an urban watershed of Chesapeake Bay (USA). Appl. Goeche. **15**, 901, **2000**.
3. JARTUN M., OTTESEN R.T., STEINNES E., VOLDEN T. Runoff of particle bound pollutants from urban impervious surfaces studied by analysis of sediments from stormwater traps. Sci. tot. Environ. **396**, 147, **2008**.
4. KRISHNAPPAN B.G., MARSALEK J. Transport characteristics of fine sediments from on-stream stormwater management pond. Urban Water **4**, 3, **2002**.
5. LARRSON P., OKLA L., CRONBERG G. Turnover of polychlorinated biphenyls in a eutrophic and an oligotrophic lake in relation to internal lake processes and atmosphere fallout. Can. J. Fish. Aquat. Sci. **55**, 1926, **1998**.
6. ZENG E.Y., YU., C.C, TRAN K. In situ measurements of chlorinated hydrocarbons in the water column of the Palos Verdes Peninsula, California. Environ. Sci. Technol. **33**, 392, **1999**.
7. BERGLUND O., LARSSON P., EWALD G., OKLA L. Influence of trophic status on PCB distribution in lake sediments and biota. Environ. Pollut. **113**, 199, **2001**.
8. ROESSINK I., KOELMAS A.A., BROCK T.C.M. Interactions between nutrients and organic micro-pollutants in shallow freshwater model ecosystems. Sci. Total Environ. **406**, 436, **2008**.
9. WETZEL, R.G. Limnology, 2nd Edition. Saundres College Publishing, New York, **1983**.
10. COBELAS M.A. DIAZ J.L.V, OLMO A.R. Settling seston in a hypertrophic lake. Arch. Hydrobiol. **127**, 327, **1993**.
11. TATRAI G., BIASCI G. Trophic status and lake sedimentation fluxes. Water, Air, Soil Pollut. **99**, 523, **1997**.
12. KUJAWA I. AND KUJAWA M. The General Project of the Sokołówka River **2003** [In Polish].
13. JOKIEL P. AND MAKSYMIUK Z. Atlas of the City of Łódź. Map IX, **2002** [In Polish].
14. BIEZANOWSKI W. Łódka and other Lodz rivers. 2nd ed; Society for the Reservation of Historical Monuments in Łódź Publishing, Zora, **2003** [In Polish].
15. WAGNER I., IZYDORCZYK K., DROBNIEWSKA A., FRATCZAK W., ZALEWSKI M. Inclusion of ecohydrology concept as integral component of systemic in urban water resources management. The City of Łódź, case study, Poland. Scientific Conference SWITCH in Birmingham and New directions in IURWM, Paris, **2007**.
16. PN-EN 1948-2: Emission from the stationary sources. Estimation of the PCBs mass concentration. Part 3: Identification and quantitative estimation, **2002** [In Polish].
17. EPA Method 1668, Revision A: chlorinated Biphenyls congeners in Water, soil, sediment and Tissue by HRGC/HRMS, **1999**.
18. BERG M. VAN DEN, BIRNBAUM L., DENISON M., FARLAND W. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. Toxicol. Sci. **93**, (2), 223, **2006**.
19. OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z. Analysis and estimation methods of soil and plants properties. Catalogue of the Institute of Environment Protection, Warsaw, **1991** [In Polish].
20. GOLTERMAN H.L., CLYMO R.S., OHSTAND M.A.M. Methods for physical and chemical analysis of freshwater. Blackwell Scientific Publication, Londres, pp. 214, **1978**.
21. HACH. Water analysis handbook. Hach Company, pp. 1309, **1997**.
22. LAWTON L., MARSALEK M., PADISAK J., CHORUS I. Determination of cyanobacterial in the laboratory. In. Chorus I., Bartram J. (Eds). Toxic cyanobacterial in water. A guide to their public health consequences, monitoring and management. E&FN Spon, pp. 347-367, **1999**.
23. WAGNER I, ZALEWSKI M. Effect of hydrological patterns of tributaries on biotic processes in a lowland reservoir – consequence for restoration. Ecol. Engin. **16**, 79, **2000**.
24. YUNUS A.J.M., NAKAGOSHI N. Effects of seasonality on streamflow and water quality of the Pinang river in Penang Islamnd, Malaysia. Chin. Geo. Sci. **14**, (2), 153, **2004**.
25. Organization for Economic Cooperation and Development (OECD). Eutrophicated water. Monitoring assessment control – technical report, Environment Directorate; Paris, pp. 154, **1983**.
26. URBANIAK M., ZIELINSKI M., WESOLOWSKI W., ZALEWSKI M. PCBs and heavy metals contamination in bottom sediments from three reservoirs of different catchment characteristics. Pol. J. Environ. Stud. **17**, (6), 941, **2008**.
27. LOGANATHAN B.G. KUMAR K.S., MASUNAGA S., SAJWAN K.S. Polychlorinated dibenzo-p-dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls in sediment and mussel samples from Kentucky Lake, USA. Arch Environ Contam Toxicol. **54**, 20, **2008**.
28. NIEMIRYCZ E., GOZDEK J., KACZMARCZYK A., TYSZKIEWICZ H. Anthropogenic organic substances: sources, locations and interaction in the water sediments of the Włocławek Reservoir.. IMGW, project report GF/POL/INV/R 22, **2003**.
29. CAMUSSO M., VIGNATI D., VAN DE GUCHTE C. Ecotoxicological assessment in the rivers Rhine (The Netherlands) and Po (Italy). Aquat. Ecosys. Health and Manag. **3**, 335, **2000**.
30. MARVIN CH.H., HOWELL E.T., KOLIC T.M., REINER E.J. Polychlorinated dibenzo-p-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls in sediments and mussels at three sits in the lower Great Lakes, North America. Environ. Toxicol. Chem. **21**, (9), 1908, **2002**.
31. ALLOCK R.E., JONES K.C. Pentachlorophenol (PCP) and Chloranil as PCDD/Fs sources to sewage sludge and sludge amended soils in UK. Chemosphere **35**, (10), 2317, **1997**.
32. BOSTIAN K., MERECHAL A.M., VONCINA E., BRONIJAK-VONCINA D. Textile dyes and pigments as a source of dioxins. Organochalogen Comp. **66**, 931, **2004**.
33. GIHR R., KLOPFFER W., RIPPEN G., PARTSCHT I. Investigations on potential sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sewage sludges. Chemosphere **23**, 1653, **1991**.

34. LEXEN K., DE WIT C., JANSSON B., KIELLER L-O., KULP S.E., LJUNG K., SODERSTROM GRAPPE C. Polychlorinated dibenzo-*p*-dioxin and dibenzofuran levels and patterns in samples from different Swedish industries analyzed within the Swedish dioxin survey. Chemosphere **27**, 163, **1993**.
35. FALANDYSZ J. Polychlorinated biphenyls in the environment: chemistry, analysis, toxicity, concentration and risk assessment. Gdansk University Development Foundation, **1999** [In Polish].
36. ZIELIŃSKI M., WESOŁOWSKI W., KUCHARSKA M. HRGC/HRMS technique in estimation of non-ortho and mono-ortho PCB in industrial products of Aroclor. Conference: Application of chromatographic techniques in environmental and clinical analysis. 16.IV.2007. Technical University in Lodz, **2007** [In Polish].
37. HOLOUBEK I. Polychlorinated biphenyls (PCBs) world-wide contaminated sites. TOCOEN Reports no. 173, http://www.recetox.muni.cz/reports/TR173/p2.htm, **2000**.
38. FALANDYSZ J, SZYMCZYK K. Data on manufacture, use, inventory and disposal of polychlorinated biphenyls (PCBs) in Poland. Pol. J. Environ. Stud. **10**, 189, **2001**.
39. SAPOZHNIKOVA Y., ZUBCOV E., ZUBCOV N., SCHLENK D. Occurrence of pesticides, polychlorinated biphenyls (PCBs), and heavy metals in sediments from the Dniestr River, Moldova. Arch. Environ. Contamin. Toxicol. **49**, 439, **2005**.
40. QI M., BLUNT J., CHEN J., GAO X. Determination of polychlorinated biphenyl congeners in sediment samples of twelve rivers in eastern China. Toxicol. Environ. Chem. **71**, 497, **1999**.
41. KOH C.H., KHIM J.S., KANNAN K., VILLENEUVE D.L., SENTHILKUMAR K, GIESY J.P. Polichlorinated dibenzo-*p*-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, **2004**.
42. URBANIAK M. Polychlorinated biphenyls (PCBs): sources, distribution and transformation in environment – literature review. Acta Toxicol. **15**, (2), 83, **2007**.
43. MULLIS R M.D., REVITT M., SHUTES R.B. The impacts of urban discharges on the hydrology and water quality of an urban watercourses. Sci. Total Environ. **189/190**, 385, **1996**.
44. POLKOWSKA Ż, GRYNKIEWICZ M., ZABIEGA B. NAMIEŚNIK J. Levels of pollutants in runoff water from roads with high traffic intensity in the city of Gdansk, Poland. Pol. J. Environ. Stud. **10**, 351, **2001**.
45. MARSALEK J., JIMENEZ-CISNEROS B.E., MALMAQUIST P.A., KARMAZUS J., GOLDENFUM B., CHOCAT. Urban water cycle processes and interactions. Technical Documents in Hydrology, UNESCO, Paris, **78**, **2006**.
46. OSTROUMOV S. A. On Some Issues of Maintaining Water Quality and Self-Purification. Water Resources, Vol. 32, No. 3, 2005, pp 305–313. Translated from Vodnye Resursy, **32**, (3), 337, **2005**.
47. KOWALEWSKA G. Phytoplankton - the main factor responsible for transport of polynuclear aromatic hydrocarbons from water to sediments in the southern Baltic ecosystem. IECS J. Mar. Sci. **56** (Suppl.), 219, **1999**.
48. KOWALEWSKA G., KONAT-STEPOWICZ J., WAWRZYNIAK-WYDROWSKA B., SZYMCZYK-ŻYŁA M. Transfer of organic contaminants to the Baltic In the Odra Estuary. Mar. Pollut. Bull. **46**, 703, **2003**.
49. LYNN S.G., PRICE D.J., BIRGE W.J., KILHAM S.S. Effect of nutrient availability on the uptake of PCB congener 2,2',2,6,6'-tetrachlorobiphenyl by a diatom (*Stephanodiscus minutulus*) and transfer to a zooplankton (*Daphnia pulicaria*). Aquat. Toxicol. **83**, 24, **2007**.
50. FITZGERALD S. A., STAUER J.J. Association of polychlorinated biphenyls (PCBs) with live algae and total lipids in rivers – a field based approach. Sci. Total Environ. **354**, 60, **2006**.
51. SHEFFER M., HOSPER S. H., MEIJER M-L., MOSS B., JEPPESEN E. Alternative equilibria in shallow lakes. Trends in Ecology and Evolution **8**, 275, **1993**.