ARCHIVES OF ENVIRONMENTAL PROTECTION
vol. 35 no. 2 pp. 125 - 132 2009
PL ISSN 0324-8461

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDDS) AND POLYCHLORINATED DIBENZOFURANS (PCDFS) COMPOUNDS IN SEDIMENTS OF TWO SHALLOW RESERVOIRS IN CENTRAL POLAND

MAGDALENA URBANIAK[1, 2*], MAREK ZIELIŃSKI[3], WIKTOR WESOŁOWSKI[3], MACIEJ ZALEWSKI[1, 2]

[1] University of Łódź, Department of Applied Ecology
ul. Banacha 12/16, 90-237 Łódź, Poland
[2] International Institute of Polish Academy of Sciences, European Regional Centre for Ecohydrology under the auspices of UNESCO
ul. Tylna 3, 90-364 Łódź, Poland
[3] Nofer Institute of Occupational Medicine
ul. Teresy 8, 91-348 Łódź, Poland
*Corresponding author e-mail: m.urbaniak@erce.unesco.lodz.pl

COMMUNICATION

Keywords: PCDDs/PCDFs, sediments, reservoirs.

Abstract: The objectives of this research were to 1) measure the concentrations of PCDDs/PCDFs in sediments from two reservoirs located in Central Poland, 2) illustrate the pollution level, and 3) identify sources affecting these contaminations. Sediment samples were collected during spring period of 2007 from Barycz Reservoir situated on the Grabia River and Lower Pond located on the Sokołówka River. Almost all of analyzed homologues were identified, except for two the most toxic congeners: 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, which were not observed. The total concentrations of PCDDs/PCDFs were 213.727 pg·g^{-1} d.w. for Barycz Reservoir and 536.266 pg·g^{-1} d.w. for Lower Pond, with dominant OCDD congener. WHO-TEQ concentrations based on TEF values ranged from 2.323 to 7.984 pg·g^{-1} for Barycz Reservoir and Lower Pond, respectively.

INTRODUCTION

Every year in Europe more than 30 000 chemicals in quantities of 1 Mg are produced and handled. Many of them are formed due to combustion processes or as manufacturing by-products. Some are highly reactive and toxic for living organisms in very low concentrations but posses relatively short lifetime; others, like polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), have been shown to be persistent in environment, bioaccumulative and hazardous for biota for several years [13].

PCDD/DFs form a group of synthetic organic chemicals that contain 210 structurally related individual congeners widely distributed in the environment. They have been detected in soil, surface water, sediments, plants, and animal tissue in all regions of the earth [6, 7, 9]. Because of their low volatility and low solubility in water they can be

strongly associated with particulates and thus most of them are contained in soil and sediments that serve as environmental reservoirs from which PCDD/DF may be released over a long period of time. They can also enter the aquatic environment by atmospheric transport and deposition, direct and indirect discharges and as a riverine input [13, 14, 16].

MATERIALS AND METHODS

Study areas

In this study we determined the concentrations of 17 PCDD/PCDF congeners in sediments collected from two shallow reservoirs: Barycz Reservoir and Lower Pond (Fig. 1). Sites were selected to represent the major land uses: agricultural – Barycz Reservoir, and urban (residential and commercial-industrial) – Lower Pond, based on dominant mapped land-use and personal observation of the surrounding area.

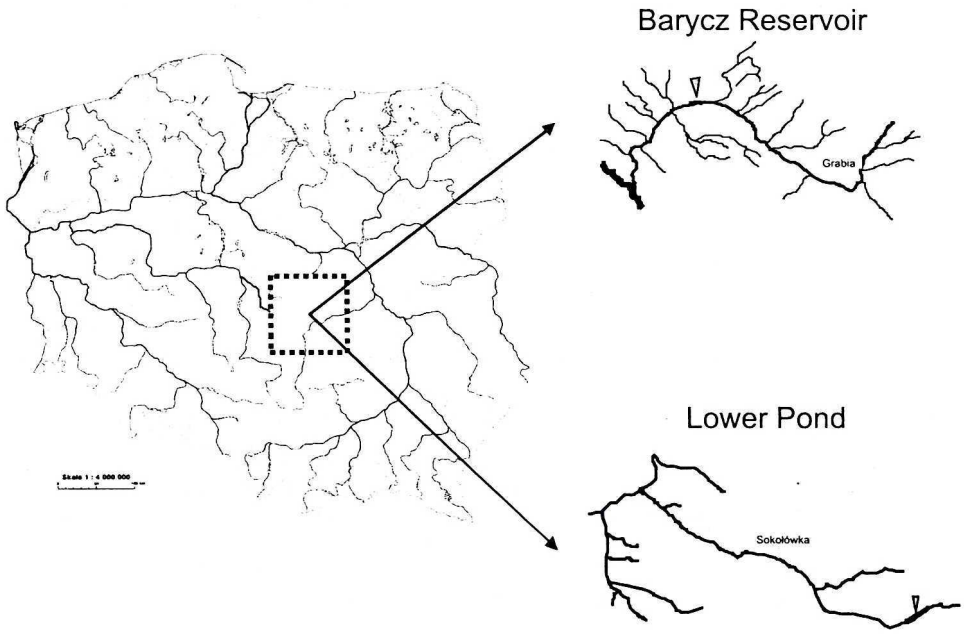

Fig. 1. Location of the sediment samples taken for the analysis

Barycz Reservoir (51°35'N; 19°12'E) is located in the middle course of the Grabia River (river basin 813 000 m^2) between Barycz and Ldzań villages [12]. The total capacity of this reservoir is 2800 m^2 and mean depth 1.78 m. The reservoir was built for water retention and irrigation of agriculture.

Lower Pond is situated on the Sokołówka River (river basin 45 400 m^2) which represent highly urbanized and industrialized catchment contaminated with heavy metals and organic compounds due to sewage and storm water disposal. The main channel was channelised by concrete slabs, to straighten the course and deepen the bed for the purpose of detention of storm waters. The total capacity of Lower Pond is 1080 m^2 and mean depth is 1.0 m [1, 17].

Sampling

Sediment samples were collected using sediment core sampler during the spring period of 2007 (06.04.2007). Samples were filled into amber containers and transported at 4°C to the laboratory. After wards the samples were freeze dried at -40°C, and put trough 2000 μm mesh sieve.

PCDDs/DFs analysis

The dried sediments were extracted by ASE (Automatic System Extraction) 200 Dionex. The 2 g of sediment were spiked with ^{13}C-labelled PCDDs/DFs standard of known quantity to monitor extraction efficiency. Extraction was performed at 150 atm (11 Mpa) at 175°C. Extracts were treated with a multilayer column packed with neutral silica and silica modified with 44% (w/w) and 22% sulphuric acid ($SiO_2 - H_2SO_4$), 3% KOH and 10% $AgNO_3$, prewashing by 150 cm^3 of hexane. Elution was performed with 200 cm^3 of hexane. The extracts were then reduced to approximately $100 \cdot 10^{-6}$ dm^3 and n-hexane was replaced by n-nonane and the internal standard was added [5].

For identification and quantification of 17 2,3,7,8-substituted PCDD/DF, HRGC/HRMS (HP6890, Hewlett Packard/Autospec Ultima, Micromass) fitted with DB-5MS columns (60 m x 0.25 mm i.d., film thickness 0.25 μm) was used. As an internal standard the perfluorokerosene (PFK) was used. The column oven temperature was programmed as follows: 150°C for 2 min, 20°C/min to 200°C (0 min), 1°C/min to 220°C for 16 min and 3°C/min to 320°C for 3 min. The injector temperature was 270°C. The MS was operated with a mass resolution of 10 000, and the electron impact ionization energy was 34.8 eV with an ion source temperature of 250°C. Helium was used as carrier gas at a flow rate 1.6 cm^3/min. Samples were quantified with an isotope dilution method [5].

Quality assurance/Quality control

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

Quantification was done by the external standard method using certified calibration standards. Each analytical batch contained a method blank, a matrix spike, and replicate samples. A reagent blank was used to assess artifacts, precision was verified by duplicate analyses and recoveries were estimated using samples spiked with PCDD/PCDF. Samples spikes were used also as an additional check of accuracy. Recoveries of ^{13}C-labeled PCDD and PCDF congeners through the analytical procedure ranged from 74 to 146%.

RESULTS AND DISCUSSION

Results showed that almost all tetra- to octachlorinated PCDDs/PCDFs were identified, except for two the most toxic congeners: 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, which were not observed (Tab. 1 and Fig. 2). The maximum concentration was observed for octachlorinated PCDD congeners: 162.483 and 409.636 $pg \cdot g^{-1}$ d.w. for Barycz Reservoir and Lower Pond, respectively (Tab. 1 and Fig. 2).

Table 1. Concentration of analyzed PCDDs/PCDFs in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007 [pg·g^{-1} d.w.]

Congener	Barycz Reservoir	Lower Pond	Barycz Reservoir	Lower Pond
			WHO-TEQ concentration	
2378-TCDD	0.000	0.000	0.000	0.000
12378-PeCDD	0.000	0.000	0.000	0.000
123478-HxCDD	0.325	0.597	0.033	0.060
123678-HxCDD	1.254	1.266	0.125	0.127
123789-HxCDD	4.083	6.207	0.408	0.621
1234678-HpCDD	4.496	29.185	0.145	0.292
OCDD	162.483	409.636	0.049	0.123
2378-TCDF	0.000	10.028	0.000	1.003
12378-PeCDF	0.639	4.738	0.019	0.142
23478-PeCDF	1.047	8.242	0.314	2.472
123478-HxCDF	3.158	7.143	0.316	0.714
123678-HxCDF	3.068	7.517	0.307	0.751
123789-HxCDF	2.228	2.472	0.223	0.247
234678-HxCDF	2.718	11.487	0.272	1.149
1234678-HpCDF	7.198	22.790	0.072	0.228
1234789-HpCDF	3.818	5.228	0.038	0.052
OCDF	7.211	9.732	0.002	0.003
Total	213.727	536.266	2.323	7.984

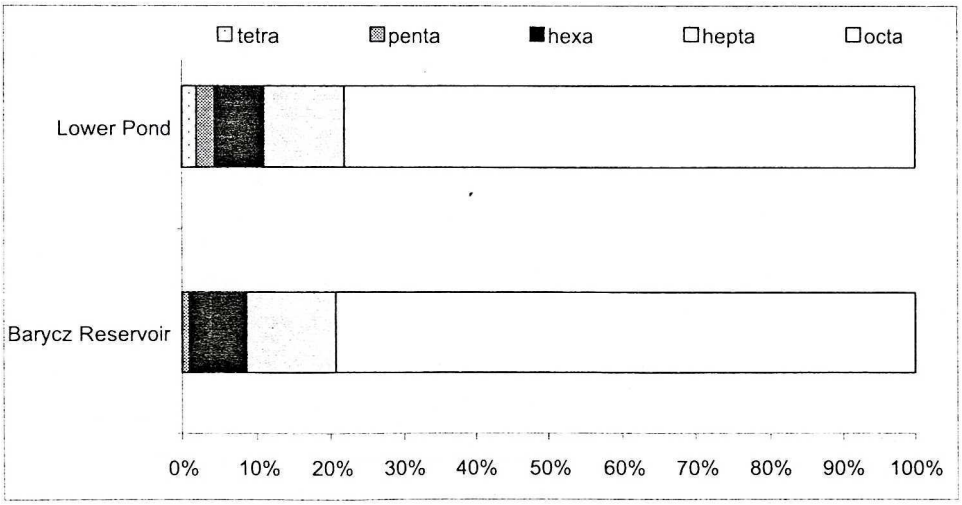

Fig. 2. Percentage content of analyzed homologues in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007

The total concentrations of PCDD/DF were 213.727 and 536.266 pg·g^{-1} d.w. for Barycz Reservoir and Lower Pond , respectively, with the predominance of PCDD (182.641 and 446.891 pg·g^{-1} d.w. for Barycz Reservoir and Lower Pond, respectively)

(Tab. 1 and Fig. 2). The total PCDD/DF TEQs concentrations were 2.323 and 7.984 pg TEQ·g^{-1} dry weight for Barycz Reservoir and Lower Pond, respectively (Tab. 1 and Fig 4). The PCDF congeners were responsible for higher contributions to 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (WHO-TEQ) values (2.06 and 5.53 times higher than PCDDs for Barycz Reservoir and Lower Pond, respectively).

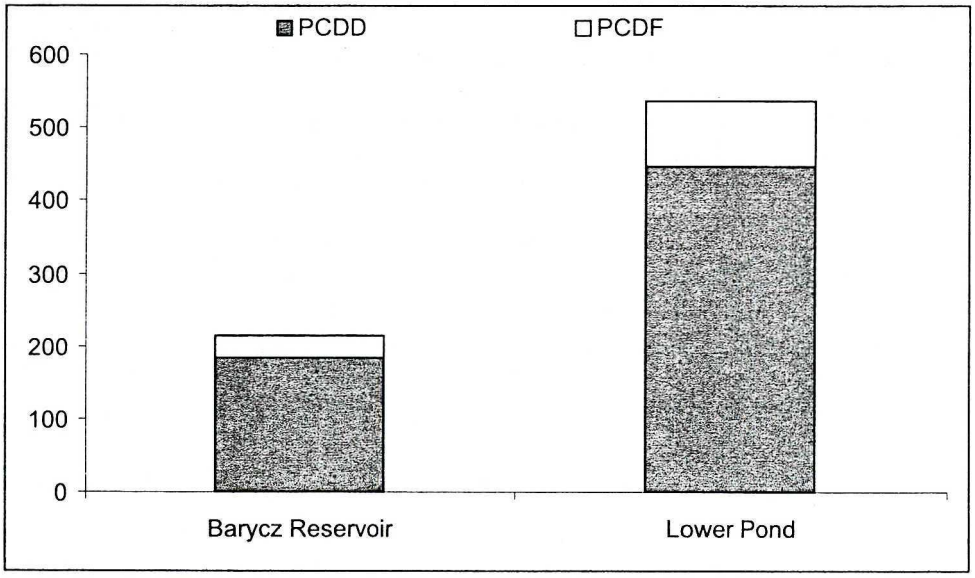

Fig. 3. Total PCDD/DF concentration in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007 [pg·g^{-1} d.w.]

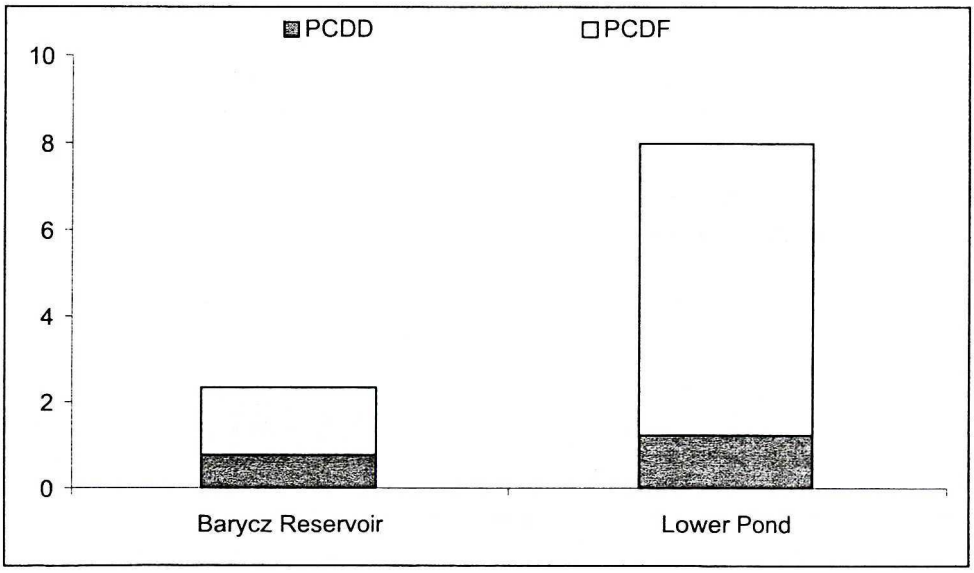

Fig. 4. Total PCDD/DF TEQ concentration in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007 [pg TEQ·g^{-1} d.w.]

The composition of 7 PCDD congeners in sediments collected from Barycz Reservoir was in order: OCDD (76.02%), 1,2,3,4,6,7,8-HpCDD (6.78%), 1,2,3,7,8,9-HxCDD (1.91%), 1,2,3,6,7,8-HxCDD (0.59%), 1,2,3,4,7,8-HxCDD (0.15%), 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD (0.00%). Similar pattern was observed for Lower Pond sample: OCDD (76.39%), 1,2,3,4,6,7,8-HpCDD (5.44%), 1,2,3,7,8,9-HxCDD (1.16%), 1,2,3,6,7,8-HxCDD (0.24%), 1,2,3,4,7,8-HxCDD (0.11%), 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD (0.00%). The PCDFs composition was more diverse and ranged from 3.37% to 0.00% for the Barycz Reservoir sample and from 4.25% to 0.46% for the Lower Pond sample.

It could be stated that no previous measurements of PCDD/PCDF concentrations were undertaken in analyzed reservoirs, thus there are not available data for comparison. Nevertheless, the obtained concentrations of PCDDs/PCDFs in the studied area were more or less comparable to the values observed in other reservoirs worldwide. Chi *et al.* [2] reported that concentration of PCDDs in northern Taiwan reservoir ranged between 0.95 to 14.40 pg TEQ·g^{-1}. In a study of Rose and McKay [15] the concentrations ranged from 1 to 100 pg TEQ·g^{-1}. Research of Koh *et al* [11] showed the PCDD/PCDF concentration values in sediment from the Hyeongsan River were between 190 to 290 pg·g^{-1} d.w. El-Kady *et al.* [4] reported that total sum of PCDD/PCDFs in sediments of the River Nile was in the range from 239.67 to 755.09 pg·g^{-1} d.w. A study of Kannan *et al.* [10] showed values from 68.7 to 1420 pg·g^{-1} d.w. with TEQ concentration ranged from 3.00 to 62.1 pg·g^{-1} d.w. Hilscherova *et al.* [8] reported concentration from 59 to 120 and from 2400 for PCDDs to 53600 pg·g^{-1} d.w. for PCDFs for upstream and downstream of the Tittabawse River, respectively.

From the study obtained by Polish researchers carried out on soils in Poland total PCDD concentrations ranged from 6.8 to 41 pg·g^{-1} d.w. and concentration of PCDFs was in range 3.9 to 19 pg·g^{-1} d.w. and in all samples highly chlorinated PCDDs/DFs dominated (OCDD, 1,2,3,4,6,7,8-HpCDD, OCDF, 1,2,3,4,7,8,9-HpCDF, 1,2,3,4,6,7,8-HpCDF were found in all investigated soils). Total toxic equivalency was in the range of 0.023–5.9 pg TEQ·g^{-1} d.w. [18].

Presented by authors values were several times lover that obtained in our study, nevertheless it could be stated that sediment samples are matrices that accumulate liphoplilic substances and can receive inputs via various pathways including atmospheric deposition, industrial and domestic effluents, storm water, spills, and other. Thus they are the ultimate sink for micropollutants and it is estimated that about 97% of released POPs in a water column are retained in sediment [3].

The main sources of PCDDs/DFs in the analyzed samples include thermal processes such as grass and trash burning as well as heating of houses by small stoves fired with hard coal with added household wastes, and former use of agrochemical formulations consisting of impurities of PCDD/DF. Thus, this kind of pollution may play an important role at agricultural site (Barycz Reservoir). In comparison, as the main sources of PCDD/PCDF in the urban region (Lower Pond), energy and fossil fuel production, co-fired power boilers, and chemical industry can be considered. Moreover, congeners 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD are reported as closely related to incineration sources, and therefore can be linked to these processes. Congeners 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD, in turn, showed similarities with the PCDD/DF homologues in pentachlorophenol (PCP), and thus their presence in the environment is explained as PCP-related contamination. The higher concentrations of OCDD/OCDF might be connected to the former

production and use of highly chlorinated polychlorinated biphenyl formulation – such as chlorofen [18].

The obtained results suggest that sediments from Barycz Reservoir and Lower Pond are contaminated with PCDD/PCDFs in a considerable rate. Industrial and urban characteristic of Lower Pond basin with combined overflows located along the Sokołówka River have influenced its higher sediment concentration.

Acknowledgements

This study was supported by grant GOCE 018530 SWITCH: Sustainable Water Management Improves Tomorrow's Cities Health (UE FP) and project no. 2 PO4 G 088 30 founded by Ministry of Science and Higher Education.

REFERENCES

[1] Bieżanowski W.: *Łódka i inne rzeki łódzkie*, Wydawnictwo Towarzystwa Opieki nad Zabytkami w Łodzi, Zora, wyd. II, Łódź 2003.

[2] Chi K.H., M.B. Chang, S.J. Kao: *Historical trends of PCDD/Fs and dioxin-like PCBs in sediments buried in a reservoir in Northern Taiwan*, Chemosphere, **68**, 1733–1740 (2007).

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

[4] El-Kady A.A., A.M. Abdel-Wahhab, B. Henkelmann, M.H. Belal, M. Khairy, S. Morsi, S.M. Galal, K.W. Schramm: *Polychlorinated biphenyl, polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran residues in sediments and fish of the River Nile in the Cairo region*, Chemosphere, **68**, 1660–1668 (2007).

[5] EPA Method 1613: *Revision B, Tetra- trough Octa-chlorinated dioxins and Furans by Isotope Dilution HRGC/HRMS*, US EPA (1994).

[6] Falandysz J.: *Polichlorowane dibenzo-p-dioksyny w środowisku naturalnym*, Farmakologia Polska, **44**, 577–581 (1988).

[7] Grochowalski A.: *Dioksyny a środowisko. Historia, dzień dzisiejszy i perspektywy*, II Ogólnopolskie Sympozjum Dioksyny – Człowiek – Środowisko, Politechnika Krakowska, Kraków, 19–20.09.1996.

[8] Hilscherova K., K. Kannan, H. Nakata, N. Yamashita, P. Bradley, J.M. Maccabe, A.B. Taylor, J.P. Giesy: *Polichlorinated dibenzo-p-dioxin and dibenzofuran concentration profiles in sediments and flood-plain soils of the Tittabawssee River, Michigan*, Environ. Sci. Technol., **37**, 468–474 (2003).

[9] Im S.H., K. Kannan, M. Matsuda, J.P. Giesy, T. Wakimoto: *Sources and distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment from Masay Bay, Korea*, Environmental Toxicology and Chemistry, **21**, 245–252 (2002).

[10] Kannan K., J.L. Kober, Y.S. Kang, S. Masunaga, J. Nakanishi, A. Ostaszewski, J. Giesy: *Polichloronated naphtalens, biphenyls, dibenzo-p-dioxins, and dibenzofurans as well as polycyclic aromatic hydrocarbons and alkylphenols in sediment from the Detriot and Rouge rivers, Michigan, USA*, Environmental Toxicology and Chemistry, **20**, 1878–1889 (2001).

[11] Koh C.H., J.S. Khim, K. Kannan, D.L.Villeneuve, K. Senthilkumar, J.P. Giesy: *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*, Environmental Pollution, **123**, 489–501 (2004).

[12] Kondracki J.: *Geografia fizyczna Polski*, PWN, Warszawa 1978.

[13] Makles Z., A. Swiatkowski, S. Grybowska: *Niebezpieczne dioksyny*, Arkady Sp. z o.o, Warszawa 2001.

[14] Moore M.R., W. Vetter, C.Gaus, G.R. Shaw, J.F. Muller: *Trace organic compounds in the marine environment*, Marine Pollution Bulletin, **45**, 62–68 (2002).

[15] Rose C.L., W.A. McKay: *PCDDs (dioxins) and PCDFs (furans) in selected UK lake and reservoir sites – concentrations and TEQs in sediment and fish sample*, Science of Total Environment, **177**, 43–56 (1996).

[16] Stronkhost J., P. Leonards, A. Murk: *Rusing the dioxin receptor-calux in vitro bioassay to screen marine harbor sediments for compounds with a dioxin-like mode of action*, Environmental Toxicology and Chemistry, **21**, 2552–2561 (2002).

[17] Wagner I., K. Izydorczyk, A. Drobniewska, W. Fratczak, M. Zalewski: *Inclusion of ecohydrology concept as integral component of systemic in urban water resources management. The City of Lodz, case study. Poland*, Scientific Conference SWITCH in Birmingham and New directions in IURWM, Paris 2007.
[18] Wyrzykowska B., J. Falandysz, N. Hanari, N. Yamashita: *Dioxins in agricultural soil of Poland*, Roczniki Państwowego Zakładu Higieny, **57**, 361–70 (2006) (in polish).

Received: July 31, 2008; accepted: February 24, 2009.

POLICHLOROWANE DIBENZO-P-DIOKSYNY I POLICHLOROWANE DIBENZOFURANY W OSADACH DENNYCH DWÓCH PŁYTKICH ZBIORNIKÓW POLSKI CENTRALNEJ

Celem niniejszych badań było: 1) zmierzenie stężeń PCDD/DF w osadach dennych dwóch zbiorników zaporowych zlokalizowanych w Polsce Centralnej, 2) zilustrowanie poziomu zanieczyszczenia powyższymi związkami oraz 3) identyfikacja źródeł wpływających na istniejący stan. Osady denne pobrano w sezonie wiosennym 2007 r. ze Zbiornika Barycz usytuowanego na rzece Grabi i Stawu Dolnego zlokalizowanego na rzece Sokołówce. Niemal wszystkie spośród 17 analizowanych kongenerów PCDD/DF zidentyfikowano w badanych próbach, wyjątkiem były dwa najbardziej toksyczne związki: 2,3,7,8-TCDD i 1,2,3,7,8-PeCDD, których nie wykryto. Całkowite stężenie PCDD/DF w Zbiorniku Barycz wynosiło 213,727 pg·g^{-1} s.m. oraz 536,266 pg·g^{-1} s.m. w Stawie Dolnym, z dominującym stężeniem kongeneru OCDD. Stężenie mierzone jako WHO-TEQ wynosiło 2,323 i 7,984 pg·g^{-1} s.m., odpowiednio dla Zbiornika Barycz i Stawu Dolnego.