Assessment of DDT, HCH and PCB pollution of lake sediments in Poland

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Abstract: In the years 2010-2013, 528 samples of surface sediments were collected from lake depths in the area of Poland. The content of 7 PCB congeners, HCH isomers and p,p'-DDT, p,p'-DDE and p,p'-DDD was determined using the GC-ECD method. The studies showed the common occurrence of organochlorine compounds in lake sediments in Poland. The presence of HCHs, at a concentration above the determination limit, was detected in 83.71% of samples, that of DDTs in 98.86% of samples, and of PCBs in 98.86% of samples. The maximum HCH concentration was 60.7 ng g⁻¹, that of DDTs 602.9 ng g⁻¹, and of PCBs 50.7 ng g⁻¹, while the averages were 6.3 ng g⁻¹, 19.2 ng g⁻¹ and 2.8 ng g⁻¹, respectively. High levels of DDTs are found in sediments of those lakes upon which major towns are located, whereas the highest HCH concentrations are observed in sediments of the lakes upon which holiday centres and agrotourism facilities have developed. The ratio of concentrations of total DDT metabolites to p,p'-DDT was above 2 in almost all samples, and the value was most frequently from several to tens (average 28.3). Sediments of some lakes contain higher concentrations of γ -HCH and DDT metabolites than their *PEC* values, the content of γ -HCH was higher in 1.89% of the analysed samples, the content of p,p'-DDE in 3.78% of the samples, and the content of p,p'-DDD in 7.38% of the samples. Concentrations of p,p'-DDT and PCB in excess of the *PEC* value were not found in any of the samples tested.

Key words: lake sediments, PCBs, DDTs, HCHs

Introduction

Water sediments are an integral part of the surface water environment, and the dwelling aquatic organisms are involved not only in biogeochemical transformations, but also play a fundamental role in maintaining the purity of water, decomposition of organic matter and primary production. The sediments are also characterised by their ability to accumulate numerous types of contaminants that pose a threat to living organisms. These include organochlorine compounds such as DDTs, HCHs and PCBs. A re-suspension of contaminated sediments can be an important source of organochlorine compounds in the water and can cause exposure of fish to their effects (Hornbuckle and Miller 2010; Schneider et al. 2007). For these reasons, water sediment pollution is one of the most important contemporary environmental problems.

Organochlorine compounds (DDTs, HCHs and PCBs) are referred to as persistent organic pollutants because of their resistance to chemical, biological and

photolytic degradation, their ease of bioaccumulation in living organisms, and the possibility of biomagnification in the trophic chain (Strandberg et al. 2000; Henny et al. 2003; Nfon et al. 2008; Erkmen et al. 2013). Although their production and use have been abandoned in most countries, they are widespread in the environment and their presence is recognised in sediments of many lakes (Erkmen et al. 2013; Bettinetti et al. 2011; Hu et al. 2010; Jiao et al. 2009; Jung et al. 2008; Yuan et al. 2013; Grimalt et al. 2004). These compounds, ending up in surface waters along with runoff, sewage and atmospheric deposits, are retained in the sediment (due to their low solubility in water) usually in forms adsorbed on fine-grained material, or they are associated with organic matter (Abbt-Braun and Frimmel 1996; Lohmann et al. 2005). Most organochlorine compounds, due to the high vapour pressure, are relatively easily released into the atmosphere and can be transported over long distances, and, in consequence, their atmospheric deposition in both dry and wet precipitation plays an important role in

the circulation of these contaminants in the environment (Shen et al. 2005; Totten et al. 2003; Hsu et al. 2003; Gryniewicz et al. 2003; Eisenberg et al. 1998; Ramamoorthy and Ramamoorthy 1997).

In modern sediments, the content of organochlorine compounds ranges from below the detection limit to as much as several hundred thousand ng g^{-1} (extreme content is recorded, e.g., in sediments of some harbours); in general, even in highly contaminated sediments, the content of these compounds does not exceed 1,000 ng g^{-1} (Kannan et al. 1997; Bremie et al. 1998; Sivey and Lee 2007; Lin et al. 2009). High levels of organochlorine pesticides and PCBs have been typically observed in sediments dated to the 1950s-1970s. It has been discovered that, in lakes located near urban and industrial areas, the maximum content of, e.g., DDTs was found in sediments dating back to the 1950s, while in lakes located far from pollution sources, the maximum DDT content was recorded in water sediments deposited in the 1970s (Rawn et al. 2001; Jung et al. 2008). Concentration of organic pollutants in the sediments is largely constrained by the concentration of organic matter. Lower concentrations are found in sandy sediments, while a much higher content is observed in organic muds (Sapota 2006).

Research scope and methods

The study uses the results obtained during the monitoring conducted under National Environmental Monitoring. In the years 2010-2013, 528 samples of surface sediments from the profundal zone were collected for monitoring, using the Van Veen sampler.

Determinations of polychlorinated biphenyls (congeners: PCB28, PCB52, PCB101, PCB118, PCB153, PCB138, PCB180), hexachlorocyclohexane isomers (α -HCH, β -HCH, γ -HCH, δ -HCH and p,p'-DDT (1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane), p,p'-DDE (1,1-dichloro-2,2-bis (4-chlorophenyl)ethylene) and p,p'-DDD (1,1-dichloro-2,2-bis (4-chlorophenyl)ethane) were made on extracts obtained after the ex-

traction of the samples using the hexane/acetone mixture. After desulphurisation, the extracts were purified from polar compounds by column chromatography (Florisil). The content of POPs in the extracts was determined using a gas chromatograph with an electron capture detector GC-ECD (Agilent). Separation of the compounds was performed on an HP-5 capillary column (30 m in length, 0.32 mm in diameter, 0.25 μm film (5%)-diphenyl-(95%) dimethylpolysiloxane), using temperature programming: with an increment of $30^\circ\text{C min}^{-1}$ from 110°C to 140°C , with a temperature increment of 2°C min^{-1} from 140°C to 170°C , isotherm at 170°C for 10 min, with an increment of 2°C min^{-1} from 170°C to 240°C , with an increment of $10^\circ\text{C min}^{-1}$ from 240°C to 300°C . The limit of determination for PCB28, PCB52, PCB101, PCB118, PCB153, PCB138, PCB180, and for p,p'-DDE and p,p'-DDD was 0.1 ng g^{-1} , and for α -HCH, β -HCH, γ -HCH, δ -HCH and p,p'-DDT – 0.5 ng g^{-1} . Organic carbon content was also determined in all the samples by coulometric titration from a solid sample using a Ströhlein COULOMAT 702 CS/LI device, after removal of carbonate carbon by concentrated HCl.

Results and discussion

In the lake sediments, the sum of HCH isomers (Σ HCH) was in the range from <2 (determination limit) to 60.7 ng g^{-1} , the calculated mean concentration was 6.3 ng g^{-1} , the geometric mean 3.5 ng g^{-1} , and the median 2.9 ng g^{-1} (Table 1). The concentration of Σ HCH, in excess of 30 ng g^{-1} , was characteristic of sediments in the following lakes: Lubiatońko (60.7 ng g^{-1}), Cichowo (55.4 ng g^{-1}), Charzykowskie (52.5 ng g^{-1}), Dominickie (49.6 ng g^{-1}), Dadaj (48.1 ng g^{-1}), Krzyckie (47.0 ng g^{-1}) and Bnińskie (46.2 ng g^{-1}) (Table 2). At a concentration in excess of the determination limit, isomer α -HCH was recorded in 442 samples, but more than half of them show a concentration of less than 2 ng g^{-1} (Figure 1). The highest concentration of this isomer was found in the sediments of Lake Lubi-

Table 1 Statistical parameters of the content of HCH isomers in lake sediments (ng g^{-1})

Parameter	Mean	Geometric mean.	Median	Minimum	Maximum
α -HCH	4.4	1.8	1.6	<0.5	51.0
β -HCH	0.5	<0.5	<0.5	<0.5	9.8
γ -HCH	1.1	0.6	0.5	<0.5	33.0
δ -HCH	<0.5	<0.5	<0.5	<0.5	16.4
Σ HCH	6.3	3.5	2.9	<2.0	60.7

Fig. 1. Histograms of α -HCH and γ -HCH in lake sediments

atówko (51 ng g^{-1}). The occurrence of isomer β -HCH, at a concentration in excess of the determination limit, was found in 100 samples. The highest levels were recorded in Lake Miejskie (Sarcz) – 9.8 ng g^{-1} . The presence of isomer γ -HCH, at a concentration in excess of the determination limit, was detected in 282 samples and most of them show values of less than 1 ng g^{-1} . The highest γ -HCH concentration was found in the sediments of Lake Dadaj – 33 ng g^{-1} γ -HCH. Isomer δ -HCH was found only in 14 samples and its highest concentrations were measured in the sediments

of Lake Charzykowskie (16 ng g^{-1}). Isomer α -HCH was not only the most frequently detected one, but also its average concentration was the highest – 4.4 ng g^{-1} , whereas the average concentration of γ -HCH, the second most frequent HCH isomer, was 1.1 ng g^{-1} . In most of the lakes, α -HCH predominates over γ -HCH. The concentration of γ -HCH is higher than the concentration of α -HCH only in the following lakes: Lubińskie, Selmęt, Kielsk, Łęgowskie, Wukśniki, Tuczno and Dadaj. The concentration of Σ HCH in the sediments shows a poor correlation with the TOC

Table 2. The content of the HCH isomers in sediments of selected lakes (ng g^{-1})

Lake	Voivodeship	α -HCH	β -HCH	γ -HCH	δ -HCH	Σ HCH
Białe-Mialkie	Greater Poland	28	0.6	5.3	<0.5	34.2
Bnińskie	Greater Poland	38	0.9	7.0	<0.5	46.2
Januszewskie	Warmian-Masuria	25	<0.5	4.3	<0.5	29.6
Lubiatówko	Warmian-Masuria	51	<0.5	9.2	<0.5	60.7
Tuczno	Kuyavian-Pomeranian	8.7	1.6	18	<0.5	28.6
Wilczyńskie	Podlasie	22	<0.5	4.1	<0.5	26.9
Krzyckie	Greater Poland	39	0.7	7.0	<0.5	47.0
Wielgie Dankowskie	Masovian	21	<0.5	3.9	<0.5	25.6
Cichowo	Greater Poland	45	1.6	8.5	<0.5	55.4
Lubinieckie	Warmian-Masuria	21	0.5	3.9	<0.5	25.7
Powidzkie Małe	Greater Poland	22	0.6	3.9	<0.5	26.8
Długie	Greater Poland	31	<0.5	5.5	<0.5	36.8
Charzykowskie	Pomeranian	30	<0.5	5.6	16.0	52.5
Dadaj	Warmian-Masuria	12	1.5	33.0	1.6	48.1
Dominickie	Greater Poland	41	<0.5	8.0	<0.5	49.5
Jeziorak	Warmian-Masuria	20	1.2	3.4	<0.5	25.1
Jeziorak	Warmian-Masuria	22	1.3	3.8	<0.5	26.9
Powidzke	Greater Poland	20	1.2	4.1	<0.5	25.6
Szczytno	Pomeranian	27	<0.5	4.5	<0.5	32.2
Niesłysz	Lubusz	28	<0.5	4.7	<0.5	33.2

($r=0.22$) and yet poorer correlation with the concentrations of DDTs ($r=0.13$) and PCBs ($r=0.17$).

The maximum recorded content of Σ HCH in lake sediments in the area of Poland is higher than that found in the sediments of China's lakes, e.g. Taihu Lake, where the content is up to 6 ng g^{-1} , Honghu Lake, up to 19.9 ng g^{-1} , and Baiyangdian Lake, up to 12.8 ng g^{-1} (Liu et al. 2009; Yuan et al. 2013; Hu et al. 2010). However, the average content of Σ HCH in lake sediments in Poland is comparable to the content of Σ HCH in sediments of those lakes, as well as to the content of HCH in the sediments of lakes from Svalbard Island (Norway), which contain from 0.8 to 6.5 ng g^{-1} Σ HCH, the sediments of Lake Victoria (Uganda), which contain up to 5.48 ng g^{-1} γ -HCH, or the sediments of Lake Manyas (Turkey), referred to as Bird Paradise, which contain 1.08 ng g^{-1} α -HCH, 1.95 ng g^{-1} β -HCH and 0.46 ng g^{-1} γ -HCH on average (Jiao et al. 2009; Erkmén et al. 2013; Wasswa et al. 2011). The maximum content of Σ HCH in the lake sediments is lower as

compared to the content of HCH in river sediments in Poland, which contain up to 122 ng g^{-1} , e.g. in the River Vistula at Oświęcim (Bojakowska et al. 2012). For comparison, in surface sediments of the southern Baltic Sea (Gdańsk Basin), where contaminants transported by the Vistula are accumulated, the content of Σ HCH is 1.73 ng g^{-1} , including 0.54 ng g^{-1} γ -HCH. In the Bornholm Basin, where contaminants transported by the River Oder are deposited, the content of Σ HCH is 2.13 ng g^{-1} (Sapota 2006; Pazdro 2004).

The total content of p,p'-DDT, p,p'-DDE and p,p'-DDD (Σ DDT) in the lake sediments was in the range from $<0.7 \text{ ng g}^{-1}$ to 602.9 ng g^{-1} , the average was 19.2 ng g^{-1} , the geometric mean was 8.9 ng g^{-1} , and the median, 10.4 ng/kg (Table 3). The highest content of p,p'-DDT and its metabolites was found in sediments of the following lakes: Urzędowskie (602.9 ng g^{-1}), Orłowskie (181.6 ng g^{-1}), Wilkowskie (195.1 ng g^{-1}), Góreckie (147.8 ng g^{-1}), Karczemne (157.6 ng g^{-1}) and Cichowo (124.1 ng g^{-1}) (Table 4).

Table 3. Statistical parameters of the content of DDT and its metabolites in lake sediments (ng g^{-1})

Parameter	Mean	Geometric mean.	Median	Minimum	Maximum
p,p'-DDE	8.9	4.6	5.9	<0.1	150.0
p,p'-DDD	9.5	2.8	3.3	<0.1	450.0
p,p'-DDT	0.8	0.5	0.3	<0.5	11.2
DDTs	19.2	8.9	10.4	0.4	602.9

Table 4. The content of DDT and its metabolites in sediments of selected lakes (ng g^{-1})

Lake	Voivodeship	p,p'-DDE	p,p'-DDD	p,p'-DDT	DDTs
Bnińskie	Greater Poland	38	38	1.8	77.8
Cichowo	Greater Poland	55.7	67	1.4	124.1
Czarne	Warmian-Masuria	34.5	89	0.9	124.0
Urzędowskie	Pomeranian	150	450	2.9	602.9
Góreckie	Greater Poland	39.8	107	1.3	147.8
Karczemne	Pomeranian	76	71	10	157.6
Kortowskie	Warmian-Masuria	30	45	3.8	78.6
Lechickie	West Pomeranian	46.0	76	1.4	122.9
Łęgowskie	Greater Poland	46	28	5.2	78.6
Miedwie	West Pomeranian	22	60	1.1	82.5
Morzycko	West Pomeranian	32	44	1.0	77.2
Narie	Warmian-Masuria	31	39	2.0	72.2
Orłowskie	Kuyavian-Pomeranian	69.2	111	1.6	181.6
Ostrów	West Pomeranian	46.4	54	2.2	102.2
Pszczewskie	Lubusz	30	67	3.9	100.7
Stępuchowskie	Greater Poland	23	47	1.3	71.6
Trześniowskie	Lubusz	39	81	1.5	121.1
Wilkowskie	Lubusz	51	137	7.3	195.1
Zajeziarskie	Pomeranian	26.3	72	0.8	98.6
Zamkowe (in Wałcz)	Podlasie	23	46	4.3	73.3

Fig. 2. Histograms of p,p' -DDT, p,p' -DDD, p,p' -DDE and (DDD+DDE)/DDT in lake sediments

The presence of metabolite p,p' -DDE was found in almost all samples (522 samples). Its maximum content (150 ng g⁻¹) was measured in the sediments of Lake Urzędowskie, but nearly 75% of the analysed samples contained less than 10 ng g⁻¹ (Figure 2).

Metabolite p,p' -DDD, at a concentration higher than the determination limit, was found in 502 samples, with the highest content (450 ng g⁻¹) also reported from Lake Urzędowskie. Despite the significantly lower geometric mean of the p,p' -DDD content than the p,p' -DDE content, the upper quartile of both isomers is comparable (8.9 ng g⁻¹ and 10.8 ng g⁻¹, respectively). The presence of p,p' -DDT, at a concentration above the determination limit, was observed in 255 samples, and the majority of samples contained less than 1 ng g⁻¹. The maximum content of p,p' -DDT (11.2 ng g⁻¹) was recorded in the sediments of Lake Ińsko. The content of DDT in the lake sediments has a weak correlation with the TOC ($r = 0.14$) and HCH content ($r = 0.13$), but a good correlation with the PCB content ($r = 0.45$).

The content of DDTs in most of the investigated lakes is comparable with the concentrations of DDTs in the sediments of China's lakes, e.g. in the sediments of Honghu Lake located in rice and cotton areas (up to 27.52 ng g⁻¹), the sediments of Baiyangdian Lake (up to 3.1 ng g⁻¹ DDTs), and the sediments of Taihu Lake (12 ng g⁻¹) (Yuan et al. 2013; Hu et al. 2010; Liu et al. 2009). However, the average DDT content in the lake sediments in Poland is much higher than the average content in the sediments of lakes on Svalbard Island, ranging from 0.07 to 5.4 ng g⁻¹, and the sediments of Lake Manyas, Turkey, with the values of 2.4 ng g⁻¹ p,p' -DDD, 0.92 ng g⁻¹ p,p' -DDE, and 1.18 ng g⁻¹ p,p' -DDT (Erkmen et al. 2013; Jiao et al. 2009). The maximum content of DDTs, recorded in the sediments of Lake Urzędowskie, is several times higher than the maximum concentration of DDT in the sediments of Lake Sibaya (123 ng g⁻¹), one of the most polluted lakes in South Africa (Humphries 2013). In the area of Poland, the presence of DDT has been much more frequently detected in lake sediments than in river sediments,

and the geometric mean content in river sediments is much lower – $1.9 \mu\text{g kg}^{-1}$. However, river sediments contain much higher amounts of DDT, up to $3,941 \text{ ng g}^{-1}$ (Bojakowska et al. 2012). For comparison, in the surface sediments of the Baltic Sea in the Gdańsk Basin, the content of DDTs is 4.39 ng g^{-1} , in the Bornholm Basin 0.98 ng g^{-1} , in the Gotland Basin $0.7\text{--}1.9 \text{ ng g}^{-1}$, and in the Gulf of Finland $2.6\text{--}5.0 \text{ ng g}^{-1}$ (Sapota 2006; Pikkarainen 2007).

The content of the sum of polychlorinated biphenyls ($\Sigma \text{ PCB}$) in the examined lake sediments var-

ied from $<0.7 \text{ ng g}^{-1}$ to 50.7 ng g^{-1} , the average was 2.8 ng g^{-1} , and the geometric mean and the median had similar values of 1.8 and 1.9 ng g^{-1} , respectively (Table 5). In the majority of samples, the PCB content does not exceed 3 ng g^{-1} (Figure 3). The highest $\Sigma \text{ PCB}$ values were reported in the sediments of the following lakes: Grzymiśławskie (50.5 ng g^{-1}), Karczemne (44.1 ng g^{-1}), Ostrów (25.4 ng g^{-1}) and Kalejty (24.8 ng g^{-1}) (Table 6). The presence of at least one PCB congener, at a concentration above the determination limit, was detected in 522 samples, including PCB28 – found in

Table 5. Statistical parameters of the content of PCBs in lake sediments (ng g^{-1})

Parameter	mean	Geometric mean.	Median	Minimum	Maximum
PCB28	0.2	0.1	<0.1	<0.1	30.0
PCB52	0.3	0.1	0.1	<0.1	12.0
PCB101	0.6	0.3	0.5	<0.1	8.3
PCB118	0.3	0.1	<0.1	<0.1	14.9
PCB153	0.6	0.3	0.4	<0.1	12.6
PCB138	0.4	0.2	0.2	<0.1	8.1
PCB180	0.4	0.2	0.2	<0.1	6.5
Suma PCB	2.8	1.8	1.9	<0.7	50.7

Table 6. The PCB content in sediments of selected lakes (ng g^{-1})

Lake	Voivodeship	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Total PCB
Bleszno	Lubusz	1.1	1.6	1.4	0.5	2.0	1.4	1.2	9.2
Borak	Lubusz	0.3	0.9	2.0	1.0	2.8	2.1	1.3	10.4
Buszno	Lubusz	0.4	0.3	1.7	1.0	3.2	3.3	2.8	12.7
Urzędowskie	Pomeranian	0.7	1.2	4.3	1.6	3.7	2.7	4.5	18.7
Ewingi	Warmian-Masuria	0.3	0.8	2.8	1.2	2.5	2.0	1.2	10.8
Góreckie	Greater Poland	0.2	0.3	1.6	1.3	3.1	2.8	1.5	10.8
Grzymiśławskie	Greater Poland	30	12	2.9	1.2	2.3	0.6	1.7	50.7
Kalejty	Podlasie	<0.1	<0.1	1.1	14.9	1.2	7.4	<0.1	24.8
Karczemne	Pomeranian	3.7	3.3	6.2	3.7	13	8.1	6.5	44.1
Klasztorne	Pomeranian	0.3	0.8	1.7	0.8	3.0	2.1	1.8	10.5
Kortowskie	Warmian-Masuria	1.3	1.2	2.6	2.9	2.4	2.9	1.1	14.4
Lechickie	West Pomeranian	0.3	0.2	2.0	0.9	2.4	2.0	1.3	9.1
Lubinieckie	Warmian-Masuria	<0.1	2.4	8.3	<0.1	2.7	1.0	0.8	15.3
Łęgowskie	Greater Poland	0.1	0.1	2.0	1.9	1.8	2.5	1.6	9.9
Miedwie	West Pomeranian	0.6	1.0	1.9	0.9	2.2	1.9	1.0	9.5
Orłowskie	Kuyavian-Pomeranian	0.8	1.3	1.7	1.5	2.2	2.4	1.8	11.7
Ostrów	West Pomeranian	0.6	1.2	4.1	1.7	7.2	6.2	4.4	25.4
Selmęt	Warmian-Masuria	<0.1	<0.1	0.4	8.7	0.7	3.3	0.3	13.5
Stelchno	Kuyavian-Pomeranian	0.7	1.4	2.6	2.2	2.1	1.7	0.8	11.5
Tuczno	Kuyavian-Pomeranian	3.4	1.3	3.0	<0.1	0.7	0.2	0.4	9.1

Fig. 3. Histograms and spectrum of PCBs in lake sediments

204 samples; PCB52 – in 280 samples; PCB101 – in 399 samples; PCB118 – in 236 samples; PCB153 – in 440 samples; PCB138 – in 311 samples; and PCB180 – in 407 samples. Among the examined congeners, PCB101 and PCB153 are predominant (Figure 3). The content of PCBs in the lake sediments shows a weak correlation with the TOC ($r = 0.19$) and with the HCH content ($r = 0.17$), and a good correlation with the DDT content ($r = 0.45$).

The range of the Σ PCB content in the lake sediments in Poland is similar to the PCB content in the sediments of China's lakes, e.g. Honghu Lake, where the concentration is up to 42.95 ng g^{-1} , or Baiyangdian Lake, where the concentration is up to 7.6 ng g^{-1} , as well as to the concentrations of PCBs in the lake sediments of Svalbard Island, attaining 18 ng kg^{-1} (Hu et al. 2010; Jiao et al. 2009; Yuan et al. 2013). The concentrations are also lower than those found in the sediments of Lake Bourget (France), which contain up to 79 ng g^{-1} PCBs and its deposition is dated to the 1970s (up to 850 ng g^{-1}), or those from Lake Michigan (USA), ranging from 0.6 to 224.9 ng g^{-1} , and yet lower than those from Järnsjön Lake (Sweden), which were up to $30,700 \text{ ng kg}^{-1}$ prior to remediation (Yaun et al. 2013; Bremie et al. 1998). Sediments of the Baltic Sea near Stockholm contain up to 100 ng g^{-1} , in the Gotland Basin up to 14.3 ng g^{-1} , in the estuary of the Warnow River 214 ng g^{-1} , and at the mouth of the Peene River 122 ng g^{-1} (Biselli et al. 2005; Dannenberg et al. 1997; Müller and Schilling 1998).

Based on the study results, it can be concluded that organochlorine compounds are common con-

stituents in the sediments of Poland's lakes. Undoubtedly, some of these compounds in the lake sediments originate from atmospheric transport, but their main source, particularly of organochlorine pesticides, was and still is primarily surface runoff from former agriculture and forestry areas. Among the POPs identified in the lake sediments, the most frequent compounds were DDTs and PCBs. The highest concentrations were reported for metabolites p,p'-DDT. The average content of p,p'-DDE was 8.9 ng g^{-1} , and p, p,-DDD 9.5 ng g^{-1} , while the average PCB content was significantly lower – 2.8 ng g^{-1} .

The presence of HCHs, at a concentration above the determination limit, was detected rarely, but their average content in the sediment was significantly higher than the content of PCBs. High DDT levels were detected in the sediments of lakes on which towns are located, e.g. Kartuzy (15,700 inhabitants) on Lake Karczemne, Olsztyn (175,500 inhabitants) on Lake Czarne (Sukiel), and Człuchów (14,000 inhabitants) on Lake Urzędowskie. Sediments of these lakes also contain elevated levels of HCHs and PCBs. Particularly striking is that the highest HCH content was observed in the sediments of lakes that are used for recreational purposes, near resorts and agrotourism centres. Sediments of these lakes are also characterised by relatively low DDT content. Although the use of HCH has been banned in agricultural production, these compounds are still present in cosmetics and medicines (shampoos against fleas and lice, anti-scabies drugs). Elevated PCB content was recorded in the sediments of lakes used for recreational purposes

as well as in those on which towns are situated. PCB compounds were used in many devices as hydraulic fluids, a lubricant component, insulation in engines, impregnation, or components of insecticide formulations, which resulted in widespread contamination of lake sediments with these compounds.

It has been found that the HCH and DDT concentrations in sediments of some lakes are higher than the PEC (Probable Effect Concentration) values, above which we can observe harmful effects of these compounds on organisms inhabiting surface fresh waters (Ingersoll et al. 2011). The γ -HCH content in the sediments of lakes Dadaj, Tuczno, Lubiatówko, Cichowo, Dominickie, Bnińskiego, Krzyckie, Charzykowskie, Długie and Białe Miątkie (1.89% of samples) exceeded 5 ng g^{-1} (PEC), but in most lakes (93.56%), the γ -HCH content was less than 3 ng kg^{-1} (TEC value – *Threshold Effect Concentration*), below which no harmful effect is observed on aquatic organisms. Contents of p,p'-DDE above 31 ng g^{-1} (PEC) was found in 20 samples (3.78%), while the values below 4.9 ng g^{-1} (TEC value) were observed only in 128 samples (24.2%). In the case of p,p'-DDD, a concentration higher than the PEC value – 28 ng g^{-1} , was observed in 39 samples (7.38%), and a content less than the TEC value (4.9 ng g^{-1}) was found in 321 samples (60.79%). No p,p'-DDT concentrations higher than the PEC value (62.9 ng g^{-1}) were found in the samples, and a content less than 1.19 ng g^{-1} (TEC) was measured in 428 samples (81.06%). None of the samples yielded PCB content greater than 676 ng g^{-1} (PEC), and a content greater than 22 ng g^{-1} (TEC) was found in only four lakes: Grzymisławskie, Karczemne, Ostrów and Kalejty.

The observations prove that p,p'-DDD is the prevalent component of the sediments that are characterised by a high content of DDTs originating presumably from local sources, indicating anaerobic conditions of p,p'-DDT degradation which probably took place in lake depths. The sediments with a lower DDTs content more frequently show prevalence of p,p'-DDE, which indicates the occurrence of aerobic conditions of degradation of p,p'-DDTs, and their likely origin from surface runoff. The content ratio of p,p'-DDT to its metabolites also shows a wide range of variation in the sediments. A low value of (DDE + DDD)/DDT (less than 1) indicates a close proximity to the source of contamination and relatively recent application of this preparation. The concentration ratio of the sum of DDT metabolites to p,p'-DDT in almost all lakes was above 2, and the ratio was commonly in single or

double figures (average 28.3). The ratio of DDT/(DDE + DDD) lower than 1 was recorded only for the sediments of lakes Kruteckie, Tumińskie and Gremzdel. For comparison, the (DDD + DDE)/DDT ratio in river sediments does not exceed 5.0 (Bojakowska et al. 2012).

The prevalence of α -HCH content over γ -HCH content in the sediments of almost all lakes, and the frequency of detection of individual HCH isomers in the sediments is constrained by several factors. It is probably related to the varying water solubility of the individual isomers: for example, δ -HCH dissolves much more readily than α -HCH. It also depends on the intensity of the isomerisation process of γ -HCH in α -HCH, particularly under reducing conditions (Różański 1992). The prevalence of α -HCH content over γ -HCH content may also indicate that preparations with a composition similar to an industrial product, but not to lindane, were used in the past. Industrial HCH, which was used in forestry in combating Black Arches (*Lymantria monacha*), generally contains 55-80% α -HCH, 5-14% β -HCH, 8-15% γ -HCH, and 2-16% δ -HCH, while lindane was characterised by a high content of γ -HCH – 99% (Erkmen et al. 2013; Wołkowicz 2010).

In water sediments, organic pollutants are associated primarily with organic matter. The analysed POPs from the lake sediments show a poor correlation with the TOC, but a very good correlation between the content of HCHs, DDTs and PCBs and the content of HCH/TOC, DDTs/TOC and PCB/TOC (Figure 4). In 90% of the samples, the $\Sigma \text{ HCH/TOC}$ ratio is below 1.8×10^{-7} (Figure 5). Most frequently, high values of this ratio were observed in samples characterised by an elevated content of $\Sigma \text{ HCH}$ (Figure 4). It can be assumed that the presence of HCHs in the sediments, at low concentrations and low values of the $\Sigma \text{ HCH/TOC}$ ratio, is due to their origin from diffuse sources of pollution, and the high content of $\Sigma \text{ HCH}$ and the high $\Sigma \text{ HCH/TOC}$ ratio point to local pollution. In 90% of the samples, the (DDT + DDE + DDD)/TOC ratio does not exceed 6.3×10^{-7} . Figure 5 depicts the (DDD + DDE + DDT)/TOC ratio histogram. Like with the case of HCH, high values of this ratio were most frequently observed in the samples characterised by increased content of DDT and its metabolites, most likely originating from local contamination sources. In 90% of the samples, the PCB/TOC ratio does not exceed 0.8×10^{-7} .

Fig. 4. Scatter plots of HCH, PCBs and DDTs terms of TOC

Fig. 5. Histograms of HCH/TOC, DDTs/TOC, PCBs/TOC

Conclusions

1. The studies have shown the common occurrence of organochlorine compounds in lake sediments in the area of Poland (99% of the analysed samples).
2. Among the analysed organochlorine compounds, the most frequent were DDTs and PCBs. The maximum content of HCH in the lake sediments was 60.7 ng g^{-1} ; DDTs – 602.9 ng g^{-1} ; and PCBs – 50.7 ng g^{-1} . Their average values were 6.3 ng g^{-1} , 19.2 ng g^{-1} and 2.8 ng g^{-1} , respectively.
3. Sediments of some lakes contain concentrations of γ -HCH and DDTs higher than the PEC values. The γ -HCH content was higher in 1.89% of the analysed samples, the p,p'-DDE content in 3.78% of the samples, and the p,p'-DDD content in 7.38% of the samples. p,p'-DDT and PCB concentrations, higher than the PEC value, were not found in any of the samples.

References

- Abbt-Braun G., Frimmel F., 1996, Interaction of pesticides with river sediments and characterization of organic matter of the sediments, [in:] Calmano W., Forstner U. (eds), *Sediments and toxic substances*, Springer, Berlin Heidelberg: 51-89.
- Bettinetti R., Quadroni S., Crosa G., Harper D., Dickie J., Kyalo M., Mavuti K., Galassi S., 2011, A preliminary evaluation of the DDT contamination of sediments in lakes Natron and Bogoria (Eastern Rift Valley, Africa), *Ambio* 40(4): 341-50.
- Biselli S., Reineke N., Heinzel N., Kammann U., Franke S., Hühnerfuss H., Theobald N., 2005, Bioassay-directed fractionation of organic extracts of marine surface sediments from the north and Baltic Sea, *J. Soil Sediment* 5(1): 171-181.
- Bojakowska I. Stasiuk M., Gąsior J., 2012, DDT i jego metabolity w powierzchniowych osadach jezior i rzek Polski (DDT and its metabolites in surface sediments of lakes and rivers of Poland), *Biul. PIG* 450: 9-16 (in Polish, English summary).

- Bojakowska I., Gliwicz T., Małecka K., 2006, Wyniki geochemicznych badań osadów wodnych Polski w latach 2003-2005 (Results of the geochemical research on water sediments of Poland in 2003-2005 years), IOŚ, Warszawa, p. 145 (in Polish).
- Bremie G., Okla L. Larsson P., 1998, PCB in water and sediment of Lake after remediation of contaminated sediment, *Ambio* 27(5):398-403.
- Dannenberg D., Andersson R., Rappe C., 1997, Levels and patterns of polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in surface sediments from the western Baltic Sea (Arkona Basin) and the Oder River estuarine system, *Mar. Poll. Bull.* 34(12): 1016-1024.
- Eisenberg J., Bennett D., McKone T., 1998, Chemical dynamics of persistent organic pollutants: a sensitivity analysis relating soil concentration levels to atmospheric emissions, *Environ. Sci. Technol.* 32(1): 115-123.
- Erkmen B., Yerli S., Erk'akan F., Kolankaya. D., 2013, Persistent organochlorine pesticide residues in water and sediment samples from Lake Manyas, Turkey, *J. Environ. Biol.* 34: 171-176.
- Grimalt J., Van Drooge B., Ribes A., Vilanova R., Fernandez P., Appleby P., 2004, Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes, *Chemosphere* 54: 1549-1561.
- Grynkiewicz M., Polkowska Z., Górecki T., Namieśnik J., 2003, Pesticides in precipitation from an urban region in Poland (Gdańsk-Sopot-Gdynia Tricity) between 1998 and 2000, *Water Air Soil Poll.* 149(1-4): 3-16.
- Henny C., Kaiser J., Grove R., Bentley V., Elliott J., 2003, Biomagnification factors (fish to osprey eggs from the Willamette River, Oregon, USA) for PCDDs, PCDFs, PCBs and OC pesticides, *Environ. Monit. Assess.* 84(3): 275-315.
- Hornbuckle K.C., Miller S.M., 2010, Spatial and temporal variations of persistent organic pollutants impacted by episodic sediment resuspension in southern Lake Michigan, *J. Great Lakes Res.* 36(2): 256-266.
- Hsu Y., Holsen T., Hopke P., 2003, Locating and quantifying PCB sources in Chicago: receptor modeling and field sampling, *Environ. Sci. Technol.* 37(4): 681-890.
- Hu G., Luo X., Li F., Dai J., Guo J., Chen S., Hong C., Mai B., Xu M., 2010, Organochlorine compounds and polycyclic aromatic hydrocarbons in surface sediment from Baiyangdian Lake, North China: Concentrations, sources profiles and potential risk, *J. Environ. Sci.* 22(2): 176-183.
- Humphries, M.S., 2013, **DDT residue contamination in sediments from Lake Sibaya in northern KwaZulu-Natal, South Africa: Implications for conservation in a World Heritage Site**, *Chemosphere* 93(8):1494-1499.
- Ingersoll C.G., MacDonald D., Wang N., Crane J.L., Field L.J., Haverland P.S., Kemble N.E., Lindskoog R.A., Severn C., Smorong D.E., 2001, Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines, *Arch. Environ. Con. Tox.* 41:8-21.
- Jiao L., Zheng GJ, Minh TB, Richardson B, Chen L, Zhang Y, Yeung LW, Lam JC, Yang X, Lam PK, Wong MH., 2009, Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: levels, sources and fluxes. *Environ Pollut.* 157(4):1342-1351.
- Jung S., Arnaud F., Bonté P., Chebbo G., Lorgeoux C., Wiński T., Tassin B., 2008, Temporal evolution of urban wet weather pollution: analysis of PCB and PAH in sediment cores from Lake Bourget, France, *Water Sci. Technol.* 57 (10): 1503-1510.
- Kannan K, Maruya K., Tanabe S., 1997, Distribution and characterization of polychlorinated biphenyl congeners in soil and sediments from a superfund site contaminated with Aroclor 1268, *Environ. Sci. Technol.* 31(5): 1483-1488.
- Lin T., Hu Z., Zhang G., Li X., Xu W., Tang J., Li J., 2009, Levels and mass burden of DDTs in sediments from fishing harbors: the importance of DDT-containing antifouling paint to the coastal environment of China, *Environ. Sci. Technol.* 43: 8033-8038.
- Liu G., Zhang G., Jin Z., Li J., 2009, Sedimentary record of hydrophobic organic compounds in relation to regional economic development: A study of Taihu Lake, East China, *Environ. Poll.* 157: 2994-3000.
- Lohmann R., MacFarlane J., Gschwend P., 2005, Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbor sediments, *Environ. Sci. Technol.* 39: 141-148.
- Müller A., Schilling P., 1998, Sedimentbelastung und Stoffhaushalt im Nördlichen Peenestrom, *BfG Mitteilung.* 15: 97-121.
- Nfon E., Cusin I., Broman D. Biomagnification of organic pollutants in benthic and pelagic marine food chain from Baltic Sea, *Sci. Total Environ.* 397: 190-204.
- Pazdro K., 2004, Trwałe zanieczyszczenia organiczne w osadach Zatoki Gdańskiej (Persistent organic pollutants in sediments from the Gulf of Gdańsk), *Rocz. Ochr. Środ.* 6: 75-76 (in Polish, English summary).
- Pikkarainen A., 2007, Polychlorinated biphenyls and organochlorine pesticides in Baltic Sea sediments and bivalves, *Chemosphere* 68: 17-24.
- Ramamoorthy S., Ramamoorthy S., 1997, Chlorinated organic compounds in the environment. Regulatory and monitoring assessment, Lewis Publishers, Boca Raton: p. 370.
- Rawn D.; Lockhart W.; Wilkinson P.; Savoie D.; Rosenberg G., Muir D., 2001, Historical contamination of Yukon Lake sediments by PCBs and organochlorine pesticides: influence of local sources and watershed characteristics, *Sci. Total Environ.* 280(1-3):17-37.
- Różański L., 1992, Przemiany pestycydów w organizmach żywych i środowisku (Transformations of pesticides in life forms and in the environment), PWRiL, Warszawa, p.274 (in Polish).
- Sapota G., 2006, Persistent organic pollutants (POPs) in bottom sediments from the Baltic Sea, *Oceanol. Hydrobiol. Stud.* 35(4): 295-306.

- Schneider A.R., Porter E.T., Baker J.E., 2007, Polychlorinated biphenyl release from resuspended Hudson River sediment, *Environ. Sci. Technol.* 15(4): 1097-103.
- Shen L., Wania F., Lei Y., Teixeira C., Muir D., Bidleman T., 2005, Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America, *Environ. Sci. Technol.* 39(2): 409-420.
- Sivey, J. D., Lee, C. M., 2007, Polychlorinated biphenyl contamination trends in Lake Hartwell, South Carolina (USA): sediment recovery profiles spanning two decades, *Chemosphere* 66(10):1821-1828.
- Strandberg B., Bandh C., Van Bavel B., Bergqvist P., Broman D., Ishaq R., Näf C., Erappe C., 2000, Organochlorine compounds in the Gulf of Bothnia: sediment and benthic species, *Chemosphere* 40(9-11): 1205-1211.
- Totten L., Gigliotti C., Offenberg J., Baker J., Eisenreich S., 2003, Reevaluation of air-water exchange fluxes of PCBs in Green Bay and Southern Lake Michigan, *Environ. Sci. Technol.* 37: 1739-1743.
- Wasswa J., Kiremire B.T., Nkedi-Kizza P., Mbabazi J., Ssebugere P., 2011, Organochlorine pesticide residues in sediments from the Uganda side of Lake Victoria, *Chemosphere* 82(1): 130-136.
- Wołkowicz W., 2010, Ocena wpływu migracji pestycydów chloroorganicznych z wybranych mogiłników, zlokalizowanych w różnych warunkach geologicznych, na zanieczyszczenie osadów i wód podziemnych (Assessment of organochlorine pesticides migration from selected disposal sites localized under different geological conditions and its impact on soil and groundwater contamination), *Prz. Geol.* 58(11): 1087-1097 (in Polish, English summary).
- Yuan L., Qi S., Wu X., Wu C., Xing X., Gong X., 2013, Spatial and temporal variations of organochlorine pesticides (OCPs) in water and sediments from Honghu Lake, China, *J. Geochem. Explor.* 132: 181-187.