Organochlorine Residues in Freshwater Sediments in Poland

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Abstract
The concentrations and spatial distribution of organochlorine compounds (HCHs, HCB, DDTs, CHLs and PCBs) were examined in freshwater and brackish water sediment collected from various sites in Poland in 1993-1994. The concentrations of PCBs were found to be highest in all samples with a range between 1.7 and 4.6 ng/g dry wt in unpolluted areas and between 46 to 1300 ng/g dry wt in highly urbanised and industrialised areas. The pattern of PCBs determined in most polluted sediment sample (1300 ng/g dry wt) collected from the coal mine pond in Katowice resembled that of technical Chlorofen. The concentrations of DDTs in sediments collected from the northern and southern regions of Poland were five to ten times, respectively, lower than of PCBs, on the average, and were followed by HCHs, HCBz and CHLs.

Key words: Organochlorine Pesticides, DDTs, HCHs, HCBz, CHLs, Chlordanes, Polychlorinated Biphenyls, PCBs, Sediment, Pollution.

Introduction
Organochlorine pesticides (OCs) such as DDT, technical BHC (benzenehexachloride) and Lindane (γ-HCH) were used in large quantities in agriculture and for other purposes in the past in Poland (1, 2). The technical DDT was applied confidently and in a relatively high rates between 1970-1990 in countries neighbour to Poland such as a former Soviet Union and Eastern Germany - imported from Romania and Soviet Union (3, 4). Poland has two own technical polychlorinated biphenyl (PCBs) mixtures: Chlorofen - a highly chlorinated type formulation (used for mining purposes) (5), and Tarpol, which is an analogue of Aroclor 1254. There is no data available about the quantity of Chlorofen produced, while in rough 100 tones of Tarpol were manufactured. Some foreign PCB mixtures (Sovol, Delor, Clophen) were also imported and used in Poland but there is no data available about the total volume and type of technical PCBs imported in detail. Additionally, some quantities

of industrial wastes contaminated with PCBs were illegally conveyed to Poland in 1989-1991.

In this study an attempt has been made to clarify organochlorine pesticides and PCBs levels in sediments in selected regions of Poland.

Materials and Methods

The sediment samples were collected at the area of the Districts of Gdańsk, Szczecin and Katowice in 1993-1994 (Figure 1).

Figure 1. Location of the sampling sites.

The surface sediment (0-10 cm) were collected using an Eckman Birge sampler. All samples were packed in chemically clean polyethylene bags and until analysis stored under temperature controlled condition. The sediment samples were ground and sieved using a 32 mesh size sieve (500 μm). A sediment sample (20 g) was mixed with 20 ml *n*-hexane-prewashed water in a 250 ml glass stoppered Erlenmayer flask and allowed to soak for 30 minutes. The sample was extracted with 150 ml of acetone for an hour. The acetone extraction was repeated twice for each sample. The combined supernatant was decanted into a 3 litre separatory funnel containing 200 ml of *n*-hexane in 1300 ml of *n*-hexane prewashed water, and the funnel was shaken for 10 minutes. The *n*-hexane extract was washed three times with 200 ml of *n*-hexane prewashed water, dried by passing it through a layer of anhydrous sodium sulphate, and then concentrated to 5 ml by using a Kuderna-Danish concentrator. The extracts were cleaned-up with concentrated sulphuric acid and subjected to column chromatography fractionation with activated Florisil gel (130°C, 12h). The first fraction eluted with *n*-hexane contained HCB, *p,p'*- DDE, PCBs and a part of

trans-nonachlor. The second fraction eluted with 20% dichloromethane in n-hexane contained chlordane compounds and metabolites (*trans*-chlordane, *cis*-chlordane and *trans*-nonachlor), *p,p'*- DDT, *p,p'*- DDD, and HCH isomers (α, β and γ). Each elute was concentrated down to 5 ml and washed with 2 ml of fuming sulphuric acid in concentrated sulphuric acid. Sulphur eluted in the first fraction was removed by treatment with copper chips. The identification and quantification of organochlorines were made using capillary column gas chromatography with a ^{63}Ni electron capture detection (HRGC-ECD; Hewlett Packard 5890). The GC system was equipped with a moving-needle-type injection system (splitless and solvent-cut mode). The capillary column of 0.25 mm i.d. and 30-m length (J & W Scientific Co. USA; 10% dimethyl polysiloxane, 0.25 μm bonded phase) for HCB and PCBs and DB-1701 (J & W Scientific Co., USA; 14% cyanopropyl phenyl polysiloxane, 0.25 μm bonded phase) for organochlorine pesticides were used. The temperature of the column oven was programmed at a rate from an initial 160°C (4 min hold) to a final temperature of 240°C, with a final holding of 20 min. Helium and nitrogen were used as carier (2 ml/min) and make-up gas (60 ml/min), respectively. The injector temperature was kept at 250°C and detector temperature was maintained at 300°C. DDTs was the sum of *p,p'*- DDT, *o,p'*- DDT, *p,p'*- DDE, *p,p'*- DDD and *o,p'*- DDD, HCHs was the sum of the α, β and γ, and CHLs was the sum of *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor. The PCB concentration in the samples was calculated by adding the concentrations of the individually resolved peaks of different PCB isomers and congeners, while an equivalent mixture of the technical Kanechlor formulations (KC 300:400:500:600) of known chlorobiphenyl composition and content (CB%) was used as an analytical standard. The detection limit of the method was 0.1 ng for pesticides and 1.0 ng/g for PCBs, and recovery rates of these compounds were between 95 and 105% (6). To clarify the pattern of PCBs some of the extracts obtained were analysed using HRGC/LRMS.

Results and Discussion

HCBz, HCHs, DDTs, CHLs and PCBs were detected in all sediment samples (Table 1). PCBs were a major compounds quantified and followed by DDTs, CHLs, HCHs and HCBz.

The concentrations of PCBs were apparently low, i.e. between 1.7 and 2.2 ng/g dry weight, in sediments collected from the drainage ditches, the canals and lakes at the areas without an evidence of a direct impact of urbanization or industrial activity. For some areas of the Szczecin Lagoon (near Karnocice and Stepnica) also a low degree of pollution with PCBs was observed (1.9 ng/g dry weight), while for those receiving untreated municipal effluents from the resort town of Międzyzdroje (Lake Wicko Małe and Lake Wicko Wielkie) a higher degree of pollution occurred (between 78 and 99 ng/g dry weight). The sediments collected at the sites under influence by human activity in Northern Poland (Dead Vistula River Channel, the canals of the sea ports and shipyards of the cities of Gdańsk, Gdynia and Świnoujście) contained PCBs in concentration between 46 and 630 ng/g dry weight. In a few sediment samples in Southern Poland the concentrations of PCBs ranged between 46 and 1300 ng/g dry weight, and a most polluted was a pond receiving effluent water from

Table 1. Organochlorine pesticides and PCBs concentrations in sediments from Poland (ng/g dry weight)

Compound	Northern Poland n = 20		Southern Poland n = 3	
HCBz	0.50±0.94	0.003-3.7	0.39*	
α-HCH	0.31±0.42	0.003-1.4	0.77±0.58	0.24-1.4
β-HCH	0.18±0.26	0.008-1.1	0.92±0.61	0.40-1.6
γ-HCH	0.25±0.31	0.012-1.2	0.93±0.75	0.21-1.7
HCHs	0.74±0.78	0.034-2.6	2.6±1.9	0.85-4.7
p,p'-DDT	4.9±12	0.022-51	4.8±2.6	1.8-6.5
o,p'-DDT	0.53±1.0	0.006-3.8	0.56±0.47	0.26-1.1
p,p'-DDD	14±33	0.009-140	38±51	5.2-97
o,p'-DDD	3.2±8.2	0.016-35	10±10	3.2-22
p,p'-DDE	2.3±4.1	0.013-14	3.5±3.6	1.4-7.7
o,p'-DDE	0.029±0.041	<0.04-0.2	<0.02	<0.02-<0.02
DDTs	24±41	0.1-150	57±55	18-120
CHLs	1.0±1.2	0.036-4.5	3.4±3.9	0.24-7.8
PCBs	110±160	1.7-630	540±670	46-1300

*One sample analysed

the coal mine in city of Katowice. The pattern of PCBs in sediments from a coal mine pond reflected that observed in the Polish technical PCB formulation Chlorofen.

The concentrations of DDTs were well below 50 ng/g dry weight in ~80% of the sediments examined and in four samples was between 72 and 150 ng/g dry weight. *p,p'*-DDD, and in a few cases *p,p'*-DDT were a major components among DDTs quantified. HCBz, HCHs and CHLs were only a minor residues and their concentrations were usually well below 5 ng/g dry weight of sediment.

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References

1. Falandysz J; The use of pesticides and their levels in food in Eastern Europe: The example of Poland. Chapter 25, p. 247-256, in *Contaminants in the Environment. Multidisciplinary Assessment of Risk to Man and other Organisms*, Eds. A. Renzoni, Lewis Publishers, **1994**; ISBN-0-87371-853-4.
2. Dąbrowski J, Siłowiecki A, Heinisch E, Wenzel-Klein S; Anwendung chlororganischer Pestizide in Polen und hieraus entstehende ökologisch-chemische und ökotoxicologische Folgen, p. 19-24, in *Schadstoffatlas Osteuropa. Ökologisch-*

chemische und ökotoxi-kologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost-Mitteleuropa. Eds. E. Heinisch, A. Kettrup, S. Wenzel-Klein, Ecomed, Landsberg am Lech, **1994**; ISBN 3-609-69540-4.

3. Fedorov LA; *Organohalogen Compd.* **1997**, 32, 41.
4. Heinish E, Wenzel-Klein S; p. 4-7. in *Schadstoffatlas Oteuropa - Ökologisch-chemische und ökotoxi-kologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost-Mitteleuropa*. Eds. E. Heinisch, A. Kettrup, S. Wenzel-Klein, Ecomed, Landsberg am Lech, **1994**, ISBN 3-609-69540-4.
5. Falandysz J, Yamashita N, Tanabe S, Tatsukawa R; Composition of PCB isomers and congeners in technical Chlorofen formulation produced in Poland. *Intern J Environ Anal Chem.* **1992**, 42, 129.
6. Kawano M., Ramesh A, Thao VD, Tatsukawa R, Submaranian AN; Persistent organochlorine insecticide residues in some paddy, upland and urban soils of India. *Intern. J. Environ. Anal. Chem.* **1992**, 48, 163.