Spatial Distribution of DDTs, HCBz and PCBz in Plankton in the Southern Part of the Baltic Proper

[1]Jerzy Falandysz, [2]Bo Strandberg, [1]Dorota Danisiewicz, [1]Lidia Strandberg, [2]Per-Anders Bergqvist, [2]Christoffer Rappe [1]Department of Environmental Chemistry & Ecotoxicology, University of Gdańsk, ul. J. Sobieskiego 18, PL 80-952 Gdańsk, Poland and [2]Institute of Environmental Chemistry, Umea University, S-901 87 Umea, Sweden

Abstract

We report here on the concentrations, composition and spatial distribution of DDT and its analogues (DDTs: *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE and DDMU), hexa- (HCBz) and pentachlorobenzene (PCBz) in subsurface mixed phyto- and zooplankton collected in the southern part of the Baltic Sea in 1992. The 1992 concentrations of DDTs were five to eight times lower than was found in mixed plankton collected from the same regions of the Baltic in 1983, and in parallel there was also high reduction of the concentration of HCBz, while PCBz remained undetected. A large reduction of the concentrations of DDTs and HCBz in plankton over the period from 1983 to 1992 seems to indicate on decreased deposition rates of these compounds from the atmosphere into the southern part of the Baltic Sea in a recent years.

Key words: Organochlorine pesticides, DDTs, hexachlorobenzene, pentachlorobenzene, plankton, Baltic Sea

Introduction

The bioaccumulation by plankton of persistent organohalogenated compounds both from the water column and food is a complex process affected by several abiotic and biotic factors, such as solubility, hydrophobicity, molecular configuration, the cell surface area and type, the growth rate of the cells, and their lipid content and composition[1]. DDTs (insecticide DDT and its analogues), HCBz (fungicide hexachlorobenzene) and PCBz (pentachlorobenzene) were determined in mixed subsurface phyto- and zoo-plankton samples to better understand possible sources of pollution and recent concentrations of those compounds in the Baltic Sea. DDTs and HCBz are lipophilic environmental micropollutants, which were introduced into the common practice in 1940 and 1915, respectively. The peak concentrations of DDTs in Baltic marine organisms was observed in the early 1970s[2]. PCBz is understudied micropollutant in the Baltic

Sea and recently its presence have been identified in Baltic herring as well as in stickleback collected from the coastal areas of the Gulf of Gdańsk[3,4].

Experimental Methods

The mixed subsurface phyto- and zoo-plankton samples were collected in four spatially distant sites in the southern part of the Baltic Sea (Fig. 1) during a research cruise of r/v "Oceania" in September 1992. The species composition of the plankton samples examined differed slightly, and in detail was presented elsewhere[5].

The analytical method used for determination of DDTs, HCBz and PCBz is a part of a multiresidue procedure of many organohalogens[6]. A final quantification of DDTs, HCBz and PCBz was achieved using capillary column (Rtx-5) gas chromatography and low resolution mass spectrometry (HRGC/LRMS) after a nondestructive extraction in an open wide bore glass tube and clean-up step using dialysis through semipermeable polyethylene membrane, and further fractionation of the extract on Florisil column. DDTs, HCBz and PCBz were eluted with *n*-hexane (fraction 1) and methylene chloride and *n*-hexane (15:85; v/v; fraction 2). $^{13}C_{12}$ -labelled *p,p'*-DDT and 2,2',4,5,5'-pentachlorobiphenyl were internal standards used to control recovery.

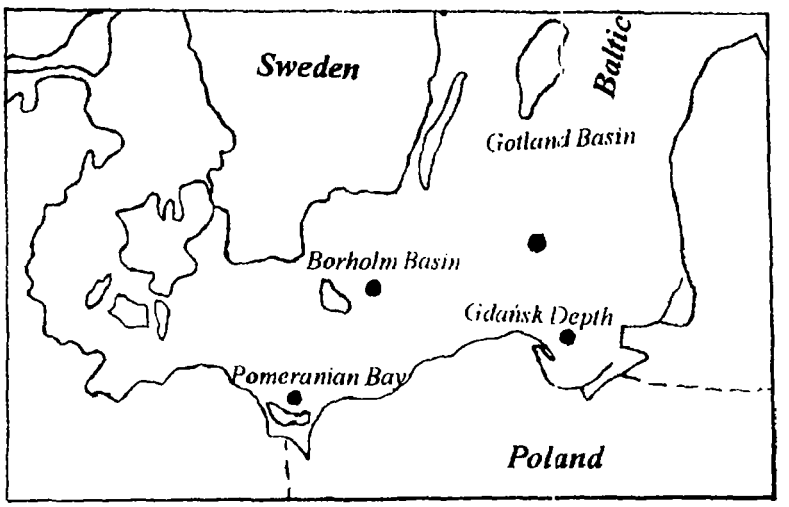

Figure 1. The sampling sites of plankton in the southern part of the Baltic Sea.

Results and Discussion

Table 1 shows the concentrations of DDTs and HCBz determined in plankton samples, while PCBz remained undetected above the detection limit of the method (<0.2 ng/g lipids). Despite of the spatially distant sampling sites of plankton the lipid weight adjusted data and composition of DDTs are nearly the same for all samples (Table 1, Figure 2), what seems to indicate on the atmosphere as a main source of those contaminants in the southern part of the Baltic Sea in recent years.

The concentrations of DDTs in plankton collected from the area of the Gdańsk Deep, Gotland Basin and Bornholm Basin in 1983 were 1300, 920-1200 and 2200 ng/g on a lipid weight basis, respectively [7]. The concentrations of DDTs noted in plankton 1992, when compared to the values reported for the same areas of the Baltic in 1983, are from five to eight times lower. A similar as for DDTs a downward trend of the concentrations in plankton can be observed for HCBz. The concentrations of HCBz in plankton in 1983 were 88, 44-100 and 93 ng/g lipid weight [6] and after nine years have decreased to 11, 10 and 12 ng/g lipid weight in the Gdańsk Deep, Gotland Basin and Bornholm Basin, respectively.

In the 1979-1989 time-trend study of organochlorines in cod-liver oil produced from the livers of cod netted from the southern part of the Baltic proper a gradual decline of DDTs was observed from 1983 to 1989, *i.e.* from 5.0 ng/g to 3.1 ng/g, respectively [2]. The rate of decline of the concentration of DDTs in plankton over the period of 1983-1992 is much higher when compared to cod-liver oil produced in 1983-1989. A relatively rapid decline of DDTs in subsurface plankton and slower in cod-liver oil can indicate on a lower deposition rates of DDTs from the atmosphere into the southern part of the Baltic Sea in recent years.

Table 1

DDTs, HCBz and PCBz in Baltic plankton (ng/g on a lipid and wet weight basis - *italics*)

Compound	Number of the sampling station and concentration			
	Gdańsk Deep	Gotland Basin	Bornholm Basin	Pomeranian Bay
	5	22	26	27
o,p'-DDT	ND	ND	ND	ND
p,p'-DDT	23/*0.41*	30/*0.32*	33/*0.26*	22/*0.23*
o,p'-DDD	28/*0.52*	44/*0.49*	55/*0.46*	22/*0.17*
p,p'-DDD	130/*2.3*	130/*1.4*	120/*0.94*	98/*1.1*
o,p'-DDE	1.6/*0.029*	ND	ND	ND
p,p'-DDE	110/*2.0*	110/*1.2*	130/*1.1*	120/*1.3*
DDMU	6.9/*0.13*	ND	7.9/*0.067*	6.7/*0.071*
DDTs	**290/*5.4***	**310/*3.4***	**340/*2.8***	**270/*2.9***
HCBz	11/*0.20*	10/*0.11*	12/*0.10*	16/*0.17*
PCBz	ND	ND	ND	ND
Lipids (%)	1.85	1.10	0.84	1.07

ND, not detected (<0.2 ng/g on a lipid weight basis)

DDT is not more used in Poland from 1975 [8]. In the former Eastern Germany the technical DDT was used until 1988, and the application rates were *ca.* 25 tones annually during 1976-1982. In 1983 and 1984 to control *Lymantria monacha* in coniferous trees the use of DDT in a former Eastern Germany reached *ca.* 140 and 480 tones, respectively [9].

The ratio of the concentrations of *p,p'*-DDT to DDTs in environmental matrices was earlier used by some authors as a possible indication of the recent use of the insecticide DDT. The ratio of *p,p'*-DDT to DDTs (*p,p'*-DDT + *p,p'*-DDD + *p,p'*-DDE) in plankton examined in

1983 was 0.26 for the Gdańsk Deep, 0.27-0.36 for the Gotland Basin, and 0.39 for the Bornholm Basin [7], and for plankton collected from the Ariste Bay in 1984 it was 0.65 [10]. When compared to the data obtained in 1983 the *p,p'*-DDT/DDTs ratios in plankton examined in 1992 are much lower, *i.e.* 0.088 (Gdańsk Deep), 0.11 (Gotland Basin), 0.12 (Bornholm Basin) and 0.092 (Pomeranian Bay). The detection of small amounts of *p,p'*-DDT in all samples of subsurface plankton examined in this study indicate on a lack of any significant local sources of pollution with that compound, and a fresh inputs, possibly due to atmospheric transportation and deposition, can be also related to a distant sources.

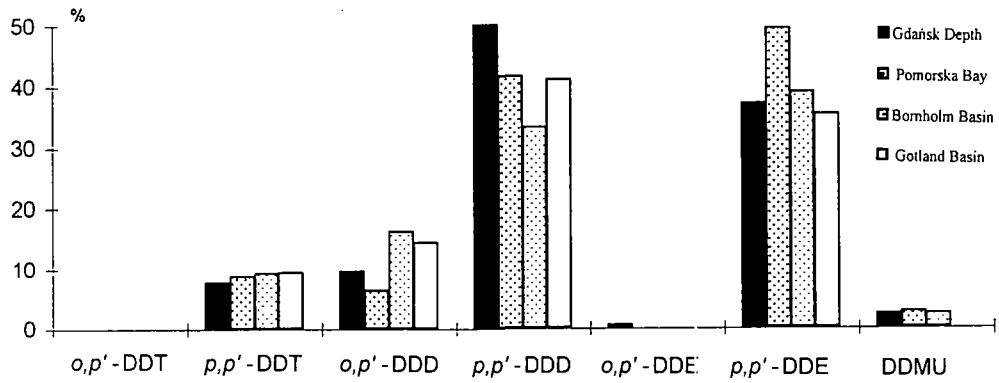

Figure 2. The composition (%) of DDT compounds in plankton.

Acknowledgements

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Literature cited

1) Skoglund, R. and D.L. Swackhamer: *In* Environmental Chemistry of Lakes and Reservoirs; Baker LA., Ed.; ACS Advances in Chemistry Series; 237; American Chemical Society Washington, DC, **1994** pp 559-574.
2) Kannan, K.; Falandysz, J.; Yamashita, N.; Tanabe, S. and R. Tatsukawa: Temporal trends of *Mar. Pollut. Bull.* **1992**, 24, 358-363.organochlorine concentrations in cod-liver oil from the southern Baltic proper, 1971-1989.

3) Falandysz, J.; Danisiewicz, D.; Strandberg, L.; Strandberg, B.; Bergqvist, P-A. and C. Rappe: DDTs, HCBz and PCBz in stickleback from various sites in the Gulf of Gdańsk. Indiannapolis, Dioxin'97, submitted.
4) Falandysz, J.; Danisiewicz, D.; Strandberg, L.; Strandberg, B.; Bergqvist, P-A. and C. Rappe: Pentachlorobenzene, hexachlorobenzene and DDTs in a pelagic food chain in the Baltic Sea. Indiannapolis, Dioxin'97, submitted.
5) Falandysz, J. and C. Rappe: Spatial distribution in plankton and bioaccumulation features of polychlorinated naphthalenes in a pelagic food chain in southern part of the Baltic proper. *Environ. Sci. Technol.* **1994**, 30, 3362-3370.
6) Bergqvist, P-A.; Strandberg, B. and C. Rappe: Analysis of dioxins and related compounds including chlorinated pesticides and PAH using semipermeable membranes. Analytical Proceedings **1993**, 30, 404-405.
7) Falandysz, J: Trace metals and organochlorines in plankton from the southern Baltic. *Mar. Pollut. Bull.* **1984**, 15, 416-418.
8) Dąbrowski, J.; Siłowiecki, A.; Heinisch, E. and S. Wenzel-Klein: Anwendung chlororganischer Pestizide in Polen und hieraus entstehende ökologische-chemische und ökotoxikologische Folgen. *In* E. Heinisch, A. Kettrup, S. Wenzel-Klein (eds). Schadstoffatlas Osteuropa. Ökologisch-chemische und ökotoxikologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost- Mitteleuropa. Ecomed, Landsberg/Lech. **1994**, pp 19-24.
9) Heinisch, E. and S. Wezel-Klein: Produktion und Anwendung von Chlorkohlenwasserstoff-Pestiziden in der ehemaligen DDR. *In* E. Heinisch, A. Kettrup, S. Wenzel-Klein (eds). Schadstoffatlas Osteuropa. Ökologisch-chemische und ökotoxikologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost- Mitteleuropa. Ecomed, Landsberg/Lech. **1994**, pp 4-7.
10) Roots, O: Polychlorierte Biphenyle und chlororganische Pestizide in der Ostsee-Estnische Daten 1976-1991. *In* E. Heinisch, A. Kettrup, S. Wenzel-Klein (eds). Schadstoffatlas Osteuropa. Ökologisch-chemische und ökotoxikologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost- Mitteleuropa. Ecomed, Landsberg/Lech. **1994**, pp 221-225.