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DDTs, HCBz and PCBz in Stickleback from Various Sites in the Gulf of Gdańsk

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Abstract

Stickleback collected from four sites in the beach zone in the western part of the Gulf of Gdańsk in 1992 contained DDTs (DDTs: *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE and DDMU), HCBz and PCBz in the concentrations between 1300-2600, 18-40 and 4.8-8.2 ng/g lipid weight, respectively. A relatively elevated concentrations of DDTs and HCBz were found in sticklebacks collected at a site with a possible impact of the contaminated with those substances water of the Dead Vistula River Channel, and at a site neighbourhood to the port and shipyards area there was a relatively higher concentration of PCBz.

Key words: Fish, stickleback, pesticides, DDT, pentachlorobenzene, hexachlorobenzene, pollution, Baltic Sea

Introduction

DDT is a highly persistent insecticide, which was intensively used and mainly for agricultural purposes in the past in Poland. The total volume of the technical DDT used in Poland from 1947 to 1980 was 48151,7 tones, and the annual rate was up to 3880,6 tones¹⁾. In neighbourhood to Poland the former Eastern Germany in 1983 and 1984 was used *ca.* 120 and 480 tones of the technical DDT, respectively²⁾. A recent data on DDTs content of herring and perch collected from the Gulf of Gdańsk has indicated on relatively elevated concentrations of that insecticide when compared to herring and perch from the various sites of the Gulf of Bothnia, in the northernmost part of the Baltic Sea³⁾. DDTs concentrations has decreased largely in fish in the southern part of the Baltic Sea from the mid 1970s^{4,5)}, however, a recent sources of this insecticide seem to be connected to atmospheric transportation and deposition from a distant sources, and partly to the past history of its use in Poland. The soils in Poland still can contain relatively elevated concentrations of DDTs, and much less of the isomers of hexachlorocyclohexane, hexachlorobenzene and chlordanes⁶⁾. HCBz was imported and used in the past in Poland as fungicide, and the application rates were relatively small (total import was 187.6 tones between 1962 and 1972)¹⁾, and there are no data available on the use of PCBz.

LEVELS IN FOOD

Stickleback *Gasterosteus aculeatus* was selected as an indicator organism to investigate concentrations and spatial distribution of DDTs, HCBz and PCBz in a coastal area of the south-western part of the Gulf of Gdańsk.

Experimental Methods

Stickleback of both sexes were caught in four sites in the beach zone in the south-western part of the Gulf of Gdańsk in June 2 - July 1, 1992 (Figure 1). From the every site examined 30 specimens were collected.

The analytical method used for determination of DDTs, HCBz and PCBz is a part of a multiresidue procedure of many organohalogen⁷⁾. 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). ¹³C₁₂-labelled *p,p'*-DDT and 2,2',4,5,5'-pentachlorobiphenyl were internal standards used to control recovery.

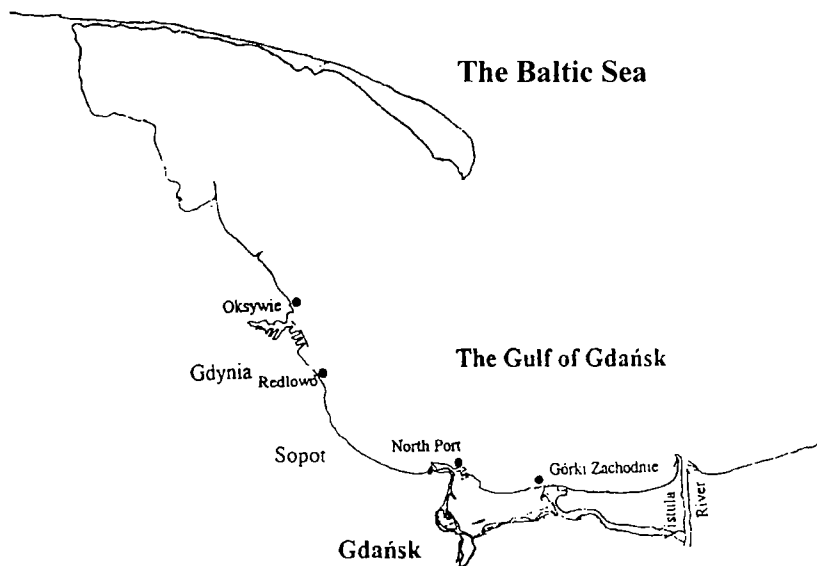


Figure 1. The sampling sites of (●) stickleback in the Gulf of Gdańsk.

Results and Discussion

The lipid weight normalised DDTs, HCBz and PCBz concentrations in fish measured in this study are presented in Table 1, and the composition of DDT and its analogues is shown in Figure 2.

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Table 1

DDTs, HCBz and PCBz in stickleback from the western part of the Gulf of Gdańsk

Compound	Sampling site and concentration			
	Redłowo	Oksywie	Westerplatte	Pleniewo
<i>o,p'</i> -DDT	77	52	53	130
<i>o,p'</i> -DDD	83	68	67	140
<i>p,p'</i> -DDT	280	250	160	390
<i>p,p'</i> -DDD	230	250	240	500
<i>o,p'</i> -DDE	6.0	7.6	4.7	12
<i>p,p'</i> -DDE	740	1100	700	1400
DDMU	22	32	21	33
DDTs	1400	1800	1300	2600
HCBz	28	18	19	40
PCBz	5.4	8.2	4.8	6.0
Lipids (%)	2.44	2.66	2.38	2.44

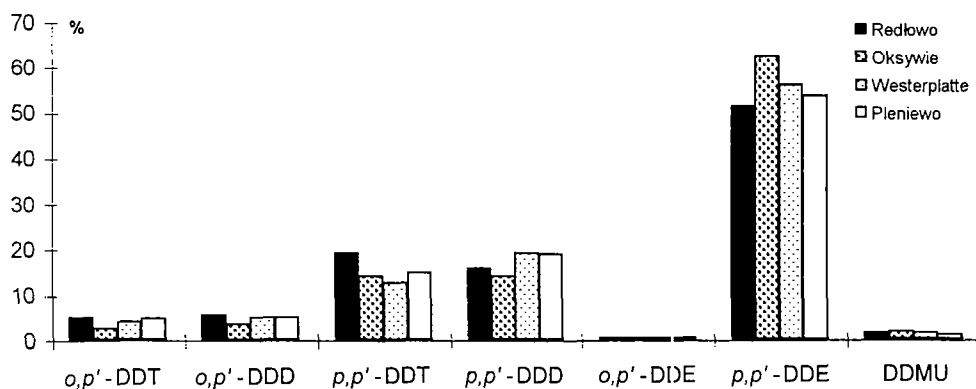


Figure 2. The composition (%) of DDT compounds in stickleback.

There are no earlier records on DDTs, HCBz or PCBz in sticklebacks from the Gulf of Gdańsk and adjacent area. *p,p'*-DDT, *o,p'*-DDT and their metabolites such as DDD, DDE and DDMU could be quantified in all sticklebacks sampled. The fish collected at the Pleniewo site when compared to other three areas were more contaminated with DDTs (Table 1). The concentrations of DDTs in sticklebacks collected at the Redłowo, Oksywie and Westerplatte sites when normalised to lipid weight are very similar to those determined in herring and perch, which contained 1300 and 1400 ng/g, respectively, and were caught in the Gulf of Gdańsk in summer 1992³⁾. The sticklebacks collected at the Pleniewo site contained elevated concentration of

LEVELS IN FOOD

DDTs when compared to other areas. Since those fish were sampled close to the outlet of the Brave Vistula River (actually a connection between the Gulf of Gdańsk and the Dead Vistula River Channel) a possibility exist, that relatively higher level of DDTs in sticklebacks from that particular site could be attributed to the past history of the use of DDT for agricultural purposes at fields around the Dead Vistula River Channel. The compositional pattern of DDTs in sticklebacks (Figure 2) is very similar for all sampling sites, and there are only a small variations in the ratio of *p,p'*-DDT to DDTs, *i.e.* from 0.12 to 0.20.

Hexachlorobenzene, like DDTs, in a somewhat elevated concentration was quantified in the sticklebacks collected at the Oksywie site (Table 1), which is localised close to the shipyards and port complex of the city of Gdynia. There are no data available on the volume and pattern of possible use of HCBz during a recent 25 years in Poland, and also no data on PCBz.

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