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Pentachlorobenzene and Hexachlorobenzene in Fish in the Gulf of Gdańsk*

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Abstract

Fish (herring, cod, eelpout, round goby, flounder, perch, lamprey, pikeperch, sand eel and lesser sand eel) caught in the Gulf of Gdansk in 1992 contained the residues of penta- (PCBz) and hexachlorobenzene (HCBz) in concentrations from 0.09 to 0.75 and from 0.36 to 3.7 ng/g wet weight (3.3-14 and 6.5-41 ng/g lipid weight), respectively. Both compounds were identified and quantified using capillary gas chromatography and low resolution mass spectrometry (HRGC/LRMS) after a non-destructive extraction and clean-up step with a semipermeable polyethylene membrane and further fractionation on the Florisil column. A higher HCBz/PCBz ratio indicated in some species of fish caught near the city of Gdynia when compared to the specimens caught close to the city of Gdansk indicated the existence of a slight local source of pollution with HCBz in the area of the seaport of the city of Gdynia.

Keywords: Hexachlorobenzene, HCBz, pentachlorobenzene, PCBz, fish, Baltic Sea

Introduction

Hexachlorobenzene (HCBz) was used world-wide as a fungicide for agricultural purposes starting in 1915. That compound was also registered in Poland and sold as a fungicide under the trade name "Śnieciotox". Around 1980 hexachlorobenzene become unpopular and finally was withdrawn from agriculture in Poland [1]. Apart from its agrotechnical application, hexachlorobenzene is also known as a substrate, intermediate product, technical impurity and by side product in various industrial - scale chemical synthesis processes (synthetic rubbers, organofluorine compounds, PVC, hexachlorophene, additive for pyrotechnic products as well as for production of electrodes and as an ingredient in formulations for preservation of wood) [2-4]. Pentachlorobenzene (PCBz) is a substrate used for the synthesis of the fungicide pentachloronitrobenzene (PCNBz), and apart from this application it has not found any other special application. Pentachlorobenzene, like HCBz, is a technical impurity in some chemical formulations (up to 0.06% in technical formulation of HCBz, and also was found in technical formulation of PCNBz) [4, 5]. Another source of environmental pollution with HCBz and PCBz are high temperature processes such as municipal solid waste incineration. All theoretically possible congeners of chlorobenzene were identified in flue gas and fly ash from municipal solid waste incinerators, and contribution from PCBz and HCBz was up to - 50% and - 13%, respectively [6, 7]. Hexachlorobenzene is highly persistent under environmental conditions. Nevertheless, depending on the environmental matrix, HCBz slowly undergoes abiotic (photochemical) and biotic (mainly metabolised by bacteria and lower fungi in soil and sediments as well as by man and animals) degradation. Pentachlorobenzene is an intermediate product in metabolism of HCBz and of the insecticide Lindane (γ-HCH) [8, 9].

Hexachlorobenzene became a global environmental

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pollutant and for many years this compound is identified and quantified in all environmental matrices, including aquatic biota and human tissues and body fluids [4, 10-20]. There is much less data available on concentrations and environmental behaviour and impact of PCBz than HCBz. Fish from the Neckar River near the city of Rottweil in Germany in 1983-1984 contained PCBz in their flesh at a mean concentration of 4 ng/g wet weight (up to 50 ng/g for an individual fish) and elevated concentrations of HCBz (52% of the samples exceeded the legal tolerance of 50 ng/g wet weight for lean fish, i.e. with fat content below 10%), while trichlorobenzene and tetrachlorobenzene remained undetected [21]. An elevated concentrations of HCBz and PCBz in fish from the Neckar River were due to pollution of the river with effluents from the industrial process, including degasing of an aluminium smelt with chlorine gas [22].

We examined degree of contamination with penta- and hexachlorobenzene and distribution of those compounds in edible species of fish in the Gulf of Gdansk. The fish species examined were herring *(Clupea harengus),* cod *(Gadus morhua),* flounder *(Platichthys flesus),* eelpout *(Zoarces viviparus),* perch *(Perca fluviatilis),* round goby *(Neogobius melanostomus),* pikeperch *(Stizostedion lucioperca),* lamprey *(Lampetra fluviatilis),* sand-eel *(Hyperoplus lanceolatus)* and lesser sand-eel *(Amodytes tobianus).*

Materials and Methods

All fish were captured in summer 1992 using gill net or bottom sack at sites close to the harbours of Gdansk and Gdynia, or near Mikoszewo at the Vistula River outlet in the Gulf of Gdansk.

The analytical method used for determination of penta- and hexachlorobenzene is part of a multi-residue procedure allowing the simultaneous determination of many organochlorines and polynuclear aromatic hydrocarbons (PAHs). After homogenization of the sample (77.0-219.2 g) with anhydrous sodium sulphate (1:7; baked at 550°C for 2 days), a powdered mixture was packed into a wide bore open glass column, spiked with an internal standard ($^{13}C_{12}$ -*p,p'* - DDT), extracted with 500 ml mixture of acetone and n-hexane (2.5:1) followed by 500 ml of n-hexane and diethyl ether (9:1), to obtain fat extract. The solvents were carefully evaporated on a water bath under vacuum pressure using a rotary evaporator. Pure ethanol was than added to remove azeotropically co-extracted water, also under vacuum and using the rotary evaporator. Bulk lipid removal was performed by means of the polyethylene film dialysis method [23]. After dissolving the extracted lipids in cyclopentane, dialysis through the polymeric membrane was accomplished by changing the dialysate after 24, 48 and 72 hours. The three dialysate fractions, containing normally between 1-10% of the original lipids, depending on sample size and matrix type, were combined and concentrated to a few millilitres using a rotary evaporator. The extract was split into two parts, of which 10% was used for analysis of penta- and hexachlorobenzene and some other organochlorine pesticides, and bulk of polychlorinated biphenyls (PCBs), while 90% was used for the analysis of planar compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), planar PCBs and polychlorinated naphthalenes (PCNs).

The remaining lipid was removed on a Florisil column (35 cm length), and the analytes were fractionated using n-hexane (28 ml; fraction 1) and methylene chloride and n-hexane (15:85 v/v; 38 ml, fraction 2). The penta- and hexachlorobenzene were eluted in fractions 1 and 2, which were combined, and the solvent was evaporated of room temperature with tetradecane added as a keeper. Before injection of the analytes to a capillary column gas chromatography/low resolution mass spectrometer system (HRGC/LRMS), a recovery standard of $^{13}C_{12}$ - hexachlorobenzene was added. Procedural blanks were performed with every set of the real samples analyzed, which only contained minor residues of PCBs and hexa-

Table 1. Mean concentrations of penta- (PCBz) and hexachlorobenzene (HCBz) in fish in the Gulf of Gdansk (ng/g wet weight).

Species	No.	Body length (cm)	Lipids (%)	PCBz	HCBz
Herring	1 (3)*	16 – 21	9.7	0.75	3.7
Cod	1 (3)	18 – 20	3.4	0.28	0.46
Flounder	3 (15)	15 – 20	4.6	0.40 ± 0.10	0.90 ± 0.30
			(4.2 – 4.8)	(0.20 – 0.60)	(0.60 – 1.5)
Lamprey	2 (6)	16 – 26	15.0	0.16	0.91
			(6.3 – 22.6)	(0.09 –0.23)	(0.89 – 0.93)
Perch	2 (16)	10 – 17	5.6	0.29	1.1
			(5.2 – 5.9)	(0.28 –0.29)	(0.79 – 1.3)
Pikeperch	1 (3)	15 – 20	4.4	0.46	0.85
Round goby	1 (6)	16 – 26	4.8	0.29	0.64
Eelpout	1 (3)	21 – 32	3.0	0.22	0.79
Sand-eel	1 (20)	12 – 16	5.7	0.25	0.75
Lesser sand-eel	1 (20)	12 – 15	5.5	0.17	0.36

* Number of samples and number of fish (in parentheses)

chlorobenzene and were well below 10% of any calculated value. The recoveries were generally between 60-120%, and the results for all samples were corrected for recovery values. Native penta- and hexachlorobenzene were used as external standards to check retention time and ion identity as well as for quantitative calculations.

Results and Discussion

The residues of HCBz at concentrations from 0.36 to 3.7 ng/g wet weight (from 4.0 to 41 ng/g lipid weight) and PCBz at concentrations from 0.09 to 0.76 ng/g wet weight (from 0.39 to 14 ng/g lipid weight) were detected in all fish species examined (Tab. 1). For lamprey, herring and perch captured close to the city of Gdynia the values of the ratio of the concentrations of HCBz/PCBz were 4.0, 4.9 and 4.5, respectively, while for all other species it was from 1.6 to 3.6. For perch and lamprey captured near the city of Gdynia the value of the quotient HCBz/PCBz was nearly twice of that for the same species captured near Gdansk, while in the case of flounder there was no spatial difference of HCBz/PCBz ratio. Hexachlorobenzene is usually found in relatively higher concentrations in various environmental matrices in industrialized areas, and especially at sites with a highly developed chemical industry [4, 20]. In Poland, for example, the surface layer of soil (0-10 cm) in the city of Krakow and the adjacent area as well as in highly industrialized Silesia (Katowice, Chorzow) is much more polluted with HCBz (0.19-30 ng/g dry weight; n = 24) than in the northern part of the country (< 0.01-0.74 ng/g dry weight; n = 7) [24].

As regards to freshwater and marine fish HCBz and also PCBz could be found in apparently high concentrations in their flesh when industrial effluents and subsequently river or seawater and sediments become highly polluted with these compounds [21, 22, 30]. Herring and perch from the Bothnian Sea at the site of Gavlebucken in Sweden when compared to the same species of fish from the other sites in the Bothnian Bay and the Bothnian Sea or to fish from the Gulf of Gdansk (Table 1) contained elevated concentrations of HCBz, *i.e.* mean concentrations were 82 and 270 ng/g lipid weight, respectively, while they were between 18 and 33 ng/g lipid weight for the other sites [30]. Unfortunately, there is no data reported for PCBz in herring and perch from the Bothnian Bay and the Bothnian Sea.

A relatively higher absolute concentration of HCBz and also a higher value of the quotient HCBz/PCBz for perch and lamprey captured near Gdynia when compared to specimens collected close to Gdansk seems to indicate a local source of pollution with HCBz. When examining the concentrations and spatial distribution of the residues of polychlorinated naphthalenes (PCNs) and polychlorinated biphcnyls (PCBs) it was observed that fish caught under the city of Gdynia were also more polluted with those compounds than the specimens from the site Gdansk in the Gulf of Gdansk, while no such relationship was noted in the case of the residues of cyclodiene insecticides (chlordan, aldrin, dieldrin, endrin, izodrin, endosulfan 1 and 2) or DDT and its analogues [21-27].

Concentrations of PCBz and HCBz reported in fish from the Gulf of Gdansk are from the hygienic point of view relatively low and do not seem to pose a threat to humans. Nevertheless, both PCBz and HCBz are only two members of the large group of persistent, toxic and bioaccumulative organochlorine compounds of anthropogenic origin identified recently in fish from the Gulf of Gdansk. This is the first report on PCBz in biota from the southern part of the Baltic Sea. On the historical perspective the concentrations of HCBs indicated for cod, herring and flounder in this study are practically the same as noted for these species of fish in the Gulf of Gdansk in 1985-1986 [29], indicating the continued pollution of the Baltic Sea with this substance or persistency.

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