Regionally Based Assessment of Persistent Toxic Substances

The Baltic Sea – Poland
(Brussels, 4-8 December, 2001 POPs Workshop 1 - by Jerzy Falandysz)

The Baltic Sea inside the Danish Straits is one of the largest brackish water areas on Earth, some 377 000 km^2 (volume 21 000 km^3), with a fourfold larger drainage area, much industry and population of 85 million. Countermeasures against toxic pollution with organochlorine pesticides, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polychlorinated terphenyls (PCTs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as well as metallic elements and metalloids gradually gave results, and today the struggle to limit toxic pollution of the Baltic Sea seems to be an international environmental success story (Falandysz et al. 2000; Elmgren 2001).

Aldrin, dieldrin and endrin

Very limited information is available on the rates or total amount of various chlorinated cyclodiene pesticides used in the past around the Baltic Sea, and also relatively scare are data on their occurrence, concentrations, fate and possible effects in this sea. Aldrin and dieldrin were used in the past rather shortly and at relatively low rates in the Baltic States (Falandysz 1994; Falandysz et al. 1998). Those compounds like many other semi-volatile and environmentally persistent organohalogenated substances are less ore more prone for atmospheric transportation and subsequent deposition on the earth surface. The number of data published on occurrence, composition, sources of origin and effects of chlorinated cyclodiene pesticides in Baltic fish and another biota is much less than for many other groups of persistent organochlorine compounds.

Aldrin and endrin but also isodrin, endosulfan 1 and endosulfan 2 were not detected in any of the samples of fish, crab, mussel and plankton (Table 1). Those substances were absent also in tissues of top predator species such as Harbour Porpoise and White-tailed Sea Eagle collected in the 1990s from the southern part of the Baltic Sea or fish and a lower food web organisms from the Gulf of Bothnia.(Strandberg et al. 1999; Falandysz et al. 2001), what implies lack of sources of pollution (isodrin, endrin) and for easy degradation (aldrin, endosulfan 1 and 2).

Dieldrin is ubiquitous trace contaminant in the Baltic Sea ecosystem (Tables 1-3). The concentrations of dieldrin quantified in biota collected from the Baltic south coast in the 1990s when based on fresh weight and extractable lipids are given in Table 1. Those concentrations based on extractable lipids were relatively small and ranged between 7.6 and77 ng/g, while between 0.10 and 6.6 ng/g were on a fresh weight. In Tables 2 and 3 are reviewed available data on residues of dieldrin in muscle tissue and organs of the Baltic Sea fish as well as some fish species and fishery products originated from the North-Eastern basin of the North Atlantic Ocean.

A various Baltic fish species, on the average, contained in their flesh in the 1970s around fivefold or more greater concentrations of dieldrin than in the 1980-90s (Table 2). The cod-liver oil produced of the Baltic cod contained dieldrin at slightly elevated concentrations when compared to cod-liver oil produced of cod caught in the Shelf of Iceland, North Sea and Norwegian Sea (Table 3).

Table 1
The concentrations of dieldrin in plankton and soft tissue of blue mussel, a whole crab and a whole fish from the Gulf of Gdańsk (Falandysz et al. 1998 and 2001)

Matrix	Sample no.	Lipids (%)	Dieldrin	
			ng/g fresh weight	***ng/g lipids****
Plankton	4		1.2±0.4 (0.82-1.9)	31±7 (23-42)
Blue mussel	2 (700)*	1.5 (1.3-1.7)	15 (11-19)	0.21 (0.18-0.24)
Crab	1 (3)	1.3	7.6	0.10
Herring	1 (3)	9.0	70	6.6
Cod	1 (3)	3.4	51	1.7
Pikeperch	1 (3)	4.4	29	0.92
Perch	2 (16)	5.6	35 (28-42)	1.9 (1.6-2.2)
Round goby	1 (6)	4.8	20	0.96
Sand-eel	1 (20)	5.7	25	1.4
Lesser sand-eel	1 (20)	5.5	15	0.84
Lamprey	2 (6)	15	23 (17-29)	3.8 (1.1-6.5)
Flounder	3 (15)	4.6	27±4 (23-31)	0.83±0.21 (0.62-1.0)
Stickleback	4 (120)	2.5	1.2±0.5 (0.92-1.9)	49±19 (35-77)

Notes: *Composite samples - number of samples and number of individuals (in parentheses); ** Aldrin (< 0.3 ng/g), endrin (< 0.5 ng/g), isodrin (< 1.5 ng/g), endosulfan 1 and 2 (< 3 ng/g)

Table 2
Arithmetic mean weighted concentrations of dieldrin in Baltic fishes (ng/g wet weight) (Falandysz 1999)

Species,. Family or group of fish	Sample no.	Mean	Range
Cod, 1970-1983	483	5	<1-<30
Cod, 1992*	3	1.7	
Herring, 1970-1983	3834	20	1-48
Herring, 1986-1992*	184	4.4	2.4-6.6
Herring, 1970-1983	29	10	8-13
Flatfishes, 1970-1983	408	5	1-<20
Flatfishes, 1990-1992*	18	1.0	0.72-1.3
Salmon, 1970-1983	1	17	
Eel, 1970-1983	29	59	51-93
Eel, 1991**	6[a]	1.8	
Perch, 1991-1992*	61	1.1	0.36-2.2
Other fish species, 1992*	55	2.0	0.84-6.5
Cod liver, 1970-1983	530	130	1-670
Herring - roe, 1970-1983	1	15	
Herring - eggs, 1970-1983	4	18	15-20

Notes: [a]Small specimens (*ca* 30 cm body length); *data after HRGC/LRMS analysis; **data after HRGC/ECD analysis

Table 3
Concentrations of dieldrin in marine fish and fishery products of the North-Eastern Basin of the Atlantic Ocean origin (Falandysz 1999)

Specimen, product and region	Sample no.	Lipids (%)	Mean and range
Herring *(ng/g lipids)*			
Baltic proper, 1986	1 (100)	5.4	81
Bothnian Bay, 1987	1 (60)	4.4	66
Bothnian Bay, 1991	5 (21)	5.6*	*70 (36-120)
Bothnian Bay, 1992	1 (3)	9.1	70
Perch			
Bothnian Bay, 1991	9 (45)	1.1*	*85 (30-120)
Gulf of Gdańsk, 1992	2 (16)	5.0	35 (28-42)
Cod-liver oil			
Baltic, southern part, 1971-1980	9	100	330 (260-410)
Baltic, southern part, 1980-1989	6	100	260 (200-310)
Baltic, western part, 1981-1986	11	100	240 (160-360)
North Sea, 1978	1	100	310
North Sea, 1982	1	100	130
Norwegian Sea, 1982	1	100	190
Shelf of Island, 1984-1987	8	100	110 (90-130)
Cod liver *(ng/g wet weight)*			
North Sea, northern part, 1978-1987	7	54.6	67 (46-90)
North Sea, central part, 1978-1987	8	51.2	130 (70-210)
North Sea, southern part, 1978-1987	9	51.8	170 (81-240)

*Arithmetic mean weighted

Chlordane and heptachlor

Technical chlordane is composed of more than 147 constituents of mainly C_9 to C_{15} skeleton, and *trans*-chlordane (24±2%), *cis*-chlordane (19±3%), heptachlor (10±2%), *trans*-nonachlor (7±3%), *cis*-nonachlor (7±1%) are major constituents, while MC4, MC5, MC6, MC7 and U82 are minor. Heptachlor, a constituent of technical chlordane (about 10%) with a highest insecticidal activity was also synthesised (65-72% of active agent) and sold separately as insecticide and fungicide.

Chlordane and heptachlor were used in the past rather shortly and at relatively low rates in the Baltic States. Heptachlor has been quite popular in Finland. Chlordanes are ubiquitous trace contaminants in the Baltic Sea ecosystem. Nevertheless, in the case of CHLs usually data for a few or all six the most abundant compounds such as *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, oxychlordane and heptachlor epoxide are reported and discussed in the articles. As noted in two retrospective studies these compounds are from many years a common residues in edible parts of the Baltic fish. For example in 1970 Baltic herring contained CHLs at the concentration 520 ng/g lipid; and in 1971 in cod-liver oil were 170 ng/g of CHLs. Salmon sampled in the Baltic proper in 1971 and 1979 contained in muscle tissue 280 and 340 ng/g lipid of CHLs, respectively. In study by Andersson *et al.* (1988) salmon caught in the Baltic proper in 1979 were more contaminated with CHLs than fish from the Canadian Atlantic Ocean waters and contained 60 ng/g lipid, while specimens caught near Greenland contained 100 ng/g lipid. A similar differences in spatial distribution of the chlordane concentrations in the Northwest and Northeast Atlantic Ocean Basins as observed for salmon in 1979 were also found for cod-liver oil manufactured in the 1980s. Again the cod-liver oil produced of the Baltic cod contained CHLs at elevated concentrations when compared to cod-liver oil produced of cod caught in the Shelf of Iceland, North Sea and Norwegian Sea. It seems that the Baltic proper is a region relatively sensitive for CHLs pollution and mainly due to its specific hydrological condition, climate and semi-enclosed nature resulting in a long residence time of semi-volatile organohalogenated compounds.

The origin of chlorinated cyclodiene pesticide residues found nowadays in abiotic and biotic matrices in the Baltic Sea can be partly explained due to the past history of use of this substances and also due to continuing atmospheric transport from the remote regions in the northern hemisphere and subsequent deposition. Pollution from the secondary sources like a locally and directly discharged municipal wastewater as well as transport *via* contaminated with effluents the reverie systems around the Baltic Sea still take place. Nevertheless, a discharge rates, total loads, fluxes and budget of various chlorinated cyclodiene pesticides in the Gulf of Gdańsk and entire Baltic Sea are largely unknown. In a recent study the annual load of CHLs discharged to the Gulf of Gdańsk with the Wisła River (Vistula River) water was assessed for 0.38 kg (between <0.01 to 0.12 kg *per* month) in 1991-1992.

The concentrations of twelve chlordane compounds in biota from the Baltic south coast based on fresh weight and extractable lipids are given in Table 4, respectively.

Table 4
The concentrations of chlordanes in soft tissue of blue mussel, a whole crab and a whole fish from the Gulf of Gdańsk (Falandysz et al. 2001)

Matrix	Sample no.	Lipids (%)	*Cis-* chlordane	*Trans-*	*Cis-* nonachlor	*Trans-*	MC4	MC5	MC6	MC7	U82	Oxy- chlordane	Heptachlor epoxide	CHLs
ng/g fresh weight														
Blue mussel	2 (700)	1.5	0.05	0.02	ND	0.05	ND	0.03	ND		ND	ND	0.02	0.18
		1.3-1.7	0.04-0.06	0.02-0.03		0.04-0.06		0.02-0.04		ND-0.02			0.02-0.03	0.16-0..20
Crab	1 (3)	1.3	0.02	0.01	ND	0.08	ND	0.01	0.01	ND	ND	0.36	0.03	0.52
Herring	1 (3)	9.0	1.3	0.21	0.33	1.1	0.05	0.33	0.15	0.07	0.04	0.54	0.35	4.4
Cod	1 (3)	3.4	0.11	0.02	0.05	0.15	0.003	0.04	0.02	0.01	0.01	0.08	0.14	0.63
Pikeperch	1 (3)	4.4	0.18	0.04	0.09	0.24	0.01	0.06	0.02	0.18	0.01	0.11	0.15	0.92
Perch	2 (16)	5.6	0.25	0.06	0.12	0.43	0.01	0.07	0.07	0.01	0.01	0.18	0.16	1.4
			0.14-0.35	0.04-0.08	0.08-0.16	0.28-0.58	0.01-0.01	0.06-0.08	0.04-0.09	0.01-0.01	0.01-0.01	0.17-0.20	0.16-0.17	1.0-1.8
Round goby	1 (6)	4.8	0.15	0.03	0.08	0.25	0.01	0.05	0.03	0.02	0.01	0.09	0.09	0.80
Sand-eel	1 (20)	5.7	0.15	0.04	0.07	0.20	0.01	0.04	0.03	0.01	0.01	0.10	0.09	0.75
Lesser sand-eel	1 (20)	5.5	0.08	0.02	0.03	0.09	0.004	0.03	0.01	0.005	0.004	0.06	0.06	0.40
Lamprey	2 (6)	15	1.8	0.31	0.61	2.1	0.08	0.54	0.30	0.08	0.08	0.83	0.03	6.8
			0.30-3.2	0.04-0.59	0.14-1.1	0.55-3.7	0.01-0.16	0.07-1.0	0.08-0.52	0.01-0.15	0.01-0.15	0.20-1.5	0.01-0.05	1.4-12
Flounder	3 (15)	4.6	0.20?0.04	0.06?0.01	0.06?0.02	0.23?0.08	0.01?0.01	0.05?0.01	0.02?0.01	0.01?0.01	0.01?0.01	0.09?0.02	0.10?0.01	0.83?0.21
			0.15-0.24	0.05-0.07	0.04-0.08	0.15-0.31	0.003-0.01	0.04-0.06	0.01-0.03	0.005-0.01	0.004-0.01	0.07-0.11	0.09-0.12	0.62-1.0
Stickleback	4 (120)	2.5	0.44?0.27	0.07?0.03	0.22?0.13	0.73?0.34	0.02?0.01	0.15?0.08	0.09?0.05	0.01?0.01	0.02?0.01	0.22?0.12	0.09?0.01	2.1?1.1
			0.24-0.82	0.04-0.12	0.13-0.41	0.48-1.2	0.01-0.03	0.08-0.27	0.05-0.15	0.005-0.02	0.01-0.03	0.11-0.37	0.08-0.11	1.3-3.5
ng/g lipids*														
Blue mussel	2 (700)		3.2	1.7	ND	3.3	ND	1.7	ND		ND	ND	1.8	12
			2.8-3.6	1.6-1.8		2.8-3.7		1.2-2.2		ND-1.4			0.92-2.6	12-12
Crab	1 (3)		1.9	0.49	ND	6.3	ND	0.92	0.76	ND	ND	28	2.3	41
Herring	1 (3)		14	2.3	3.6	12	0.54	3.7	1.7	0.73	0.43	6.0	3.9	49
Cod	1 (3)		3.1	0.71	1.6	4.5	0.09	1.0	0.56	0.18	0.17	2.5	4.2	19
Pikeperch	1 (3)		4.0	0.91	1.9	5.4	0.12	1.4	0.46	0.55	0.13	2.4	3.5	21
Perch	2 (16)		4.5	1.0	2.3	7.9	0.16	1.3	1.3	0.20	0.18	3.3	2.9	35
			2.4-6.6	0.60-1.5	1.4-3.1	4.7-11	0.09-0.22	1.0-1.5	0.72-1.8	0.12-0.27	0.11-0.25	2.8-3.8	2.7-3.2	28-42
Round goby	1 (6)		3.2	0.55	1.7	5.2	0.11	1.1	0.53	0.33	0.13	1.9	1.9	17
Sand-eel	1 (20)		2.5	0.75	1.2	3.6	0.11	0.76	0.46	0.11	0.13	1.8	1.6	13
Lesser sand-eel	1 (20)		1.5	0.39	0.49	1.7	0.07	0.5	0.19	0.08	0.07	1.1	1.1	7.2
Lamprey	2 (6)		9.6	1.6	3.5	13	0.42	2.8	1.8	0.39	0.44	4.8	2.3	40
			4.8-14	0.62-2.6	2.2-4.8	9.0-16	0.13-0.72	1.1-4.5	1.2-2.3	0.12-0.66	0.23-0.65	3.1-6.5	1.7-2.9	24-56
Flounder	3 (15)		4.3?1.0	1.4?0.2	1.3?0.4	5.0?1.7	0.12?0.05	1.1?0.2	0.46?0.18	0.16?0.05	0.14?0.04	1.9?0.5	2.3?0.3	18?5
			3.2-5.1	1.1-1.5	0.86-1.7	3.1-6.4	0.06-0.15	0.79-1.3	0.26-0.59	0.10-0.20	0.09-0.18	1.4-2.3	1.9-2.5	13-22
Stickleback	4 (120)		18?11	2.8?1.4	9.1?5.4	30?14	0.75?0.56	6.2?3.4	3.6?2.0	0.42?0.22	0.77?0.47	8.8?4.9	3.7?0.6	84?44
			8.9-34	1.6-1.7	5.3-17	19-49	0.19-1.2	2.9-11	2.0-6.3	0.17-0.70	0.33-1.4	4.1-15	3.1-4.3	48-150

*Heptachlor (< 0.3 ng/g)

Table 5
Chlordanes content of Baltic fish and fish products (ng/g wet weight) (Falandysz, 2000a)

Species or family and year of sampling	Mean	Range	Sample no.
Herring			
1970	8.3		24
1978	17	10-27	8
1978	19		1 (40)*
1979	10	7.4-15	3 (75)
1982	38	25-53	7
1986	10[a]		1 (100)
1987	8.1[a]		1 (60)
1987	1.8[a]		1 (100)
1991	4.5		3 (9)
1991	5.9		3 (9)
1992	4.4		1 (3)
Herring - eggs			
1975	4	4-4	1
1975	3	1-4	1
Herring - roe			
1975	8	7-9	2
1975	3	3-3	2
Salmonidae			
1971	36		14
1979	29		5
1979	3.8		3
1979	3.7	3.5-4.1	2
Mackerel			
1979	9.4		3
Cod			
1992	0.63		
Cod - eggs			
1975	1		1
1975	2		1
Flounder			
1990	3.1		1 (3)
1992	0.83	0.62-1.0	3 (15)
Perch			
1991	0.69		4 (20)
1991	1.9		2 (10)
1991	0.62		1 (5)
1991	0.73		2 (10)
1992	1.4	1.0-1.8	2 (16)
Pikeperch			
1992	0.92		1 (3)

Table 5, continued

Species or family and year of sampling	Mean*	Range	Sample no.
Round goby			
1992	0.80		1 (6)
Lamprey			
1992	6.8	1.4-12	2 (6)
Lesser sand eel			
1992	0.75		1 (20)
Greater sand eel			
1992	0.40		1 (20)
Eel			
1990	2.6		1 (6)
Pike			
1971	5	1-8	4
1972	4	1-9	6
1973	1		1
1974	6		1
1975	15		1
1978	22	21-23	2
1982	34	18-45	8
1982	13	2-40	8
Cod - liver			
1975	<1	<1-<1	4
1975	79	1-180	4
1982	30	20-50	53
1990 (canned)	24±5	12-30	3
Cod-liver oil			
1971-1980 (southern part)	280	170-350	
	11[he]	4-18	
1980-1989	310	190-420	
	18[he]	13-23	
1980s	340	190-520	11
	19[he]	11-24	
1980s (western part)	240	36-550	9
1980s (North Sea and Norwegian Sea)	250	210-280	2
	22[he]	14-29	
1980s (Island)	140	40-200	8
	18 [he]	12-25	

[*] number of samples and number of individuals (in parentheses)
[a] *cis*- and *trans*-chlordane and *trans*-nonachlor
[he] heptachlor epoxide

DDT

DDT from the early 1970s. is not used in Poland. Nevertheless, 48151.7 tonnes of technical DDT was used in Poland between 1947 and 1980, while 1350 tonnes was used in the former East Germany between 1972 and 1989 (473 t in 1984) (Falandysz et al. 1999b). Technical DDT was both synthesized and used confidently in the former USSR also after 1970, *e.g*. ≥10000 tonnes in 1986 (>70000 tonnes in Uzbekistan in 1970-1983), while in Romania it was produced at least until 1995 (after Falandysz et al. 1999d). A relatively high concentration of DDTs in fish from the Gulf of Gdańsk in this study when compared to other areas of the Baltic Sea (Strandberg et al. 1998), like of DDTs residues still found in soils and sediments in Poland (Falandysz et al. 2000a), seem to be mainly due to the past history of the use of DDT in Poland. Nevertheless, aerial transport from the sites of fresh use of DDT in the countries neighbour to Poland and south off the Baltic Sea was reported earlier to be a source of that pesticide deposited on the matrix surfaces in Poland in 1980s, and what resulted also in temporal increase in *p,p′*-DDT/DDTs ratio, a higher frequency of appearance of *o,p′*-DDT and higher concentration of DDTs in several species of fishes in the southern part of the Baltic Sea in the early 1980s (Falandysz et al. 1999b).

Concentrations of DDT and its metabolites (DDTs; *p,p′-DDT, o,p′-DDT, p,p′-DDD, o,p′-DDD, p,p′-DDE, o,p′-DDE i p,p′-DDMU*) decreased considerably in plankton collected from the Baltic Sea in the 1990s when compared with levels in the early 1980s. Residues measured in 1992 (Table 6) were five to eight times lower than in comparable samples analysed in 1983 and were reported as being in the region of 300 ng/g lipids in recent studies. Apart from plankton the residues of DDTs as well as TCPM-H and TCPM-OH has been still quantified in flesh of various edible fishes caught in the southern part of the Baltic Sea in 1992 (Table 6). All fish examined contained detectable residues of DDTs, and the concentrations ranged from 28 to 310 ng/g wet weight. *o,p′*-DDT accounted from 0.4 to 2.5% to DDTs content. As the base of the Baltic Sea food web, the presence of DDTs in plankton will result in the transfer and biomagnification of these contaminants to each successive predator. The data presented in Table 6 give a good example of DDTs biomagnification process. Reported concentrations of DDTs in the 1990s are greater in each successive level of the food web rising from around 300 ng/g lipids in plankton to around 4 500 000 ng/g lipids in breast muscles of predator species such as White-tailed Sea Eagle.

On historical perspective the mean weighted residue concentrations of DDTs in herring (110 ng/g wet weight and 1100 ng/g lipid weight) in 1992 was threefold lower than in the years 1979-1983 and fourteen times lower than in 1969-1973 (Table 7).

Table 6
Concentrations of DDTs and TCPM-H/OH in sediment (ng/g dry wt) and biota (ng/g lipid wt) from the Baltic south coast (Falandysz et al. 1999b)

Matrix	No	Lipid (%)	TCPM-H	TCPM-OH	TCPM-H/OH	*p,p′*-DDT	*o,p′*-DDT	*p,p′*-DDD	*o,p′*-DDD	*p,p′*-DDE	*o,p′*-DDE	*p,p′*-DDMU	DDTs
Sediment	2	NA	ND	ND	ND	9.1 (2.8-15)	1.8 (a)	21 (5.9-36)	5.0 (2.3-7.3)	8.4 (2.8-14)	ND	1.9 (0.6-3.1)	46 (15-77)
Plankton	4	1.8	ND	ND	ND	26± 3 (21-32)	ND	120±7 (100-130)	37±7 (22-55)	120±5 (110-130)	1.6 (a)	5.4±1.8 (ND-7.9)	300±120 (270-340)
Blue mussel	2 (700)*	1.5	ND	ND	ND	80 (60-100)	26 (23-28)	370 (320-430)	76 (73-79)	310 (290-330)	ND	50 (26-66)	910 (840-980)
Crab	1 (3)	1.3	ND	ND	ND	120	7	580	15	1300	ND	17	2000
Three- spined stickleback	4 (120)	2.5	11±3 (6.4-18)	5.9±1.7 (2.4-11)	17±9 (8.8-29)	270±47 (170-390)	78±18 (52-130)	310±65 (230-500)	90±17 (67-140)	990±170 (700-1400)	7.5±1.5 (5-12)	27±3 (21-33)	1800±420 (1300-2600)
Lesser sand-eel	1 (20)	5.5	2.3	3.6	5.9	35	12	130	36	280	3.9	14	510
Sand eel	1 (20)	5.7	1.4	2.7	4.1	72	14	140	59	250	5.5	26	560
Herring	1 (3)	9.0	3.7	ND	3.7	120	6.6	470	22	590	ND	45	1300
Lamprey	2 (6)	6.3	5.4	1.4	6.9 (5.2-8.5)	100 (77-120)	12 (11-12)	350 (270-440)	15 (14-16)	670 (590-750)	1.6 (1.4-1.8)	50 (17-49)	1200 (980-1400)
Pikeperch	1 (3)	4.4	19	8.2	27	180	26	750	51	720	9.3	130	1900
Eelpout	1 (3)	3.0	5.5	8.4	14	180	17	640	40	3700	22	100	4700
Cod	1 (3)	3.4	13	3.2	16	36	8	320	36	780	4.8	36	1200
Round goby	1 (6)	4.8	14	2.2	16	120	ND	460	4.6	740	1.2	63	1400
fFlounder	3 (15)	4.8	17±5 (11-24)	4.5±2.0 (2.8-7.3)	22±7 (13-31)	80±11 (58-92)	20±1 (18-22)	630±67 (560-750)	72±23 (46-120)	680±54 (590-700)	9.8±3.2 (5.8-16)	65±16 (50-96)	1600±53 (1500-1700)
Perch	2 (8)	6.0	20 (9.2-30)	4.9 (2.7-7.1)	25 (12-37)	100 (80-120)	15 (12-18)	420 (400-440)	44 (36-51)	770 (740-800)	6.1 (3.9-8.3)	51 (51-51)	1400 (1300-1500)
Harbour porpoise	4	87.0	6.8±1.7 (2.9-12)	15±2 (10-19)	21±7 (13-30)	730±210 (390-1300)	62±9 (39-79)	2600±1600 (670-1800)	54±11 (32-82)	5900±1600 (2300-9600)	24±7 (13-43)	35±10 (18-57)	7800±1900 (3400-11000)
Black cormorant													
-breast muscles	3	4.5	19±8 (25-77)	170±14 (93-190)	230±77 (120-300)	0.9±1.4 (0.6-1.4)	ND	95±19 (70-120)	1.2 (a)	4300±1200 (4000-16000)	ND	70±7 (20-160)	9500±1300 (4100-16000)
-liver	3	4.6	75±16 (60-82)	550±58 (530-580)	620±5 (620-630)	1.5±0.2 (1.0-2.3)	ND	160±15 (120-190)	1.7±0.4 (1.1-2.2)	8100±3300 (5800-10000)	ND	110±40 (20-250)	8300±3400 (6000-11000)
White-tailed sea eagle													
-breast muscles#	10	8.8	6800±11000 (13-33000)	8700±18000 (<1-54000)	16000±28000 (<13-73000)	140±260 (ND-900)	2800 (a)	33000±40000 (240-120000)	29±43 (ND-150)	720000±1400000 (4200-4700000)	110±180 (4.8-580)	20000±34000 (330-110000)	780000±1500000 (4800-4800000)
-liver#	3	4.8	39000±62000 (200-110000)	10000±11000 (600-22000)	50000±72000 (800-130000)	17±14 (4-37)	ND	22000±15000 (1700-37000)	8.9±8.3 (ND-20)	4400000±4500000 (67000-11000000)	160±200 (20-440)	100000±140000 (5000-300000)	4500000±4700000 (73000-11000000)
-breast muscles†	3	11.2	210±280 (9-530)	260±280 (14-560)	460±560 (23-1100)	2.1±2.3 (ND-5.3)	11 (a)	2300±1900 (520-5000)	25±5 (20-32)	120000±160000 (2400-350000)	19±15 (4.7-40)	2700±2900 (97-6800)	130000±170000 (3000-360000)
-liver†	3	7.8	300±520 (<1-900)	200±350 (<1-600)	500±870 (<1-1500)	4.8±3.6 (0.8-9.5)	ND	3200±4500 (400-8400)	35±16 (14-53)	61000±84000 (2100-180000)	11±8 (4-22)	2200±2900 (66-6300)	69000±93000 (2700-200000)
-adipose fat†	2	80.9	4.5 (2-7)	10 (9.0-10)	14 (12-16)	130 (23-230)	18 (4.1-31)	1000 (760-1400)	68 (55-80)	4000 (3600-4400)	14 (10-18)	130 (120-130)	5400 (5400-5400)

*number of samples and number of animals (in parentheses); #Baltic coast, †inland Poland; NA, not analysed; ND, not detected (<1 ng/g lipid wt); ±S.E.; (a) detected in one sample; (b) detected in two samples - 11 and 2800 ng/g lipids

Table 7
Concentrations of DDTs in herring from the southern part of the Baltic Sea (Falandysz et al. 1999c)

Year	Sample no.	DDTs ng/g wet weight.	ng/g lipids weight
1980-81	23 (339)*	320 (150-560)	2500
1981	2 (30)	320 (280-370)	5900
1981	13	360 (87-870)	2900
1981	295	120 (15-410)	1300
1983	187	250 (59-1100)	3500
1985	4 (40)	380 (330-450)	6000
1986	3 (47)	200	5800
1987	1 (60)	190	4300
1992	20-25	100	1000
1992	1 (3)	110	1100

*number of samples and number of individuals (in parentheses)

HCB

Hexachlorobenzene (HCB) was used world-wide as a fungicide for agricultural purposes from 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 the agriculture in Poland (Falandysz, 1994). Apart from its agrotechnical application hexachlorobenzene is also known as a substrate, intermediate product, technical impurity and by side product in various of 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) (Falandysz et al. 2000c).

Another source of environmental pollution with HCB 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 the municipal solid waste incinerators, and contribution from PCBz and HCB was up to ~50 % and ~13 %, respectively (after Falandysz, 2001b). Hexachlorobenzene is highly persistent under environmental conditions. Nevertheless, depending on the environmental matrix, HCB 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.

The residues of HCB in concentration from 0.36 to 3.7 ng/g wet weight (from 4.0 to 41 ng/g lipid weight) were detected in all fish species collected from the Gulf of Gdańsk in the southern part of the Baltic Sea in 1992 (Table 8).

Herring and perch from the Bothnian Sea at the site Gävlebucken 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 Gdańsk did contain elevated concentration of HCB, *i.e.* the 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 (Strandberg et al. 1998).

Table 8
Mean concentrations of penta- (PCBz) and hexachlorobenzene (HCB) in fish in the Gulf of Gdańsk (ng/g fresh weight) (Falandysz et al. 2000)

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

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

On the historical perspective the concentrations of HCB indicated for cod, herring and flounder in early the 1990s were practically the same as noted for these species of fish in the Gulf of Gdańsk in 1985-1986 (Table 9), what indicates the continued pollution of the Baltic Sea with this substance or persistency. Nevertheless, concentrations of HCB reported for herring from various regions of the Baltic Sea in the 1980s and 1990s seem to be substantially smaller than noted in the 1970s (Table 9). The hot spots of HCB around the Baltic Sea are industrial sites like Gävlebucken in Sweden, what has a long-term effect resulting in increased concentrations of this compound in biota from the neighboured waters (Strandberg et al. 1998).

Table 9
The concentrations of HCB in Baltic fish and fishery products (ng/g fresh weight) (Falandysz et al. 2000b)

Family, species and year	Sample no.	Mean	Range
Gadidae			
Cod *Gadus morhua*, whiting *Merlangius merlangus*			
1981	98	0.77	0.2-6.1
1982-1983	47	<10*	<10-<10
1983	232	0.66	<0.1-2.7
1985	181	0.60	0.35-1.3
1986	13	0.45	0.43-0.47
1992	3	0.46	
Clupeidae			
Herring *Clupea harengus*			
1973	20	14	8-19
1974	63	11	8-18
1975	10	12	6-17
1976	15	40	
1977	1124	30	7-70
1979	205	28	10-48
1980-1981	1218	17	0.5-39
1982-1983	33	<10	<10-30
1983	299	12	2.1-150
1983	88	9	1-39
1985	40	15	14-16
1986	100	0.35	0.29-0.42
1986	47	5.1	4.4-5.5
1986	100	6.3	
1987	100	6.2	
1991	21	2.5	1.6-3.3
1992	3	3.7	
Sprat *Sprattus sprattus*			
1971-1974	42	<5	
1975	30	18	
1978	177	18	17-20
1981	102	6.4	0.8-62
1982-1983	47	<10	<10-10
1983	225	17	1.5-71
1983	31	18	8.1-35
1985	285	14	10-20
Pleuronectidae and Bothidae			
Flounder *Platichthys flesus*, plaice *Pleuronectes platessa,* turbot, *Psetta maxima*			
1974-1975	61	1.6	ND-20
1981	125	4.2	ND-27

Table 9, contn'd

Table 9, continued.

Family, species and year	Sample no.	Mean	Range
Pleuronectidae and Bothidae			
1983	170	0.98	0.2-3.6
1985	15	3.0	
1986	10	1.1	0.54-1.6
1992	15	0.90	0.60-1.5
Salmonidae			
Salmon *Salmo salar*, brown trout *Salmo trutta,* trout *Salmo gairdneri irideus*			
1976	20	3.5	3-4
1978	8	63	32-110
1979	4	19	10-31
1980-1981	61	3.9	1-7.3
1982	58	1.4	0.5-13
Anguillidae			
European eel *Anguilla anguilla*			
1981	125	18	3-66
1982	128	13	1.5-210
1983	227	12	<0.5-330
Percidae			
Perch *Perca fluviatilis*, pikeperch *Stizostedion lucioperca*			
1983	6	0.9	0.5-1.9
1991	35	0.27	0.23-0.36
1991	10	3.2	
1992	16	1.1	0.79-1.3
1992	3	0.85	
Various other fish species			
Garfish *Belone belone,* Fourbearded rockling *Enchelyopus cimbrius*, Lamprey *Lampetra fluviatilis*, Eelpout or Viviparous blenny *Zoarces viviparus,* Round goby *Neogobius melanostomus,* Greater sand eel *Hyperoplus lanceolatus,* Lesser sand eel *Ameodytes tobianus*			
1981	15	0.72	0.1-2.8
1981	7	1.1	0.42-2.8
1983	1	0.4	
1983	2	31	27-35
1983	24	2.2	0.89-6.7
1986	20	3.1	
1986	68	4.5	1.6-18
1992	55	0.62	0.36-0.93
Cod liver			
1973	42	220	10-1600
1974	5	190	50-310
1975	4	190	110-240

Table 9, contin'd

Table 9, continued

Family, species and year	Sample no.	Mean	Range
1978	10	280	
1978	11	78	<1-230
1979	25	45	22-96
1980	9	44	30-110
1981	585	89	<10-530
1982-1983	43	70	<10-170
1983	210	96	<10-330
1985	40	34	
1986	3	36	
1990 (canned)	3	60	50-76
Cod-liver oil			
1971-1980	9	370	290-460
1981-1989	6	260	200-310
1980s	11	280	170-370
1980s (western Baltic Sea)	9	160	110-260
1980s (North Sea and Norwegian Sea)	2	120	110-130
1980s (Iceland)	8	87	73-100
Cod hard roe			
1975	1	8	
Herring hard roe			
1975	2	6	4-8
Herring soft roe (milt)			
1975	2	4	3-4

Notes: *value omitted when calculating arithmetic mean weighted; ND, not detected

Mirex

Technical grade formulations of mirex consist of 95.19% mirex and by side products, and including keptone. Mirex, however was not detected in any sample of blue mussel or fish from the Gulf of Gdańsk sampled in early 1990s (detection limit < 0.15 ng/g lipid) but was quantified in small concentrations in perch and herring from the Swedish coastal waters (Strandberg et al. 1998), while up to 26000 ng/g lipid in breast muscles of a top prey species such as white-tailed sea eagle (*Haliaeetus albicilla*) from the breeding sites in the Baltic south coast and at much smaller concentrations in specimens originating from inland Poland (Strandberg et al. 1998a)

Toxaphene

The polychlorinated bornanes, -bornenes and –bornandienes as well as polychlorinated camphenes and –dihydrocamphenes with thousands of congeners are possible constituents of ver complex technical mixture of toxaphene (or Melipax) but only polychlorinated bornanes are major contaminants in fish. Melipax (< 100 tons) and used for in Poland between 1985 and 1971and more extensively in former Eastern Germany. There is no data available on residue concentrations of toxaphene compounds in fish or other biota from the southern part of the Baltic Sea. A recent time-trend study of toxaphene in cod-liver oil of the Baltic proper origin sampled in 1971-1993 has indicated on downward trend of this substance (Unpublished).

PCBs

Concentrations and composition profiles of polychlorinated biphenyls (PCBs) were investigated in composite samples of ten species of edible fish from the Gulf of Gdańsk, to understand the status of contamination and possible human exposure risk. Apart from the total PCBs also planar non-ortho (IUPAC nos. 77, 126, 169) and mono-*ortho* (nos. 105, 114, 118, 123, 156 ,157, 167, 189) chlorobiphenyls were quantified and their dioxin-like toxicity was assessed. The absolute values of total PCB concentrations in fish ranged from 43 to 490 ng/g wet wt (910-11000 ng/g lipids), while of TCDD TEQs of planar members were from 0.15 to 3.1 pg/g wet wt (8.1-81 pg/g lipids). The penta- and hexa CBs usually comprised 70-80% of the total PCBs and followed by hepta-, tetra- and tri-CBs, and for a specific site tri- and tetra-CBs comprised as much as 22%. Among of individual CB congeners nos. 118, 153 (+132) and 138 (+160+163+164) were the most abundant, while no. 110 comprised between 6.8 and 9.3% of total PCBs in some species.

Apparently an actual degree of contamination with total PCBs of seafood resources from the Gulf of Gdańsk is much below known tolerance limits set for fresh fish and fishery products elsewhere. Nevertheless, the concentration of total PCBs are relatively elevated when expressed on extractable lipids, *i.e.* the mean is around 2000 ng/g (Table 10). When taking into account the historical perspective a much higher concentrations of PCBs and ranging between 6300 and 17000 ng/g were noted in liver lipids of cod caught in the southern part of the Baltic Sea in 1971-1989.

Table 10
Concentrations of non- and mono-*ortho* coplanar congeners and total PCBs (ng/g lipid weight) and their total TCDD TEQs in whole-body homogenates of edible fishes from the Gulf of Gdańsk (Falandysz et al. 2002)

PCB Congener (IUPAC No.)	Round goby *Neogobius melanogaster*	Greater sand eel *Hyperoplus lanceolatus*	Lesser sand eel *Amodytes tobiasus*	Cod *Gadus morhua*	Lamprey *Lamperta fluviatilis*	Perch *Perca fluviatilis*	Pikeperch *Stizostedion lucioperca*	Flounder ***Platichtys flesus***		Herring ***Clupea harengus***	Eelpout ***Zoarces viviparus***
Non-*ortho* chlorobiphenyls											
77	9.7	6.7	5.2	1.2	1.1 (0.56 –1.6)	9.1 (3.2-15)	12	6.2 ± 3.6	(2.2-9.2)	1.4	7.6
126	6.7	1.5	1.2	1.1	1.1 (0.61-1.6)	5 (2.6-7.4)	5.8	2.2 ± 1.9	(0.41-4.1)	0.62	8.9
169	0.14	0.027	0.024	0.086	0.10 (0.089-0.11)	0.09 (0.064-0.11)	0.11	0.06 ± 0.02	(0.04-0.074)	0.14	0.14
Mono-*ortho* chlorobiphenyls											
105	620	170	150	110	200 (69-270)	460 (240-680)	1100	683 ± 683	(38-1400)	96	1700
114	29	7.1	5.1	4.8	2.3 (3.2-13)	22 (12-31)	31	39 ± 38	(2.6-79)	5	93
118	1600	340	270	290	400 (180-610)	1100 (660-1600)	2400	1300 ± 1200	(100-2500)	240	4100
123	84	20	16	21	17 (11-22)	55 (23-87)	120	86 ± 87	(7.4-180)	11	100
156	240	40	44	54	60 (26-100)	190 (87-300)	340	199 ± 211	(16-430)	35	750
157	69	12	13	13	15 (6.3-24)	48 (21-74)	84	54 ± 60	(3.1-120)	7.5	180
167	200	35	33	39	51 (19-83)	130 (62-190)	290	141 ± 146	(14-300)	29	510
189	7.5	0.96	0.96	2.4	2.4 (1.6-3.1)	5.0 (3.4-6.4)	7.8	4.2 ± 4.0	(0.97-8.6)	1.3	17
TEQs (l. w.)	50	11	9	8.1	8.9 (4.7-13)	35 (17-53)	51	24 ± 22	(3.1-46)	5.3	81
TEQs (w. w.)	2.3	0.64	0.50	0.28	0.97 (1.1-0.84)	2.0 (0.89-3.1)	2.3	1.1 ± 1.0	(0.15 –2.2)	0.48	2.4
Total PCBs	330	97	57	46	170 (110 – 230)	270 (160 – 380)	490	231 ± 205	(43 – 450)	120	350
Lipids (%)	4.8	5.7	5.5	3.4	15 (6.3 – 23)	5.6 (5.2 - 5.9)	4.4	4.60 ± 0.35	4.2 – 4.8	9.0	3.0
No.	1 (6)*	1 (20)	1 (20)	1 (3)	2 (6)	2 (16)	1 (3)	3 (15)		1 (3)	1 (3)

PCDD/PCDFs

There are only a few data on PCDD/Fs in fish and other biota from the Polish coast of the Baltic Sea. Flounder, herring and cod caught in the Gulf of Gdańsk in 1992 had PCDD/Fs in their flesh in concentration of 8.4, 81 and 7.8 pg iTEQs/g lipids, respectively (Falandysz et al. 1997).

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