PCB and organochlorine pesticides in perch (*Perca fluviatilis*) from the Baltic area

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Abstract: PCB, hexachlorobenzene (HCB), the hexachlorocyclohexanes (HCH) α- and γ- (lindane), and p,p'-DDT and metabolites were measured in perch (*Perca fluviatilis*) from the Väinameri Region of Estonia. The concentrations are within the range reported by others for perch from the Baltic watershed, with the exception of elevated levels of p,p'-DDT and metabolites in perch, caught in September 1999, as compared to fish caught in the same area in August 1999. In female perch, the median concentrations of ΣPCB, HCB, α-HCH, γ-HCH, and ΣDDT were 355, 10, 2, 29, and 1018 ng/g lipid in the September perch, and 659, 13, 3, 41, and 390 ng/g lipid in the August perch. The September fish had an unusually low concentration of lipid and a chlorobiphenyl profile different from the August fish. The reasons for the difference are not known. Even the maximum contents of organochlorine compounds in the investigated perch are considerably lower than the norms set by FAO/WHO.
Keywords: Baltic Sea, Estonia, PCB, DDT, HCH, HCB, perch

Since 1994, the analysis of hazardous substances from Baltic fish is a part of the national environmental monitoring program (Roots and Saare, 1996,1998) and receives financing from the state budget (Keskkonnauuringud, 1999). Our knowledge of the presence persistent organic pollutants (POPs), their concentrations and trends in the Eastern Baltic Sea perch is limited to only a few studies (Olsson, 1999; Olsson et al., 1999; Roots and Kakum, 1999). Perch is one of the most abundant fish species in Estonian waters. The Estonian total annual catch (from the sea) in the years 1994-1997 was from 300 to 600 t and has a decreasing trend. The main coastal fishing areas are Matsalu Bay, the Väinameri (Moonsund) Archipelago, and Pärnu Bay in the Gulf of Riga.

The migration of perch was for the first time studied in Matsalu Bay between 1994-1999. During the autumns of 1994 and 1995, and in the spring of 1995, a total of 2146 perch were tagged in Matsalu Bay. By the end of 1999, 286 fish were recaptured (Järv 2000). The activity area of perch seems to be relatively restricted, with 98.3% of the recaptures within < 20 km, and 58.2 % recaptures within 10 km from the tagging place. Further, it is interesting to note that the migrations are longer in the north-south direction (about 25 km), than in the east-west direction (0.5-1.0 km, Järv 2000). On the other hand, in the autumn of 1994, three perch were recaptured in Pärnu Bay, in the Gulf of Riga, > 160 km from the tagging site. However, on the whole, perch are likely to reflect a fairly localised contamination of the environment. In particular, the Väinameri Archipelago contains one large perch population, whose fish undertake only short spawning and feeding migrations (Mihkelsaar 1984).

This paper reports the concentrations of PCB, hexachlorobenzene (HCB), the hexachlorocyclohexanes (HCH) α- and γ- (lindane), and p,p'-DDT and metabolites, in the muscle of perch caught in the Väinameri Region of the Estonian Republic. The results are compared with results obtained by Blomkvist et al (1993), Edgren et al (1981), Valters et al (1999), and Olsson et al (2000) on perch from the Baltic watershed between 1976 and

1997. The relationship between the concentrations of PCB and p,p'-DDE is compared with that found in the European minnow (*Phoxinus phoxinus*) from the Alps (Hofer et al 2001), to see the effects of regional differences in uses and transport of the organochlorine compounds in the environment.

Materials and Methods

Perch from the Väinameri Region (the western coast of the Estonian Republic) were collected in August and in September 1999 (Tab. 1). The description of the sampling techniques as well as the analytical procedures can be found in Roots (1995) and Roots and Talvari (1997, 1999).

Table 1. Biological parameters* of the perch from the Väinameri Region, August 1999, Nos 1-9, and September 1999, Nos 10-20 (Keskkonnauuringud, 1999)

No	Length, mm	Weight, g	Sex, m/f	Maturity	Age, years	Lipid, %
1	297	289.9	m	II	7	0.49
2	362	621.3	f	VI-II	10	0.43
3	332	591.4	f	VI-II	10	0.41
4	310	413.5	f	VI-II	7	0.51
5	248	172.7	m	II	6	0.68
6	258	246.8	f	VI-II	6	0.69
7	256	206.7	m	II	6	0.65
8	256	238.4	f	II	6	0.64
9	280	290.9	f	II	6	0.56
10	285	290	f	III	6	0.21
11	245	199	f	III	5	0.22
12	260	241	f	III	5	0.47
13	295	388	f	III	6	0.23
14	245	219	f	III	6	0.33
15	305	387	f	III	7	0.12
16	390	825	f	III	11	0.21
17	375	629	f	III	9	0.34
18	310	377	f	III	7	0.36
19	365	593	f	III	8	0.27
20	300	400	f	III	7	0.37

* Analyzed by Ms M. Järve from Estonian Marine Institute

Principal Component Analysis (PCA, see for example Zitko 1994) of chlorobiphenyl profiles was performed by the software of Wise and Galagher (1998), running under MATLAB 5.0 (The Math Works Inc., South Natick, MA 01760, USA).

Results and Discussion

The region of the study

The Väinameri Region was chosen to be the research area since it is probably the best breeding area for seals in the Baltic (The Estonian Fund for Nature, 1992; Roots, 1999; Roots and Talvari, 1997, 1999). Consequently, it was of interest to determine the levels of organochlorine compounds in fish of this area. Salinity affects the uptake and excretion of hydrophobic organic chemicals (Tulp et al., 1979). The decrease in the salinity Baltic seawater has had a significant effect on the ecosystem of the Baltic (especially of its northern and eastern part). It may have changed the patterns of the acumulation of lipophilic chemicals in aquatic fauna and diminished the difference between perch from lakes and perch from the coastal areas of the Baltic.

Table 2. Concentrations (ng/g lipid) of organochlorine pesticides and PCBs in the muscle of perch from the Väinameri Region, August 1999, Nos 1-9, and September 1999, Nos 10-20 (Keskkonnauuringud, 1999)

	α-HCH	γ-HCH	HCB	DDE	DDD	DDT	28*	52*	101*	118*	153*	105*	138*	180*
1	3.6	44.6	16.1	452.4	204.2	381.2	54.6	99.8	138.4	112.7	254.4	91.8	198.5	47.2
2	2.7	40	1.9	240.3	109.1	242.6	43.6	64.4	92	89.4	145.7	59.7	152.5	30.5
3	3.7	41.3	32.1	228.1	174.4	321	36.1	40.4	102.1	102.5	156.6	76.1	189.7	27.9
4	2.5	16.9	15.4	121.5	86.1	176.9	235.7	149.6	85.2	158.6	107.9	55.2	103.8	17.1
5	2.1	16.3	12.6	151.8	44.2	103.5	10.9	33	48.2	69.9	102.2	37.4	100.3	20.5
6	1.5	195.3	13.1	199.1	61.7	133.8	18.4	41	78.7	123.5	144.3	67	129.9	22.8
7	1.3	22.8	4.2	81.5	33.4	73.2	26.4	30.2	28.5	34.8	58.5	26.9	55.4	7.6
8	1.9	40.7	9.5	93.9	53.6	107.3	5.4	15	25.4	28.3	61.3	21	52.8	17.7
9	5.2	478.5	13.3	168.6	54.9	148.2	115.8	98.6	83	66.7	102.8	62.7	93.1	16.5
10	3.5	36.4	24.5	544.7	253.1	255.3	17.9	33.2	28.8	58.6	53.6	18.8	54.2	22
11	10.1	67.7	37.9	327.8	224.7	465.1	459.3	220.1	251.8	321.3	202.2	201.6	269.3	57.8
12	1.2	0.9	0.5	457.7	186.5	211.4	3.6	13	28.1	53.3	68	19.8	56.9	42
13	3.4	28.5	11.6	823.7	435.9	450.8	35.9	43.7	29.3	1.1	50.1	26.2	56.3	47.2
14	1.1	12.1	5.6	32.7	134.2	63.9	7.5	6.7	10.7	1.7	30.3	11.4	28.9	11.7
15	2.9	63.2	21	803.3	522.8	283.8	5.3	29.8	64.8	80.8	173	43.5	239.5	55.1
16	0.2	27.5	5.9	1466.2	637.6	281.6	6.7	19.9	58.5	46.7	196.5	55.5	194.1	67
17	2	36.8	16.8	561.7	247.6	123.2	16.8	17.2	46.2	56.3	104.3	26.3	147.9	39.5
18	1.3	26.2	7.8	104.7	93.5	119.9	2.1	24.5	26.9	17.6	46.9	15.4	60.1	58.4
19	0.6	34.9	5.7	983.1	398.5	265.7	1.6	7	45	47	95.4	42.4	85.3	31.6
20	4.3	15.3	9.5	211.2	236.2	209.1	26.1	14.5	30.8	52.6	81	39.5	88.6	27.5

- PCB IUPAC numbers

The size of the fish

The concentrations of organochlorine pesticides and chlorobiphenyls and their means, medians and coeffcients of variaton are in Tables 2 and 3, respectively. Since the concentration of organochlorine compounds in fish is usually a function of fish size, it is important to take this into consideration. The fish analyzed in this study are larger (Fig.1) than fish analyzed by Blomkvist et al (1993), Valters et al (1999), and Olsson et al

(2000), however, their length and weight deviate only slightly from the curve derived for the other fish (Fig.1, dotted line). Fish sizes were not reported in the study of Edgren et al. (1981).

Table 3. Means, medians, and coefficients of variation of the perch data in Tables 1 & 2 (f = female, m= male).

	Aug f	Aug m	Sept f		Aug f	Aug m	Sept f		Aug f	Aug m	Sept f
Age	7.5	6.3	7.0		6.5	6.0	7.0		26.3	9.1	25.6
Length, mm	299.7	267.0	306.8		295.0	256.0	300.0		14.2	9.8	16.4
Weight, g	400.4	223.1	413.5		352.2	206.7	387.0		42.9	27.0	47.1
Fat %	0.54	0.61	0.28		0.54	0.65	0.27		20.75	16.84	34.80
a-HCH	2.9	2.3	2.8		2.6	2.1	2.0		46.2	50.0	99.3
g-HCH	135.5	27.9	31.8		41.0	22.8	28.5		133.0	53.1	63.0
HCB	14.2	11.0	13.3		13.2	12.6	9.5		70.1	55.8	81.6
p,p'DDE	175.3	228.6	574.3		183.9	151.8	544.7		33.4	86.2	73.8
p,p'DDD	90.0	93.9	306.4		73.9	44.2	247.6		51.8	101.8	55.5
p,p'DDT	188.3	186.0	248.2		162.6	103.5	255.3		42.4	91.3	50.9
28+31	75.8	30.6	53.0		39.9	26.4	7.5		115.0	72.3	255.2
52	68.2	54.3	39.1		52.7	33.0	19.9		71.6	72.5	156.4
101	77.7	71.7	56.4		84.1	48.2	30.8		34.6	81.7	118.1
118	94.8	72.5	67.0		96.0	69.9	52.6		47.6	53.8	131.2
153	119.8	138.4	100.1		126.1	102.2	81.0		30.1	74.3	62.2
105	57.0	52.0	45.5		61.2	37.4	26.3		33.4	67.0	117.8
138+158+163	120.3	118.1	116.5		116.9	100.3	85.3		39.9	62.0	71.4
180	22.1	25.1	41.8		20.3	20.5	42.0		27.2	80.5	41.3
PCB	635.7	562.7	519.4		658.5	422.4	355.3		35.5	68.3	99.1
sddt	453.5	508.5	1128.8		389.6	299.5	1017.6		37.7	90.8	57.7

The concentration of lipids

The concentration of lipids in perch mussel decreases with increasing length of the fish (Fig. 2). Interestingly, the concentration of lipids in the fish collected in September 1999 is, in most of these fish, less than predicted by the regression line. The length and weight of these fish correspond to the age of perch in this and in the studies referred to above (Fig. 3). In addition, Edgren et al.(1981) have not detected an annual trend in the lipid concentration in perch. Consequently, one can only postulate that either the difference in maturity (see Table 1), a sudden starvation, a disease or the presence of higher concentrations of the DDT compounds or some other toxicants is the cause of the low lipid concentrations. At the same time, the concentration of PCBs is lower in the September fish than in those from August. One would expect the opposite, had the low lipid concentration been the cause of higher concentrations of organochlorine compounds, expressed on a lipid basis.

PCB and DDT

The concentration of PCB depends only slightly on the length of perch (Fig. 4). The very large variations in PCB concentrations, observed by Blomkvist et al (1993) are obviously caused by the different sampling sites. The same large variations are observed for the concentration of ΣDDT regardless the length of the fish in the data of Blomkvist et al (Fig. 5). In our fish, the concentration of ΣDDT increases with their length. As mentioned already, the concentration is much higher in the fish sampled in September 1999 than in those sampled in August 1999 (Fig. 4). Olsson et al (2000) did not measure p,p'-DDT because of interference by a chlorobiphenyl peak. However, in their study, the concentration of p,p'-DDT appeared to be below the quantitation limit of their method (Valters, personal communication, 2001). Consequently, our data may indicate a localised, 'sudden' change in the concentration of p,p'-DDT and its metabolites. The concentration of ΣDDT in some of our September, as well as August fish is well outside the range of the expected ΣDDT *vs* PCB relationship (Fig. 6). On the other hand, the concentrations of DDD and DDE in the September fish do no deviate from the DDD *vs* DDE line (Fig. 7).

HCHs and HCB

The concentration of α-HCH is lower in our fish than in those analyzed by Olsson et al (2000). This may indicate that it decreases with increasing length of the fish (Fig. 8). The concentration of lindane (γ-HCH) is slightly higher in our fish than in fish analyzed by Olsson et al (2000), except for two fish, in which the concentration is much higher (Fig. 9). On the whole, it seems that the concentration of lindane is practically independent of the size of the fish. The same seems to be the case for the concentration of HCB (Fig. 10).

Chloropbiphenyl profiles

The chlorobiphenyl profiles of the August and September 1999 perch differ from each other and are more scattered than those of the perch studied by Olsson et al (2000), as can be seen from Fig. 11. The more chlorinated chlorobiphenyls # 138, 118, and 153 tend to predominate in the September 1999 fish, as may be seen from Fig. 11 in conjunction with Fig. 12. The latter shows the effects of the individual chlorobiphenyls on the principal componets 1 and 2 of Fig. 11. The 'outliers', August fish Nos. 4 and 9, and the September fish No. 11 contain unusually high relative concentrations of the chlorobiphenyl #28. On the other hand, the 'outlier' No. 13 has a very low proportion of the chlorobiphenyl #118 and a high proportion of the chlorobiphenyl #180. The fish Nos. 14 and 18 contain relatively low proportions of chlorobiphenyls #118 and #28, respectively, and both are relatively enriched in the chlorobiphenyls # 138 and #180. It is impossible to tell whether the 'outlier' profiles are analytical artifacts. However, the data clearly indicate that the September 1999 fish have chlorobiphenyl profiles different from the August fish. Whether this is the cause of the lower lipid concentrations in the former, remains an open question.

A comparison with OC in herring and salmon

The average concentrations of PCB, HCB, α-HCH, γ-HCH, and ΣDDT between 1985 and 1989 in the Baltic were 1030, 57, 111, 72, and 770 ng/g lipid in herring, and 4243, 153, 70, 37, and 3254 ng/g lipid in salmon (Paasivirta, 2000). In comparison, the concentrations of HCB, α-HCH, and ΣDDT in perch (Table 3) are lower, and the concentration of γ-HCH in the August perch is higher. As for PCB, it is difficult to make comparisons, since it is not known which chlorobiphenyls were included in the data of Paasivirta. The concentration of the chlorobiphenyl #105 is between the concentrations reported for herring and salmon, 17 and 73 ng/g lipid, respectively.

Human risk assessment

From the human health risk point our data indicate that even the maximum levels of organochlorines found in the organism of Baltic fish (at the coastal areas of Estonia) do not represent any human health risk, as they are lower than the standards set by the World Health Organization. In addition, our calculations with ADI and NOEL values based on the literature data (Reports and Studies 1991; Roots 1996; 1999 a) were made on the ground of 150g of edible fish per day, compared with the European average of 60g per day (Roots, 1996; 1999).

Concluding remarks

Even though the current levels of the investigated organochlorine compounds in perch do not represent a risk to humans, a continuing monitoring is warranted to document the effectivness of the international ban of the selectd Peristent Organic Pollutants. In addition, animals at high levels of the aquatic food webs still contain unacceptably high concentrations, and possibly significant toxicologically levels of these compounds. A continuous monitoring is necessary to ensure that no additional discharges into the environment take place. At the same time, attention should be given biological, physiological, and biochemical characterisation of the analysed fish to be able to better assess the status of their health.

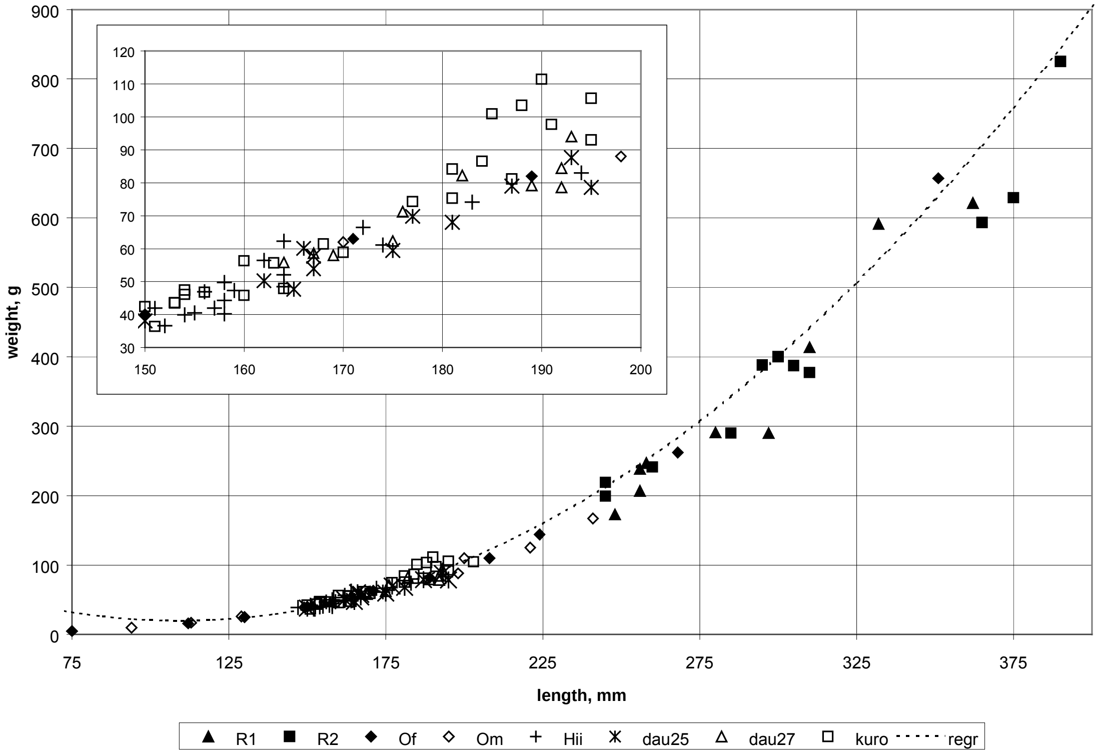

Fig. 1. Length vs weight relationship. R1, R2 =August and September 1999 perch in this study, Of, Om, Hii, dau25, dau27, and kuro = data of Olsson et al. (2000) for female (f) and male (m) perch, and of Blomkvist et al. (1993) for perch from Hiiumaa (Estonia),Daugavriva (Latvia), stations 25 and 27, and Kuronian Bay (Lituania), respectively. Dotted line fitted to data of Olsson et al., and Blomkvist et al.

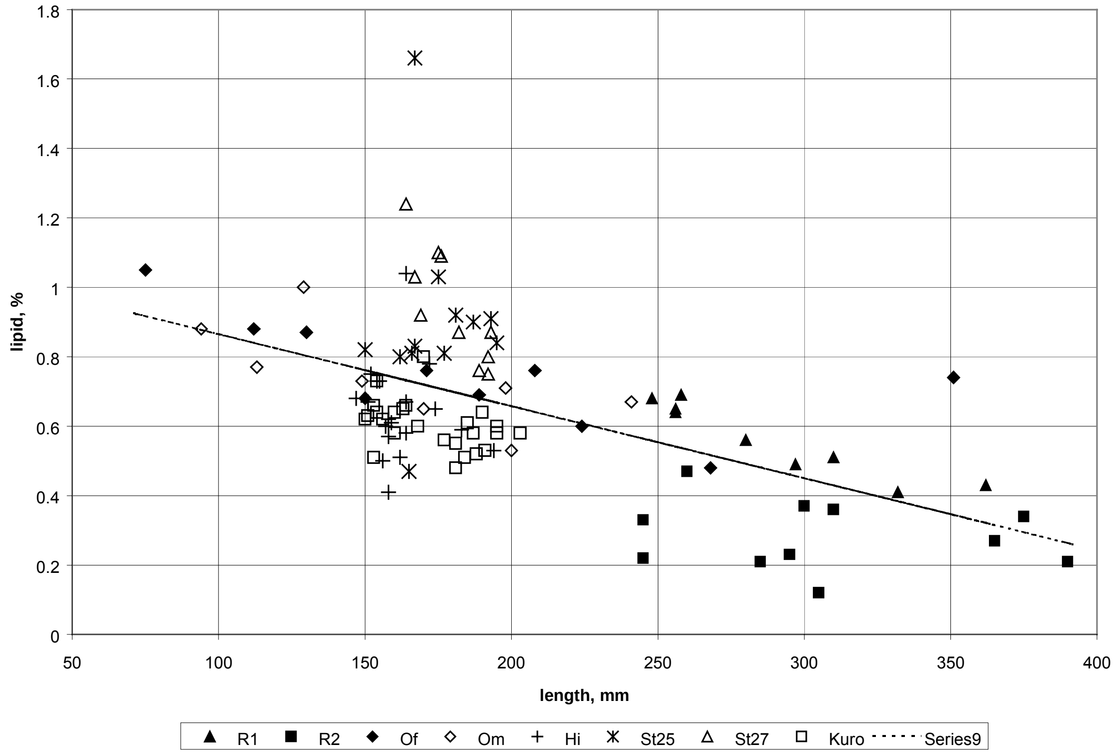

Fig. 2. The lipid concentration vs length relationship. See Fig. 1 for details

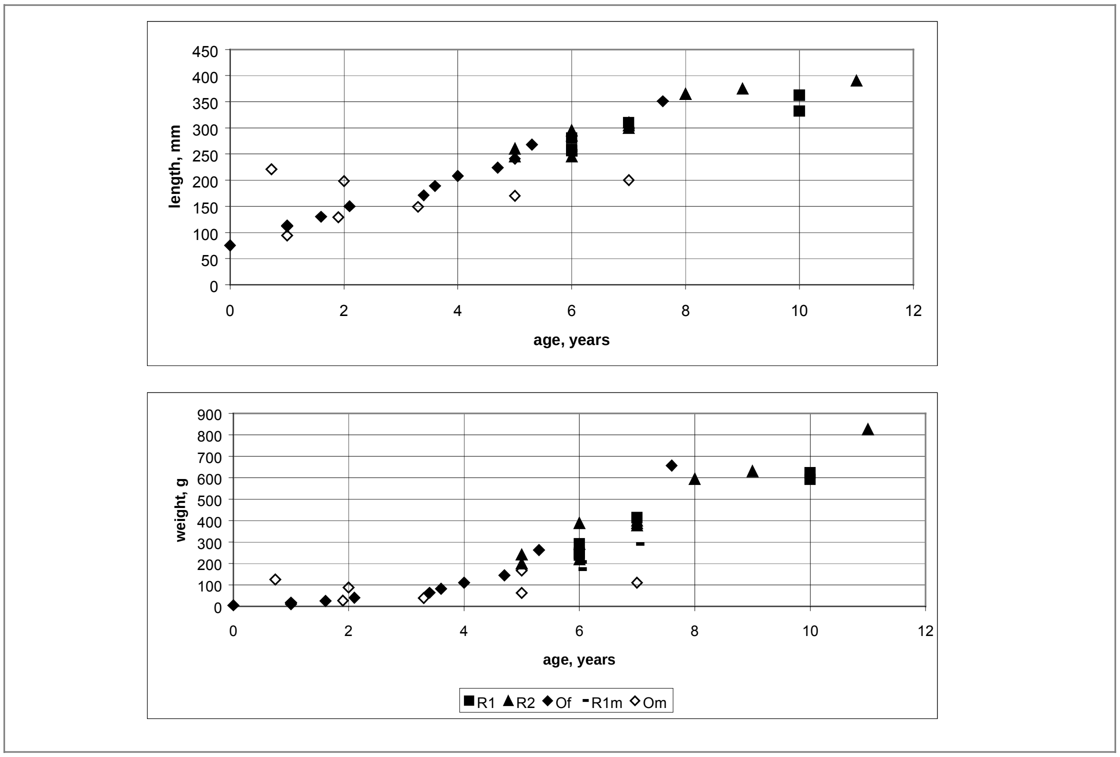

Fig. 3. Length and weight vs age relationships. R1 and R2 are only female fish of this study. Male August 1999 fish are designated R1m. Of and Om have the same meaning as described in Fig.1.

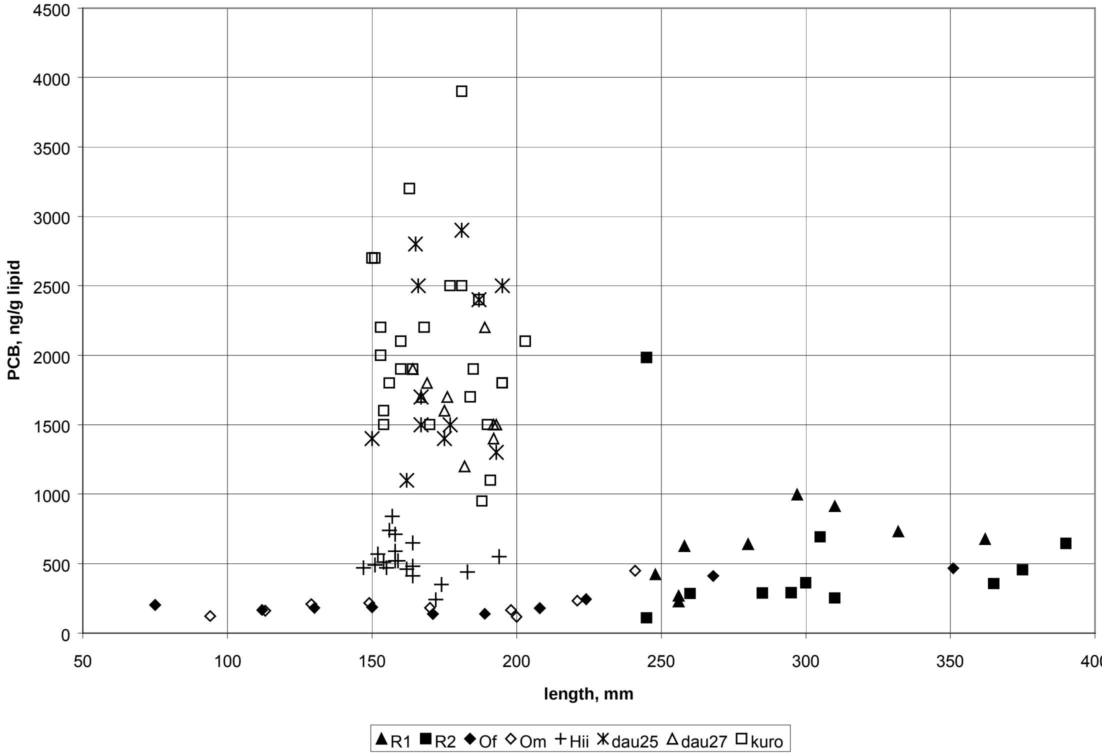

Fig.4. PCB vs length relatioship. The point symbols are as in Fig. 1.

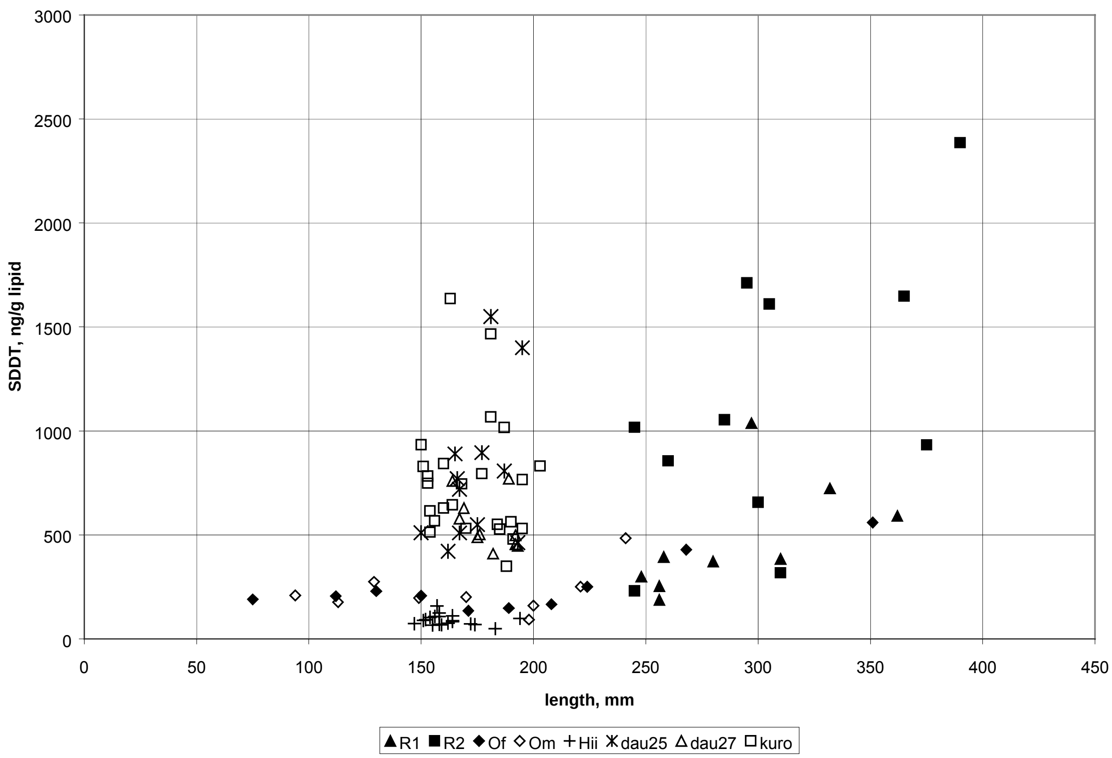

Fig. 5. ΣDDT vs length relationship. Points identification is as in Fig. 1.

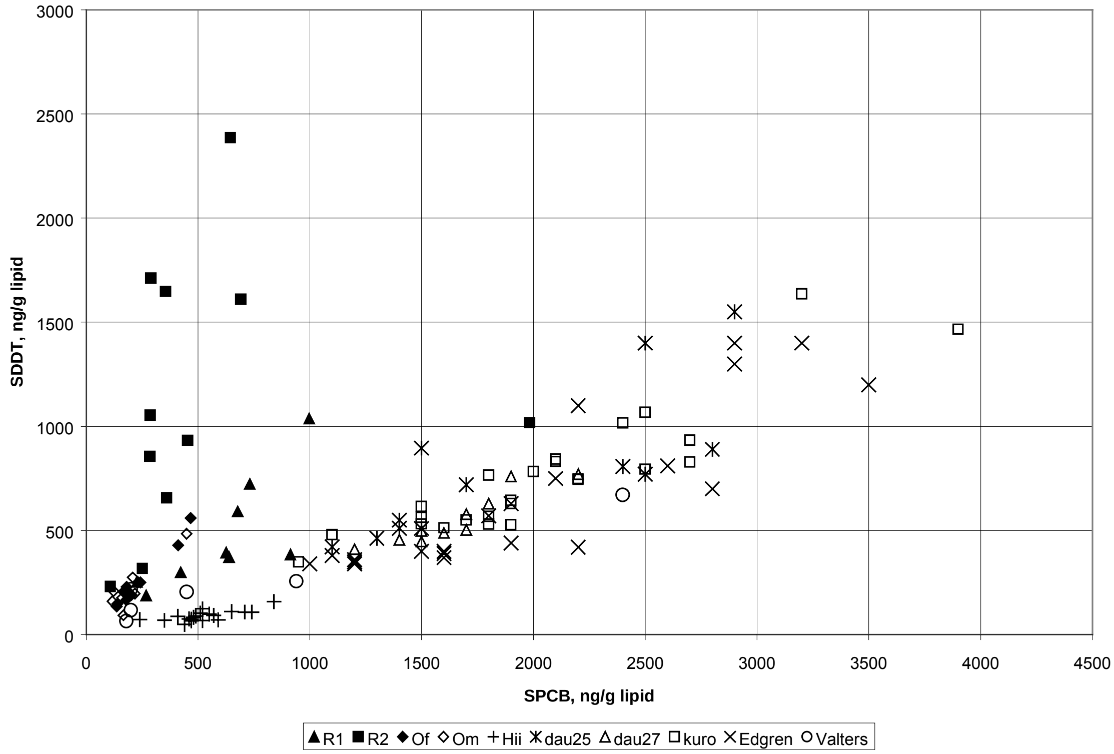

Fig. 6. ΣDDT vs ΣPCB relationship. Points identification is as in Fig. 1.

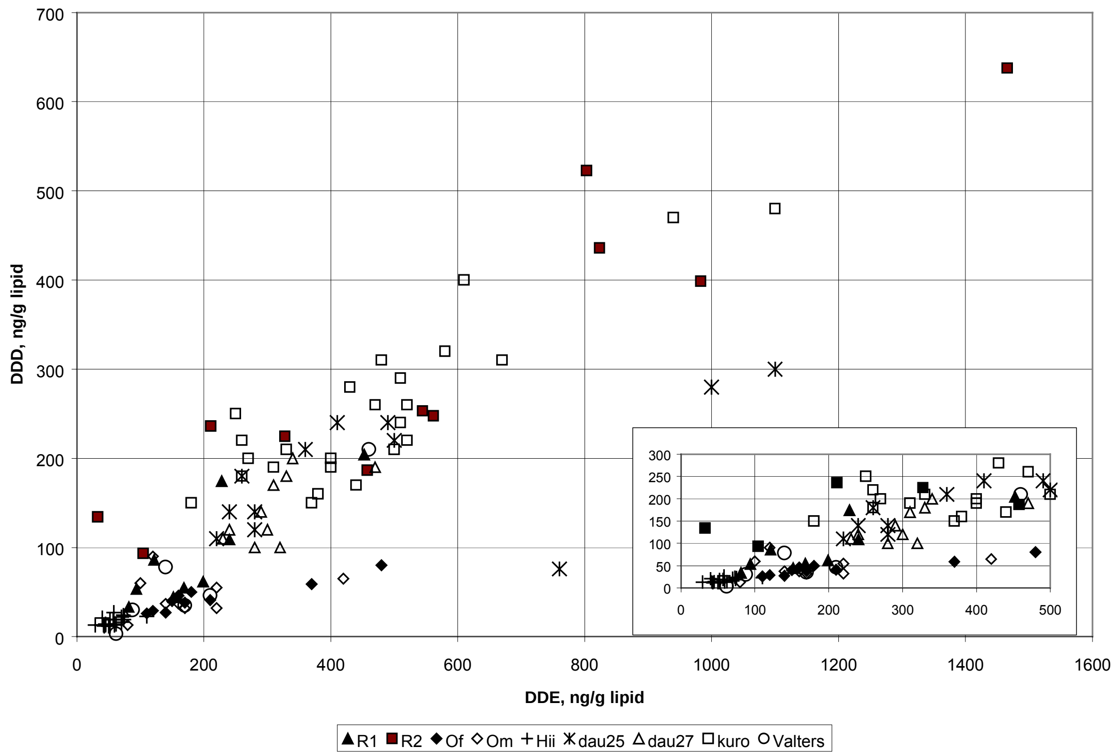

Fig. 7. P,p'-DDD vs p,p'-DDE relationship. Points identification is as in Fig. 1.

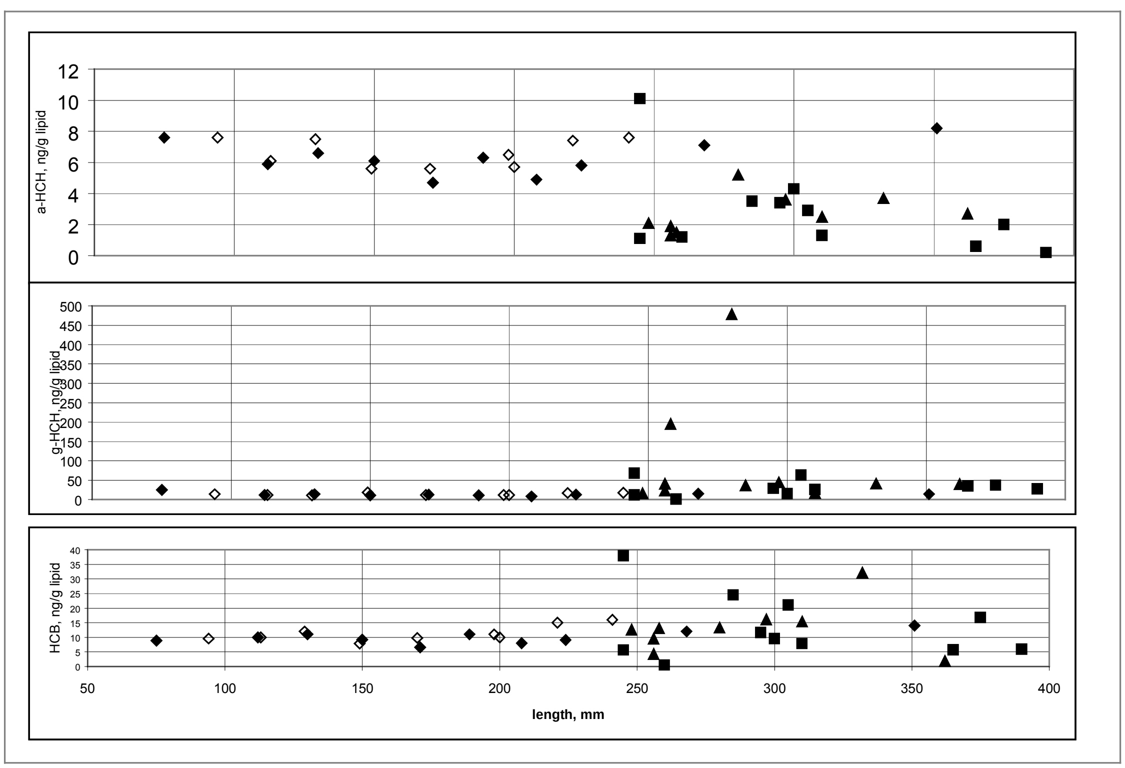

Fig. 8. Concentration vs length relationships for α- and γ-HCH (lindane), and HCB (hexachlorobenzene)

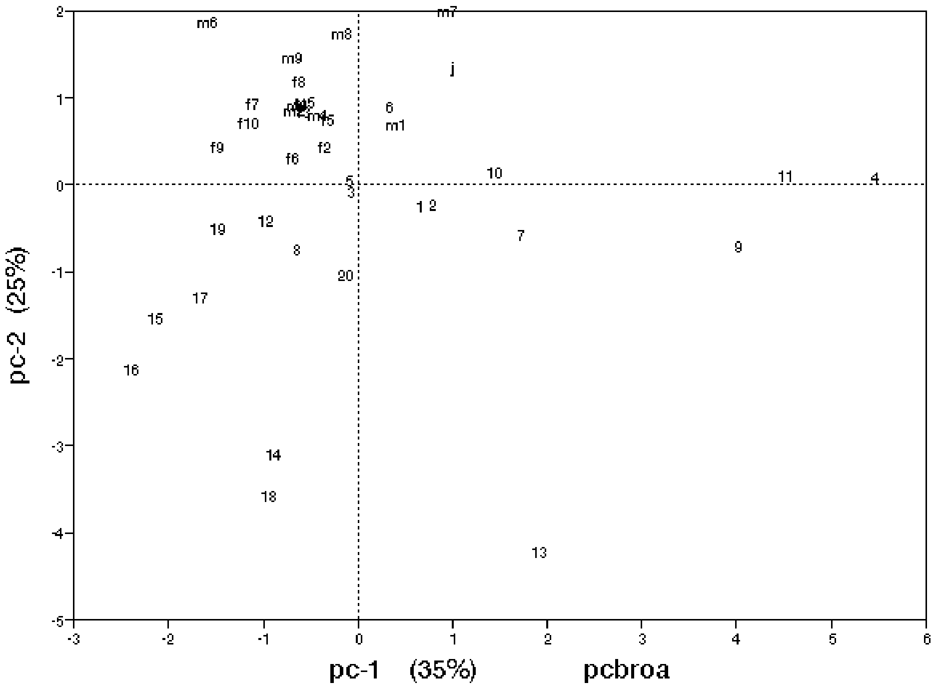

Fig. 9. Chlorobiphenyl profiles (Chlorobiphenyl concentrations scaled to a sum of 100), projected on the plane of the first two principal components. Portions of the original variance captured by the principal components are indicated on the axes. Points 1-9 and 10-20 are perch caught in August and September 1999, respectively. Points marked j, m, and f are juvenile, male, and female perch of Olsson et al. (2000). Similar profiles are located in close proximity.

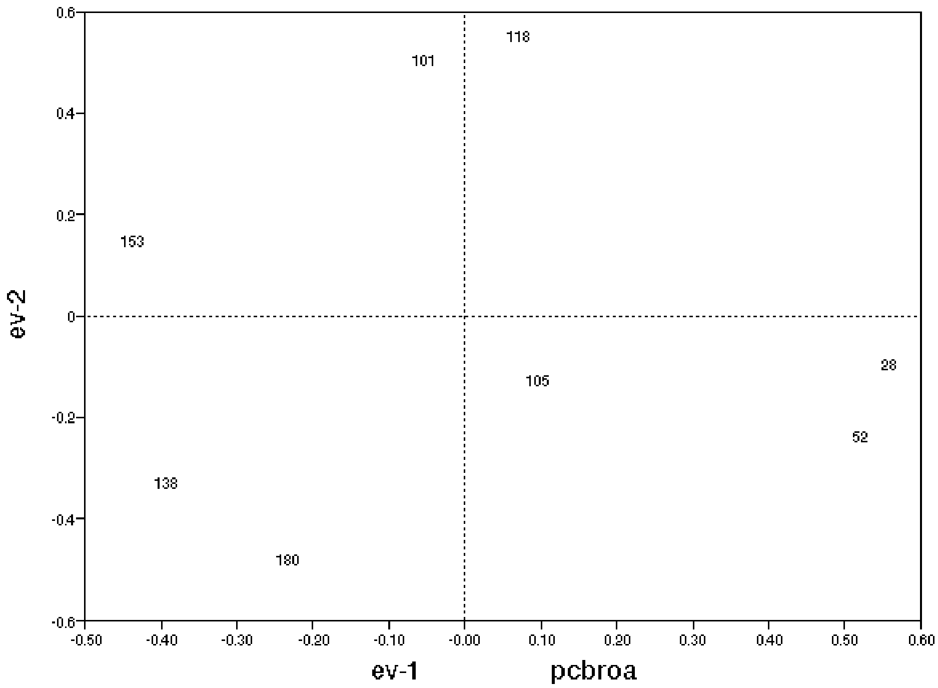

Fig. 10. The loadings of the individual chlorobiphenyls on the principal components 1 and 2 in Fig. 9. A close proximity indicates correlation.

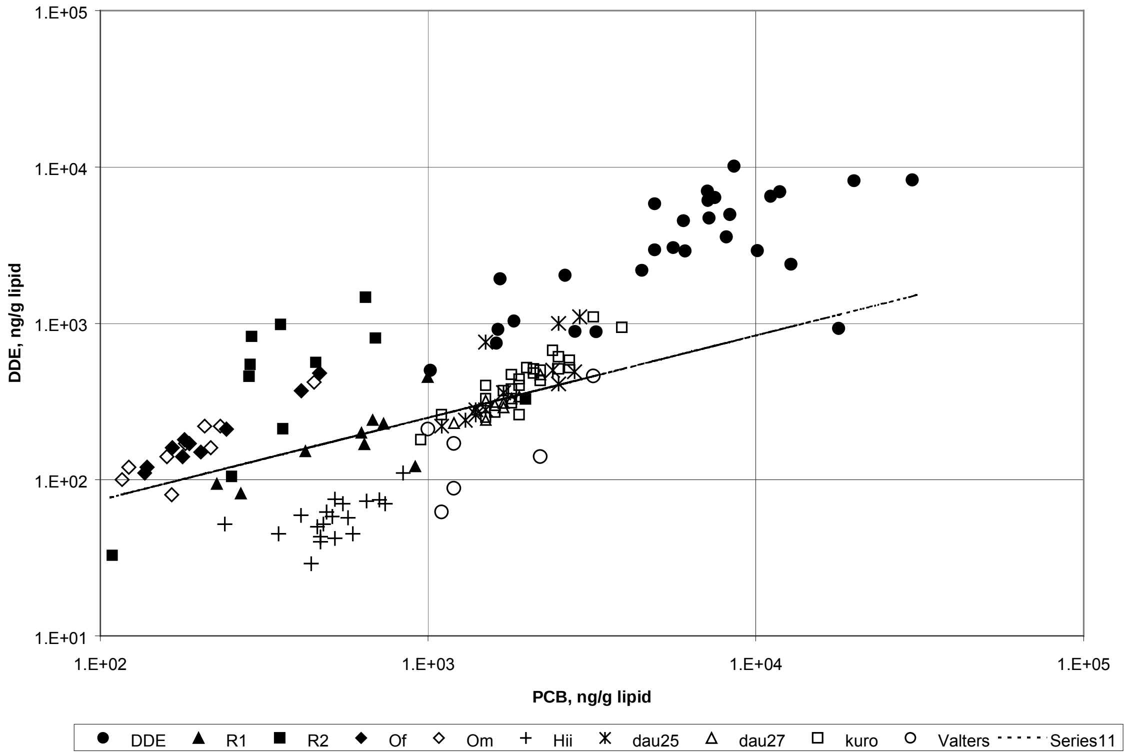

Fig. 11. The relationship between the concentration of p,p'-DDE and PCB. In addition to points identified as in Fig. 1, the data of Valters et al. (1999) and of Hofer et al. (2001, 'DDE') are included. The line was fitted to all points, except the latter.

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