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# Accumulation of PCBs and Organochlorine Pesticides in River-Caught European River Lamprey (*Lampetra fluviatilis*) in Finland

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The polychlorinated biphenyls (PCBs) are a group of toxic, persistent, and lipophilic organic compounds that have been used worldwide since 1929. The PCBs are composed of various numbers of chlorine atoms in the biphenyl moiety. About 150 congeners among the 209 possible are reported to be present in the environment. In 1998 the World Health Organization (WHO) driven consensus for the toxic properties of 12 selected PCBs - the so-called toxic equivalency factors (TEFs) - was launched (van den Berg et al. 1998). However, the remaining congeners may have toxicological effects in the environment and also in humans. Giesy and Kannan (1998) reported dioxin-type toxic effects caused not only by congeners with dioxinlike structure but also those with a different substitution pattern of chlorine atoms. Recently, various methods for estimating the total nondioxinlike PCB mass in fish tissue samples have been examined (Connor et al. 2005). Specific accumulations of PCBs and their congeners in edible fish, including lampreys, in the southern part of the Baltic Sea were reported. The level of PCBs in lampreys varied between 110 and 230 $\mu g\ kg^{-1}$ (Falandysz et al. 2002).

PCBs and organochlorine residues are very commonly found in fish, fishery products, and marine biota in which they are often reported as contaminants (Strandberg et al. 2000; Roots 2001; Nakari et al. 2002; 2004; Kiviranta et al. 2003; Storelli et al. 2003; 2004). The concentrations of PCBs and organochlorine pesticides are increasing in the food chain. This property of the compounds causes severe problems in piscivorous animals such as seals and sea birds, especially in their reproduction (Hario et al. 2000; 2004; Routti et al. 2005). As far as human exposure is concerned one of the main sources of PCBs and other organochlorine compounds are fish and fishery products (Asplund et al. 1994). Organochlorine compounds are widely used as bioindicators to assess the degree of environmental contamination with persistent pollutants and especially to monitor the quality of the aquatic environment (Strandberg et al. 1998a; b; Falandysz et al. 2001).

European river lamprey (*Lampetra fluviatilis*) are commonly found along the western coast of Finland. Most rivers in Finland support lamprey stocks; however, due to engineering projects and establishment of hydroelectric power plants in

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several rivers, many stocks have been depleted or have almost completely disappeared. Lamprey larvae spend 4-6 y in the bottom sediments of rivers and later migrate to the sea, where they remain for 2 y before they migrate back to the rivers to spawn. In the sea lamprey feed on fish such as Baltic herring (*Clupea harengus membras*), European sprat (*Clupea sprattus*), and Atlantic cod (*Gadus morhua*), but they stop feeding when they begin the spawning migration to the rivers. Lamprey are caught during the spawning period and the largest catches are taken in September and October in Finland. Lampreys are processed for human consumption in small enterprises and marketed as a seasonal delicacy during autumn.

Nakari et al. (2002; 2004) reported bioaccumulation levels of toxic compounds in fish and bivalves from fresh and coastal waters in Finland. However, no information is available on the PCB and organochlorine pesticide residues in lamprey in the northern part of the Baltic Sea.

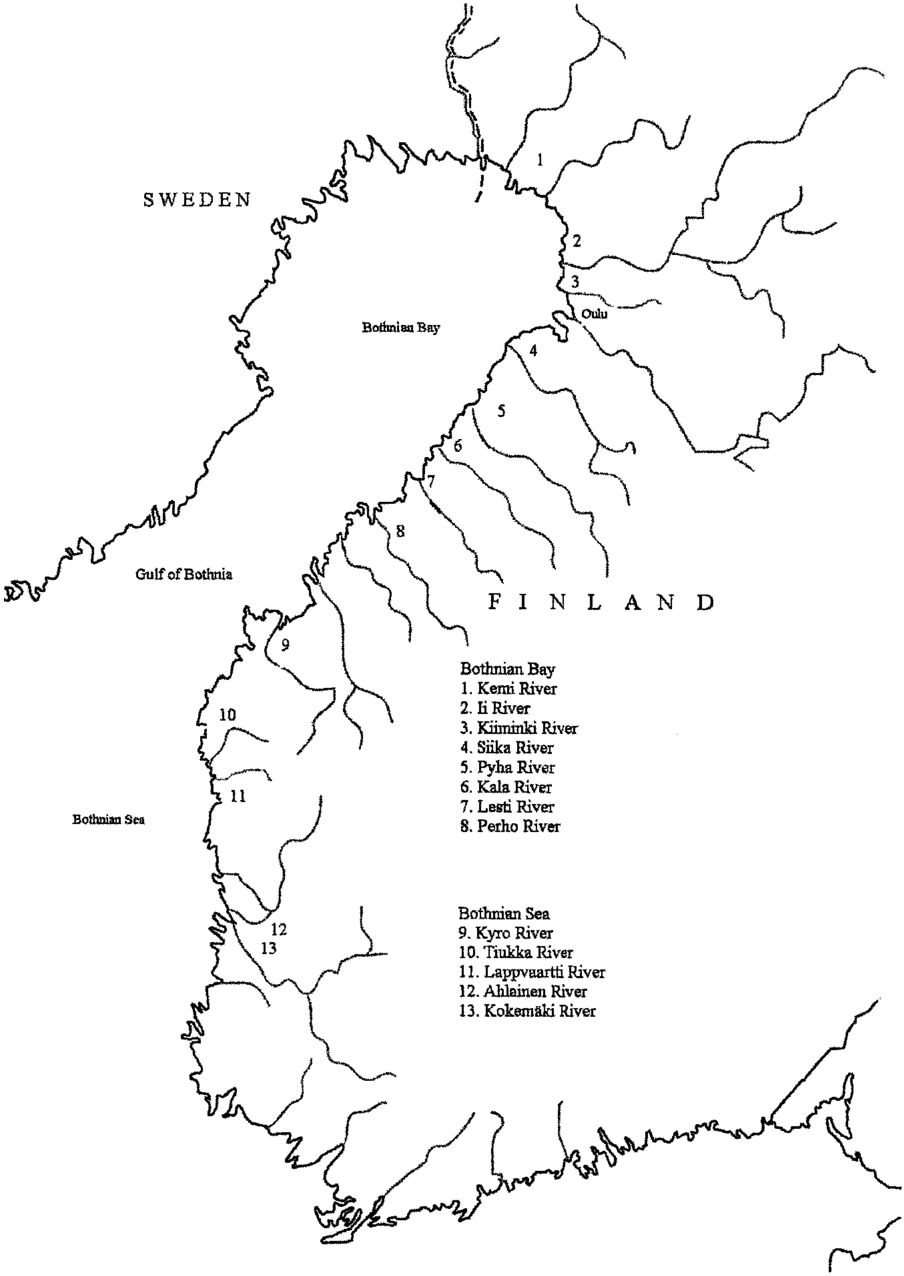
Here we report the levels of various congeners of PCBs and some pesticides in river-caught lamprey from Finland. The sampling locations are shown in Figure 1. The aim was to use the data to determine the feasibility of using lamprey as bioindicator species for aquatic environmental quality in the Gulf of Bothnia.

## MATERIALS AND METHODS

A total of 50 fresh lamprey samples were analyzed in 13 rivers flowing downstream to the Bothnian Bay (northern area, 31 samples) and the Bothnian Sea (southern area, 19 samples). Each sample consisted of 6 lamprey. The lamprey were homogenized and stored in a freezer at -18 °C before analysis.

Hexachlorocyclohexanes (alpha-HCH, beta-HCH, lindane), hexachlorobenzene (HCB), heptachloroepoxide, dieldrin, chlordanes (oxychlordane, transchlordane, cischlordane, transnonachlor [TNCL]), DDTcompounds (p,p'- DDE, p,p'- DDD, p,p'- DDT, o,p'- DDT), and 15 PCB congeners were determined from all samples. The method used was an in-house modification of the methods described by the AOAC (1995) and Specht (1987).

Ten grams of homogenized sample were mixed with sodium sulphate and sand and blended in a mortar until homogeneity was achieved. Extraction was performed twice with hexane/acetone (2+1) in a rotary shaker. After filtration the organic phase was evaporated and the lipid residue weighed. The pesticides were removed from the lipid with automated gel permeation chromatography. The elution solvent was dichloromethane-cyclohexane (1+1). Further cleanup and separation were achieved using a 3% deactivated silica gel column. The compounds were eluted with hexane (fraction 1, with PCBs and some organochlorine pesticides) and toluene (fraction 2, with organochlorine pesticides). The lipid content was determined gravimetrically according to a standard procedure after extraction of the sample with diethyl ether and light petroleum.




**Legend to Figure 1.** Sampling locations of the river lampreys in some rivers in Finland.

The PCBs and organochlorine pesticides were determined in the National Veterinary and Food Research Institute (EELA) using a capillary gas chromatograph equipped with dual column and dual electrochemical (EC) detector systems. The gas chromatograph used was an Agilent 6890 Series (Agilent Technologies Inc., Palo Alto, CA, USA) and the capillary columns used were a DB-1701; 30 m, 0.25 mm i.d., 0.25 μm film thickness and a DB-1; 30 m, 0.25 mm i.d., 0.25 µm film thickness. The following conditions were used: helium at a flow rate of 2.3 ml/min and oven temperature programmed to start at 80 °C, at which it was held for 2 min, followed by a linear increase to 190 °C at a rate of 30 °C/min at which the temperature was held for 13 min. The temperature was then linearly increased to 220 °C at a rate of 3 °C /min and held there for 2 min. Finally the temperature was increased to 260 °C at a rate of 10 °C/min and held there for 10 min. The injection volume was 2 µl and a splitless mode was applied.

The organochlorine compounds were quantified against a 5-point calibration curve; the final results were not corrected with recoveries. The recovery of the indicative PCB congeners were: PCB 28 111 % ± 5 %, PCB 52 101 % ± 10 %, PCB 101 100 % ± 15 %, PCB 118 93 % ± 23 %, PCB 138 103 % ± 15 %, PCB 153 92 % ± 16 %, PCB 180 102 % ± 19 %. Recoveries of the measured pesticides varied from 68 % to 111 % and the individual recovery was for alpha-HCH 96 % ± 14 %, beta-HCH 84 % ± 9 %, lindane 98 % ± 14 %, HCB 68 % ± 14 %, heptachlorepoxide 84 % ± 12 %, dieldrin 88 % ± 13 %, cischlordane 75 % ± 5 %, oxychlordane 109 % ± 7 %, transchlordane 78 % ± 8 %, transnonachlor 78 % ± 12 %, p,p'DDE 104 % ± 11 % and p,p'DDD 99 % ± 4 % respectively.

The laboratory has participated in several intercomparison studies organized by the European Union (EU) reference laboratory, ISS, Rome, Italy (pesticides in an isooctane solution, in Soya oil, and the PCBcompounds naturally present in crude fish oil) and by Fapas (PCBcompounds in vegetable fat). All results showed Z scores better than ± 2. The differences between the pesticide and ΣPCB concentrations in lampreys from the Bothnian Bay and Bothnian Sea areas were analyzed using Student's t-test.

## RESULTS AND DISCUSSION

The mean ΣPCB value (Table 1) in samples from rivers flowing downstream to the Bothnian Bay was 110 $\mu g\ kg^{-1}$, which was significantly lower than the corresponding value of 130 $\mu g\ kg^{-1}$ in samples from the Bothnian Sea area ($p < 0.01$). The maximum values for ΣPCB in the northern and southern areas were 160 $\mu g\ kg^{-1}$ and 180 $\mu g\ kg^{-1}$, respectively. The mean concentrations of individual congeners were statistically higher in lampreys taken from the southern area than the northern area with regard to PCB congeners 128, 149, 151, 170 and 180 ($p < 0.01$). The major congeners were 138 and 153, and there were no differences in concentrations between the areas. Congener 15 was not detected in any sample. The level of dioxinlike PCB congeners 114 and 118 did not differ in the 2 catchment areas.

Our data clearly demonstrate that the concentrations of DDT were significantly higher in lamprey taken from rivers in the southern area compared with those from the northern area ($p < 0.01$), with maximum values of 87 $\mu g\ kg^{-1}$ and 66 $\mu g\ kg^{-1}$, respectively (Table 2). The mean concentrations of beta-HCH, HCB, dieldrin, and oxychlordane were significantly higher in samples from rivers flowing downstream to the Bothnian Sea in comparison to the Bothnian Bay ($p < 0.01$). The mean residue levels of lindane were also lower in the northern area ($p < 0.05$). There were no statistical differences between the areas with regard to the concentrations of alpha-HCH, heptachloroepoxide, transchlordane, cischlordane and TNCL. The mean fat concentrations were 15.2% in river lampreys from the Bothnian Sea and 16.1% from the rivers of Bothnian Bay.

**Table 1.** Residue levels of PCBs (µg $kg^{-1}$ fresh weight) in European river lamprey from rivers flowing downstream to the Bothnian Bay and Bothnian Sea, Finland.

| | Bothnian Bay (n = 31) | | | Bothnian Sea (n = 19) | | |
|---|---|---|---|---|---|---|
| Congener | Mean | Min | Max | Mean | Min | Max |
| PCB 8 | ND[a] | ND | 0.74 | ND | ND | 0.23 |
| PCB 15 | ND | ND | ND | ND | ND | ND |
| PCB 28 | 1.3 | 0.74 | 2.4 | 1.5 | 0.90 | 2.3 |
| PCB 52 | 1.1 | 0.19 | 6.7 | 0.90 | 0.24 | 1.9 |
| PCB 101 | 6.7 | 4.0 | 9.7 | 7.1 | 5.0 | 9.0 |
| PCB 114 | 4.4 | 2.7 | 15 | 5.3 | 3.1 | 9.5 |
| PCB 118 | 10 | 6.5 | 29 | 10 | 6.7 | 16 |
| PCB 128 | 3.4 | 0.92 | 5.7 | 4.4 | 2.4 | 7.4 |
| PCB 138 | 19 | 12 | 32 | 20 | 13 | 27 |
| PCB 141 | 2.4 | 1.3 | 4.9 | 2.4 | 1.3 | 3.6 |
| PCB 149 | 8.8 | 4.3 | 13 | 13 | 7.1 | 24 |
| PCB 151 | 8.1 | 2.9 | 13 | 11 | 5.6 | 21 |
| PCB 153 | 28 | 18 | 41 | 32 | 20 | 46 |
| PCB 170 | 4.6 | 1.2 | 8.3 | 6.6 | 3.1 | 10 |
| PCB 180 | 11 | 8.3 | 16 | 13 | 7.6 | 24 |
| Σ PCB | 110 | 81 | 160 | 130 | 80 | 180 |

[a]ND = not detected

**Table 2.** Residue levels of ΣDDT and some pesticides (µg $kg^{-1}$ fresh weight) in European river lamprey from rivers flowing downstream to the Bothnian Bay and Bothnian Sea, Finland.

| | Bothnian Bay (n = 31) | | | Bothnian Sea (n = 19) | | |
|---|---|---|---|---|---|---|
| Pesticide | Mean | Min | Max | Mean | Min | Max |
| Alpha-HCH | 1.2 | 0.19 | 2.4 | 1.6 | 0.18 | 4.0 |
| Beta-HCH | 0.63 | 0.15 | 1.7 | 1.1 | 0.19 | 2.2 |
| Cischlordane | 2.7 | 1.3 | 4.1 | 3.1 | 1.8 | 4.9 |
| ΣDDT | 46 | 34 | 66 | 68 | 28 | 87 |
| Dieldrin | 3.7 | 2.0 | 6.2 | 5.3 | 2.4 | 7.6 |
| HCB | 3.1 | 1.1 | 5.6 | 4.4 | 1.1 | 7.3 |
| Heptachlorepoxide | 0.74 | 0.38 | 1.1 | 0.86 | 0.40 | 1.7 |
| Lindane | 1.2 | 0.59 | 2.0 | 1.5 | 0.24 | 3.0 |
| Oxychlordane | 1.1 | 0.50 | 1.6 | 1.3 | 0.79 | 2.2 |
| Transchlordane | 0.49 | 0.17 | 1.1 | 0.41 | 0.087 | 0.72 |
| Transnonachlor | 9.5 | 3.6 | 17 | 9.8 | 1.4 | 19 |

We demonstrated that the mean residues ΣPCB, ΣDDT, beta-HCH, alpha-HCH, lindane, HCB, dieldrin, and oxychlordane were higher in catches from the rivers flowing to the Bothnian Sea than the rivers flowing to the Bothnian Bay. The differences seen in the levels of PCBs and organochlorine compounds in lamprey taken from the Bothnian Bay and Bothnian Sea may have resulted entirely for geographical reasons. Industrial sites are more commonly found in the southern regions, while the northern catchment area is wilderness with abundant forestland and less agriculture. The drainage basin for the northern rivers consists of approximately 329 000 ha of land under cultivation and the southern drainage basin of 679 000 ha (Information Center of the Ministry of Agriculture and Forestry 2003). The total sale of fungicides in Finland has increased during 1996-2002 from 231.6 to 512.6 tons and that of herbicides from 1585.7 to 2929.8 t. The sale of insecticides varied in the same period from 107.5 to 190.4 t (Information Center of the Ministry of Agriculture and Forestry 2003). Since the amount of land under cultivation is double in the southern area, it may be assumed that the use of pesticides is also higher. The amount of forestland in the northern and southern drainage basins is similar: being 767 600 ha and 856 200 ha, respectively. The yearly use of pesticides in forestland has diminished during 1996-2002 from 45.3 t to 8.5 t (Information Center of the Ministry of Agriculture and Forestry 2003). Therefore the pesticide contamination probably originated from agriculture.

In a recent study of Falandysz et al. (2002) the level of total PCB in lamprey from the Gulf of Gdansk was 170 $\mu g\ kg^{-1}$, which appears to be higher than the value reported here. Nakari et al. (2002; 2004) monitored the residues of PCB, DDT, and some pesticides in Baltic herring and northern pike (*Esox lucius*) from the Bothnian Bay and Bothnian Sea during 1997-1999 and 2000-2002. They showed that the concentrations of the analytes were higher in Baltic herring than in pike. In line with our results, Nakari et al. (2004) observed that the concentrations of beta-HCH, alpha-HCH, lindane, HCB, TNCL, and ΣDDT in Baltic herring from the Bothnian Sea and Bothnian Bay were 0.61 and 0.18, 1.3 and 0.11, 5.9 and 0.093, 3.5 and 0.56, 3.1 and 0.76, and 29.8 and 5.98 $\mu g\ kg^{-1}$, respectively. The compounds measured are lipid-soluble and their concentrations were higher in fish species with higher fat content, even those caught in the same area. In general the percentage of fat in pike, Baltic herring, and lamprey varies 0.36-0.43%, 2.3-3.50% and 15.2-16.1%, respectively. The high fat concentration together with a high position in the food chain probably explain, at least partially the higher amounts of various organohalogen residues in river lamprey than in Baltic herring. Since lamprey are very fat, they are excellent biomarkers evaluating marine pollution caused by persistent lipophilic compounds.

The national authorities (Anonymous 2003) have set action limits for some residues in fish. In our study the maximum residue level in lampreys was 3.0 (action limit 200) $\mu g\ kg^{-1}$ for lindane, 7.3 (action limit 200) $\mu g\ kg^{-1}$ for HCB, 1.7 (action limit 100) $\mu g\ kg^{-1}$ for heptachloroepoxide, 87 (action limit 500) $\mu g\ kg^{-1}$ for ΣDDT, and 180 (action limit 2000) $\mu g\ kg^{-1}$ for ΣPCB, respectively. All residues were thus well below the action limits. Although the concentrations of organic compounds were higher in river lamprey than in pike and Baltic herring, lamprey appear to be a safe foodstuff with respect to the residues measured here.

On the other hand, most developed countries and the EU have severely restricted the use of PCB-containing products since 1976. In addition Finland has banned several pesticides during recent decades. The use of dieldrin and DDT was prohibited in 1972, lindane in 1987 and heptachloroepoxide, HCB, and chlordane in 1996. The use of PCB was prohibited in 1990 and transformers containing PCBs were removed by 1994. Depending on the half-lives of these compounds, in the long run the levels of organohalogen residues will probably be further reduced (Mackenzie et al. 2004). A total of 390 products were listed in the pesticide register in Finland in 2002 (Savela et al. 2003). Although the active ingredients in these new products are less toxic than in the old products and the rate of application of pesticides in Finland is among the lowest in Europe (Savela et al. 2003), future investigation on the occurrence of the residues in biomarker species and foodstuffs will be justified. The present study implies that there are differences in the concentrations of some residues between different basins of the Gulf of Bothnia and gives basic information on evaluation of foodstuffs of marine origin.

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