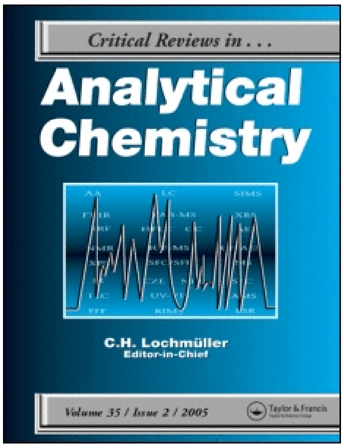

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ANALYSIS OF ORGANOHALOGEN SUBSTANCES IN LATVIAN FRESHWATER FISH - CONCENTRATIONS OF PCB AND DDE IN PERCH *(Perca Fluviatilis)*

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INTRODUCTION

Polychlorinated biphenyls (PCB), 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) and its metabolites, as well as numerous other organohalogen substances (OHS) of anthropogenic origin, are ubiquitous environmental contaminants (1, 2). During the last decades the distribution and concentrations of these contaminants have been intensively studied in different parts of the world, including the Baltic Sea. Fish, birds, and mammals have been analysed for OHS (3, 4).The toxicological impact, that these compounds may have on organisms and ecosystems, has also been studied (5). Among others a few articles have been published on concentrations of OHS in biota from the Gulf of Riga. (6-9). In comparison, very little information is available on OHS levels in fish and mammals in the inland waters of the Baltic states, e.g. Latvia (10).

The aim of the present study was to make a survey for OHS in pike from a fresh-water lake, Baltezers, which is located in the vicinity of Riga. Furthermore PCB and DDE were quantified in perch from 6 lakes and 3 river locations in the territory of Latvia. The overall goal is to screen for OHS and to make quantifications for a future baseline study, which should be the fundament for a programme of environmental monitoring of OHS in Latvia.

MATERIALS AND METHODS

Samples

Perch (*Perca fluviatilis*) were sampled in six lakes and two pikes (*Esox lucius*) were caught in lake Baltezers during July - August, 1995. Perch were also collected from three river locations in June of the same year (Figure 1 and Table 1).

Chemicals

All chemicals used were of analytical grade. Dichloromethane (DCM) and n-hexane were purchased from Fisons Scientific Equipment (Loughborough, England). Methyl *tert*-butyl ether (MTBE) was obtained from Rathburn Chemical Ltd. (Walkerburn, Scotland) and acetone from Riedel-de Haen AG (Seelze, Germany). Sulfuric acid was produced by Merck (Darmstadt, Germany).

2,3,2′,6′-Tetrachlorobiphenyl (CB-46), 3,4,3′,4′,-tetrachlorobiphenyl (CB-77), and 2,3,4,5,3′,4′,5′-heptachlorobiphenyl (CB-189) were synthesised as described elsewhere (11, 12). The commercial PCB mixture Clophen A50 was obtained from Bayer A (Germany).

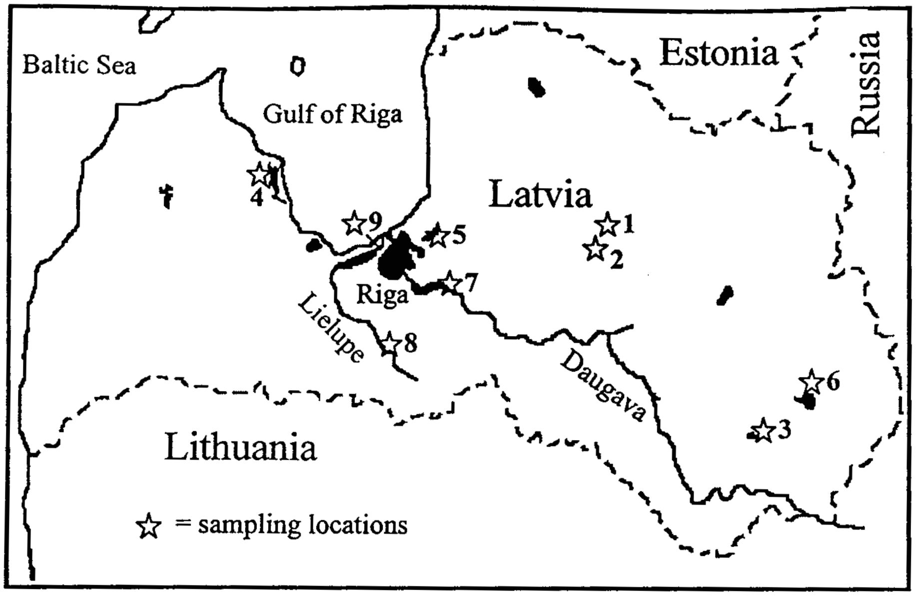

FIGURE 1 Lakes and locations in rivers, where perch and pike samples were collected during the summer of 1995. The location numbers correspond to those in Tables 1 and 2.

TABLE 1 Sampling locations and length range (cm) of the perch. Locations in the rivers: a - upstream Riga; b - near Bauska; c - near Jurmala.

No.	Location	Length range cm
	Lakes:	
1	Alauksts	11.5 - 12.5
2	Inesis	12.0 - 13.0
3	Rusons	12.5 - 14.0
4	Engures	14.0 - 16.0
5	Baltezers	17.5 - 20.0
6	Raznas	19.5 - 20.5
	Rivers:	
7	Daugava (a)	15.0 - 16.7
8	Lielupe (b)	15.0 - 18.0
9	Lielupe (c)	15.0 - 17.0

Instruments

The fish muscle samples were homogenised with an IKA T25 homogenizor from Labassco AB, Partille, Sweden.

Gel permeation chromatography (GPC) was performed on an SR 25 column (450 mm, 25 mm i. d.) from Pharmacia Fine Chemicals AB (Uppsala, Sweden) packed with Bio-Beads SX-3 (50 g; 200-400 mesh) from Bio-Rad Laboratories (Richmond, CA, USA). The solvent delivering system consisted of a HPLC pump (model 2150) and UV-detector (model 2158 Uvicord SD), both from LKB (Bromma, Sweden).

The high performance liquid chromatography (HPLC) system consisted of a nitrophenylpropyl derivatized silica column (Nucleosil-NO_2, 5 μm, Jones Chromatography Ltd., Mid Glamorgan, UK) supplied with LC-6A pump and SPD-2AS UV-detector from Shimadzu (Japan).

A Varian 3400 gas chromatograph equipped with an electron capture detector (ECD) and a Varian 8200 autosampler were used for the analysis. The injector and detector temperature were 250°C and 360°C, respectively. The column was DB-5 (length 30 m, i. d. 0.25 mm, film thickness 0.25 μm) from J&W Scientific (Folsom, CA, USA). Hydrogen was used as carrier gas and nitrogen as make-up gas for the ECD. The GC temperature programme was: 80°C (2 min.), 10°C/min. to 300°C (10 min.). GC-data acquisition and quantification was performed by ELDS 900 from Chromatography Data System (Svartsjö, Sweden).

Gas chromatography/mass spectrometry (GC/MS) was performed on a Finnigan MAT TSQ-700 (Bremen, Germany) mass spectrometer, equipped with a Varian 3400 gas chromatograph. The GC column was same type as described above and helium was used as carrier gas. The oven temperature was programmed: 60°C (4 min.), 30°C/min. to 180°C and 5°C/min. to 320°C (10 min.). Mass spectra were collected in the negative ion chemical ionisation (NICI) mode, with methane as a reagent gas, the ion source temperature was 120°C and the scanning interval - between 30 and 700 amu (0.5 sec/scan). In the electron ionisation (EI) mode the electron energy was 70 eV and the GC column and temperature programme was the same as for NICI.

Analytical procedure

Pooled perch samples with aliquots (approximately 3 g of muscle) of 4 individuals were taken from each of the six lakes. The homogenates of perch from the rivers were made of 8 individuals from Lielupe near Bauska and 10 individuals from each of the other two locations (Table 1). Equal parts of muscle were taken from each perch, so that the total pooled sample from each river location was approximately 10g. The pooled muscle was homogenised and extracted as described previously (13). The extracts were spiked with a surrogate standard (CB-189).The mass of extracted lipids was determined gravimetrically (Table 2). Two different sample clean-up methods were applied prior to analysis by GC(ECD) or GC-MS. Perch samples from the rivers were treated with sulfuric acid (method 1), while GPC and subsequent fractionation on HPLC was used for the rest of the perch samples and the pikes (method 2).

Clean-up method 1

The extracted material was treated with sulfuric acid as described by Jensen and co-workers (13). In order to remove remaining lipids, small columns with 0.5g silica gel:sulfuric acid (2:1,w:w) were used prior to GC(ECD) analyses.

Clean-up method 2

The method has been described elsewhere (6). The method consists of three steps. After the extraction GPC was used to separate xenobiotics from lipids. Small silica gel column was used to complete lipid removal from the fractions containing xenobiotica. Furthermore, xenobiotica were separated in non-polar and polar compounds by a Nucleosil-NO_2 column.

Total PCB concentrations were quantified in relation to Clophen A50 with the relative congener composition as reported by Shultz and co-workers (14).

None of the analysed compounds was detected in the blank sample (pure solvent treated similarly as the fish samples) corresponding to the HPLC first fractions of the perch samples.

However the blank sample representing the second fractions was contaminated. Therefore concentrations of xenobiotica of these fractions are not reported.

Two pikes (*Esox lucius*) from lake Baltezers were selected for qualitative analysis. All lipid material (1.75 g) extracted from the muscle of both pikes was pooled in a single sample. The extraction and work-up procedure of this sample was essentially the same as described above (method 2), except for the following differences. No internal standards were added to the extracted material. The lipid material was divided into portions of 250 mg to improve lipid removal and each of the seven portions was run on the GPC system. The OHS fractions were pooled again prior to separation by the Nucleosil-NO_2 column into three fractions. All three fractions were qualitatively analysed by GC-MS (EI and NICI).

RESULTS

The concentrations of total PCB and DDE of the pooled perch samples are shown in Table 2.

Table 2 The concentrations of total PCB and DDE, based on lipid weight, in pooled perch samples from Latvian lakes and rivers. Locations in the rivers: a - upstream Riga; b - near Bauska; c - near Jurmala.

No.	Location	Lipid content %	Total PCB ng/g	DDE ng/g
	Lakes:			
1	Alauksts	0.89	230	110
2	Inesis	0.97	590	300
3	Rusons	0.76	1200	770
4	Engures	0.77	350	79
5	Baltezers	0.77	790	220
6	Raznas	0.77	280	200
	Rivers:			
7	Daugava (a)	0.82	940	210
8	Lielupe (b)	0.75	200	88
9	Lielupe (c)	0.73	1400	340

The total ion chromatogram (TIC), determined in the NICI mode, of the pike muscle sample first fraction was dominated by PCB. A number of peaks of polybrominated diphenyl ethers (PBDE) were present in the first and second fractions. Hexachlorobenzene, the DDT family compounds, and, notably, the recently described environmental contaminant BCPS (6) were tentatively identified. Structures of numerous other substances were indicated: octachlorostyrene (OCS), several congeners of Chlordane, and others. However, it should be stressed, that the identity of these compounds have not been confirmed by comparison to the corresponding standards. Several substances, observed in the total ion chromatograms, have not yet been identified. More details will be presented at the workshop regarding OHS in pike from lake Baltezers.

CONCLUSIONS

According to the present results the background levels of PCB in perch in Latvian lakes is between 200 and 400 ppb (based on lipid weight). The concentrations of PCB and DDE in Latvian lakes, as shown by analysis of perch homogenates, are in the same range as in perch from e. g. Swedish lakes (15). Excluding lake Rusonu, the highest PCB concentration was found in the perch from lake Baltezers (Table 2), which is located in the vicinity of the industrialised Riga area (Figure 1). Similarly PCB concentration in the perch caught in river Daugava just upstream Riga is notably higher then those in the lakes of rural areas. This study shows, that Riga and its surroundings is the most polluted area in Latvia, concerning PCB and possibly other OHS.

A large number of environmental contaminants are present in the Latvian environment, as well as elsewhere in the Northern hemisphere. PBDE, tentatively identified in the pike sample, are widespread environmental contaminants, which are used as flame retardants (16). Octachlorostyrene is an indicator of inadequate regional combustion or long range transport of this compound.

The present study may serve as a base for future work on analysis of environmental contaminants in Latvia. It is of interest to select e.g. two of the lakes to be included in a monitoring programme that also should involve coastal areas of Latvia in order to detect any changes to concentrations of PCB, DDT, PBDE, and BCPS. The perch may serve as a monitoring species since we now have some rather extensive analytical data on this species (partly unpublished).

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