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Metals and Organochlorine Compounds in Fish from Latvian Lakes

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Organochlorines and metals have high toxicity and worldwide distribution in the aquatic environment. They are known to accumulate in sediments. In mollusks and fishes, they are bioconcentrated, even when released in minute quantities into the environment. This is important, as these chemicals have an adverse impact on species diversity, and accumulate in humans when seafood is consumed (Jaffar et al. 1988; Ruiter 1995). The nature and extent of accumulation and impact of persistent xenobiotics in water bodies depend on their sources; i.e. whether they are from industry, agricultural activities, transboundary transport with air masses (Sharif et al. 1993), geochemically determined elevated concentrations, or dissolution of mineral phases due to acidification of the environment (Iivonen et al. 1992). It is, therefore, important to analyze persistent xenobiotics (metals and organochlorines) in biota, even if the impact of anthropogenic pollution is minimal. Metal and organochlorine concentrations in fish in Latvia have never been reported. In Latvia direct point sources are found only in a few regions, while dominant metal sources in many cases appear to be transboundary transport of pollutants (Nikodemus and Brumelis 1994). Comparatively high biota contamination levels (HELCOM 1996) have been found in neighbouring countries (Sweden, Poland, Russia and Denmark), but data for comparison in Latvia is lacking.

The objectives of the present study were to determine metal (Pb, Cu, Co, Ni, Cd, Mn, Zn, Hg) and organochlorine (PCB, DDT and α-HCH) concentrations in water, sediments and 2 fish species (perch and pike) in lakes of Latvia with minimal levels of anthropogenic impacts and in polluted sites, to evaluate environmental contamination levels and to the study accumulation of persistent xenobiotica in aquatic biota.

MATERIALS AND METHODS

Sixteen lakes situated throughout Latvia (Figure) were studied during June-August in 1994-1996. The lakes were chosen to represent the range of existing natural and anthropogenic environmental factors. Water samples were collected from a depth of 0.5 m in 250 ml polypropylene (Nalgene) bottles. Basic water chemistry was determined using standard methods (Fresenius et al. 1988). Samples for metal analysis were preserved by the addition of 1 ml 35 % suprapur HNO_3 (Merck).

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Metal concentrations in 0.45 µm filtered water were determined after pre-concentration using dithizone (extraction of Pb, Cd, Cu, Zn, Co dithizonate from a citrate-buffered medium at pH 9 with chloroform) with re-extraction to the aqueous phase by 1M HCl Fresenius et al. 1988). The upper sediment layer (0 - 2 cm) was sampled by Ekman grab. The lyophilized and fractionated (< 63 µm) samples (- 10 g) were digested in 15 ml conc. HNO_3 and then by 10 ml conc. HNO_3 + 5 ml 60 % $HClO^4$ (Van Loon 1985).

Three to fifteen both male and female fish (Northern pike *Essox lucius L.*, and perch *Perca fluviatilis L.*) were caught using gill nets. Each fish weighed 90± 5 g. Muscle before analysis was dried at 105°C for 48 h and 0.2 g sub-samples were decomposed with 2 ml conc. HNO_3 and 0.5 ml H_2O_2 (Van Loon 1985). Concentrated samples were diluted to 25 ml (10 ml $KMnO_4$ added to 10 ml sub-samples for Hg analysis). Metal concentrations were expressed as fresh weight. Metal concentrations were determined by furnace atomic absorption (Perkin Elmer 1100 equipped with a HGA graphite furnace system) and Hg by cold vapor atomic absorption (Perkin Elmer Mercury Analysis System) analysis. The identification limits were (µg/l in 100 µ1 measuring solution): Cd-0.003; Co-0.02; Cu-0.02; Mn--0.01; Zn-0.001; Pb-0.05; Hg- 0.01. For analytical quality control, Dogfish Muscle Tissue (DORM-l NRC, Canada) was used. The analysis results of SRM were all within the 95 % confidence level of the SRMs. The normal distribution of variables was tested using the Kolmogorov-Smirnov test. Metal bioconcentration patterns were investigated using correlation analysis as described by Babukutty and Chacko (1995).

For organochlorine analysis, six fish from each sampling station were used. Ten g of muscle tissues were homogenized to extract lipids with acetone, acetone/hexane (50/50) and hexane according to the method of Larsson et al. (1991). The extract after the phase separation was concentrated to 10 ml in a water bath under a gentle stream of N_z. H_2SO_4 destruction was carried out as described by Larsson et al. (1991). The cleaned extracts were analyzed for organochlorines by capillary gas chromatography/ECD on a Hewlett Packard 5980 gas chromatograph. A 30 m DBl capillary column (i.d. 0.32 mm) was used with H_2 (1 ml/min) as a carrier gas and N_2 as the make -up gas (30 ml/min). The temperature regime was 80°C; 4°C/min to 200°C; 3°C/min to 230°C and 15 °C/min to 250°C over 5 minutes. Clophen A 60 was used as a standard.

RESULTS AND DISCUSSIONS

The selected sixteen lakes were chosen because of their water and community composition, pollution sources common and representative to Latvia and the low pollution background levels representative for Northern Europe. The basic water chemistry data of the surveyed lakes are sumarized in Table 1. Some of the lakes in the study area lack major known point sources of anthropogenic pollution; hence their metal concentrations were due to local geochemistry (natural sources) and transboundary transport, and their waters may be regarded as pristine. Anthropogenic pollution sources are evident only for Lake Liepajas, Lake Kišezers and Lake Juglas. Waters of all studied lakes are medium hard to hard (with the exception of brown-water lakes), and nutrient levels in them are generally low (Table 1). Water pH was neutral to alkaline (6.8-7.8), except for brown-water lakes (pH 3.4-6.2).

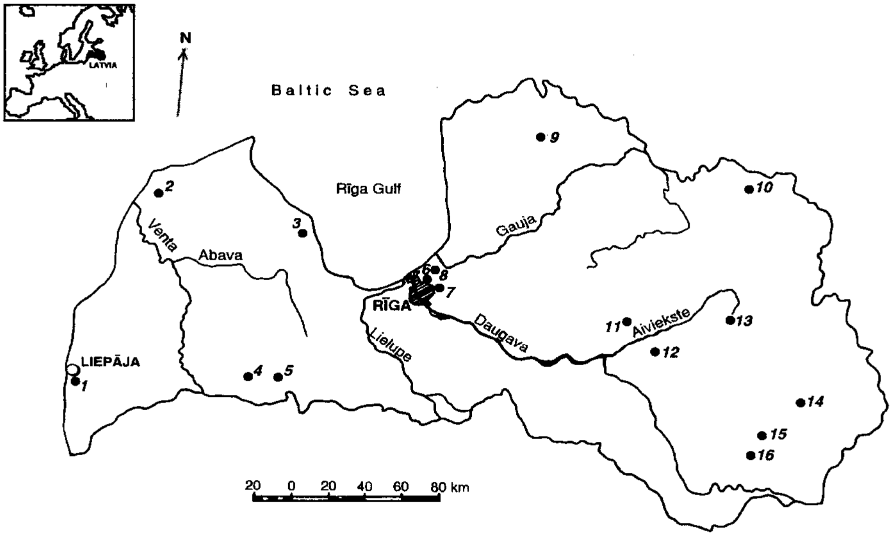

Figure. Locations of sampling sites in Latvia. 1-Lake Liepajas; 2-Bušnieku; 3-Engures; 4-Cieceres; 5-Zebrus; 6-Kišezers; 7-Juglas; 8-M.Baltezers; 9-Burtnieku; 10-Aluksnes; 11-Dreimanu; 12-Tolkojas; 13-Lubans; 14-Raznas; 15-Rušonu; 16-Certogs

Table 1. Sampling stations (1993-1995) and mean water chemical composition

Sampled lake	pH	Ca^{+2}, mg/l	SO_4^{-2}, mg/l	Pb, µg/l	Cu, µg/l	Cd, µg/l	Ni, µg/l	Zn, µg/l	Mn, µg/l	Co, µg/l
Burtnieku	8.06	34.0	18.9	0.06	0.32	0.01	0.23	3.00	1.50	0.04
Juglas	7.40	70.5	57.6	0.17	0.96	0.04	0.73	3.45	4.50	0.09
Ķīšezers	7.70	59.5	62.6	0.18	0.93	0.05	0.85	2.87	3.50	0.09
M.Baltzers	8.10	59.0	48.0	0.04	0.48	0.02	0.18	4.35	2.25	0.05
Rušons	7.40	42.6	11.6	0.03	0.35	0.01	0.24	5.12	5.60	0.06
Rāznas	7.60	35.5	10.1	0.03	0.32	0.01	0.28	3.28	3.00	0.05
Liepājas	7.60	52.9	19.0	0.14	0.79	0.08	0.85	4.07	1.80	0.09
Bušnieku	7.30	28.0	20.0	0.09	0.65	0.03	0.43	3.29	7.90	0.06
Zebrus	7.90	31.1	29.6	0.06	0.54	0.01	0.23	6.80	3.50	0.04
Cieceres	7.30	32.6	27.5	0.05	0.52	0.01	0.15	4.25	3.05	0.03
Engures	8.00	28.9	16.0	0.09	0.61	0.04	0.21	3.55	4.20	0.08
Alūksnes	7.60	25.5	12.0	0.08	0.55	0.03	0.38	2.90	4.60	0.06
Dreimaņu	7.80	52.3	16.0	0.04	0.43	0.02	0.29	3.10	4.15	0.07
Čertogs	6.90	4.4	7.9	0.08	0.59	0.03	0.31	4.25	7.00	0.05
Tolkojas	6.50	1.5	9.0	0.08	0.61	0.04	0.25	3.90	3.50	0.04
Lubāns	7.90	74.1	38.9	0.06	0.48	0.03	0.29	3.20	4.00	0.05

Generally, the pollution levels, as indicated by metal concentrations in Latvian lakes, in comparison with other regions of the world, are relatively low (Klavinš et al. 1995).

Table 2. Characteristics of lake sediments

Lake	NO^-_3, mg/kg	NH^+_4, mg/kg	Pb, mg/kg	Cu, mg/kg	Ni, mg/kg	Cd, mg/kg	Zn, mg/kg	Mn, mg/kg
Burtnieks	8.5	1.8	18.75	4.37	4.06	0.41	23.75	31.25
Juglas	5.5	2.5	68.71	15.34	11.18	2.08	78.43	79.12
M.Baltezers	30.3	3.1	28.31	6.15	4.18	0.96	25.65	54.12
Engures	3.7	4.7	15.32	13.52	10.75	1.53	22.53	78.36
Rušonu	6.2	2.5	19.44	3.04	3.25	0.42	48.17	28.47
Rāznas	14.9	3.8	16.67	6.15	4.15	0.43	64.31	48.31
Čertogs	2.5	6.7	21.43	9.13	7.14	0.53	36.54	58.43
Alūksnes	18.2	21.8	19.35	8.39	9.35	1.58	25.39	41.21
Lubāns	9.3	11.4	12.35	3.76	3.31	0.76	65.24	41.55
Zebrus	3.6	6.2	13.24	1.33	2.48	0.41	29.73	37.85
Cieceres	11.8	9.5	14.40	6.48	6.42	036	56.38	72.56
Bušnieku	5.21	6.8	35.21	9.58	13.27	2.35	49.24	28.27
Tolkojas	3.8	12.4	8.45	2.85	3.11	0.28	18.32	14.28
Ķīšezers	12.7	15.3	83.21	16.34	6.74	2.75	69.73	81.17
Liepājas	8.6	11.8	55.62	9.81	6.95	5.31	68.35	49.55
Dreimaņu	3.4	1.1	6.64	4.32	2.04	0.43	15.32	15.38

Metal concentrations in the upper (0-2 cm) layer of lake sediments vary greatly within Latvia. A distinct group of sediments are those from Lake Liepajas, Lake Juglas and Lake Kišezers which are polluted by anthropogenic sources. Metal concentrations in the other lakes are much lower, but metal concentrations in brown-water lakes (Tolkojas and Dreimanu) are the lowest.

Metal concentrations in pike and perch muscle also varied significantly. Higher concentrations were found in fish from polluted lakes (Kišezers, Juglas and Liepajas). Increased Pb concentrations were found in Lake Baltezers close to highways, but possible point sources may also exist. The largest variations in metal concentrations were observed for Pb, Cu, Co and Ni which clearly are of anthropogenic origin. Concentrations of Zn and Mn were less variable, except in Lakes Kišezers and Liepajas which receive industrial waste. Increased Mn and Zn concentrations were found in several lakes in which Pb, Cd, Cu, Ni, Co were at background levels. This could be due to natural Mn and Zn deposits. Acidification of surface waters increases metal concentrations in fish tissues (Iivonen et al. 1992, Rask and Metsalu 1991). However, in naturally acidic brown-water lakes with water pH 3.4-6.2, there was no significant increase of metal concentrations in biota mainly due to binding of metals by dissolved organic matter (Klavinš 1995).

Generally, increased metal concentrations in water resulted in increased metal concentrations in biota. To evaluate metal bioconcentration patterns, bioconcentration factors (BCR, Babukutty and Chacko 1995) and their relationships to metal concentrations

Table 3. Concentrations of metals (means and standard deviations) in muscle of Northern pike (*Essox lucius L.*) and perch (*Perca fluviatilis L.*) from lakes in Latvia (mg/kg fresh wt.)

Lake	Species	n	Co	Cu	Ni	Pb	Zn	Cd	Mn	Hg
Alūksnes	*E. lucius*	6	0.27±0.08	0.53±0.08	0.41±0.08	1.12±0.30	16.03±3.40	0.08±0.01	2.89±0.74	-
	P. fluviatilis	12	0.32±0.09	0.58±0.09	0.87±0.09	1.86±0.14	11.27±3.26	0.07±0.01	2.78±0.89	0.12 ±0.01
Cieceres	*P. fluviatilis*	7	0.37±0.05	0.64±0.07	0.86±0.07	0.91±0.07	21.43±2.13	0.07±0.01	2.76±0.65	0.43± 0.03
Engures	*E. lucius*	14	0.26±0.04	0.94±0.06	0.27±0.03	0.93±0.11	9.67±1.18	0.06±0.02	1.93±0.37	-
	P. fluviatilis	5	0.21±0.05	0.92±0.06	0.25±0.04	0.97±0.07	11.27±2.18	0.05±0.01	1.99±0.26	0.16± 0.02
Burtnieku	*E. lucius*	32	0.25±0.03	0.56±0.05	0.25±0.09	0.65±0.07	10.85±1.89	0.05±0.01	1.86±0.54	-
	P. fluviatilis	16	0.22±0.04	0.52±0.06	0.28±0.07	0.66±0.08	8.88±1.34	0.06±0.03	1.75±0.51	0.34± 0.03
M.Baltezers	*P. fluviatilis*	8	0.72±0.11	0.63±0.05	0.39±0.03	1.64±0.15	19.14±1.89	0.09±0.02	3.24±0.71	-
Ķīšezers	*P. fluviatilis*	6	1.38±0.21	0.88±0.12	0.89±0.14	2.62±0.42	26.25±2.67	0.10±0.02	4.13±0.98	-
Juglas	*P. fluviatilis*	24	1.95±0.34	1.21±0.18	0.86±0.09	4.12±0.34	21.09±3.10	0.09±0.03	3.17±0.76	-
Liepājas	*P. fluviatilis*	5	3.05±0.28	2.31±0.13	0.85±0.16	3.29±0.21	29.13±3.18	0.13±0.05	8.23±0.72	-
Rāznas	*E. lucius*	16	0.24±0.03	0.38±0.03	0.28±0.06	0.48±0.04	10.15±1.28	0.04±0.01	1.15±0.23	-
	P. fluviatilis	15	0.19±0.04	0.32±0.05	0.32±0.07	0.42±0.04	9.26±0.98	0.04±0.01	1.31±0.28	0.05± 0.01
Rušonu	*E. lucius*	12	0.28±0.03	0.34±0.05	0.36±0.04	0.53±0.06	13.18±1.37	0.04±0.02	1.24±0.15	-
	P. fluviatilis	14	0.19±0.02	0.28±0.04	0.29±0.04	0.61±0.05	12.01±1.82	0.05±0.02	1.47±0.15	-
Lubāns	*P. fluviatilis*	5	0.31±0.02	0.32±0.02	0.34±0.06	0.46±0.05	13.14±1.72	0.05±0.02	1.47±0.19	0.18 ±0.01
Dreimaņu	*P. fluviatilis*	5	0.18±0.03	0.19±0.01	0.21±0.03	0.28±0.03	14.03±1.12	0.04±0.02	0.64±0.11	-
Bušnieku	*P. fluviatilis*	5	0.95±0.03	0.87±0.03	0.68±0.05	1.13±0.14	13.18±2.10	0.09±0.04	6.54±0.37	-
Zebrus	*P. fluviatilis*	6	0.46±0.02	0.34±0.03	0.42±0.04	0.93±0.09	10.87±1.67	0.07±0.01	2.15±0.17	-
Čertogs	*P. fluviatilis*	3	0.21±0.03	0.28±0.02	0.31±0.03	0.54±0.10	8.75±1.10	0.03±0.01	1.14±0.14	-
Tolkojas	*P. fluviatilis*	4	0.27±0.04	0.31±0.03	0.26±0.03	0.61±0.06	7.56±0.74	0.03±0.01	1.21±0.11	-

in different phases were studied.
$BCR = M_{soft\ tissues}/M_{diss}$ where: M_{diss} - metal concentration in the dissolved phase; $M_{soft\ tissue}$ - metal concentrations in soft tissues.

Table 4. Correlation coefficients between metal concentration in water (Me_{aq}, μg/l) and bioconcentration ratio (BCR)

	Co_{aq}	Pb_{aq}	Cd_{aq}	Zn_{aq}	Mn_{aq}	Ni_{aq}	Cu_{aq}
Co_{BCR}	0.725**						
Pb_{BCR}	0.148	0.109					
Cd_{BCR}	-0.091	-0.069	-0.799**				
Zn_{BCR}	0.557*	0.683**	0.436*	-0.367*			
Mn_{BCR}	0.752**	0.745**	0.190	-0.035	-0.557*		
Ni_{BCR}	0.153	-0.035	0.071	0.188	0.338	0.226*	
Cu_{BCR}	0.674**	0.624**	0.345	-0.050	-0.408	0.225	0.515*

n = 34; *$p < 0.01$; **$p < 0.001$

The correlation coefficients between the metal concentrations in fish and waters are presented in Table 4. The metal BCR and aqueous concentration were found to be significantly correlated for Co, Ni, Cu. However, BCR was found to be negatively correlated with metal aqueous concentrations of Cd, Zn and Mn. This may indicate that metal total concentrations can be regarded as a poor estimates of metal bioconcentration in biota (Hare and Tessier 1996), especially if concentrations of natural organic and particulate matter in waters are high (as in the case of studied lakes). Accumulation of metals in fish tissues depends on metal type, interaction with natural factors, ability to bind metals in forms that are not biologically available, and the character of mechanisms determining bioaccumulation and excretion of metals.

Metal concentrations in fish tissues depend on the type of tissue, fish species, size and age (Taylor et al. 1995) but the major factor affecting metal concentration in the environment is environmental pollution. Cu in *Gadus morhua* ranged from 0.2- 1.0 mg/kg (Harms 1975). Zn concentrations in rainbow trout muscles can be as low as 25.1 mg/kg (Carpene et al. 1990). Also, metal concentrations found in Turkey (Gümgüm et al. 1994) and in the Baltic Sea (HELCOM 1996) were much higher than those found in this study.

Similar conclusions may be reached by comparing concentrations of organochlorines in different environments (Table 5,6). Generally, concentrations of various organochlorines in fish tissues were correlated; higher PCB concentrations are associated with higher DDT and α-HCH concentrations. The general levels of organochlorine concentrations in fish tissues found in Latvia are much lower than those found in other studies, even in the Baltic Sea area. Still in lakes (Kišezers, Juglas, Liepajas) where direct anthropogenic impacts are evident, concentrations similar to those found in contaminated regions are found. Thus, the obtained results indicate that the transboundary transport of organochlorines is the dominant source in Latvia, but in several places also the presence of higher pollutant concentrations is evident, due to the presence of point sources.

Table 5. Concentrations (mean and range) of persistent organochlorines (ng/g fresh weight) in muscle tissues of Northern pike *(Essox lucius L.)* from lakes in Latvia

Lake	Σ PCB	DDT	α-HCH
Cieceres	0.94 (0.92-0.98)	1.26 (1.06-1.51)	0.014 (0.012-0.015)
Dreimaņu	0.85 (0.82-0.87)	0.96 (0.90-0.98)	0.011 (0.009-0.015)
Engures	1.77 (1.23-1.95)	4.35 (4.01-4.55)	0.008 (0.006-0.009)
Burtnieku	1.73 (1.67-1.87)	4.21 (4.12-4.34)	0.009 (0.007-0.010)
Ķīšezers	13.35 (11.02-15.82)	12.24 (9.43-14.65)	0.031 (0.028-0.034)
Juglas	7.82 (7.31-7.90)	9.12 (8.12-10.18)	0.024 (0.020-0.028)
Liepājas	7.25 (6.32-9.05)	8.43 (6.32-9.63)	0.028 (0.022-0.030)
Rāznas	1.40 (1.34-1.55)	4.75 (4.12-5.21)	0.014 (0.012-0.018)
Rušonu	0.93 (0.83-0.98)	9.67 (9.05-9.89)	0.010 (0.008-0.012)
Lubāns	1.71 (1.23-1.93)	5.84 (5.12-6.33)	0.015 (0.013-0.016)
Zebrus	2.10 (2.02-2.34)	6.02 (5.45-6.62)	0.012 (0.010-0.014)

Table 6. Comparison of organochlorine concentrations in fish muscle tissues (ng/g fresh weight)

Substance	NW Atlantic, 1991[a]	Baltic Sea, 1983[b]	Bothnian Bay, 1993[c]	Finland, 1978[a]	This study
Σ PCB	<0.2-2	58 (8-210)	4-20	32	3.62
DDT	<0.02-2	10 (2-58)	1-8	9 (6-12)	6.07
α-HCH					0.016
ΣHCH	<0.02-2	13 (5-48)			

[a]Hellou et al. 1993; [b]Falandusz 1986; [c]HELCOM 1996

The persistent contaminant levels in waters, their sediments and biota in Latvia are much lower (excepting of few evidently contaminated sites) than those in relatively unpolluted lakes in other countries. Therefore, the pollution levels in Latvian lakes can serve as background levels for Northern Europe.

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