Contamination of Fish by PCDDs and PCDFs in the Kymijoki River and its Estuary

Markku, Korhonen, Finnish Environment Institute, Impacts Research Division, P.O.Box 140, FIN-00251 Helsinki, Finland,
Matti Verta, Finnish Environment Institute, Impacts Research Division, P.O.Box 140, FIN-00251 Helsinki, Finland and
Terttu Vartiainen, National Public Health Institute, Division of Environmental Health, P.O.Box 95, FIN-70701 Kuopio, Finland

Abstract

Concentrations of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) were studied in several fish species: burbot (*Lota lota*), pike (*Esox lucius*), perch (*Perca fluviatilis*), pike perch (*Stizostedion lucioperca*), bream (*Abramis brama*) and Atlantic salmon (*Salmo salar*), in the contaminated Kymijoki River and its estuary. The river has been heavily polluted by effluents from pulp mills and the chemical industry. The levels were low, approximately 1 ITEQ pg/g, fresh weight (fw) or less, in muscle in all other fishes exept salmon. The lipid content in salmon muscle was more than 10 times that of other fishes. The reason for higher bioaccumulation values in salmon was the high lipid content. Concentrations in the liver and spawn were higher mainly also because of the higher lipid content. The main congeners found in fishes as calculated ITEQ fw were 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,3,7,8-PD.

Introduction

The Kymijoki, the fourth largest river in Finland, has a drainage basin of 37,160 km^2, and is situated in the south-eastern corner of the country (Fig. 1). The maximum water discharge is about 700 m^3/s with an average discharge of about 300 m^3/s. The average residence time is only three to four days.

The area has a long tradition in the paper industry and the river has been heavily polluted by pulp mill effluents as well as the chemical industry. Inspite of the recent positive development of cleaner industrial processes, signs of past chemical contamination are still seen in the bottom sediments of the river[1]. Recent findings in sediments from the river show extremely high concentrations of PCDD/Fs, which occurred as impurities of a wood preservative Ky-5, manufactured in Kuusankoski on the upper Kymijoki from the 1940s to 1984. The main impurities of the product were 123468-HxCDF, 124678-HxCDF, 124689-HxCDF, 1234689-HpCDF and 12346 78-HpCDF[2].

High levels of PCDDs and PCDFs in sediment were found in the Pilkanmaa - Koria - Myllykoski[1] area as well as gill abnormalities in hydropsychid larvae (Trichoptera and Hydropsychidae) in the Langinkoski area[3] near the river outlet. These findings initiated a joint project on 'Occurrence and impacts of organochlorine compounds and heavy metals in the river Kymijoki - (KYPRO)'. In this paper we present some preliminary results of PCDD/F concentrations in fish caught from several locations along the Kymijoki River and its estuary in the Gulf of Finland.

Experimental Methods

The fish were caught in 19 localities along the Kymijoki River and its estuary by the local fishing authorities with the help of several local fishermen (Fig 1). Burbot were taken during the winter (January - February, 1996), perch, pike perch, pike and bream in the spring and salmon in the summer (May - July, 1996). The fish were deep-frozen within one day and transported to Helsinki to the laboratory of the Finnish Environment Institute (FEI).

Length, weight, sex and age of fish were measured and muscle, liver and spawn samples were taken from half thawed fish and the homogenates were prepared for the chemical analyses. Determination of PCDDs and PCDFs was carried out in National Public Health Institute, Division of Environmental Health, Kuopio.

In the beginning of the determination of PCDD/Fs about 10 g of freeze-dried fish sample was soxhlet extracted for 24 h with toluene. Fat content was weighed and the raw extract was purified over a silica gel column, fractionated using an activated carbon column containing Celite, and further cleaned with an activated alumina column. The analyses were performed with a fused silica capillary column (60 m, DB-DIXIN) and a VG 70 SE mass spectrometry (resolution 10,000). A total of 16 13C-PCDD/Fs congeners (100 pg/sample, Cambridge Isotope Laboratories) were used as internal DIOXIN standards, added to the samples before silica gel column extraction. To test the recoveries, 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD were added to the final concentrate before GS-MS analyses.

Results and Discussion

The total PCDD and PCDF concentrations were low, about 1 ITEQ pg/g fw, or less, in the muscle of burbot, pike and pike perch (Table 1, Fig 2) even very near the pollution source Kuusankoski (Keltti). When calculated by lipid weight (lw), the concentrations of PCDDs and PCDFs were at the same level in salmon as in other fish. However, when calculated by fresh weight the levels in salmon were about 10 times higher. The age of fish studied varied most in bream (12-28 years old) and perch (4-12), while the age of other species varied little (burbot 4-8, pike 4-9, pike perch 5-7 and salmon 4 years).

The PCDD/F accumulation in liver was particularly high in burbot (Table 1, Fig 3). This was due to a very high lipid content in the burbot liver. A clearly lower accumulation of PCDD/Fs was observed in spawn than in the liver in burbot. In contrast, the accumulation of PCDD/Fs was clearly stronger in spawn than in the liver of bream. This could not be explained by the - differences in lipid content (Table 1).

The congeners that showed the highest ITEQ values were (Fig 4) 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,3,7,8-PD. The amount of 2,4,7,8-TCDF was at the same level in pike muscle as was analysed three years earlier[4]. Clearly smaller amounts were found in congeners 2,3,4,7,8-PF and 1,2,3,4,6,7,8-HpF (as ITEQ), the latter being the main impurity of Ky-5 manufacturing.

In the estuary of the Kymijoki River as well as in the open sea area the Ky-5 impurity congener 1,2,3,4,6,7,8-HpF could only be observed in burbot in Ahvenkoskenlahti Bay (Fig 5). The congeners 2,3,4,7,8-PF and 1,2,3,7,8-PD had most strongly accumulated in salmon. In all other species the dominating congener was 2,3,7,8-TCDD.

Table 1. The amount of fish studied (n) and homogenates (=analyses; h), lipid % (l), weight (g), PCDD/PF ITEQ pg/g fw and 1,2,3,4,6,7,8-F pg/g fw.

	n/h	l	g	PCDD/PF (ITEQ)	1,2,3,4,6, 7,8-F
Kymijoki river					
burbot/muscle	18/5	0.3	700	0.7	5 -10
burbot/liver	18/5	24.6	700	122	20 -1400
burbot/spawn	5/2	10.1	400	22.8	150-250
pike/muscle	12/4	0.4	950	0.9	0.8
pike/liver	12/4	4.1	950	5.1	11.8
pike/spawn	5/2	1.1	850	6.4	10.2
perch/liver	8/1	3.8	22	3.9	23.9
perch/spawn	8/1	4.1	22	2.7	1.5
bream/muscle	1/1	1.3	1350	1.0	17.4
bream/liver	1/1	3.0	1350	4.1	106
Kymijoki Estuary					
burbot/muscle	31/10	0.3	950	0.4	0.5
burbot/liver	2/2	31.2	1350	82.4	75
burbot/spawn	2/2	7.6	1350	16.0	5
perch/muscle	6/1	0.4	250	0.4	0.2
perch/spawn	6/1	4.0	250	6.1	0.2
bream/muscle	8/2	0.3	1000	0.4	0.2
bream/liver	5/1	1.8	960	4.9	7.2
bream/spawn	5/1	3.0	960	13.1	2.9
pike perch/muscle	8/2	0.4	600	0.3	0.1
pike perch/liver	8/2	1.1	600	4.0	0.6
pike perch/spawn	2/1	7.8	570	4.6	0.1
salmon/muscle	3/3	7.0	4700	7.1	0.1

The concentrations of PCDDs and PCDFs in muscle in all other species, apart from salmon, were low. The Nordic Council of Ministers have recommended the Tolerably Daily Intake (TDI) of 35 TEQ pg/kg body weight/week[5]. According to these recommendations an individual weighing 70 kg can have a daily intake of about 350 g of all other studied fish muscle except salmon. The maximum daily meal of salmon is about 40 g. The calculated maximum of liver and spawn of pike, pike perch, perch and bream is about 10 times smaller than the maximum of the muscle of other species other than salmon. Because of the very high lipid content in the liver of burbot, these recommended maximum consumption values can be as much as 100 times smaller in burbot liver.

Acknowledgements

The authors wish to thank the steering group of the KYPRO-project and express gratitude for the financial support of the Ministry of the Environment and UPM-Kymmene.

Literature Cited

(1) Koistinen, J.; Paasivirta, J.; Suonperä, M. and Hyvärinen, H. *Env. Sci. and Tech,* Vol. 29, 1995, 2541-2547.
(2) Humppi, T.; Heinola, K. *J. Chromatogr.* 331 . 1985, 410-418.
(3) Vuori, K. M. *Univ. of Joensuu Publ.* no 32. 1995
(4) Koistinen,J.; Paasivirta,J. and Lehtiperä,M. *Chemosp.* Vol 27. Nos 1-3. 1993, 149-156.
(5) Nordisk dioxinriskbedömning. *NORD* 1988:49.

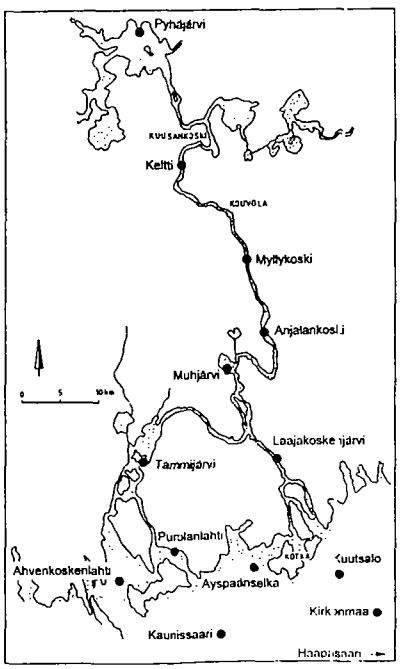

Figure 1. The map of the study areas downstream of the Kymijoki River and its estuary.

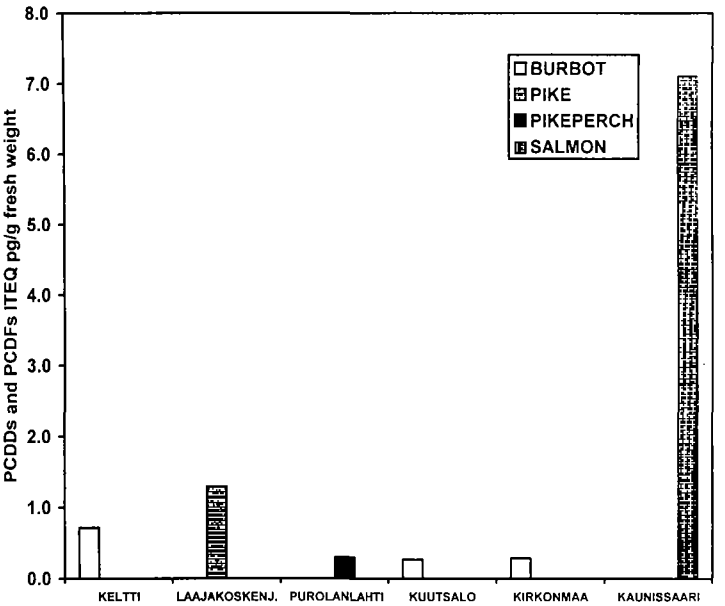

Figure 2. The concentrations of PCDDs and PCDFs (ITEQ pg/g, muscle, fw) in different fish species in the Kymijoki River and its Estuary.

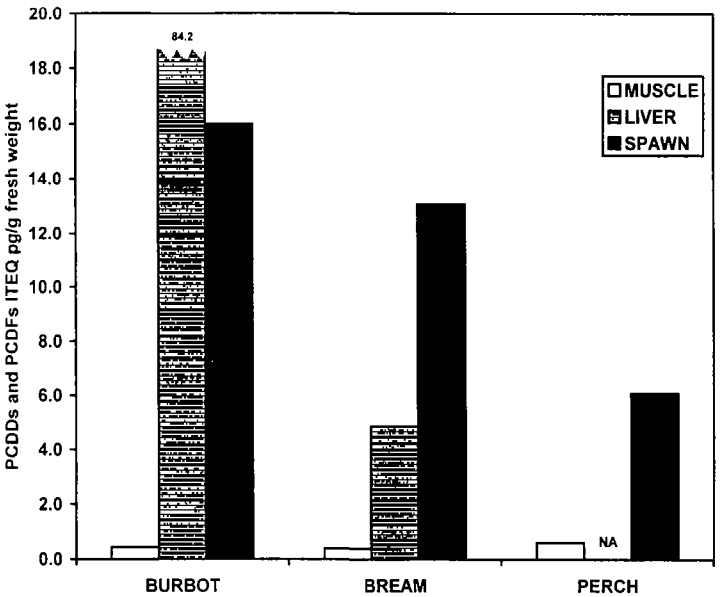

Figure 3. The concentrations of PCDDs and PCDFs (ITEQ pg/g, fw) in burbot, bream and perch muscle, liver and spawn in Ahvenkoskenlahti Bay.

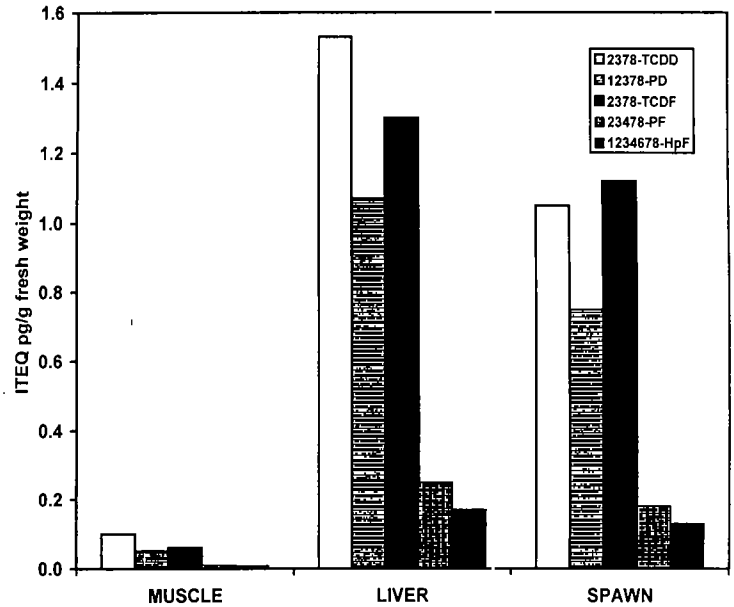

Figure 4. The most toxic PCDDs and PCDFs and also 1234678-HpF (ITEQ pg/g, fw) in pike muscle, liver and spawn in Myllykoski, Kymijoki River.

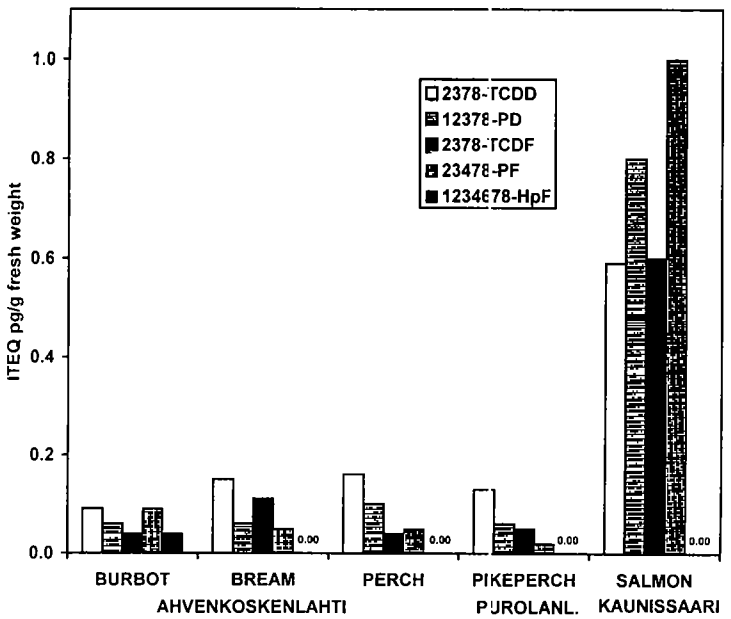

Figure 5. The most toxic PCDDs and PCDFs and also 1234678-HpF (ITEQ pg/g, muscle, fw) in different fish species in the estuary of the Kymijoki River.