

## Human exposure to Ky-5 originating PCDD/Fs in Kymijoki area, Finland

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### Introduction

Fourth largest river in Finland, Kymijoki, situated in the south eastern corner of the country has been heavily polluted by pulp, paper and chemical industry. A wood preservative, Ky-5 was manufactured from 1940s to 1984 in Kuusankoski, situated 30-35 kilometers upstream from the Gulf of Finland. Findings in river sediments south from Kuusankoski reveal extreme concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). PCDD/F compounds, especially higher chlorinated dibenzofurans occur as impurities of KY-5 (1). In order to evaluate the possible human exposure to Ky-5 PCDD/F impurities via food chain, we examined PCDD/F concentrations in sediment, fish, human milk and human blood samples. This paper reports levels of the most abundant PCDF impurity congeners (1,2,3,4,6,7,8- HpCDF and OCDF) and their percentage of 2,3,7,8-substituted congeners.

### Materials and methods

Sediment samples were collected from 16 locations with a pistonless corer and sliced in the field before transportation to the laboratory. Along the river area four species of fish were caught: perch (*Perca fluviatilis*), northern pike (*Esox lucius*), bream (*Abramis brama*) and burbot (*Lota lota*). In addition Baltic herring (*Clupea harengus membras*), pike perch (*Stizopedion lucioperca*) and salmon (*Salmo salar*) were caught from the Gulf of Finland near river Kymijoki estuary. Muscle PCDD/F concentrations of fish were determined. Mother milk samples from primiparae mothers and fishermen blood samples along the river area and coastal area of the estuary of Kymijoki river were collected.

HRGC/HRMS analysis of PCDD/Fs in sediment, fish and human fat samples are described in more detail in references 2 and 3. The median percentage of 1,2,3,4,6,7,8-HpCDF (HpCDF) and OCDF is calculated from the total concentration of 2,3,7,8-substituted congeners.

Mann-Whitney U nonparametric test was used to test the statistical significance of human results.

## Results and Discussion

A summary of the percentages of HpCDF and OCDF in sediment, fish and human samples in three districts in Kymijoki river area is presented in Table 1.

In impurities of Ky-5 product the percentages of HpCDF and OCDF are 61 and 25, respectively. In Kymijoki river sediments the percentages of HpCDF and OCDF were similar to Ky-5 and in most of the sampling places these two congeners contributed 97-99% of the total load of 2,3,7,8-substituted PCDD/Fs. In the river area the concentrations of HpCDF and OCDF varied from 15.2 to 148,000 ng/g and there was a declining gradient towards the Gulf of Finland. The concentrations of HpCDF and OCDF in the sediments of sea area varied from 0.29 to 17 ng/g, but the percentages were similar to river percentages. In sediment upstream from the Ky-5 manufactory HpCDF and OCDF covered only 10.3 % of the total concentration of 2,3,7,8-substituted congeners.

The percentages of HpCDF in fish species in the river area were between 13 and 64 and were higher than corresponding percentages in the coastal area. The percentages of OCDF in fish species in the river area were low and identical to upstream and coastal areas. One may conclude that because of congener specific differences in elimination and metabolism the percentages of HpCDF and OCDF are considerably lower in fish species than in sediments. The median concentrations of HpCDF in perch, pike, bream, and burbot in the river area were 0.42, 0.47, 0.66, and 7.5 pg/g f.w., respectively. The corresponding values in upstream area were 0.01, 0.02, 0.23, and 0.01, respectively and in coastal area 0.14, 0.10, 0.20, and 0.43, respectively.

The concentrations of HpCDF and OCDF in mother milk in river area were 3.87 and < 1 pg/g fat, respectively. In the coastal area the corresponding concentrations were 8.42 and 0.85, respectively. The differences were not statistically significant. These concentrations are similar to concentrations of HpCDF and OCDF measured in primiparae mother milks from Kuopio and Helsinki in 1992-94 (HpCDF 8.45 and 5.05 pg/g fat in Helsinki and Kuopio, respectively) (4). The percentages of HpCDF in mother milk in Kymijoki river area, coastal area, Helsinki, and Kuopio were equal; 2.04, 3.93, 2.28 and 2.45, respectively. Consequently there is no additional exposure of Kymijoki river area mothers to PCDD/F originating from Ky-5 production. Based on the questionnaire mothers at the area rarely eat Kymijoki fish.

Fishermen were chosen as another study group because of their frequent use of fish and consequently being exposed to PCDD/Fs. The concentration of HpCDF was the highest in the river area, 67.9 pg/g fat, 40.5 in coastal area, and 30.7 in upstream area. Between river area and upstream area the difference was statistically significant with p value 0.017. These concentrations are due to fish use and are considerably higher than values measured in males of the same age in the general population in Finland; 9.84 pg/g fat. The percentage of HpCDF in the river area is however only twice that in coastal area and in upstream area, table 1, and accounts only about 4 % of the total PCDD/F. The OCDF concentrations in blood were all under 1 pg/g fat. A small additional exposure to PCDD/Fs originating from Ky-5 production can thus be obtained if large amounts of Kymijoki fish is used for nutrition.

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Table 1. Median percentages of 1,2,3,4,6,7,8-HpCDF and OCDF in sediment, fish, and human samples in three areas in Kymijoki river area.

		n	1,2,3,4,6,7,8-HpCDF		OCDF	
			Median Percentage	Range	Median Percentage	Range
Upstream from Ky-5 Manufactory	<b>Sediment</b>	1	4.6		5.7	
	<b>Fish</b>					
	Perch	1	0.6		0	
	Pike	2	2.1	1.8-2.5	3.8	3.2-4.5
	Bream	1	0.7		0.3	
	Burbot	1	1.4		3.0	
	<b>Mothersmilk</b>	-				
	<b>Fishermen</b>	11	2.5	0.7-7.6	0.1	0-1.7
Downstream from Ky-5 Manufactory	<b>Sediment</b>	27	42	10-77	57	20-77
	<b>Fish</b>					
	Perch	3	18	17-46	3.7	3.3-22
	Pike	10	13	7.4-36	4.6	0-37
	Bream	5	21	18-72	2	1.5-4.1
	Burbot	6	64	55-69	5.0	2.8-14
	<b>Mothersmilk</b>	12	2.0	0.5-4.4	0	0-4.8
	<b>Fishermen</b>	11	4.2	1.7-24	0	0-42
Coast of the Gulf of Finland	<b>Sediment</b>	6	46	34-52	49	43-50
	<b>Fish</b>					
	Perch	4	6.6	2.3-15	2.1	0-7.8
	Pike	4	6.4	1.5-12	4.0	3.0-9.1
	Bream	5	5.1	3.2-13	0.9	0-4.8
	Burbot	12	18	9.2-44	20.5	8.7-55
	Baltic herring	2	1.0	0.9-1.1	0.1	0-0.3
	Pike perch	5	3.5	0-21	0	0-11
	Salmon	12	0.7	0.2-1.9	0.9	0-3.1
	<b>Mothersmilk</b>	6	3.9	1.1-7.5	0.5	0-5.9
<b>Fishermen</b>	14	2.4	1.4-7.6	0	0-0.2	