

HIGH CONCENTRATIONS OF PCDD=S, AND PCDF=S IN RIVER KYMIJOKI SEDIMENTS, SOUTH-EASTERN FINLAND, CAUSED BY WOOD PRESERVATIVE Ky-5

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Introduction

Kymijoki, the fourth largest river in Finland, locates in the south-eastern corner of the country. The area has long traditions in paper industry and the river has been heavily polluted by e.g. pulp mill effluents as well as the chemical industry. Up to 24 000 t of wood preservative, called Ky-5, was manufactured at the upper reaches of Kymijoki from 1940 to 1984, from which an unknown amount of the product and impurities ended in the river and finally to the Gulf of Finland. The product consisted mainly of polychlorinated phenols (PCP). Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), especially higher chlorinated dibenzofurans occurred as impurities. Estimates of the total amount of PCDD/Fs in river and marine sediments, based on echo sounding of loose contaminated sediments and a river sediment transport model, accounted for from 16 to 21 kg of PCDD/Fs (as I-TEQ) in the contaminated area. This is an order of magnitude more than the amount of 2,3,7,8-tetrachloro-*p*-dibenzodioxin emitted to the atmosphere in Seveso in 1976 (1).

We present here the spatial extent of surface sediment concentrations of PCDD/Fs in the river, river estuary and the reference stations upstream and in the coastal area in the Gulf of Finland. Concentrations in sedimenting material as well as estimate of the present and historical contaminant fluxes is also given.

Materials and methods

Samples of river and coastal sediments were collected by gravity sediment corer and sampled for surface sediment (0-3 cm river stations, 0-2 cm coastal stations) in 1996-1998. From each river location at least four surface sediment samples were pooled to two subsamples and analysed separately. Analyses from coastal sediments represent one sample. Sediment traps (diameter/depth ratio 1/5) were placed one meter above the sediment surface at six stations for the collection of sedimenting material in 1997 and 1998. Samples were collected monthly during ice-free seasons. HRGC/HRMS analysis of PCDD/Fs are described in more detail elsewhere (2). The percentage of 1,2,3,4,6,7,8-HpCDF, other HpCDFs, and OCDF is calculated from the total concentration of PCDD/Fs (19-49 compounds analysed).

Results and discussion

Environmental Levels in Sediment, Sewage, Sludge and Food

River sediments

The highest concentrations of Σ PCDD/F in sediments were measured at the upper course of the river (Table 1). Within the distance of about 30 km from the manufactory the Σ PCDD/F concentrations in river sediments were up to two orders of magnitude higher than the limit values proposed for contaminated soils in Finland. River sediments can be classified as extremely contaminated, with maximum areal mean concentration of above 70 000 000 pg g^{-1} (dw) as Σ PCDD/F and 130 000 pg g^{-1} (dw) as I-TEQ (4) (Table1). The concentrations decreased with the distance from the pollution source.

Hepta- and octa-chlorinated dibenzofurans, typical to Ky-5 fungicide, dominated in river sediments at all stations downstream the manufactory (Table 1). HpCDFs and OCDF represented from 79 to 95 percent of the Σ PCDD/F in sediments. This is comparable with the few analyses from the product (77 %, 3). Reference sites upstream had notably lower Σ PCDD/F concentrations and revealed only from 12 to 26 % of HpCDFs and OCDF from the total amount. Clearly, OCDF was more abundant in river sediments (23-74 %) than in the product (5.4 %). Instead, the main impurity 1,2,3,4,6,7,8-HpCDF was less represented in sediments. This was especially true at the most contaminated sites (Table 1). This may be an indication of different physical and chemical properties of congeners with different chlorine substitution and /or sparse data of the composition of the contaminant entering the river.

Estuarine and coastal sediments

At the estuary clearly lower Σ PCDD/F concentration were measured, all being below the limit values for soils, but still an order of magnitude higher than at other locations on the coast. HpCDFs and OCDF accounted for from 80 to 84 percent of Σ PCDD/F at the inner estuary and was similar to that in the river. The same congeners were dominant at all sites along the coast, although at a decreasing fraction (57-80 %). It should be noted that Ky-5 product was previously routinely used in most sawmills in Finland, which may partly explain the presence of these congeners in the coastal sediments, different from those in reference sites upstream the manufactory (Table 1).

Sediment traps

The total concentrations in sediment traps behaved similarly to concentrations in sediment surface (both the level and the congener pattern) indicating that substantial amounts of these pollutants are transported from the river channel to the estuary. Multiplying the mean yearly suspended particle discharge of river Kymijoki at each station with the mean concentration of PCDD/Fs in traps yields a mean yearly Σ PCDD/F transport of about 73 kg (220 g I-TEQ) from the most contaminated area (upstream Keltti) of which 41 kg (140 g I-TEQ) is transported to the estuary.

Different estimates (sediment transport model, present flux estimate above, dated sediment cores) give an estimate of a total historical transport of about 2000-2300 kg Σ PCDD/F, i.e. (6-7 kg I-TEQ) to the

Environmental Levels in Sediment, Sewage, Sludge and Food

Gulf of Finland. Assuming the same retention for PCDD/Fs in the estuary as that calculated for suspended material (5), about 55 % would have retained at the limited estuarine area and 45 % would have been transported forward.

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Table 1. Mean total PCDD/F concentrations and percentage of HpCDFs and OCDF in surface sediments and sedimenting material at different sites along the river Kymijoki, its estuary and coastal area in the Gulf of Finland. Distance from the pollution source is indicated in kilometers. Note that at

Environmental Levels in Sediment, Sewage, Sludge and Food

the estuary and coastal areas the distance is from the river inlet.

	km	1,2,3,4,6,7,8- HpCDF %	Other HpCDF	OCDF %	Other %	□ PCDD/F pg g ⁻¹
Ky-5 -chemical		42.0	29.8	5.4	22.8	
Upstream Ky-5 manufactory						
Pyhäjärvi	-24	3.8	3.4	4.8	88.0	120 000
Urajärvi	-36	8.2	5.9	11.6	74.3	795
Downstream Ky-5 manufactory						
Kuusaansaari	0	20.0	23.9	34.8	21.3	17 200 000
Ruotsula	3	11.0	9.7	73.8	5.5	73 000 000
Keltti	7	17.0	21.3	48.6	13.1	9 270 000
Koria	10	24.2	29.8	33.9	12.1	3 350 000
Lopotti	19	37.3	24.5	33.4	4.8	10 000 000
Myllykoski	28	35.0	28.9	28.4	7.7	2 960 000
Koskenalusjärvi	33	32.1	22.6	39.1	6.2	1 800 000
Muhjärvi	48	30.8	23.2	36.1	9.9	130 000
Hirvivuolle	61	38.1	27.6	23.4	10.9	740 000
Vanhala	64	33.5	23.5	37.7	5.3	970 000
Vastila	68	41.6	21.6	23.1	13.7	230 000
Kyminlinna	69	32.4	21.2	41.6	4.8	560 000
Tammijärvi	73	30.3	22.7	39.7	7.3	910 000
Ahvenkoski	88	33.6	22.8	34.5	9.1	200 000
Estuary and coastal area						
Kuutsalo	7	30.1	24.5	24.8	20.6	30 000
Ahvenkoskenlahti	8	32.3	18.5	33.1	16.1	52 900
Äyspäänselkä	8	27.4	21.8	30.9	19.9	20 200
Vahterpää	17	28.5	22.0	29.3	20.2	11 800
Huovari	42	23.0	16.2	28.3	32.5	1 990
Emäsalo	66	22.9	17.0	25.6	34.5	2 230
Kaunissaari	80	21.7	16.6	31.6	30.1	1 350
Vuosaari	90	16.1	16.4	24.9	42.6	1 030
Sediment traps, river						
Ruotsula	5	24.8	24.4	40.8	10.0	16 900 000
Keltti	7	25.4	23.8	41.6	9.2	5 400 000
Koskenalus	33	28.6	24.9	36.8	9.7	1 300 000
Tammijärvi	73	28.6	24.1	36.7	10.6	710 000
Sediment traps, estuary						
Ahvenkoskenlahti	8	32.0	24.3	32.2	11.5	150 000
Äyspäänselkä	8	30.8	20.3	30.2	18.7	37 600