THE DEPOSITION AND SEDIMENTATION OF PCDD/FS IN THE GULF OF FINLAND

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Introduction

Recent analyses have shown that the Kymijoki River, with high levels of PCDD/Fs in sediments, up to 350 000 ng TEQ/kg dry weight (d.w.)[1], is also the main contributor of dioxins to the Gulf of Finland[2], a sub basin of the Baltic Sea. Concern of whether this has an impact on the dioxin concentration in fish has been raised.

The main component of the Kymijoki load is the impurity of a wood preservative Ky 5 (mainly 1,2,3,4,6,7,8-HpCDF). This is different from the main dioxin component in fatty fish in the Baltic (e.g. Baltic herring and Baltic salmon), which is 2,3,4,7,8-PeCDF[3]. Possible other sources of 2,3,4,7,8-PeCDF include atmospheric deposition and other point sources. Consequently the causal relationship between Kymijoki load and PCDD/Fs in fish is unclear.

The aim of this study was to investigate whether the PCDD/F data from recent studies that is presently available from the Gulf of Finland can give more information of the possible source of PCDD/Fs to fish. The study summarizes the results of total and special PCDD/F congeners of interest in summertime deposition in southern Finland, and in sedimentation and surface sediments in the Finnish coastal area of the Gulf of Finland.

Material and Methods

The research includes several collaborating activities from 1996 to 2001 devided here in three compartments: 1) deposition, 2) sedimentation and 3) surface sediment. Deposition was collected during summertime (May-October) in 1998-2001 in southern Finland (Evo). Sedimenting material was collected with sediment traps within case studies at Kymijoki estuary (Kotka area), Porvoonjoki estuary (Porvoo area) and at one open sea area (GF2). Surface sediment was collected from sites along the coast in order to define the backround concentrations of PCDD/Fs.

1) The precipitation sampling was done with two glass funnels (30 cm in diameter). Rainwater was collected through funnels into 5-litre Pyrex bottles using a teflon tube. 100 ml dichloro-methane and 100 ml deionized water was added to the bottles. The sampling period was about 4-5 weeks. The method used was a bulk sampler modified by DMU, The National Environmental Research Institute, Denmark.

2) Sediment trap material was collected in 1996-1999 in two coastal areas, Kotka and Porvoo and one open sea station (GF2). Sediment traps were placed a few meters above the bottom. The traps in the coastal area had a small collection area of 0.004-0.008 m^2 and the large automatic trap in the open sea had a collection area of 1 m^2 .

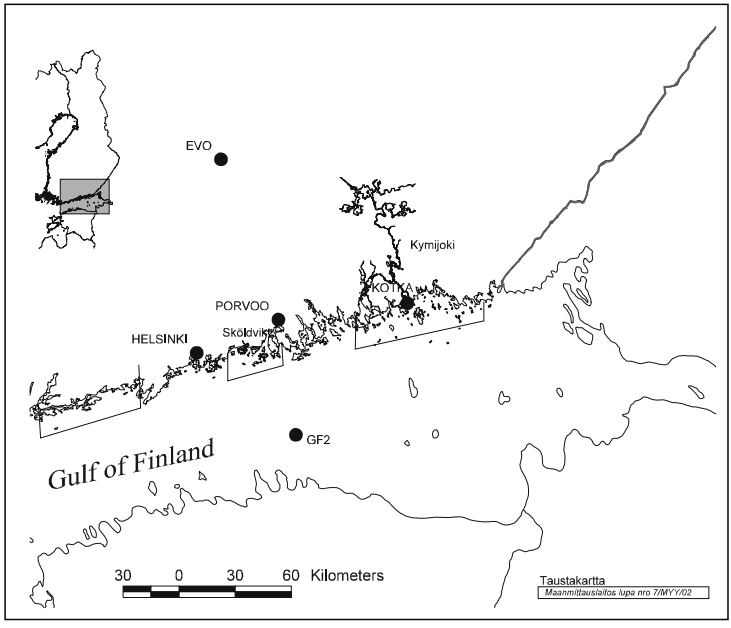

Figure 1. The map of the study area showing regions for deposition (Evo), sedimenting material (Kotka, Porvoo, GF2) and surface sediment (Kotka, Porvoo-Helsinki, Helsinki west) samples

3) Sediment studies were carried out in 1996-1997 between the eastern part of the Finnish coast and the western area of Helsinki. The morphology of the northern part of the Gulf is characterized by rugged rocky areas in the shallow zone alternating with late and post-glacial clay- and silt sediment infill in the deeper parts. The rugged coastline with a large number of islands disturbs the westerly and parallel current pattern. The conditions of erosion and transportation prevail but also large accumulation areas are found at the study area.

For the PCDD/F analyses, the rainwater precipitation samples were extracted with toluene in a glass funnels. Extracts were dried with activated Na_2SO_4 before fractionation and purification.

Lyophilized and homogenized sediment and sediment trap samples (1.5 g) were Soxhlet-extracted with toluene for 20 h. All the extracts were fractionated and purified by eluting them through three columns consisting of (1) sodium sulfate and silica gel, (2) activated carbon and Celite, and (3) aluminum oxide. Sulfur was precipitated from the sediment and sediment trap samples with activated copper powder. The quantification of PCDD/Fs was achieved by measuring the native compounds and ^{13}C-labeled internal standards by high-resolution gas chromatography-mass spectrometry.

Results and Discussion

Mean concentration of the sum of toxic PCDD/F components both in sediment traps and in surface sediments clearly decreased by orders of magnitude when the distance from the Kymijoki estuary (Kotka region) increased (Fig. 1, Table 1). This was mainly due to Ky 5-originating congeners such as 1,2,3,4,6,7,8 HpCDF (Table 1). The mean concentration of OCDD also decreased indicating that this congener is also originating at substantially large amounts from Kymijoki. Extremely large variation of

Table 1. Mean concentrations of some specific PCDD/F congeners and the sum of all toxic congeners in sedimenting material (traps), in surface sediments (0-2 cm or 2-4 cm) and in deposition (open bottle)

Site	n	23478PeCDF	1234678HpCDF	OCDD	tox. All
Sediment traps (pg g^{-1}, dw)					
Trap 1 Kotka	13	14	29011	608	57076
Trap 2 Porvoo - Sköldvik	13	<5	106	312	1859
Trap 3 Gulf of Finland / GF2	2	16	313	<5	884
Surface sediments (pg g^{-1}, dw)					
Sed 1 Kotka	6	16	3834	100	8008
Sed 2 Porvoo - Helsinki	3	8	323	63	894
Sed 3 Helsinki, west	2	6	106	9	268
Deposition (pg l^{-1})					
Dep Evo	19	0.09	1.23	2.83	9.26

this congener (<5-5700 pg/g,dw) was measured in sediment traps both in Kotka and in Porvoo regions. Instead 2,3,4,7,8-PeCDF showed only a minor variation in concentration both in traps and in surface sediments and as high concentration in trap samples at the open Gulf of Finland (GF2) than in Kotka region (Table 1).

In deposition OCDD was the main congener representing 39 % of all of the toxic congeners. In sediment traps and in surface sediments the portion of OCDD was always less than 20 %, and usually less than 5 % (Fig. 2a). Different from OCDD, the share of Ky 5-originating 1,2,3,4,6,7,8-HpCDF usually varied from 35 % to 54 % in sediments and in traps (Fig. 2b). This was notably higher that the share of 1,2,3,4,6,7,8-HpCDF in deposition (20 %). The only exception was locally polluted Porvoo – Sköldvik traps with only 6 % HpCDF. The main congener at this area was OCDF that originates from vinylchloride monomer production at the area[4].

The most abundant congener in fish - (2,3,4,7,8-PeCDF) - was found only at a minor portion (< 2.5 %) in traps and in sediments (Fig.2c). The share of 2,3,4,7,8-PeCDF increased with increasing distance from Kymijoki estuary and exceeded the share of PeCDF in deposition at the furthest regions.

The findings indicate that, regardless of the major importance of Kymijoki to the dioxins in the Gulf of Finland, other sources may contribute more to the 2,3,4,7,8-intake of fish in the studied sea area.

References:

1. Verta M., Korhonen M., Lehtoranta J., Salo S., Vartiainen T., Kiviranta H., Kukkonen J., Hämäläinen H., Mikkelson P., Palm H. (1999). Organohalogen Compd. 43, 239
2. Isosaari, P., Kankaanpää, H., Mattila, J., Kiviranta, H., Verta,M., Salo,S.,Vartiainen, T. 2002. (This conference).
3. Rappe, C., Bergqvist, P.-A., Kjeller, O., 1989. Chemosphere, 18(1-6), 651.
4. Isosaari, P., Kohonen, T., Kiviranta, H., Tuomisto, J., Vartiainen, T. 2000. Environ. Sci. Technol. 34; 2684.

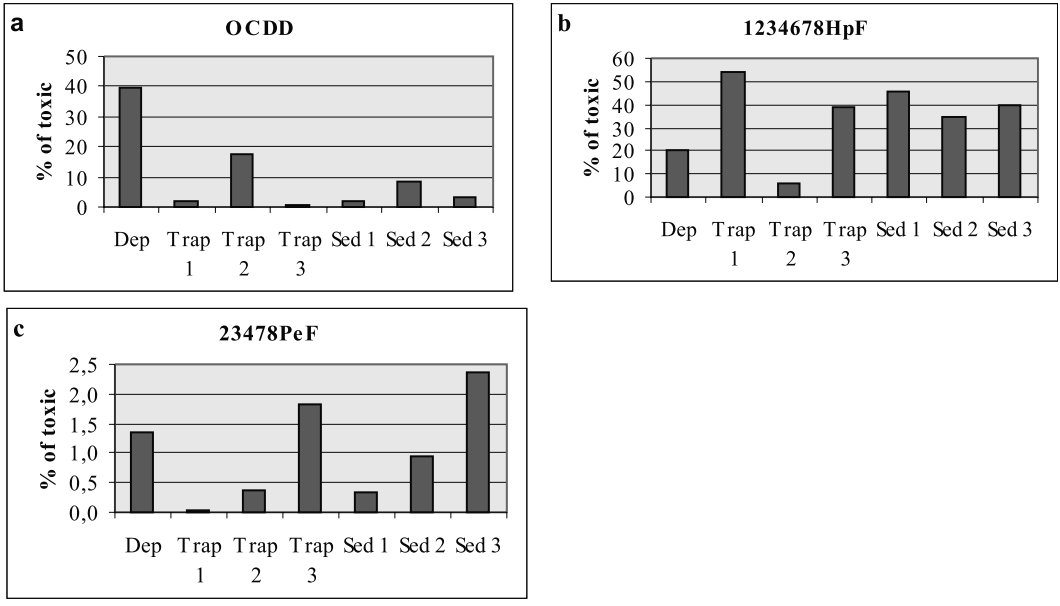

Figure 2. The relative proportion of selected congeners from the sum of all toxic PCDD/F congeners (for sampling site codes, see Table 1): a) Octachlorodibentzo-p-dioksin; b) 1,2,3,4,6,7,8-Heptachlorodibentzofuran; c) 2,3,4,7,8-Pentachlorodibentzofuran