Concentrations of PCDDs and PCDFs in Baltic herring (*Clupea harengus*) and Northern pike (*Esox lucius*) in Finnish coastal area from 1989-1993

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Abstract

The concentrations of PCDDs and PCDFs in Baltic herring were studied in seven coastal areas and in Northern pike in six areas. The concentrations were usually less than 1 ITEQ pg/g, fresh weigth (fw) in Baltic herring muscle. Only in the eastern part of the Gulf of Finland was the concentration 3.6 ITEQ pg/g fw. The concentrations in all study areas were less than 1 ITEQ pg/g fw in northern pike muscle.

Introduction

Dioxins and furanes are formed in very different kinds of processes. One general way of producing dioxins and furanes as impurities is to heat material such as carbon and chlorine together. Such kinds of processes occur in paper bleaching, in chemical processes to produce chlorinated compounds as well as in many types of combustion processes including waste incineration, vehicle operation and metal production[1].

The estimated amount of dioxin and furane emissons in Finland in late the 80s and early 90s has been about 100-150g TEQ/year[2]. The main sources of emissions have been in the calculations industry, traffic, waste burning and fires in dumping grounds.

The Finnish Environment Institute has been monitoring dioxins and furanes in coastal waters since 1989. The monitoring species have been pike (*Esox lucius*), Baltic herring (*Clupea harengus*), Baltic mussel (*Macoma baltica*) and an isopod crustacean (*Mysis relicta*). Pike are piscivorous and feed mainly on detrivorous fishes. Baltic herring consume mainly plankton.

The monitoring sites are situated all along the Finnish coast from the easternmost areas of the Gulf of Finland (Virojoki) to the northernmost areas of the Gulf of Bothnia (Kuivaniemi) (Fig 1). The places were chosen mainly in areas far from local pollution. Two places were selected in the estuaries of big rivers receiving pollution from agriculture, municipal wastewaters and industry. They were Ahvenkoskenlahti Bay in the estuary of the River Kymijoki and Pihlavanlahti Bay in the estuary of the River Kokemäenjoki.

Eutrofication, as calculated by the amount of chlorophyll *a*, has been worst at the time of this study in the Gulf of Finland, where it has increased from the Archipelago Sea (Seili, about 3 mg/m^3) to the eastern part of the Gulf of Finland (Virolahti Bay, about 5.5 mg/m^3)[3]. In the big bays and inner island areas the values have been about 5-10 mg/m^3. In the Gulf of Bothnia the amount of chlorophyll *a* has been about 2 mg/m^3 up to the Mikkelinsaaret Island area while in the northern part less than 2 mg/m^3. The Pihlavanlahti Bay has been heavily polluted from agriculture and industry; amount of chlorophyll *a* there has been 10-15 mg/m^3.

Salinity has been decreasing in the Archipelago Sea (less than 7 $‰$) in the east of the Gulf of Finland (Virojoki more than 4 $‰$) and to the north (outside the Pihlavanlahti Bay area less than 6 $‰$ and in the Kuivaniemi area about 3 $‰$)[3].

Experimental Methods

Fish were caught by local environmental centres along the coast with the help of fishing authorities. Pike was taken at spawning in the spring and Baltic herring in autumn from August to October. The fish were deep-frozen within one day and transported to Helsinki to the laboratory of the Finnish Environment Institute (FEI). The fishes were prepared in the laboratory of FEI. Length, weight, sex and age of the fish were measured and muscle samples were taken for chemical analyses. Analyses have been carried out by the National Public Health Institute.

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 performd 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 concentrations of PCDDs and PCDFs in Baltic herring muscle have been approximately 1 (or less) ITEQ pg/g fw (Fig 2). Only in the Gulf of Finland have the concentrations been clearly larger (3.6 ITEQ pg/g fw). In 1990 the concentrations were smaller than in 1993, which could not be explained by the differences in the specimens (Table 1). In 1993 the concentrations were smaller in the Archipelago sea than in either the Gulf of Finland or Bothnian Bay.

The concentrations of PCDDs and PCDFs in pike muscle have been less than 0.5 ITEQ pg/g fw (Fig 3). Only in 1992 in Ahvenkoskenlahti Bay did the concentration almost exeed 1 ITEQ pg/g fw. The levels were high at all the most toxic congeners (Fig 5).

In 1993, the dominating congeners were 2,3,7,8-TCDD, 1,2,3,7,8-PD and 2,3,7,8-TCDF in Baltic herring as calculated in ITEQ fw (Fig 4). The only difference was in the Virolahti where the concentration of 2,3,7,8-TCDD was very high (almost 3 ITEQ pg/g fw) and the amount of 2,3,7,8-TCDF was also small. The dominating congeners in 1992 in pike were 2,3,7,8-TCDD

and 2,3,4,7,8-PF. The concentrations were somewhat less with the congeners 1,2,3,7,8-PD and 2,3,7,8-TCDF as calculated in ITEQ fw (Fig 5).

When comparing the concentrations on the lipid weight basis, the bioaccumulating levels were about 10 times larger in pike than in Baltic herring. This is because the lipid content in pike (about 0.4 %) was about 10 times smaller than in Baltic herring (about 5 %).

Table 1. The length, weight, sex and age (dispersion in parentheses) of the Baltic herring and pike studied (n=amount of specimens used in the homogenate, h=amount of homogenates=analyses, f=female, m=male, y=year)

	Baltic herring				
place/year	n/h	length/cm	weigth/g	sex	age/y
Kuivaniemi/90	48/2	18(1.5)	41(4)	f	5(1)
Kuivaniemi/93	22/1	17.5(0.5)	36(3)	f	4(1)
Mikkelinsaaret/93	11/1	17(0.5)	32(3)	f	4(1)
Ahvenanmaa/90	85/3	17(0.5)	31(2)	f	4(1)
Seili/93	31/1	17.5(0.5)	37(3)	f	5(1)
Tvärminne/93	20/1	16.5(0.5)	29(3)	f	5(1)
Ahvenkoskenlahti/90	17/1	17(1)	35(5)	-	6(1)
Virolahti/93	25/1	16(0.5)	27(2)	f	5(1)
	Northern pike				
Kuivaniemi/92	5/1	50(1)	900(100)	f	6(1)
Mikkelinsaaret/92	4/1	62(2)	1350(100)	f	8(1)
Pihlavanlahti/92	7/2	55(4)	1250(200)	f	7(1)
Ahvenanmaa/89	9/3	50(3)	900(200)	f	7(1)
Ahvenkoskenlahti/89	6/2	60(6)	1600(400)	f	8(2)
Ahvenkoskenlahti/92	3/1	52(3)	1100(300)	f	6(1)
Virolahti/92	5/1	57(3)	1200(150)	f	6(1)

Literature Cited

(1) Corinair, Programme CORINE, EC Commission.
(2) Holopainen, T. *VYH moniste* 530, 1993.
(3) Kauppila, P. Unpublished data, FEI.

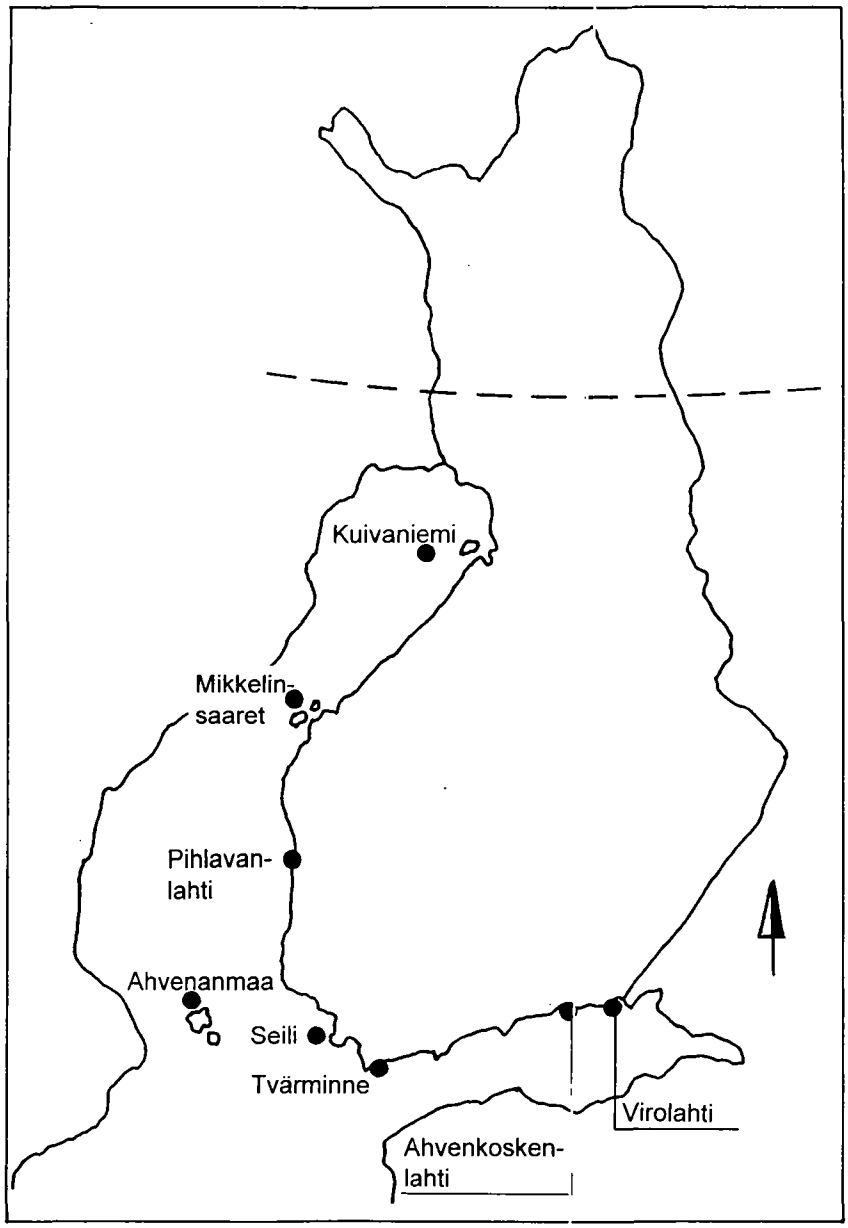

Figure 1. The map showing monitoring sites along the coastal areas of Finland

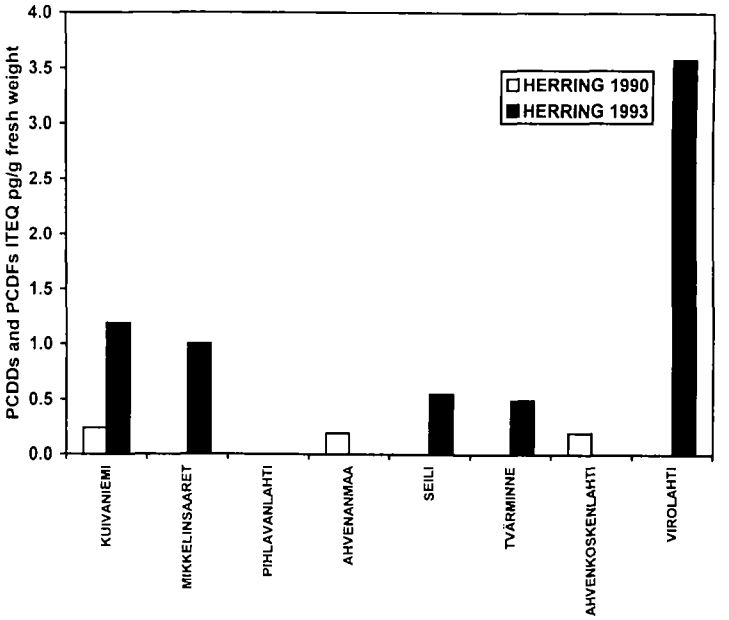

Figure 2. The concentrations of PCDDs and PCDFs (ITEQ pg/g, muscle, fresh weight) in Baltic herring along Finnish coastal areas in 1990 and 1993.

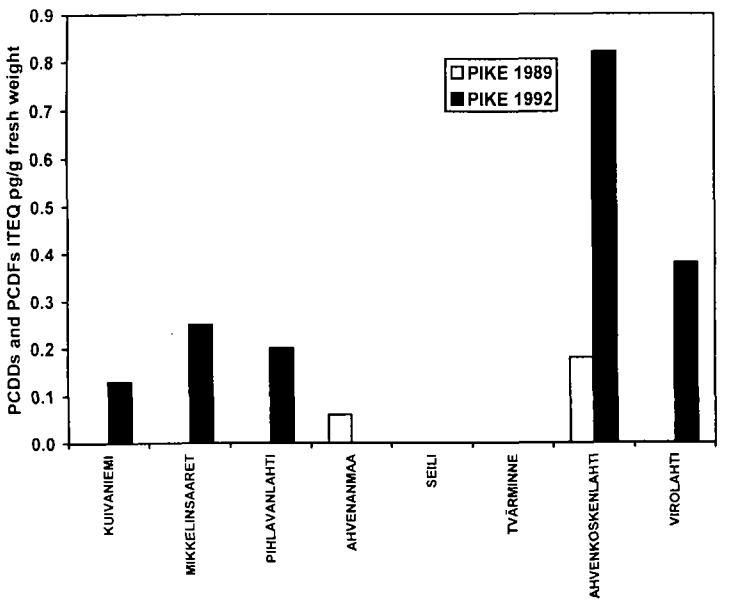

Figure 3. The concentrations of PCDDs and PCDFs (ITEQ pg/g, muscle, fresh weight) in pike along Finnish coastal areas in 1989 and 1992.

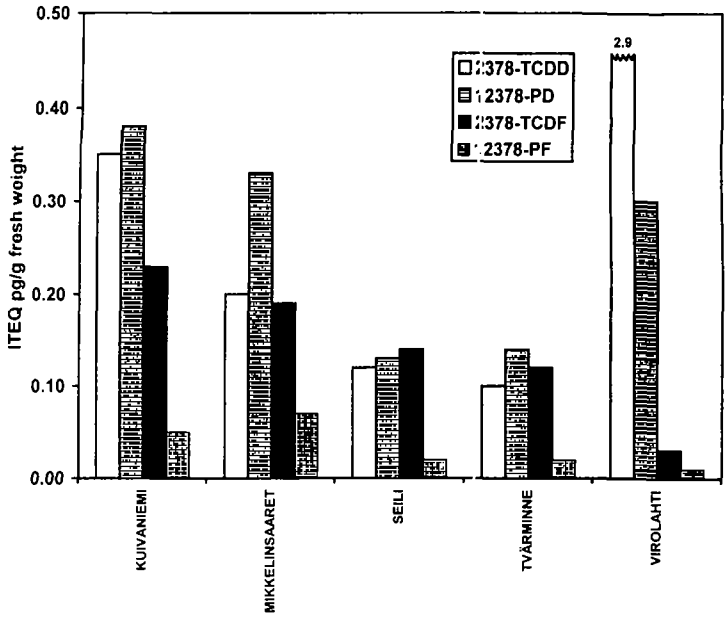

Figure 4. The most toxic PCDD and PCDF congeners (ITEQ pg/g, muscle, fresh weight) in Baltic herring along Finnish coastal areas in 1993.

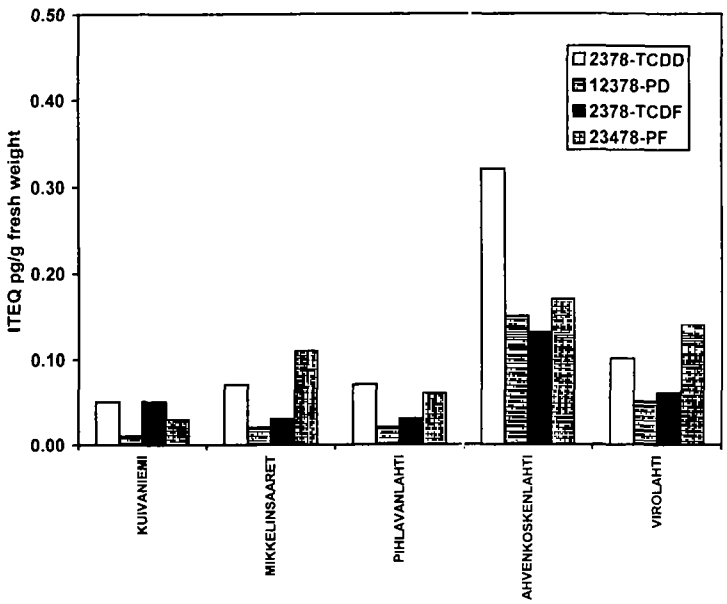

Figure 5. The most toxic PCDD and PCDF congeners (ITEQ pg/g, muscle, fresh weight) in pike along Finnish coastal areas in 1992.