PCDDS, PCDFs AND DIOXIN-LIKE PCBs IN FISH FROM TUNG KANG, KAO PING RIVERs IN TAIWAN

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Introduction

As part of an extension background survey to assess the contaminant in Tung Kang and Kao Ping rivers on southern part of Taiwan, polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (non-*ortho*- and mono-*ortho*-substituted CBs, DLPCBs) congeners were determined for 20 fish fillet samples. The analytical method was designed to determine to low parts-per-trillion (ppt-pg/gram) concentration for fish by using large sample weight and high sensitivity HRGS/HRMS analytical methods. Sample concentrations of PCDDs/PCDFs and DLPCBs were determined using EPA M1613B[1] and M1668A[2] respectively. In this paper, we present data on the significance of the DLPCBs to total toxic equivalent (TEQ) and suggest the advantages of conducting a full scan for all the PCB congeners.

Materials and Methods

Sample Collection

Fishes of the same species from the same place were pooled as one sample.Twenty fish samples were collected from Tung Kang and Kao Ping rivers in 1999. Sixteen fish samples were collected from Tung Kang river with four sampling sites, via down stream direction such as Lung Tung bridge (n=2), Hsing She bridge (n=1), Kang Hsu water-pumping station (n=7) and Tung Kang bridge (n=6). Four fish samples were collected from Kao Ping river with sampling site Shuang Yuan bridge (n=4).

Determination of PCDDs/DFs and dioxin-like PCBs

Pooled fish fillet samples were homogenized, freeze-dried.Approximately 10 to 20 gram dry sample were extracted using Soxhlet apparatus with dichloromethane/n-Hexane(=1 : 1). Lipids were removed from the Soxhlet extract using acidified silica gel. Fractionation was carried out with an acid silica-gel and an acid alumina column. In the AX-21 charcoal impregnated Celite (8%) mixture column fractionation step, adsorbed PCDDs/PCDFs and dioxin-like PCBs were elute into

fractions. The first fraction, eluted with dichloromethane/benzene(1 : 1) through forward direction (the same direction as sample inlet), consisted of dioxin-like PCBs. The second fraction, eluted with toluene via reverse charcoal column, comprised PCDDs/PCDFs. Instrument analysis was conducted according to Method 1613B and Method 1668A using an Micromass Autospec Ultima magnetic sector high resolution MS equipped with HP 6890 gas chromatograph. Dioxin-like PCBs and PCDDs/PCDFs analyses were conducted using DB-5 (60m× 0.25mm i.d.× 0.25 um film) chromatography column. The concentrations of not detected congeners were calculated with L.O.D.(limit of detection)

Result and Discussion

Seven 2,3,7,8-substituted PCDDs, ten 2,3,7,8-substituted PCDF, and twelve DLPCBs were normalized by multiplying their measured concentrations by the appropriate WHO toxicity-equivalence factors (TEFs). The summation of these products yields a TEQ, which expresses these analyte concentrations as a single number, equivalent to that of a toxicity drived exclusively from 2,3,7,8-TCDD. Table 1 summarizes the TEQ concentrations in fish from Tung Kang, Kao Ping rivers.

Table1 : WHO-TEQ concentrations of PCDDs/PCDFs, DLPCBs in fish fillet samples

Analyte	Tung Kang river				Kao Ping river
(pg-TEQ/g w.w.)	Lung Tung bridge(n=2)	Hsing She bridge(n=1)	Kang His water-pumping station(n=7)	Tung Kang bridge(n=6)	Shuang Yuan bridge(n=4)
PCDDs/PCDFs	0.106-0.840	0.069	0.050-2.625	0.065-0.780	0.057-0.521
DLPCBs	0.286-1.65	0.179	0.112-24.4	0.057-8.82	0.082-2.91
Total TEQ	0.392-2.49 (mean:1.44)	0.248	0.196-27.1 (mean:4.28)	0.138-9.60 (mean:2.00)	0.139-3.43 (mean:1.29)
DLPCBs(%)	66-73	72	53-90	41-92	59-85

TEQ concentrations drived from PCDDs/PCDFs in fishes ranged from 0.05 to 2.625 pg-TEQ/g w.w. and only one out of 20 fish samples exceeded 1.0 pg-TEQ/g (5%). Combined TEQ concentrations from DLPCBs in fish ranged 0.138 to 27.1 pg-TEQ/g w.w. from Tung Kang river and 0.139 to 3.43 pg-TEQ/g w.w. from Kao Ping river. The percentages of TEQ concentrations exceeded 1.0 pg-TEQ/g w.w were 25% and 50% respectively. Table 1 also showed that DLPCBs played an important role in the contribution of TEQ values. In nighteen fish samples, a single PCB congener, IUPAC 126 (3,3',4,4',5-PeCB) was found to be the highest source of TEQ [3]due in large part to its high TEF-0.1. DLPCBs enter the environmental from two potential sources[4] ; firstly as a

commercial PCB formulations and secondly by combustion processes. Although PCB had been banned for several decades, they still became an important worldwide contamination.

Figure 2 shows the distribution of PCDDs/PCDFs and DLPCBs from Tung Kang river (Kang His water-pumping station, Tung Kang bridge) and Kao Ping river (Shuang Yuan bridge). The distributions of DLPCBs in fish look alike among two rivers at three different sampling sites. All twelve DLPCB congeners can be detected in twenty fish samples, with the exception of IUPAC 169. The highest concentrations are IUPAC 118、105 and 156. The patterns of PCDDs/PCDFs from Tung Kang river at two different sites are almost the same. The fish data from Tung Kang river were dominated by OCDD、2,3,7,8-TCDF、OCDF、1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, while 1,2,3,7,8,9-HpCDF and 1,2,3,4,7,8,9-HpCDF were not detected for sixteen samples. For Kao Ping river, the fish data were dominated by OCDD、OCDF and 1,2,3,4,6,7,8-HpCDD. The isomer distribution betweenTung Kang and Kao Ping rivers are not the same showing that they may be suffered by different PCDDs/PCDFs contamination sources.

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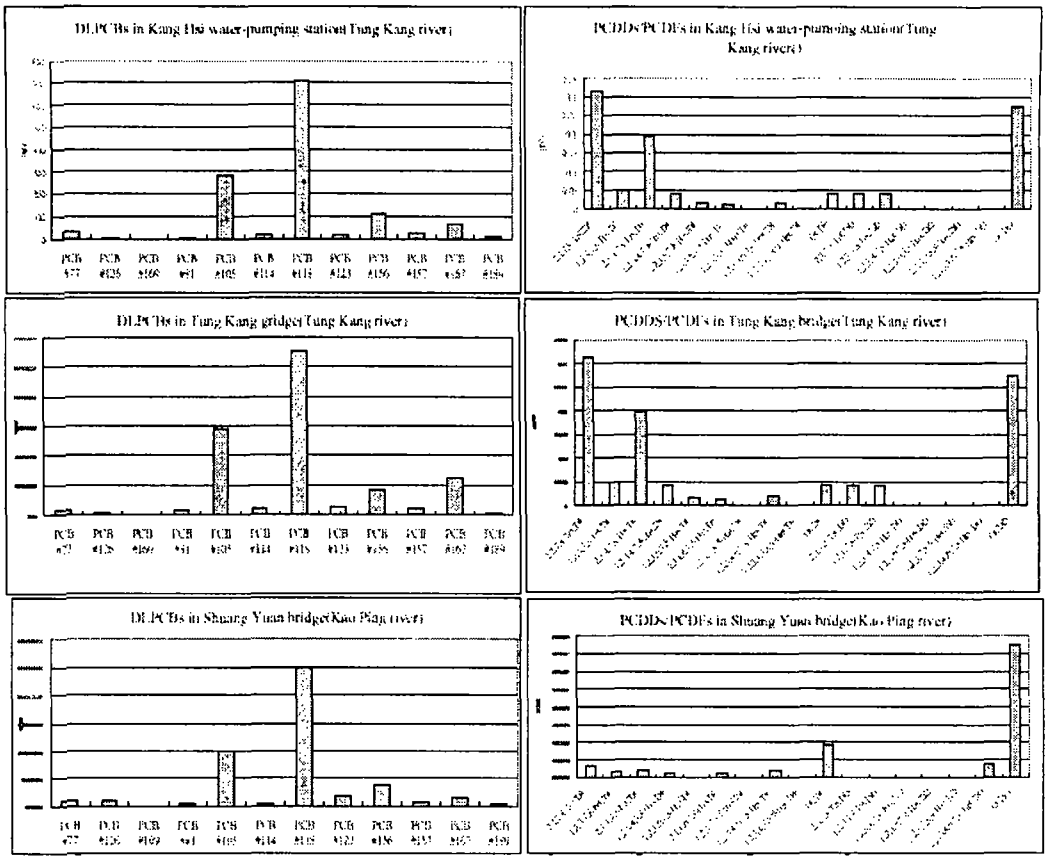

Figure 1 : Profiles of PCDDs/PCDFs and DLPCBs in fish from Tung Kang, Kao Ping rivers