LEVELS OF PCDDS, PCDFS, DIOXIN-LIKE PCBS, AND PBDES IN FISH SAMPLES FROM RIVERS AND ESTUARIES IN TAIWAN

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Abstract

The concentrations of polychlorinated dibenzo-*p*-dioxin (PCDDs), polychlorinated dibenzo- *p*-furan (PCDFs), dioxin-like polychlorinated biphenyls (DLPCBs), and polybrominated diphenyl ethers (PBDEs) were measured in fifty-nine fish samples collected from rivers and estuaries in Taiwan. Determination of PCDDs/PCDFs/ DLPCBs and PBDEs was carried out using HRGC/HRMS. For all fish of all species from all sampling areas, the concentration range for PCDDs/PCDFs and DLPCBs World Health Organization Toxic Equivalent (WHO-TEF) were 0.024 ~ 1.02 pg WHO-TEQ/g wet weight and 0.023 ~ 14.1 pg WHO-TEQ/g wet weight respectively. The concentration range for PBDEs were 12.1 ~ 380 ng/g lipid weight, with BDE-47＞BDE-154＞BDE-100 ~ BDE-99＞BDE-153＞BDE-183。The highest concentrations of both PCDDs/PCDFs and PBDEs were found in the area of Erren river and the highest concentrations of DLPCBs was found in Dahan river. The average recoveries of the ^{13}C-labelled internal standards for PCDDs/PCDFs, Dioxin-like PCBs and PBDEs were in the range of 63 ~ 95 %, 54 ~ 78 % and 37 ~ 126 % respectively. The average recoveries of the method blank spike samples for PCDDs/PCDFs, Dioxin-like PCBs and PBDEs were in the range of 86 ~ 99 %, 105 ~ 112 % and 86 ~ 119 % (133% for BDE-209) respectively.

Introduction

Polychlorinated dibenzo-*p*-dioxin (PCDDs), polychlorinated dibenzo- *p*-furan (PCDFs), dioxin-like polychlorinated biphenyls (DLPCBs) are a group of toxic and highly persistent organic compounds that consist of 75, 135 and 209 congeners, respectively. Due to its chemical stability, their lipid solubility, and its ubiquitous prevalence in environmental, PCDDs, PCDFs and PCBs constitute which is called persistent organic pollutants (POPs). Polybrominated diphenyl ethers (PBDEs) are one of several types of brominated flame retardants and are also bioaccumulative, lipophilic, and persistent[1-4]. Human chronic exposure to those highly lipophilic and persistent compounds via food chain has led to the accumulation of both parent compounds and its metabolites in lipid rich tissues such as adipose tissues and human breast milk[5,6]. One possible exposure pathway by which humans and other upper trophic level species can be exposed to POPs is through consumption of dietary fish, This paper presented the analytical results of 17 PCDDs/PCDFs, 12 DLPCBs and 25 PBDEs congeners in all the

samples. The purpose of the current study was to evaluate the distribution of PCDDS/PCDFs, DLPCBs and PBDEs in fish samples from eight rivers and estuaries in Taiwan. These data will be used to evaluate temporal and spatial trends of these POPs, and may also be used in health risk assessment.

Materials and Methods

PCDDs/PCDFs/Dioxin-like PCBs and PBDEs standards were purchased from Wellington Laboratories. 10 g of freeze-dried muscle and tissue samples were extracted with Soxhlet extraction. Before extraction, the sample was fortified with internal standards (6 ^{13}C-PCDDs, 9 ^{13}C- PCDFs, 12 ^{13}C-Dioxin-like PCBs and 10 ^{13}C-PBDEs). The lipid extracts were removed by mixing with 30 g acidified silica gel in hexane. A CAPE carbon column was used to separate interferences, PCDDs/PCDFs/Dioxin-like PCBs and PBDEs. Dioxin-like PCBs and PBDEs portion were collected using 5 mL of hexane/toluene eluent in forward direction of carbon column, and then reverse carbon column and PCDDs/PCDFs fraction was eluted by 30 mL toluene. Before instrument analysis, 13C-labeled injection standards were added and the vials were vortexed to mix completely. All analyses were performed with the isotope dilution method. Quantification of PCDDs/PCDFs/Dioxin-like PCBs and PBDEs were performed by GC-HRMS using a JMS-700 high resolution mass spectrometer (JEOL, Tokyo, Japan) equipped with a Hewlett-Packard (HP) model 6890 series gas chromatograph and a CTC PAL autosampler. The instrument operates at 10,000 resolution for PCDDs/PCDFs/Dioxin-like PCBs analysis and at 8,000 resolution for PBDEs analysis, The details of the MS analysis and quality control are described in the EPA method 1613B, 1668A and method 1614.

Results and Discussion

A total of 59 composite fish samples were analyzed. Table 1 shows the sampling location, no.of samples and average concentrations (min ~ max concentration) for each river site. The column headed “WHO-TEQ” refers to the total toxicity from all 17 2,3,7,8-substituted PCDDs/PCDFs congeners based on the World Health Organization Toxic Equivalents’ method. The column headed “PCB-TEQ” refers to the Dioxin-like toxicity, using the WHO-TEF method, containing 4 non-ortho PCBs and 8 mono-ortho PCBs. For PBDEs, there is no analogous concept to WHO-TEQ. Thus, we report the concentrations of the individual congeners, BDE-47, -99, -100, -153, -154 and -183, and their sum. For the purpose of calculating WHO-TEQ for PCDDs/PCDFs/ DLPCBs and total level of PBDEs, a concentration of 1/2 of the detection limit was used for each nondetect. The concentration of total PCDDs/PCDFs ranged from 0.024 ~ 1.02 pg-WHO-TEQ/g ww. The highest level of PCDDs/PCDFs occurring at Ye-cu-jia Bridge, downstream of Erh-Jen River and the main congeners of the *Nematalosa come* species are 2,3,7,8-TCDF(26.1%), 2,3,4,7,8-PeCDF(22.9%), OCDD(7.8%) and 1,2,3,7,8-PeCDF(7,5%). As might be expected, Erh-Jen River is in southwestern Taiwan and is considered among one of the most polluted rivers in Taiwan. Decades ago, a number of metal reclamation activities

including acid washing, open-air incineration of waste computer components and scrap electrical wires/cables, disposal of waste motors and electrical transformers/capacitors, as well as numerous of municipal and agricultural activities, are believed to have discharged waste water effluent containing large amounts of heavy metals, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) into this river. In Taiwan, fish in rivers is not the primary protein source in the diet of resident. Judging from the European Union regulation limit of fish products (4.0 pg TEQ/g ww), all the concentrations in this study were lower than that of the criteria.

The levels of PCB-TEQ ranged from 0.023 ~ 14.1 pg-WHO-TEQ/g ww. The highest level of PCB-TEQ was found at midstream of Dahan River. The average toxicity of DLPCBs collected from 3 sampling sites were exceed 1.0 pg-WHO-TEQ/g ww including Erren River, Dahan River and Houjin Creek. Houjin Creek. flows through several industrial zones in southern part of Taiwan. Contamination of DLPCBs may come from factories from that area. Dahan River in midstream is the most contaminated in the Tamsui River Basin. The main pollution sources of water quality may come from domestic sewage and industrial wasted water. Seven fish samples were collected from Dahan River, and there is only one *Oreochromis sp.* was in 14.1 pg-WHO-TEQ/g ww., 10 times higher than other sampling points. Due to the wide dispersion of PCB-TEQ (0.069 ~ 14.1 pg-WHO-TEQ/g ww.) in Dahan River, further investigation should be continued. The main congeners of DLPCBs in fish samples are PCB-118>PCB-105 > PCB-156. The sum concentrations of PCB-118, PCB-105 and PCB-156 constituted 79 ~ 99 % of the total of DLPCBs in all fish samples collected from the different sites. Considering toxicity of dioxin-like compounds, DLPCBs accounted for 74 % (a the range of 33 ~ 97%) of total TEQ in fish samples.

The table 1 gives the concentration for all congeners in ng/g on lipid weight basis for PBDEs. At most sites, individual PBDE congeners were present at detectable levels in fish tissue, with the mean ∑PBDE concentration ranging from 69.1 to 230 ng/g lipid. The highest average levels of PBDEs were measured from Houjin Creek, while the lowest levels were measured from Laojie River. The highest value of PBDEs was 380 ng/g lipid and was measured in Chongde Bridge from Erren River. These data are mostly in good agreement with data published by other investigators[7-9]. The highest values are found for samples originating from the San Francisco Bay Area[7] and San Francisco Estuary[8]。The average concentration of major PBDEs congeners in each rivers are presented in Figure1. As already reported in literature[9] BDE 47 was the dominant congeners in tissue followed by BDE 154、BDE 99 and BDE 100. The PBDE profile was similar in all fish species.

References

1. Harrad S., Wijesekera R., Hunter S., Halliwell C., and Baker R. *Environ Sci Technol* 2004; 38: 2345.

2. Harrad S., Hazrati S., and Ibarra C. *Environ Sci Technol* 2006; 40: 4633.

3. Harrad S., Ibarra C., Diamond M., Melymuk L., Robson M., Douwes J., Roosens L., Dirtu, A. C., and Covaci

A. *Environ Int* 2008; 34: 232.

4. Thomas G. O., Wilkinson M., Hodson S., and Jones K. *Environ. Pollut* 2006; 141: 30.
5. Birnbaum L. S. and Staskal D. F. *Environ Health Persp* 2004; 112: 9.
6. Darnerud P. O. *Environ Int* 2003; 29: 841.
7. Holden A., She J., Tanner M., Lunder S., Sharp R., Hooper K. Organohalogen Compounds, 61, 255-258, 2003
8. Daniel R. O., Dale H., Francois R., David C., Jose S.; Environ. Sci. Technol., 39,33-41, 2005
9. Lepom P., Karasova T., Sawal G., Organohalogen Compounds, 58, 209-212, 2002

Table 1. Concentrations of PCDD/Fs, PCB and PBDE in fish samples from rivers and estuaries

Location	n	PCDD/F-TEQ (pg/g w.w.)	PCB-TEQ (pg/g w.w.)	PBDE (ng/g lipid)
Laojie River	3	0.275 (0.099 ~ 0.618)	0.395 (0.067 ~ 0.935)	69.1 (40.7 ~ 85.2)
Tung-shan River	7	0.234 (0.058 ~ 0.646)	0.541 (0.071 ~ 1.20)	89.2 (51.2 ~ 182)
Wu River	5	0.136 (0.033 ~ 0.416)	0.260 (0.023 ~ 0.442)	124 (37.0 ~ 216)
Houjin Creek	5	0.248 (0.071 ~ 0.552)	1.20 (0.247 ~ 2.0)	230 (103~ 366)
Erren River	14	0.291 (0.057 ~ 1.02)	3.31 (0.089 ~ 10.4)	187 (40.2 ~ 380)
Niouchou River	5	0.117 (0.057 ~ 0.179)	0.144 (0.034 ~ 0.328)	104 (57.2 ~ 147)
Dahan River	7	0.337 (0.034 ~ 0.584)	2.91 (0.069 ~ 14.1)	74.3 (12.1 ~ 148)
Keelung River	13	0.111 (0.024 ~ 0.407)	0.449 (0.028 ~ 1.63)	152 (25.1 ~ 287)

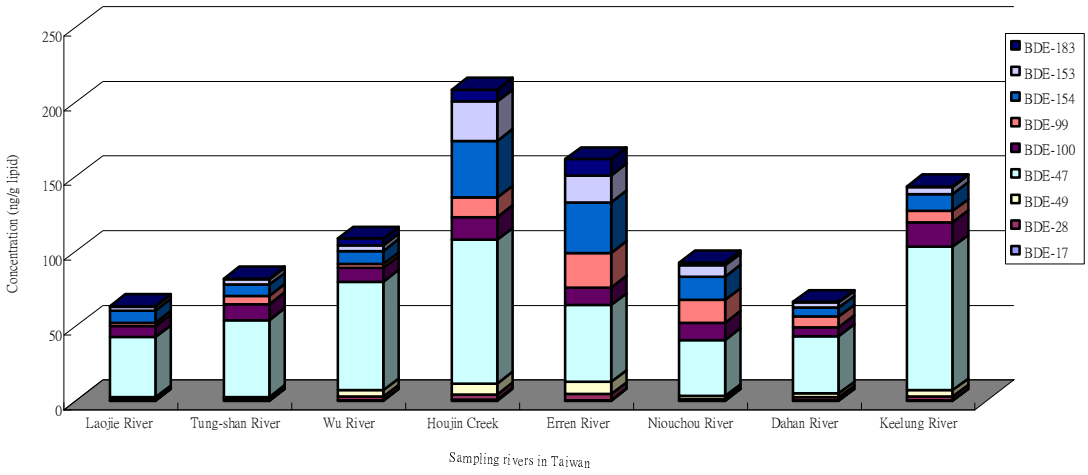

Figure 1. The average concentration profile of major PBDEs congener in fish samples.