

POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN TISSUES FROM SOUTH KOREA

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Introduction

Tissues of shellfish and fish are often used to monitor for environmental contaminants that bioaccumulate and have the potential to adversely affect aquatic organisms and the wildlife and people who eat them ¹. Because of their stable structure and lipophilic properties, PCDDs/DFs have been the focus of many environmental and toxicological studies over the last several years, and these chemicals have been identified in diverse environmental samples from a range of countries ²⁻⁴, however little information was available on the isomer characterization and concentrations of PCDDs/DFs in South Korea. To identify distributions of PCDDs/DFs, and assess potential environmental exposure to total concentrations of PCDDs/DFs, including estimations of 2378-tetrachlorinated dibenzo-*p*-dioxin (2378-TeCDD) equivalents (TEQs), samples of shellfish and fish were collected from South Korea.

Materials and Methods

Samples of shellfish (mussel and clam) and fish (mullet, herring and flounder) were collected respectively from Masan Bay, South Korea. Samples of the mussel (*Septifer virgatus*) (n=150) and clam (*Anomalocardia sp.*) (n=150) were collected in May 1993. Mullet (*Liza macrolepis*) (n=3) were collected in November 1991, and herring (*Konosirus punctatus*) (n=5) and flounder (*Cleisthenes pinetorum herzensteini*) (n=23) were collected in December 1993. All shellfish samples were processed into whole-body minus shell edible portions. Edible portions of fish were prepared as skin-on fillets from which scales and bones had been removed. Each sample was rinsed with purified water to remove all foreign particles, wrapped with clean aluminum foil, and stored at -20°C until analyzed. To increase the mass of fat available for extraction, all fillet and whole-body samples within a given species were composited into a single pooled sample. The lipid-fractions of the tissues were: 1.9, 1.3, 2.7, 2.4 and 2.1% for mussel, clam, mullet, herring and flounder, respectively. PCDDs/DFs analyses were completed on each respective lipid fraction. Known amounts of ¹³C-labeled PCDDs/DFs were added to samples as internal standards. The extract containing the lipids and PCDDs/DFs was transferred to hexane and treated with concentrated sulfuric acid. The resulting extracts, from which the lipids had been removed were passed through a series of silica gel, alumina, activated carbon, and Sep-pak columns to purify and separate the PCDDs/DFs from possible interferences. PCDDs/DFs were identified and quantified using a high resolution gas chromatograph interfaced with a high resolution mass spectrometer (HRGC-HRMS). Recoveries of ¹³C-labeled internal standards ranged from 83% to 105%. Analytical methods for PCDDs/DFs have been reported in detail elsewhere ^{5,6}

Results and Discussion

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs), including 2378-substituted isomers, were present in edible portions of shellfish and fish collected from Masan Bay, South Korea. From the individual isomers detected, total concentrations of PCDDs/DFs and TEQs were calculated, and given on both a lipid-weight and wet-weight basis (Table 1). Shellfish tissues contained a greater number of PCDD/DF isomers, including most of the tetrachlorinated dibenzo-*p*-dioxins and furans (TeCDD and TeCDF), and greater total concentrations of PCDDs/DFs compared to fish collected from the same locations. The mean concentrations were 25-fold greater than those in fish. Total concentrations of PCDDs/DFs in mussel and clam were 750 and 3418 pg/g, lw, respectively, and those of mullet, herring and flounder were 52, 82, and 121 pg/g, lw, respectively.

Concentrations of TEQs in mussel and clam were 0.97 and 12 pg/g, lw, respectively. TEQ concentrations in mullet, herring and flounder were 12, 22, and 18 pg/g, lw, respectively. Although the total concentrations of PCDDs/DFs in fish were less than those in shellfish, 2378-substituted were the predominant isomers in fish, affecting great TEQs (Table 1). In fish 2378-substituted PCDD accounted for 100% of the total PCDD concentrations. The 2378-substituted PCDF accounted for from 59 % of the total concentration of PCDF in flounder to 73 % in mullet. The 2378-substituted isomers accounted for only 3% of the total PCDDs/DFs in shellfish. The limited presence of 2378-substituted isomers in shellfish resulted in small concentrations of TEQs. These results indicate 2378-substituted isomers are more accumulated or retained in fish. Total TEQs in Masan Bay fish, ranging from 0.32 to 0.53 pg/g, wet weight basis, were similar or slightly less than those reported in other comparable studies. Total TEQs in fish from Tokyo Bay ⁷, and Lake Kasumigaura in Japan ⁸ ranged from 0.32 to 2.07 pg/g, ww, and 0.4 to 2.64 pg/g, ww, respectively. Total TEQs in fish from the Sacramento-San Joaquin River in the U.S.A ranged from 0.96 to 3.49 pg/g, ww ⁹.

The concentrations of PCDDs/DFs were similar within species of each trophic level (shellfish vs. fish). Both mussel and clam samples contained a wide range of PCDD/DF isomers. The most frequently observed and highly concentrated isomers included non-2378-substituted PCDDs/DFs, contributing roughly 97% of total PCDDs/DFs, with isomers 1368- and 1379-TeCDD predominating. Total concentrations of PCDDs in shellfish were slightly greater than PCDFs, PCDD/PCDF = 1.34 and 1.37 in mussel and clam, respectively. TeCDD/DF and PeCDD/DF predominated accounting for 97% of total PCDDs/DFs in mussel, and TeCDD/DF alone accounted for greater than 90% of the total. Similarly, TeCDD/DF and PeCDD/DF accounted for 98 % of total PCDDs/DFs in clam tissues, with TeCDD/DF, accounting for 92% of the total. Six of the seventeen 2378-substituted isomers were detected in clam tissue (Table 1). Of 2378-substituted PCDDs, only isomer 1234678-HpCDD was identified. Isomer 2378-TeCDF occurred at the greatest concentration followed by 1234678-HpCDD, whereas concentrations of 123478+123479-HeCDF and 123678-HeCDF were the least. In mussel tissue, only two isomers of 2378-substituted PCDDs/DFs, including OCDD and 2378-TeCDF were detected.

2378-TeCDD, the most toxic isomer of total PCDDs/DFs, was observed in two each of the herring and flounder. Of the total PCDDs, only three 2378-substituted isomers, 2378-TeCDD, 12378-PeCDD and OCDD, were observed in fish. Of the total PCDFs, four of 2378-TeCDF, 12378+12348-PeCDF, 23478-PeCDF, and 234678-HeCDF, were predominant in all three species

of fish, with high concentrations of 2378-TeCDF. Together these four isomers accounted for 73%, 69%, and 58% of the total concentration of PCDFs in mullet, herring, and flounder, respectively. Notable among the non-2378-substituted PCDF isomers found in fish was 2348-TeCDF which was found at relatively great concentrations in all samples. Along with 2378-TeCDF and 23478-PeCDF, these three PCDFs were found in all fish samples at relatively great concentrations. These findings are consistent with the results of other studies, which have found that these three PCDF compounds are both strongly accumulated and retained. Several species of fish collected from Saginaw Bay in USA ¹⁰ contained 2378-TeCDF and 23478-PeCDF at concentrations greater than all of the other observed isomers. Isomer profiles for fishes from Tokyo Bay in Japan ⁷ were also dominated by 2378-TeCDF and 23478-PeCDF.

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Table 1. Concentrations of TEQs and total PCDDs/DFs (pg/g) in shellfish and fish samples collected from South Korea

PCDDs/DFs	Shellfish		Fish		
	Mussel (n=150)	Clam (n=150)	Mullet (n=3)	Herring (n=5)	Flounder (n=23)
2378-TeCDD	0	0	0	7.6	4.3
12378-PeCDD	0	0	4.6	5.9	0
123478-HeCDD	0	0	0	0	0
123678-HeCDD	0	0	0	0	0
123789-HeCDD	0	0	0	0	0
1234678-HpCDD	0	30	0	0	0
OCDD	15	0	9.3	0	0
Other TeCDD	381	1774	0	0	0
Other PeCDD	25	135	0	0	0
Other HeCDD	0	32	0	0	0
Other HpCDD	9.8	7.4	0	0	0
2378-TeCDF	9.6	61	9.2	24	45
12378+12348-PeCDF	0	9	0	4.9	6.7
23478-PeCDF	0	9.3	17	18	18
123478+123479-HeCDF	0	3.1	0	0	0
123678-HeCDF	0	3.1	0	0	0
123789-HeCDF	0	0	0	0	0
234678-HeCDF	0	0	1.4	0	0
1234678-HpCDF	0	0	0	0	0
1234789-HpCDF	0	0	0	0	0
OCDF	0	0	0	0	0
Other TeCDF	286	1276	10	21	43
Other PeCDF	24	80	0	0	5.4
Other HeCDF	0	0	0	0	0
Other HpCDF	0	0	0	0	0
Lipid weight basis (pg/g)					
Total PCDDs	430	1977	14	14	4.3
Total PCDFs	320	1441	38	68	117
Total PCDDs+PCDFs	750	3418	52	82	121
TEQs	0.97	12	12	22	18
Wet weight basis (pg/g)					
Total PCDDs	8.2	26	0.38	0.34	0.09
Total PCDFs	6.1	19	1	1.6	2.5
Total PCDDs+PCDFs	14	44	1.4	2	2.5
TEQs	0.02	0.16	0.32	0.53	0.38

TeCDD/DF = Tetrachlorinated dibenzo-*p*-dioxin/furan
 PeCDD/DF = Pentachlorinated dibenzo-*p*-dioxin/furan
 HeCDD/DF = Hexachlorinated dibenzo-*p*-dioxin/furan
 HpCDD/DF = Heptachlorinated dibenzo-*p*-dioxin/furan
 OCDD/DF = Octachlorinated dibenzo-*p*-dioxin/furan
 TEQs = Toxic equivalency quotients