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Concentrations and accumulation profiles of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in aquatic tissues, and ambient air from South Korea

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Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs), including 2378-substituted isomers were present in samples of shellfish and fish, and ambient air collected from Masan Bay, and Masan City, South Korea. Total concentrations of PCDDs/DFs in mussel and clam were 750 pg g^{-1}, lipid weight (lw), and 3418 pg g^{-1}, lw, respectively. Total concentrations of PCDDs/DFs in mullet, gizzard and flounder were 52, 82, and 122 pg g^{-1}, lw, respectively. Shellfish tissues contained a greater number of PCDD/DF isomers, contributing greater total concentrations of PCDDs/DFs compared to fish collected from the same locations. The predominance of 2378-substituted PCDDs/DFs in fish is represented in greater total concentrations of 2378-TeCDD equivalents (TEQs), whereas there was very limited occurrence of 2378-substituted isomers in shellfish. TEQ concentrations in samples of mussel and clam were 0.97 and 12 pg g^{-1}, lw, respectively. Total TEQs in mullet, gizzard and flounder were 12, 22 and 18 pg g^{-1}, lw, respectively. In fish 2378-substituted PCDDs accounted for 100% of the total concentrations of PCDDs, and 2378-substituted PCDFs accounted from 59% to 73% of the total PCDFs. The 2378-substituted isomers accounted for only 3% of the total PCDDs/DFs in shellfish. Ambient air collected from two sites contained a wide range of isomers of tetra- through heptachlorinated PCDDs/DFs. Even though the total concentration of PCDDs/DFs in ambient air (12.8 pg m^{-3}) collected from an industrial area was 2-fold greater than that in air samples (6.3 pg m^{-3}) collected from an urban/rural area, total TEQs (0.07 and 0.08 pg m^{-3}) there was no statistical difference between the two samples.

Keywords: PCDDs; PCDFs; Shellfish; Fish; Air; Masan Bay

1. Introduction

Previous studies have reported concentrations and characteristics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) and polychlorinated biphenyls (PCBs) in soils and sediments collected from South Korea (Im et al., 1994, 1995, 2002a,b). Tissue samples, such as shellfish and fish, and ambient air were

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collected concurrently for this study. Shellfish and fish samples often used to monitor for environmental contaminants that bioaccumulate and have the potential to adversely affect aquatic organisms and wildlife, and to evaluate potential risk of PCDDs/DFs to people who eat them (Giesy et al., 1994). However, very limited information was available on the isomer distribution of PCDDs/DFs and bioaccumulative characteristics in aquatic trophic levels, such as shellfish and fish, in South Korea. Ambient air is useful for monitoring of terrestrial environment of PCDDs/DFs. Once distributed to ambient air, organohalogen compounds, such as PCDDs/DFs, are easily transported from sites with sources to long distance locations, deposited and accumulated into various environmental media, such as vegetation, soils, grazing livestock and human diet and human exposure (Kevin and Duarte-Davidson, 1997; Lohmann et al., 1999).

PCDDs/DFs are released into the environment from many possible sources including incineration, industrial processes, and internal combustion engines. PCDDs/DFs have been identified as agents responsible for many toxic responses in exposed individuals, including cancer and developmental/reproductive dysfunctions (Murray et al., 1979; Peterson et al., 1993; Aylward et al., 1996). 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 (Gardner and White, 1990; Eitzer, 1993; Kucklick and Baker, 1998; Giesy et al., 1999). A previous study reported concentrations of PCDDs/DFs of dairy products from 39 countries, among which samples from Korea contained the greatest total concentrations (Weiss et al., 2001). The objectives of this research were to identify distributions of PCDDs/DFs in samples of shellfish, fish and ambient air collected from South Korea, including estimations of 2378-tetrachlorinated dibenzo-*p*-dioxin (2378-TeCDD) equivalents (TEQs), and to characterize accumulative and exposure properties of PCDDs/DFs between trophic levels such as shellfish and fish.

2. Materials and methods

Samples of shellfish (mussel and clam) and fish (mullet, gizzard and flounder) and ambient air were collected from Masan Bay and Masan City, South Korea (Fig. 1). Masan Bay is a semi-closed estuary, in southeastern South Korea that has productive fishing areas in the near the open sea. About 150 samples of the mussel (*Septifer virgatus*) and clam (*Anomalocardia* sp.) were collected respectively in May 1993. Five samples of gizzard (*Konosirus punctatus*) and 23 flounder (*Cleisthenes pinetorum herzensteini*) were collected in December

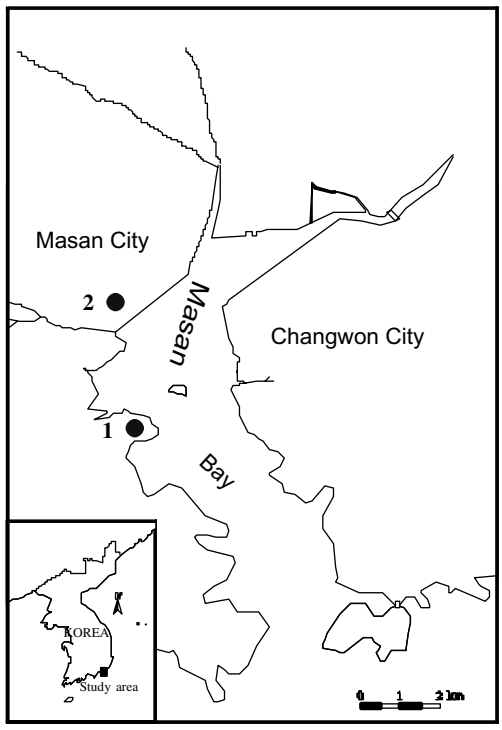

Fig. 1. Map of Masan Bay and Masan City, South Korea, indicating sampling locations for shellfish and fish, and air. Tissues were collected from the bay, and ambient samples were collected from two sites ((●) sites 1 and 2) in the city.

1993, and three Mullet (*Liza macrolepis*) samples were collected in November 1991. Mussel and clam samples were collected by hand from near-shore habitats. All shellfish samples were processed into whole-body minus shell edible portions. Fish samples were collected via hook-and-line (sport fishing) and gill netting (census) methods. Ranges of the size of fish were: mullet (20–30 cm), gizzard (10–16 cm), and flounder (12–16 cm). Fish samples 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 mussel tissue samples within a given species a single pooled sample composite was made. Pooled sample weights for mussel, clam, mullet, gizzard and flounder were 643, 401, 230, 145, and 483 g, respectively. Wet tissue was homogenized with anhydrous sodium sulfate, and Soxhlet extracted with acetone (6 h) and dichloromethane (24 h) to extract lipid and associated PCDDs/DFs. The lipid-fractions of the tissues were: 1.9%, 1.3%, 2.7%, 2.4% and 2.1% for mussel, clam, mullet, gizzard and flounder, respectively. PCDDs/DFs analyses were completed on each respective lipid fraction. Known amounts of ^{13}C-labeled

PCDDs/DFs were added to samples as internal standards. The extract containing the lipids and PCDDs/DFs were transferred to hexane and treated with concentrated sulfuric acid, followed by a series of silica gel, alumina, activated carbon, and Sep-pak columns to purify and separate the PCDDs/DFs from possible interfering compounds (Im et al., 1995).

Ambient air was collected from two sites in Masan City during March 1995 (sites 1 and 2, Fig. 1). Initial air sampling activities included four collection sites, however two of the four samples were lost during sampling, and data from the two sites are discussed here. Site 1 was located in an industrial area where local conditions are influenced by industrial activities, such as metal processing and waste incineration. Site 2 was on the roof of a building in an urban/rural area. Air samples were taken continuously for 5 days with a flow rate of approximately 18 m^3/h. An air pump sampler (model AP-240Z, Iwaki Co., Japan) equipped with cleaned glass fiber filters and three polyurethane foam plugs (PUF; diameter, 4 cm; length, 5 cm) was used to capture PCDDs/DFs associated with particulate matter and the gaseous phase. Air flow rate was measured with a gaseous flow meter (model RK-1450-002, Koshima Co., Japan). Following sample collection, the filters and PUF plugs were Soxhlet extracted with 500 ml acetone for 6 h followed by 500 ml toluene for 24 h. Known amounts of ^{13}C-labeled PCDDs/DFs were added to samples as internal standards. After Kuderna-Danish concentration, the solvent was transferred to hexane and treated with concentrated sulfuric acid. A series of silica gel, alumina, activated carbon, and Sep-pak column clean-up procedures were completed.

PCDDs/DFs were identified and quantified using a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS). Instrumentation included a Hewlett Packard (HP) 5890 series II gas chromatograph (Avondale, PA, USA), connected to a JEOL SX102A high-resolution mass spectrometer. The capillary column was 50 m long with a 0.25-mm i.d. and 0.2-μm stationary phase film thickness (CP-Sil 88, Chromopack, Supelco, Bellefonte, PA, USA). The mass spectrometer was operated in EI mode at 70 eV. PCDDs/DFs were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster. Recoveries of ^{13}C-labeled internal standards ranged from 83% to 105%. Reported concentrations were corrected for the recoveries of internal standards. Identification and quantification of PCDDs/DFs were performed by means of internal and external standards. A fly ash sample containing known compositions of PCDD/DF isomers was used as a reference to identify individual PCDDs/DFs. Procedural blanks were analyzed for every five samples to check for interferences and laboratory contamination. Interferences were not found in blanks. Concentrations of PCDDs/DFs are reported as the sum of all the quantifiable isomers. Concentrations that were less than the method detection limits (MDL) were assigned a value of zero when calculating means. Total TEQ concentrations are calculated for the 17 2378-substituted PCDDs/DFs using international toxic equivalency factors (I-TEFs) (Kutz et al., 1990).

3. Results and discussion

3.1. Shellfish and fish

From the individual isomers of tetra- through octachlorinated PCDDs/DFs detected, total concentrations of PCDDs/PCDFs, and TEQs were calculated, and given on both a lipid-weight and wet-weight basis (Table 1). Total concentrations of PCDDs/DFs in shellfish tissues, such as mussel and clam were 750 and 3418 pg g^{-1}, lw, respectively, and those of mullet, gizzard and flounder were 52, 82 and 122 pg g^{-1}, lw, respectively. Shellfish tissues contained a wide range of PCDD/DF isomers, affecting greater PCDD/DF concentrations, than did fish, and mean concentrations were 25-fold greater than those in fish. Chromatograms of all the tetra- through octachlorinated PCDD/DF isomers detected in clam samples are shown (Fig. 2).

Among PCDD/DF isomers, 2378-substituted PCDDs/DFs are more toxic and persistent than the other isomers of PCDDs/DFs, and can interact with the aromatic hydrocarbon receptor (AhR). Total concentrations of 2378-TeCDD equivalents (TEQs) in samples of mussel and clam were 0.97 and 12 pg g^{-1}, lw, respectively. Total TEQs in mullet, gizzard and flounder were 12, 22 and 18 pg g^{-1}, lw, respectively. Although the total concentrations of PCDDs/DFs in fish were much less than those in shellfish, 2378-substituted were the predominant isomers in fish, affecting great TEQs (Table 1). In fish 2378-substituted PCDD isomers accounted for 100% of the total PCDD concentrations, and the 2378-substituted PCDF accounted for from 59% of the total PCDFs in flounder to 73% in mullet, whereas 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 that 2378-substituted isomers are more likely to be stable and retained in fish tissues, and less biodegradation of a range of PCDD/DF isomers occurred in shellfish. These findings are similar to those observed in shellfish and fish tissues in other relevant studies (Naito et al., 2003). Total TEQs, expressed on a wet weight basis, in fish collected from Masan Bay ranging from 0.32 to 0.53 pg g^{-1}, ww (Table 1), were similar or slightly less than those reported in other comparable studies. Total TEQs in fish from Tokyo Bay (Sakurai et al., 2000), and Lake Kasumigaura, Japan

Table 1
Total PCDDs/DFs and TEQs in shellfish and fish ($pg\,g^{-1}$), and in air ($pg\,m^{-3}$) from Masan Bay and Masan City

PCDDs/DFs	Shellfish		Fish			Air	
	Mussel	Clam	Mullet	Gizzard	Flounder	Site 1	Site 2
TeCDD[a]							
1368	247	1196	<0.02	<0.02	<0.02	2.56	0.89
1379	75	417	<0.02	<0.02	<0.02	1.1	0.32
1378	8.5	<0.02	<0.02	<0.02	<0.02	0.17	0.2
1247 + 1248 + 1369	17	51	<0.02	<0.02	<0.02	0.05	<0.02
1268	2.1	36	<0.02	<0.02	<0.02	<0.02	<0.02
1478	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2378	<0.02	<0.02	<0.02	7.6	4.3	0.03	0.05
1234 + 1246 + 1249	<0.02	24	<0.02	<0.02	<0.02	0.24	<0.02
1237 + 1238	15	51	<0.02	<0.02	<0.02	<0.02	<0.02
1279 + 1236	2.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1469 + 1278	<0.02	<0.02	<0.02	<0.02	<0.02	0.05	<0.02
1239	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1269	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1267	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1289	15	<0.02	<0.02	<0.02	<0.02	0.03	<0.02
Total	381	1774	<0.02	7.6	4.3	4.2	1.5
PeCDD[b]							
12479 + 12468	18	76	<0.02	<0.02	<0.02	0.6	0.2
12368	6.8	40	<0.02	<0.02	<0.02	0.2	0.07
12478	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12379	<0.02	13	<0.02	<0.02	<0.02	0.1	0.05
12469 + 12347	<0.02	6.6	<0.02	<0.02	<0.02	0.03	0.02
12378	<0.02	<0.02	4.6	5.9	<0.02	<0.02	<0.02
12369	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12467	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12489	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12346	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12367	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12389	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Total	25	135	4.6	5.9	<0.02	0.89	0.33
HeCDD[c]							
124679 + 124689 + 123468	<0.02	26	<0.02	<0.02	<0.02	0.32	0.19
123679 + 123689	<0.02	5	<0.02	<0.02	<0.02	0.14	0.1
123478	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
123678	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.05
123469	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
123789	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
123467	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Total	<0.02	31	<0.02	<0.02	<0.02	0.46	0.34
HpCDD[d]							
1234679	9.8	7.4	<0.02	<0.02	<0.02	0.16	0.08
1234678	<0.02	30	<0.02	<0.02	<0.02	0.24	0.13
Total	9.8	37	<0.02	<0.02	<0.02	0.4	0.21
OCDD[e]							
12346789	15	<0.02	9.3	<0.02	<0.02	<0.02	<0.02
TeCDF[f]							
1368	<0.02	<0.02	<0.02	<0.02	<0.02	0.19	0.1
1378 + 1379	26	86	<0.02	<0.02	<0.02	0.22	0.13
1347	9.6	47	<0.02	<0.02	<0.02	0.26	0.16
1468	14	12	<0.02	<0.02	<0.02	0.18	0.08
1247 + 1367	19	111	<0.02	<0.02	<0.02	0.14	0.07
1348	7.7	22	<0.02	<0.02	<0.02	0.23	0.13

Table 1 (*continued*)

PCDDs/DFs	Shellfish		Fish			Air	
	Mussel	Clam	Mullet	Gizzard	Flounder	Site 1	Site 2
1346 + 1248	9.6	69	1.1	<0.02	<0.02	0.09	0.1
1237 + 1369 + 1478 + 1246 + 1268	42	215	<0.02	<0.02	<0.02	0.67	0.42
1234 + 1678	12	52	<0.02	<0.02	<0.02	0.11	0.57
1238 + 1467 + 1236 + 2468	17	85	<0.02	<0.02	<0.02	0.52	0.19
1349	16	76	<0.02	<0.02	<0.02	<0.02	<0.02
1278	9.6	50	<0.02	<0.02	<0.02	<0.02	<0.02
1267 + 1279	13	36	<0.02	<0.02	<0.02	<0.02	<0.02
1469 + 2368 + 1249	19	85	<0.02	<0.02	<0.02	0.33	<0.02
2467	19	66	<0.02	<0.02	<0.02	0.44	0.1
1239 + 2347	8.8	50	<0.02	<0.02	<0.02	0.09	0.06
1269	<0.02	2.5	<0.02	<0.02	<0.02	<0.02	<0.02
2378	9.6	61	9.2	24	45	0.08	0.04
2348	9.6	59	9.2	21	43	0.1	0.09
2346	9	26	<0.02	<0.02	<0.02	0.16	0.1
2367	19	97	<0.02	<0.02	<0.02	0.13	<0.02
3467	5.8	33	<0.02	<0.02	<0.02	0.09	0.07
1289	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Total	295	1337	20	45	88	4.0	2.4
PeCDF[g]							
13468	3	<0.02	<0.02	<0.02	<0.02	0.08	0.08
12468	12	<0.02	<0.02	<0.02	<0.02	0.1	0.08
13678	2.8	4.5	<0.02	<0.02	<0.02	0.05	0.04
13478	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
13479 + 12368	4.9	21	<0.02	<0.02	5.4	0.17	0.07
12478	<0.02	9	<0.02	<0.02	<0.02	0.09	0.03
12479 + 13467	1.9	12	<0.02	<0.02	<0.02	0.07	0.06
12467	<0.02	12	<0.02	<0.02	<0.02	0.06	0.05
12347 + 14678	<0.02	6	<0.02	<0.02	<0.02	0.04	0.02
13469	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	<0.02
12378 + 12348	<0.02	9	<0.02	4.9	6.7	0.11	0.06
12346 + 12379	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03
12367	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12469 + 23468	<0.02	<0.02	<0.02	<0.02	<0.02	0.08	0.03
13489	<0.02	<0.02	<0.02	<0.02	<0.02	0.13	0.07
12369	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12678	<0.02	6.2	<0.02	<0.02	<0.02	<0.02	<0.02
12349	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12489	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23478	<0.02	9.3	17	18	18	<0.02	<0.02
12389	<0.02	<0.02	<0.02	<0.02	<0.02	0.08	0.06
23467	<0.02	9	<0.02	<0.02	<0.02	0.13	0.07
Total	24	98	17	23	30	1.2	0.8
HeCDF[h]							
123468	<0.02	<0.02	<0.02	<0.02	<0.02	0.12	0.04
124678 + 134679	<0.02	<0.02	<0.02	<0.02	<0.02	0.23	0.09
134678	<0.02	<0.02	<0.02	<0.02	<0.02	0.23	<0.02
124679	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.11
123478 + 123479	<0.02	3.1	<0.02	<0.02	<0.02	0.02	<0.02
123678	<0.02	3.1	<0.02	<0.02	<0.02	0.08	0.06
124689	<0.02	<0.02	<0.02	<0.02	<0.02	0.12	0.06
123467	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
123679	<0.02	<0.02	<0.02	<0.02	<0.02	0.18	0.18
123469 + 123689	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
123789	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

(*continued on next page*)

Table 1 (*continued*)

PCDDs/DFs	Shellfish		Fish			Air	
	Mussel	Clam	Mullet	Gizzard	Flounder	Site 1	Site 2
123489	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
234678	<0.02	<0.02	1.4	<0.02	<0.02	0.11	0.09
Total	<0.02	6.2	1.4	<0.02	<0.02	1.1	0.6
HpCDF[i]							
1234678	<0.02	<0.02	<0.02	<0.02	<0.02	0.45	0.13
1234679	<0.02	<0.02	<0.02	<0.02	<0.02	0.06	<0.02
1234689	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1234789	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Total	<0.02	<0.02	<0.02	<0.02	<0.02	0.5	0.1
OCDF[j]							
12346789	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
	Lipid weight basis ($pg\,g^{-1}$)					($pg\,m^{-3}$)	
Total PCDDs	431	1977	14	14	4.3	6	2.4
Total PCDFs	319	1441	38	68	118	6.8	3.9
Total PCDDs + PCDFs	750	3418	52	82	122	12.8	6.3
TEQs[k]	0.97	12	12	22	18	0.07	0.08
	Wet weight basis ($pg\,g^{-1}$)						
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		

[a] TeCDD = Tetrachlorinated dibenzo-*p*-dioxin.
[b] PeCDD = Pentachlorinated dibenzo-*p*-dioxin.
[c] HeCDD = Hexachlorinated dibenzo-*p*-dioxin.
[d] HpCDD = Heptachlorinated dibenzo-*p*-dioxin.
[e] OCDD = Octachlorinated dibenzo-*p*-dioxin.
[f] TeCDF = Tetrachlorinated dibenzofuran.
[g] PeCDF = Pentachlorinated dibenzofuran.
[h] HeCDDF = Hexachlorinated dibenzofuran.
[i] HpCDF = Heptachlorinated dibenzofuran.
[j] OCDF = Octachlorinated dibenzofuran.
[k] TEQs = Toxic equivalency quotients.

(Sakurai et al., 1996) ranged from 0.32 to 2.1 $pg\,g^{-1}$, ww, and 0.4–2.6 $pg\,g^{-1}$, ww, respectively. Total TEQs in fish from the Sacramento-San Joaquin River in the USA ranged from 0.96 to 3.5 $pg\,g^{-1}$, ww (Petreas et al., 1992).

Distributions of relative concentrations of PCDDs/DFs and the isomer profiles may be explained by trophic level as well as the duration, extent of exposure and potential for metabolism. Although total PCDDs/DFs, including TEQs, varied considerably among tissue samples, a positive relationship was observed between the trophic position (shellfish vs. fish) and the concentrations/accumulation profiles of PCDDs/DFs. More individual PCDDs/DFs occurred at quantifiable concentrations in shellfish tissues of mussel and clam. The isomers that were observed most frequently and at the greatest concentrations included non-2378-substituted PCDDs/DFs, contributing roughly 97% of the total PCDDs/DFs. 1368- and 1379-TeCDD are the most dominant isomers, contributing 85% and 91% of the TeCDD concentrations in mussel and clam tissue, respectively, which findings are consistent with the results of earlier study on sediment samples (Im et al., 2002b), suggesting that the herbicide CNP which contains these isomer pair as major impurities, could have been the possible source of these isomer (Yamagishi et al., 1981). Total concentrations of PCDDs in shellfish were slightly greater than PCDFs, PCDDs/PCDFs = 1.35 and 1.37 in mussel and clam, respectively. Less chlorinated PCDDs/DFs, in particular, tetrachlorinated dibenzo-*p*-dioxin/furan (TeCDD/DF) predominated in shellfish tissues. TeCDD/DF alone accounted for greater than 90% of the total PCDDs/DFs in mussel. Similarly, TeCDD/DF accounted for 91% of the total in clam tissues. Of the 17 2378-substituted PCDDs/DFs, clam tissues contained a relatively greater number of isomers

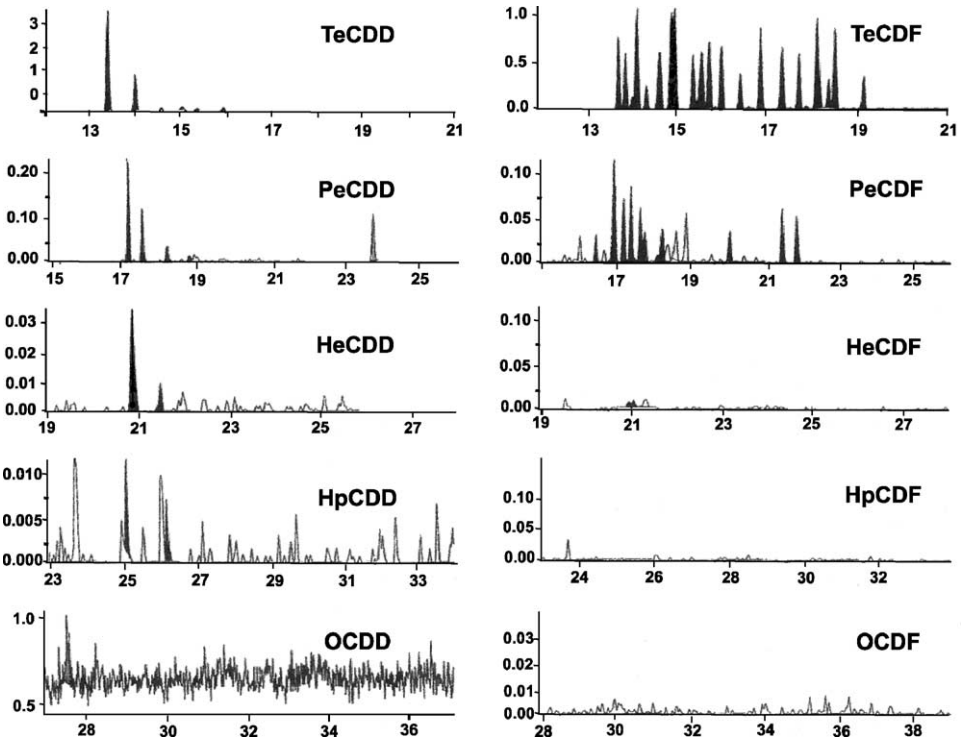

Fig. 2. Mass chromatograms of tetra- through octachlorinated PCDD/DF isomers observed in clam tissue from Masan Bay, South Korea.

than did mussel (Fig. 3). Six isomers were detected, including two isomers that co-eluted. 2378-TeCDF occurred at the greatest concentration, whereas 123478 + 123479-, and 123678-HeCDF were the least. In mussel tissue, only two isomers, 2378-TeCDF and OCDD, were detected. The OCDD concentration exceeded that of 2378-TeCDF, however, due to a relatively small TEF for OCDD, it did not contribute significantly to the total concentration of TEQs.

Although fish tissues contained a limited number of PCDD/DF isomers, of which 2378-substituted isomers predominated, resulting in greater TEQ concentrations (12–22 pg g^{-1}, lw) compared to shellfish (0.97 and 12 pg g^{-1}, lw). Of a wide range of PCDDs, only three 2378-substituted PCDDs, 2378-TeCDD, 12378-PeCDD and OCDD, were detected (Fig. 3). Both total concentrations of PCDDs and PCDD-TEQs were contributed by only those three isomers. Among PCDFs, 2378-substituted were also the major isomers found, which are 2378-TeCDF, 12378 + 12348-PeCDF, 23478-PeCDF, and 234678-HeCDF. Together these four 2378-substituted isomers of PCDFs, accounted for 73%, 69%, and 59% in mullet, gizzard, and flounder, respectively. 2378-TeCDD, the most toxic isomer of total PCDDs/DFs, was observed in gizzard and flounder. 2378-TeCDF was detected in all tissue samples of shellfish and fish analyzed, with relatively great concentrations, and 23478-PeCDF were also observed as a predominant isomer in

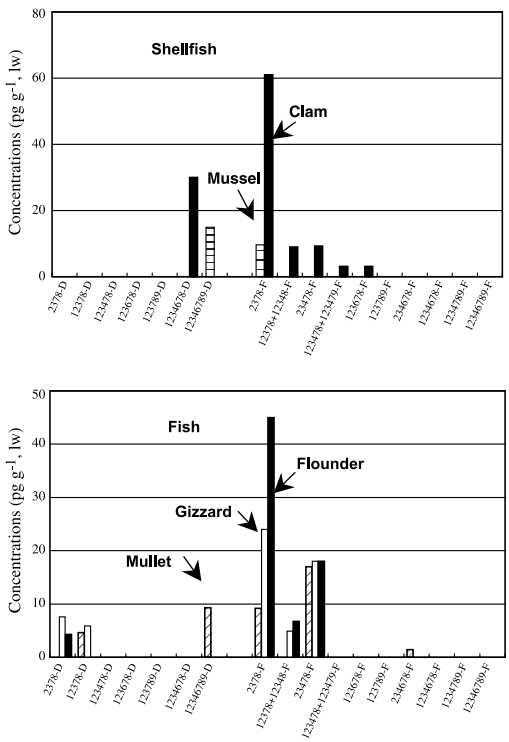

Fig. 3. Concentrations and distributions of 2378-substituted PCDD/DF isomers detected in tissues of shellfish and fish.

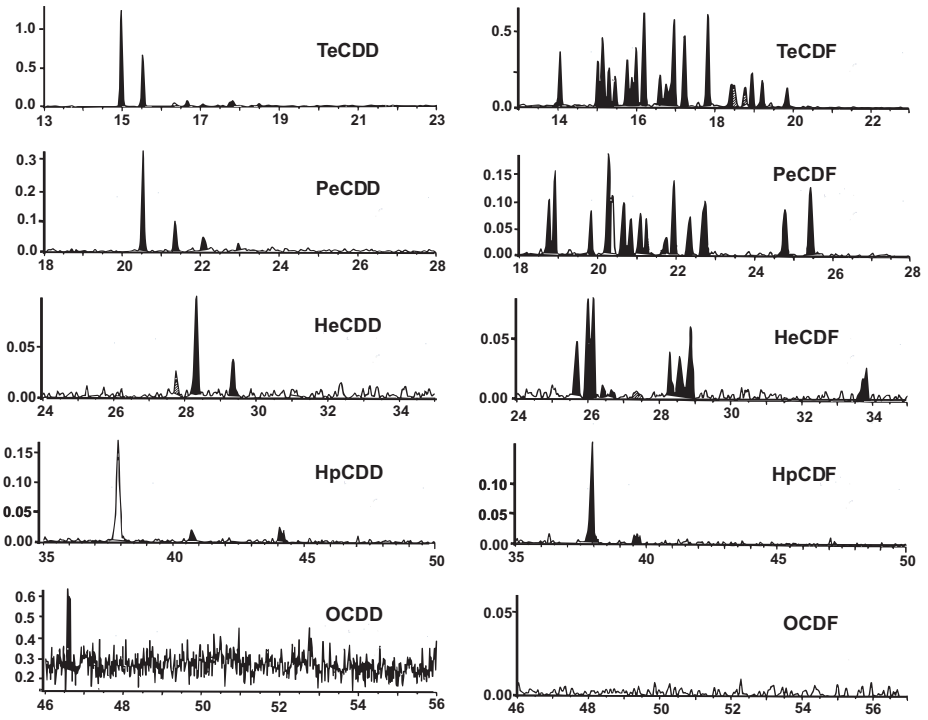

Fig. 4. Mass chromatograms of tetra- through octachlorinated PCDD/DF isomers observed in air sample from site 1 in Masan City, South Korea.

tissues. These results show that those three isomers are persistent and preferentially accumulated with less biodegradation in tissues. This pattern is similar to those measured in diverse environmental bio-samples (Giesy et al., 1997; Iseki et al., 2001; Kannan et al., 2003). Several studies have reported that technical PCBs contain 2378-TeCDF and 23478-PeCDF as a major impurity (Van den Berg et al., 1985; Wakimoto et al., 1988).

Notable among the non-2378-substituted PCDF isomers found in tissues was 2348-TeCDF which was found at relatively great concentrations nearly similar to that of 2378-TeCDF. 2348-TeCDF has none of TEFs, however, likely to be retained and accumulated in tissue samples.

3.2. Air

Ambient air was collected from two sites. Site 1 was located in an industrial area where local conditions are influenced by industrial activities. The site 2 sample was from an urban/rural area. All isomers of tetra- through octachlorinated PCDDs/DFs and 2378-substituted isomers observed are reported in Table 1. Chromatograms of all isomers detected in the sample from site 1 are shown (Fig. 4). A few more individual PCDDs/DFs were observed in air from site 1. Total PCDDs/DFs at sites 1 and 2 were 12.8 and 6.3 $pg\,m^{-3}$, respectively. Air from site 1 contained approximately twice as much total PCDDs/DFs than did air at site 2. Industrial processes at site 1 included possible combustion and incineration-related sources for PCDDs/DFs formation. Industrial sites that lack suitable emissions controls may be major sources of PCDDs/DFs, which influenced the concentrations of PCDDs/DFs in ambient air at both a local and regional level. Total concentrations of PCDDs/DFs measured in air samples (12.8 and 6.3 $pg\,m^{-3}$) were greater than those of other relevant studies in other countries. Concentrations of PCDDs/DFs in air samples collected from Gothenburg, Sweden, a mid-sized industrial city, ranged from 1.0 to 1.8 $pg\,m^{-3}$ (Tysklind et al., 1993). Total concentrations of PCDDs/DFs in air samples from Lancaster, United Kingdom ranged from 0.71 to 1.5 $pg\,m^{-3}$ (Lohmann et al., 1999). Air at McMurdo Station, Antarctica ranged from 0.04 to 4.6 $pg\,m^{-3}$ (Lugar et al., 1996).

Nine of the seventeen 2378-substituted PCDDs/DFs were detected in air from both sites (Table 1). Total concentrations of TEQs were similar at the two sites, with concentrations of 0.07 and 0.08 $pg\,m^{-3}$, respectively, despite the significant difference in total concentrations and local conditions between the two sites. Contributions and isomer patterns of 2378-substituted PCDDs/DFs detected were similar at the two sites,

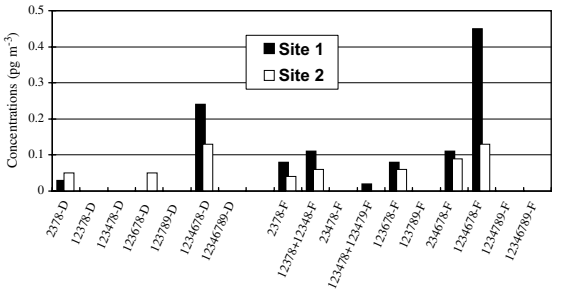

Fig. 5. Contributions and isomer patterns of 2378-substituted PCDDs/DFs detected in ambient samples.

excepting that 123478-HeCDF was identified only at site 1, and 123678-HeCDD was found only at site 2 (Fig. 5). The 2378-substituted isomers found in the greatest concentrations were 1234678-HpCDD and 1234678-HpCDF. The most toxic PCDD/DF, 2378-TeCDD, was detected in both samples, at concentrations of 0.03 and 0.05 pg m^{-3}. At site 1, TeCDD/DF were the most abundant PCDDs/DFs, contributing 63% to the total concentrations of PCDDs/DFs. Air at site 2 also contained TeCDD/DF (63%) at the greatest concentrations. The relative proportions of TeCDD/DF in both air samples generally followed in decreasing order of: PeCDD/DF > HeCDD/DF > HpCDD/DF > OCDD/DF. These results are similar to the profile of PCDDs/DFs for soil collected from near the air sampling sites in previous study (Im et al., 2002a). The presence of predominantly less chlorinated PCDDs/DFs has been linked to atmospheric discharges from ongoing manufacturing activities at chemical-related works (Jones and Davidson, 1997). Combustion and incineration can also produce a range of PCDD/DF isomers (Yasuhara et al., 1987; Erickson et al., 1989; Sakai et al., 2000). Many isomers of tetra- through heptachlorinated PCDDs/DFs were observed in air samples, indicating that combustion and incineration-related processes have also contributed to PCDDs/DFs in ambient air.

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