Contamination of Dioxins and Dienzo-furans in Shellfish from Western Coastal Area in Korea

Jong-Guk Kim*, Kyoung-Sim Kim

Department of Environmental Engineering, Chonbuk National University
Research Institute of Industrial Technology in Chonbuk National University*
664-14 Duckjin-Dong, Duckjin-gu, Chonju, Chonbuk, 561-756, Korea

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have never been manufactured intentionally from incineration and combustion process, pulp bleaching and chemical process. Once these compounds are released to the environment, they have tendency to accumulate in land and water bodies through dry/wet deposition, and then finally exposed to human through inhalation, skin contact and food consumption. The main sources of PCDDs/PCDFs are well known from food ingestion, it has some kind of difference according to the dietary life pattern. Especially, in Korea and Japan, contribution of PCDDs/PCDFs was estimated to be about 40-60 percent by fish/shellfish intake.

On the other hand, Shellfish are used as bio-indicator organisms to assess available contaminant concentrations in coastal area because of their abundance, wide distribution, sedentary behavior and accumulation of ambient trace pollutants.

With the above information the objective of this study is to investigate levels of PCDDs/PCDFs using shellfish as bio-indicator in western-coastal area of Korea and from the results we intend to understand the characteristics of PCDDs/PCDFs distribution from this result.

2. Material and Methods

2.1. Sampling and sample preparation

Eleven sampling sites are to locate in western-coastal area of Korea as shown in Fig. 1. During the periods of October and November, shellfish samples (clam, oyster) were collected and kept frozen until analysis.

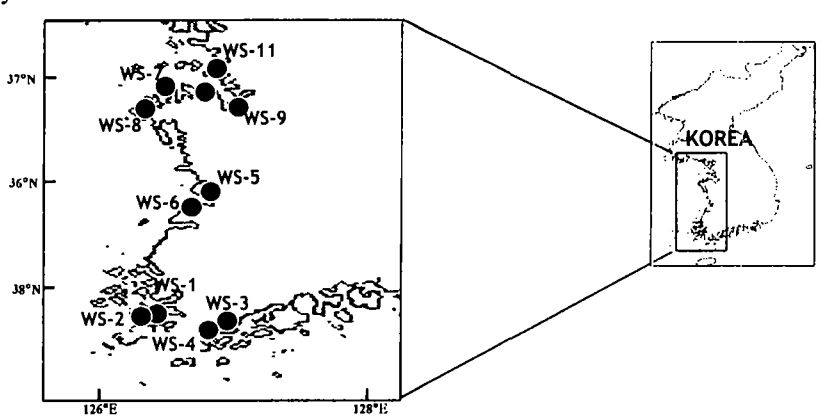

Fig. 1. Sampling location of shellfish in western-coastal area of Korea.

2.2 Analytical method

All samples were finely homogenized with anhydrous Na_2SO_4 and extracted using a Soxhlet apparatus with dichloromethane (DCM) about 20hours(sample information is shown in Table 1). The solvents were allowed to evaporate and the fat content was determined gravimetrically. The $^{13}C_{12}$-surrogate standards were added to each samples and the fat was di-resolved in n-hexane and treated with concentrated sulfuric acid. Crude extract from every sample was transferred to silica gel column, basic alumina column and finally, in activated carbon impregnated silica gel column chromatography.

Table 1. Sample information

Sample code	Sample Name	Scientific Name	Total Sample weight (g)	Fat content (%)	Shell length (cm)	Each soft tissue weight (g)*
WS-1	Little neck Clam	*Tapes philippinarum*	61.84	0.74	2.4 - 4.2	0.7
WS-2	Little neck Clam	*Tapes philippinarum*	44.24	0.67	3.3 - 3.7	1.0
WS-3	Little neck Clam	*Tapes philippinarum*	45.62	1.09	3.5 - 4.2	0.5
WS-4	Clam	*Meretrix lamarkii*	45.32	0.43	5.4 - 5.7	3.2
WS-5	Bivalve	*Pelecypoda*	53.21	0.69	5.0 - 5.8	3.0
WS-6	Little neck Clam	*Tapes philippinarum*	78.01	0.87	3.1 - 4.6	1.4
WS-7	Oysters	*Crassostrea gigas*	51.23	1.36	2.5 - 3.0	1.8
WS-8	Oysters	*Crassostrea gigas*	27.10	1.18	3.4 - 4.1	2.0
WS-9	Oysters	*Crassostrea gigas*	25.86	1.66	2.8 - 4.5	3.1
WS-10	Oysters	*Crassostrea gigas*	39.13	1.27	3.4 - 5.0	3.2
WS-11	Little neck Clam	*Tapes philippinarum*	39.88	1.10	3.8 - 4.2	2.5

Note : asterisk is the approximately weight of soft-sample

Quantifications were performed with J&W Scientific DB-5 column(60m× 0.25mm i.d× 0.25㎛ film thickness) and Supelco SP2331(60m×0.32mm i.d× 0.20㎛ film thickness) on Autospec Ultima NT at >10,000 resolutions. The levels were expressed in 2,3,7,8-TCDD toxic equivalents using calculations of International Toxic Equivalent Factors (I-TEFs) for PCDDs/PCDFs.

3. Results and Discussion

3.1 Levels of PCDDs/PCDFs in shellfish on the western-coastal area of Korea

At the beginning of this study we selected four regions as the sampling area where are located in western-coastal area of Korea and collected samples. From this region, the measured total concentrations of PCDDs/PCDFs in shellfish are shown in Table 2. WS-1 and WS-4(Little neck clam, clam) ranged from 0.754 to 1.160pg/g wet weight, WS-5 and WS-6(little neck clam, bivalve) are 2.451, 0.391pg/g wet, WS-7 and WS-10(Oyster) are from 0.832 to 3.844pg/g wet and WS-11(little neck clam) is 0.875pg/g wet respectively.

At that time of collecting the samples, we could not compare exactly the difference of regional pollution by PCDDs/PCDFs, because we could not help but selecting the different shellfish what the organisms are ubiquitous inhabiting in sampling region. However in the same kinds samples they appeared similar levels in western coast.
In the case of TEQ levels for shellfish, it appeared to the range from 3.128 pgTEQ/g fat(WS-6) to 31.877 pgTEQ/g fat(WS-7) and in order of oyster, bivalve, little neck clam. These results are lower than the previous surveys by Kim et al(1998), Hashimoto et al(1998).

3.2 Congener profiles of shellfish
The congener profile of shellfish are generally similar within all samples as shown in Figure 2, on the whole the total proportion of PCDFs is higher than that of PCDDs with a percentile range much as 50~80%. OCDD was especially predominant in all samples and the contribution of 2378-TCDF is comparatively higher than other isomer in WS-7 and WS-11 point.

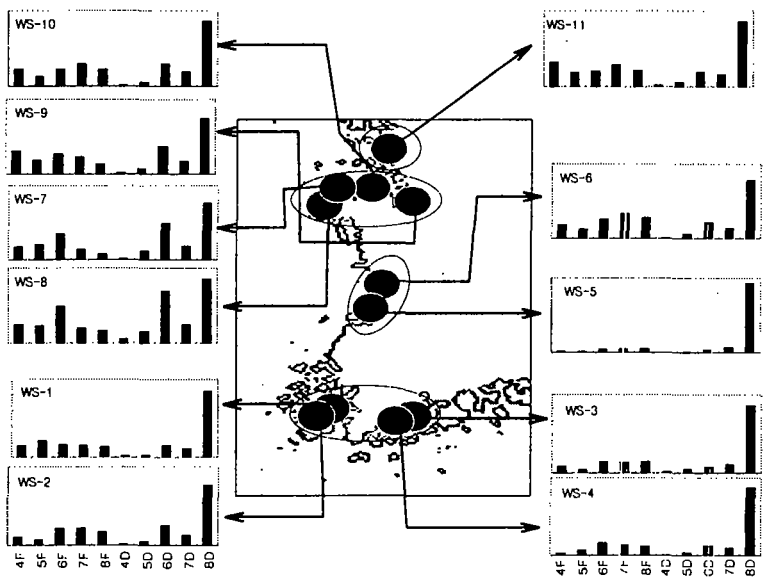

Figure 2. Congener profiles of shellfish in western-coastal area of Korea

Acknowledgement
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References
1) Shunji Hashimoto et al. Polychlorinated dibenzo-p-dioxin and Polychlorinated dibenzofuran in shellfishes from south coast of Korea Chemosphere, Vol.37, No.5, pp951-959(1998)
2) Jong-guk Kim. Survey of Polychlorinated dibenzo-p-dioxin and dibenzofuran in shellfishes from coastal area in Korean, KSEE proceeding, pp.511~514. (1997)

Table 2. Concentration of PCDDs/PCDFs in shellfish on the western-coastal area of Korea

(pg/g wet weight)

	WS-1	WS-2	WS-3	WS-4	WS-5	WS-6	WS-7	WS-8	WS-9	WS-10	WS-11
4F	0.094	0.042	0.038	0.023	0.043	0.031	0.262	0.177	0.296	0.075	0.114
5F	0.134	0.031	0.016	0.048	0.038	0.022	0.311	0.168	0.175	0.041	0.064
6F	0.101	0.089	0.067	0.115	0.092	0.043	0.536	0.358	0.261	0.075	0.069
7F	0.097	0.089	0.061	0.095	0.109	0.054	0.201	0.148	0.220	0.097	0.098
8F	0.085	0.067	0.065	0.087	0.104	0.045	0.122	0.122	0.131	0.074	0.073
PCDFs	0.511	0.317	0.247	0.367	0.385	0.195	1.433	0.972	1.083	0.362	0.418
I-pgTEQ/g fat	10.786	4.175	1.517	7.422	4.164	1.869	17.515	11.771	8.500	2.872	4.119
4D	0.014	0.005	0.007	0.005	0.005	0.002	0.028	0.041	0.020	0.006	0.007
5D	0.019	0.021	0.021	0.024	0.017	0.011	0.176	0.113	0.077	0.017	0.020
6D	0.097	0.102	0.036	0.089	0.076	0.036	0.753	0.513	0.355	0.096	0.068
7D	0.072	0.052	0.052	0.071	0.144	0.024	0.281	0.177	0.171	0.062	0.056
8D	0.527	0.311	0.390	0.603	1.824	0.123	1.173	0.623	0.710	0.288	0.305
PCDDs	0.729	0.491	0.507	0.793	2.066	0.195	2.411	1.468	1.333	0.470	0.457
I-pgTEQ/g fat	4.650	3.933	2.081	6.393	3.511	1.259	14.362	12.860	5.828	2.015	2.290
PCDF+PCDD	1.240	0.807	0.754	1.160	2.451	0.391	3.844	2.441	2.416	0.832	0.875
Total I-pgTEQ/g fat	15.437	8.107	3.598	13.815	7.675	3.128	31.877	24.631	14.328	4.888	6.409
Fat content (%)	0.74	0.67	1.09	0.43	0.69	0.87	1.36	1.18	1.66	1.27	1.10

Note D=dibenzo-p-dioixns F=dibenzo furan 4 = Tetera 5 = Penta 6 =Hexa 7 = Hepta 8 = Octa