

Distribution Characteristics of Dioxins in Marine Sediment from Busan Port in Korea

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Eight marine sediments from Busan port in Korea were annually analyzed to examine the concentration distribution of dioxins from 2006 to 2010. Yearly mean concentration of dioxins ranged from 186.3 to 383.3 pg g⁻¹ in real values and 5.087 to 8.541 pg-TEQ (Toxicity equivalency) based on dry weight of samples. The dioxin concentration at the site near fishing market was the highest concentration among all sampling sites. Also the dioxin concentration at the sites with various pollutant sources such as large ships, sewage influx and thermal power station as well as fishing market was higher than that of the sites without specific pollutant sources. Another main factor that affects the dioxin concentration is topography characteristics of the bay. The bay has relatively high dioxin concentration because of the lack of the pollutant diffusion. This study demonstrated that the dioxin concentration in the site with pollutant sources and the lack of the pollutant diffusion was relatively high as compared with the other sites. As a result of contribution ratio of dioxin congeners, OCDD (Octachlorodibenzodioxin) in all sites was major contributor in real value, in contrast, dioxin congeners in TEQ values were dominated by 2,3,4,7,8-PeCDF.

Key words: Sediment, Dioxin, Distribution, Contribution rate

Introduction

Busan metropolitan city, the second largest city in Korea is located on southeastern tip of Korean peninsula and faced with the East Sea. Busan port, the world's 5th busiest container port and the largest transshipment port in Northeast Asia, handled more than 16million TEU (twenty foot equivalent units) in 2011. It is estimated that there are many pollutants from ships in Busan port. Also the pollutants that flow in the river and the sewer pipe, were accumulated inside the Busan port because of the topography characteristics of the bay. Especially, dioxins with hydrophobic properties tend to accumulate in sediments that are the final reservoir of pollutants (Choi et al, 2011). Because of

the higher density and low water solubility of dioxins, dioxins released from sources tend to adsorb and accumulate in soil or sediments.

Dioxins are unintentionally generated by various thermal processes including waste incinerator, cement kilns firing hazardous waste, production of pulp using elemental chlorine, a sintering plant (Guerzoni et al, 2004). Dioxins released in the atmosphere return to the soil, plants or organisms by dry and wet deposition process and finally accumulate to human beings through food chains (Moon et al, 2008). It is assumed that soil and sediments are the largest reservoir media of dioxins. Especially, marine sediments are main route for marine life to adsorb dioxins. The monitoring of dioxins in marine sediments from the Korean coast including Busan port has been regularly undertaken on a national scale by the ministry of land, transport and maritime affairs (Choi et al, 2011). Because this monitoring can't represent the characteristics of Busan

port, we are monitoring the marine sediments from Busan port divided into eight sites. This study focused on an evaluation of the concentration and spatial distribution of dioxins in sediments.

Materials and Methods

Samples of the marine sediments were yearly collected in eight different sites from 2006 to 2010 using a box core sampler according to Korean standard method. Sampling sites selected for this study are summarized in Fig. 1. Site A, B, C and D have various pollutant sources such as sewage, thermal power station and fisheries products market, while site E, F, G and H have no specific pollutant sources.

The collected samples were individually stored in

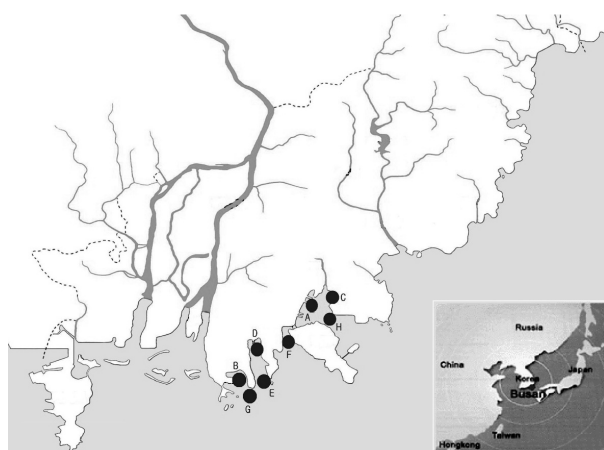


Fig. 1. Marine sediment sampling locations in Busan port, South Korea.

a wide-mouth and amber glass bottle at -4°C and the sample were dried with freezing for about 2 days in later for analysis of dioxins. The freeze-dried samples were passed through a 2 mm of sieve. And the samples were extracted in a soxhlet extraction apparatus using 300 mL of toluene for about 24 hours after spiking internal standards of dioxins. The extracted samples were concentrated to 1 to 2 mL using a rotary evaporator. Multi-silica column, alumina column and carbon column were used to cleanup sample extracts according to Korean standard method and JIS method K 0311 and 0312. Silica gel was activated by heating in dry oven at 180°C for 2 hours after washing with dichloromethane. Basic alumina was used after activation by heating in muffle furnace at 600°C for 24 hours. Dioxins were eluted by 100 mL hexane in multi-silica column consisting of 2% KOH-silica gel, 44% H_2SO_4 -silica gel, 22% H_2SO_4 -silica gel and 10% AgNO_3 -silica gel, followed by basic alumina column. There are two fractions in alumina column. The first fraction of alumina column was used with 100 mL hexane containing dichloromethane (2% vol/vol) and discarded. After then, the second fraction with 150 mL hexane containing dichloromethane (50% vol/vol) was received. Finally, carbon column was performed for eliminating trace interfering compounds using hexane solution containing dichloromethane (25% vol/vol). After this fraction was discarded, then dioxins were eluted by toluene 200 mL.

Table 1 shows the operating conditions of gas chromatograph and mass spectrometer. Instrumental analysis was performed by using a high resolution

Table 1. The operating conditions of gas chromatograph and mass spectrometry.

Descriptor	GC Condition	Descriptor	Mass Condition
Instrument	HP 6890	Instrument	Autospec Ultima
Column	SP-2331 (60 m \times 0.25 mm ID \times 0.2 μm)	Source temp.	260°C
Carrier gas	Helium 1.0 mL/min	Electron energy	35.0 eV
Injection mode	Splitless mode	Resolution	Over 10,000 at 10% valley
Inlet temp.	260°C	Ionization mode	EI positive mode
Oven ramping	Initial temp. 100°C (5 min.) $20^{\circ}\text{C}/\text{min.} \rightarrow 200^{\circ}\text{C}$ (7 min.) $5^{\circ}\text{C}/\text{min.} \rightarrow 260^{\circ}\text{C}$ (36 min.) $10^{\circ}\text{C}/\text{min.} \rightarrow 270^{\circ}\text{C}$ (2 min.)	Selected Ion Mode (SIM)	M/M+2 or M+2/M+4
Injection volume	1 μL	Interface temp.	
		- Capillary line 1	260°C
		- Capillary line 2	260°C
		- Re-entrant	260°C
		- PFK septum	160°C

gas chromatograph (HP 6890 series plus) equipped with a CTC A200SE auto sampler and coupled to an Autospec Ultima mass spectrometer (Micromass, UK), by using a positive electron ionization source and operating in the selected ion monitoring mode at over 10,000 resolution at 10% valley definition. The SP-2331 (supelco, USA) fused-silica capillary column (60 m length \times 0.25 mm ID \times 0.20 μ m film thickness) was used for separation each dioxin congener.

The identification and quantification of each dioxin congener were performed by the isotope dilution method using relative response factors obtained from five standard solutions.

The recovery of each dioxin congener was always in the range from 50 to 120%.

Results and Discussion

Marine sediment samples collected from 2006 to 2010 showed yearly mean concentration ranging from 186.3 to 383.3 μ g g^{-1} dry weight in real values and 5.087 to 8.541 μ g-TEQ g^{-1} in TEQ values as shown in Table 2. There was only a slight change of dioxin concentration in the other samples ranging from 5.087

to 6.657 μ g-TEQ g^{-1} in TEQ values except sample in 2010. In the case of 2010, it was similar in real value to 2006. But TEQ value in 2010 was higher than that in 2006 by approximately 67.9%. Most congeners except OCDD in 2010 were detected in higher concentration than 2006. Especially the concentration of 2,3,7,8-TeCDD having the highest TEQ value in 2010 was approximately seven fold more than that in 2006. There are many previous studies on dioxin in sediments. Choi et al. (2011) measured dioxins of 25 samples up to 12.22 μ g-TEQ g^{-1} in Korean coast. Kurunthachalam et al. (2001) reported that the dioxin concentration in sediments from the Detroit and Rouge River in USA ranged from 3.99 to 62 μ g-TEQ g^{-1} . Concentrations of dioxins at Niagara river over the period 1980-2002 ranged from about 12 to 28 μ g-TEQ g^{-1} (Chris et al., 2007). Ethel et al. (2001) reported that the dioxin concentrations in Mediterranean sediments were ranging from 0.06 to 8.14 ng g^{-1} and 0.4 to 39.24 μ g-TEQ g^{-1} . Dioxin concentrations in Tokyo bay and Hong Kong were 3.2-49 μ g-TEQ g^{-1} (Masaaki et al., 2003) and 3.0-33 μ g-TEQ g^{-1} (Jochen et al., 2002), respectively.

Fig. 2 shows the mean concentrations of dioxins by sampling sites. Both real values and TEQ values

Table 2. Yearly mean concentration of each dioxin congener in marine sediments.

	2006		2007		2008		2009		2010	
	Real values ($\mu\text{g g}^{-1}$)	TEQ values ($\mu\text{g-TEQ g}^{-1}$)	Real values ($\mu\text{g g}^{-1}$)	TEQ values ($\mu\text{g-TEQ g}^{-1}$)	Real values ($\mu\text{g g}^{-1}$)	TEQ values ($\mu\text{g-TEQ g}^{-1}$)	Real values ($\mu\text{g g}^{-1}$)	TEQ values ($\mu\text{g-TEQ g}^{-1}$)	Real values ($\mu\text{g g}^{-1}$)	TEQ values ($\mu\text{g-TEQ g}^{-1}$)
2,3,7,8-T _c CDF	1.818	0.182	4.622	0.462	1.100	0.110	1.656	0.166	2.903	0.290
1,2,3,7,8-P _c CDF	4.123	0.206	7.351	0.368	3.900	0.195	4.480	0.224	6.612	0.331
2,3,4,7,8-P _c CDF	3.615	1.808	4.601	2.300	2.939	1.469	3.197	1.599	6.076	3.038
1,2,3,4,7,8-H _x CDF	5.826	0.583	5.058	0.506	7.044	0.704	5.318	0.532	7.395	0.740
1,2,3,6,7,8-H _x CDF	4.104	0.410	4.167	0.417	6.175	0.617	4.243	0.424	7.715	0.772
2,3,4,6,7,8-H _x CDF	4.855	0.485	4.151	0.415	7.393	0.739	4.968	0.497	8.958	0.896
1,2,3,7,8,9-H _x CDF	0.000	0.000	0.436	0.044	2.532	0.253	0.096	0.010	0.196	0.020
1,2,3,4,6,7,8-H _p CDF	21.437	0.214	16.321	0.163	48.483	0.485	106.178	1.062	31.675	0.317
1,2,3,4,7,8,9-H _p CDF	0.467	0.005	1.842	0.018	6.626	0.066	0.811	0.008	2.043	0.020
OCDF	0.000	0.000	15.309	0.015	50.180	0.050	43.449	0.043	17.926	0.018
2,3,7,8-T _c CDD	0.029	0.029	0.615	0.615	0.034	0.034	0.038	0.038	0.213	0.213
1,2,3,7,8-P _c CDD	0.721	0.361	1.314	0.657	0.438	0.219	1.011	0.506	1.316	0.658
1,2,3,4,7,8-H _x CDD	0.647	0.065	0.849	0.085	0.588	0.059	0.667	0.067	1.275	0.128
1,2,3,6,7,8-H _x CDD	1.930	0.193	1.827	0.183	1.196	0.120	1.324	0.132	3.207	0.321
1,2,3,7,8,9-H _x CDD	0.901	0.090	1.408	0.141	1.121	0.112	0.590	0.059	2.785	0.279
1,2,3,4,6,7,8-H _p CDD	24.587	0.246	16.854	0.169	18.806	0.188	21.158	0.212	35.131	0.351
OCDD	209.930	0.210	99.581	0.100	154.530	0.155	184.122	0.184	150.928	0.151
Total	284.991	5.087	186.305	6.657	313.084	5.576	383.307	5.761	286.355	8.541

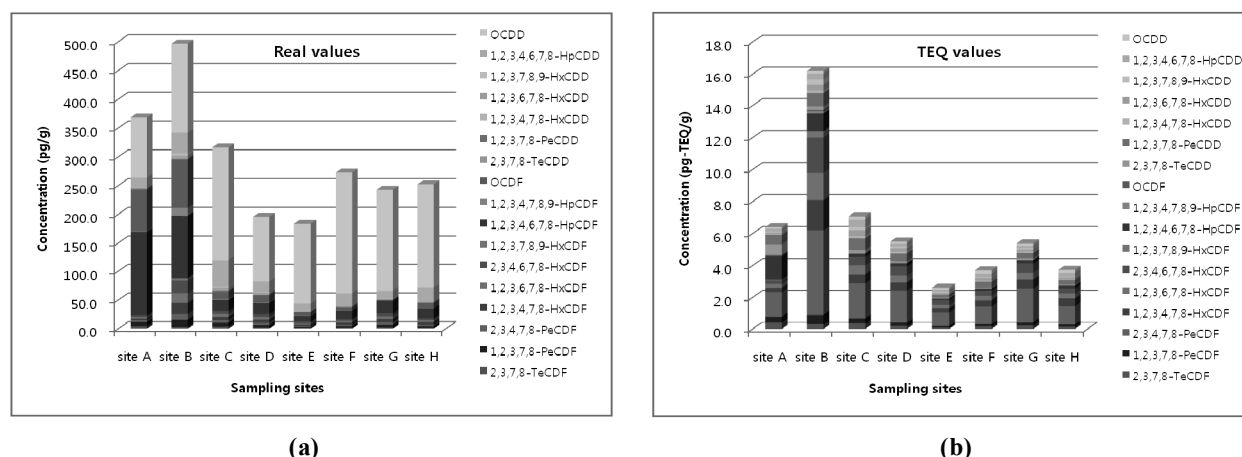


Fig. 2. The mean concentration of each dioxin congener by sampling sites (a, real values; b, TEQ values).

Table 3. The mean concentration and contribution ratio of real values and TEQ values in dioxin congeners.

	Contaminated areas of the sea				General areas of the sea			
	Real value		TEQ value		Real value		TEQ value	
	Conc. (pg g ⁻¹)	Contribution ratio (%)	Conc. (pg-TEQ g ⁻¹)	Contribution ratio (%)	Conc. (pg g ⁻¹)	Contribution ratio (%)	Conc. (pg-TEQ g ⁻¹)	Contribution ratio (%)
2,3,7,8-TeCDF	3.290	1.0	0.329	3.7	1.550	0.7	0.155	4.0
1,2,3,7,8-PeCDF	7.500	2.2	0.375	4.3	3.087	1.3	0.154	4.0
2,3,4,7,8-PeCDF	5.518	1.6	2.759	31.4	2.654	1.1	1.327	34.4
1,2,3,4,7,8-HxCDF	8.073	2.3	0.807	9.2	4.184	1.8	0.418	10.8
1,2,3,6,7,8-HxCDF	7.436	2.2	0.744	8.5	3.126	1.3	0.313	8.1
2,3,4,6,7,8-HxCDF	8.648	2.5	0.865	9.8	3.482	1.5	0.348	9.0
1,2,3,7,8,9-HxCDF	1.193	0.3	0.119	1.4	0.111	0.0	0.011	0.3
1,2,3,4,6,7,8-HpCDF	73.594	21.4	0.736	8.4	16.043	6.8	0.160	4.2
1,2,3,4,7,8,9-HpCDF	4.314	1.3	0.043	0.5	0.402	0.2	0.004	0.1
OCDF	45.347	13.2	0.045	0.5	5.399	2.3	0.005	0.1
PCDF	164.912	47.9	6.822	77.6	40.036	16.9	2.896	75.1
2,3,7,8-TeCDD	0.305	0.1	0.305	3.5	0.066	0.0	0.066	1.7
1,2,3,7,8-PeCDD	1.324	0.4	0.662	7.5	0.596	0.3	0.298	7.7
1,2,3,4,7,8-HxCDD	1.143	0.3	0.114	1.3	0.467	0.2	0.047	1.2
1,2,3,6,7,8-HxCDD	2.540	0.7	0.254	2.9	1.254	0.5	0.125	3.2
1,2,3,7,8,9-HxCDD	1.940	0.6	0.194	2.2	0.782	0.3	0.078	2.0
1,2,3,4,6,7,8-HpCDD	29.564	8.6	0.296	3.4	17.050	7.2	0.170	4.4
OCDD	142.292	41.4	0.142	1.6	177.344	74.6	0.177	4.6
PCDD	179.108	52.1	1.967	22.4	197.560	83.1	0.963	24.9
Total (PCDF+PCDD)	344.021	100.0	8.790	100.0	237.596	100.0	3.859	100.0

in contaminated areas of the sea were higher than those in general areas of the sea. Especially, site B with 496.6 pg g⁻¹ in real value and 16.191 pg-TEQ g⁻¹ in TEQ value showed the highest concentration among all sampling sites probably due to inflow of the various pollutants from fishing market and fishing boat because site B is adjacent to the fisheries products market and a busy port of small fishing boat. And site A with

busy port of large container ships, site C with influx of sewage and site D nearby thermal power station as well as site B showed higher dioxin concentrations than site E, F, G and H that are general areas of the sea without specific pollutant sources. In addition, the inner location of site A, B, C and D closed to harbors made dioxins accumulated in marine sediments. These results were consistent with the results of some researchers

that contaminants were easily accumulated more in inner bay than in outer bay (Jung et al., 2007; Kim et al., 1997; Moon et al., 2008).

The dioxin congener profiles in sediments from selected sites divided into contaminated areas of the sea and general areas of the sea are presented in Table 3. In the case of real values, the contribution ratio of PCDF was similar to that of PCDD in the contaminated areas of the sea, while that of PCDD was about five times higher than that of PCDF in the general areas of the sea. But the similar level of contribution ratio of PCDF and PCDD were observed in both site groups in TEQ value. Our monitoring showed that the concentrations and contribution ratios of OCDD in real value and 2,3,4,7,8-PeCDF in TEQ value were the highest among all congeners. Jung et al. (2007) reported that OCDD was the most predominant congener in all monitoring sites and the concentration of PCDFs was higher than that of PCDDs in TEQ values. Also, the same results were reported by Moon et al. (2008).

Acknowledgments

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