EVALUATION OF PCDD/DFs AND DLPCBs FOR SOUTHEAST-MARINE SEDIMENT, KOREA

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Abstract

This study was carried out in order to a practical use as data for management of PCDD/DFs and DLPCBs by monitoring in marine environment and evaluated concentration levels and characteristics of contamination of PCDD/DFs and DLPCBs from 38 sediments samples of Masan Bay, Jinhae Bay, Nakdong estuary and Ulsan Bay of southeast marine in Korea.
In this result, WHO_{98}-TEQ concentration of PCDD/Fs and DLPCBs observed 2.46, 5.53, 2.20 and 17.70 pg WHO_{98}-TEQ/g d.w. in surface sediments of Ulsan Bay, Busan Bay, Nakdong river estuary and Jinhae-Masan Bay of each group areas, respectively.
PCA analysis was carried out for 17 congeners 2, 3, 7, 8 – substituted PCDD/DFs and 12 congeners DLPCBs. In the results, PC- 1, PC-2, PC-3 and PC-4 accounted for 42%, 24%, 11%, and 8%, respectively, and accounted by 85% for substances in all area sites. Especially, surfaces sediments of Masan Bay inside have a high correlation with PC-3 and appropriate substances has 1, 2, 3, 4, 6, 7, 8 - HpCDD, 2, 3, 7, 8 - TeCDF, and OCDD, and positive correlation between these substances.

Introduction

Dioxins(Polychlorinated dibenzo-p-dioxins ; PCDDs, Polychlorinated dibenzo furans ; PCDFs, Dioxin liked polychlorinatedbephenyls ; DL PCBs) can be persistency, bio-accumulation, toxicity and potent possibility of long rang transfer is one of the high persistent organic pollutants (POPs).[1] Also, it is one of chemical species that dioxins among priority substance is based to PBT(Persistent, Bioaccumulative, and Toxic) and becomes screening at the first step in OSPAR treaty to preserve northeast Atlantic Ocean's marine environment.
Especially, these substances sources is indicating combustion process of waste incineration, including industry activity that is exhausted to environment as unintentionally produced substance.[2-4].
Also, these organic substances exhausted into atmosphere from air emission can be scavenging through precipitation and atmospheric process of wet/dry deposition to ground surface. Finally these compounds were indicated as that is flowed in surface area and can be accumulated to water, soil, vegetation and sediments. Especially, coastal and ocean sediments were indicated as important pathway into the body absorption in marine organism and role as sink and reservoir of PCDD/Fs and DLPCBs.[5-7]
The study for PCDD/DFs and DLPCBs in sea sediments were reported to characteristics of concentration levels and distribution, origination, historical trend etc. in Baltic Sea, Spain, Sweden, Japan, and Korea in all the countries of the world.[8-15]
In the case of Korea, there were some monitoring studies for concentration levels and it‘s characteristics assessment of PCDD/DFs and DLPCBs in coastal and ocean sediments,[13-15] but it is necessary that storage of enough data of PCDD/DFs and DLPCBs are to evaluate of ecological risk assessment for a long terms and cover a wide area in marine environment. Therefore, this study were carried out in order to a practical use as data for management of PCDD/DFs and DLPCBs by monitoring in marine environment and evaluated for concentration levels and characteristics of contamination for PCDD/DFs and DLPCBs in sediments of Masan Bay, Jinhae Bay, Nakdong estuary and Ulsan Bay of southeast marine in Korea.

Materials and Methods

Sampling and Study Area
Sediment samples were collected in following area; Masan Bay, Jinhae Bay, Naekdong estuary and Ulsan Bay of which 38 sediment samples on July, 2003 from March, 2002. Sampling site was showed Fig.1. Sediment

samples were collected using a box-corer sampler, and samples were stored by freeze-dried at -20℃ until extraction.

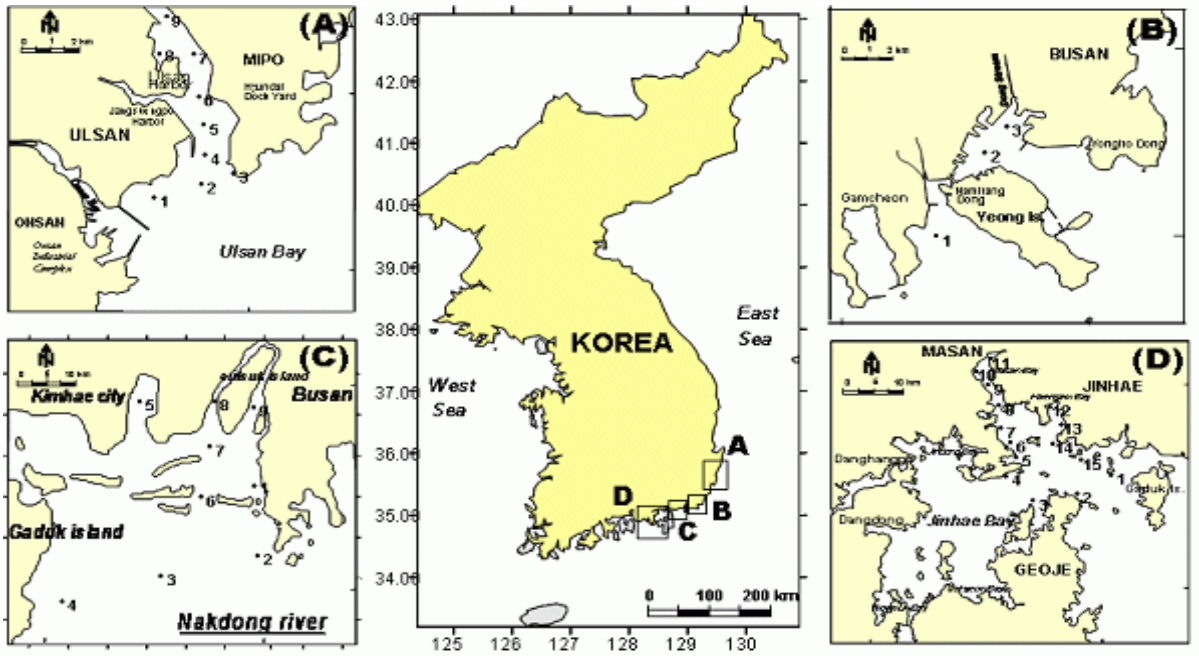

Fig. 1. Map of the study area of sampling sites.

Sample preparation and Instrumental analysis

After freeze-dried, samples were homogenized by below 2mm mesh and added labeled standard solution(EPA-1613LCS, Wellington Laboratories, Canada) to sediment 30g, and Soxhlet extracted for 16hr using Toluene 300 ml. Extracted solutions were passed through using a Multi-layer silica-based absorbents (70-230 mesh, Neutral, Merck) column and alumina column for clean-up with spiked labeled internal standard(EDF-8999 and 68A-LCS, Wellington Laboratories, Canada). Clean-up solutions were concentrated using a rotary evaporate about 2ml, finally concentrated until 50 uL at room temperature and were analyzed using a HRGC/HRMS(Agelent 6890 GC coupled to a JEOL JMS-700D HRMS). Capillary column were used sp-2331, DB-5MS(Tetra – HeCDD/DFs ; Sp - 2331, 60m x 250 um x 250 um and Hepta – OCDD/DFs ; DB - 5ms, 30m x 250m x 250m) for PCDD/Fs for analysis, and HT-8 column was used DLPCBs for analysis. Detailed descriptions have been presented elsewhere.[16]

Results and Discussion

Concentration levels of PCDD/DFs and DLPCBs in surface marine sediment

PCDD/DFs and DLPCBs concentration(WHO98-TEQ) levels are presented in Fig.2 for each sites area. In case of Ulsan Bay, PCDD/Fs homologue concentration were ranged from 199 to 446 pg/g d.w. by mean concentration of 355 pg/g d.w.(standard deviation is ±0.54) in 9 surface sediment samples. Also, the concentration of 2,3,7,8-substituted PCDD/DFs(WHO_{98}-TEQ) and DLPCBs(WHO_{98}-TEQ) were 2.23 pg - TEQ/g d.w and 0.22 pg - TEQ/g d.w. respectively. The variance of concentration between site was confirmed less than in the all site of Ulsan Bay. The concentration levels of PCDD/DFs from surface sediment samples of Busan Bay were within the range of 254 - 1,257 pg/g d.w. and mean concentration was 628 pg/g d.w. The PCDD/DFs WHO_{98}-TEQ mean concentration of 2, 3, 7, 8 –substituted PCDD/DFs and DLPCBs showed 5.45 pg WHO - TEQ/g d.w. and 0.08 pg WHO-TEQ/g d.w. respectively. Particularly, the trends of variance of concentration between sites were confirmed in the inside of harbor highest level rather than open side of Bay. The concentration levels of surface

sediment for homologues PCDD/DFs have a ranged from 35 to 246 pg/g d.w. (mena concentration is 116 pg/g d.w.) in Nakdong river estuary, and 2, 3, 7, 8 –substituted PCDD/DFs(WHO_{98}-TEQ) and DLPCBs were 2.05 pg WHO_{98}-TEQ/g d.w , and 0.145 pg WHO_{98}-TEQ/g d.w. by mean concentration, respectively. Finally, for Jinhae Bay showed that the concentration of homologues PCDD/DFs were 234 - 4,610 pg/g d.w.(mean concentration was 1,136 pg/g d.w.) and average concentration of 2,3,7,8-substitued PCDD/DFs and DLPCBs were 16.8 pg WHO-TEQ/g d.w. and 0.862 pg WHO_{98}-TEQ/g d.w. respectively. And trend of distribution was presented highest level at surface sediment samples of Masan Bay inside. When compared with result by Moon et al (2002)[14] in the adjacent sites sediment that concentration levels were confirmed almost the same levels, but was low rather than in the worldwide.[10-12]

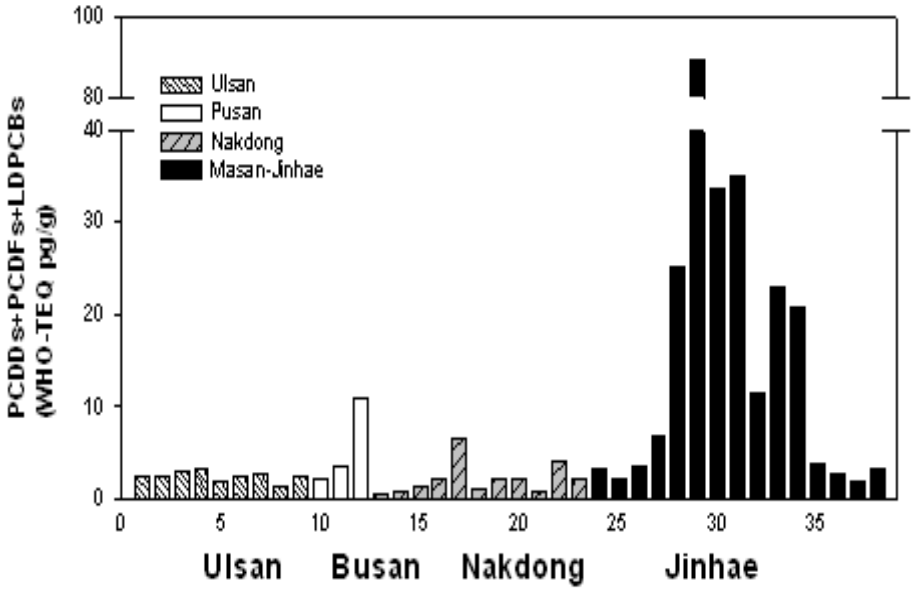

Fig. 2. Concentration levels of PCDD/DFs and DLPCBs for surface sediments in each sites.

Characteristics of Profile and contribution for PCDD/Fs and DLPCBs

Fig.4 shows the contribution rate(%) of a average Total WHO-TEQ concentration for 17 congeners of 2, 3, 7, 8-substituted PCDD/DFs and 12 DLPCBs congeners in each area sites for the surface sediments.

As can be seen in Fig.3, a gape of contribution rate (%) was not a great in according to the area site, but WHO_{98}-TEQ concentrations exhibited that followed sequence PCDFs $_{WHO98\text{-}TEQ}$> PCDDs $_{WHO98\text{-}TEQ}$> DLPCBs $_{WHO98\text{-}TEQ.}$ and in the contribution of Total-TEQ concentration which is 2, 3, 7, 8-substituted PCDFs of 57 - 69%, 2, 3, 7, 8-substituted PCDDs is 27 - 35%, and DLPCBs showed as 1.4 - 9.2%. Also, among the 2, 3, 7, 8-substituted PCDDs that 1, 2, 3, 7, 8 - PeCDD was dominated and 2, 3, 4, 6, 7, 8- HxCDF was dominated in case of 2, 3, 7, 8-substituted PCDFs. Such tendency showed similar pattern in surface sediment samples of all area sites. Particularly, in the case of Busan Bay that contribution(%) of DLPCBs are lowest, and although, in generally highest contribution among the DLPCBs were 3, 3 '4, 4', 5 - PeCBs (PCB 126) but only contribution of Pusan Bay surface sediments were exhibited higher by 2 '3, 4, 4', 5 - PeCB (PCB 123), 2, 3, 3 '4, 4', 5 - HxCB (156) and 2, 3 '4, 4', 5, 5' - HxCB(167) than 3, 3 '4, 4', 5 - PeCBs (PCB 126) .

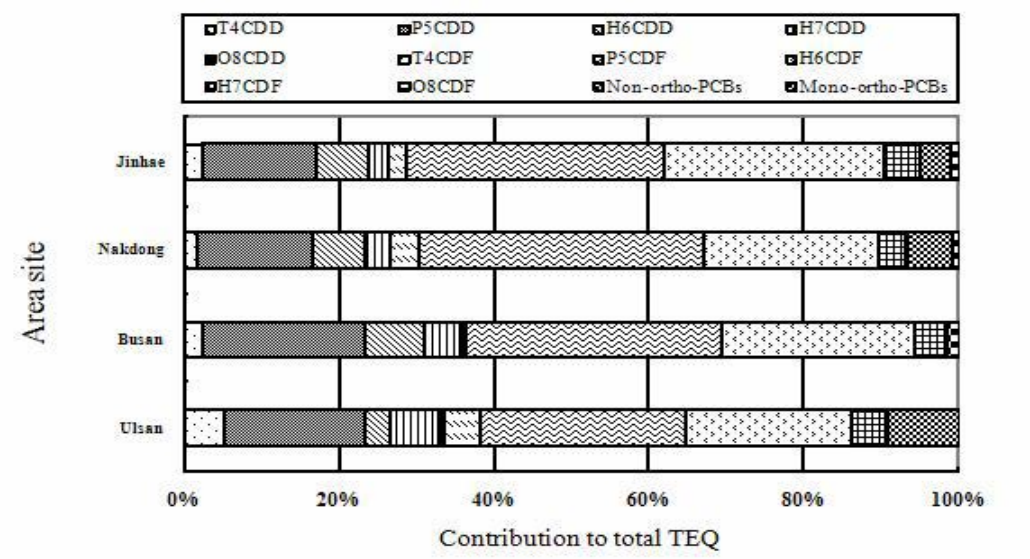

Fig. 3. Contribution (%) of PCDD/DFs and DLPCBs to tatal WHO-TEQ98 in each area

Statistical analysis

PCA analysis was carried out for 17 congeners 2, 3, 7, 8 – substituted PCDD/DFs and 12 congeners DLPCBs. Four PC was accounted from analyzed data of PCDD/Fs and DLPCBs in 38 surface sediment samples by PCA, The results showed that PCA loading rate and correlation($r > 0.7$) with all substance of PCDD/DFs and DLPCBs, PC- 1, PC-2, PC-3 and PC-4 accounted for 42%, 24%, 11%, and 8%, respectively, and accounted by 85% for substances in all area sites. In this study, results of PCA for PCDD/Fs and DLPCBs in surface sediment of southeast coastal area, in generally these substances presented by very same patterns, but in a except for partial surface sediment samples of Jinhae-Msan Bay. Specially, Among Jinhae-Msan Bay surface sediments samples that inside surface sediment samples shows can be difference statistically. From this result was confirmed that surfaces sediments of Masan Bay inside have a high correlation with PC-3 and appropriate substances has 1, 2, 3, 4, 6, 7, 8 - HpCDD, 2, 3, 7, 8 - TeCDF, and OCDD, and positive correlation between these substances.

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