EVALUATION OF PCDDS/DFS ORIGIN IN MARINE SEDIMENTS FROM THE INDUSTRIALISED REGIONS OF KOREA

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Introduction

Polychlorinated dibenzo-*para*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have in recent decades generated wide interest in both scientific and public setting as a result of the pronounced toxicity and persistence of members within these compound classes. PCDDs/DFs, especially the isomers with chlorines substituted in 2,3,7 and 8 positions are thought to pose a risk to human health due to their high toxicity, carcinogenic potency and potential effects on animal reproductive and immunological systems [1,2]. Environmental pollution by toxic organic contaminants has arisen exclusively from human activities and their heavily contaminated areas tend to be located around the industrial regions. PCDDs/DFs are inadvertently produced from various combustion sources and manufacturing processes, such as municipal solid waste incineration [3], motor vehicles [4], steel mills [5], and chemical production processes [6]. These contaminants derived from various emission sources are mainly transported to the aquatic systems through the atmospheric dry and wet deposition and/or directly via rivers. Because of their low water solubility and vapour pressure, the parts of these chemicals tend to be strongly bound or adsorbed onto surface of particulate matter [7,8], which are then deposited in the underlying sediments. Thus, the deposited sediments will work as conservative matrices that provide valuable information on loading of contaminants to the marine environment [8,9]. The objective of this investigation was to assess contamination distribution and origin of PCDDs/DFs in marine sediments from the industrialized regions of Korea using congener-specific characterisastion.

Materials and Method

Surface sediments were sampled at 144 stations from the industrialized regions of Korea during the period of March 2000 to July 2001 (Figure 1). Sediments were collected with a box-corer sampler and then kept frozen at -20 until extraction. They were freeze-dried and sieved through 2 mm. Twenty grams of sediments were extracted in a soxhlet apparatus with 200 mL of toluene for 24 hours after the spike of internal standard (EPA-1613LCS, Wellington Laboratories). The extracts were reduced to 1-2 mL in a rotary evaporator and then were transferred to *n*-hexane. After pre-cleaned up with a multi-layer slilica gel column chromatography containing $AgNO_3$-silica gel, H_2SO_4-silica gel and KOH-silica gel, the extract was cleaned up on an activated alumina column chromatography with successive elutants of 3% methylene dichloride in *n*-hexane and 50% methylene dichloride in *n*-hexane. The second fraction was concentrated to less than 1 mL, and left at a room temperature for one or two days to evaporate to dryness. The residue was dissolved with 30 μL of *n*-nonane and determined for PCDDs/DFs using HRGC/HRMS (JMS 700D, JEOL). Further details of the experimental procedure and instrumental analysis of PCDDs/DFs are presented elsewhere [10,11].

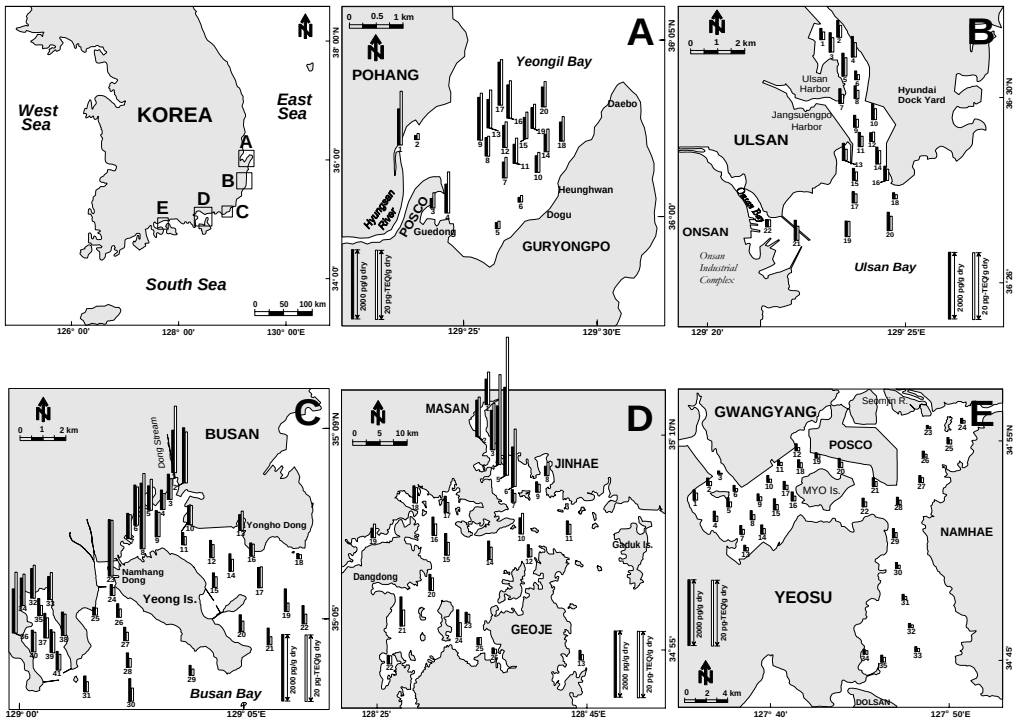

Figure 1. Map showing the sampling stations and PCDDs/DFs concentrations in marine sediments from the industrialized regions of Korea. A: Pohang coast, B: Ulsan coast, C: Busan coast, D: Jinhae coast, E: Gwangyang coast.

Results and Discussion

Contaminant levels of PCDDs/DFs in marine sediments

The horizontal distributions of total and 2,3,7,8-substituted PCDDs/DFs in sediments from five coastal areas of Korea are presented in Figure 1. PCDDs/DFs were detected in all the sediments analysed. Total concentrations of PCDDs/DFs in marine sediments from the five coastal areas of Korea varied from 87 to 2,663 pg/g dry weight. Toxic 2,3,7,8-substituted PCDDs/DFs concentrations in surface sediments from five coastal areas of Korea ranged from 0.5 to 42 pg-TEQ/g dry weight. Total concentrations of PCDDs/DFs in sediments from Pohang coast were in the range of 141-1,265 pg/g dry weight. TEQ concentrations in this coast varied from 2.0 to 16 pg-TEQ/g dry weight. The highest concentration was found at Station P1 at the mouth of Hyungsan River. The central part (Stations P7-P20) of this coast showed the similar contamination by PCDDs/DFs. The PCDDs/DFs concentrations in surface sediments from Ulsan Bay varied from 191 to 674 pg/g dry weight and TEQ levels in this bay ranged between 1.3 and 5.5 pg-TEQ/g dry weight. Maximum concentration was found at Station 5 in the vicinity of Ulsan Harbor. However, in general, there were no significantly differences of dioxin contaminations among sampling stations from Ulsan Bay. Total concentrations of PCDDs/DFs in sediments from Busan coast varied from 164 to 1,991 pg/g dry weight. TEQ concentrations in this bay ranged between 1.23 and 22.7 pg-TEQ/g dry weight. The highest concentrations were found at Stations B1, B2, B8 and B23, which were potentially influenced by the contaminant loading from Dong Stream. North Port showed the higher contamination status by PCDDs/DFs in sediments than those from three ports

of Busan coast. In particular, the distribution of PCDDs/DFs from the inner stations (Stations B1 to B9) to outer stations (Stations B10 to B22) showed the decreasing gradient. Total concentrations of PCDDs/DFs in sediments from Jinhae Bay varied from 174 to 2,663 pg/g dry weight and TEQ concentrations ranged from 1.4 to 41.7 pg-TEQ/g dry weight. In particular, Stations J1 to J6, which were located at the inner part of Masan Bay, showed the highest concentrations of PCDDs/DFs in this bay. Other stations from central part of Jinhae Bay showed relatively uniform distribution of PCDDs/DFs in coastal sediments. Concentrations of PCDDs/DFs in sediments from Gwangyang coast varied from 87 to 340 pg/g dry weight and TEQ levels of PCDDs/DFs in this coast ranged between 0.5 and 2.1 pg-TEQ/g dry weight. PCDDs/DFs concentrations in sediments from Gwangyang Bay had the low value in comparison with those of different coastal areas sediments surveyed. The low levels of PCDDs/DFs in sediments from Gwangyang Bay may be due to physical effects such as sediment dredging, seawater diffusion and/or advective particle transport.

Congener-specific characterisation of PCDDs/DFs

Average congener distribution of PCDDs/DFs in marine sediments from the industrialized regions of Korea are presented in Figure 2. Each congener was normalized by total concentration of each homologue. Ulsan, Busan, Jinhae and Gwangyang coastal areas showed the similar congener pattern of PCDDs/DFs in sediments. For these four coastal areas, the 1368- and 1379-TCDD were dominant species in TCDD homologue and the 12468/12479-, 12368-,12379-PeCDD were predominant species in the PeCDDs. 123468/124679/124689-HxCDD was the most abundant species in HxCDD congener groups. For PCDFs, the congener abundances of all sediment samples were similar except some species. The 1347- and 2468/1238/1467/1236-TCDF were predominant congeners in TCDF homologue and 12478-, 12368/13478- and 12348/12378-PeCDF were present in higher proportions in PeCDFs. HxCDF congener patterns were dominated by 12468- and 134678/134679-HxCDF. However, Pohang coast was characterised by high proportions of 12478-PeCDD and 12478-PeCDF in PeCDD/DF homologue groups. It may suffer from certain point source of contamination. Indeed, these sampling stations seem to be influenced by toxic contaminants generated from combustion process of steel mill in the vicinity of this bay.

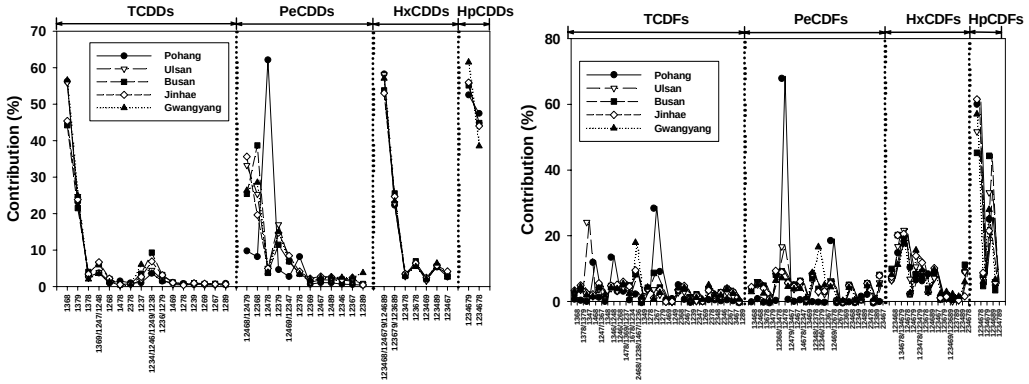

Figure 2. Average congener profiles of PCDDs (left) and PCDFs (right) in marine sediments from the industrialised regions of Korea. Congener group which coelutes on SP-2331 and DB-5MS column is described by '/'.

Origin of PCDDs/DFs in marine sediments from the industrialized regions

Although the examination of congener profiles of PCDDs/DFs can explain the relationships among congeners within each homologue, it is difficult to identify the relationships among all congeners of different homologues, including OCDD and OCDF [12]. Hence, principal component analysis (PCA) has been used to investigate the similarities, differences, and relationships of the variations in PCDDs/DFs profiles among all congeners [12,13]. In this study, 106 chromatograhic peaks resolved by two used columns of 136 congeners from tetra- to octa-chloro dioxins and furans were subjected to PCA. The variance of each peak was normalized to total values of PCDDs/DFs congeners. The eigenvectors were varimax-rotated to clearify the interpretability of the results.

The results showed that most of congeners within each homologue group were located close inner or near except some species. These results indicated that the congener profiles of primary source for each sediment sampling station were similar and that most of congeners within each homologue behave identically in marine environment.

Generally, the inputs of airborne particulate matters formed as various combustion processes identified the primary source of PCDDs/DFs in marine environment for Pohang, Ulsan, Busan and Jihnae coastal areas of Korea. In addition, the influence of impurities of pentachlorophenol (PCP) and the discharge of domestic and/or industrial wastewater were investigated as sources of PCDDs/DFs in these coastal marine environments. However, the usage of PCP was a major origin of PCDDs/DFs in sediments from Gwangyang coastal areas.

References

1. Huff J.E. (1992) Chemosphere 25, 173-176.
2. Safe S. (1998) Terat. Carcin. Mut. 17, 285-304.
3. Olie K., Vermeulen P.L. and Hutzinger O. (1977) Chemosphere 8, 455-459.
4. Marklund S., Rappe C., Tsyklind M. and Egebäk K. E. (1987) Chemosphere 16, 29-36.
5. Tsyklind M., Söderström G., Rappe C., Hägerstedt L.-E. and Burström E. (1989) Chemosphere 19, 705-710.
6. Hutzinger O., Blumich M. J., Berg M.V.D. and Olie K. (1985) Chemosphere 14, 581-611.
7. Beurskens J.E.M., Mol G.A.J., Barreveld H.L., Van Munster B. and Winkels L. (1993) Environ. Toxicol. Contam. 12, 1549-1566.
8. Tyler A.O., Millward G.E., Jones P.H. and Turner A. (1994) Estuar. Coast. Shelf Sci. 39, 1-13.
9. Dannenberg D., Andersson R. and Rappe C. (1997) Mar. Pollut. Bull. 34, 1016-1024.
10. Moon H.B., Choi H.G., Kim S.S. and Lee P.Y. (2002) J. Fish. Sci. Technol. 4, 51-57.
11. Moon H.B., Choi H.G., Kim S.S., Jeong S.R., Lee P.Y. and Ok G. (2002) J. Kor. Soc. Environ. Anal. 5, 225-235.
12. Ogura I., Masunaga S. and Nakanishi J. (2001) Chemosphere 45, 173-183.
13. Wehrmeier A., Lenoir D., Schramm K.W., Zimmermann R., Hahn K., Henkelmann B. and Kettrup A. (1998) Chemosphere 36, 2775-2801.