CONGENER-SPECIFIC CHARACTERIZATION AND SOURCES OF PCDD/FS AND DIOXIN-LIKE PCBS IN MARINE SEDIMENTS FROM INDUSTRIALIZED BAYS OF KOREA

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Abstract

PCDDs, PCDFs and dioxin-like PCBs were determined in 122 coastal sediments from heavily industrialized areas in Korea. Concentrations of PCDD/Fs and DLPCBs ranged from 0.48 to 44.5 pg TEQ/g dry wt and from 0.02 to 27.7 pg TEQ/g dry wt, respectively. Overall PCDD/F and DLPCB concentrations were elevated in estuarine and inner bay locations close to industrial complexes, indicating that these contaminants derived from local discharges. PCDD/F concentrations measured in our study were comparable to those in industrialized areas of other countries. Non-parametric multidimensional scaling ordination and congener-specific characterization showed that combustion processes occurring in industrial complexes, including the steel industry, are the major source of PCDD/Fs in Korean coastal waters. There were no significant correlations among PCDD/Fs, DLPCBs and TOC; however, there was moderate correlation between PCDD/Fs and DLPCBs in some coastal bays, suggesting that these chemicals have similar sources and movements in these locations.

Introduction

The Korean Ministry of Environment has launched a nationwide inventory project, to identify the sources of PCDD/F and DLPCB emissions into the atmosphere. In 2001, the annual emission of PCDD/Fs and DLPCBs from various sources was estimated to be 1,219–1,233 g WHO-TEQ/yr.[1] The main source of dioxins in Korea was found to be MSWIs, which account for about 85% of the total TEQ emissions. The second most important source is the steel industry, with a contribution of about 9.2%.[1] PCDD/Fs and DLPCBs derived from various sources can be transported to aquatic environments via riverine inputs and atmospheric deposition.[2] The existence of PCDD/Fs and related compounds in marine sediments from industrialized and heavily populated areas in Korea is a cause for concern.[3,4] The objective of this study was to describe the concentrations and congener patterns of PCDD/Fs and DLPCBs in coastal sediments and to evaluate the sources of these compounds in industrialized regions of Korea.

Materials and Methods

Surface sediments were sampled at 122 locations from five industrialized bays from February 2000 to March 2002. Detailed descriptions of preparation procedures and instrumental analysis have been presented elsewhere.[2] Briefly, 20 g of sediments were extracted in a Soxhlet apparatus after spiking with ^{13}C-labelled internal standards of PCDD/Fs and DLPCBs. For PCDD/F analysis, the extracts were cleaned by passing them through a multi-layer silica gel column with successive eluants of 150 mL of hexane. The eluted fractions were cleaned up on an activated neutral alumina (70–230 mesh, Neutral, Merck) column with successive portions of 3% methylene chloride in hexane and 50% methylene dichloride in hexane. The second fraction was concentrated to less than 1 mL. Cleanup of the DLPCBs was performed using the same multi-layer silica gel column that was used for the pre-cleaning of the PCDD/Fs. Quantification was performed using a high-resolution gas chromatograph interfaced with high-resolution mass spectrometer (JMS 700D, JEOL). The capillary column used was an SP 2331 (60 m length, 0.25 mm i.d., 0.25 µm film thickness, Supelco) for the separation of tetra- to hexa-CDD/Fs. Hepta- to octa-CDD/Fs were analyzed using a DB5-MS (60 m length, 0.25 mm i.d., 0.25 µm film thickness; J&W Scientific). An HT-8 (50 m, 0.22 mm i.d., 0.25 µm film thickness, SGE) was used for DLPCB analysis.

Results and Discussion

Spatial distribution of PCDD/Fs and DLPCBs

In Yeongil Bay, total TEQ concentrations in marine sediments from Yeongil Bay ranged from 2.55 to 19.6 pg TEQ/g dry wt. The highest TEQ concentration was found at the locations near the mouth of the Hyeongsan River and steel factory. The contribution of DLPCBs to the total TEQ concentrations in all sampling locations was small. In Ulsan Bay, concentrations of PCDD/F in the sediments were in the range of 1.36–5.58 pg TEQ/g dry wt and those of DLPCB ranged from 1.62 to 27.7 pg TEQ/g dry wt. DLPCBs had a wide range of concentration compared with PCDD/F. There was no great difference in PCDD/F contamination among the sampling locations in the bay. For DLPCBs, the concentrations in the sediments from the inner part of the bay were higher than those from the outer part of the bay. Our findings suggest that shipping and industrial activities were an important source of dioxin-like contaminants in Ulsan Bay. Sediments from Busan Bay showed relatively high concentrations of PCDD/Fs and DLPCBs compared with the other bays studied. Concentrations of PCDD/Fs ranged from 2.33 to 24.0 pg TEQ/g dry wt and DLPCB concentrations ranged from 0.68 to 23.9 pg TEQ/g dry wt, which accounted for 30 ± 14 % of the total TEQ concentrations. The overall concentrations of PCDD/Fs and DLPCBs in marine sediments from Busan Bay were higher at the inner close to the harbors than in the outer locations, suggesting that harbor and shipyard activities contributed to the PCDD/F and DLPCB contamination in this bay. In Jinhae Bay, concentrations of PCDD/F and DLPCB ranged from 1.58 to 44.5 and from 0.10 to 1.80 pg TEQ/g dry wt, respectively. Jinhae Bay was characterized by high concentrations of PCDD/F in the sediments from the inner part of the bay, which is a semi-enclosed system. Gwangyang Bay sediments showed the lowest concentrations and a homogenous distribution of PCDD/F and DLPCB. This may have been due to physical effects such as regular reclamation and dredging, strong seawater diffusion and advective particle transport in this region.

Congener-specific characterization and pollution sources of PCDD/Fs

Two-dimensional ordination was performed by non-parametric multidimensional scaling (MDS) using PRIMER for Windows (PRIMER Version 5.2.9, Plymouth, UK), to characterize further the spatial variability and potential sources of PCDD/F contamination. The 106 chromatographic peaks, resolved by two columns, of 136 congeners from tetra- to octa-CDD/Fs were subjected to MDS ordination. Four clusters were identified on the variable plot, each containing data grouped according to their sampling locations. In general, the sampling locations from each of the bays were located either within or close to one of the clusters, indicating that each bay had a similar source and behavior of PCDD/Fs in the marine environment. The first cluster (Group A) included Ulsan Bay, Busan Bay and some locations in Jinhae Bay. At all the sampling locations, 1,3,6,8- and 1,3,7,9-TCDD were the dominant congeners in TCDD homologue groups. These patterns were similar to the typical isomer patterns of PCDD/Fs found in combustion processes across various samples and conditions.[5] The PCDF patterns in our samples were similar to those in sediments from Tokyo Bay in Japan, which were contaminated by the deposition of combustion emissions.[6] The second group, Group B, was represented by the inner locations (Masan Bay) from Jinhae Bay. It is difficult to explain the difference in the congener distributions for PCDD/Fs between Group A and B, although some congeners such as 1,3,4,6,7,8/1,3,4,6,7,9-HxCDF and 1,2,3,4,6,7,8-HpCDF were present in higher proportions than other congeners of the same homologue groups. This result indicates that PCDD/F contamination of this area, such as in Masan Bay, is influenced by combustion processes as well as other sources. The third group (Group C) represented all of the sampling locations in Yeongil Bay. This group corresponded to high contributions of specific congeners of tetra- and penta-CDD/Fs such as 1,2,6,7-, 1,2,7,9-, 1,4,6,8-TCDF, 1,2,4,7,8-PeCDD, 1,2,4,7,8-, 1,2,4,6,9/1,2,6,7,8-PeCDF, suggesting that a specific source of contamination exists in the bay. The fourth group (Group D) comprised the sampling locations from Gwangyang Bay. Gwanyang Bay has a large steel making facility and a petrochemical factory, but no specific congener patterns associated with these industrial activities could be discerned. This may have been due to the regular reclamation and dredging of sediments in this region and the effect of PCDD/F removal facilities at the steel industry. However, this bay was dominated by more highly chlorinated homologues such as OCDD and OCDF, which are the main components of PCP emitted to the environment.[6]

Correlation among PCDD/Fs, DLPCBs and TOC

Although PCDD/Fs and DLPCBs were expected to be associated with organic-rich particles, the correlation between PCDD/Fs and TOC was not high (r = 0.381, p = 0.001) and that between DLPCBs and TOC was not significant (r = 0.078, p = 0.395) for any of the sediment samples. This may have been due to the combined effect of local contaminant sources, transport, mixing and deposition. However, moderate correlations of PCDD/Fs (r = 0.642, p = 0.002) and DLPCBs (r = 0.540, p = 0.014) with TOC were found in the sediments from Yeongil Bay, consistent with the results found by Koh et al. (2007). There was no significant correlation (r = 0.082, p>0.05) between the concentrations of PCDD/Fs and DLPCBs in any of the sediment samples. Sakurai et al.[7] reported that PCDD/Fs were different from DLPCBs in their emission sources and their movement in the environment. However, moderate correlations were found between PCDD/Fs and DLPCBs in the sediments from Busan Bay (r = 0.554, p = 0.009) and Jinhae Bay (r = 0.413, p = 0.036), suggesting that these contaminants in the two bays originated from similar sources.

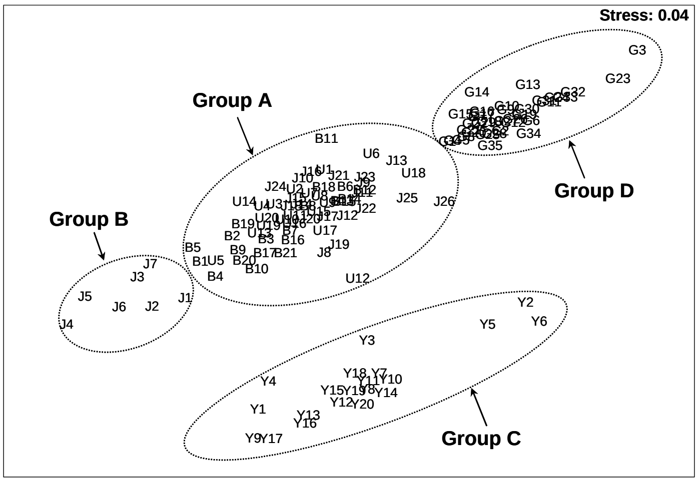

Fig. 1. Non-parametric multidimensional scaling (MDS) ordination plots of PCDD/F congener distribution in marine sediments from industrialized bays of Korea.

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