PCDDS, PCDFS AND CO-PCBS IN TOKYO BAY: SOURCES AND CONTRIBUTION

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and dioxin-like coplanar polychlorinated biphenyls (Co-PCBs) are persistent, bioaccumulative, and toxic environmental contaminants. To control human exposure to these compounds, a full understanding of the sources of PCDD/Fs and Co-PCBs and the relative contributions of these sources is required. The objective of this study was to investigate the levels of PCDD/Fs and Co-PCBs in a sediment core from Tokyo Bay, to elucidate the key sources of PCDD/Fs and Co-PCBs and their historical contribution in the Japanese aquatic system.

Methods and Materials

A sediment core sample was collected from Tokyo Bay in 1993 at the position of 35°33' N latitude and 139°55' E longitude. The core was sliced into 1-cm-interval disks on-site and the disks were dried by the freeze-drying method. The average sedimentation rate was estimated to be 0.27 g/cm^2/yr and 0.26 g/cm^2/yr by the ^{210}Pb method and the ^{137}Cs method, respectively. Furthermore, a molecular stratigraphy approach was also performed and good agreement between the deposition dates estimated using the radionuclides and molecular markers was observed[1]. For our analysis, the disks were further subsampled to make up thirteen samples at depths of 0-3, 3-6, 6-9, 9-15, 15-20, 20-25, 25-30, 30-35, 35-40, 40-45, 45-50 and 55-58 cm. The ages of these samples, shown in this paper, were determined by the ^{210}Pb method.

After the addition of twenty ^{13}C-labeled internal standards, each sample (5~10 g) was Soxhlet-extracted with toluene for 20 h. Then they were treated with alkaline hydrolysis, sulfuric acid oxidation, and sulfur removal. Sample cleanup included chromatography on silica gel, aluminum and activated carbon columns. The final PCDD/F and Co-PCB fractions were further concentrated and spiked with two ^{13}C-labeled recovery standards for HRGC/HRMS analysis. The tetra- to octachlorinated PCDD/Fs and four Co-PCBs (PCB-77, PCB-81, PCB-126, and PCB-169) were analyzed by congener-specific analysis. The TEQ concentrations were calculated based on the TEFs for humans revised by the WHO in 1998.

STATISTICA software was used for data analysis. Source identification was performed using principal component analysis (PCA). For our PCDD/F and Co-PCB congener-specific data set, each congener or congener cluster was constituted as a variable, while each disk was treated as a case. Principal components (PCs) were obtained by varimax rotation and then identified by comparing their characteristic congeners with those of known sources. Furthermore, multiple regression analysis was carried out for dioxin source apportioning. The congener-specific data of PCDD/F concentrations in PCP, CNP[2], and atmospheric deposition obtained in the Kanto area, Japan[3] were used to estimate the historical contributions of different sources to dioxin pollution in Tokyo Bay.

Results and Discussion

Nearly all the tetra- to octachlorinated PCDD/Fs were detected from the samples examined. Based on the obtained data, the historical trends of PCDD/Fs in the Tokyo Bay sediment core were reconstructed, as shown in Figure 1. The PCDD/F concentration increased during the period 1935-1972, in which a drastic increase occurred from the late 1950s and peaked around 1970. During 1972-1981, the total dioxin concentration decreased continuously and then generally leveled off. A distinct homolog profile, dominated by OCDD, was observed throughout the sediment core. On the other hand, some trends in the profile and pattern were also found from the bottom to the top of the core. OCDD, HpCDDs, OCDF, HpCDFs, HxCDFs, and HxCDDs showed similar trends. They increased dramatically during 1956-1972, decreased rapidly during 1972-1981, and then leveled off. In contrast to the highly chlorinated dioxins, TCDDs, PeCDDs and TCDFs, especially 1,3,6,8-TCDD and 1,3,7,9-TCDD, increased during 1962-1977, decreased rapidly during 1977-1981, and subsequently leveled off. Moreover, PeCDFs showed a different trend from those of the other homologs mentioned above, increasing slowly to date. These characteristics indicate the existence of different dioxin sources in the Tokyo Bay area. To identify these sources, PCA was performed using a correlation matrix calculated from the PCDD/F data set, and three PCs with proportions of approximately 35, 33, and 28 % were extracted. PC-1 includes OCDD, HpCDDs, OCDF, and most HpCDFs as its characteristic congeners. Considering the fact that these compounds are known impurities of PCP[2] and their trends described above correspond with the history of PCP use in Japan, PC-1 was judged to be the dioxin impurities of PCP. In the case of PC-2, most PeCDFs, particularly 1,2,3,4,9-PeCDF and 2,3,4,6,7-PeCDF, are the characteristic congeners. Based on the homolog pattern of a typical combustion process reported by Hutzinger and Fiedler[4], in which PeCDFs and HxCDFs are the main components, it was assumed that PC-2 corresponds to combustion processes in which incineration is considered to be the main factor. The characteristic congeners of PC-3 include some TCDD, PeCDD, and TCDF congeners, especially 1,3,6,8-TCDD, 1,3,7,9-TCDD, 1,2,3,6,8-PeCDD, 1,2,3,7,9-PeCDD, and 2,4,6,8-TCDF. Since these compounds are reported to be the primary impurities of CNP and their trends mentioned above are consistent with the history of CNP use in Japan[2], PC-3 was identified to be the dioxin impurities of CNP. After source identification, we carried out multiple regression analysis for source apportioning. The congener-specific concentrations of HpCDDs, OCDF, and HpCDFs in PCP[2] were modified using the typical homolog pattern of PCP reported by Hutzinger and Fiedler[4] and used in this analysis. Based on the obtained apportionment of each source, the historical contributions of PCP, CNP, and atmospheric deposition to the PCDD/F and TEQ (PCDD/Fs) concentrations in Tokyo Bay were estimated and the results are presented in Figures 2 and 3, respectively. It can be seen that herbicides (PCP and CNP) have contributed mainly to the PCDD/F and TEQ (PCDD/Fs) concentrations since the late 1950s; PCP has been the greatest contributor to dioxin burdens. The inputs originating from PCP and CNP did not significantly decrease even after the decline of their use. This suggests that dioxins remaining in agricultural land will continue to run off and pollute the aquatic environment in Japan for a long time.

For Co-PCBs, the four target congeners were found to be ubiquitous in all the core layers examined. Figure 4 shows the historical trends of Co-PCB concentration in the sediment core. The Co-PCB concentration increased drastically from 1951 to 1972. Subsequently, a decrease occurred during 1972-1986 and then the concentration generally leveled off. PCB 77 was the dominant congener, contributing more than 88 % of the Co-PCB concentration throughout the core. The TEQ (Co-PCBs) was dominated by PCB 126 due to its largest TEF within the coplanar PCB group. Since only four Co-PCBs in the sediment core were analyzed, it was difficult to apply PCA for Co-PCB source identification. However, from the historical trends of individual Co-PCB congeners, we found something interesting. PCB-77, PCB-81, and PCB-126 showed very similar trends. They increased drastically during 1951-1972, and then decreased quickly during 1972-1977. These trends agree well with the situation of PCB production and use in Japan[5]. These trends are also generally in agreement with that of total PCBs in the same sediment core[6]. In addition, the observed Co-PCB pattern with the predominance of PCB-77 mentioned above is similar to the finding of Kannan et al. that Kanechlor mixtures contain PCB-77 as the key Co-PCB congener[7]. Based on these comparisons, we believed that PCB formulations were the greatest contributing Co-PCB source in this area. On the other hand, PCB-169 showed a different trend from those of PCB-77, PCB-81 and PCB-126. The PCB-169 level has generally been increasing slowly to date, being consistent with the trend of PeCDFs recorded in the sediment core. Since PeCDFs are thought to be the main combustion-related dioxin components, as described previously[4], and incineration has been estimated to be a greater source of PCB-169 than PCB formulations and herbicides[8], we estimated that incineration was another significant source of Co-PCB pollution in Tokyo Bay. It is noteworthy that the PCB-169/Co-PCB ratio had been increasing by a factor of 3 from the late 1960s to 1993, thus suggesting increasing Co-PCB emissions from incineration.

Furthermore, it was found that the total TEQ (PCDD/Fs and Co-PCBs) concentration increased drastically form the late 1950s and reached its maximum around 1970. PCDD/Fs contributed more than 90 % of the total TEQ throughout the sediment core. Our findings are of significance for the establishment of comprehensive dioxin and PCB control measures in Japan.

Acknowledgements

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Fig. 1. Historical trends of PCDD/F concentration in the sediment core from Tokyo Bay

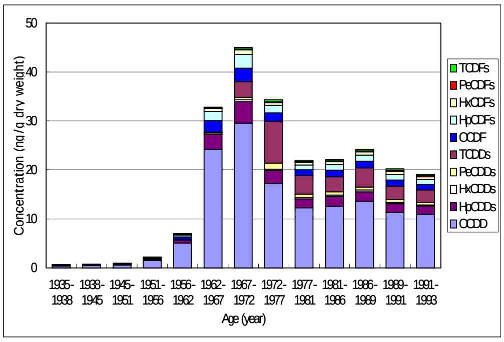


Fig. 2. Historical contribution of different sources to the PCDD/F concentration in Tokyo Bay

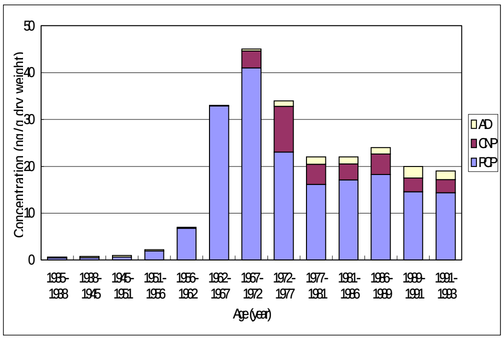


Fig. 3. Historical contribution of different sources to the TEQ (PCDD/Fs) in Tokyo Bay

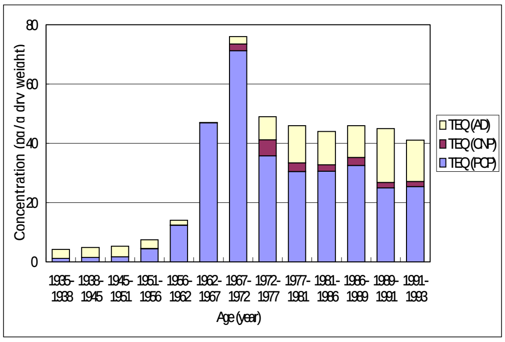
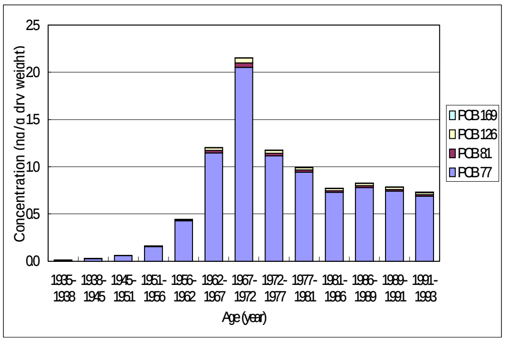


Fig. 4. Historical trends of Co-PCB concentration in the sediment core from Tokyo Bay



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