THE VERTICAL DISTRIBUTION OF PCDDS, PCDFS AND CO-PCBS IN ARIAKE BAY, JAPAN

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Introduction

Endocrine disruptor chemicals, such as dioxins and coplanar polychlorineated biphenyls (co-PCBs) were well known to be accumulating into the tidal flat. Suspended solids in Ariake Bay are very important factor to keep the coastal ecosystem because they are abundantly deposit into the tidal flat with terrestrial nutrient through river. This implies that Ariake Bay has had been the land-derived toxic organochlorine compounds. However, nowadays in Ariake Bay, there is very little information about the effect of chemical pollution and has not been reported with any relationship between marine production and toxic chemical compounds. This study will provide valuable information to understand and assess the behavior of persistent organic pollutants (POPs), in particular polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibezofurans (PCDFs) and co-PCBs in the environment from the point of view of environmental pollution in Ariake Bay, Japan.

Materials and Methods

Commercially available PCDDs/Fs and PCBs were used. A sediment core, which was a cylindrical sample with a diameter of 11cm and a length of 350cm was obtained from the northern part of Ariake Bay, the Yanagawa coast (St.2; N33˚ 05' 477" and E130˚ 23' 431") by the scuba divers on 2005. Surface sediment samples were also collected at 2 other stations, St.1 (N33˚ 09' 123" and E130˚ 21' 482") and St.3 (N33˚ 05' 370" and E130˚ 24' 735") in the Ariake Bay using an Ekman-Berge dredge. The sediment samples were extracted, fractionated and analyzed following the methods reported by Eun et al. (2003)[1]. Determinations of hepta- to OCDD/Fs and coplanar PCBs were accomplished by using a 60m of DB-5MS column (J&W Scientific; 0.25mm i.d. with 0.25μm film thickness). Similarly, SP-2331 (J&W Scientific; 60m × 0.32mm i.d. with 0.20μm film thickness) fused silica capillary column was used to separate for tetra- to hexaCDD/Fs. The HRMS was operated in an electron impact (EI) and SIM mode at resolution more than 10,000 (10% valley). Recovery range for ^{13}C-labeled PCDDs, PCDFs and coplanar PCBs were 61-115 % (average 88 ± 14 %, n=22), 62-115 % (average 87 ± 14 %, n=22) and 82-120 % (average 99 ± 9 %, n=22), respectively. Mean blank value was subtracted from the sample data. The sediment cores were analyzed for ^{210}Pb, ^{226}Ra and ^{137}Cs by direct gamma assay using a high purity germanium detector (Canberra; BE5025). The sedimentation rate and radiometric dates were calculated from the ^{210}Pb records based on the Constant Initial Concentration model. The age determination with ^{210}Pb isotope revealed that the sedimentary rate in Ariake Bay (St.2) is 0.52 g/cm^2 per year.

Results and Discussion

PCDDs/Fs The vertical variation of ^{210}Pb concentration was obviously observed as decreasing downward. This trend implies that the top 40cm of the core spans a little more than a century. Most of the tetra- to octachloroinated dibenzo-p-dioxins (PCDDs) and dibezofurans (PCDFs) were determined in this study. The total concentration of PCDDs and PCDFs in surface sediments of the Yabe River (17 ng/g dry wt) was approximately 2.5-fold higher than that of the Chikugo River (7 ng/g dry wt), which has the highest flow amount of about 40% input to part of the northern Bay. In particular, with respect to the PCDFs concentration in the Yabe River was approximately 3-fold higher than that of the Chikugo River. This fact in the Yabe River may imply the influence of pollution sources, including pentachlorophenol (PCP) more than the Chikugo River area. Because of the PCP profiles are generally characterized by relatively high concentrations of PCDFs[2,3]. The vertical distribution of both PCDDs and PCDFs concentration in sediment cores increased gradually from the 1930s. The maximum concentration was exhibited during 1967 to 1971 and thereafter the concentration was decreased until the 1990s. Subsequently, the concentration of PCDDs homologues showed rising again toward the upper sediment core but PCDFs kept level. The concentration and composition profiles of PCDDs and PCDFs congeners in all samples were predominated by higher chlorinated PCDDs, in particular OCDD which contributed an average 53% to the total PCDDs/Fs concentration. In the 1950s and 1960s, the most abundant OCDD in sediment core slice 10-28cm of depth could be assumed that it was attributed to the herbicide, PCP. Homologue profiles of PCP samples revealed that the most abundant impurity of dioxin was OCDD[4] and there were many widely used in Japan during that period[5]. However, they are lower than the concentration in the sediment cores of Tokyo Bay, which is the region of the most PCDDs and PCDFs polluted areas in the world[6], Japan[7,8,9]. Since the ratio of ΣPCDD to ΣPCDF concentration in PCP profiles ranges from 1-10 and relatively high PCDFs, the ratio observed in this study was significantly different between the period of time using (ratio, 4 to 5) and not using (ratio, 6 to 9 and 10 to 31) for the PCP[3]. In addition, a large number of fish and shellfish were suddenly killed in Ariake Bay during 1961 and 1962. Ikematsu et al., (1963) reported that this phenomenon might be caused from the use of PCP in rice fields[10]. Therefore, the PCDDs/DFs pollutions in sediment core during the early 1950s to 1970s in Ariake Bay, based on the possibility of PCP contamination, could be assumed occurred in the early 1960s.

PCBs The concentration of coplanar PCBs in surface sediments of St.3 was approximately 2-fold higher than that of the St.1 as well as described the total concentration trend of PCDDs/Fs. However, the concentration in surface sediments of PCBs, which was previously determined by Nakata et al. (2002)[11], was higher than that of the center and southern part of this Bay. This result might be attributed to a large amount of river flow through the Chikugo River and the tidal flow from southern to northern in the Ariake Bay. The vertical profile of coplanar PCBs concentration in sediment cores increased gradually from the 1930s and drastically increased from the early of the 1950s to the late 1960s. Then the concentration was decreased until the 1990s. It is interesting to note that the maximum concentration was presented in the top sediment core, corresponding to the 2002-2005 period in our present study (Figure 1). In the predominance homologue among the PCBs was observed the pentachloro biphenyl which contributed to ΣPCBs concentration more than 70%. The composition

of PCB 118 presented the most dominant congener in all detectable samples and then followed by PCB 105 and 77. The contributions of PCB 118, 105 and 77 to the ΣPCBs concentration in sediment cores accounted for about 53%, 19% and 11%, respectively. The pattern of compositions for coplanar PCB congeners in atmospheric and water environment of Hiroshima, Japan, was similar to our result in sediment core[12]. It could be assumed that the high PCBs concentration of top core determined in Ariake Bay might have originated from atmospheric environment or a remote area through the seawater.

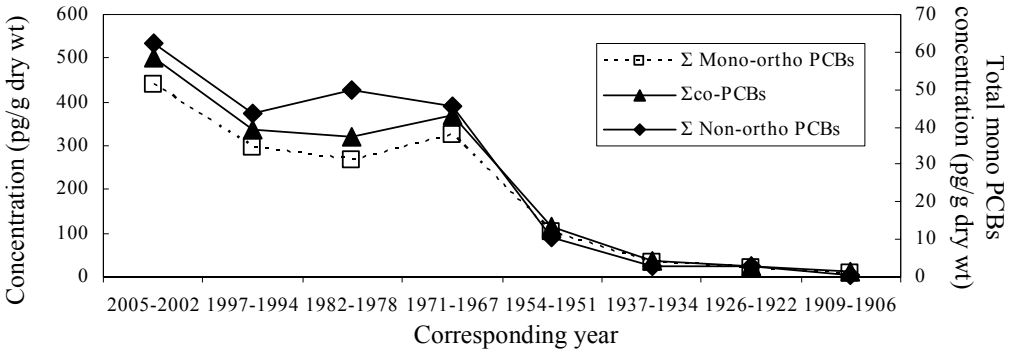

Figure 1 Concentration vertical profiles of coplanar PCB, including mono- and non-*ortho* congeners in sediment cores from Ariake Bay

TEQs The 2,3,7,8-tetrachlorodibezo-*p*-dioxin (2,3,7,8-TCDD) toxic equivalent quantity (TEQ-pg/g) was estimated by WHO TEF (toxic equivalent factor) for dioxins and PCBs. According to the Ministry of the Environment in Japan (2004)[13], the concentration of dioxins TEQ in surface sediment on upstream and midstream of river, Yabe was found to be 0.68 and 0.30pg-TEQ/g, respectively. Thus it is generally assumed that sources of dioxins pollution are caused by upstream conditions. In this study, however, concentration of total dioxins in surface sediment from the mouth of the river was approximately 10-fold (31pg-TEQ/g) higher than those of total dioxins. This implied that the pollution source of dioxins might be emitted from nearby St.3 in southern part of the Ariake Bay. This assumption was supported by the tidal flow in this Bay. It has been found to be in a counter-clockwise rotation and the high concentration, 300pg-TEQ/g in surface sediment of Omuta River where was located in 5km south of St.3, Yabe River[14]. The profiles of contribution of PCDDs, PCDFs and PCBs to total TEQs was exhibited the vertical trends (Figure 2). Result in this study could be explained by the influence of PCP, which was widely used at that time in Ariake Bay. And then, the PCDDs profile from 1978-1982 showed a general increase toward the top core, indicating that might be more representative of CNP than PCP.

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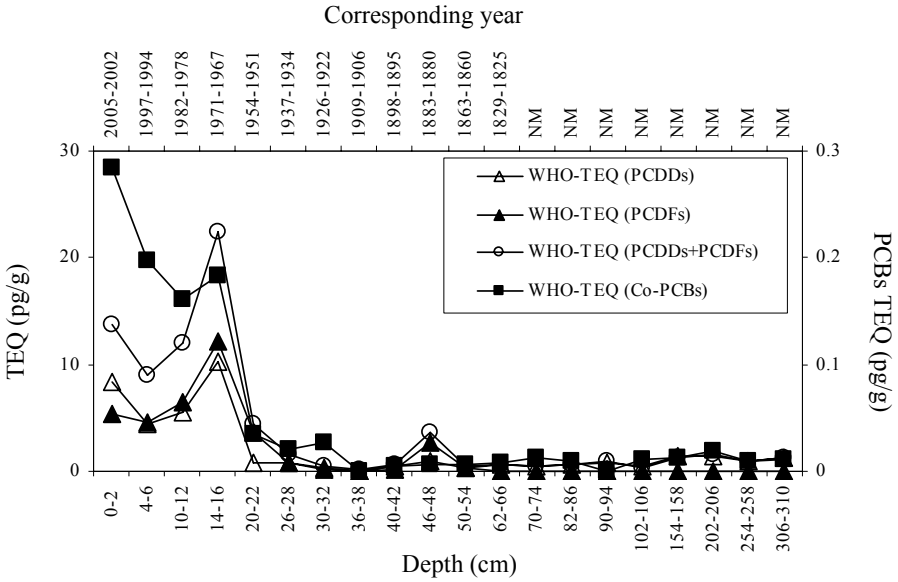

Figure 2 Vertical TEQs profiles of PCDDs, PCDFs and coplanar PCBs in Ariake Bay

References

1. Ikenaka Y, Eun H, Watanabe E, Miyabara Y. *Organohalogen Comp* 2003;60-65
2. Hagenmaier H, Brunner H. *Chemosphere* 1987;16:1759.
3. Gaus C, Papke O, Dennision N, Haynes D, Shaw G, Connell DW, Muller JF. *Chemosphere* 2001;43:549.
4. Stern GA, Braekevelt E, Helm PA, Bidleman TF, Outridge PM, Lockhart WL, McNeeley R, Rosenberg B, Ikonomou MG, Hamilton P, Tomy GT, Wilkinson P. *Sci Total Environ* 2005;342:223.
5. Masunaga S, Yao Y, Ogura I, Nakai S, Kanai Y, Yamamuro M, Nakanishi J. *Environ Sci Technol* 2001;35: 1967.
6. Ogura I, Masunaga S, Nakanishi J. *Chemosphere* 2001;44:1473.
7. Yao Y, Masunaga S, Takada H, Nakanishi J. *Environ Toxci Chem* 2002;21:991.
8. Choi JW, Fujimaki S, Kitamura K, Hashimoto S, Ito H, Sakurai T, Suzuki N, Nagasaka H, Tanabe K, Sakai SI. *Organiohalogen Comp* 2003;61: 119.
9. Shimizu J, Yamao S, Nosaka T, Noguchi K, Mine M, Matsumoto K, Oichi K, Tsutsumi K, Miyamoto T, Ikeda Y. *Report of Hydrographic and Oceanographic Researches* 2005;41:35. (in Japanese)
10. Ikematsu W, Tanaka Y, Azeta Y, Ehira S, Morokuma H, Yamaguchi S. *Bulletin of the Seikai National Fisheries Research Institute. Nagasaki* 1963;28:1. (in Japanese)
11. Nakata H, Miyawaki T, Sakai Y. *J Environ Chem* 2002;12:127. (in Japanese)
12. Hiura M, Oohara T, Odahara M, Okamoto T. *Report of Hiroshima Prefecture Health Environment Center Research* 2004;12:47. (In Japanese)
13. Ministry of the Environment in Japan. <*http://www.env.go.jp/press/press.php?serial=3048*> 2004.
14. Ministry of the Environment in Japan. <*http://www.env.go.jp/air/report/h17-03/04.pdf*>2000.