A COMPARISON ON LEVELS OF PCDDS, PCDFS AND NON-ORTHO CHLORINE SUBSTITUTED COPLANAR PCBS IN SEDIMENTS FROM FRESHWATER FISH CULTURE PONDS, RIVERS AND A COASTAL AREA NEAR INCINERATION SITES FOR METAL RECLAMATION IN WAN-LI, TAIWAN

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1. INTRODUCTION

We previously found that six surface soil samples from incineration sites in Wan-Li, southern Taiwan, Republic of China, where waste electric wire and/or magnetic card had been combusted directly on the earth for metal reclamation, were polluted with PCBs, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Especially, the samples from the incineration sites only with waste electric wire were heavily polluted by these chlorinated compounds[1]. Furthermore, some of sediment samples from nine culture ponds for freshwater fish in this Wan-Li area were revealed to be heavily polluted with PCDDs and PCDFs, showing their levels to be similar to those of surface soil specimen from waste incineration sites for metal reclamation[2].

In this study, a comparison on the levels of PCDDs, PCDFs and non-ortho chlorine substituted coplanar PCBs (Co-PCBs) in sediment samples from culture ponds for freshwater fish , rivers and coastal area near the waste combustion sites in Wan-Li area was carried out in order to estimate an influence from the waste combustion.

2. EXPERIMENTAL

Sample

Surface sediment samples were collected from nine freshwater fish culture ponds, three rivers and one coastal area near waste incineration sites for metal reclamation in Wan-Li, southern Taiwan in February, 1993 (Fig. 1). The marks of "P", "R" and "S" in Fig. 1 mean

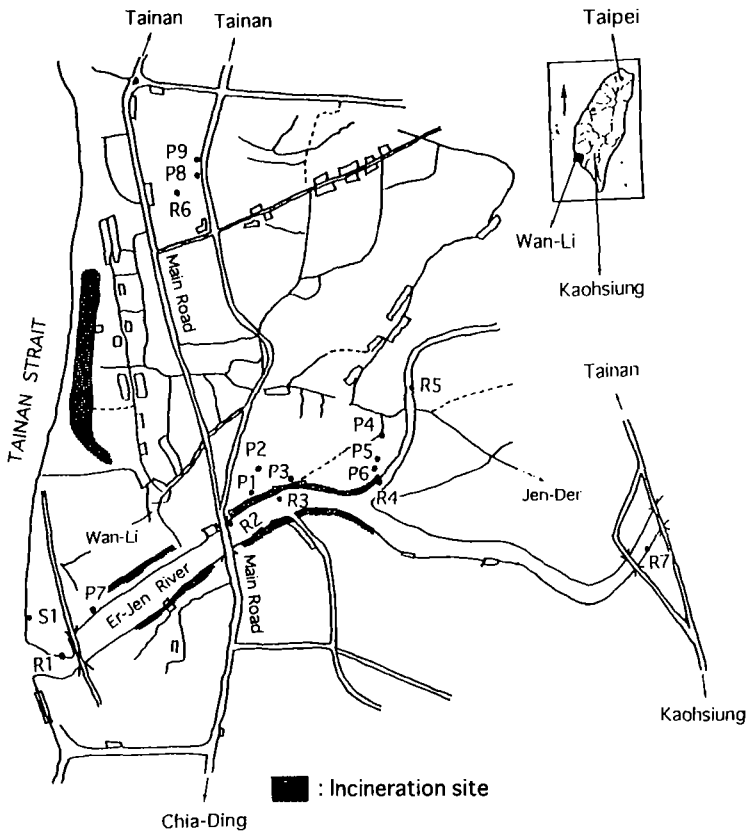

Fig. 1. Sampling sites of sediment samples

respectively the sampling points of pond, river and coastal areas. All samples were took within a depth of less than 20 cm.

Extraction

The sediment specimens were thinned in a thickness of 1 cm, left for 2 days at outdoor for complete dryness, and then pulverized into small pieces. Each poured samples (60 g) was extracted with 300 ml of toluene for 8 hours under reflux. The toluene extract was filtered through a 1 μm glass fiber filter in order to remove sediment particles.

Clean-up

After addition of keeper solvent (n-decane, 0.3 ml), a sixth aliquot of the filtered toluene extract was concentrated to a volume of less than 0.3 ml and adjusted to a volume of 20 ml with n-hexane. After spiking of internal standards (five $^{13}C_{12}$-PCDDs and five $^{13}C_{12}$-PCDFs, each 500 pg; three $^{13}C_{12}$-Co-PCBs, each 1000 pg), the extract was purified on a multi-layer column containing Ns_2SO_4-silica (12 g), 10% (w/w) $AgNO_3$-silica (8 g), silica (2.4 g), 22% (w/w) H_2SO_4-silica (12 g), 44% (w/w) H_2SO_4-silica (12 g), silica (2.4 g) and 2% (w/w) KOH-silica (8 g) with an eluent of n-hexane (360 ml). The eluate was concentrated to 5 ml and chromatographed into three fractions with successive eluents of 90 ml of n-hexane, 70

ml of 1% methylene chloride in n-hexane and 160 ml of 50% methylene chloride in n-hexane on an alumina column (10 g, Merck neutral, activate I). The third eluate containing PCDDs, PCDFs and Co-PCBs was concentrated to 3 ml. After addition of keeper solvent (n-decane, 30 μl), the concentrated eluate was left for complete evaporation of n-hexane in room temperature and then adjusted to a volume of 30 μl with n-decane.

Above finally purified extract was analyzed on J&W DB-5 (30 m x 0.32 mm, 0.20 μm)(held for 1 min at 120℃ and programmed to 180℃ at 20℃ /min, to 260℃ at 4℃ /min and to 310 ℃ at 20℃ /min) for Co-PCBs, (held for 1 min at 140℃, programmed to 220℃ at 20℃ /min and 310 ℃ at 8℃ /min, and held for 4 min) for hepta- and octachlorinataed PCDDs and PCDFs, and on Supelco 2331 (60 m x 0.32 mm, 0.20 μm)(programmed from 150 to 180℃ at 20℃/min and to 250℃ at 3/min, and held for 29 min) for tetra- through hexachlorinated PCDDs and PCDFs in an electron impact-single ion monitoring mode at a resolution of 7000 using a Hewlett Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer. The result were corrected for the recovery of $^{13}C_{12}$-labeled internal standards.

3. RESULTS AND DISCUSSION

Wastes of wire, magnetic card and electric instrument part, etc. have been incinerated at the areas around northwest part of Main road and around both river sides of the Er-Jen River (see the mesh mark in Fig. 1). In the latter case, the area was the surrounding both river sides of the marks of P7 through P6 as shown in Fig. 1.

Figure 2 shows concentrations of 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8- and 1,2,3,4,6,7,8,9-HpCDFs and OCDF in sediment samples from various locations in Wan-Li shown in Fig. 1. In a case of pond survey, the highest concentrations of HpCDD and OCDD were seen in a sediment sample from P3 with the levels of 4380 and 3440 pg/g, respectively. The samples of P6 and P7 also showed high levels of HpCDD and OCDD with 1440 and 1560 pg/g and 676 and 1990 pg/g, respectively. In general, the pollution degree was high in the samples from ponds (P3, P5, P6, P7 and P2) in just close vicinity to the incineration sites. Pond P2 was located at a distance of ca. 100 m from P3, and P4 and P5 were respectively located at a distance of ca. 150 and 300 m from P6. As shown in Fig. 2, the contamination levels of HpCDD and OCDD in P2 was remarkably lower than that in P3. In addition, the level was arranged in the order of P6, P5 and P4 in a magnitude. This indicates that an influence on exposure to the both chemicals derived from burning of waste materials decreases with an increase of the distance from the incineration site. Compared to samples from ponds except P1 near the river side, those from ponds P8 and P9, both of which were located at a distance of ca. 2500 m from the river side and of ca. 300 m from the northwest incineration site, gave lower concentrations with levels 18 and 10 pg/g in HpCDD and 43 and 17 pg/g in OCDD, respectively.

Similar results above described were also observed in cases of 1,2,3,4,6,7,8-HpCDF, 1,2,3,6,7,8,9-HpCDF and OCDF (Fig. 2).

In river sediments, it was revealed that R3 and R4 closely adjacent to P3 and P6 heavily polluted by PCDDs and PCDFs gave also high levels of 1,2,3,4,6,7,8-HpCDD with 314 and 531 pg/g, of OCDD with 939 and 1430 pg/g, of 1,2,3,4,6,7,8-HpCDF with 118 and 742 pg/g, of 1,2,3,6,7,8,9-HpCDF with 6.46 and 36.3 pg/g, and of OCDF with 14 and 150 pg/g,

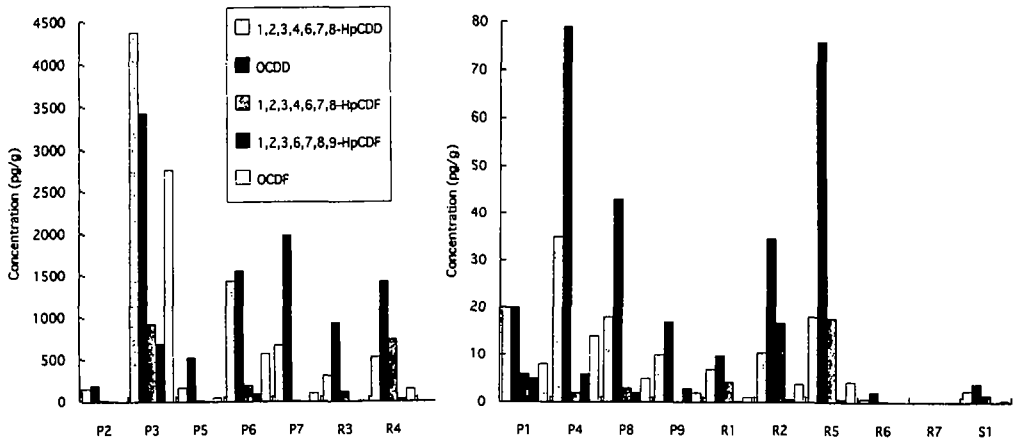

Fig. 2. Concentrations of HpCDD, OCDD, HpCDFs and OCDF in sediments from freshwater culture ponds, rivers and a costal area in Wan-Li

respectively. The ratios (3.0 and 2.7, respectively) of OCDD versus HpCDD in R3 and R4, however, were remarkably higher than those (0.79 and 1.1, respectively) in P3 and P6 (Fig. 2). R1, R6 and R7 showed lower levels of PCDDs than did R2, R3, R4 and R5 near the incineration site. Especially, the levels in R7 at the upper stream of ca. 3500 m from R3 was extremely low (0.05 in 1,2,3,4,6,7,8-HpCDD and 0.22 pg/g in OCDD, respectively). These results also cleared the pollution in the river to be closely related to a distance from the combustion site. In addition, a sample from a coastal area S1 was confirmed to have similar contamination level to one from the river mouth R1.

As shown in Fig. 2, similar observations were also recognized in a case of PCDFs.

On the other hand, both sediments from P3 and P6 among nine sites were heavily polluted by Co-PCBs as well as PCDDs and PCDFs, showing the concentrations to be 54.9 and 278 ng/g, respectively (Fig. 3). The contamination level (ng/g) in other pond samples was arranged in the order of P2 (11.8), P5 (0.46), P-7 (8.13), P1 (3.05), P4 (1.86), P8 (0.14) and P-9 (0.04) in a magnitude. Here again, this insists that the exposure to Co-PCBs as well as PCDDs and PCDFs has a close correlation with a distance from the combustion site. In river sediments, R3 and R4 showed high concentrations of Co-PCBs at a level of 157 and 7.96 ng/g, respectively. In addition, R2 and R5 also lifted levels with 4.49 and 2.88 ng/g, respectively. The exposure levels (0.061 to 278 ng/g) in samples except R7 and S1 was equivalent to 2.4 to 1120 greater times one from north of Galve on the Swedish east cost (0.025 ng/g)[3]. All sediment samples collected in this study contained 3,3',4,4'-tetrachlorinated Co-PCB (3,3',4,4'-TCB) as a major at the isomer ratio of 90.7 to 98.4%. Similar results were also reported in sediments from east cost in Sweden[3] and from Eman River[4]. The isomer ratio of 3,3',4,4',5-pentachlorinated Co-PCB (3,3',4,4',5-PeCB) having the highest toxicity (2,3,7,8-TCDD toxicity equivalency factor = 0.1)[5] among three Co-PCB isomers was in the range of 1.6 to 8.6%. The ratios in high contamination sediments from P3, P6 and R3 were 5.6, 1.9 and 6.2%, respectively. In the meantime, 3,3',4,4',5,5'-hexachlorinated Co-PCBs (3,3',4,4',5,5'-HxCB) had an extremely low level with the range of

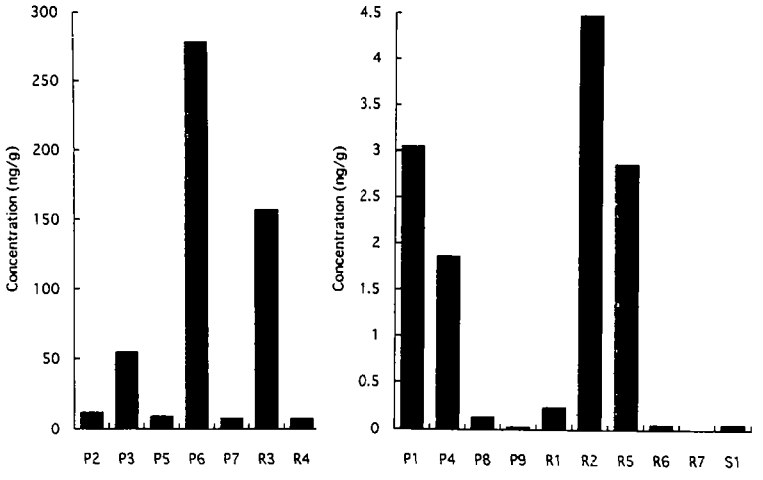

Fig. 3. Concentrations of total Co-PCBs in sediments from freshwater culture ponds, rivers and a costal area in Wan-Li

<0.0 to 1.4%.
We will present the data on lower chlorinated PCDDs and PCDFs in above examined sediment samples in Wan-Li.

4. REFERENCES

1) Huang, C.-W., Miyata, H., Lu, J-R., Ohta, S., Chang, T. and Kashimoto, T.(1992): Levels of PCBs,PCDDs and PCDFs in soil samples from incineration sites for metal reclamation in Taiwan, Chemosphere 24, 1669-1676
2) Lu, J-R, Miyata, H., Huang, C.-W., Tsai, H.-T., Sheng, V.-Z., Mase, Y., Aozasa, O. and Ohta, S. (1993): Survey on PCDDs and PCDFs in sediment from freshwater fish culture ponds near incineration sites for metal reclamation in Taiwan, Republic of China, Organohalogen Compounds 12, 321-323
3) Bergquist, P.-A., Bandh, C., Broman, D., Ishaq, R., Lundgren, K., Naf, C., Patterson, H., Rappe, C., Rolff, C., Strranberg, B., Zebuhr, Y. and Zook, D.R. (1992): Multi-residue analytical method including planar PCB, Dioxines and other organic contaminants for marine samples, Organohalogen Compounds 9, 17-16
4) Kjeller, L.-O., Kulp, S.-E., Bergek, S., Bostrom, M., Berguist, P.-A. and Rappe, C. (1990): Levels and possible sources of PCDD/PCDF in sediment and pike samples from Swedish lakes and river, Chemosphere 20, 1489-1496
5) Safe, S. (1993): Polychlorinated biphenyls-toxicology and risk assessment, Organohalogen Compounds 14, 53-58