

SURVEY OF BACKGROUND LEVELS OF PCDDS, PCDFS AND NON-ORTHO CHLORINE SUBSTITUTED COPLANAR PCBs IN SEDIMENTS FROM RIVERS IN TAIWAN, REPUBLIC OF CHINA

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1. INTRODUCTION

We already revealed that sediments and fish culture ponds surrounding air-open waste incineration areas for metal reclamation in Wan-Li, southern Taiwan, Republic of China, were heavily polluted by polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non-ortho chlorine substituted coplanar PCBs (Co-PCBs)¹⁾. In addition, fish samples from the contaminated ponds showed also their high exposure levels²⁾.

Apart from above local contaminated area, no data concerning the background levels of above toxic chlorinated pollutants have been reported until today in Taiwan.

PCDDs, PCDFs and Co-PCBs are generated as by-products from various combustion and chemical processes. In addition, Co-PCBs are derived from commercial PCB products used widely in developed countries. They are released to the environment through the use and disposal products, and the combustion of various wastes. The pollutants released in the environment are surmised to accumulate in the estuary and ocean through atmospheric deposition and rain flow transportation.

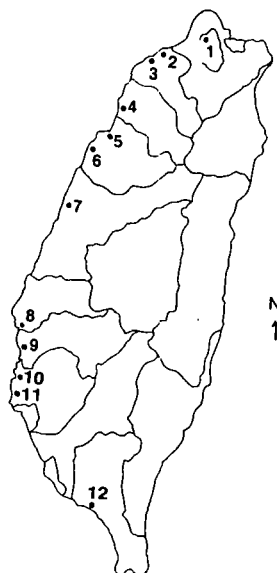
From above view points, we investigated the background levels of PCDDs, PCDFs and Co-PCBs in sediments from the estuary and the neighboring areas in Taiwan.

2. EXPERIMENTAL

Sampling

Surface sediment samples were collected from the estuary and the neighboring area of 12 rivers over northern to southern Taiwan, Republic of China in January, 1994. The sampling locations and the details were shown in Fig. 1 and Table 1, respectively. All samples were took within a depth of less than 20 cm.

Fig. 1. Sampling locations of river sediments



Analytical procedure

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 powdered samples (50 g) was extracted with 350 ml of toluene for 5 hrs. under reflux. The toluene extract was filtered through a 1 μ m glass fiber filter in order to remove sediment particles.

After addition of keeper solvent (n-decane, 0.3 ml), a fifth 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 $^{13}\text{C}_{12}$ -PCDDs and five $^{13}\text{C}_{12}$ -PCDFs, each 500 pg; three $^{13}\text{C}_{12}$ -Co-PCBs, each 400 pg), the extract was purified according to our previous method^{1,2)} composing essentially of multi-layer column chromatography and alumina column (10 g, Merck neutral, activate I) chromatography, followed by determination for PCDDs, PCDFs and Co-PCBs in an electron impact-single ion monitoring mode at a resolution of 8000 using a Hewlett Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer under similar conditions described elsewhere^{1,2)}.

3. RESULTS AND DISCUSSION

As shown in Fig. 1, sediment samples except for No. 1 used in this study were all obtained from the estuary of various rivers. The main reason is derived from a fact that the pollution at the upper stream has naturally an influence on the estuary area. Therefore, the detection of contamination by pollutants at the river mouth means that there is the source at the area surrounding the upper position.

Table 2 shows concentrations of 2,3,7,8-chlorine substituted PCDDs and PCDFs, and Co-PCBs in river sediments from 12 locations. The total concentration of three chemicals was in a wide range of 51 to 3758 pg/g dry weight. Especially, sample Nos. 2, 3 and 9 gave a high contamination level of 865, 1679 and 3758 pg/g, respectively.

Both sampling locations 2 and 3 are situated at industrial areas with a high population

Table 1. The details of sampling locations

Sample No.	River name	Sampling location	Character of surrounding area
1	Tansui River	Kuantu Bridge	Urban and industrial area
2	Nankan Rivulet	Haihu	Industrial area
3	Laochieh Rivulet	Tayuan Bridge	Industrial area
4	Touchang Rivulet	Nan-Liao	Industrial area
5	Chungkang Rivulet	Chungkang Bridge	Industrial area
6	Houlung Rivulet	Sungtzuchiao	Rural area
7	Tachia Rivulet	Hsin-Tachiao Bridge	Rural area
8	Peigaang Rivulet	Yunchia Bridge	Rural area
9	Putzu Rivulet	Tangshi Bridge	Rural area
10	Chiangshun Rivulet	Chan-Liao	Rural area
11	Tsengwen Rivulet	Kausing Bridge	Rural area
12	Kaoping Rivulet	Shuangyuan Bridge	Rural area

Table 2. Concentrations of PCDDs, PCDFs and Co-PCBs in river sediments from various locations

Sample No.	Actual concentration (pg/g dry weight)				TEQ concentration (pg/g dry weight)			
	PCDDs	PCDFs	Co-PCBs	Total	PCDDs	PCDFs	Co-PCBs	Total
1	157	11.1	75.9	244	2.76	0.025	0.361	3.14
2	250	48.4	565	865	0.458	0.064	0.210	0.732
3	241	14.4	1425	1679	0.802	0.048	2.843	3.69
4	123	7.12	80.1	210	0.140	0.059	0.076	0.275
5	103	3.37	11.8	118	0.096	0.003	0.012	0.111
6	193	15.4	45.2	253	1.10	0.065	0.022	1.18
7	37.1	4.19	9.74	51.0	0.050	0.004	0.010	0.064
8	123	17.9	60.5	201	0.278	0.020	0.045	0.343
9	3624	95.4	38.5	3758	9.63	0.004	0.045	9.68
10	298	15.5	20.9	332	0.232	0.011	0.108	0.351
11	24.6	6.14	1.54	32.3	0.024	0.007	0.001	0.031
12	48.2	8.59	15.9	72.6	0.061	0.010	0.008	0.079

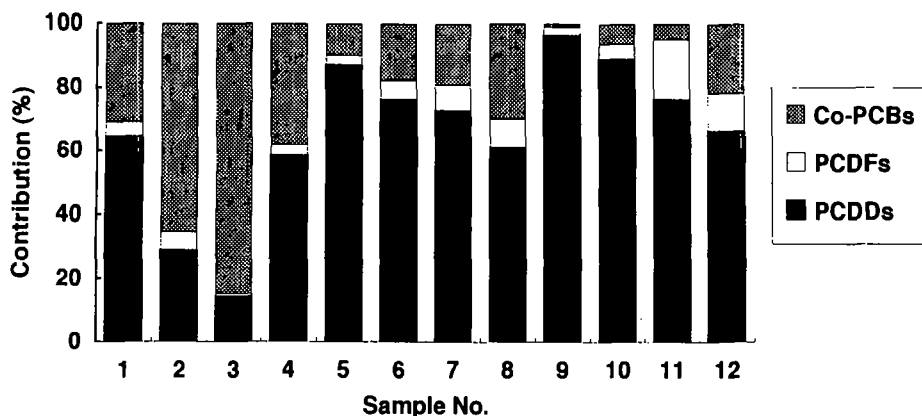


Fig. 2. Contributions of PCDDs, PCDFs and Co-PCBs to the total levels in river sediments from various locations

density.

As illustrated in Fig. 2, sample Nos. 2 and 3 contained Co-PCBs as a main component with 566 and 1425 pg/g, being equivalent 65 and 85% of the total, respectively. On the other hand, the contributions of PCDDs were 29 and 14%, respectively. Furthermore, the less contribution was seen in PCDFs, showing to be only 5.6 and 0.9% of the total. Taking into consideration that both locations belong to the industrial area, the high contribution of Co-PCBs is considered to be derived from commercial PCB products used large;y in the past.

Contrary to our expectation, the sediment from Location 1 in urban and industrial area with a high population density showed a low total pollution level of 244 pg/g. The major was PCDDs with 64% of the total (Fig. 2). The PCDDs included OCDD as a main congener at a level of 73% of the total PCDDs (Fig. 3). Thus high contribution of OCDD to the total was also seen in sample Nos. 2 (94%) and 3 (78%).

In the case of Locations 4 and 5 in another industrial areas, PCDDs were the most important contaminant (Fig. 2). A magnitude of the contamination level was arranged in order of PCDDs >> Co-PCBs > PCDFs in both locations. The PCDDs in both samples had similar composition to that in sample No. 2 and a little different one from those in sample Nos. 1 and 3. Therefore, it is considered that there might be different contamination sources of PCDDs between Locations 1 and 3 and Locations 2, 4 and 5.

A river sediment from Location 9 in the rural area gave the highest total contamination level of 3758 pg/g dry weight (Table 2). As illustrated in Fig. 2, 96% of the total was attributable to PCDDs. The congener profile of PCDDs was significantly different from those of sample Nos. 1 to 5, that is, the major congener was 2,3,7,8-TCDD (shown as TCDD in Fig. 2) with the contribution level of 82%. In addition, our gas chromatograph-mass spectrometer analysis revealed that TCDDs were composed of numerous isomers with main components of 1,3,6,8-TCDD and 1,3,7,9-TCDD. Form these results, it is surmised that the PCDDs might be mainly brought from the herbicide CNP (4-nitrophenol 2,4,6-trichlorobiphenyl ether) sprayed in the farm, because the agent contains 1,3,6,8- and 1,3,7,9-TCDD isomers as majors of PCDDs³). Similar observation was also reported in samples of paddy soil in Japan⁴). Sample No. 10 as well as No. 9 showed also the similar pollution profile (Figs. 2 and 3).

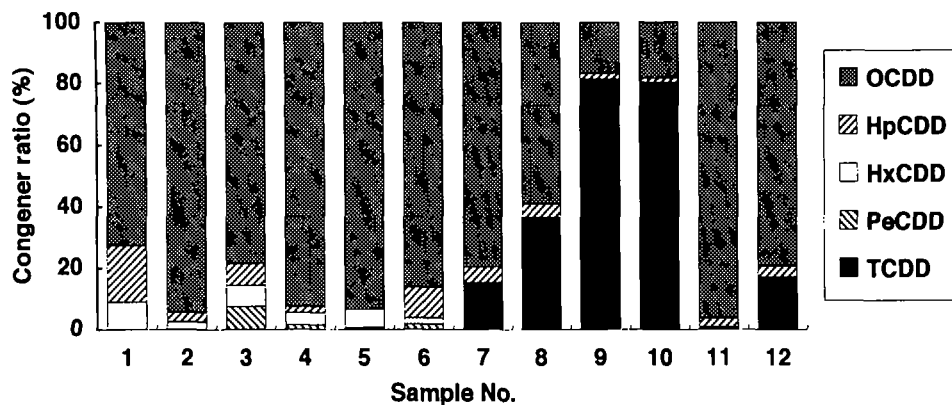


Fig. 3. Congener ratios of PCDDs in river sediments from various locations

On the other hand, sample Nos. 6, 7, 8, 11 and 12 in another rural regions included also PCDDs as a major, showing the PCDDs to occupy at a range of 61 to 76% of the total (Fig. 2). However, their congener patterns of PCDDs were distinguishably different from above cases of sample Nos. 9 and 10, namely, the majority of PCDDs in these samples was OCDD with the congener ratio of 59 to 96% (Fig. 3). Especially, both sample Nos. 6 and 11 showed the remarkably high OCDD ratio of 86 and 96%, respectively. This indicates that the main contamination source might be the herbicide pentachlorophenol (PCP) including HpCDD and OCDD as majors of PCDDs⁵⁾.

In the case of specimen Nos. 7, 8 and 12, TCDD was detected at the congener ratio of 15, 36 and 17%, respectively. Therefore, the contamination might be derived from both herbicides of CNP and PCP.

This survey made clear that PCDFs was the minor contaminant in all locations, showing the contribution to be only 0.9 to 19% of the total concentration (Fig. 2).

From above results, it was found that responsible pollutants were Co-PCBs and/or PCDDs in urban and/or industrial areas, and PCDDs in agricultural areas.

In order to compare the total toxicity levels of PCDDs, PCDFs and Co-PCBs in analyzed samples, the values of 2,3,7,8-TCDD toxic equivalent quantity (TEQ) were calculated for PCDDs and PCDFs using International 2,3,7,8-TCDD Toxicity Equivalence Factors (TEFs) reported by Kuts et al.⁶⁾ and for Co-PCBs using TEF proposed by Safe⁷⁾.

As shown in Table 2, the total TEQ levels of three pollutants in river sediments were in a wide range of 0.079 to 9.68 pg/g dry weight. Especially, the high level was recognized in Nos. 1, 3, 6 and 9 among analyzed samples, showing it to be 3.14, 3.69, 1.18 and 9.68 pg/g, respectively.

In the case of sample No. 3, Co-PCBs occupied 75% of the total TEQ (Fig. 4). In sample No. 1, however, the major was attributable to PCDDs with 89% of the total. The similarity was observed also in sample No. 5. On the other hand, PCDFs was a negligible contributor in Locations 1, 3 and 5 in urban and/or industrial regions. While, the noticeable participation was confirmed in Locations 2 and 4, indicating the contribution to be 8.8 and 21%, respectively.

In sample No. 9 having the highest contamination level of 9.68 pg/g, PCDDs was responsible for the most total (99.5%). PCDDs was also the main contributor in all samples

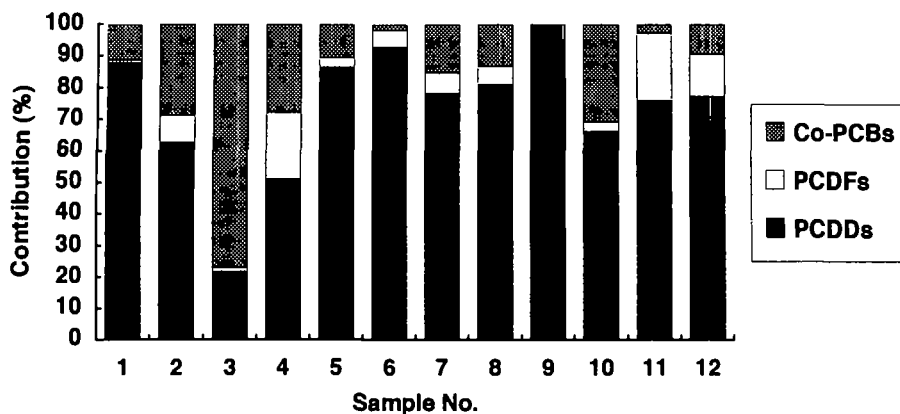


Fig. 4. Contributions of PCDDs, PCDFs and Co-PCBs to the total TEQ levels in river sediments from 12 locations in Taiwan

from another agricultural regions.

From above results, it was concluded that the majority of total TEQ was attributable to PCDDs. Hereafter, it is very important to detect the contamination sources for the high contamination locations.

4. REFERENCES

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