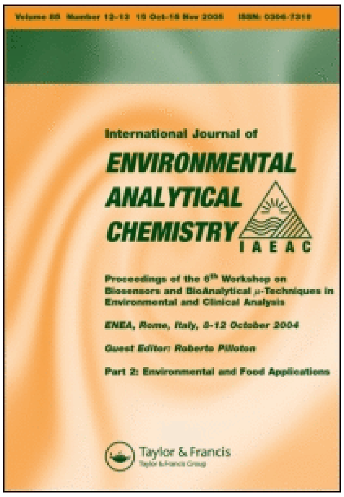

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LEVELS OF COPLANAR PCBs, PCDDs AND PCDFs IN FLY ASHES AND POND SEDIMENTS

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Non-*ortho* chlorine substituted coplanar PCBs (Co-PCBs), polychlorinated dibenzo-p-dioxin (PCDDs) and polychlorinated dibenzofuran (PCDFs) in fly ash and sediment samples of an irrigation pond near a municipal waste incineration facility were analyzed using ^{13}C-labeled respective internal standards and a selected ion monitoring method of high resolution GC-MS. The average concentrations of total Co-PCBs, total PCDDs and total PCDFs in the fly ash samples (n = 3) were 1200, 33000 and 16000 pg/g of dry weight, respectively. The average levels of total Co-PCBs, total PCDDs and total PCDFs in the sediment samples (n = 10) were 270, 10000, and 290 pg/g of dry weight, respectively. Though the concentrations of Co-PCBs, PCDDs and PCDFs in the sediment were much lower than those in the fly ash, these findings might suggest that one minor source of Co-PCB pollution was municipal waste incineration as well as PCDDs and PCDFs.

KEY WORDS: Non-*ortho* coplanar polychlorinated biphenyl, polychlorinated dibenzo-p-dioxin, polychlorinated dibenzofuran, gas chromatography-mass spectrometry, fly ash, pond sediment.

INTRODUCTION

Non-*ortho* coplanar polychlorinated biphenyls (Co-PCBs) are known to be similar in structure and toxicity to those of polychlorinated dibenzo-p-dioxin (PCDDs) and polychlorinated dibenzofuran (PCDFs), which are the most toxic among the PCB congeners. Recently, Co-PCBs were detected in high concentrations in fish[1], food[2], human serum[3], human milk[4,5] and wildlife[6–9] and in greater concentrations in animals than PCDDs or PCDFs. They are significant compounds of toxic importance to animals. The source of Co-PCB contamination in the environment was found to be commercial PCB preparations distributed throughout the world[7,10]. Another source of Co-PCB pollution was examined by the assessment of the levels of Co-PCB in fly ash and sediment samples. Simultaneously, the concentrations of PCDDs and PCDFs were measured to compare them with the Co-PCB levels. The findings of these studies are reported herein.

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MATERIALS AND METHODS

Sampling

Three fly ash samples were taken from a municipal waste incineration facility and ten sediment samples were collected from an irrigation pond (0.5 km radius) which is 0.6 km away from the facility. Samples were collected from April to December in 1986.

Chemicals

Dichloromethane and *n*-hexane were pesticide-grade solvents from Wako pure chemical ltd (Osaka, Japan). Toluene was the same grade solvent from Kishida chemical ltd (Osaka, Japan). Sulfuric acid, silver nitrate and anhydrous sodium sulfate were analytical grade products from Wako. Alumina and silica gel were purchased from Merck (Darmstadt, Germany). Standard and internal standard were purchased from Cambridge isotope laboratories (Woburn, Massachusetts, USA).

Sample preparation

Sediment samples were air dried and powdered. Fly ash samples were examined without additional preparation.

Extraction and cleanup

Five g of fly ash or 20 g of dried sediment samples were extracted with 200 ml of toluene using Soxhlet extractors for 24 hrs without pretreatment of the fly ash sample with diluted hydrochloric acid[11].

The extract after concentration was diluted with 50 ml of *n*-hexane and spiked with 500 pg of ^{13}C- labeled Co-PCBs PCDDs and PCDFs ranging from tetra- to heptachloro congener, and with 5000 pg ^{13}C- labeled octachloro dibenzo-p-dioxin (O_8CDD) and dibenzofuran (O_8CDF). The *n*-hexane solution was treated with 10 ml of sulfuric acid until be color of the aqueous layer disappeared. After treatment with sulfuric acid, the *n*-hexane solution was washed with 30 ml of 1N sodium hydroxide aqueous solution. The *n*-hexane solution was passed through anhydrous sodium sulfate and evaporated to 1 ml at < 40°C under reduced pressure. Subsequently, the concentrated hexane solution was cleaned up on 2 g of silver nitrate silica packed in a glass column (10 mm internal diameter × 300 mm length). Co-PCBs, PCDDs and PCDFs were eluted with 200 ml of *n*-hexane. The eluate was evaporated in the same conditions as described above. Furthermore, the concentrate was passed through a glass column (10 mm internal diameter × 300 mm length) packed with activated silica gel (2 g) and sodium sulfate (2 g). Co-PCBs, PCDDs and PCDFs were eluted with 150 ml of *n*-hexane. The eluate was concentrated as described above. Finally, the concentrated solution was transferred into a glass column (10 mm internal diameter × 300 mm length) packed with activated alumina (2 g) and sodium sulfate (2 g). Initial elution employing 50 ml of *n*-hexane provided a fraction containing other PCBs and chlorinated hydrocarbons which interfere with analysis[12]. This fraction was discarbed. A second fraction eluted with 150 ml of 50% dichloromethane in *n*-hexane contained Co-PCBs, PCDDs and PCDFs.

The residue after evaporation was dried under a nitrogen stream and dissolved in 20 µl of nonane.

Gas chromatography-mass spectrometry (GC-MS)

The analysis of extracts was performed on a Finnigan Mat 90 high resolution mass spectrometer equipped with a Varian 3400 gas chromatograph. The operating conditions are listed below.

Gas chromatographic conditions: 1) for tetra-hexa PCDDs and PCDFs; column: SP-2331 (Supelco), 60 m, 0.25 mm, 0.2 µm film thickness, Oven temp.: 130°C, isothermal for 1 min, 20°C/min to 200°C, 3°C/min to 220°C, 1°C/min to 250°C, isothermal for 30 min. 2) for hepta-octa PCDDs, PCDFs and Co-PCBs; column: MPS-50 (Quadrex), 25 m, 0.25 mm, 0.1 µm film thickness, oven temp.: 120°C, isothermal for 1 min, 10°C/min to 260°C, isothermal for 10 min.

Injector temp.: 260°C, interface temp.: 260°C, carrier gas: helium, 15 psi., injection: splitless.

Mass spectrometric conditions: ion source: positive ion electron ionizing, accelating voltage: 5 kv, Ion source temp.: 260°C, analyzer: selected ion monitoring mode, resolving power: 7000.

RESULTS AND DISCUSSIONS

Chromatograms

Figure 1 shows typical GC-MS SIM chromatograms of Co-PCBs and ^{13}C-labeled Co-PCBs in a sediment sample. As shown in Figure 1, the retention time of each Co-PCB congener exactly coincided with that of the ^{13}C-labeled respective internal standard. Accordingly, each Co-PCB congener was specifically identified and determined.

Co-PCB concentrations

Table 1 shows Co-PCB concentrations in the pond sediment samples and Table 2 shows those in the fly ash samples. As shown in Table 1, all the sediments were polluted by Co-PCBs. As presented in Table 2, Co-PCBs were fairly found in the fly ashes. The concentrations of the Co-PCB congeners in the sediment sample were lower than those in the fly ash sample. The average concentration of the total Co-PCBs was about one-fortieth of that of the total PCDDs and was nearly equal to that of the total PCDFs in the sediment samples. These findings might show that a small amount of Co-PCBs were discharged from the municipal waste incineration facility as well as the case of PCDDs and PCDFs

PCDD and PCDF concentrations

As shown in Tables 1 and 2, the average concentrations of total PCDDs and total PCDFs

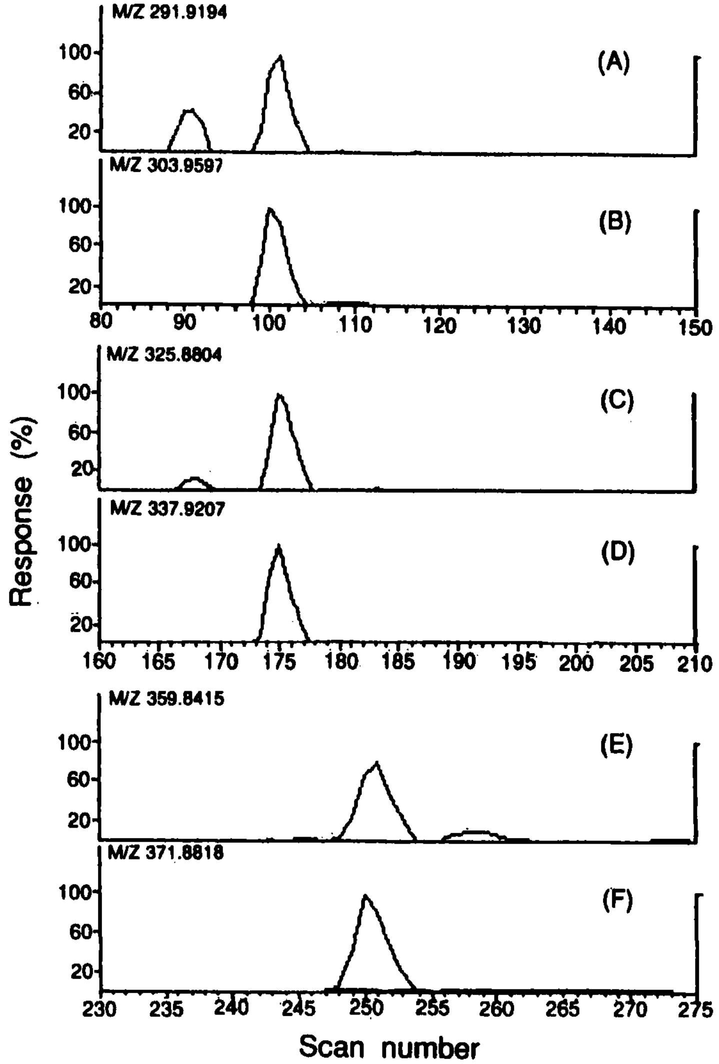

Figure 1 Typical GC-MS SIM chromatograms of Co-PCBs and ^{13}C-labeled Co-PCBs in soil extract.
(A) T_4CB (B) ^{13}C-T_4CB (C) P_5CB (D) ^{13}C-P_5CB (E) H_6CB (F) ^{13}C-H_6CB

in the fly ash were higher than those in the sediment. The average concentration of 2,3,7,8-TCDD in the fly ash was much higher than that in the sediment. Then, the average concentration of total PCDDs was about two times that of the total PCDFs in the fly ash and was about thirtyfive times that of the total PCDFs in the sediment.

PCDD and PCDF congeners

The concentrations of PCDD congeners in the sediment increased with the increased degree of chloro-substitution, while a decrease in those concentrations was observed in

Table 1 The concentrations of Co-PCBs, PCDDs and PCDFs in the sediment samples.

Sample	*Sed. 1*	*Sed. 2*	*Sed. 3*	*Sed. 4*	*Sed. 5*	*Sed. 6*	*Sed. 7*	*sed. 8*	*Sed. 9*	*Sed. 10*	*Sed. av.*
3,3', 4,4'–T_4CB	160	400	86	370	120	320	280	340	130	360	260
3,3',4,4',5–T_5CB	3.4	8.2	1.7	8.2	7.8	2.3	5.8	3.6	1.3	5.7	4.8
3,3',4,4',5,5'–H_6CB	0.9	2.7	0.5	3	1.8	1.5	1.7	0.5	0.5	1.5	1.5
Total Co-PCBs	160	410	88	380	130	320	290	340	130	370	270
2,3,7,8–T_4CDD	0.03	0.21	0.3	0.09	0.03	0.1	0.17	0.14	0.2	0.34	0.16
T_4CDD	150	270	180	300	87	260	240	210	110	540	230
P_5CDD	44	130	45	76	46	62	86	56	26	90	66
H_6CDD	61	110	100	130	71	130	170	120	120	64	110
H_7CDD	510	730	750	720	330	1400	1000	1000	1100	350	790
O_8CDD	4500	6300	12000	11000	6500	11000	12000	11000	9900	7400	9100
Total PCDDs	5300	7500	13000	12000	7000	13000	13000	12000	11000	8400	10000
T_4CDF	42	60	87	84	110	61	71	54	28	140	73
P_5CDF	30	45	39	56	97	43	53	43	17	76	50
H_6CDF	32	49	43	53	120	53	65	54	30	54	56
H_7CDF	42	63	46	57	110	72	70	73	39	69	64
O_8CDF	39	56	30	51	38	71	65	60	37	45	49
Total PCDFs	180	270	240	300	470	300	320	280	150	390	290

The concentration units are ng/kg of dry weight, sed. means sediment, av. means average.

the analyzed fly ash. Fly ashes possessing similar tendency have sometimes been found[13]. On the other hand, the percentage of O$_8$CDD concentration was 91% of total PCDDs in the sediment as well as in the soil[14].

The congener profile of PCDFs in the fly ash was similar to that of PCDDs, while the congener concentrations of PCDFs were lower than those of PCDDs. However, in the sediment, the congener levels of PCDFs were similar to those of Co-PCBs and much lower than those of PCDDs.

Table 3 shows the ratios of PCDDs to PCDFs in the sediment and the fly ash samples. The value of H$_7$CDD/H$_7$CDF in the sediment was fairly higher than that in the fly ash. The value of O$_8$CDD/O$_8$CDF in the former was much higher than that in the latter. This fact might be caused from the stability and the abundance of O$_8$CDD in the environment[15]. However, the values of T$_4$CDD/T$_4$CDF, P$_5$CDD/P$_5$CDF and H$_6$CDD/H$_6$CDF in the sediment and those in the fly ash were at the same level, so they showed a good similarity of congener patterns of less chlorinated isomers between the sediment and the fly ash, indicating that further investigation should be continued.

Table 2 The concentrations of Co-PCBs, PCDDs and PCDFs in the fly ash samples.

Sample	*Fly ash 1*	*Fly ash 2*	*Fly ash 3*	*Fly ash av.*
3,3', 4,4'-T$_4$CB	1900	400	450	910
3,3',4,4',5-T$_5$CB	260	140	150	180
3,3',4,4',5,5'-H$_6$CB	250	88	87	140
Total Co-PCBs	2400	630	690	1200
2,3,7,8-T$_4$CDD	45.5	16.3	16.8	26.2
T$_4$CDD	15700	12500	12500	13500
P$_5$CDD	13000	6100	5900	8300
H$_6$CDD	14000	3700	3800	7300
H$_7$CDD	3300	2400	2500	2700
O$_8$CDD	1200	1300	1100	1200
Total PCDDs	48000	26000	26000	33000
T$_4$CDF	17000	2800	2900	7500
P$_5$CDF	12000	2000	2200	5500
H$_6$CDF	2800	1700	1700	2000
H$_7$CDF	680	620	650	650
O$_8$CDF	180	180	170	180
Total PCDFs	33000	7300	7600	16000

The concentration units are ng/kg of dry weight, av. means average.

Table 3 The ratios of PCDDs/PCDFs in the sediment and the fly ash samples.

PCDDs/PCDFs	*Sediment*	*Fly ash*
T$_4$CDD/T$_4$CDF	3.2	1.8
P$_5$CDD/P$_5$CDF	1.3	1.5
H$_6$CDD/H$_6$CDF	2	3.7
H$_7$CDD/H$_7$CDF	12	4.2
O$_8$CDD/O$_8$CDF	180	6.7

These data were calculated from average values.

Co-PCB congeners

The average concentrations of Co-PCBs in the fly ash samples (n = 3) were 910, 180 and 140 pg/g of dry weight for 3,3',4,4'-tetrachlorinated biphenyl (T_4CB, IUPAC no. 77), 3,3',4,4',5-pentachlorinated biphenyl (P_5CB, IUPAC no. 126), and 3,3',4,4',5,5' -hexachlorinated biphenyl (H_6CB, IUPAC no. 169), respectively. The average concentrations of Co-PCBs in the sediment samples (n = 10) were 260, 4.8, and 1.5 pg/g of dry weight for T_4CB, P_5CB and H_6CB, respectively. Table 4 shows the percentage of Co-PCB congeners in the sediment, the fly ash samples and the technical PCB product[7,10]. As given in Table 4, there was observed a difference in a composition of Co-PCBs among the sediment, the fly ash and the PCB product. The percentages of T_4CB were in the order of the PCB product > the sediment > the fly ash, while the percentages of P_5CB and H_6CB were in the order of the fly ash > the sediment > the PCB product.

The magnitude of Co-PCB congeners was in the order of T_4CB > P_5CB > H_6CB in both the fly ash and the sediment samples as in the case of fish[1,2]. A decrease in Co-PCB concentration was observed from T_4CB to H_6CB, while the levels of the PCDDs increased with the degree of chloro-substitution. However, in the case of human serum[3] and milk[4,5], the ratios of Co-PCB congeners were in the order of P_5CB > H_6CB > T_4CB. The most toxic P_5CB(4) was mostly seen in the human samples. Thus, there was a great difference in the order of the distribution of Co-PCB congeners between the sediment and human samples.

Source of Co-PCBs

Though twenty years have elapsed since the restriction of the manufacture and use of PCBs in Japan, PCBs still exist in the environment. The source of Co-PCB contamination to the environment is thus commercial PCB preparations. However, as presented in Table 4, the profiles of Co-PCB congeners in the sediment were slightly different and those in the fly ash were entirely different from those of the technical PCB product. Moreover, PCBs can be formed by dimerisation of chlorobenzenes in municipal incinerators[16]. Accordingly, another source of Co-PCB contamination may be from the combustion of municipal waste as in the case of PCDDs and PCDFs. The Co-PCBs exhausted from a municipal waste incinerator may still be prevalent and pollute the environment.

Table 4 The percentages of Co-PCB congeners in PCB product, the sediment and the fly ash sample.

Co-PCB	*Sediment*	*Fly ash*	*PCB product**
3,3', 4,4'-T_4CB	97.64	73.98	98.89
3,3',4,4',5-T_5CB	1.80	14.64	1.10
3,3',4,4',5,5'-H_6CB	0.56	11.38	0.01

The percentages were calculated from average values.
*These data are cited from Kannan *et al.* 1989.

CONCLUSION

In conclusion, although the Co-PCB concentrations were much lower than those of PCDD in both the sediment and fly ash samples, one source of Co-PCB contamination in the environment may be, besides the input by technical PCB products, the combustion of municipal wastes.

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