DETERMINATION OF CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN FISH FROM CONTAMINATED AREAS IN TAIWAN

Der-Kau Soong, Cheng-Chuan Lu
Union Chemical Laboratories, Industrial Technology Research Institute
Hsinchu, Taiwan 300, R.O.C.
Yong-Chien Ling
Department of Chemistry, National Tsing Hua University
Hsinchu, Taiwan 300, R.O.C.

ABSTRACT

Fish coming from Er-Jen River and nearby fish ponds situated around an abandoned pentachlorophenol factory in Tainan (located in the south/western part of Taiwan) were examined for residues of dioxins and furans. Er-Jen River area was previously an electronic and metal recycling side, in which many PVC cables were burned along the river during the reclaiming process. Additionally, sediment collected from both sites indicated the contamination of dioxins and furans.

1. INTRODUCTION

For many years, the Er-Jen River was known for it's contamination of dioxins and furans by the recycling process, even though surveys of this area have been quite scarce(1). A recent investigation(2) of the sediment along side and in the river indicated various degrees of contamination. Another nearby contaminating source,i,e., an abandoned pentachlorophenol factory, was surrounded by fish ponds and also contained high concentrations of dioxins and furans in sediment and soil(3). The samples collected from both sites were pretreated using combinations and modifications of the methods of Kapila, et.al.(4), Yamada, et.al.(5),and Afghan, et.al.(6). The cleaned sample extracts were analyzed by high resolution gas chromatograph/negative chemical ionization/mass spectrometry and high resolution gas chromatograph/ high resolution mass spectrometry.

2. EXPERIMENT

Sample Preparation

The fish fillets were freeze dried and grounded to fine powder. A 10 gm portion of the dried fish powder was weighed and addition of ^{13}C-2378-tetrachloroinated dibenzo-p-dioxin, ^{13}C-12378-penta-chloroinated dibenzo-p-dioxin, ^{13}C-123478-hexachloroinated dibenzo-p-dioxin, ^{13}C-1234678-heptachloroinated dibenzo-p-dioxin, ^{13}C-octachloroinated dibenzo-p-dioxin was used as internal standards. The fish power was subsequently

extracted with a soxhlet extractor using 200 mL of benzene as extraction solvent. The extract was concentrated to 2 mL and cleaned with a multi-layer silica gel column (1.5 cm i.d.) containing sulfuric acid-on-silica, sodium hydroxide-on-silica and silver nitrate-on-silica. Following reduction in volume of the organic extract, the sample was passed through an alumina column to remove PCBs and organochlorine pesticides. Final clean-up and isolation of dioxins and furans were carried out using a carbon-silica column. Additionally, The eluting solvent was purged to dryness and 50 µL of ^{13}C-1234-tetrachloroinated dibenzo-p-dioxinprior at 0.5 µg/mL was added prior to instrument analysis as recovery standard.

Instrumental Analysis

The dioxin and furan were analyzed via two instrumental systems. The first was a HP5890/5989 gas chromatograph/mass spectrometer under methane negative chemical ionization (150 ^{o}C for source temperature) mode with a 60 m x 0.25 mm i.d. HP-5ms columns. The GC temperature was programmed from 170 ^{o}C(3 min) to 250 ^{o}C at a rate of 30 ^{o}C/min, then rose to 280 ^{o}C at a rate of 1.5 ^{o}C/min, and finally to 320 ^{o}C(10min) at a rate of 15 ^{o}C/min. The second system was a HP5890GC/Jeol SX-102A high resolution mass spectrometer under EI (70 eV ,250 ^{o}C) mode at resolution 10000. The GC conditions were: 30 m x 0.25 mm i.d. DB-5ms columns; programmed from 170 ^{o}C(10 min) to 320 ^{o}C(10 min) at a rate of 10 ^{o}C/min. Both systems used helium carrier gas at a constant flow of 1 mL/min, splitless injection at 280 ^{o}C, and direct GC/MS interface at 300 ^{o}C.

3. RESULTS

Fish collected from both areas were found to be contaminated with dioxins and furans. The fish from the fish ponds near the abandoned pentachlorophenol factory show an abnormally high concentrations of OCDD (Table 1). The concentrations of hepta- and octa- PCDD/Fs are also noticed to be clearly higher than the tetra- and penta-PCDD/Fs(Figure 1), thereby making negative chemical ionization more suitable for analysis. The fact that the main impurity in commercial pentachlorophenol samples is OCDD might explain this finding. The TEQ of sample No. 1 is much higher than the other samples, even though the average weight of sample No. 1 is smaller than the other samples. This is ascribed to the differences in diet and living capability. Sample No. 1 are *Tilapia mossambica*. These fish feed on miscellaneous foods and adapt well to environmental fluctuations. Sample No. 2 to 4 are *Chanos chanos* and feed on algae. Significantly higher TEQ in sample No. 2 when comparing to sample No. 3 and 4 is noticed. This implies that when the *Chanos chanos* have grown beyond a critical weight their capability to retain PCDD/Fs would significantly increase.

The fish from the Er-Jen River show higher concentrations of PCDDs than PCDFs in all the tetra- to octa-chlorinated homologue (Table 2). The concentrations of OCDD are also the highest among all PCDD/Fs. Thus, based on these data the major contributor to the PCDD/Fs in these fish can't be identified yet. Sample No. 3 are *Clarisa fuscus*. These fish feed on miscellaneous aquatic species including small fish and shrimp and have strong living capability. Sample No. 3 also has the largest weight among the eight

samples studied. Thus, the highest TEQ found in sample No. 3 is expected. Sample No. 2, 4, 6, and 7 are *Megalips cyprinoides* and have similar size as sample No. 3. However, their TEQs are quite smaller than sample No. 3. This is ascribed to their difference in diet. Sample No. 1 and 5 are *Tilapia mossambica*. Their diet and environmental adapting capability might explain although their size are comparatively smaller but the corresponding TEQ are quite higher. Support by the National Science Council of the Republic of China under grant No. NSC83-0208-M-007-065 (to Y.-C. Ling) and Union Chemical Laboratories of Industrial Technology Research Institute (to D.-K. Soong) is gratefully acknowledged.

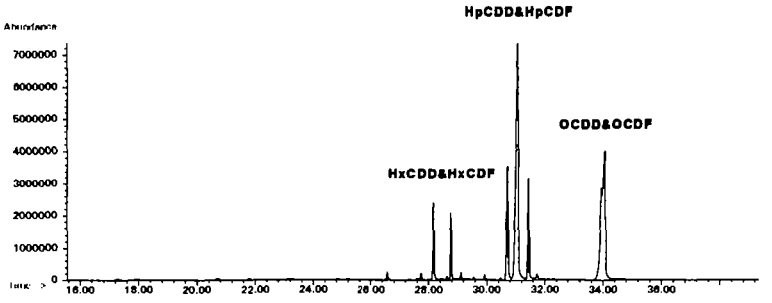

Figure 1. NCI/MS chromatogram of dioxins and furans in fish from pentachlorophenol factory area

Table 1. PCDD/Fs in fish from fish ponds near an abandoned pentachlorophenol factory

Compound	1	2	3	4
2378-TCDD	0.018	0.006	0.008	0.008
2378-TCDF	0.076	0.012	0.012	0.033
12378-PeCDD	0.032	0.065	0.004	0.013
12378-PeCDF	0.147	0.061	0.009	0.043
23478-PeCDF	0.271	0.018	0.009	0.018
123478-HxCDD	0.041	0.015	0.019	0.035
123678-HxCDD	0.011	0.005	0.008	0.012
123789-HxCDD	0.006	0.010	0.005	0.007
123478-HxCDF	0.212	0.149	0.009	0.024
123678-HxCDF	0.117	0.317	0.004	0.003
234678-HxCDF	0.049	0.033	0.009	0.008
123789-HxCDF	0.077	0.017	0.007	0.008
1234678-HpCDD	0.319	0.342	0.060	0.076
1234678-HpCDF	0.257	0.214	0.037	0.095
1234789-HpCDF	0.039	0.011	0.006	0.005
OCDF	2.545	7.848	0.693	0.629
OCDD	2.172	3.097	0.203	0.239
TEQ	0.301	0.174	0.030	0.054
Average weight(g)	101	229	173	116
Number of fish	7	5	7	5

Table 2. PCDD/Fs in fish Er-Jen River

Compound	1	2	3	4	5	6	7	8
2378-TCDD	0.087	0.016	0.008	0.014	0.018	0.007	0.041	0.009
2378-TCDF	0.078	0.010	0.007	0.006	0.018	0.008	0.009	0.006
12378-PeCDD	0.071	0.007	0.040	0.033	0.022	0.011	0.112	0.017
12378-PeCDF	0.061	0.007	0.011	0.014	0.024	0.006	0.093	0.022
23478-PeCDF	0.003	0.003	0.009	0.001	0.023	0.007	0.033	0.082
123478-HxCDD	0.145	0.017	0.132	0.050	0.041	0.028	0.139	0.036
123678-HxCDD	0.013	0.010	0.281	0.018	0.017	0.007	0.116	0.018
123789-HxCDD	0.007	0.011	0.314	0.026	0.023	0.020	0.111	0.053
123478-HxCDF	0.127	0.014	0.070	0.016	0.012	0.015	0.071	0.019
123678-HxCDF	0.005	0.004	0.045	0.006	0.004	0.006	0.033	0.011
234678-HxCDF	0.012	0.009	0.111	0.105	0.118	0.011	0.023	0.017
123789-HxCDF	0.006	0.003	0.015	0.008	0.006	0.012	0.066	0.011
1234678-HpCDD	0.268	0.064	16.457	0.150	0.593	0.059	0.452	1.083
1234678-HpCDF	0.246	0.068	10.278	0.144	0.397	0.059	0.447	0.732
1234789-HpCDF	0.010	0.025	0.027	0.005	0.027	0.019	0.089	0.032
OCDD	3.418	0.324	156.8	6.063	84.78	0.723	1.298	10.93
OCDF	0.937	0.142	60.19	0.600	8.221	0.166	0.998	3.734
TEQ	0.211	0.041	2.084	0.085	0.282	0.037	0.250	0.214
Average weight(g)	55	400	600	37	46	405	515	46
Number of fish	5	1	1	7	6	1	1	6

4. REFERENCES

1. C.-W. Huang, H. Miyata, J.-R. Lu, S. Ohta, T. Chang and T. Kashimoto, Chemosphere, 24(11), 1669-1676 (1992).

2. Mei-Kuei Lee, Der-Kau Soong, Yong-Chien Ling, The Eigth Symposium of Environmental Analytical Chemistry(1993).

3. Der-Kau Soong, Cheng-Chuan Lu, unpublished results.

4. C. Orazio, J. Meadows, S. Kapila, C. Palmer and A.F. Yanders, Chemosphere, 18(1-6), 69-76 (1989).

5. H. Miyata, K. Takayama, J. Ogaki, M. Mimura, T. Kashimoto and T. Yamada, Chemosphere, 18(1-6), 407-416 (1989).

6. J. Lawrence, F. Onuska, R. Wilkinson and B.K. Afghan, Chemosphere, 15(9-12), 1085-1090 (1986).