

Survey on PCDDs and PCDFs in sediment from fresh water culture ponds near incineration sites for metal reclamation in Wan-Li, Taiwan, Republic of China

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Introduction

We previously revealed that surface soil samples from six incineration sites of waste electric wires and/or magnetic cards for metal reclamation in Wan-Li, Taiwan, Republic of China, were polluted with PCBs at a level of 0.45 to 77 µg/g dry weight, polychlorinated dibenzo-p-dioxins (PCDDs) at n.d. to 540 ng/g dry weight and polychlorinated dibenzofurans (PCDFs) at 1.8 to 310 ng/g dry weight¹. Especially, the samples from the incineration sites handling only waste electric wires were heavily polluted by these chlorinated compounds¹. In this Wan-Li area, there are a lot of culture ponds (diameter: ca. 20 to 30 m) for fresh water fish. This suggests to us a possibility that the culture fish might be polluted by the chlorinated compounds. In recent years, PCDDs and PCDFs have been the subject of much concern in the environmental field in various countries, because some of PCDD and PCDF isomers are extremely toxic^{2,3}.

In this study, sediment samples from culture ponds in Wan-Li were analysed for PCDDs and PCDFs in order to estimate fish exposure to these compounds.

Experimental

Sampling

Surface sediment samples were collected from nine culture ponds for fresh water fish at and near waste incineration sites for metal reclamation in Wan-Li, southern Taiwan, in February 1993. All samples were taken within a depth of less than 20 cm.

Extraction

The sediment specimens were spread in a thickness of 1 cm, stored two days outdoors to dry completely, and then pulverized into small pieces. Each powdered sample (60 g) was extracted with 300 ml of toluene for eight hours under reflux. The toluene extract was filtered through a 1 µm glass fibre filter in order to remove sediment particles.

Clean-up

After adding a keeper solvent (n-decane, 0.3 ml), a tenth 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 ¹³C₁₂-PCDDs and five ¹³C₁₂-PCDFs, each 625 pg), the extract was purified on a multi-layer column containing Na₂SO₄ (16 g), 10 % (w/w) AgNO₃-silica (8 g), silica (2.4 g), 22 % (w/w) H₂SO₄-silica

(12 g), 44 % (w/w) H₂SO₄-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 two fractions with successive eluents of 90 ml of 1 % methylene chloride in n-hexane and 200 ml of 50 % methylene chloride in n-hexane on an alumina column (10 g, Merck neutral, activate I). The second eluate containing PCDDs, PCDFs and Co-PCBs was concentrated to 3 ml. After adding a keeper solvent (n-decane, 30 µl), the concentrated eluate was left for complete evaporation of n-hexane at room temperature and then adjusted to a volume of 30 µl with n-decane.

The finally purified extract was analyzed on J & W DB-5 (30 m x 0.32 mm, 0.25 µm) (held for 1 min at 140 °C, programmed to 220 °C at 20 °C/min and to 310 °C at 8 °C/min, and held for 4 min) for hepta- and octachlorinated PCDDs and PCDFs, and on Chrompack CP-Sil 88 (50 m x 0.32 mm, 0.20 µm) (programmed for 150 to 180 °C at 30 °C/min and to 230 °C at 2 °C/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 8000 using a Hewlett Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer. The results were corrected for the recovery of ¹³C₁₂-labeled internal standards.

Results and Discussion

Tables 1 and 2 show respectively the concentrations of PCDDs and PCDFs in surface sediment samples from nine fish culture ponds at and near waste combustion sites for metal reclamation in Wan-Li, and in two control surface soil samples in Wan-Li. The total levels of PCDDs ranged from 0.069 to 33.7 ng/g dry weight. The levels were 0.11 to 53 times greater than the average in the controls. This result revealed that the sediment samples no. 3 and 6 were heavily polluted by PCDDs.

Similar to PCDDs, the total levels of PCDFs also varied widely between 0.113 and 360 ng/g dry weight. The level ratios of the sediment versus the control were in the range of 0.1 to 315. A high exposure to PCDFs was found in the samples no. 2, 3 and 6.

In all sediments except sample no. 7, the level of PCDFs was higher than that of PCDDs, showing the ratio of PCDFs versus PCDDs to be 1.5 to 140.

On the other hand, 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) levels of PCDDs were 0.0 to 263 pg/g dry weight in the sediments. As well as the total PCDDs level, samples no. 3 and 6 showed high TEQ levels of 263 and 94 pg/g, respectively, i.e. levels 886 and 136 times greater than the controls. In the case of PCDFs, the TEQ levels were 4.4 to 11900 pg/g in the pond sediment. Especially, samples no. 2, 3, 5 and 6 showed high levels of 642, 11900, 247 and 1820 pg/g. The total of PCDDs and PCDFs in samples no. 2, 3, 5 and 6 were 657, 12163, 257 and 1914 pg/g, respectively. These levels correspond to those in surface soil samples from waste incineration sites for metal reclamation in Wan-Li reported previously by us¹.

From the above results, it can be concluded that some of the fish culture ponds in Wan-Li are heavily polluted by PCDDs and PCDFs.

Conclusion

Four of nine sediment samples from fish culture ponds at and near waste combustion sites for metal reclamation in Wan-Li, southern Taiwan, Republic of China, were heavily polluted by PCDDs and PCDFs. The TEQ levels of PCDDs and PCDFs were in the range of 257 to 12163 pg/g dry weight.

Compound	Sediment from fish culture pond									Control soil	
	1	2	3	4	5	6	7	8	9	1	2
2,3,7,8-TCDD	-	0.005	0.068	-	0.003	0.017	-	0.001	0.001	0.003	0.002
Others	0.026	0.407	3.224	0.103	0.204	1.053	0.056	0.040	0.018	0.217	0.348
1,2,3,7,8-PeCDD	-	0.014	0.128	0.003	0.008	0.100	0.002	-	-	0.006	0.005
Others	0.010	0.383	14.156	0.386	0.145	1.738	0.053	0.026	0.007	0.074	0.055
1,2,3,4,7,8-HxCDD	-	0.003	0.136	0.006	0.002	0.025	-	-	-	0.003	0.004
1,2,3,6,7,8-HxCDD	-	0.008	0.235	0.005	0.004	0.041	0.002	0.001	0.001	0.007	0.006
1,2,3,7,8,9-HxCDD	-	0.006	0.267	-	0.003	0.043	0.002	-	0.001	0.005	0.006
Others	0.032	0.186	4.42	0.010	0.057	0.663	0.060	0.006	0.005	0.063	0.058
1,2,3,4,6,7,8-HpCDD	0.020	0.158	4.38	0.035	0.172	1.44	0.676	0.018	0.010	0.027	0.030
Others	0.018	0.191	3.17	0.027	0.248	1.60	0.890	0.021	0.009	0.036	0.027
OCDD	0.020	0.198	3.44	0.079	0.524	1.56	1.99	0.043	0.017	0.100	0.190
Total	0.126	1.56	39.7	0.663	1.37	8.28	3.73	0.156	0.069	0.540	0.720
Total TEQ (pg/g)	0.0	15	263	3	10	94	10	1	1	8	7

-: Not detected

Tab. 1.: Levels (ng/g dry weight) of PCDDs in sediments from fish culture ponds at and near waste incineration sites for metal reclamation in Wan-Li, southern Taiwan

Compound	Sediment from fish culture pond									Control soil	
	1	2	3	4	5	6	7	8	9	1	2
2,3,7,8-TCDF	0.004	0.065	0.919	0.014	0.037	0.381	0.010	0.003	0.002	0.045	0.015
Others	0.101	1.70	42.5	0.308	1.03	9.48	0.226	0.070	0.031	0.935	0.315
1,2,3,7,8-PeCDF	0.005	0.081	2.50	0.011	0.052	0.607	0.011	0.004	0.001	0.020	0.012
2,3,4,7,8-PeCDF	0.004	0.071	2.04	0.008	0.049	0.537	0.007	0.002	0.001	0.015	0.010
Others	0.046	1.01	23.5	0.108	0.522	6.56	0.106	0.026	0.008	0.063	0.058
1,2,3,4,7,8-HxCDF	0.042	0.858	33.6	0.066	0.259	5.51	0.105	0.018	0.015	0.018	0.004
1,2,3,6,7,8-HxCDF	0.023	1.29	27.4	0.071	0.168	4.12	0.057	0.013	0.007	0.014	-
1,2,3,7,8,9-HxCDF	-	-	2.12	-	1.54	-	0.017	-	-	-	-
2,3,4,6,7,8-HxCDF	0.085	3.81	42.9	0.062	0.193	5.19	0.076	0.008	0.014	0.019	-
Others	0.227	12.8	174	0.302	6.09	29.8	0.514	0.274	0.026	0.108	0.040
1,2,3,4,6,7,8-HpCDF	0.006	0.020	0.932	0.002	0.020	0.197	0.012	0.003	-	0.070	0.031
1,2,3,6,7,8,9-HpCDF	0.005	0.013	0.893	0.006	0.009	0.095	0.006	0.002	0.003	0.031	0.019
Others	0.030	0.194	5.99	0.032	0.124	1.86	0.079	0.009	0.004	-	-
OCDF	0.008	0.075	2.765	0.014	0.050	0.567	0.104	0.005	0.002	0.060	0.060
Total	0.588	22.0	360	1.03	7.15	64.9	1.42	0.433	0.113	1.57	0.720
Total TEQ (pg/g)	17.8	642	11900	25.9	247	1820	30.8	5.50	4.40	18.9	7.90

-: Not detected

Tab. 2.: Levels (ng/g dry weight) of PCDFs in sediments from fish culture ponds at and near waste incineration sites for metal reclamation in Wan-Li, southern Taiwan

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