

## Dioxin in soil samples at a chlorophenol manufacturing site in Taiwan

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### 1. Introduction

Chlorophenols have been used in Taiwan as biocides or as starting compounds for pesticide production. Pentachlorophenol and its sodium salt (PCPs) have been widely used as wood preservative owing to their toxic effect on bacteria, mold, algae, and fungi. The R.O.C. government in Taiwan has banned the production and use of PCPs in 1989. The production of PCPs was stopped and the facilities were closed since then. High levels of PCPs were detected in soils of these facilities. The contaminated soils were not subjected to any treatment yet. High temperatures and/or alkaline conditions are known to enhance the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs) from PCPs<sup>1</sup>). It is highly possible that the facility sites and the neighboring environment might be contaminated by PCDD/DFs.

The purpose of this study is to investigate the magnitude of pollution and to determine the polluting sources in one of these PCPs manufacturing sites. To answer these questions, 13 soil samples collected at and near a PCPs manufacturing site, 5 years after the facility was closed, were analyzed for PCDD/DFs.

### 2. Materials and methods

A total of 13 soil samples (S1 to S13) were collected. The sampling locations are shown in Figure 1. Most samples were collected from the surface (depth 0 - 5 cm), except samples S10, S12 and S13. Samples S1 to S9 were collected inside the facility site. Samples S10 to S12 were collected outside the facility site. Sample S10 was a sediment collected from a nearby fish culturing pond. Samples S12 and S13 were sludges collected from another nearby pond which was previously used by the facility to dump the manufacturing effluents and waste.

The samples were analyzed using isotope-dilution GC/MS for PCDD/DFs as described in the previous study<sup>2</sup>). In summary, the samples were freeze dried and grounded to fine powder. A 20-g portion of the dried soil powder was spiked with internal standards of <sup>13</sup>C<sub>12</sub>-2,3,7,8-TCDD, <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PeCDD, <sup>13</sup>C<sub>12</sub>-1,2,3,4,7,8-

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HxCDD, <sup>12</sup>C<sub>12</sub>-1,2,3,4,6,7,8-HpCDD, and <sup>12</sup>C<sub>12</sub>-OCDD. The spiked sample was then Soxhlet extracted in 200-ml benzene for 16 hours. The extract was concentrated to 2 ml and cleaned with a Na<sub>2</sub>SO<sub>4</sub> / silica gel / H<sub>2</sub>SO<sub>4</sub> silica gel / silica gel / NaOH silica gel / silica gel / AgNO<sub>3</sub> silica gel / glass wool column. The PCDD/DFs were eluted by 60% dichloromethane/hexane. Final separation of PCDD/DFs was carried out using a Caropak B / silica gel column. The PCDD/DFs were collected using toluene eluent. The eluate was concentrated and analyzed using a HP-5890/5971 GC/MS equipped with a J&W DB-5ms column (60 m x 0.25 mm i.d, 0.25 mm film thickness) for PCDD/DFs. We used the I-TEF/89 system<sup>3)</sup> to calculate the toxic equivalents (TEQ). The reported concentration and TEQ values were based on dry matter.

### 3. Results and discussion

The concentrations of PCDD/DFs and the TEQ are summarized in Table 1. The TEQ ranges from 0.239 ng TEQ/g in sample S10 to 1357 ng TEQ/g in sample S7. For 7 out of the 8 samples collected around the factory, i.e., S2 to S8, the TEQ are all above the reference value (>10 ng TEQ/g) for remediation of contaminated soil in industrial areas.<sup>4)</sup> The highest content of TEQ was found for sample S7 (1357 ng TEQ/g) taken from the center of the facility site. The TEQ content decreases with soil samples collected further away from the central site. This findings indicate that there might be a leaking during the manufacturing process. This presumption is not valid for sample S9 which was collected at the exit gate. The high TEQ content at this location was ascribed to the required weighing operation of the PCP products before they were delivered out. Some PCPs might leak during the weighing operation.

Figure 2 shows the PCDD/DFs patterns of the soil samples. Similar patterns were observed for all samples. They were all dominated by OCDD/DFs and HpCDD/DFs. The findings indicate that they were all contaminated by a similar source, presumably a PCPs manufacturing facility.<sup>5)</sup> The unusually high OCDF content is unexpected. The soil surface at these sampling locations had the sign of previous burning activity, i.e., dark in color and residual ash. We therefore ascribed this high OCDF content to the previous burning activity.

### 4. Conclusions

Dioxin contamination from PCPs is a well-known issue. The exceptionally high TEQs found in soils samples collected from the PCPs manufacturing facility located at the southern part of Taiwan, after 5 years of ceased operation, deserved special concern. This is because the lifetime of these pollutants is more than 10 years and the manufacturing site is located at a fish culturing area. The possibility of fish cultured at nearby culturing ponds contaminated by dioxins is high. More study is needed to confirm this speculation. The synergetic risk from dioxins and PCPs can not be overlooked. Remediation of this site is suggested before any new industrial activity is planned and should be of prime priority.

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## 5. References

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Table 1. Concentrations (ng/g, dry matter) of PCDD/DFs and the TEQ in various soil samples.

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
TCDD	0.21	4.09	0.35	0.62	0.36	3.99	14.44	1.19	0.04	0.06	0.00	0.06	0.05
TCDF	0.99	18.76	23.33	22.48	5.01	10.12	377.1	3.50	0.67	0.44	0.76	0.63	0.77
PeCDD	0.85	40.68	6.69	7.43	2.36	20.66	136.4	3.15	0.10	0.19	0.20	0.43	0.16
PeCDF	7.91	335.9	236.3	448.6	81.14	186.1	1234	48.34	12.22	1.70	6.31	1.20	2.08
HxCDD	2.89	317.3	84.60	72.34	25.64	109.0	2187	19.81	2.56	1.13	1.95	1.65	2.88
IxCDF	56.5	1616	1354	2376	529.8	1060	19132	354.2	83.99	10.15	52.80	4.24	25.69
HpCDD	55.3	2966	1068	1956	585.3	1544	27637	309.5	77.54	5.52	27.91	27.95	56.70
HpCDF	183.8	5335	5231	6838	1873	3274	81259	948.7	267.4	12.23	68.33	10.51	155.4
Total	1175	49299	21195	19581	18394	30534	810514	7592	2062	61.74	438.2	237.0	1204
2,3,7,8-TCDD	0.019	0.980	0.102	0.045	0.024	0.230	2.646	0.041	0.004	0.005	ND	0.004	0.002
2,3,7,8-TCDF	0.311	0.695	6.278	0.470	0.225	0.628	44.67	0.316	0.033	0.055	0.041	0.087	0.066
1,2,3,7,8-PeCDD	0.069	14.61	1.599	0.908	0.375	2.868	28.85	0.536	0.046	0.026	0.040	0.033	0.028
1,2,3,7,8-PeCDF	2.596	2.835	3.733	0.399	0.280	0.675	16.55	0.305	0.028	0.483	3.167	0.303	0.339
2,3,4,7,8-PeCDF	0.065	1.689	0.580	0.092	0.286	0.372	7.946	0.052	0.032	0.048	0.043	0.019	0.013
1,2,3,4,7,8-HxCDD	0.192	28.60	4.171	2.702	1.063	4.895	50.77	0.856	0.085	0.036	0.111	0.083	0.079
1,2,3,6,7,8-HxCDD	0.794	60.99	24.07	29.33	6.273	19.00	1137	6.706	1.001	0.163	0.547	0.324	0.846
1,2,3,7,8,9-HxCDD	0.375	60.95	9.975	5.811	2.582	13.10	130.6	2.107	0.188	0.085	0.228	0.158	0.171
1,2,3,4,7,8-IxCDF	0.221	9.283	7.500	3.979	0.744	4.577	142.0	0.693	0.185	0.160	0.093	0.097	0.167
1,2,3,6,7,8-HxCDF	0.162	11.76	4.000	1.733	0.260	0.605	37.33	0.059	0.061	0.079	0.048	0.030	0.055
2,3,4,6,7,8-HxCDF	0.293	16.75	773.1	1393	339.5	671.9	93.96	251.4	0.174	0.103	0.180	0.087	0.543
1,2,3,7,8,9-HxCDF	0.172	10.48	4.144	14.85	2.886	10.78	248.4	1.122	0.268	0.053	0.210	0.029	0.179
1,2,3,4,6,7,8-HpCDD	39.53	2173	882.7	1737	485.0	1113	23670	246.5	62.85	3.793	20.53	20.24	42.19
1,2,3,4,6,7,8-HpCDF	41.15	1028	915.9	1448	350.7	682.4	22470	200.1	50.63	3.003	14.39	2.590	34.87
1,2,3,4,7,8,9-HpCDF	1.089	5.618	6.771	54.44	15.44	28.24	672.5	6.622	1.732	0.135	0.514	0.090	1.144
OCDD	433.9	17210	2123	1175	4292	10380	206900	2472	597.1	19.95	193.4	175.3	408.1
OCDF	432.7	21450	11070	6685	11000	13950	471700	3431	1020	10.38	86.50	14.94	552.5
TEQ	2.15	99.95	115.9	186.0	59.53	117.0	1357	37.12	3.013	0.239	0.980	0.554	1.993

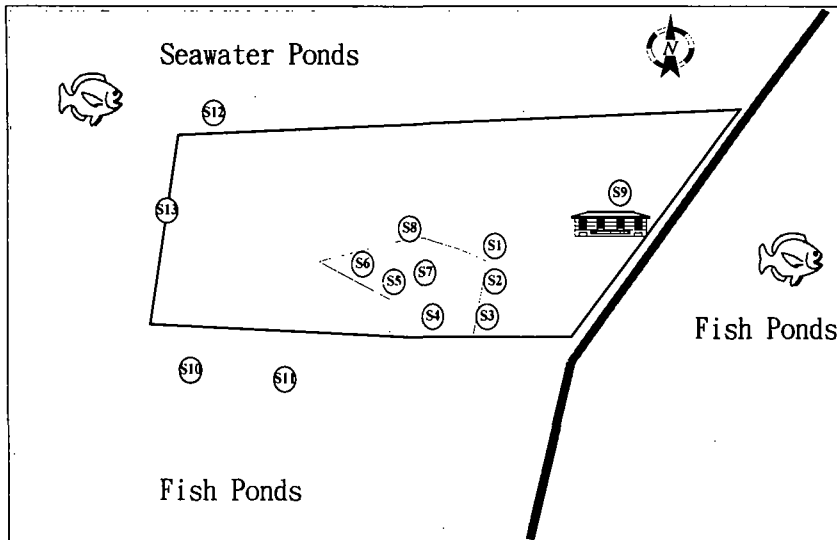


Figure 1. Sampling locations. The length is 50 m in N-S and 100 min E-W.

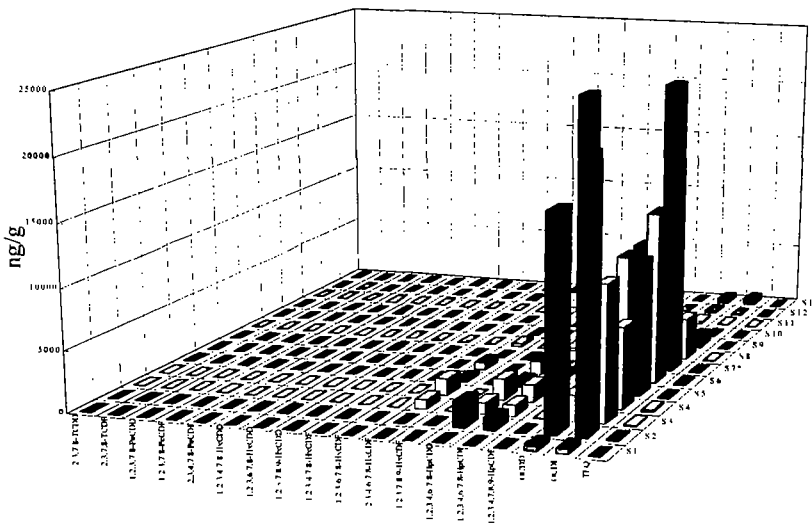


Figure 2. PCDD/DFs patterns of soil samples.  
 (\* The concentration of sample S7 is scaled down by 1/20)