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Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from a heavy oil-fueled power plant in northern Taiwan

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ABSTRACT

We measured the concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from the flue gas and the ambient atmosphere of a power plant fueled by heavy oil in northern Taiwan. The mean emission concentration and I-TEQ concentration of total PCDD/Fs were 0.292 ng/N m^3 and 0.016 ng I-TEQ/N m^3, respectively. All PCDD/F emission concentrations in the flue gas were supposed to meet the Environmental Protection Administration Executive Yuan, R.O.C. standard (1.0 ng I-TEQ/N m^3 from 2008). Furthermore, the mean I-TEQ concentration in the ambient atmosphere was 0.011 pg I-TEQ/N m^3, which was much lower than the environmental quality standards for dioxins in Japan (0.6 pg TEQ/N m^3). Also, the PCDD/F emission factor was 0.188 ng I-TEQ/L fuel, which was comparable to the data issued in US EPA [EPA, Locating and estimating air emissions from sources of dioxins and furans, Office of Air Quality Planning and Standards, Research Triangle Park, NC, DCN No. 95-298130-54-01, 1997] (0.2 ng I-TEQ/L of fuel). Also, the result of the correlations of PCDD/Fs and operational parameters illustrated that the positively significant correlation ($r = 0.502$, $p = 0.048$) was found only between PCDD/Fs (I-TEQ) and the flue gas emission temperature (125–157 °C). However, PCDD-TEQ/PCDF-TEQ ratios were statistically significantly associated with the decreased flue gas flow ($r = -0.659$, $p = 0.006$), moisture ($r = -0.612$, $p = 0.012$) and flue gas temperature ($r = -0.503$, $p = 0.047$). For proper environmental management of dioxins, it is necessary to establish a complete emission inventory of PCDD/Fs, and, in particular, the government should pay more attention to power plants to address the information shortage.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have recently emerged as hot topics in Taiwan. In 2005, pollutants from the Taiwan Steel Union Co., Ltd., were suspected as the source of the high levels of dioxin found in duck eggs in central Taiwan, requiring the destruction of millions of duck eggs and thousands of ducks. In 2006, 50 sheep on a ranch in northern Taiwan were slaughtered because of excessive dioxin residue in their bodies. In 2007, a new report of Lee's study [1] of the elevated dioxin-TEQ levels (53.4 pg WHO-TEQ/g of lipid) in serum for residents living near a seriously polluted area was compared to those of the Taiwanese general population (16.1 pg WHO-TEQ/g of lipid) [2]. All these facts encouraged people to deliberate upon the issue. Consequently, the EPA in Taiwan set new dioxin emission standards for all new industrial facilities at 0.5 ng TEQ/N m^3 in 2006. The standards for existing operations involving dioxin pollution were set at the much stricter level of 2.0 ng TEQ/N m^3 in 2006; the level was then lowered to just 1.0 ng TEQ/N m^3 in 2008. Accordingly, the dioxin issue became a matter of common observation in Taiwan.

On the basis of previous research, municipal solid waste incinerators (MSWIs) have been identified as the largest contributors to the environmental pollution levels in the United States [3], England, and Japan [4]; however, the situation is different in Taiwan because sintering plants contribute the largest amounts

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[5]. Most of the dioxins are emitted from combustion, which a power plant also contributes to. At present, a variety of thermal processes have been widely investigated, such as MSWIs, industrial waste incinerators, sinter plants, secondary aluminum smelters, electric arc furnaces, and coal boilers. However, little information about power plants/stations is available. There is only Fernandez-Martinez et al.'s [6] study that showed that the mean concentration of dioxin emissions from coal-fired power stations in Spain was 0.41 pg I-TEQ/N m^3. However, Lin et al. [7] indicated that the emission factor of PCDD/Fs from coal-fired power plants was 0.62 μg I-TEQ/ton. Though low, the total amount of PCDD/F emissions from coal-fired power plants cannot be neglected owing to the high volume of flue gas.

In this study, we investigated the characteristics and emission factors of PCDD/Fs from a power plant fueled by heavy oil. Besides the influence of the power plant emission on the nearby atmosphere, we also evaluated the relationship between PCDD/Fs and the operational parameters to provide more information for further research on the effect of the flue gas from the power plant.

2. Experimental

2.1. Sampling information

For this study, we selected the largest northern power plant, which is near the Pacific Ocean and located in Keelung City in northern Taiwan (Fig. 1). Sixteen samples were collected from the stack of the power plant fueled by low-sulfur heavy oil from March 2006 through January 2007. The power plant is equipped with four sets of boilers configured with lower NO_x burners and with electrostatic precipitators as air pollution control devices. All samples were collected from the stack flue gas in accordance with US EPA modified Method 23. The sampling train adopted in this study is comparable to that specified by the US EPA modified Method 5. Before sampling, we spiked XAD-2 resin with PCDD/F surrogate standards labeled with isotopes. The sampling time for each stack flue gas sample was approximately 3.0 h. To ensure that the process of sampling and transportation were free of contamination, we also took one trip blank and one field blank when conducting the field sampling. After completing the flue gas sampling, we brought the samples back to the laboratory and placed them in a refrigerator at a temperature below 10 °C.

Six ambient air samples were collected by using a PS-1 sampler (Graseby Andersen, GA) according to the revised EPA Reference Method T09A. The sampling site is shown in Fig. 1. The samples were collected separately in August and November. The sampling flow rate was specified at ~0.225 m^3/min, and each sample was collected continuously on three consecutive days. The PS-1 sampler was equipped with a quartz fiber filter for sampling particle-phase PCDD/Fs and followed by a glass cartridge for sampling the gas-phase PCDD/Fs. A known amount of surrogate standard was spiked in the glass cartridge in the laboratory before sampling. Also, we collected two fly ash samples in November.

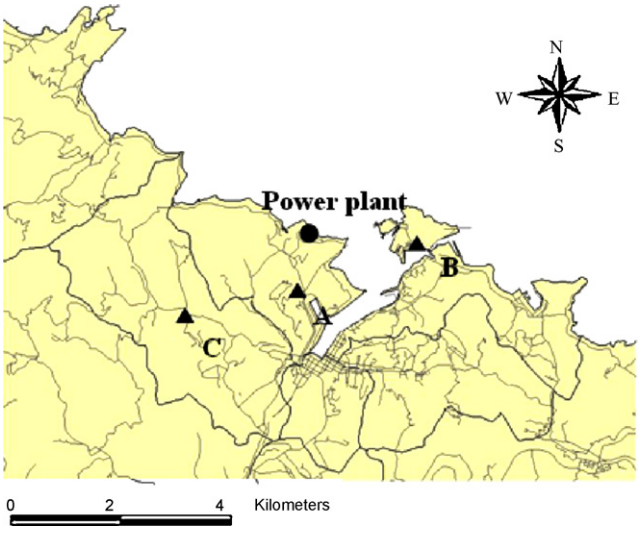

Fig. 1. The sampling sites were located in northern Taiwan.

Analyses of stack flue gas and ambient air samples followed the US EPA modified Method 23 and EPA Reference Method T09A, respectively. All chemical analyses were performed in the Super Micro Mass Research and Technology Centre of the Cheng Shiu Institute of Technology. This facility is the first lab certified by the Taiwan EPA to analyze PCDD/Fs in Taiwan, and it passes international intercalibration standards test on PCDD/Fs in fly ash, sediment, mother's milk, human blood, and cod liver. We performed the sample analysis according to standard procedures. We spiked each collected sample with a known amount of the internal standard. After being extracted for 24 h, the extract was concentrated, treated with concentrated sulfuric acid, and then followed by a series of sample cleanup and fractionation procedures. The eluate was concentrated to ~1 mL, transferred to a vial, and then further concentrated to near-dryness with a nitrogen stream. Before analyzing PCDD/Fs, we added the standard solution to the sample to ensure recovery during the analysis process [8].

We used high-resolution gas chromatography, coupled with a high-resolution mass spectrometer, for PCDD/F measurements. We used a Hewlett-Packard 6970 Series gas chromatograph, equipped with a DB-5 (J&W Scientific, CA) fused silica capillary column (60 m, 0.25-mm internal diameter, 0.25-μm film thickness) and splitless injection. The initial oven temperature was 150 °C. The temperature was programmed as follows: 150 °C, held for 1 min, then increased by 30 °C/min to 220 °C and held for 12 min; then increased again at 1.5 °C/min to 240 °C and held for 20 min. Helium was used as the carrier gas. We used a Micromass Autospec Ultima (UK) mass spectrometer with a positive electron impact (EI^+) source. The analyzer mode of selected ion monitoring with a resolving power at 10,000 was used. The electron energy was set at 35 eV, and the source temperature was set at 250 °C.

We followed the protocol for quality analysis/quality control strictly; e.g., immediately before analysis, we added the standard solution to the sample to ensure recovery during the analysis process. The recovery efficiency of known-addition analysis ranged from 75 to 118%. The MDLs ranged from 0.0001 to 0.0035 ng/N m^3.

Measurements below the limits of detection were recorded as zero. Half of the PCDD/DF-congener levels did not follow a normal distribution curve according to Kolmogorov–Smirnov tests, and so we used the Kruskal–Wallis *H* tests to compare the differences among the groups (i.e., PCDD/F concentrations in four stacks' gas). We calculated Spearman rank correlation coefficients for associations of continuous variables (i.e., moisture content) with dioxin or dioxin-TEQ levels. Multiple regression models, including the stepwise, forward, and backward tests, were tested to find the relationships between dioxins and operation parameters. We performed statistical analyses by using the Statistical Package for Social Sciences, version 15.0 (SPSS, Chicago, IL).

3. Results and discussion

3.1. PCDD/Fs in stack flue gases of a heavy oil-fueled power plant

Table 1 lists the PCDD/F concentrations in the stack flue gases of a power plant, which to our knowledge is the first report for a

Table 1
Concentrations of PCDD/Fs in the flue gases of four stacks

PCDD/Fs (ng/N m^3, dry)	Stack 1 (n = 4)				Stack 2 (n = 4)				Stack 3 (n = 5)				Stack 4 (n = 3)				P[a]
	Mean	S.D.	Median	Range	Mean	S.D.	Median	Range	Mean	S.D.	Median	Range	Mean	S.D.	Median	Range	
2,3,7,8-TeCDD	0.0008	0.001	0.0002	ND[b]–0.003	0.0018	0.002	0.00125	0.001–0.004	0.00038	0.0003	0.0003	ND–0.001	0.00083	0.0002	0.001	0.001–0.001	0.133
1,2,3,7,8-PeCDD	0.003	0.005	0.001	ND–0.010	0.005	0.004	0.002	0.002–0.01	0.001	0.0001	0.001	0.001–0.001	0.003	0.002	0.002	0.001–0.006	0.171
2,3,4,7,8-HxCDD	0.003	0.004	0.002	ND–0.009	0.004	0.003	0.004	0.001–0.001	0.001	0.0003	0.0009	0.001–0.002	0.003	0.002	0.002	0.001–0.005	0.483
1,2,3,6,7,8-HxCDD	0.006	0.007	0.004	0.001–0.016	0.007	0.005	0.006	0.002–0.014	0.002	0.0003	0.002	0.002–0.002	0.008	0.010	0.002	0.002–0.019	0.146
1,2,3,7,8,9-HxCDD	0.004	0.005	0.003	ND–0.011	0.006	0.005	0.005	0.001–0.011	0.001	0.0006	0.001	0.001–0.002	0.004	0.004	0.002	0.002–0.009	0.320
1,2,3,4,6,7,8-HpCDD	0.053	0.047	0.050	0.012–0.101	0.041	0.034	0.031	0.014–0.088	0.011	0.006	0.009	0.007–0.022	0.034	0.040	0.013	0.010–0.080	0.104
OCDD	0.198	0.151	0.213	0.028–0.337	0.099	0.103	0.059	0.023–0.251	0.031	0.019	0.022	0.015–0.052	0.053	0.051	0.030	0.018–0.112	0.134
2,3,7,8-TeCDF	0.007	0.009	0.003	0.001–0.020	0.015	0.010	0.014	0.004–0.028	0.004	0.002	0.004	0.003–0.006	0.010	0.011	0.005	0.003–0.022	0.164
1,2,3,7,8-PeCDF	0.009	0.013	0.003	0.0013–0.028	0.017	0.013	0.014	0.005–0.035	0.004	0.001	0.004	0.003–0.006	0.008	0.006	0.006	0.003–0.014	0.168
2,3,4,7,8-PeCDF	0.013	0.018	0.005	0.002–0.040	0.02	0.014	0.018	0.007–0.039	0.005	0.001	0.005	0.004–0.007	0.013	0.009	0.011	0.005–0.020	0.126
1,2,3,4,7,8-HxCDF	0.015	0.021	0.006	0.002–0.046	0.023	0.018	0.020	0.007–0.045	0.006	0.004	0.005	0.004–0.013	0.012	0.009	0.009	0.005–0.021	0.296
1,2,3,6,7,8-HxCDF	0.014	0.020	0.006	0.001–0.044	0.021	0.017	0.017	0.006–0.043	0.005	0.002	0.005	0.004–0.007	0.013	0.010	0.009	0.005-0.024	0.210
1,2,3,7,8,9-HxCDF	0.001	0.002	0.00	ND–0.003	0.002	0.002	0.001	0.00–0.004	0.0002	0.0004	0.00	ND–0.0009	0.0004	0.001	0.000	ND–0.001	0.656
2,3,4,6,7,8-HxCDF	0.016	0.021	0.008	0.001–0.047	0.021	0.020	0.016	0.006–0.049	0.004	0.001	0.004	0.003–0.006	0.014	0.011	0.009	0.006–0.026	0.150
1,2,3,4,6,7,8-HpCDF	0.052	0.058	0.030	0.012–0.135	0.063	0.054	0.056	0.014–0.127	0.017	0.011	0.012	0.011–0.037	0.029	0.024	0.016	0.015–0.056	0.148
1,2,3,4,7,8,9-HpCDF	0.007	0.009	0.004	ND–0.02	0.011	0.009	0.009	0.003–0.022	0.003	0.002	0.002	0.002–0.007	0.006	0.006	0.003	0.002–0.013	0.391
OCDF	0.063	0.046	0.066	0.013–0.109	0.065	0.053	0.060	0.010–0.130	0.029	0.028	0.012	0.009–0.076	0.020	0.017	0.012	0.010–0.040	0.258
PCDDs	0.269	0.172	0.289	0.045–0.454	0.163	0.155	0.110	0.046–0.385	0.048	0.025	0.037	0.027–0.081	0.106	0.110	0.049	0.036–0.232	0.147
PCDFs	0.196	0.200	0.123	0.047–0.491	0.259	0.207	0.215	0.082–0.522	0.078	0.048	0.055	0.042–0.161	0.124	0.102	0.076	0.056–0.241	0.241
PCDDs/PCDFs ratio	1.95	1.44	1.88	0.51–3.52	0.608	0.115	0.610	0.47–0.74	0.658	0.203	0.520	0.500–0.880	0.773	0.265	0.890	0.47–0.96	0.289
Total PCDDs/PCDFs	0.465	0.277	0.514	0.090–0.740	0.421	0.359	0.325	0.130–0.910	0.126	0.07	0.083	0.080–0.240	0.230	0.210	0.112	0.110–0.470	0.136
PCDDs (I-TEQ)	0.005	0.006	0.003	0.001–0.013	0.007	0.006	0.005	0.002–0.014	0.001	0.001	0.001	0.001–0.002	0.004	0.003	0.002	0.002–0.008	0.179
PCDFs (I-TEQ)	0.013	0.017	0.006	0.002–0.039	0.020	0.015	0.017	0.007–0.040	0.005	0.001	0.005	0.004–0.006	0.012	0.009	0.009	0.005–0.023	0.099
PCDDs/PCDFs (I-TEQ ratio)	0.380	0.098	0.350	0.300–0.520	0.300	0.055	0.320	0.220–0.340	0.320	0.103	0.280	0.230–0.490	0.333	0.086	0.350	0.240–0.410	0.564
Total PCDD/Fs (I-TEQ)	0.018	0.023	0.008	0.002–0.052	0.027	0.020	0.022	0.009–0.053	0.006	0.001	0.006	0.005–0.008	0.017	0.013	0.012	0.007–0.031	0.097
Moisture content (%)	11.1	0.632	11.3	10.3–11.7	11.5	1.29	11.7	9.75–12.7	11.9	0.806	11.4	11.1–12.7	11.9	0.179	12.1	11.7–12.1	0.501
Oxygen content (%)	5.37	0.268	5.35	5.10–5.70	5.79	0.773	5.83	5.00–6.50	5.42	0.217	5.50	5.20–5.70	4.77	0.513	4.90	4.20–5.20	0.162
CO_2 content (%)	12.5	0.141	12.5	12.4–12.7	12.4	0.760	12.2	11.7–13.4	12.3	0.409	12.2	119–13.0	12.7	0.529	12.9	12.1–13.1	0.612
CO content (%)	<0.1	–	–	–	<0.1	–	–	–	<0.1	–	–	–	<0.1	–	–	–	–
Flue gas temperature (°C)	133	10.4	130	125–148	139	12.3	135	130–157	135	13.1	125	125–149	147	16.7	156	128–157	0.298
Flue gas flow (m/sec)	12.9	3.31	13.1	8.53–16.6	14.9	4.76	15.1	9.02–20.6	18.1	6.07	15.3	11.1–25.3	18.2	5.41	21.3	12.0–21.4	0.472
Fuel consumption (kL/h)	64.1	13.5	70.2	44.0–72.1	65.5	21.2	64.8	41.1–91.2	72.7	14.7	64.6	60.0–89.0	78.3	16.2	87.5	59.5–87.8	0.870
Boiler steam temperature (°C)	532	9.80	536	517–538	526	16.6	526	512–541	519	17.9	509	502–539	525	18.0	532	505–539	0.648
Boiler operation pressure (kg/cm^2)	151	31.1	165	105–170	138	32.1	144	93.4–170	164	10.7	161	152–177	167	15.5	171	150–180	0.209

[a] Kruskal–Wallis H tests.
[b] ND: Not detectable, the value less than method detection limit.

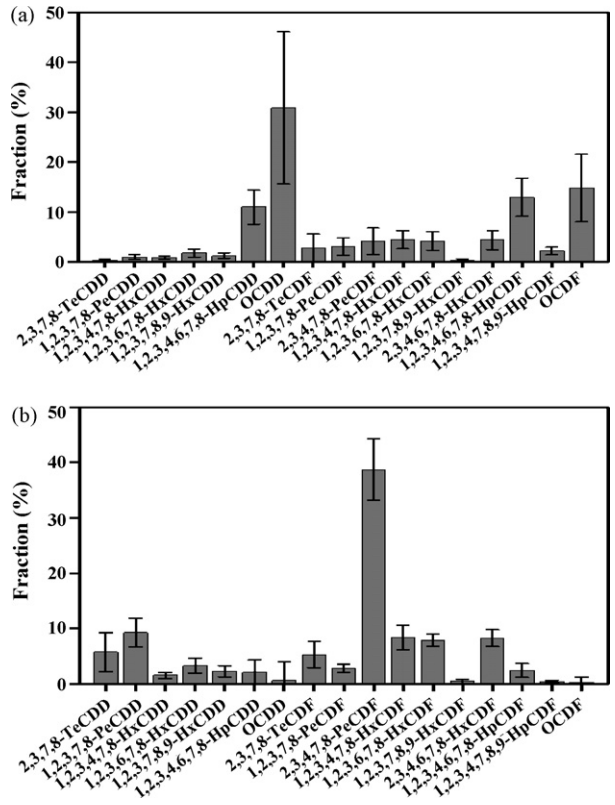

Fig. 2. Congener profiles of 17 PCDD/Fs in the flue gas of a heavy-oil power plant. (a) Based on concentration; (b) based on I-TEQ level.

power plant fueled by heavy oil in Taiwan. The PCDD/F concentrations ranged from 0.002 to 0.053 ng I-TEQ/N m^3, with an average of 0.016 ng I-TEQ/N m^3. Our value was similar to Lin et al.'s result [7] (a mean of 0.017 ng I-TEQ/N m^3 for a power plant fueled by coal). The PCDD/F emission concentrations in our study meet the new emission standard (1.0 ng I-TEQ/N m^3 from 2008) regulated by Taiwan EPA; however, it exceeded Fernandez-Martinez et al.'s results [6] (an average of 0.41 pg I-TEQ/N m^3) but was lower than the Taiwan MSWIs PCDD/F emission standard (0.1 ng I-TEQ/N m^3). There were no significant differences in all variables among the four stack gases per the nonparametric Kruskal–Wallis *H* tests (Table 1).

We selected the congener profiles of the 17 PCDD/Fs as the fingerprints of emission sources. Fig. 2a shows the congener profiles of PCDD/Fs measured from the flue gases of the heavy oil-fueled power plant on the basis of emission concentration. OCDD was the dominant congener, followed by OCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD, which is not very similar to the congener profiles reported by Lin et al. [7]. Fig. 2b shows the congener profiles of PCDD/Fs measured from the flue gases of the heavy oil-fueled power plant on the basis of the I-TEQ concentration. 2,3,4,7,8-PeCDF was the dominant congener, followed by 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDF. The chlorine-substituted profiles of PCDD/Fs from the flue gases of the heavy oil-fueled power plant showed that OCDD, HpCDF, and OCDF were the three dominant chlorine-substituted PCDD/Fs on the basis of emission concentrations. However, PeCDF, HxCDF, and PeCDD were the three dominant chlorine-substituted PCDD/Fs, which account for more than 75% of the ng I-TEQ/N m^3 from the flue gases (data not shown).

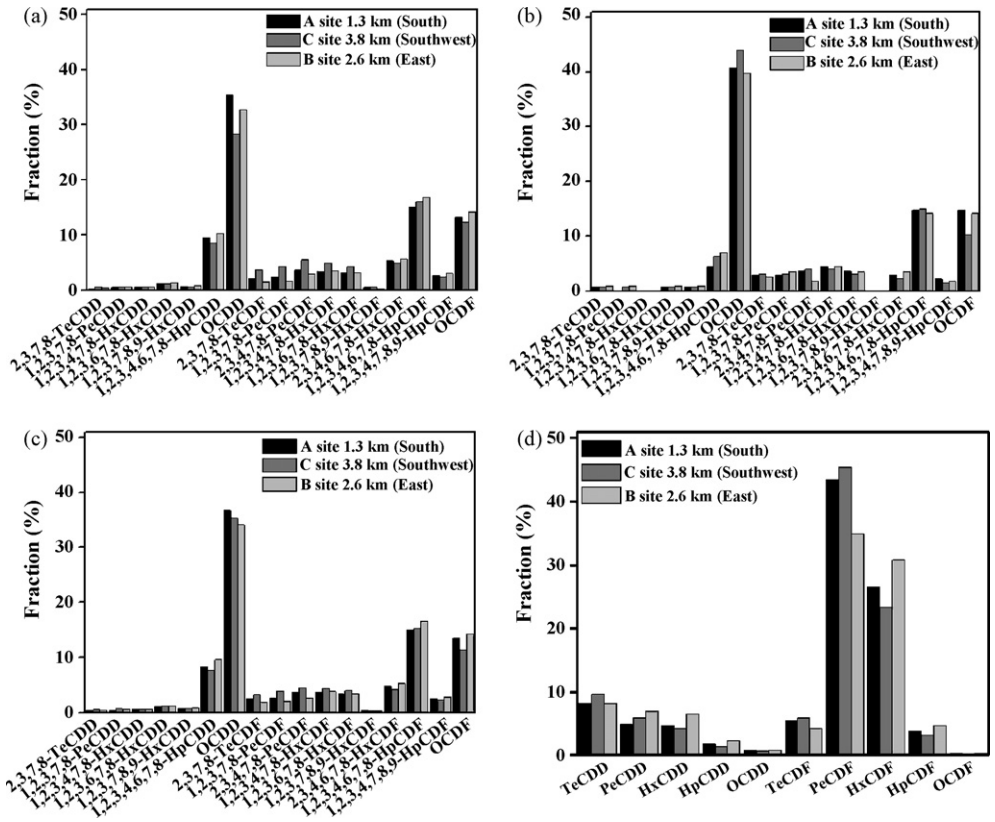

Fig. 3. (a) Congener profiles of PCDD/Fs in the ambient atmosphere in August. (b) Congener profiles of PCDD/Fs in the ambient atmosphere in November. (c) Averaged congener profiles of PCDD/Fs in the ambient atmosphere. (d) Chlorine-substituted profiles of PCDD/Fs in the ambient atmosphere.

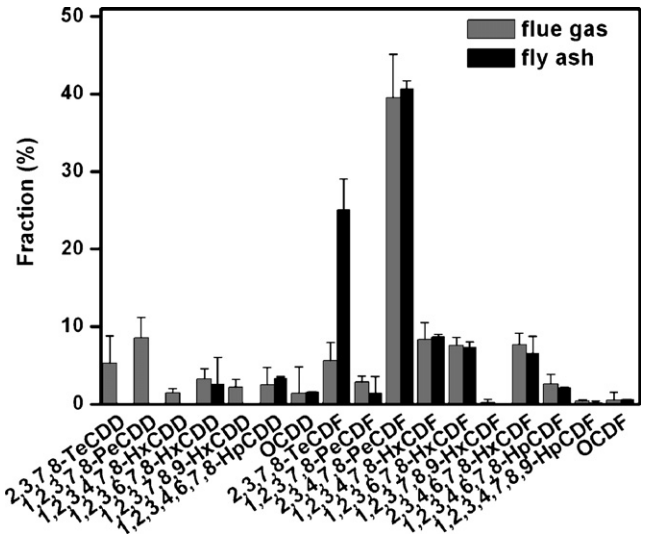

Fig. 4. Fractional differences of stack flue gas and fly ash based on concentrations.

3.2. PCDD/Fs in ambient air of the heavy oil-fueled power plant

PCDD/F concentrations ranged from 0.004 to 0.022 pg I-TEQ/N m^3, with an average of 0.011 pg I-TEQ/N m^3 (Fig. 3). This value was much lower than the air quality standard in Japan (0.6 pg I-TEQ/N m^3). It was also lower than the value in Shih's study [8], which illustrated the PCDD/F concentrations in the ambient air of the surrounding environment of two MSWIs (~0.0216–0.155 pg I-TEQ/N m^3). The environmental analysis laboratory of the EPA issued a report in 2002, having surveyed 80 ambient samples in Taiwan [9]. The results indicated that the highest mean concentration was found in the middle of Taiwan (0.112 pg I-TEQ/N m^3), followed by southern Taiwan (0.105 pg I-TEQ/N m^3) and northern Taiwan (0.038 pg I-TEQ/N m^3), and the lowest concentration was in eastern Taiwan (0.035 pg I-TEQ/N m^3). The mean ambient PCDD/F concentration in this study was much lower than those in the EPA's survey mentioned above.

Fig. 3a and b shows the congener profiles of PCDD/Fs measured from the ambient atmosphere of the heavy oil-fueled power plant in August and November, respectively. OCDD was the dominant congener, followed by 1,2,3,4,6,7,8-HpCDF, OCDF, and 1,2,3,4,6,7,8-HpCDD for August and November. Fig. 4c indicates the mean congener profiles of PCDD/Fs in the ambient atmosphere. The pattern was similar to that of the stack flue gases from the power plant, however, the contribution from the power plant to the ambient in Keelung city was only 0.18% (averaged) according to ISCST 3 model simulation (data not shown). It warrants further investigation if the transportation or incinerators contribute more to the ambient.

The chlorine-substituted profiles of PCDD/Fs from the flue gases of the heavy oil-fueled power plant are shown in Fig. 4d. PeCDF and HxCDF were the two dominant chlorine-substituted PCDD/Fs, which account for more than 65% of the ng I-TEQ/N m^3 from the flue gases. The pattern was also similar to that of the stack flue gases from the power plant.

3.3. PCDD/Fs in the fly ash of the heavy oil-fueled power plant

The mean PCDD/F concentration in fly ash was 0.00074 ng I-TEQ/g dw. Fig. 4 compares the fraction difference of stack flue gas and fly ash on the basis of the concentrations. 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD showed a weaker affinity to fly ash; however, TeCDF showed a stronger affinity to fly ash, which possibly decreases its toxicity in the flue gas. The efficiency of fly ash particles as a sink for PCDD/Fs has been investigated by Matzing et al. [10], which showed that the gaseous dioxin fraction decreased with decreasing temperature. However, the available particle surface is not a limiting parameter for the gas/particle partitioning of the PCDD/Fs. The temperature and the chemical composition of the fly ash particles appear to be more important parameters for adsorption of PCDD/Fs. This hypothesis warrants further investigation.

3.4. Annual release of PCDD/Fs to the air from major sources

Developing the PCDD/F source inventory was not the objective of this study. The various emission factors are compared in Table 2. The emission factor of PCDD/Fs in this study was 0.188 ng I-TEQ/L. This value was comparable to the results of the US EPA (1997) [11] and a little higher than the results of the US EPA (2006) [12]. The emission factor for an oil-fired power plant is lower than it is for coal-fired power plants and much less than it is for domestic heating with wood, coal, and coke [13], although the available information is limited. However, the situation differs for the data measured in Fernandez-Martinez et al.'s results [6], whose emission factor is the lowest in Table 2. The variability for these data might be due to different types of coal or oil used. Furthermore, the following APC is also different.

Roughly calculated, there is a total annual emission of 0.431 and 109 g I-TEQ in Keelung City and in Taiwan, respectively [14]. The dominant source of PCDD/Fs in Keelung City was heat and power generation, mostly from the heavy oil-fueled power plant, which contributed 78.24% of the total. However, this amount constitutes only 7.84 and 0.31% of the total oil combustion and total PCDD/Fs in Taiwan, respectively.

3.5. Correlation of PCDD/Fs and operational parameters

We tried to apply nonparametric statistical analyses in the evaluation of the relationship of PCDD/Fs and the operational parameters during operation. The operational parameters included emitted CO_2, O_2, flue gas emission temperature, flue gas emission rate, heavy oil consumption rate, steam temperature, operational pressure, and water content. The sampling size was not large

Table 2
Emission factors comparison among various heat and power generation

No.	Subcategories of main category	TEQ emission factors		
		Value	Unit	References
1	Heavy-oil fire power plants	0.188	ng L^{-1}	This study
2	Coal/oil-fired industrial boilers	0.200	ng L^{-1}	US EPA [11]
3	Domestic heating with wood, coal and coke	1.6–2500	ng kg^{-1}	Moche and Thanner [13]
4	Coal-fired industrial boilers	0.079	μg ton^{-1}	US EPA [12]
5	Oil-fired power plants	0.083	ng L^{-1}	US EPA [12]
6	Coal-fired power plants	1–5	pg kg^{-1}	Fernandez-Martinez et al. [6]
7	Coal-fired power plants	0.62	μg ton^{-1}	Lin et al. [7]

Table 3
Spearman's correlation coefficients between PCDD/Fs and operation parameters in a power plant

	PCDD/Fs I-TEQ (ng I-TEQ/N m^3)	PCDDs/PCDFs (%)	PCDD-TEQ/PCDF-TEQ (%)	CO_2 (%)	O_2 (%)	Flue temperature (°C)	Flue gas flow (°C)	Moisture (%)	Fuel consumption (KL/hr)	Steam temperature (°C)
PCDDs/PCDFs (%)	−0.42(0.105)[a]									
PCDD-TEQ/PCDF-TEQ (%)	0.103(0.704)	0.370(0.158)								
CO_2 (%)	0.108(0.692)	−0.117(0.665)	0.115(0.672)							
O_2 (%)	−0.061(0.823)	0.121(0.656)	−0.042(0.878)	−0.719(0.002)**						
Flue gas temperature (°C)	0.502(0.048)*	−0.415(0.110)	−0.503(0.047)*	0.260(0.332)	−0.138(0.611)					
Flue gas flow (m/s)	−0.171(0.528)	−0.504(0.046)*	−0.659(0.006)**	0.031(0.909)	−0.015(0.956)	0.693(0.003)**				
Moisture (%)	−0.124(0.648)	−0.331(0.211)	−0.612(0.012)*	−0.091(0.738)	−0.177(0.511)	0.404(0.121)	0.556(0.025)*			
Fuel consumption (kL/h)	−0.202(0.454)	−0.167(0.535)	−0.305(0.251)	0.145(0.591)	−0.288(0.280)	0.339(0.199)	0.674(0.004)**	0.699(0.003)**		
Boiler steam temperature (°C)	0.409(0.115)	0.032(0.905)	0.159(0.556)	0.109(0.687)	−0.130(0.631)	0.482(0.059)	0.124(0.648)	0.277(0.299)	0.396(0.128)	
Boiler pressure (kg/cm^2)	−0.293(0.271)	−0.038(0.890)	−0.246(0.359)	0.250(0.350)	−0.502(0.048)*	0.264(0.324)	0.536(0.032)*	0.608(0.013)*	0.814(<0.001)***	0.258(0.34)

[a] Spearman's rho coefficient (p value).
* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.

enough to reach statistical significance; therefore, we chose the nonparametric Spearman correlation coefficient test. The results (Table 1) show that there was no significant difference for PCDD/Fs (I-TEQ), the PCDD/PCDF ratio, and PCDD-TEQ/PCDF-TEQ among four stack flue gases. This finding indicated no obvious emission concentration variations for the mean annual values. Furthermore, we used the Spearman correlation test for all 16 samples collected in four stack gases to determine the correlations of PCDD/Fs (I-TEQ), the PCDD/PCDF ratio, PCDD-TEQ/PCDF-TEQ, and the operational parameters of the heavy oil-fueled power plant in the process. In Table 3, no statistically significant associations are shown among dioxin–I-TEQs, PCDD/PCDF, PCDD-TEQ/PCDF-TEQ, carbon dioxide emission, and oxygen emissions. A significant positive correlation ($r = 0.502$, $p = 0.048$) was found between dioxin-I-TEQ and flue gas emission temperature (125–157 °C). The flue gas emission temperature significantly correlated with an increased emission of dioxin-I-TEQs. However, the values of PCDD-TEQ/PCDF-TEQ were significantly related to the decreasing of flue gas flow ($r = -0.659$, $p = 0.006$), moisture ($r = -0.612$, $p = 0.012$), and flue gas temperature ($r = -0.503$, $p = 0.047$). Furthermore, a significant negative correlation was found between PCDD/PCDF ratio (%) and the flue gas flow ($r = -0.504$, $p = 0.046$). Multiple linear regression models were used to evaluate the major operation factors for the influence of dioxin emission. Levels of dioxin-I-TEQs and PCDD/PCDF were log-transformed to fulfill the normal distribution for the further statistical tests. Levels of log dioxin-I-TEQs ($R^2 = 0.611$, $p = 0.002$) were significantly correlated with the increased flue gas temperature ($\beta = 0.034$, $p = 0.001$) and the decreased fuel consumption ($\beta = -0.022$, $p = 0.003$) by the multiple backward linear regression. The increased values of PCDD-TEQ/PCDF-TEQ were significantly associated with the decreased flue gas temperature ($R^2 = 0.305$, $\beta = -0.012$, $p = 0.026$) by the multiple stepwise linear regression. The log values of PCDD/PCDF were not significantly related with the operation parameters. In a previous report [15], the higher flue gas temperature was related to the higher dioxin–I-TEQ emissions in the incinerator. The borderline significant correlation of dioxin-I-TEQs and flue gas temperature may be associated with well-known dioxin reproduction with de novo synthesis at the temperature of 250–500 °C. Yan et al. [16] also indicated no direct correlation between PCDD/F levels and CO, O_2, and HCl concentrations in flue gas. Our study did not make a conclusion with the relationship between the dioxin levels and operation parameters because of the small sample size. Larger sample sizes are needed for further investigation. Nevertheless, to our knowledge this is the first report attempting to interpret the correlations between PCDD/Fs and operational parameters.

4. Conclusions

The government in Taiwan has made great efforts in establishing the PCDD/Fs source inventory. It was interesting to find that MSWIs were not the largest contributors of PCDD/Fs in Taiwan [7]. At present, a variety of thermal processes have been widely investigated, such as MSWIs, industrial waste incinerators, sinter plants, secondary ALSs, EAFs, and coal combustion. However, little information about power plants/stations is available. The annual emission factor of this study, 0.097 g I-TEQ/yr, is higher than that of Fernandez-Martinez et al.'s study (~0.0005–0.045 g I-TEQ/yr). Also, Lin et al. [7] indicated that the emission factor of PCDD/Fs from coal-fired power plants was 0.62 μg I-TEQ/ton. Though low, the total amount of PCDD/F emissions from power plants cannot be neglected owing to the high volume of flue gas. For proper environmental management of dioxins, it is necessary to establish a complete source inventory of PCDD/Fs, and in particular, the gov-

ernment should pay more attention to power plants to address the information shortage.

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