



Thermal treatment of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from contaminated soils

Wen-Jhy Lee^{a,b}, Shun-I Shih^{c,*}, Chih-Yuan Chang^{a,b}, Yi-Chieh Lai^{a,b},
Lin-Chi Wang^d, Guo-Ping Chang-Chien^d

^a Department of Environmental Engineering, National Cheng Kung University, No. 1, University Road, Tainan City 70101, Taiwan

^b Sustainable Environment Research Center, National Cheng Kung University, No. 1, University Road, Tainan City 70101, Taiwan

^c Department of Environmental Engineering, Kun Shan University, No. 949, Da-Wan Road, Yung-Kang 710, Tainan County, Taiwan

^d Department of Chemical and Materials Engineering, Cheng Shiu University, 840 Chengching Road, Kaohsiung 833, Taiwan

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ABSTRACT

Thermal treatment technology was used to remove polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from heavily contaminated soil. For a soil with an original PCDD/F content of 35,970 ng International Toxic Equivalents (I-TEQ)/kg, >99.99% PCDD/F removal efficiency was obtained with a primary furnace at two different treatment temperatures (750 °C and 850 °C), while a secondary furnace at 1200 °C gave >98% decomposition efficiency. The total PCDD/F I-TEQ contents in treated soils at 750 °C and 850 °C were 1.56 ng I-TEQ/kg and 2.15 ng I-TEQ/kg, respectively, which were far below the soil pollution standard of Taiwan (1000 ng I-TEQ/kg soil). Although air pollution control devices had significant effects on the removal of PCDD/Fs, the total I-TEQ concentrations in the upstream flue gas of PUF cartridge at 750 °C and 850 °C (2.61 ng I-TEQ/Nm³ and 2.38 ng I-TEQ/Nm³, respectively) were still higher than the stationary emission limit of the Taiwan EPA (0.5 ng I-TEQ/Nm³). The above results also suggested that additional APCDs, such as activated carbon injection in front of the filter are needed to enhance PCDD/F removal efficiency.

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1. Introduction

In the 1950s, a production factory (abbreviation as CPDC-ASS) for pentachlorophenol (PCP) was established in Tainan City, Taiwan, to manufacture chemicals for fungicides, versatile wood preservatives and disinfectants for industrial, agricultural and domestic applications. Due to adverse effects on humans and the environment, associated with PCP and its derivatives, their use was banned by many developed countries (Sweden in 1978, UK in 1981 and Germany in 1986) [1–3].

The CPDC-ASS was closed down in 1982; however, PCP and its production residues, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and Hg, were left behind or in open dumps without proper treatment [4]. Due to the necessity of site remediation, in 2004, the Environmental Protection Agency (EPA) of Taiwan sampled the site and its surroundings to estimate the extent of contamination of the local environment. According to the EPA reports, high contents of PCP (0.312–110 mg/kg), PCDD/Fs (36,000 ng I-TEQ/kg) and Hg (0.212–12,000 mg/kg) were detected in an area around the factory.

Such results indicated that the soils were heavily contaminated [5].

In general, PCDD/Fs are not produced intentionally; PCDD/Fs are a by-product of PCP production (i.e., during thermal decomposition or uncontrolled incineration) [1,6–8]. Because of their low volatility and limited solubility in water, the PCDD/F congeners are deposited onto soil and are extremely persistent in the environment [9]. For example, the half-life of 2,3,7,8-TCDD is 1–10 years in soils [10], thus providing the potential for adverse effect on human health and the environment [11–12].

Recently, several technologies have been developed and applied to the remediation of PCDD/Fs contaminated soil, including physical/chemical, thermal and biological technologies [13–17]. The choice of treatment depends on toxicity removal efficiency, detoxification of soils and energy consumption rates. Of these, the thermal remediation process is usually preferred, due to advantages of reliability, high capacity and lower cost [14]. There have been numerous studies of thermal treatment technology applied to soils, contaminated by Hg [18–19], various organic chemicals [20–22] and fly ash [23]. However, few studies have reported thermal treatment technology in PCDD/F-contaminated soils.

This paper investigated the behavior of PCDD/Fs when the contaminated soil was explored in a thermal treatment system. The effects of two thermal treatment temperatures (750 °C and 850 °C)

* Corresponding author. Tel.: +886 6 2050110; fax: +886 6 2050540.
E-mail address: ssi10@mail.ksu.edu.tw (S.-I. Shih).

on the PCDD/F contents of contaminated soils were evaluated. Particularly, for examining the efficiencies of three different air pollution control devices (APCDs) on PCDD/F removal, the mass distributions and removal efficiencies of PCDD/Fs in these APCDs were determined.

2. Experimental

2.1 Soil samples

The soil samples were from the contaminated area in the CPDC-ASS, containing PCP, PCDD/F and Hg residues. The sampling method was based on the National Environment Analysis Method of Taiwan (NIEA SS102.60B). The samples had leaves, trunks, branches and large stones removed and were then dried in the air for 7–10 days. All results in this study were reported on dry basis.

2.2 Laboratory thermal treatment system

The laboratory-scale thermal treatment system consisted of a primary furnace, a secondary furnace, and a set of APCDs, which included a cooling unit (to collect condensed water with dissolved PCDD/Fs and certain amount of dust), a filter (to collect particles) and three glass cartridges (plugged with polyurethane foam (PUF) in sequence to collect gas phase PCDD/Fs) as illustrated in Fig. 1 [24]. To ensure that the gaseous PCDD/Fs are insignificant, three separate tests were performed by measuring PCDD/Fs in the last stage of the PUF cartridge. The results showed that <2% of PCDD/F mass was found at the last stage of the PUF cartridge.

As mentioned previously, the soil samples were contaminated by both PCDD/Fs and Hg. Due to their toxicity and associated adverse health effects, both PCDD/Fs and Hg should be removed from these soils. Pretests were carried out to observe the behavior of Hg at different temperatures. There was greater removal efficiency of Hg at a higher temperature. When the temperature was 750 °C, the removal efficiency of Hg was >99.5%. Based on these results, the two temperatures (750 °C and 850 °C) were chosen.

A graphite crucible, containing 40 g of soil was placed in the primary furnace. The crucible inside diameter was 70 mm and height 95 mm. The experiments were performed by raising the primary furnace temperature at 5 °C min⁻¹ from room temperature and maintaining at 750 °C or 850 °C, respectively, for 1 h. This ensured that after the thermal process, more than 99.95% of the Hg was removed from the feed soil. The temperature of the secondary furnace was constant at 1,200 °C. Gaseous samples were withdrawn after the secondary furnace at 12 L min⁻¹, and the residence time of the gas stream in the secondary furnace was approximately 3 s. The batch experiment was repeated twice for consistency. After the thermal treatment experiments, the soil, aqueous, particulate, and the flue gas samples were collected and analyzed for PCDD/F contents or concentrations.

Table 1

Volume or weight of samples collected to be extracted in treated soil, cooling unit, filter and PUF cartridge at 750 °C and 850 °C thermal treatment temperature, respectively ($n = 2$)

Treated soil	Cooling Unit		Filter		PUF cartridge		
	750 °C (g)	850 °C (g)	750 °C (mL)	850 °C (mL)	750 °C (set)	850 °C (set)	
22.9	21.4	121	115	0.0524	0.0133	3	3

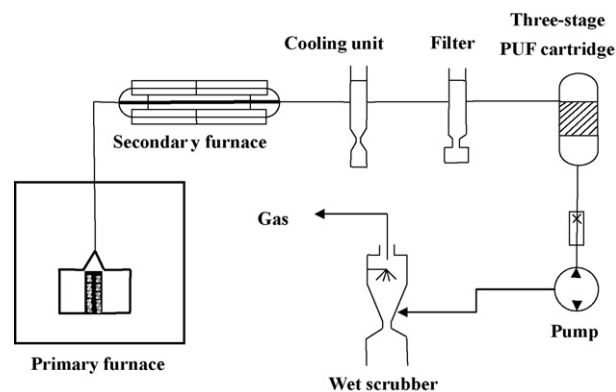


Fig. 1. Sketch of the thermal treatment system.

2.3 PCDD/F analysis

There are four kinds of samples to be analyzed in the present study. Volume or weight of samples collected to be extracted for analyses in treated soil, cooling unit, filter and PUF cartridge at 750 °C and 850 °C thermal treatment temperature, respectively, are listed in Table 1.

Samples collected from cooling unit were divided into two parts. The first one was called solution part A, which was collected directly via condenser; it was aqueous solution and contained dissolved PCDD/Fs and certain amount of solid dusts. In the 750 °C and 850 °C treatment temperature, the mean collected volume of solution part A were 21 mL and 15 mL, respectively. Another one was called solution part B, which was collected due to tube washing by using *n*-hexane. Normally, the volume of solution part B was 100 mL. The solution part A and B were pooled together, filtered the particulates and shaken for the liquid/liquid extraction and then for the PCDD/F analyses. Solution part B was the major part of PCDD/F mass collected from the cooling unit, while the PCDD/F mass contributed by solution part A was less than 3% of total (summation of solution part A and B).

Analyses were performed in a laboratory certified in Taiwan to analyze PCDD/Fs. Each sample was spiked with a known standard and extracted for 24 h. Then the extract was concentrated and treated with sulfuric acid; followed by a series of cleanup and fractionation procedures. A standard solution was added to the sample before PCDD/F analysis to estimate recovery during analysis. A high resolution gas chromatography with mass spectrometer (HRGC/MS) was used to determine the concentrations of 17 individual PCDD/Fs. The HRGC was equipped with a DB-5 fused silica capillary column ($L = 60$ m, i.d. = 0.25 mm, film thickness = 0.25 μ m) and splitless injection. The oven temperature was programmed as follows: initial temperature at 150 °C, increased to 220 °C at 30 °C min⁻¹, then increased to 240 °C at 1.5 °C min⁻¹, then increased to 310 °C at 1.5 °C min⁻¹. Helium was used as the carrier gas. The HRMS was equipped with a positive electron impact source. The analyzer mode was selected ion monitoring with resolving power at 10,000. The electron energy and the source temperature were set at 35 eV and 250 °C, respectively. The recoveries for the 17 individual PCDD/Fs compounds were 60–115%.

Table 2
PCDD/F contents in feed soil, treated soil and their removal efficiencies at 750 °C

PCDD/PCDFs (ng/kg of soil ^a)	Feed soil	Treated soil	Removal efficiency
2,3,7,8-TeCDD	159.2	<0.0171 ^b	~100
1,2,3,7,8-PeCDD	712.7	<0.0135 ^b	~100
1,2,3,4,7,8-HxCDD	1,080	<0.0257 ^b	~100
1,2,3,6,7,8-HxCDD	2,406	<0.0323 ^b	~100
1,2,3,7,8,9-HxCDD	2,149	0.0629	99.9983
1,2,3,4,6,7,8-HpCDD	110,000	0.734	99.9996
OCDD	2,155,000	8.07	99.9998
2,3,7,8-TeCDF	43,890	11.3	99.9852
1,2,3,7,8-PeCDF	45,790	0.868	99.9989
2,3,4,7,8-PeCDF	29,060	0.559	99.9989
1,2,3,4,7,8-HxCDF	63,150	0.278	99.9999
1,2,3,6,7,8-HxCDF	15,710	0.197	99.9992
2,3,4,6,7,8-HxCDF	2,046	0.162	99.9955
1,2,3,7,8,9-HxCDF	6,379	<0.0282 ^b	~100
1,2,3,4,6,7,8-HpCDF	93,190	1.10	99.9993
1,2,3,4,7,8,9-HpCDF	11,530	0.129	99.9994
OCDF	656,600	3.23	99.9997
PCDDs	2,272,000	8.87	99.9998
PCDFs	967,400	17.8	99.9999
PCDDs/PCDFs ratio	2.35	0.496	—
Total PCDD/Fs	3,239,000	26.7	99.9995
PCDDs ng I-TEQ/kg	4,334	0.0227	99.9997
PCDFs ng I-TEQ/kg	31,640	1.54	99.9972
PCDDs/PCDFs I-TEQ ratio	0.14	0.0148	—
Total ng I-TEQ/kg	35,970	1.56 ^c	99.9975

^a Dry basis.^b Method detection limit (MDL).^c In case the measurement lower than MDL, then neglect the contribution of that congener.**Table 3**
PCDD/F contents in feed soil, treated soil and their removal efficiencies at 850 °C

PCDD/PCDFs (ng/kg of soil ^a)	Feed soil	Treated soil	Removal efficiency
2,3,7,8-TeCDD	159.2	<0.0156 ^b	~100
1,2,3,7,8-PeCDD	712.7	0.0804	99.9940
1,2,3,4,7,8-HxCDD	1,080	<0.0394 ^b	~100
1,2,3,6,7,8-HxCDD	2,406	0.131	99.9971
1,2,3,7,8,9-HxCDD	2,149	0.0822	99.9980
1,2,3,4,6,7,8-HpCDD	110,000	2.82	99.9986
OCDD	2,155,000	19.1	99.9995
2,3,7,8-TeCDF	43,890	14.0	99.9830
1,2,3,7,8-PeCDF	45,790	0.944	99.9989
2,3,4,7,8-PeCDF	29,060	0.931	99.9983
1,2,3,4,7,8-HxCDF	63,150	0.292	99.9998
1,2,3,6,7,8-HxCDF	15,710	0.292	99.9990
2,3,4,6,7,8-HxCDF	2,046	<0.0464 ^b	~100
1,2,3,7,8,9-HxCDF	6,379	0.372	99.9969
1,2,3,4,6,7,8-HpCDF	93,190	2.92	99.9983
1,2,3,4,7,8,9-HpCDF	11,530	0.191	99.9991
OCDF	656,600	7.68	99.9994
PCDDs	2,272,000	22.2	99.9995
PCDFs	967,400	27.7	99.9985
PCDDs/PCDFs ratio	2.35	0.805	—
Total PCDD/Fs	3,239,000	49.7	99.9992
PCDDs ng I-TEQ/kg	4,334	0.108	99.9987
PCDFs ng I-TEQ/kg	31,640	2.04	99.9966
PCDDs/PCDFs I-TEQ ratio	0.14	0.0532	—
Total ng I-TEQ/kg	35,970	2.15 ^c	99.9968

^a Dry basis.^b Method detection limit (MDL).^c In case the measurement lower than MDL, then neglect the contribution of that congener.

3. Results and discussion

3.1 PCDD/Fs in the feed and treated soils

Tables 2 and 3 list the mean PCDD/F contents in the feed and treated soils and their removal efficiencies at treatment

temperature of 750 °C and 850 °C, respectively. To assess the toxicologically relevant information on PCDD/Fs, the I-TEQ values for PCDD/Fs were calculated by using the contents of seventeen 2,3,7,8-chlorinated congeners and their International Toxicity Equivalency Factors (I-TEFs). The means of total PCDD/F and total I-TEQ contents (summation of 17 individual PCDD/Fs and TEQs) in the feed soil

Table 4
PCDD/F mass in feed soil, treated soil, and collected by each APCD at 750 °C

PCDD/Fs (pg)	Feed soil	Treated soil	Cooling unit	Filter	PUF cartridge
2,3,7,8-TeCDD	6,368	<0.4	426.0	32.3	182.3
1,2,3,7,8-PeCDD	28,508	<0.3	1,041.2	155.2	583.9
1,2,3,4,7,8-HxCDD	43,200	<0.6	960.1	196.6	740.6
1,2,3,6,7,8-HxCDD	96,240	<0.7	1,379.6	300.7	1,043.4
1,2,3,7,8,9-HxCDD	85,960	0.8	1,223.3	265.7	984.2
1,2,3,4,6,7,8-HpCDD	4,400,000	9.6	9,795.0	2,012.9	8,217.1
OCDD	86,200,000	105.8	18,195.4	3,082.8	22,051.4
2,3,7,8-TeCDF	1,755,600	148.6	4,530.7	374.1	1,907.5
1,2,3,7,8-PeCDF	1,831,600	11.4	5,319.5	728.8	3,174.5
2,3,4,7,8-PeCDF	1,162,400	7.3	6,986.1	1,192.1	4,392.6
1,2,3,4,7,8-HxCDF	2,526,000	3.6	12,137.9	2,159.7	8,221.7
1,2,3,6,7,8-HxCDF	628,400	2.6	10,702.2	1,871.2	6,601.9
2,3,4,6,7,8-HxCDF	81,840	2.1	7,323.8	1,504.8	5,198.1
1,2,3,7,8,9-HxCDF	255,160	<0.6	597.5	71.9	391.5
1,2,3,4,6,7,8-HpCDF	3,727,600	14.5	51,082.1	9,404.6	34,621.8
1,2,3,4,7,8,9-HpCDF	461,200	1.7	7,399.3	844.7	3,035.9
OCDF	26,264,000	42.4	60,700.9	5,190.6	24,244.7
PCDDs	90,880,000	116.3	33,020.6	6,046.1	33,803.0
PCDFs	38,696,000	233.6	166,780.1	23,342.4	91,790.2
PCDDs/PCDFs ratio	94	11.4	0.2	0.3	0.4
Total PCDD/Fs	129,560,000	350.4	199,800.7	29,388.5	125,593.2
PCDDs pg I-TEQ	173,360	0.3	1,402.7	206.6	835.5
PCDFs pg I-TEQ	1,265,600	20.1	7,879.2	1,333.7	4,966.1
PCDDs/PCDFs (I-TEQ) ratio	5.6	0.3	0.2	0.2	0.2
Total pg I-TEQ	1,438,800	20.4	9,281.8	1,540.2	5,801.6

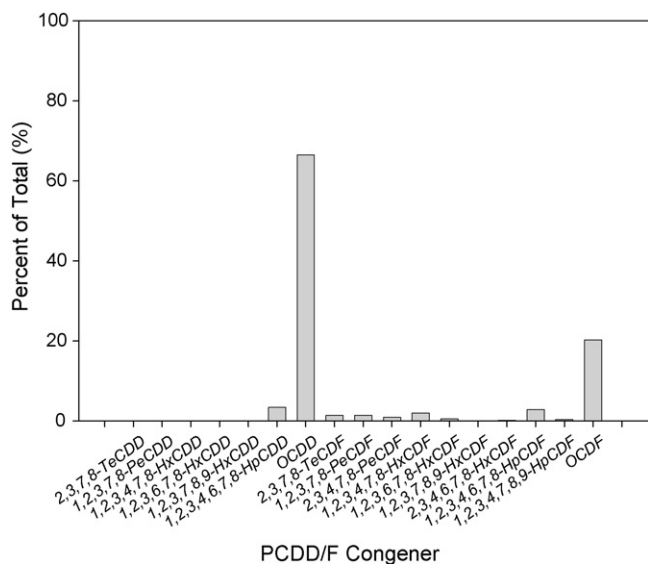


Fig. 2. Congener profiles of PCDD/Fs in the contaminated feed soil.

were 3,239,000 ng/kg and 35,970 ng I-TEQ/kg, respectively. Thus the mean total PCDD/F I-TEQ contents in the feed soil greatly exceeded the soil pollution standard of the Taiwan EPA (1000 ng I-TEQ/kg) [25]. The above results showed the CPDC-ASS is a heavily PCDD/F-contaminated site. The PCDDs/PCDFs ratio in the feed soil was 2.35 (Table 2), indicating that more PCDDs were produced than PCDFs by the precursor reaction from pentachlorophenol (PCP).

The congener profiles of the 17 PCDD/Fs were selected to characterize the dominant species and possible formation mechanisms. Each selected congener was normalized by dividing its content by that of the summation of the 17 PCDD/F congeners. The congener profiles of PCDD/Fs in the feed soil were shown in Fig. 2. Out of the total 3,239,000 ng/kg, OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,6,7,8-HpCDF were the top four dominated congeners in the feed soil. These results were very similar to previous studies that reported PCDD/F in PCP contaminated soil was characterized by congener profiles dominated by OCDD/F and Hp-CDD/Fs [26].

At the thermal treatment temperature of 750 °C and 850 °C, the mean total PCDD/F contents in the treated soils were 26.7 ng/kg and 49.7 ng/kg, respectively, while those of total PCDD/F I-TEQ were 1.56 ng I-TEQ/kg and 2.15 ng I-TEQ/kg, respectively (Tables 2 and 3). Compared with the feed soils, after thermal treatment, the PCDD/F contents were reduced very significantly in the treated soil. In addition, the total I-TEQ contents in these two treated soils at above two temperatures were far below the soil pollution regulated standard in Taiwan (1000 ng I-TEQ/kg).

The PCDD/F removal efficiency (RE) for a contaminated soil was calculated according to the following formula: $RE = [(A - B)/A] \times 100\%$, where RE (%) is removal efficiency for the contaminated soil, *A* is the PCDD/F mass in the feed soil and *B* is that in the treated soil at either 750 °C or 850 °C (Tables 2 and 3). At treatment temperature of 750 °C, the RE (%) of total PCDD/Fs and total PCDD/F I-TEQ were significantly up to 99.9995% and 99.9975%, respectively, which were similar to those of at 850 °C. Among 17 PCDD/F congeners, only the 2,3,7,8-TeCDF had lower REs (99.9852% at 750 °C and 99.9830% at 850 °C). The above results showed that thermal treatment for PCDD/F contaminated soil at 750 °C or 850 °C for 1 h was well enough for PCDD/F removal from contaminated soil.

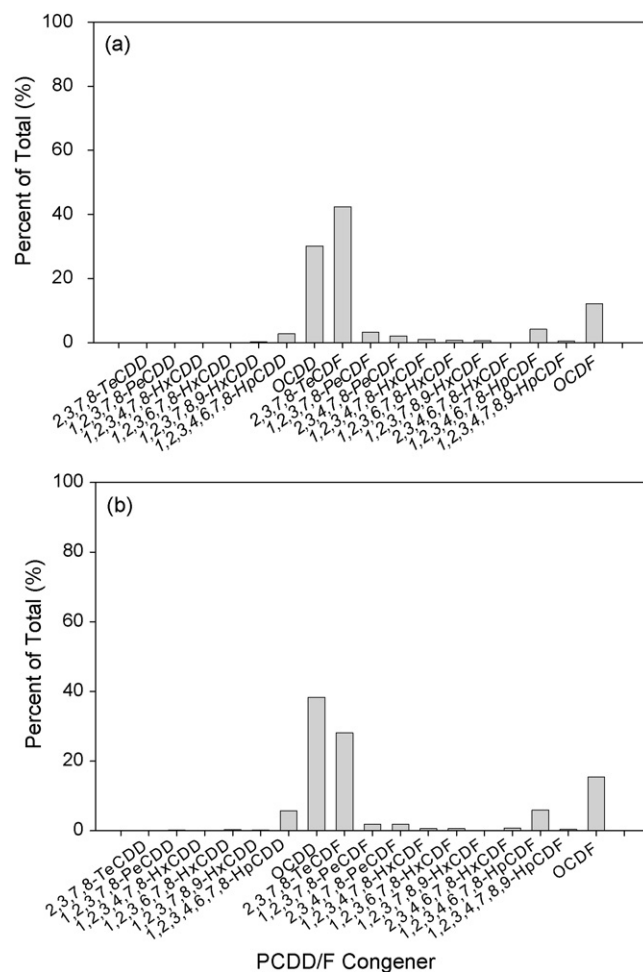


Fig. 3. Congener profiles of PCDD/Fs in the treated soil (a) at 750 °C and (b) at 850 °C thermal treatment temperature, respectively.

After 750 °C and 850 °C thermal treatment, the PCDDs/PCDFs ratios in treated soil were 0.496 and 0.805, respectively, indicating that contents of PCDFs were higher than PCDDs. The above results differed from that of feed soil, where PCDFs content was lower than PCDDs (PCDDs/PCDFs ratio was 2.35). In addition, after thermal treatment, in the treated soil, contents of the lower chlorinated PCDDs (i.e. 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD) were very low, and in several cases below the detection limit. This was probably due that PCDFs have the closed-shell configuration of delocalized electrons and thus increase their chemical stability [23]. Therefore, when thermal energy was added, the degradation of PCDDs was more rapid than PCDFs. The above results were similar to those of Visez and Sawerysyn [27], who found that no detectable PCDDs remained after thermal treatment, while 30% of PCDFs were still present. The increase in proportion of PCDFs in the treated soil could be also a result of formation of PCDFs from other constituents during the cooling process (de novo synthesis).

The congener profiles of PCDD/Fs in the treated soil at 750 °C and 850 °C are in Fig. 3. The more stable octa-chlorinated congeners (OCDD and OCDF) have lower vapor pressures and were predominant in the treated soil compared to other congeners. The above results were similar to those by Kim et al. [28]. However, it is interesting that lower chlorinated PCDF (2,3,7,8-TeCDF) became an abundant congener in the treated soil. Possibly the higher chlorinated congeners were not only destroyed in the thermal process,

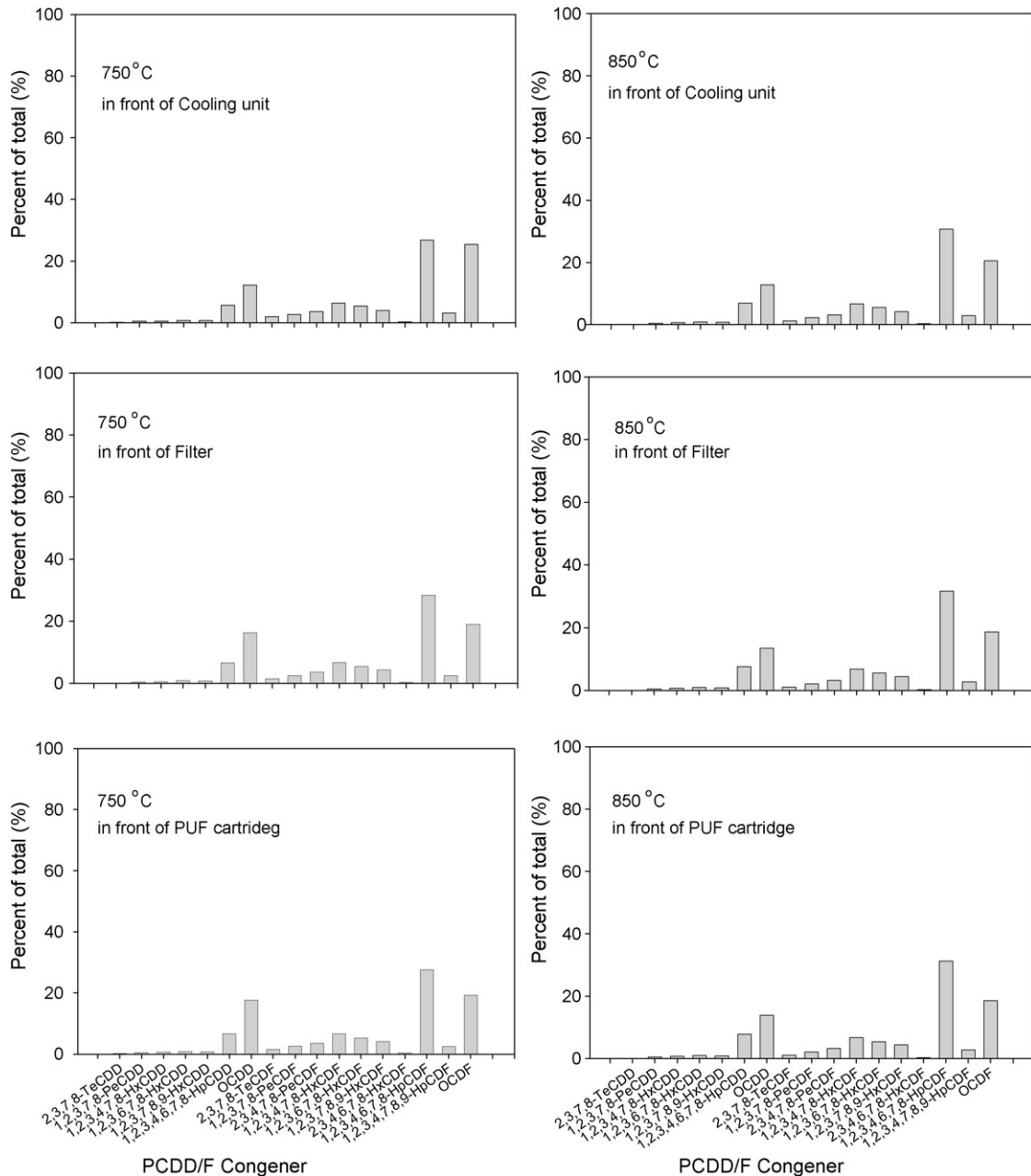


Fig. 4. Congener profiles of PCDD/Fs in the upstream flue gas of cooling unit, filter and PUF cartridge.

but also reacted and enhanced the formation of lower chlorinated congeners by dechlorination [23].

3.2 Distributions of PCDD/F mass

After the thermal treatment process, the survival PCDD/F mass leaving secondary furnace was partitioned into three phases: aqueous (condensed water containing dissolved PCDD/Fs and certain amount of solid dust), particulate and gaseous phases; they were collected in the cooling unit, filter and PUF cartridge, respectively. Tables 4 and 5 list the PCDD/F mass collected by cooling unit, filter and PUF cartridge at 750 °C and 850 °C, respectively. After treatment of the 1,200 °C secondary furnace, the total PCDD/F I-TEQ mass distribution in cooling unit, filter and PUF cartridge at two temperatures (750 °C and 850 °C) were 55.8%, 9.3%, 34.9% and 26.5%, 12.6%, 60.9%, respectively (Tables 6 and 7). The cooling unit had the highest

fraction (55.8%) at 750 °C, whereas the PUF cartridge had the highest fraction (60.9%) at 850 °C. The probable reason for the elevated partitions for cooling unit is that, at 750 °C, more PCDD/F mass were formed in form of particulate coating on the wall of cooling unit by de novo synthesis during cooling down process. Since PCDD/Fs could be removed by APCDs and it is assumed that PCDD/Fs were totally captured by these three APCDs (i.e. the removal efficiency of the PUF cartridge was 100%), the PCDD/F removal efficiencies were calculated based on the following: removal efficiency (%) in cooling unit = $C/(C+D+E) \times 100\%$; in filter = $D/(D+E) \times 100\%$, where C , D , and E are the mass of PCDD/Fs collected by the cooling unit, filter, and PUF cartridge, respectively. Based on the above definition, the removal efficiencies of total PCDD/Fs (emitted from secondary furnace) by the cooling unit and filter at 750 °C were 56.3% and 19.0% and those at 850 °C were 26.3% and 17.2%, respectively. These results revealed that, although the APCDs did not have very high removal

Table 5
PCDD/F mass in feed soil, treated soil, and collected by each APCD at 850 °C

PCDD/Fs (pg)	Feed soil	Treated soil	Cooling unit	Filter	PUF cartridge
2,3,7,8-TeCDD	6,368	<0.3	89.9	16.3	145.2
1,2,3,7,8-PeCDD	28,508	0.9	276.4	104.8	591.9
1,2,3,4,7,8-HxCDD	43,200	<0.8	290.0	169.6	868.2
1,2,3,6,7,8-HxCDD	96,240	1.5	407.6	229.4	1,153.2
1,2,3,7,8-HxCDD	85,960	0.9	379.1	206.0	1,034.1
1,2,3,4,6,7,8-HpCDD	4,400,000	32.3	2,934.6	1,837.1	10,057.0
OCDD	86,200,000	218.3	6,291.9	3,100.2	17,957.5
2,3,7,8-TeCDF	1,755,600	160.1	1,084.4	199.0	1,346.1
1,2,3,7,8-PeCDF	1,831,600	10.8	1,482.1	516.3	2,717.6
2,3,4,7,8-PeCDF	1,162,400	10.7	1,787.5	841.8	4,081.1
1,2,3,4,7,8-HxCDF	2,526,000	3.3	3,713.3	1,927.6	8,663.5
1,2,3,6,7,8-HxCDF	628,400	3.3	3,114.0	1,600.1	7,044.0
2,3,4,6,7,8-HxCDF	81,840	<1.0	1,973.0	1,219.1	5,612.4
1,2,3,7,8,9-HxCDF	255,160	4.3	157.6	61.3	310.6
1,2,3,4,6,7,8-HpCDF	3,727,600	33.4	15,667.2	8,960.4	40,529.4
1,2,3,4,7,8,9-HpCDF	461,200	2.2	1,753.8	783.4	3,538.2
OCDF	26,264,000	88.0	14,517.2	5,130.9	24,071.0
PCDDs	90,880,000	254.7	10,669.6	5,663.3	31,807.1
PCDFs	38,696,000	316.7	45,250.1	21,240.0	97,914.0
PCDDs/PCDFs ratio	94	17.2	0.2	0.3	0.3
Total PCDD/Fs	129,560,000	569.2	55,919.7	26,903.3	129,721.0
PCDDs pg I-TEQ	173,360	1.2	365.8	147.9	849.1
PCDFs pg I-TEQ	1,265,600	23.3	2,147.7	1,045.4	4,917.2
PCDDs/PCDFs (I-TEQ) ratio	5.6	1.1	0.2	0.1	0.2
Total pg I-TEQ	1,438,800	24.6	2,513.5	1,193.3	5,766.3

efficiencies of total PCDD/Fs, they did significantly reduce PCDD/F emissions.

Decomposition of PCDD/Fs in the 1,200 °C secondary furnace was mostly a chemical reaction process. The PCDD/F decomposition

efficiencies were calculated according to the following formula: $DE = [1 - (C + D + E)/(A - B)] \times 100\%$, where DE (%) is decomposition efficiency of the PCDD/Fs in the secondary furnace, A, B, C, D and E were the PCDD/F mass in the feed soil, in the treated soil, collected

Table 6
Mass distributions of PCDD/Fs in cooling unit, filter and PUF cartridge at 750 °C thermal treatment temperature (n = 2)

PCDD/Fs	Cooling unit (%)	Filter (%)	PUF cartridge (%)	Total (%)
2,3,7,8-TeCDD	66.5	5.0	28.5	100
1,2,3,7,8-PeCDD	58.5	8.7	32.8	100
1,2,3,4,7,8-HxCDD	50.6	10.4	39.0	100
1,2,3,6,7,8-HxCDD	50.7	11.0	38.3	100
1,2,3,7,8,9-HxCDD	49.5	10.7	39.8	100
1,2,3,4,6,7,8-HpCDD	48.9	10.1	41.0	100
OCDD	42.0	7.1	50.9	100
2,3,7,8-TeCDF	66.5	5.5	28.0	100
1,2,3,7,8-PeCDF	57.7	7.9	34.4	100
2,3,4,7,8-PeCDF	55.6	9.5	34.9	100
1,2,3,4,7,8-HxCDF	53.9	9.6	36.5	100
1,2,3,6,7,8-HxCDF	55.8	9.8	34.4	100
2,3,4,6,7,8-HxCDF	52.2	10.7	37.1	100
1,2,3,7,8,9-HxCDF	56.3	6.8	36.9	100
1,2,3,4,6,7,8-HpCDF	53.7	9.9	36.4	100
1,2,3,4,7,8,9-HpCDF	65.6	7.5	26.9	100
OCDF	67.3	5.8	26.9	100
PCDDs	45.3	8.3	46.4	100
PCDFs	59.2	8.3	32.6	100
Total PCDD/Fs	56.3	8.3	35.4	100
PCDDs I-TEQ	57.4	8.5	34.2	100
PCDFs I-TEQ	55.6	9.4	35.0	100
Total I-TEQ	55.8	9.3	34.9	100

Table 7
Mass distributions of PCDD/Fs in cooling unit, filter and PUF cartridge at 850 °C thermal treatment temperature (n = 2)

PCDD/Fs	Cooling unit (%)	Filter (%)	PUF cartridge (%)	Total (%)
2,3,7,8-TeCDD	35.8	6.5	57.8	100
1,2,3,7,8-PeCDD	28.4	10.8	60.8	100
1,2,3,4,7,8-HxCDD	21.8	12.8	65.4	100
1,2,3,6,7,8-HxCDD	22.8	12.8	64.4	100
1,2,3,7,8,9-HxCDD	23.4	12.7	63.9	100
1,2,3,4,6,7,8-HpCDD	19.8	12.4	67.8	100
OCDD	23.0	11.3	65.7	100
2,3,7,8-TeCDF	41.2	7.6	51.2	100
1,2,3,7,8-PeCDF	31.4	10.9	57.6	100
2,3,4,7,8-PeCDF	26.6	12.5	60.8	100
1,2,3,4,7,8-HxCDF	26.0	13.5	60.6	100
1,2,3,6,7,8-HxCDF	26.5	13.6	59.9	100
2,3,4,6,7,8-HxCDF	22.4	13.8	63.7	100
1,2,3,7,8,9-HxCDF	29.8	11.6	58.7	100
1,2,3,4,6,7,8-HpCDF	24.0	13.8	62.2	100
1,2,3,4,7,8,9-HpCDF	28.9	12.9	58.2	100
OCDF	33.2	11.7	55.1	100
PCDDs	22.2	11.8	66.1	100
PCDFs	27.5	12.9	59.6	100
Total PCDD/Fs	26.3	12.7	61.0	100
PCDDs I-TEQ	26.8	10.9	62.3	100
PCDFs I-TEQ	26.5	12.9	60.6	100
Total I-TEQ	26.5	12.6	60.9	100

Table 8

Mean decomposition efficiencies (%) of PCDD/Fs by the secondary furnace (1200 °C) at 750 °C and 850 °C thermal treatment temperature in primary furnace, respectively ($n = 2$)

PCDD/PCDFs	750 °C (%)	850 °C (%)
2,3,7,8-TeCDD	89.94	96.05
1,2,3,7,8-PeCDD	93.76	96.59
1,2,3,4,7,8-HxCDD	95.61	96.93
1,2,3,6,7,8-HxCDD	97.17	98.14
1,2,3,7,8-HxCDD	97.12	98.12
1,2,3,4,6,7,8-HpCDD	99.54	99.66
OCDD	99.95	99.97
2,3,7,8-TeCDF	99.61	99.85
1,2,3,7,8-PeCDF	99.50	99.74
2,3,4,7,8-PeCDF	98.92	99.42
1,2,3,4,7,8-HxCDF	99.11	99.43
1,2,3,6,7,8-HxCDF	96.95	98.13
2,3,4,6,7,8-HxCDF	82.86	89.24
1,2,3,7,8,9-HxCDF	99.58	99.79
1,2,3,4,6,7,8-HpCDF	97.45	98.25
1,2,3,4,7,8,9-HpCDF	97.55	98.68
OCDF	99.66	99.83
PCDDs	99.92	99.95
PCDFs	99.27	99.58
Total PCDD/Fs	99.73	99.84
PCDDs ng I-TEQ/kg	98.59	99.21
PCDFs ng I-TEQ/kg	98.88	99.36
Total ng I-TEQ/kg	98.84	99.34

by cooling unit, by filter and by the PUF cartridge, respectively (Tables 4 and 5). Based on its definition, PCDD/F decomposition is used to evaluate the extent of PCDD/Fs destroyed in secondary furnace. As shown in Table 8, in general, PCDD decomposition efficiencies increased with higher molecular weight chlorinated congeners at both 750 °C and 850 °C. Higher chlorinated PCDD congeners could be destroyed and dechlorinated to form lower chlorinated congeners, resulting in lower decomposition efficiencies of lower chlorinated congeners.

Table 9

PCDD/F concentrations in the upstream flue gas of cooling unit, filter, and PUF cartridge

PCDDs/PCDFs (ng/Nm ³)	750 °C			850 °C		
	Cooling unit	Filter	PUF cartridge	Cooling unit	Filter	PUF cartridge
2,3,7,8-TeCDD	0.289	0.0967	0.0821	0.104	0.0667	0.0600
1,2,3,7,8-PeCDD	0.802	0.333	0.263	0.402	0.288	0.245
1,2,3,4,7,8-HxCDD	0.855	0.422	0.334	0.549	0.429	0.359
1,2,3,6,7,8-HxCDD	1.23	0.605	0.470	0.740	0.571	0.477
1,2,3,7,8-HxCDD	1.11	0.563	0.443	0.669	0.512	0.427
1,2,3,4,6,7,8-HpCDD	9.02	4.61	3.70	6.13	4.91	4.16
OCDD	19.5	11.3	9.93	11.3	8.70	7.42
2,3,7,8-TeCDF	3.07	1.03	0.859	1.09	0.638	0.556
1,2,3,7,8-PeCDF	4.15	1.76	1.43	1.95	1.34	1.12
2,3,4,7,8-PeCDF	5.66	2.52	1.98	2.77	2.03	1.69
1,2,3,4,7,8-HxCDF	10.1	4.68	3.70	5.91	4.38	3.58
1,2,3,6,7,8-HxCDF	8.64	3.82	2.97	4.86	3.57	2.91
2,3,4,6,7,8-HxCDF	6.32	3.02	2.34	3.64	2.82	2.32
1,2,3,7,8,9-HxCDF	0.478	0.209	0.176	0.219	0.154	0.128
1,2,3,4,6,7,8-HpCDF	42.8	19.8	15.6	26.9	20.5	16.7
1,2,3,4,7,8,9-HpCDF	5.08	1.75	1.37	2.51	1.79	1.46
OCDF	40.6	13.3	10.9	18.1	12.1	9.95
PCDDs	32.8	18.0	15.2	19.9	15.5	13.1
PCDFs	127	51.9	41.3	67.9	49.2	40.5
PCDDs/PCDFs ratio	0.258	0.346	0.368	0.293	0.314	0.325
Total PCDD/Fs	160	69.8	56.6	87.8	64.7	53.6
PCDDs ng I-TEQ/Nm ³	1.10	0.469	0.376	0.563	0.412	0.351
PCDFs ng I-TEQ/Nm ³	6.39	2.84	2.24	3.35	2.46	2.03
PCDDs/PCDFs (I-TEQ) ratio	0.172	0.165	0.168	0.168	0.167	0.173
Total ng I-TEQ/Nm ³	7.49	3.31	2.61	3.91	2.88	2.38

After the treatment of contaminated soils, at primary furnace of 750 °C or 850 °C, and secondary furnace of 1200 °C, the PCDD/F mass survived after the secondary furnace was approximately 0.274% of PCDD/F mass in the feed soil. This result indicated that the combination of both primary (750 °C or 850 °C) and secondary furnace temperature (1200 °C) had a great efficiency in PCDD/F decomposition. Exception of insufficient removal efficiency of APCDs, after secondary furnace, the de novo synthesis of PCDD/Fs may occur during the cooling down process. A preliminary experiment were undertaken to evaluate the PCDD/F reformation caused by de novo synthesis during cooling down process. Results indicated that the contents of PCDD/Fs after thermal treatment from 750 °C to 25 °C were approximately 50 times higher than those before thermal treatment, meaning that de novo synthesis did occur very significantly during the cooling process of gas streams. After secondary furnace, the increase of PCDD/F mass due to the de novo (F mass) was approximately 50 times more than that no de novo synthesis. If the F mass was not included in the calculation of decomposition efficiency (DE) in secondary furnace, the DE (%) in secondary furnace will be 99.987% and 99.978% at 750 °C and 850 °C, respectively, which were very close to 99.999%.

3.3 PCDD/F concentrations in the upstream flue gas of each APCD

At 750 °C treatment temperature, the total PCDD/Fs I-TEQ concentrations in the upstream flue gas of cooling unit, filter, and PUF cartridge were 7.49 ng/Nm³, 3.31 ng/Nm³ and 2.61 ng/Nm³, respectively, while those at 850 °C were 3.91 ng/Nm³, 2.88 ng/Nm³ and 2.38 ng/Nm³, respectively (Table 9). Although after the thermal process, the total PCDD/F mass was destroyed by approximately 99.726%, the total I-TEQ concentrations in the upstream flue gases of PUF cartridge (2.61 ng I-TEQ/Nm³ and 2.38 ng I-TEQ/Nm³ at 750 °C and 850 °C, respectively) were still higher than the stationary emission limit of the Taiwan EPA (0.5 ng I-TEQ/Nm³) [25]. The above results also suggested that additional APCDs, such as activated carbon injection in front of the filter are needed to enhance PCDD/F removal efficiency.

At 750 °C treatment temperature, the PCDDs/PCDFs and PCDDs/PCDFs (I-TEQ) ratios in the upstream flue gas of PUF cartridge were 0.368 and 0.168, respectively, while those at 850 °C were 0.325 and 0.173, respectively. Both total PCDFs and total PCDDs I-TEQ concentrations were higher than those of total PCDDs and total PCDDs I-TEQ, respectively. It revealed that PCDFs were the main contributor to total PCDD/Fs and total PCDD/Fs I-TEQ concentrations in the upstream flue gas of PUF cartridge. The probable reason is that de novo synthesis of PCDD/Fs may occur during the cooling down process and primarily form PCDFs other than PCDDs.

Congener profiles of PCDD/Fs in the flue gases in front of cooling unit, filter and PUF cartridge, respectively, are illustrated in Fig. 4. The top four dominated congeners were 1,2,3,4,6,7,8-HpCDF, OCDF, OCDD and 1,2,3,4,6,7,8-HpCDD. During the thermal treatment process, the PCDD/Fs displayed a different reaction characteristic in the solid (soil) (Fig. 3) and gas (flue gas) phases (Fig. 4), respectively. Both 1,2,3,4,6,7,8-HpCDF and OCDF were the most two dominant congeners in the flue gases, while those in the treated soils were 2,3,7,8-TeCDF and OCDD.

4. Conclusions

- (1) Thermal treatment is an effective technology to remove PCDD/Fs from heavily contaminated soils (3,239,000 ng/kg and 35,970 ng I-TEQ/kg). Removal efficiency of >99.99% was obtained at two primary furnace temperatures (750 °C and 850 °C), while >98% of decomposition efficiency was achieved by using a secondary furnace at 1200 °C. Moreover, the total I-TEQ contents in treated soils at 750 °C and 850 °C (1.56 ng I-TEQ/kg and 2.15 ng I-TEQ/kg, respectively) were far below the soil pollution standard of Taiwan (1000 ng I-TEQ/kg).
- (2) The mean PCDDs/PCDFs ratio in the feed soil was 2.35, indicating that more amount of PCDD mass were produced than that of PCDFs by the precursor reaction from pentachlorophenol (PCP).
- (3) After 750 °C and 850 °C thermal treatment, the PCDDs/PCDFs ratios in treated soil were 0.496 and 0.805, respectively, indicating that contents of PCDFs were higher than PCDDs. The above results revealed that when thermal energy was added, the degradation of PCDDs in soil was more rapid than PCDFs and the formation of PCDFs during the soil cooling process due to the de novo synthesis might occur.
- (4) The total I-TEQ concentrations in the upstream flue gas of PUF cartridge at 750 °C and 850 °C (2.61 ng I-TEQ/Nm³ and 2.38 ng I-TEQ/Nm³, respectively) were still higher than the Taiwan stationary emission limit (0.5 ng I-TEQ/Nm³). The above results also suggested that additional APCDs, such as activated carbon injection in front of the filter are needed to enhance PCDD/F removal efficiency.

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References

- [1] Environmental Protection Bureau of Tainan City, <http://www.tnepb.gov.tw/anshuen/index.asp>.

- [2] World Health Organisation, Pentachlorophenol, 1987.
- [3] K. Jiang, Y. Chen, X. Xu, Dioxins in Chinese technical pentachlorophenols, *Chemosphere* 25 (1992) 1493–1497.
- [4] G. Eduljee, Secondary exposure to dioxins through exposure to PCP and its derivatives, *Sci. Total Environ.* 232 (1999) 193–214.
- [5] Environmental Protection Bureau of Tainan City, The pollution survey of two-ninth path (1K + 800 to 2K + 815 section) of Tainan city, Report Number 2004-09-25, 2004.
- [6] R.E. Alcock, K.C. Jones, Dioxins in the environment: a review of trend data, *Environ. Sci. Technol.* 30 (1996) 3133–3143.
- [7] C. Gaus, O. Pöpke, N. Dennison, D. Haynes, G.R. Shaw, D.W. Connell, J.F. Müller, Evidence for the presence of widespread PCDD source in coastal sediments and soils from Queensland, Australia, *Chemosphere* 43 (2001) 549–558.
- [8] S. Masunaga, T. Takasuga, J. Nakanishi, Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations, *Chemosphere* 44 (2001) 873–885.
- [9] R.E. Alcock, K.C. Jones, Pentachlorophenol (PCP) and chloranil as PCDD/F sources to sewage sludge and sludge amended soils in the UK, *Chemosphere* 35 (1997) 2317–2330.
- [10] R.A. Freeman, J.M. Schroy, Environmental mobility of 2,3,7,8-TCDD, *Chemosphere* 14 (1985) 873–876.
- [11] S.M. Ayres, K.B. Webb, R.G. Evans, J. Mikes, Is 2,3,7,8-TCDD (dioxin) a carcinogen for humans? *Environ. Health Perspect.* 62 (1985) 329–335.
- [12] US EPA, Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds, EPA/600/Bp-92/001c Estimating Exposure to Dioxin-Like Compounds, EPA/600/6-88/005Cb, Office of Research and Development, Washington, DC, 1994.
- [13] A. Miyamura, H. Shimmura, S. Taniguchi, R. Uchida, M. Takada, H. Toda, M. Hosomi, A. Murakami, C. Rappe, Remediation of dioxin contaminated soil and degradation of PCDDs and PCDFs by the base catalyzed decomposition (BCD) process, *Organohalogen Compd.* 36 (1998) 27–32.
- [14] E. Kasai, S. Harjanto, T. Terui, T. Nakamura, Y. Waseda, Thermal remediation of PCDD/Fs contaminated soil by zone combustion process, *Chemosphere* 41 (2000) 857–864.
- [15] H. Habe, K. Ide, M. Yotsumoto, H. Tsuji, H. Hirano, J. Widada, T. Yoshida, H. Nojiri, T. Omori, Preliminary examinations for applying a carbazole-degrader, *Pseudomonas* sp. strain CA10, to dioxin-contaminated soil, *Appl. Microbiol. Biotechnol.* 56 (2001) 788–795.
- [16] S. Harjanto, E. Kasai, T. Terui, T. Nakamura, Behavior of dioxin during thermal remediation in the zone combustion process, *Chemosphere* 47 (2002) 687–693.
- [17] S. Hashimoto, K. Watanabe, K. Nose, M. Morita, Remediation of soil contaminated with dioxins by subcritical water extraction, *Chemosphere* 54 (2004) 89–96.
- [18] T.C. Chang, J.H. Yen, On-site mercury-contaminated soils remediation by using thermal desorption technology, *J. Hazard. Mater.* B128 (2006) 208–217.
- [19] G. Liu, J. Cabrera, M. Allen, Y. Cai, Mercury characterization in a soil sample collected nearby the DOE Oak Ridge Reservation utilizing sequential extraction and thermal desorption method, *Sci. Total Environ.* 369 (2006) 384–392.
- [20] E.E. Uzgiris, W.A. Edelstein, H.R. Philipp, I.E.T. Iben, Complex thermal desorption of PCBs from soil, *Chemosphere* 30 (1995) 377–387.
- [21] D.M. Hamby, Site remediation techniques supporting environmental restoration activities—a review, *Sci. Total Environ.* 191 (1996) 203–224.
- [22] R.C. Thurnau, J.A. Manning, Low temperature desorption applications of a direct fired rotary kiln incinerator, *J. Air Waste Manage. Assoc.* 46 (1996) 12–19.
- [23] L. Lundin, S. Marklund, Thermal degradation of PCDD/Fs, PCB and HCB in municipal solid waste ash, *Chemosphere* 67 (2007) 474–481.
- [24] Y.C. Lai, W.J. Lee, H.W. Li, L.C. Wang, G.P. Chang-Chien, Inhibition of polybrominated dibenzo-p-dioxin and dibenzofuran formation from the pyrolysis of printed circuit boards, *Environ. Sci. Technol.* 41 (2007) 957–962.
- [25] Environmental Protection Agency of Taiwan, 2001, <http://www.edb.epa.gov.tw/>.
- [26] H. Hagenmaier, H. Brunner, Isomer specific analysis of PCP and NaPCP for 2,3,7,8-substituted PCDD and PCDF at sub-ppb levels, *Chemosphere* 16 (1987) 1759–1764.
- [27] N. Visez, J.P. Sawerysyn, On the thermal degradation of PCDD/Fs promoted by CuCl or CuCl₂ at 350 °C, *Organohalogen Compd.* 67 (2005) 2195–2199.
- [28] B.H. Kim, S.J. Lee, S.J. Mun, Y.S. Chang, A case study of dioxin monitoring in and around an industrial waste incinerator in Korea, *Chemosphere* 58 (2005) 1589–1599.