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Influence of start-up on PCDD/F emission of incinerators

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Abstract

This study aims to evaluate the influence of start-up on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) concentration in the stack flue gas of incinerators and its contributing PCDD/F emission. The PCDD/F emission of the first sample among three consecutive stack flue gas samples of five intermittent incinerators, which sampled at a stable combustion condition after start-up, is 2–3 times higher than the mean of the others. For verifying the PCDD/F characteristics of incinerators during start-up, one continuous MSWI was investigated for two years. The elevated PCDD/F emissions of the MSWI during start-up could reach 96.9 ng I-TEQ N m^{-3} and still maintained a high PCDD/F emission (40 times higher than the Taiwan emission limit) even 18 h after the injection of activated carbon, indicating the memory effect. Taking the MSWI for example, which consists of four incinerators, the estimated annual PCDD/F emission from normal operational conditions was 0.112 g I-TEQ. However, one start-up procedure can generate ~60% of the PCDD/F emissions for one whole year of normal operations. And the PCDD/F emission, which is the result of the start-ups of four incinerators, was at least two times larger than that of a whole year's normal operations, without consideration for the PCDD/F emission contributed by the long lasting memory effect.

Keywords: PCDD/Fs; Start-up; Incinerator; Memory effect

1. Introduction

After polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were discovered in the flue gases and fly ash of municipal solid waste incinerators (MSWIs) in 1977 (Olie et al., 1977), PCDD/Fs have become a serious issue in many countries because of their toxicological effects and associated adverse health implications.

Most research investigated the PCDD/F characteristics and the induced hazardous effect of incinerators during normal operations. Till recently, several studies (Gass et al., 2002; Löthgren and van Bavel, 2005; Neuer-Etscheidt et al., 2006) have focused on the high PCDD/F emission during the start-up of incinerators. The start-up of continuous MSWIs is usually a cold start-up, which occurs after a plant revision and consists of the following procedures: (1) Oil burning with a maximum fuel feed rate until the suitable temperature for incineration (850 °C) is reached. (2) Start of waste feeding and increasing feed rate until design load is reached (Gass et al., 2002). However, for intermittent incinerators, the start-up procedure is a warm start-up, which can be characterized by the furnace's remaining temperature when it is started up again the next day.

Löthgren and van Bavel (2005) measured the PCDD/F levels after a polishing wet scrubber continuously for

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18 months using long-time sampling equipment at a hazardous waste incineration facility in Sweden. Each sampling period lasted two weeks. Two dramatic risings of TEQ levels were observed, both in the period just after a maintenance stop of the plant, from 0.02 to 0.25 ng TEQ m^{-3} and from 0.03 to 0.15 ng TEQ m^{-3}. Gass et al. (2002) reported raw flue gas PCDD/F concentrations during the start-up of a MSWI of up to 250 ng I-TEQ m^{-3} in the heat-up phase. In contrast, Neuer-Etscheidt et al. (2006) reported that PCDD/F I-TEQ crude gas concentrations during the heat-up period were a little lower than those during normal operations with waste as the fuel. One reason for this difference may be the state of cleaning of the boiler section. Immediately after waste was fed, PCDD/F concentrations (46 ng I-TEQ m^{-3}) in the crude gas increased by one order of magnitude compared to normal operating conditions (3–4 ng I-TEQ m^{-3}). Even for a ship's main engine, the highest PCDD/F emissions have been measured for the start-up samples (0.1–0.4 ng WHO-TEQ $kW\ h^{-1}$ vs 0.03–0.1 ng WHO-TEQ $kW\ h^{-1}$ during normal operations), which are characterized by relatively poor combustion conditions (also high CO emissions) (Cooper, 2005). However, still little research estimated the generated PCDD/Fs during start-up to what extent. Consequently, it is not yet possible to evaluate the exposures and potential health risks during these conditions (Mckone and Hammond, 2000).

In this study, five intermittently operating incinerators, including one industrial waste incinerator (IWI), one waste liquid incinerator (WLI) and three medical waste incinerators (MWIs) were measured for PCDD/Fs in the stack flue gases when combustion condition reached stabilization after start-up to evaluate the influence of memory effect caused by start-up on PCDD/F emission. For verifying the PCDD/F characteristics of incinerators during start-up, one large scale continuously operating MSWI was chosen to be investigated for two years. In the first year, a total of five start-up stack flue gas samples were collected. For more detailed characterization, the next year, a total of 10 stack flue gas samples were sampled and the sampling time was changed so it's more accordant with the start of waste feeding. Only the 2,3,7,8-PCDD/F congeners in the stack flue gases of the incinerator were measured because of their toxicities. The obtained results were not only compared to the typical concentrations during normal operations of the MSWI but also evaluated for the PCDD/F emission during start-up.

2. Experimental section

2.1. Basic information concerning the incinerators

The basic operation information concerning the intermittent incinerators, including one IWI, one WLI and three MWIs is described in Table 1. The feeding waste and air pollution control devices (APCDs) between these three categories of incinerators are not similar, but each kind of incinerator possesses its representation.

The continuously operating MSWI investigated for two years in this study consists of four 450 ton day^{-1}, two-stage, starved-air modular incinerators, each of which includes its own heat recovery system, dry scrubber, activated carbon injection, bag filter and stack. During start-up, the incinerators were preheated by burners operated with diesel.

2.2. PCDD/F sampling

On a usual day, the intermittent incinerators were started up in the morning and operated during the day. At night, the combustion chamber cooled down. However, in this study, the feeding waste was accumulated to enough for three consecutive 3 h stack flue gas samples during normal operations after start-up, which is characterized by the stable reading of combustion temperature and traditional pollutant, like CO concentration.

The sampling time of each stack flue gas sample of the MSWI during start-up was about 2–3 h and a total of five samples were collected in the first year. For more detailed characterization, the next year, the sampling time was changed to once an hour and a total of 10 stack flue gas samples were sampled.

The PCDD/F samples were collected isokinetically from the stack flue gas of the selected incinerators according to US EPA modified Method 23. The sampling train adopted in this study is comparable with that specified by US EPA

Table 1
Basic information concerning these five intermittent incinerators

Emission sources	IWI	WLI	MWI	MWI	MWI
Denotation	A	B	C	D	E
Feeding waste ($kg\ h^{-1}$)	Industrial waste (420)	Waste liquid (200)	Infectious and pathological waste (400)	Infectious and pathological waste (300)	Infectious and pathological waste (300)
Auxiliary fuel ($l\ h^{-1}$)	–	Diesel (0.1)	Diesel (22)	Diesel (21)	Diesel (19)
APCDs in sequence (operation temperature) (°C)	Cyclone (200) BF (160)	VS (90)	DS (250) ACI BF (150)	QC VS (90)	DS (250) ACI BF (160)
Mean stack flue gas flow ($N\ m^3\ h^{-1}$)	8500	2900	4500	4000	6000

Activated carbon injection: ACI; Bag filter: BF; Dry scrubber: DS; Quench chamber: QC; Venturi scrubber: VS.

Modified Method 5. Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF. The recoveries of PCDD/F surrogate standards were 101–123%, and met the criteria within 70–130%. To ensure the free contamination of the collected samples, one trip blank and one field blank were also taken during the field sampling was conducted. Details are similar to that given in our previous work (Wang et al., 2003).

2.3. Analyses of PCDD/Fs

Analyses of stack flue gas followed the US EPA modified method 23. All chemical analyses were carried out by the Super Micro Mass Research and Technology Center at Cheng Shiu University – the accredited laboratory in Taiwan for PCDD/F analyses. Prior to analysis, each collected sample was spiked with a known amount of the $^{13}C_{12}$-labeled internal standard to the extraction thimble. Add toluene to fill the reservoir approximately 2/3 full. Adjust the heat source to cause the extractor to cycle three times per hour. 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, including multilayer silica gel column, alumina column and activated carbon chromatography. The eluate was concentrated to approximately 1 ml and transferred to a vial. The concentrate was further concentrated to near dryness, using a stream of nitrogen. Immediately prior to analysis, the standard solution for recovery checking was added to the sample. The recoveries of PCDD/F internal standards for the tetra- through hexachlorinated homologues were between 65% and 98%, and met the criteria within 40–130%, while that for the hepta- and octachlorinated homologues were between 52% and 101%, and met the criteria within 25–130%.

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/Fs analyses. The HRGC (Hewlett Packard 6970 Series gas, CA, USA) was equipped with a DB-5MS fused silica capillary column ($L = 60$ m, ID = 0.25 mm, film thickness = 0.25 μm) (J&W Scientific, CA, USA), and with a splitless injection. Helium was used as the carrier gas. However, if a valley between peaks is more than 25% of the lower of the two peaks for 2,3,7,8-TCDD and 2,3,7,8-TCDF, the column had to be changed to DB-225 to recheck isomer. The oven temperature program was set according to follows: begin at 150 °C (held for 1 min), then increased at 30 °C min^{-1} to 220 °C (held for 12 min), then increased at 1.5 °C min^{-1} to 240 °C (held for 5 min), and finally increased at 1.5 °C min^{-1} to 310 °C (held for 20 min). The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with resolving power at 10000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. Details of analytical procedures are given in our previous work (Wang et al., 2003).

3. Results and discussion

3.1. Influence of memory effect resulted from start-up on PCDD/F emissions of the intermittent incinerators

The PCDD/F profiles of three consecutive stack flue gas samples of these five intermittent incinerators were illustrated in Fig. 1 and revealed that the PCDD/F emission of the first stack flue gas sample, which was sampled at a stable combustion condition after start-up, was considerably higher than that of the follow-up samples. For toxicity basis, the first stack flue gas sample was 2–3 times higher than the mean PCDD/F emission of the second and third one. Fig. 1 also revealed that the PCDD/F profiles of the three consecutive stack flue gas samples for each incinerator declined with time. The reason for this is that the memory effect that resulted from the high PCDD/F emission of the start-up contributed and changed the subsequent concentration and profiles significantly. But as time went by, the influence of the memory effect on the PCDD/F emission faded away.

The memory effect caused by the wet scrubber resulted from that PCDD/Fs are adsorbed on scrubber fillings (typically polypropylene (PP) plastics) and thus leading to unexpected PCDD/F releases when the plant is running under more stable conditions (Hunsinger et al., 1998; Adams et al., 2000; Takaoka et al., 2003). Compared to that caused by start-up procedure, the memory effect caused by the start-up can occur in all kinds of incinerators with different APCDs, not only for those with wet scrubbers, for examples, the incinerators in this study are no exception to this.

3.2. PCDD/F emission in the stack flue gases of the MSWI under normal conditions

For more understanding of the memory effect that resulted from the start-up, one continuous MSWI was chosen to characterize the PCDD/F emission during start-up. In the first instance, we need to establish the PCDD/F characteristics of the MSWI during normal operation.

The stack flue gases of the MSWI were sampled five times in different months under normal operation conditions and a total of 25 samples were collected for PCDD/F measurement. The mean PCDD/F concentration (normalized to the dry flue gas conditions of 273 K and 11% O_2) in the stack flue gas was 0.0358 ng I-TEQ N m^{-3} (range: 0.00273–0.0946 ng I-TEQ N m^{-3}, relative standard deviations (RSD): 66.4%), while their corresponding mean PCDD/F emission factor was 0.249 μg I-TEQ ton $waste^{-1}$ (RSD: 69.0%), which is close to that (mean: 0.251 μg I-TEQ ton $waste^{-1}$, range: 0.0512–0.561 μg I-TEQ ton $waste^{-1}$) of the other 13 MSWIs in Taiwan (Lee et al.,

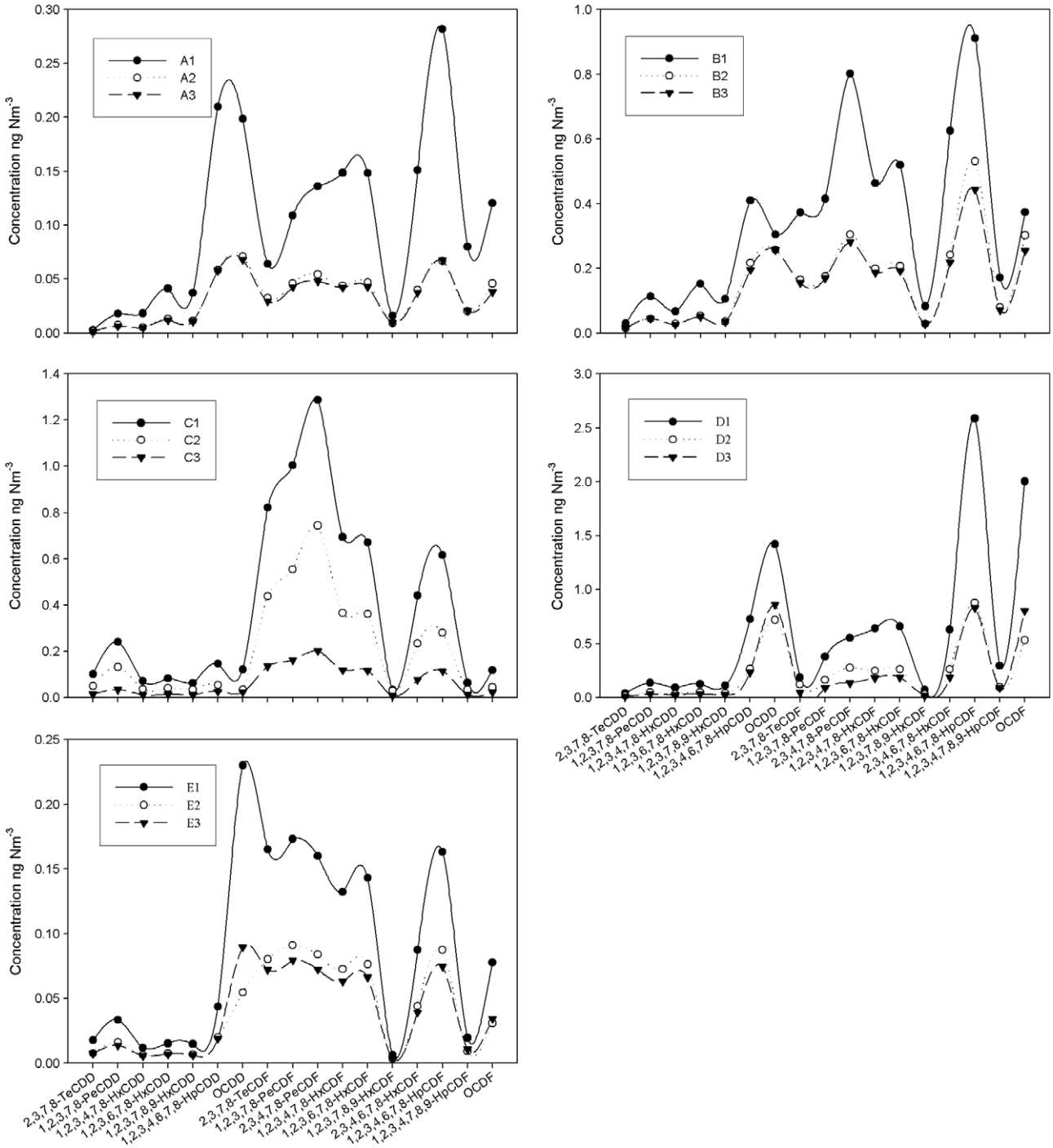

Fig. 1. The PCDD/F profiles of three consecutive stack flue gas samples of the five intermittent incinerators.

2005) and is comparable to that (0.17 μg I-TEQ ton waste^{-1}) of the MSWI (400 ton day^{-1}) in accordance with the best control technologies (Giugliano et al., 2002). Furthermore, five raw flue gas samples sampled in front of the activated carbon injection and bag filter were also measured for PCDD/Fs and the mean PCDD/F concentration was 0.610 ng I-TEQ N m^{-3} (range: 0.231–1.52 ng I-TEQ N m^{-3}, RSD: 86.1%).

According to statistical data, there were ~448 000 tonnes of waste incinerated by the MSWI investigated in this study in 2005. By directly adopting the mean emission factors that were obtained from this study (0.249 μg I-TEQ ton waste^{-1}), the total emission amount of PCDD/Fs from the MSWI is ~0.112 g I-TEQ yr^{-1}.

3.3. PCDD/F emission in the stack flue gases of the MSWI during start-up

Table 2 listed the operation conditions and their corresponding PCDD/F emission in the stack flue gases during

Table 2
PCDD/F emission in the stack flue gases of the MSWI during start-up in the first year's investigation

Sample denotations	Sampling day				
	Day one		Day two		
	a	b	c	d	e
Sampling time	15:30–17:40	19:25–20:55	23:40–3:15	10:10–12:35	13:42–16:10
Passed time after burner started (h)	5.5–7.7	9.4–11	13.7–17.3	24.2–26.6	28–30.2
Passed time after waste fed (h)	–	–	–	5.2–7.6	9–11.2
Auxiliary fuel ($l\,h^{-1}$)	660	830	650	4	7
Temperature of combustion chamber (°C)	310	490	850	900	920
Primary air flow rate ($N\,m^3\,h^{-1}$)	37500	34300	30900	50400	51000
Temperature in the inlet of superheater (°C)	190	240	360	490	500
Temperature in the inlet of economizer (°C)	150	210	300	330	340
O_2 Concentration after economizer (%)	22	22	22	11	7.3
Temperature of dry scrubber (°C)	130	160	210	240	230
Lime feeding rate ($m^3\,h^{-1}$)	0	0	0.6	2.2	4.0
Temperature of bag filter (°C)	120	150	180	160	150
Activated carbon feeding rate ($kg\,h^{-1}$)	0	0	6	10	10
CO concentration in the stack flue gas (ppm)	–	–	–	42	32
O_2 concentration in the stack flue gas (%)	18	17	14	8.3	8.7
PCDFs/PCDDs ratio	0.66	0.62	0.72	0.92	0.75
Total PCDD/Fs ($ng\,N\,m^{-3}$)	83.8	328	68.2	42.9	10.7
PCDFs/PCDDs TEQ ratio	3.0	2.1	2.4	2.6	2.4
Total I-TEQ ($ng\,I\text{-}TEQ\,N\,m^{-3}$)	2.09	12.2	3.34	2.28	0.507

–: No data.

the cold start-up of the MSWI in the first year's investigation. The PCDD/F concentrations (normalized to the dry flue gas conditions of 273 K) in the stack flue gases during the heat-up phase (samples a–c) were ranged at 2.09–12.2 ng I-TEQ $N\,m^{-3}$ while those that were ranged at 0.507–2.28 ng I-TEQ $N\,m^{-3}$ were observed 5 h after the waste feeding process had started.

For more detailed characterization, during the following year, the sampling time was changed to once an hour so it's more accordant with the start of waste feeding (see Table 3). The PCDD/F concentration in the stack flue gases during the heat-up phase (samples a–d) was between 5.16 and 41.5 ng I-TEQ $N\,m^{-3}$, which was higher than the first year's results (2.09–12.2 ng I-TEQ $N\,m^{-3}$). However, the drastic PCDD/F emissions in the stack flue gases during the heat-up phase of the two years' investigation both occurred at the combustion chamber's temperature reaching 490 °C. When the combustion chamber's temperature reaching 490 °C, the temperatures in the inlet of the superheater and economizer were between 210 °C and 290 °C, which were a little below the temperature region (250–450 °C) of the PCDD/F optimal formation. Otherwise, Clarke (2000), Gass et al. (2003) and Neuer-Etscheidt et al. (2006) reported that PCDD/F precursors (e.g., benzenes, phenols and chlorinated forms) are created in the furnace at the highest rate in these temperature regions. In fact, Benestad et al. (1990) reported that PAHs concentration during the start-up period was 2–16 times higher than that during normal operation for three small MSWIs. Yasuda and Takahashi (1998) also determined the PAHs emission of four MSWIs during start-up, burning, and burn-out and reported that during start-up conditions, PAH concentrations (7.7–248 $\mu g\,N\,m^{-3}$) have been shown to be 12–77 times higher during burning (0.1–63.2 $\mu g\,N\,m^{-3}$). Consequently, the drastic PCDD/F emissions occurred during the heat-up phase is more related to the operational temperature of the combustion chamber than to that of superheater and economizer.

But when the temperature of the combustion chamber raised from 490 °C to 850 °C, the PCDD/F emissions decreased from 12.2 ng I-TEQ $N\,m^{-3}$ (no activated carbon injection) to 3.34 ng I-TEQ $N\,m^{-3}$ (activated carbon feeding rate: $6\,kg\,h^{-1}$) during the heat-up phase in the first year's investigation. The injection of activated carbon and the elevated temperature of the combustion chamber, i.e. the more completely combustion condition, may be the reasons of drastic reduction of the PCDD/F emissions, however, due to the intervals of up to several hours where no samples were taken, which one is the most influence factor is needed to be clarified further.

In the first year, the temperature of the combustion chamber reached 490 °C after burning for 10 h with the average auxiliary fuel feeding rate of $710\,l\,h^{-1}$ and the average primary air of $35900\,N\,m^3\,h^{-1}$ while in the second year's investigation, reaching the same combustion condition with a higher average auxiliary fuel feeding rate of $1150\,L\,h^{-1}$ and a less primary air of $27700\,N\,m^3\,h^{-1}$. The results revealed that the worse combustion efficiency occurred in the second year and might result in the PCDD/F concentration in the stack flue gases during the heat-up phase (5.16–41.5 ng I-TEQ $N\,m^{-3}$) which has a recording that is higher in the second year than that of the first year (2.09–12.2 ng I-TEQ $N\,m^{-3}$). Otherwise, Neuer-Etscheidt et al. (2006) proposed that the state of

Table 3
PCDD/F emission in the stack flue gases of the incinerator during start-up in the second year's investigation

Sample denotations	Sampling day									
	Day one			Day two						
	a	b	c	d	e	f	g	h	i	j
Sampling time	18:00–19:00	20:30–21:25	23:10–00:07	01:50–02:57	05:00–06:08	09:50–11:09	12:45–13:58	15:20–16:30	18:04–19:09	20:30–21:41
Passed time after burner started (h)	2–3	4.5–5.4	7.2–8.1	9.8–11	13–14.1	17.8–19.2	20.8–22	23.3–24.5	26.1–27.2	28.5–29.7
Passed time after waste fed (h)	–	–	–	–	1–2.1	5.8–7.2	8.8–10	11.3–12.5	14.1–15.2	16.5–17.7
Auxiliary fuel ($l\,h^{-1}$)	1100	1150	1300	1060	525	2	0	0	0	0
Temperature of combustion chamber (°C)	155	230	400	490	900	900	910	880	900	900
Primary air flow rate ($N\,m^3\,h^{-1}$)	32 000	28 700	26 700	23 200	53 800	39 100	39 800	44 100	48 600	43 900
Temperature in the inlet of superheater (°C)	140	190	220	290	360	460	490	490	500	500
Temperature in the Inlet of economizer (°C)	110	160	190	250	310	330	340	340	350	350
O_2 concentration after economizer (%)	19	19	17	17	7.0	9.2	9.1	10	8.6	8.8
Temperature of dry scrubber (°C)	90	140	180	210	210	220	230	230	230	230
Lime feeding rate ($m^3\,h^{-1}$)	0	0	0	0	0	0	0	0	0	0
Temperature of bag filter (°C)	80	130	170	170	160	160	150	150	150	150
Activated carbon feeding rate ($kg\,h^{-1}$)	0	0	0	0	6	6	6	6	6	6
CO concentration in the stack flue gas (ppm)	–	–	–	–	–	49	43	53	37	21
O_2 concentration in the stack flue gas (%)	19	19	13	9.2	8.9	9.1	8.3	8.9	10	8.8
PCDFs/PCDDs ratio	0.64	0.59	0.95	1.0	1.0	0.69	0.74	0.67	0.69	0.68
Total PCDD/Fs ($ng\,N\,m^{-3}$)	180	259	111	384	909	339	86.3	99.7	66.5	64.3
PCDFs/PCDDs TEQ ratio	4.1	3.4	4.0	1.7	2.0	1.9	2.0	2.0	2.1	2.0
Total I-TEQ ($ng\,I\text{-}TEQ\,N\,m^{-3}$)	6.19	8.64	5.16	41.5	96.9	23.1	6.18	6.41	4.30	4.19

–: No data.

cleaning of the boiler section could also resulted in the PCDD/F crude gas concentrations during the heat-up period ranging from a little lower than those during normal operations to 250 ng I-TEQ N m^{-3}, which was reported by Gass et al. (2002).

Another drastic elevated PCDD/F concentrations (from 41.5 to 96.9 ng I-TEQ N m^{-3}) in the stack flue gas occurred one hour after waste feeding (Table 3) and it declined to 23.1 ng I-TEQ N m^{-3} five hours after waste feeding, but still maintained high PCDD/F concentration, 4.19 ng I-TEQ N m^{-3}, 40 times higher than the Taiwan emission limit of 0.1 ng I-TEQ N m^{-3} even 18 h after the injection of activated carbon, indicating the long lasting memory effect. Neuer-Etscheidt et al. (2006) also observed that immediately after waste was fed, PCDD/F concentrations (46 ng I-TEQ m^{-3}) in the crude gas increased by one order of magnitude compared to normal operating conditions (3–4 ng I-TEQ m^{-3}). In this study, the raw gas in front of the APCD had not been sampled so that it is unclear that if the raw gas PCDD/F levels were still elevated at 18 h after the injection of activated carbon. However, the CO concentration (21 ppm, see Table 3) at that time was already in the range of normal operation condition, representing the well combustion condition and little PCDD/F precursors, like benzenes, phenols and PAHs formed, so we extrapolated that the high PCDD/F concentration, 4.19 ng I-TEQ N m^{-3} at 18 h after the injection of activated carbon, resulting from rather the memory effect than the incomplete combustion at that time.

During the heat-up phase, no activated carbon is injected prior to the bag filter in order to avoid ignitions of the activated carbon due to the high oxygen concentration in the flue gas (see Tables 2 and 3). Although it may be one of the reason that the PCDD/F concentration in the stack flue gases was between 5.16 and 41.5 ng I-TEQ N m^{-3}, however, by comparing to the PCDD/F concentration in the raw flue gases in front of the activated carbon injection and bag filter of the MSWI during normal operation (mean: 0.610 ng I-TEQ N m^{-3}, range: 0.231–1.52 ng I-TEQ N m^{-3}), it revealed that a high PCDD/F emission during the heat-up phase occurred due to the low furnace temperature and the poor combustion condition. The surfaces of the boiler and pipe were thus contaminated by the soot particles as well as hydrocarbons, which improved de novo synthesis of PCDD/F formation during the subsequent increase of the temperatures at these locations. Otherwise, the high PCDD/F emission occurred during the start-up procedure also increased the PCDD/F adsorption on the APCDs, like wet scrubber and bag filter and then released over a longer period of time.

3.4. PCDD/F emission quantity of the MSWI during start-up

The profile of the PCDD/F emission rate of stack flue gas with time during start-up of a two year investigation is illustrated in Fig. 2 and the shadowed areas represent

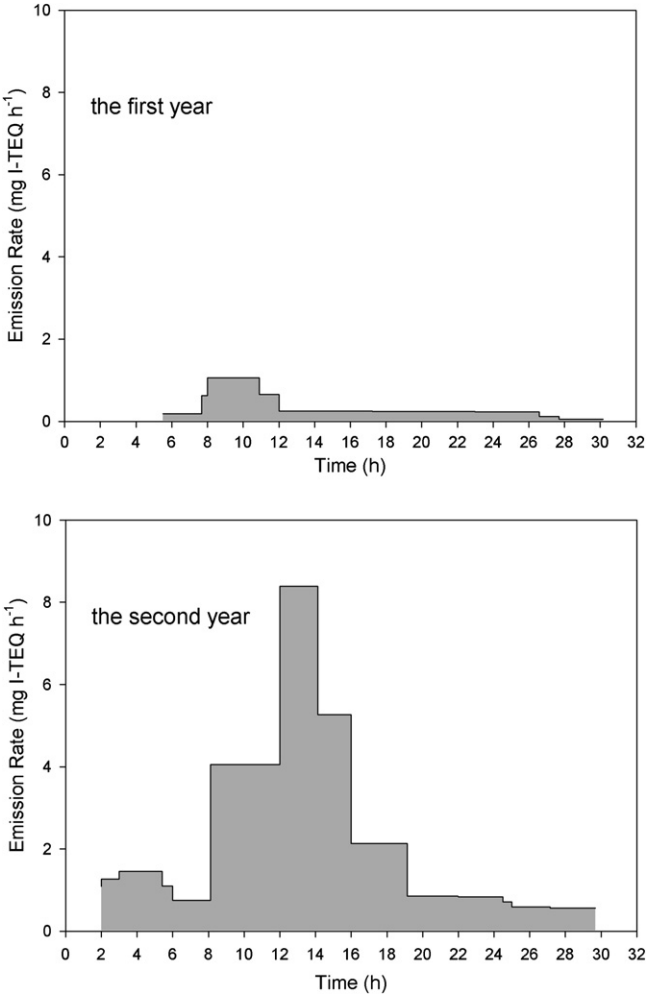

Fig. 2. PCDD/F emission rate from the stack flue gases of the MSWI during startup.

the PCDD/F emission quantity of MSWI during start-up. It revealed that one PCDD/F emission peak exists when the combustion chamber's temperature reaches 490 °C in both the first and second year. However, owing to the inexperience regarding the sampling strategy, another high PCDD/F emission peak resulted from the poor combustion when waste being fed was not observed in the first year's investigation. After changing the sampling time to be more accordant with the start of waste feeding, the PCDD/F profile clearly showed the phenomenon of PCDD/F generation and two high PCDD/F emission peaks with subsequently slow declination on emission in the second year's investigation. After calculating the shadowed areas, the estimated PCDD/F emission quantity during start-up was 0.0658 g I-TEQ in the second year's investigation.

Incinerators are usually at least shut-down and started-up once a year for maintenance. Taking the MSWI investigated in this study for example, which consists of four incinerators, the estimated annual PCDD/F emission from normal operational conditions was 0.112 g I-TEQ. However, one start-up procedure can generate ~60% of that and the PCDD/F emission quantity resulted from

the start-ups of four incinerators were at least two ($=0.0658 \times 4/0.112$) times larger than that of a whole year's normal operations, without consideration for the PCDD/F emission contributed by the long lasting memory effect because in this study the sampling period ended two days after start-up.

According to the legislation of most countries, PCDD/F measurements of incinerators only have to be conducted once or twice annually and are usually under normal and good operational conditions. Well over a 1000-fold increase in PCDD/F concentration and a two-fold increase in annual PCDD/F emission during the start-up procedures. The days when a cold start-up occurs will thus be much more significant than on the other days of normal operations. After properly evaluating the real total PCDD/F emission, an effective risk management strategy can be developed by assessing the relationship between exposure and health.

4. Conclusions

The memory effect that resulted from the start-up caused the PCDD/F concentration of the first stack flue gas sample of the intermittent incinerators, which was sampled at a stable combustion condition after start-up, elevated as much as 2–3 times higher than the mean of the follow-ups. During the start-up procedure of the MSWI, two high PCDD/F emission peaks in the stack flue gas were observed. One occurred when the combustion chamber's temperature reached 490 °C and the other occurred at the moment when waste was first fed. The elevated PCDD/F concentrations could reach 96.9 ng I-TEQ N m^{-3} and still maintained a high PCDD/F concentration (40 times higher than the Taiwan emission limit) even 18 h after the injection of activated carbon, indicating the long lasting memory effect. The PCDD/F emission over several days resulted from the start-ups of the MSWI were at least two times larger than that from a whole year's normal operations, without consideration for the PCDD/F emission contributed by the subsequent memory effect.

The obtained results revealed that the intermittent incinerators, due to their design or operational characteristics, are prone to start-up procedure and should be replaced by continuous incinerators or the operation schedule from 8 h to 5 days a week should be changed to a continuous two day operation.

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