



Influence of memory effect caused by aged bag filters on the stack PCDD/F emissions

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ARTICLE INFO

Article history:

Received 20 May 2010

Received in revised form

12 September 2010

Accepted 6 October 2010

Available online 14 October 2010

Keywords:

PCDD/Fs

Memory effect

Bag filter

Incinerator

Electric arc furnace

Start-up

ABSTRACT

To our best knowledge, this study is the first research which investigates whether the PCDD/F memory effect could also be caused by bag filters. In this study, the PCDD/F characteristics of the flue gases in front of and behind the bag filters of one municipal solid waste incinerator (MSWI) and two electric arc furnaces (EAFs) were investigated to clarify the memory effect of PCDD/Fs and their influence on emissions. After the bag filters were operated for over four years, the PCDD/F concentrations in the stack flue gases were all higher than those prior to the aged bag filter, rendering a negative PCDD/F removal. This memory effect is because gaseous phase PCDD/Fs are released from the contaminated filters of the aged bag filters. The release of 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF from the contaminated filters of the EAFs increased the PCDD/F concentration and their fractions in the stack flue gases. In contrast, the MSWI exhibited increasing fractions of 1,2,3,4,6,7,8-HpCDD, OCDD after flue gases passed through its aged bag filter. The activated carbon of the MSWI adsorbed more lower chlorinated-substituted PCDD/Fs in the raw flue gases, and the remaining higher chlorinated congeners gradually accumulated on the aged filters, and were released in lower PCDD/F concentration conditions.

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1. Introduction

Being poorly soluble and resistant to degradation, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) persist in the environment and bioaccumulate in animals and humans. In many countries, the public is seriously concerned about the PCDD/F emissions from incineration and/or industrial thermal processes. The important sources of PCDD/Fs have been reported as the waste incinerators, iron ore sintering, coal-fired power plants, electric arc furnaces (EAFs), and open burning of rice straw [1]. The atmospheric PCDD/F concentrations have been observed influenced by stationary sources nearby, such as sinter plant, secondary metallurgical melting processes [2–5]. During the biomass burning season, the total PCDD/F I-TEQ concentrations in the ambient air were even approximately 4–17 times higher than those without biomass open burnings [6].

To reduce PCDD/F emissions from stationary sources, air pollution control devices (APCDs) such as bag filters and electrostatic precipitators (EP) are used to removal particulate phase PCDD/Fs,

while methods like activated carbon injection and catalytic destruction/oxidation are used to adsorb or destroy gaseous phase PCDD/Fs. Other research adopted inhibitors to control PCDD/F emissions, for example, addition of natural organic enzyme-7F (NOE-7F) in the raw materials of EAF dust treatment plant dechlorinated PCDD/Fs, and inhibited highly chlorinated PCDD/F formation [7]. Adding CaO to adsorb HBr inhibits the formation of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) by more than 90% [8]. Although EP also collects fly ashes with high efficiency (>98%), the electric field in an EP can increase gaseous phase PCDD (and perhaps PCDF) formation potential [9]. Consequently, bag filters are more effective than EPs in controlling PCDD/Fs [10].

The chlorine contents in the feeding wastes of municipal solid waste incinerators (MSWIs) are usually below the threshold at 0.8%–1.1%, representative of unfavorable condition for high PCDD/F formation [11]. Nevertheless, even during stable combustion and good APCD operating conditions, MSWIs may emit higher PCDD/F emissions than expected, revealing a “memory” of the previous worse operating conditions. There are two types of PCDD/F memory effects defined as *de novo* based memory effect and adsorptive memory effect by Weber et al. [12]. The *de novo* based memory effect may be caused by high PCDD/F emissions resulting from the start-up procedure [13], incomplete combustion and disturbed

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Table 1
Basic information concerning the MSWI and EAFs.

Emission sources	MSWI	EAF 1	EAF 2
Feeding waste/materials (t h ⁻¹)	Municipal solid waste (12.5)	Faulty iron products (2.26) Scrap (0.98) Cast iron (2.32) Total (5.56)	Faulty iron products (2.30) Scrap (0.97) Cast iron (2.16) Total (5.43)
APCDs in sequence (operational temperature, °C)	Dry scrubber, activated carbon injection, bag filter (165)	Cyclone, bag filter (40)	Bag filter (40)
Information concerning bag filters	Polytetrafluoroethylene Diameter: 14.5 cm Length: 550 cm Number: 700	Polyethylene Diameter: 15 cm Length: 355 cm Number: 400	Polytetrafluoroethylene Diameter 14.5 cm Length: 550 cm Number: 200
Mean stack flue gas flow (Nm ³ h ⁻¹)	58,400	11,200	21,200
Temperature of stack flue gases (°C)	161	37	38

combustion conditions [14]. In these situations, the surfaces of the boiler and pipe are contaminated by soot particles containing high PCDD/F contents as well as hydrocarbons, which improve de novo synthesis of PCDD/F formation at these locations [12,14,15]. In addition to these “high temperature” memory effects [16], the desorbed PCDD/Fs from the filling surfaces of wet scrubbers, which occurs in the low temperature, increases the PCDD/F concentrations over a longer period of time [17].

For the “high temperature” memory effects, even 18 h after the injection of activated carbon, the memory effect caused by the start-up (96.9 ng I-TEQ Nm⁻³) maintains the PCDD/F concentrations at the level of 4 ng I-TEQ Nm⁻³ (40 times higher than Taiwan’s emission limit) [13]. As for the “low temperature” memory effects, most studies focus on the memory effect of wet scrubbers on PCDD/Fs [17–19]. The PCDD/F concentrations in the outlets of the wet scrubbers have been reported to be higher than those in their inlets among three MSWIs, and the PCDD/F concentrations in the inlets vs. outlets of the wet scrubbers were 0.29 ng I-TEQ Nm⁻³ vs. 0.50 ng I-TEQ Nm⁻³ [18], 0.30 ng I-TEQ Nm⁻³ vs. 4.80 ng I-TEQ Nm⁻³, and 0.35 ng I-TEQ Nm⁻³ vs. 0.54 ng I-TEQ Nm⁻³ [20]. To our best knowledge, no study address whether the PCDD/F memory effect could also be caused by bag filters.

In this study, the bag filters of one MSWI and two EAFs were investigated for their memory effect on PCDD/Fs by simultaneously sampling flue gases from the inlets of bag filters and stacks after four years and one month usage of the filters. Furthermore, gaseous and particulate phase PCDD/Fs in the stack flue gases of the MSWI were sampled two weeks after start-up and during normal conditions to clarify how the contaminated filters affect PCDD/F concentrations in the treated flue gases.

2. Experimental

2.1. Background information concerning the MSWI and EAFs

The basic operating information concerning the MSWI and EAFs is described in Table 1. The continuously operating MSWI investigated in this study consists of four 450 t 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. The operation type of the EAFs is intermittent, with scrap, faulty iron products and cast iron as their feeding materials, and cyclone and bag filters as their APCDs.

2.2. Sampling procedures

All the stack flue gas and ash samplings, as well as chemical analyses were carried out by our accredited laboratory, which specializes in PCDD/F samplings and analyses in Taiwan. For each

facility, the flue gases were simultaneously sampled from the inlet of the bag filter and stack after four-year and one-month usage of bag filters. Three flue gas samples were collected from each sampling port of the MSWI and the EAFs. Furthermore, each five stack flue gas samples were collected two weeks after start-up of the MSWI and during its normal condition.

The stack flue gas samples were collected isokinetically following U.S. EPA Modified Method 23 [21] using a U.S. EPA Modified Method 5 sampling train [22]. The sampled flue gas volumes were normalized to the dry condition of 760 mmHg and 273 K, and denoted as Nm³. The collection time of each flue gas sample of MSWI lasted for three hours, while those of the EAFs lasted two to three hours and combined three whole batch operating process.

Furthermore, the filters (thickness: 1 cm) along with the adhered ash cakes (1–2 mm) were cut (10 cm × 10 cm) from the upper, middle and lower parts of the aged bag filters for PCDD/F analyses. Each sample was a composite from at least ten filters. The fly ashes collected by the bag filters were also sampled, and then the ash samples were well-mixed and diagonally sectioned for PCDD/F analyses.

2.3. Analyses of PCDD/Fs

Analyses of the flue gas samples were performed following U.S. EPA Modified Method 23 [21], while those of the filter and fly ash samples conformed to the U.S. EPA Modified Method 1613 [23]. Prior to analysis, each collected sample was spiked with a known amount of the ¹³C₁₂-labeled internal standard to the extraction thimble. Toluene was added to fill the reservoir approximately 2/3 full, and the heat source was adjusted to cause the extractor to cycle three times per hour. After being extracted for 24 h, the extract was concentrated and treated with concentrated sulfuric acid, and this was followed by a series of sample cleanup and fractionation procedures, including multilayer silica gel column, alumina column and activated carbon column. 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.

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. The oven temperature was programmed with an initial temperature of 150 °C (held for 1 min), followed by 30 °C min⁻¹ ramping to 220 °C (held for 12 min), followed by a 1.5 °C min⁻¹ ramping to 240 °C (held for 5 min), then to 310 °C (held for 20 min). The HRMS (Micromass

Table 2
PCDD/F concentrations in the flue gases in front of and behind the aged bag filters.

PCDD/Fs	MSWI				EAF 1				EAF 2			
	Before bag filters (<i>n</i> = 3)		After bag filters (<i>n</i> = 3)		Before bag filters (<i>n</i> = 3)		After bag filters (<i>n</i> = 3)		Before bag filters (<i>n</i> = 3)		After bag filters (<i>n</i> = 3)	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
Total PCDDs	1.16	16.0	8.69	29.6	0.0569	29.6	0.0434	14.4	0.103	24.2	0.238	19.7
Total PCDFs	0.782	16.9	2.44	22.9	0.0677	34.4	0.0911	12.3	0.346	26.0	0.900	22.4
PCDFs/PCDDs Ratio	0.676	2.2	0.284	6.4	1.18	6.4	2.11	2.3	3.35	3.9	3.77	2.9
Total PCDD/Fs (ng Nm ⁻³)	1.94	16.3	11.1	28.1	0.125	32.2	0.134	12.9	0.449	25.6	1.14	21.9
Total PCDD/Fs I-TEQ (ng I-TEQ Nm ⁻³)	0.122	10.9	0.390	17.6	0.00529	35.3	0.0105	15.1	0.0442	28.8	0.142	23.4

Table 3
PCDD/F concentrations in the flue gases in front of and behind bag filters, and their PCDD/F removal efficiencies one month after deploying the new filters.

PCDD/Fs	MSWI				EAF 1				EAF 2									
	Concentrations				Removal efficiency (%)		Concentrations				Removal efficiency (%)							
	Before bag filters (<i>n</i> = 3)		After bag filters (<i>n</i> = 3)		Mean	RSD (%)	Before bag filters (<i>n</i> = 3)		After bag filters (<i>n</i> = 3)		Mean	RSD (%)	Before bag filters (<i>n</i> = 3)		After bag filters (<i>n</i> = 3)		Mean	RSD (%)
	Mean	RSD (%)	Mean	RSD (%)			Mean	RSD (%)	Mean	RSD (%)			Mean	RSD (%)	Mean	RSD (%)		
Total PCDDs	2.32	47.6	0.992	18.7	49.1	56.7	0.158	19.8	0.119	25.4	24.5	53.9	0.235	1.4	0.115	24.0	65.8	35.2
Total PCDFs	1.25	43.7	0.0832	12.1	92.0	5.2	0.813	11.8	0.118	23.2	85.6	2.6	0.657	5.5	0.319	5.6	65.6	37.6
Total PCDD/Fs (ng Nm ⁻³)	3.57	46.2	1.08	18.0	64.4	30.0	0.969	13.1	0.236	24.2	75.7	5.4	0.893	3.7	0.433	10.2	65.9	36.4
Total PCDD/Fs I-TEQ (ng I-TEQ Nm ⁻³)	0.207	44.2	0.0305	11.8	82.7	11.1	0.127	14.0	0.0145	20.4	88.7	1.3	0.117	12.9	0.0549	10.7	66.9	36.2

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 10,000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. Details of the analytical procedures are given in our previous work [24]. The recoveries of PCDD/F internal standards for the tetra- through hexa-chlorinated homologues were between 75% and 102%, and met the criteria within 40%–130%, while that for the hepta- and octachlorinated homologues were between 65% and 105%, and met the criteria within 25%–130%.

3. Results and discussion

3.1. Elevated PCDD/F concentrations in the stack flue gases of the facilities with the aged bag filters

The PCDD/F concentrations in the raw flue gases and flue gases treated by the aged bag filters (that is, the stack flue gases) which had been operated for over four years, are shown in Table 2. The PCDD/F concentrations in the stack flue gases were all higher than those in front of the aged bag filter, and were 0.122 ng I-TEQ Nm⁻³ vs. 0.390 ng I-TEQ Nm⁻³ for MSWI1, 0.00529 ng I-TEQ Nm⁻³ vs. 0.0105 ng I-TEQ Nm⁻³ for EAF1 and 0.0442 ng I-TEQ Nm⁻³ vs. 0.142 ng I-TEQ Nm⁻³ for EAF2. That is, after the flue gases passed through the bag filters which were originally designed to remove pollutants, the PCDD/F I-TEQ concentrations in the stack flue gases were elevated 3.0, 2.0 and 3.2 times for the MSWI, EAF1 and EAF2, respectively, rendering a negative PCDD/F removal. It needs to

mention EAF2 with levels of below 0.1 ng I-TEQ Nm⁻³ inlet concentration to levels of above 0.1 ng I-TEQ Nm⁻³ and therefore to levels above legislation level often applied. Similar phenomena have been reported for the use of wet scrubbers [17,20], and recognized as a memory effect resulting from the fact that PCDD/Fs are adsorbed on scrubber fillings and thus lead to unexpected PCDD/F releases when the plant is running under more stable conditions [20,25,26].

The negative PCDD/F removal of the bag filters could result from the inner walls of the ducts behind the bag filters are fouled by the soot particles generated from start-up procedure or disturbed combustion conditions. Under this circumstance, PCDD/F formation is improved through de novo synthesis by the soot particles at these favorable sites [12,15]. However, the operating temperatures of the bag filters in this study, which were only 40 °C and 165 °C for the EAFs and MSWI, are too low for de novo synthesis [27,28]. The temperatures of the flue gas in the ducts behind the bag filters were about the same, so the PCDD/F formation through de novo synthesis should be very minor. Consequently, we concluded that the negative PCDD/F removal that occurred in the MSWI and EAFs resulted from the memory effect of the aged bag filters, not likely formed in the inner walls of the ducts behind the bag filters or the adhered ash cakes of bag filters.

3.2. PCDD/F removal efficiencies of the new bag filter

The aged filters of the bag filters were the potential sources of PCDD/Fs for the three facilities, because the low PCDD/F concentrations in the raw flue gases of the EAFs revealed the furnace

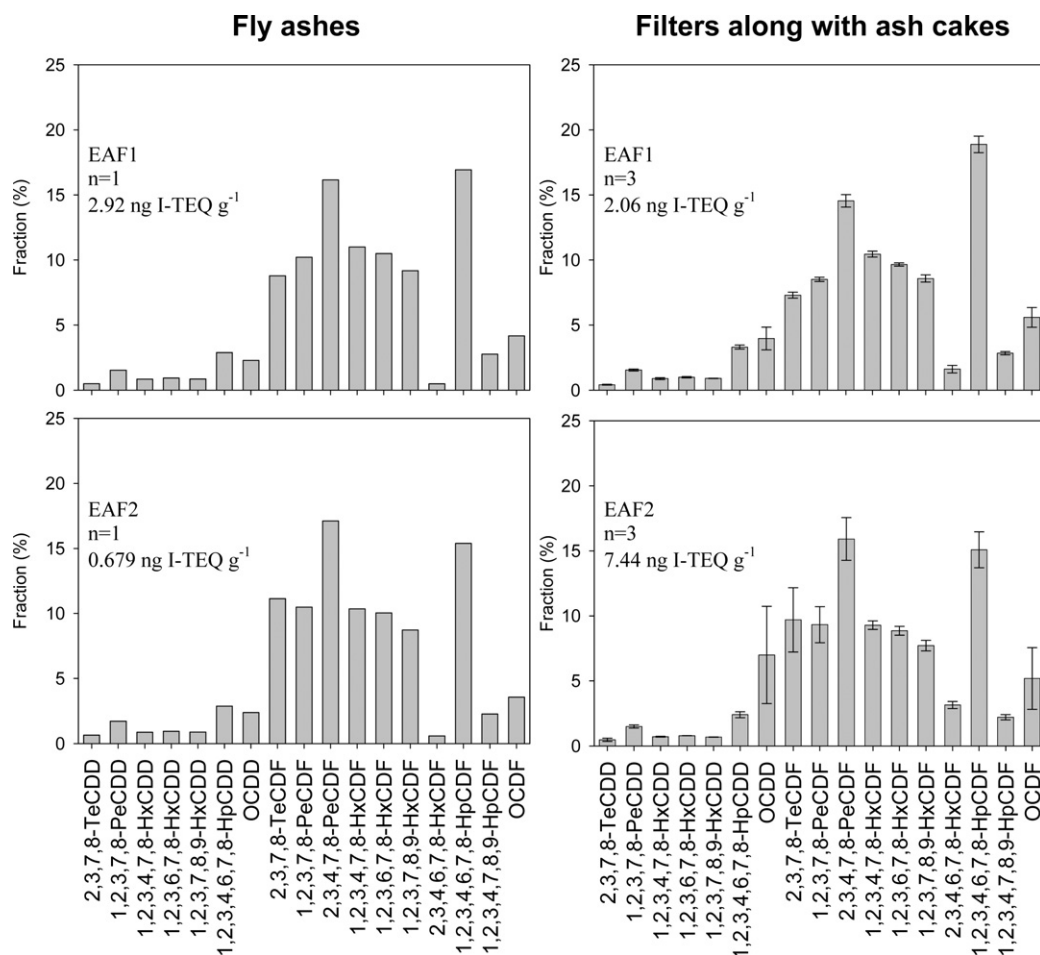


Fig. 1. PCDD/F characteristics in the collected fly ashes and the samples of the filters along with the adhered ash cakes.

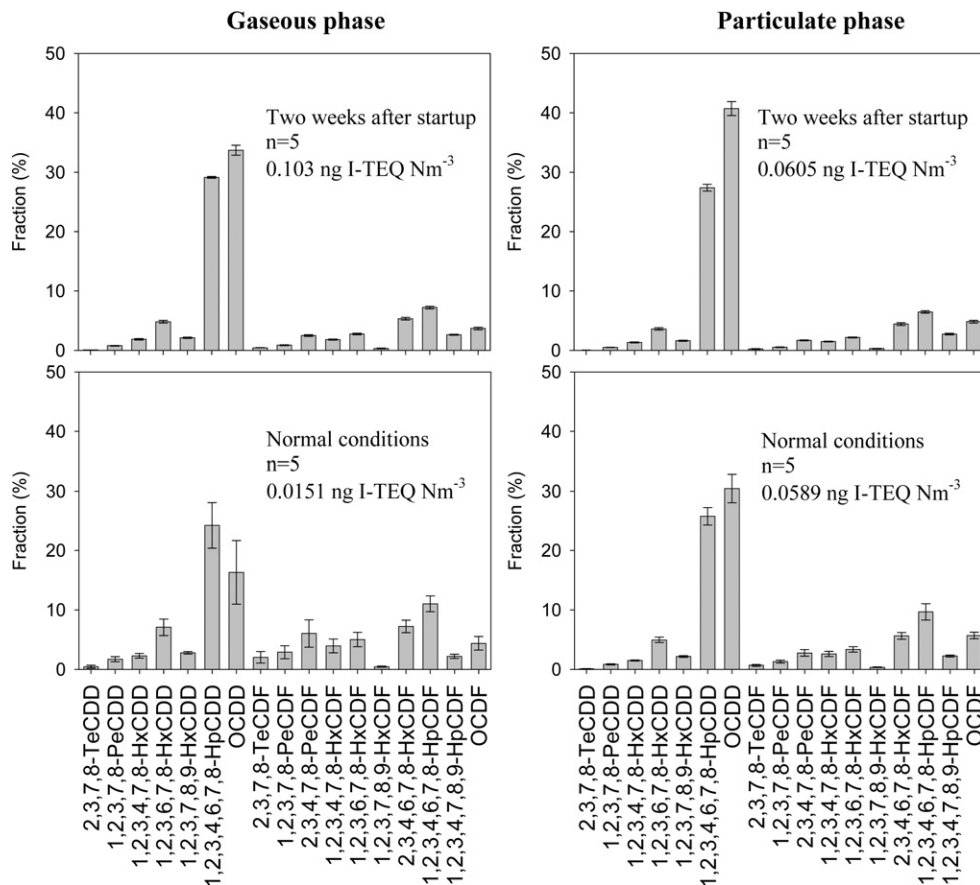


Fig. 2. PCDD/F congener profiles in the stack flue gases of the MSWI sampled in two weeks after start-up and during normal conditions.

operations and combustion conditions should be unfavorable for PCDD/F formation. Consequently, we replaced all the aged filters with the brand new ones for the three facilities. In order to prevent the memory effect caused by the cold start-up, especially for that of the MSWIs [13], one month after deploying the new filters, the PCDD/F concentrations in the flue gases were sampled in front of and behind the bag filters for evaluating their PCDD/F removal efficiencies, as shown in Table 3. For the MSWI, the PCDD/F concentration in front of the bag filters ($0.207 \text{ ng I-TEQ Nm}^{-3}$) was close to the previous measurement ($0.122 \text{ ng I-TEQ Nm}^{-3}$), while for the EAFs, the PCDD/F concentrations in front of the bag filters (0.127 and $0.117 \text{ ng I-TEQ Nm}^{-3}$) showed significant higher levels compared to those measured the previous time (0.00529 and $0.0442 \text{ ng I-TEQ Nm}^{-3}$).

The wide range of PCDD/F concentrations in the stack flue gases of EAFs has been observed as $0.041\text{--}0.83 \text{ ng I-TEQ Nm}^{-3}$ [29], $0.02\text{--}0.1 \text{ ng I-TEQ Nm}^{-3}$ [30] and $0.7\text{--}9.2 \text{ ng I-TEQ Nm}^{-3}$ [31]. Similar results also occurred in secondary aluminum smelters, and reported as $0.041\text{--}40 \text{ ng I-TEQ Nm}^{-3}$ [29] and $0.02\text{--}21.5 \text{ ng I-TEQ Nm}^{-3}$ [31]. The range could reach one to three orders, and the intrinsic differences in the feeding materials involved (scrap metal contaminated by PVC plastics and cutting oils) in each batch and the operational conditions of furnaces have been seen as the most influential factors affecting the PCDD/F concentrations [29,32]. Assuming that the worst and best scenarios for the PCDD/F removal efficiencies of bag filters are between 30% and 80%, the operating conditions of bag filters only affect the PCDD/F concentrations in stack flue gases within one order. Consequently, we consider that the impurity and contamination levels of the feeding materials may be the reason for the large PCDD/F concentration range in front of the bag filters in this study.

The mean PCDD/F concentrations in front of the bag filters of the MSWI, EAF1 and EAF2 were 0.207 , 0.127 and $0.117 \text{ ng I-TEQ Nm}^{-3}$, respectively, while those in the stack flue gases were 0.0305 , 0.0145 and $0.0549 \text{ ng I-TEQ Nm}^{-3}$. For MSWI, the PCDD/F removal efficiencies of the bag filter with activated carbon injection (feeding rate of activated carbon: $0.67 \text{ kg/tonne-waste}$) were 82.7% on toxicity bases, which were much lower than those (99%) of similar APCD combinations [33]. Similar results have been reported earlier [34], and attributed to the memory effect. That is, the soot deposits (enriched in PCDD/Fs and precursors) on the surfaces of the pipes behind bag filters could act as favorable sites for de novo synthesis, and increasingly desorb into the flue gases when the PCDD/F concentration in the flue gas is lower [18]. Both phenomena raise the PCDD/F concentration in the stack flue gases. Continuously injecting activated carbon will increase the removal efficiencies to the normal level after a period of time. Therefore, it is important to consider this effect when putting new filters in the bag filters [34]. For EAFs, the PCDD/F I-TEQ removal efficiencies of the bag filters were between 66.9% and 88.7%, which were somewhat higher than those (55.1%–64.0%) reported by previous studies [18,24]. The higher removal efficiencies in this study may be due to the much lower operational temperature (40°C) of the bag filters than those (200°C) in previous work, resulting in more gaseous phase PCDD/Fs being adsorbed onto fly ashes, and then removed by the bag filters.

3.3. PCDD/F contents in the collected fly ashes and the filters of the aged bag filters

In order to find out how the aged filters of the bag filters became the potential sources of PCDD/Fs, the PCDD/F contents in the brand

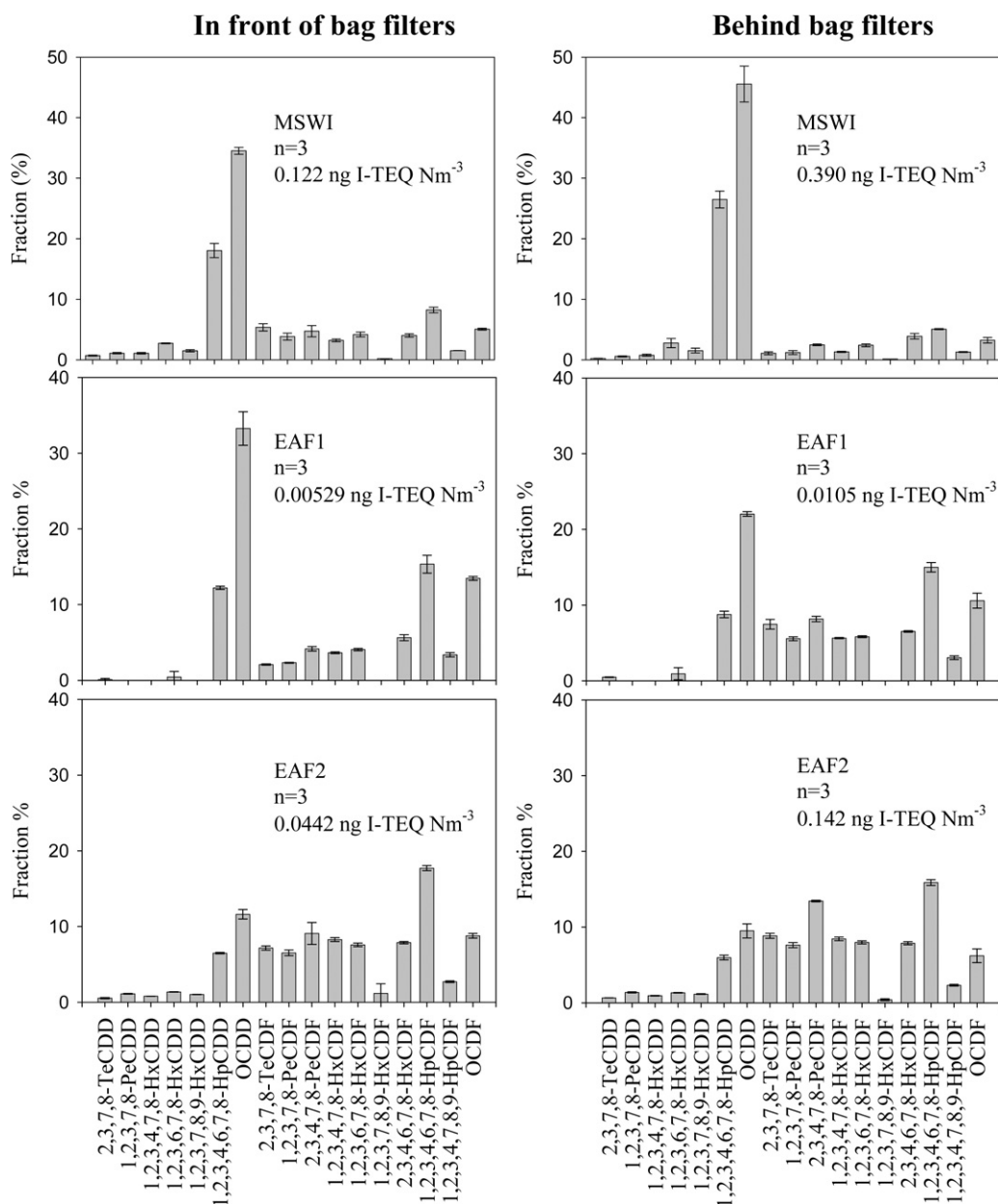


Fig. 3. PCDD/F congener profiles in the flue gases in front of and behind the aged bag filters.

new and aged filters were analyzed. The PCDD/F measurements of the brand new filters were all below the detection limit (data not shown), but the PCDD/F contents in the aged filters along with the adhered ash cakes (2.06 and 7.44 ng I-TEQ g⁻¹) were comparable or even higher than those in the collected fly ashes (2.92 and 0.679 ng I-TEQ g⁻¹) (see Fig. 1). Although we did not individually measure the PCDD/F contents in the filters and the adhered ash cakes, the cut filters were much heavier than the adhered ash cakes, so the PCDD/F contents in the filters should be close to those in the samples (filters along with ash cakes). These results suggest that the aged filters were contaminated by the raw flue gases and fly ashes, and PCDD/Fs can accumulate among the filters.

The calculated total accumulations of PCDD/Fs for all the aged filters were 2.57 and 1.73 mg I-TEQ for EAF1 and EAF2, respectively. Assuming the elevation of PCDD/F concentrations in the stack flue gases is 0.1 ng I-TEQ Nm⁻³ due to PCDD/F desorption, the influence periods of the memory effects of the aged filters are about 96 and 34 consecutive days for EAF1 and EAF2, respectively.

3.4. Memory effect caused by the start-up of the MSWI

To investigate how the contaminated filters affect the PCDD/F emission, the gaseous and particulate phase PCDD/Fs in the stack flue gases of the MSWI were sampled two weeks after start-up and during normal conditions. The congener profiles of both gaseous and particulate phase PCDD/Fs and their corresponding I-TEQ concentrations in the stack flue gases are illustrated in Fig. 2. The gaseous phase PCDD/F concentration (mean: 0.103 ng I-TEQ Nm⁻³) obtained two weeks after start-up was 6.8 times higher than that (mean: 0.0151 ng I-TEQ Nm⁻³) sampled during normal conditions, while the particulate phase PCDD/F concentrations were close to each other (0.0605 ng I-TEQ Nm⁻³ vs. 0.0589 ng I-TEQ Nm⁻³), revealing that the influence of the memory effect caused by the start-up was mainly on the gaseous phase PCDD/Fs in later stable conditions. In other words, the accumulated PCDD/Fs from the start-up were released in the form of a gaseous phase.

The congener profile of the gaseous phase PCDD/Fs obtained two weeks after start-up was dominated by 1,2,3,4,6,7,8-HpCDD and OCDD. Although 1,2,3,4,6,7,8-HpCDD and OCDD were still the most dominant congeners in the gaseous phase PCDD/Fs sampled during normal conditions, the fractions of the lower chlorinated-substituted PCDD/Fs, such as 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, increased compared to those sampled two weeks after start-up. For the congener profiles of the particulate phase PCDD/Fs, the difference between those samples was not so obvious.

The lower chlorinated-substituted PCDD/F congeners with higher vapor pressure have more mass fraction in the gaseous phase, and are more easily removed due to the gaseous phase adsorption of activated carbon [35]. In other words, the mass fractions of the higher chlorinated-substituted congeners in the gaseous phase PCDD/Fs will increase after flue gases are treated by activated carbon. During the start-up procedure, these remaining PCDD/F congeners with elevated concentrations in gaseous phase may contaminate the surface of the bag filters. In the later stable conditions, these accumulated PCDD/F congeners slowly desorbed from the contaminated filters into the gas phase, and this resulted in the elevated levels in the flue gases obtained two weeks after start-up being more dominated by higher chlorinated-substituted PCDD/F congeners.

3.5. Memory effect caused by the aged bag filters

PCDD/F congener profiles in the flue gases in front of and behind the bag filters over a four-year operation are illustrated in Fig. 3. The MSWI utilized activated carbon injection to remove the gaseous phase PCDD/Fs, while the EAFs did not. This resulted in the difference between EAFs and the MSWI in the change of PCDD/F congener profiles after flue gases passed through the aged bag filters which adsorbed an appreciable amount of PCDD/Fs. For EAFs, the fractions of the lower chlorinated-substituted PCDFs, such as 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, were elevated, due to the release of the contaminated filters of the bag filters with 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF as abundant congeners (see Fig. 1). In addition, those congeners with a higher vapor pressure than those of the higher chlorinated PCDD/F congeners lead to higher desorption into the gaseous phase.

In contrast, the MSWI exhibited increasing fractions of 1,2,3,4,6,7,8-HpCDD and OCDD after flue gases passed through its aged bag filters. This was because the activated carbon of the MSWI adsorbed more lower chlorinated-substituted PCDD/Fs in the raw flue gases, and the remaining higher chlorinated congeners gradually accumulated on the aged filters, and were released in lower PCDD/F concentration conditions.

Most of the important PCDD/F emission sources, including sinter plants, EAFs, secondary aluminum smelters, and waste incinerators, have bag filters as one of the APCDs or the only one APCD [36,37]. These important PCDD/F emission sources may all face PCDD/F memory effect caused by aged bag filters. To reduce the influence, the frequency of the operation of furnaces in unstable conditions should be reduced. Furthermore, the bag filters should be checked for the level of PCDD/F contamination by simultaneously sampling flue gases in front of and behind bag filters, when the elevated PCDD/F concentrations in the stack flue gases continuously occur in the stable and normal operation of facilities.

4. Conclusions

The gaseous phase PCDD/F concentration (mean: 0.103 ng I-TEQ Nm⁻³) in the stack flue gases of the MSWI obtained two weeks after start-up was 6.8 times higher than that (mean: 0.0151 ng I-TEQ Nm⁻³) sampled during normal conditions, revealing that the

influence of the memory effect was mainly on the gaseous phase PCDD/Fs in later stable conditions. To reduce the PCDD/F memory effect caused by bag filters, unstable combustion conditions should be avoided or at least minimized by responsible and educated operation of the facilities, and aged filters need to be replaced after a certain operational period.

Acknowledgment

The authors gratefully acknowledge Professor Cary T. Chiou for his insightful discussions related to this paper.

References

- [1] L.F. Lin, W.J. Lee, H.W. Li, M.S. Wang, G.P. Chang-Chien, Characterization and inventory of PCDD/F emissions from coal-fired power plants and other sources in Taiwan, *Chemosphere* 68 (2007) 1642–1649.
- [2] L.C. Wang, W.J. Lee, P.J. Tsai, W.S. Lee, G.P. Chang-Chien, Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from stack flue gases of sinter plants, *Chemosphere* 50 (2003) 1123–1129.
- [3] W.S. Lee, G.P. Chang-Chien, L.C. Wang, W.J. Lee, P.J. Tsai, K.Y. Wu, C. Lin, Source identification of PCDD/Fs for various atmospheric environments in a highly industrialized city, *Environ. Sci. Technol.* 38 (2004) 4937–4944.
- [4] L.F. Lin, W.J. Lee, G.P. Chang-Chien, Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from various industrial sources, *J. Air Waste Manag. Assoc.* 56 (2006) 1707–1715.
- [5] H.W. Li, W.J. Lee, K.L. Huang, G.P. Chang-Chien, Effect of raw materials on emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from the stack flue gases of secondary aluminum smelters, *J. Hazard. Mater.* 147 (2007) 776–784.
- [6] S.I. Shih, W.J. Lee, Significance of biomass open burning on the levels of polychlorinated dibenzo-p-dioxins and dibenzofurans in the ambient air, *J. Hazard. Mater.* 153 (2008) 276–284.
- [7] H.W. Li, W.J. Lee, P.J. Tsai, J.L. Mou, G.P. Chang-Chien, K.T. Yang, A novel method to enhance polychlorinated dibenzo-p-dioxins and dibenzofurans removal by adding bio-solution in EAF dust treatment plant, *J. Hazard. Mater.* 150 (2008) 83–91.
- [8] Y.C. Lai, W.J. Lee, H.W. Li, L.C. Wang, G.P. Chang-Chien, Inhibition of polychlorinated dibenzo-p-dioxin and dibenzofuran formation from the pyrolysis of printed circuit boards, *Environ. Sci. Technol.* 41 (2007) 957–962.
- [9] E.R. Altwickler, Formation of PCDD/F in municipal solid waste incinerators: laboratory and modeling studies, *J. Hazard. Mater.* 47 (1996) 137–161.
- [10] J.D. Kilgroe, Control of dioxin, furan, and mercury emissions from municipal waste combustors, *J. Hazard. Mater.* 47 (1996) 163–194.
- [11] L.C. Wang, W.J. Lee, W.S. Lee, G.P. Chang-Chien, P.J. Tsai, Effect of chlorine content in feeding wastes of incineration on the emission of polychlorinated dibenzo-p-dioxins/dibenzofurans, *Sci. Total Environ.* 302 (2003) 185–198.
- [12] R. Weber, T. Sakurai, S. Ueno, J. Nishino, Correlation of PCDD/PCDF and CO values in a MSW incinerator—indication of memory effects in the high temperature/cooling section, *Chemosphere* 49 (2002) 127–134.
- [13] L.C. Wang, H.C. Hsi, J.E. Chang, X.Y. Yang, G.P. Chang-Chien, W.S. Lee, Influence of start-up on PCDD/F emission of incinerators, *Chemosphere* 67 (2007) 1346–1353.
- [14] R. Zimmermann, M. Blumenstock, H. Heger, K. Schramm, A. Ketrup, Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: delayed emission effects, *Environ. Sci. Technol.* 35 (2001) 1019–1030.
- [15] E. Wikström, S. Ryan, A. Touati, B.K. Gullett, In situ formed soot deposit as a carbon source for polychlorinated dibenzo-p-dioxins and dibenzofurans, *Environ. Sci. Technol.* 38 (2004) 2097–2101.
- [16] K. Neuer-Etscheidt, H. Nordsieck, Y. Liu, A. Ketrup, R. Zimmermann, PCDD/F and other micropollutants in MSWI crude gas and ashes during plant start-up and shut-down processes, *Environ. Sci. Technol.* 40 (2006) 342–349.
- [17] C.J. Löthgren, B. van Bavel, Dioxin emissions after installation of a polishing wet scrubber in a hazardous waste incineration facility, *Chemosphere* 61 (2005) 405–412.
- [18] M. Giugliano, S. Cernuschi, M. Grosso, R. Miglio, E. Aloigi, PCDD/F mass balance in the flue gas cleaning units of a MSW incineration plant, *Chemosphere* 46 (2002) 1321–1328.
- [19] C.J. Löthgren, S. Andersson, Numerical modelling of the memory effect in wet scrubbers, *Chemosphere* 73 (2008) 101–105.
- [20] M. Takaoka, P. Liao, N. Takeda, T. Fujiwara, K. Oshita, The behavior of PCDD/Fs, PCBs, chlorobenzenes and chlorophenols in wet scrubbing system of municipal solid waste incinerator, *Chemosphere* 53 (2003) 153–161.
- [21] U.S. EPA Modified Method 23, Determination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from stationary sources, Code of federal regulations, Title 40, Part 60, Appendix A, 2001.
- [22] U.S. EPA Modified Method 5, Determination of particulate emission from stationary sources, Code of federal regulations, Title 40, Part 60, Appendix A, 2001.

- [23] U.S. EPA Modified Method 1613, Tetra- through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS, Office of Water Engineering and Analysis Division, 1994.
- [24] L.C. Wang, W.J. Lee, W.S. Lee, G.P. Chang-Chien, P.J. Tsai, Characterizing the emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from crematories and their impacts to the surrounding environment, *Environ. Sci. Technol.* 37 (2003) 62–67.
- [25] H. Hunsinger, S. Kreis, H. Seifert, PCDD/F behavior in wet scrubbing systems of waste incineration plants, *Chemosphere* 37 (1998) 2293–2297.
- [26] B. Adams, A. Buekens, W. Ex, J. Joannès, Dioxin emissions from a MSWI related to memory effects in a two stage wet scrubber, *Organohalogen Compd.* 46 (2000) 178–181.
- [27] R. Addink, D. Drijver, K. Olie, Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in the carbon/fly ash system, *Chemosphere* 23 (1991) 1205–1211.
- [28] M. Lasagni, E. Collina, M. Tettamanti, D. Pitea, Kinetics of MSWI fly ash thermal degradation. 1. Empirical rate equation for native carbon gasification, *Environ. Sci. Technol.* 34 (2000) 130–136.
- [29] W.S. Lee, G.P. Chang-Chien, L.C. Wang, W.J. Lee, K.Y. Wu, P.J. Tsai, Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from stack gases of electric arc furnaces and secondary aluminum smelters, *J. Air Waste Manage. Assoc.* 55 (2005) 219–226.
- [30] J. Jager, PCDD/F and PCB emission from steel producing, processing and reclamation plants with varying input, *Toxicol. Environ. Chem.* 40 (1993) 201–211.
- [31] H. Fiedler, Formation and sources of PCDD/PCDF, *Organohalogen Compd.* 11 (1993) 221–228.
- [32] L.C. Wang, Y.F. Wang, H.C. Hsi, G.P. Chang-Chien, Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes, *Environ. Sci. Technol.* 44 (2010) 1240–1246.
- [33] W.S. Lee, G.P. Chang-Chien, S.J. Chen, L.C. Wang, W.J. Lee, Y.H. Wang, Removal of polychlorinated dibenzo-p-dioxins and dibenzofurans in the flue gases by venturi scrubber and bag filter, *Aerosol Air Qual. Res.* 4 (2004) 24–34.
- [34] M.B. Chang, J.J. Lin, Memory effect on the dioxin emissions from municipal waste incinerator in Taiwan, *Chemosphere* 45 (2001) 1151–1157.
- [35] W.Y. Lin, L.C. Wang, Y.F. Wang, H.W. Li, G.P. Chang-Chien, Removal characteristics of PCDD/Fs by the dual bag filter system of a fly ash treatment plant, *J. Hazard. Mater.* 153 (2008) 1015–1022.
- [36] L. Wang, W. Lee, W. Lee, G. Chang-Chien, Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources, *Environ. Pollut.* 158 (2010) 3108–3115.
- [37] L.C. Wang, G.P. Chang-Chien, Characterizing the emissions of polybrominated dibenzo-p-dioxins and dibenzofurans from municipal and industrial waste incinerators, *Environ. Sci. Technol.* 41 (2007) 1159–1165.