

Evaluation of PCDD/Fs emission from fluidized bed incinerators co-firing MSW with coal in China

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Abstract

The levels and homologue profile of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from stack gas of three typical fluidized bed incinerators co-firing municipal solid waste (MSW) with Chinese coal were measured. The PCDD/Fs emission was in the range of 0.0054–0.1961 ng I-TEQ/N m³. Comparison of PCDD/Fs detection results by HRGC/HRMS and HRGC/LRMS suggested that it was feasible to detect fly ash with high PCDD/Fs concentration by HRGC/LRMS. Several factors on PCDD/Fs emission were discussed. The primary reason for the lower PCDD/Fs emission was the inhibition mechanism of relatively high sulfur in feeding coal on PCDD/Fs formation. The emission results also showed that there was no directly correlation between PCDD/Fs levels and CO, O₂ and HCl concentration in flue gas. It was estimated that about 0.1034 g I-TEQ was annually emitted to atmosphere from the tested three MSW incinerators (total daily treatment capacity is 800 tonnes MSW). © 2005 Elsevier B.V. All rights reserved.

Keywords: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs); Fluidized bed incinerator (FBI); Municipal solid waste (MSW); Coal

1. Introduction

Accelerated industrial development and enhanced living standards in China have led to the generation of more municipal solid wastes (MSW). Consequently, disposal of these MSW has become a serious problem with which China is currently confronted. MSW incineration has been used in some cities of China due to its advantages including significant volume reduction (about 90%), mass reduction (about 70%), and toxicity reduction of the waste and energy recovery. In 1988 the first MSW incinerator plant imported from Japan was built in Shenzhen, China. In the following years Beijing, Shanghai and other big cities have built a few MSW incineration plants. Among these incineration plants, there are three major types of MSW incineration technologies, i.e., fluidized bed (FB), stoker and rotary kiln. Most of stoker technologies are imported from abroad until now and cover more than 50% of total incineration capacity in China. In 1998 the first fluidized bed based domestic MSW incinerator (MSWI) with 150 tonnes/day developed by Zhejiang University

was built in Hangzhou, China [1]. Fluidized bed incinerators (FBI) of co-firing MSW with coal have been widely applied due to its characteristics that can deal with low heat value MSW (the heat value of MSW in most of Chinese cities is about 4200 kJ/kg) and keep stable burning. Up to 20 wt.% auxiliary coal is co-fired in the fluidized bed. There are more than 20 large scale fluidized bed incinerators (unit capacity is from 150 to 400 tonnes MSW/day) that have been commercially operated in China since 1998. Coal resource is very abundant and has relatively low price compared to oil in China. Therefore FBI technology of co-firing MSW with coal is a promising technology compared with the other current technologies in China.

MSW incineration is sometimes considered as the secondary pollution source by general public, whose concern is toxic combustion by-products (TCBs). Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are the most toxic compounds among the TCBs. Since Olie et al. reported that PCDD/Fs were present in MSWI flue gas and fly ash, the formation mechanism and control technologies of these toxic compounds have been studied intensively [2]. On the other hand, it has also been approved by Gullett et al. that co-firing MSW with coal containing sulfur can reduce PCDD/F emissions considerably [3–5]. This phenomenon has also been supported by the archival PCDD/F literature [6,7]. The emission measurements

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Table 1
The composition of MSW

Combustible matter (%)					Incombustible matter (%)			Heat value (kJ/kg)	Bulk weight (kg/l)
Kitchen waste	Paper	Plastic	Textile	Bamboo and wood	Earth ash	Metal	Glass		
64.00	4.90	10.50	2.80	1.41	13.10	1.16	2.48	4187	0.35

Table 2
The ultimate analysis of MSW and coal

	Percentage								Heat value (kJ/kg)
	C	H	O	N	Ash	H ₂ O	S	Cl	
MSW	13.72	1.91	7.75	0.35	24.14	52.00	0.12	0.54	4186
Coal	59.16	3.82	6.44	1.10	20.20	8.51	0.76	0.01	23940

from operated MSW FB incinerators in China also show that the co-firing of coal with MSW has significant suppression on PCDD/F emissions [8].

In this paper, the levels, homologue and congener distributions of PCDD/F emissions from flue gas of three FB incinerators which co-fire MSW and coal are determined. In the meantime, the difference between experimental results by two different resolution mass spectrometric methods is reported. The factors that influence PCDD/Fs emission are identified. Finally, emission estimates of PCDD/Fs from the MSW power plant are presented.

2. Experimental

The MSWI power plant mentioned in this study consists of three fluidized bed incinerators, i.e., FBI-A, FBI-B, FBI-C, each with its own air pollutant control devices (APCDs) which are composed of bag filter and semi-dry scrubber. Then, all of the flue gases from the three FBIs are induced to the same stack with a height of 60 m. The capacity of FBI-A, FBI-B and FBI-C is 200, 300 and 300 tonnes MSW/day, respectively. The ratio of MSW to coal of each incinerator is 80:20. FBI-A and FBI-B have been in commercial operation since 2002. FBI-C was put into operation after 1 year. The composition of MSW and ultimate analysis of MSW and coal used are given in Tables 1 and 2, respectively.

Sampling and quantification for PCDD/Fs in the flue gas and fly ash from bag filter are carried out according to European

Method EN 1948 and Chinese standard measurement procedure (modified version of US EPA 1613). The sampling point of FBI-A is shown in Fig. 1 and the sampling points of other two incinerators are the same. Sampling time is about 180–240 min, resulting in sampling volumes of approximately 2–3 N m³. Each of FBI was sampled twice, so the following data is the average value of two sampling times.

3. Discussion and results

3.1. PCDD/F emissions from three FBIs

Table 3 lists the results of PCDD/F emissions from three FBIs. The international toxic equivalents (I-TEQ) and the World Health Organization toxic equivalents (WHO-TEQ) are both presented in Table 3. The TEF value of 1,2,3,7,8-PeCDD, OCDD and OCDF decided by the WHO is 1, 0.0001 and

Table 3
The PCDD/Fs emissions from three FBIs

	FBI-A	FBI-B	FBI-C
I-TEQ (ng/N m ³)	0.0108	0.1961	0.0054
WHO-TEQ (ng/N m ³)	0.0117	0.2158	0.0061
PCDDs (ng/N m ³)	0.5465	7.9045	0.0618
PCDFs (ng/N m ³)	1.3985	24.5030	0.0774
PCDDs/PCDFs	0.3908	0.3226	0.7978

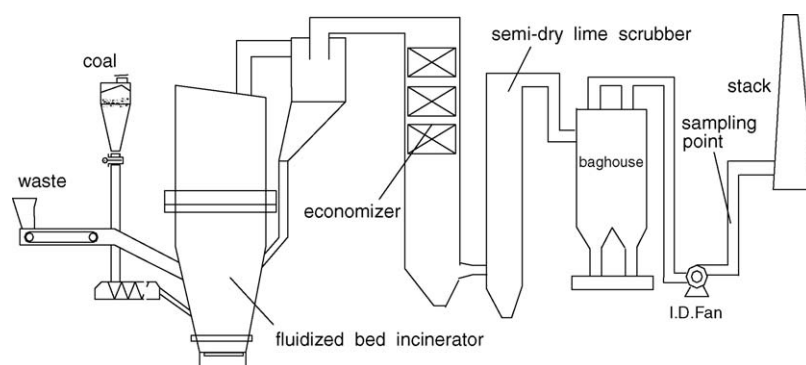


Fig. 1. The flow diagram and sampling point of FBI-A.

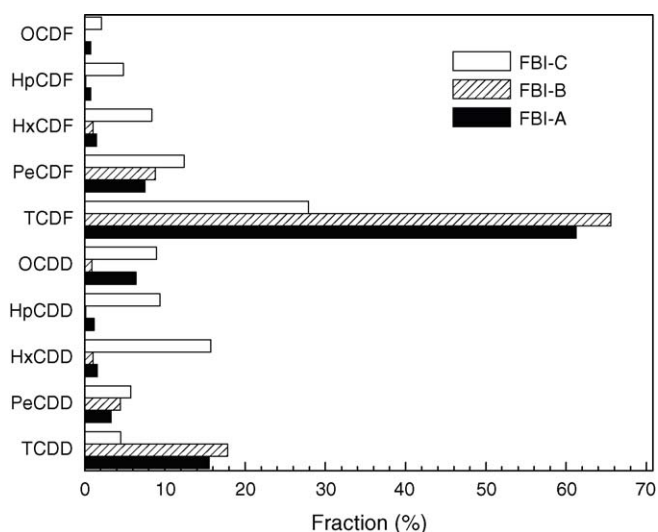


Fig. 2. The PCDD/Fs homologue profile of three FBI.

0.0001, respectively, while the TEF value of I-TEQ for the three congeners is 0.5, 0.001 and 0.001. All of the WHO-TEQ is higher than I-TEQ, which is due to the high TEF value of 1,2,3,7,8-PeCDD. The calculated I-TEQs are all greatly lower than the standard of PCDD/F emission regulation in China (1.0 I-TEQ ng/N m³). Compared with other developed countries such as USA, Germany, the PCDD/Fs emission of FBI-B is slightly higher than their standard regulations, i.e., 0.1 I-TEQ ng/N m³.

The ratios of PCDDs/PCDFs are all less than 1 for three incinerators. As shown in Fig. 2, the PCDD/Fs homologue profile of FBI-C is a little different compared with that of FBI-A and FBI-B. The reason may be resulted from the different sampling time. The concentration of PCDFs decreased with the increase of chlorine number and the concentration of PCDFs was larger than that of PCDDs, which was consistent with the PCDD/F emission performance from Korean MSW incinerators [9].

3.2. Comparison of analyzed results by HRGC/HRMS and HRGC/LRMS

The detection of PCDD/Fs in fly ash collected from bag filter of FBI-A was implemented by HRGC/HRMS and HRGC/LRMS in parallel. Table 4 and Fig. 3 give the comparison data of PCDD/Fs by the two instruments. The total I-TEQ results showed a very good fitting between HRGC/HRMS and HRGC/LRMS. The 2,3,7,8-substituted congener profiles were similar, although 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and OCDF could not be detected by HRGC/LRMS due to the detection

Table 4
The PCDD/Fs concentrations in fly ash detected by HRGC/HRMS and HRGC/LRMS

	HRGC/HRMS	HRGC/LRMS
I-TEQ (ng/g)	0.234	0.242
PCDDs (ng/g)	2.384	2.068
PCDFs (ng/g)	9.214	7.250
PCDDs/PCDFs	0.259	0.285

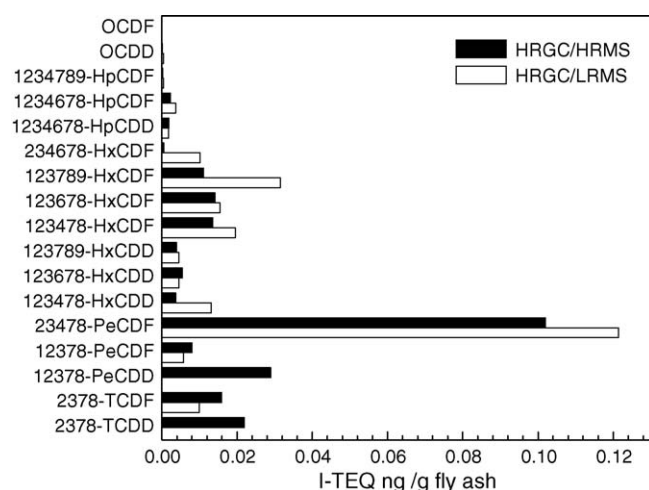


Fig. 3. The concentration of 2,3,7,8-substituted congener of fly ash detected by HRGC/HRMS and HRGC/LRMS.

limit. Thus, it is reasonable for HRGC/LRMS to detect the PCDD/Fs in high concentration of environmental samples such as fly ash and stack gas from FBI-A.

3.3. Factors on the formation of PCDD/Fs

3.3.1. Composition and property of fuel

A number of factors influence the PCDD/F emissions from MSW incinerators. Composition and property of fuel is one of the factors. It is well known that emissions of PCDD/Fs from co-firing MSW with coal are lower than those from MSW mass incineration. The major reason for the low PCDD/F emission is thought to be the relatively high sulfur to chlorine (S/Cl) ratio of coal compared to MSW. Griffin noted that the S/Cl ratio for MSW ranges between 0.286 and 0.4 while the S/Cl ratio in coal is larger than 5 [10]. Even the addition of a small quantity of coal (as little as 5 wt.%) with MSW can dramatically reduce PCDD/F emissions [4].

The ratio of S/Cl of the feeding fuel in three MSW incinerators is about 0.64 based on Table 2, which is equal to the S/Cl value in a pilot scale combustor using natural gas to which fly ash and HCl had been added [11]. The results of PCDD/F emissions from these three incinerators may support that the co-firing MSW with coal has resulted in significant reduction of PCDD/F formation.

3.3.2. Composition of flue gas

Composition of flue gas such as CO, O₂, HCl, etc. may affect PCDD/F emissions [9]. Table 5 shows the typical composition

Table 5
The main components of flue gas

Parameter	FBI-A	FBI-B	FBI-C
CO (mg/N m ³)	127.5	126.5	28.5
HCl (mg/N m ³)	13.5	33.5	23.8
SO ₂ (mg/N m ³)	110.5	178.5	70.8
O ₂ (%)	7.8	10.7	8.4

Table 6
PCDD/Fs emission from MSWIs

MSWI	PCDD/Fs emission (ng I-TEQ/N m ³)	Emission factor (ng I-TEQ/tonnes MSW)	Annual activity rate (thousand tonnes/yr)	Emission (g I-TEQ/yr)
FBI-A	0.0108	59.40	60.00	0.0036
FBI-B	0.1961	1078.55	90.00	0.0971
FBI-C	0.0054	29.70	90.00	0.0027

of flue gas from above mentioned three MSW incinerators. CO, as an indicator of efficient combustion conditions, has been used for a parameter related to PCDD/F emissions in many studies. However, there were some contradictory reports. For example, some studies showed increased PCDD/Fs emission at higher CO concentration [9]. Other studies found no significant relation between CO values and PCDD/F levels in MSWIs or pilot incinerators [12]. In this paper, CO values show a positively correlation with PCDD/F emission levels, however it is not a strong support due to few data.

O₂ is an essential parameter for the de novo synthesis of PCDD/Fs. PCDD/F formation increases with O₂ concentration between 0% and 10% [13]. Addink and Olie's research also showed that PCDD/F formation depended on O₂ level. A maximum PCDD/Fs formation was found at O₂ ≥ 5% [14]. However our results showed there was not a linear relation between O₂ and PCDD/Fs levels.

There are some papers in the literature demonstrating a relationship between Cl in the feed and PCDD/Fs formation. Almost all organic and part of inorganic chlorine is released during combustion of MSW to form HCl. So many studies focused on the correlation of HCl and PCDD/Fs concentration in flue gas. Takeshita et al. found that lower levels of HCl resulted in PCDD/Fs concentrations reduction in the stack gases of a MSW incinerator [15]. Rigo and Chandler summarized the PCDD/Fs emission data of more than 1900 waste incinerators and suggested the majority of the data showed no relationship between PCDD/Fs and HCl leaving the combustion chamber [16]. Our results also showed there was no noticeable correlation between HCl and PCDD/Fs.

3.4. Estimation of dioxin emission from the MSW incineration power plant

PCDD/Fs emission from the MSW plant with the above three FBIs can be predicted based on the data of this paper. The amount of flue gas is around 5500 N m³ per tonnes MSW burned and the operating time is 7200 h per year. Thus, estimation of annual PCDD/Fs emission can be received by the following equation:

$$\begin{aligned} & \text{Dioxin emission (g I-TEQ/yr)} \\ &= \text{emission factor (ng I-TEQ/tonnes MSW)} \\ & \quad \times \text{annual activity rate (thousand tonnes/yr)} \end{aligned}$$

The estimation of PCDD/Fs emission is described in Table 6. The emission factor of FBI-B is higher than the other two. So

the emission control technologies should be carried to reduce the PCDD/Fs emission from FBI-B.

The annual PCDD/Fs emission of this MSWI power plant is estimated to be 0.1034 g I-TEQ/yr based on the test results and calculation.

4. Conclusion

According to the emission results, all of the PCDD/F emissions from three FBIs are greatly lower than the standard of the PCDD/Fs emission regulation in China (1.0 I-TEQ ng/N m³). But the PCDD/Fs emission from FBI-B is higher than the standard regulation of some developed countries such as USA, Germany, i.e., 0.1 I-TEQ ng/N m³. The ratios of PCDDs/PCDFs are all less than 1.

It is reasonable that HRGC/LRMS can be used to detect the PCDD/Fs emission for environmental samples with high concentration such as fly ash produced from MSWI.

The primary reason for very low PCDD/Fs emission from three FBIs was the relatively high sulfur in coal that inhibited the formation of PCDD/Fs. The results also showed there was no directly correlation between PCDD/Fs levels and CO, O₂ and HCl concentration in flue gas, respectively.

It was estimated that about 0.125 g I-TEQ was annually released from the MSWI power plant with the three FBIs.

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References

- [1] X.D. Li, J.H. Yan, M.J. Ni, K.F. Cen, Study on mixing performance of municipal solid waste (MSW) in differential density fluidized beds (FBs), *Chem. Eng. J.* 84 (2001) 161–166.
- [2] K. Olie, P.L. Vermeulen, O. Hutzinger, Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace compounds of fly ash and flue gas of some municipal incinerators in The Netherlands, *Chemosphere* 6 (1977) 455–459.
- [3] B.K. Gullett, K.R. Bruce, L.O. Beach, Effect of sulfur dioxide on the formation mechanism of polychlorinated dibenzodioxin and dibenzofuran in municipal waste combustors, *Environ. Sci. Technol.* 26 (1992) 1938–1943.
- [4] B.K. Gullett, K. Raghunathan, E.D. James, The effect of co-firing high sulfur coal with municipal waste on formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, *Environ. Eng. Sci.* 15 (1998) 59–70.
- [5] B.K. Gullett, J.E. Dunn, K. Raghunathan, Effect of cofiring coal on formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans during waste combustion, *Environ. Sci. Technol.* 34 (2000) 282–290.

- [6] R.L. Lindbauer, F. Wurst, T. Prey, Combustion dioxin suppression in municipal solid waste incineration with sulfur additives, *Chemosphere* 25 (1992) 1409–1414.
- [7] H. Ogawa, N. Orita, M. Horaguchi, T. Suzuki, M. Okada, S. Yasuda, Dioxin reduction by sulfur component addition, *Chemosphere* 32 (1992) 151–157.
- [8] The Report of Institute for Thermal Power Engineering, Zhejiang University, 1999–2003.
- [9] J.E. Oh, K.T. Lee, J.W. Lee, Y.S. Chang, The evaluation of PCDD/Fs from various Korean incinerators, *Chemosphere* 38 (1999) 2097–2108.
- [10] R.D. Griffin, A new theory of dioxin formation in municipal solid waste combustion, *Chemosphere* 15 (1986) 1987–1990.
- [11] B.R. Stanmore, The formation of dioxins in combustion systems: review, *Combust. Flame* 136 (2004) 398–427.
- [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] H. Vogg, M. Metzger, L. Stieglitz, Recent finding on the formation and decomposition of PCDD/Fs in MSW incineration, *Waste Manage. Res.* 5 (1987) 285–294.
- [14] R. Addink, K. Olie, Role of oxygen in formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans from carbon on fly ash, *Environ. Sci. Technol.* 29 (1995) 1586–1590.
- [15] R. Takeshita, Y. Akimoto, S. Nito, Relationship between the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and the control of combustion, hydrogen chloride level in flue gas and gas temperature in a municipal waste incinerator, *Chemosphere* 24 (1992) 589–598.
- [16] H.G. Rigo, A.J. Chandler, Is there a strong dioxin: chlorine link in commercial scale systems? *Chemosphere* 37 (1998) 2031–2046.