

Effect of MSW source-classified collection on the emission of PCDDs/Fs and heavy metals from incineration in China

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Abstract

Municipal solid waste (MSW) source-classified collection represents a change in MSW management in China and other developing countries. Comparative experiments were performed to evaluate the effect of a newly established MSW source-classified collection system on the emission of PCDDs/Fs (polychlorinated dibenzo-*p*-dioxins and dibenzofurans) and heavy metals (HMs) from a full-scale incinerator in China. As a result of presorting and dewatering, the chlorine level, heavy metal and water content were lower, but heat value was higher in the source-classified MSW (classified MSW) as compared with the conventionally mixed collected MSW (mixed MSW). The generation of PCDDs/Fs in flue gas from the classified MSW incineration was 9.28 ng I-TEQ/Nm³, only 69.4% of that from the mixed MSW incineration, and the final emission of PCDDs/Fs was only 0.12 ng I-TEQ/Nm³, although activated carbon injection was reduced by 20%. The level of PCDDs/Fs in fly ash from the bag filter was 0.27 ng I-TEQ/g. These results indicated that the source-classified collection with pretreatment could improve the characteristics of MSW for incineration, and significantly decrease formation of PCDDs/Fs in MSW incineration. Furthermore, distributions of HMs such as Cd, Pb, Cu, Zn, Cr, As, Ni, Hg in bottom ash and fly ash were investigated to assess the need for treatment of residual ash.

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1. Introduction

With rapid economic development and urbanization in China, the quantity of municipal solid waste (MSW) generated has increased at a rate between 8% and 10% per year over the past decades [1]. Expanding MSW production could have a great effect on the environment and public health as the disposal of MSW has become a serious problem in China. Landfilling presently accounts for more than 80% of MSW disposal in China [2]. With rising landfill costs, a severe scarcity of landfill sites, and enhancement of people's environmental consciousness, the government of China has been urged to consider alternative disposal methods. Thermal treatment using incineration technology has been proven as an attractive method of MSW disposal for many years due to the primary advantages of

hygienic control, volume reduction (about 90%), mass reduction (about 70%) and energy recovery [3,4]. Thus, incineration meets the requirements of relative harmlessness, mass decrement and resource recovery. Therefore, when the first MSW incinerator plant imported from Japan was built in Shenzhen in 1988, other incineration plants were constructed in Beijing, Shanghai, Hangzhou, Zhuhai and other big cities of China in the following years. At present, more than 140 incineration plants are in operation or under construction in China [1]. In Zhejiang Province there have been 9 incineration plants constructed with a capacity of 4400 t MSW/day and 12 others designed to dispose of 6600 t MSW/day under construction [5,6]. Among incineration plants in China, there are three major types of MSW incineration technologies, i.e., stoker, fluidized bed and rotary kiln. Most stoker technologies have been imported from abroad to this point, and cover more than 50% of the total incineration capacity in China [7].

However, incineration of MSW is sometimes considered a secondary pollution source because it generates many pollutants,

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including acid gases, heavy metals (HMs) and PCDDs/Fs (Polychlorinated dibenzo-*p*-dioxins and dibenzofurans). Although various kinds of air pollution control devices (APCD) have been developed and successfully operated to ensure exhaust gases meet the environmental protection standards, concerns about PCDDs/Fs, the most toxic compounds among the toxic combustion by-products (TCBs), and HMs in flue gas and fly ash, have been increasing. It is reported that there are three major factors that affect the formation of PCDDs/Fs and the transport of heavy metals in full scale incinerators: (1) composition of the waste feed (chlorine, water, and metal content), (2) furnace design (temperature, air supply methods, residence time), and (3) the types of APCD [8]. Up to now, most studies have focused on the determination of PCDDs/Fs and HMs emission in different types of incineration plants [1,9–11]. Little is known about the effect of type of feed waste on the emission of PCDDs/Fs and HMs in incineration.

Although MSW separation has been popularized in developed countries such as Germany, United States and Japan, almost all the MSW in China is mixed, and transported directly to incineration plants without sorting and separation. Due to the lack of source-classified collection, a large amount of recyclable material is lost through combustion. Establishing a ‘recycling-based society’ is the goal for reducing natural resource consumption and lessening the environmental burden. Therefore, MSW source-classified collection for recycling represents the future direction in China and other developing countries. On the other hand, unlike most western countries, net caloric value of Chinese MSW is relatively low because of higher water content. It is reported that the heat value of MSW in most Chinese cities is only around 4200 kJ/kg [7], which barely meets the lowest caloric value needed for incineration. As a result of source-classified collection and pretreatment, it is likely that the characteristics of MSW will be altered. Any variation of MSW properties will surely affect combustion performance. However, whether the change of MSW from source-classified collection and the resultant combustion performance will pose a negative influence on the generation of hazardous pollutants such as PCDDs/Fs and HMs during incineration has not yet been clarified.

Therefore, the main objective of this study was to evaluate the effect of a newly established MSW source-classified collection in China on the generation and emission of PCDDs/Fs during MSW incineration as compared with the conventional mixed MSW. In addition, distribution of HMs in bottom ash and fly ash was also investigated. Results of the study will be helpful to assess the efficiency of the established MSW source-classified collection system on the generation and control of hazardous pollutants in MSW incineration.

2. Materials and methods

2.1. MSW source classification and collection

MSW for the experiment was collected from Wenxin district, located in the west part of Hangzhou, the capital city of Zhejiang province, China. This district has been designated as a residential

area according to municipal planning. A national pilot program has been carried out in this district to explore an MSW source separation system since March 2006. Residents in the selected communities of the district were instructed to classify the domestic waste as harmful waste, dry waste and food waste, and place them separately into proper waste containers with colors of red, blue and grey, respectively. Harmful waste included batteries, fluorescent lamps, mercury thermometers, expired medicines, and pesticides having potential hazard to human health or the environment, and was sent to a plant especially designed for hazardous waste treatment. Dry waste containing many recyclables such as waste paper, metal cans, plastic bottles, glass bottles, old clothes and shoes was transported to a separation center for further sorting. Food waste included uneaten portions of meals, and trimmings and peelings from food preparation activities in kitchens. Due to its high content of water, food waste was collected by compaction vehicles and unloaded at a transfer station where it was further dewatered.

2.2. Pretreatment of source-separated MSW

In the separation center, dry waste such as newspaper, plastics, metal, and glass were manually sorted on the drag conveyor. In order to avoid leakage of leachate, food waste was hermetically loaded and transported to the transfer station. A vertical compress machine (YJC400A, Zoomlion Heavy Industry & Science, China) was used there for dewatering. It consists of a vertical compressor, a two-box waste bin (3700 mm × 1600 mm × 1400 mm), hydraulic system, sewage discharge system, and an electric operating system. With a working pressure and time of 9.8×10^5 Pa and 10 min, respectively, food waste was compressed and dewatered mechanically. The pre-sorted dry waste and dewatered food waste were then transported together to an incineration plant. Mixed MSW for comparative research was also collected from the same communities of the district without source separation and additionally dewatered by compressive machine according to the conventional collection system. Both kinds of waste were stockpiled in the storage pit of the incineration plant for 36 h before combustion. Characteristics of the feed waste such as density, composition, moisture, combustibles, ash, heat value and chemical elements were analyzed according to the ‘sampling and physical analysis method for MSW’ [12].

2.3. Incineration facility

The comparative experiments were performed in Green Energy MSW Incineration Plant in Hangzhou (Green Energy Environmental Protection Power Co. Ltd.). The plant began to operate in 2004, and consists of three parallel stoker incinerators. Each one has its own heat recovery system and semi-dry air pollution control device (APCD). A schematic flow diagram of the incinerating facility is shown in Fig. 1. Each Mitsubishi Martin inversely-transported style incinerator with a capacity of 150 t/d was imported from Japan. The semi-dry APCD is composed of a semi-dry scrubber, activated carbon injector and a bag filter. $\text{Ca}(\text{OH})_2$ was sprayed into the semi-dry scrubber which is

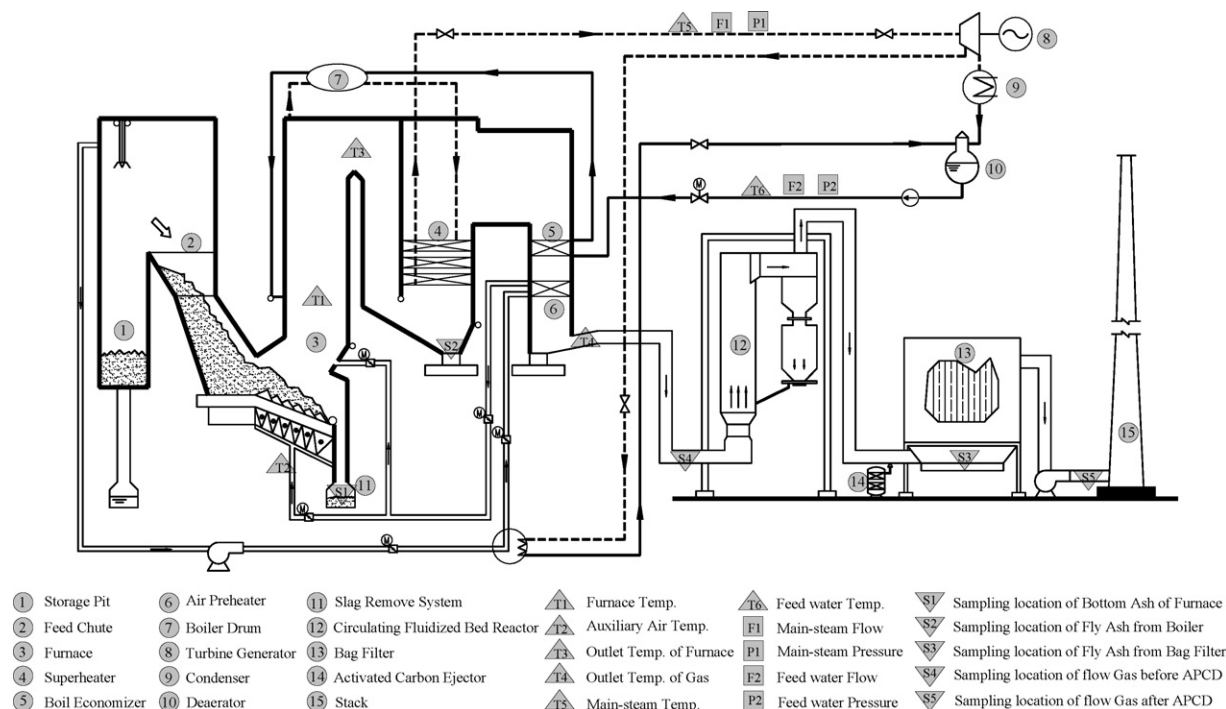


Fig. 1. System configuration of the municipal solid waste incineration process.

a circulating fluidized bed reactor. Following combustion, bottom ash is collected at the bottom of the chamber and quenched by water. After quenching, a magnetic separation is performed to recover iron and ferrous metals. The remaining residue is carried out by a drag conveyor to a chute for temporary stockpiling before loading onto disposal trucks. Fly ashes captured by the bag filter are solidified with ordinary Portland cement (OPC) and then transported to a plant where hazardous wastes are specially treated.

2.4. Combustion process analysis

More than 100 t of the classified MSW and 100 t of the mixed MSW were fed to the same stoker incinerator (150 t/d) on May 9th and May 22nd, 2006, respectively. The incinerator was continuously operated for about 10 h with an adequate supply of feed waste. The furnace temperature ($^{\circ}\text{C}$) of the incinerator representing MSW combustion temperature, and parameters of the heat recovery system including temperature ($^{\circ}\text{C}$), pressure (KPa), flow rates (m^3/h) of the main-steam and feed water were automatically recorded at a computer control center at 10 s intervals during the whole 10 h combustion process for each kind of MSW incineration. Data collected over 7 h, considered to represent the most steady operating conditions, were selected for analysis. Net energy produced from MSW incineration was calculated by subtracting total energy of feed water from total energy of main-steam during the combustion process. Net power output (Kwh) of the steam-turbine generator was also calculated according to the net energy produced and the energy conversion coefficient of the steam-turbine generator.

2.5. PCDDs/Fs emission analysis

As illustrated in Fig. 1, flue gas of the incinerator was sampled before entering the semi-dry air pollution control device and the stack flue gas was sampled at the end of the bag filter, which represented flue gas generated from combustion and flue gas treated by semi-APCD, respectively. Sampling and quantification of PCDDs/Fs in the flue gases were carried out according to US EPA Method 23 and Chinese standard measurement procedure (modified version of US EPA1613). Sampling time was about 180 min, resulting in sampling volumes of approximately 3 Nm^3 . The detection of PCDDs/Fs was implemented by HRGC/HRMS (JMS800D Japan JEOL). Chromatographic separation was carried out on a 60 m DB-5 quartz capillary column ($250 \mu\text{m}$ i.d. \times $0.25 \mu\text{m}$ film thickness). The temperature program for the GC oven was initial temperature 150°C , held for 1 min; $150\text{--}190^{\circ}\text{C}$ at $25^{\circ}\text{C}/\text{min}$ held for 2 min; $190\text{--}280^{\circ}\text{C}$ at $3^{\circ}\text{C}/\text{min}$ held for 20 min. The carrier gas was helium (99.999%) at a $1.2 \text{ ml}/\text{min}$ flow rate. The temperature of injector was 280°C . Mass spectrometer conditions were: electron impact ionization, 38 eV; ion source temperature, 280°C ; interface temperature, 280°C ; ion monitoring mode selected (SIM). All isotope standards were purchased from Wellington Laboratories, Canada and CIL, USA. Emissions of PCDDs/Fs before the APCD and after the APCD were calculated from each concentration and the flue gas volume.

2.6. HMs analysis

Bottom ashes of incinerator sampled at the bottom ash belt conveyor were slags on the grate of the incinerator (Fig. 1).

Samplings were carried out once every half hour in the 7 h that were under steady state operating conditions. Meanwhile, fly ash from boiler and bag filter were collected at the same sampling time. Bottom ash samples were magnetically separated to remove ferrous substances, then dried at 105 °C for 24 h. Concentrations of heavy metal elements in the ash, including lead, copper, zinc, chromium, nickel, arsenic and manganese, were measured by X-ray fluorescence spectrometry (XRF, ZSX 100ex). Cadmium was analyzed by atomic absorption spectrometry (AAS, SOLA ARM6). Mercury was determined by atomic fluorescence spectrometry (AFS-2202a).

3. Results and discussion

3.1. Physicochemical characteristics of feeding wastes

The compositions of the classified MSW and the comparative mixed MSW are presented in Table 1. Total content of

Table 1
Comparative analysis of the characteristics of the classified and the mixed MSW

	Classified MSW	Mixed MSW
Component (%)		
Kitchen waste	62.95	46.10
Paper	15.39	17.71
Plastics	6.83	15.61
Textiles	2.70	3.08
Bamboo and wood	0.73	0.49
Garden trimmings	0.39	0.15
Metal	0.17	1.22
Glass	0.75	1.50
Ceramics	0.04	0.16
Earth ash	10.05	13.98
Moisture (%)		
Before mechanical dewatering	63.63	57.96
After mechanical dewatering	51.73	– ^a
After stockpile dewatering	48.76	54.83
Moisture reduction rate	14.87	3.13
Bulk density (kg/m ³)		
Before mechanical dewatering	568	375
After mechanical dewatering	– ^b	– ^a
After stockpile dewatering	463	359
Bulk density reduction rate (%)	18.49	4.27
Chemical composition (on wet basis) (%)		
C	15.59	14.67
H	2.19	2.18
N	0.70	0.53
S	0.10	0.16
O	8.49	7.12
Cl	0.37	0.65
Proximate analysis (on wet basis) (%)		
Moisture	48.76	54.83
Ash	23.80	19.86
Combustibles	27.44	25.31
Heat value (kJ/kg)		
HHV	6235	5966
LHV	5043	4626

^a Not performed.

^b Not available.

incombustibles in the classified MSW decreased to 11.0% after classified collection. Due to the artificial sorting in the separation center, significant decreases of plastics, metal and glass were observed. In contrast, the content of kitchen waste was increased from 46.1% to 63.0%.

Table 1 shows the variations in the properties of both kinds of MSW after dewatering. Due to the removal of metal, glass and plastic materials which contain little water and the increase of high moisture kitchen waste, water content and bulk density of the stock classified MSW were both higher than that of the corresponding stock mixed MSW. On the other hand, source classification and collection facilitated the dewatering of waste. In comparison to a 3.13% moisture reduction rate for the mixed MSW through stockpiling, a considerably higher moisture reduction rate for the stock classified MSW was found, amounting to 14.87% through vertical compressing and stockpiling. As a result, water content of the dewatered classified MSW declined to 48.76%, which was lower than that of the dewatered mixed MSW. Although bulk density of the classified MSW decreased significantly after dewatering, it was still higher than that of the mixed MSW, as the porosity of the dewatered classified MSW was relatively lower.

Elemental and heat value analyses of the dewatered classified MSW and the dewatered mixed MSW for incineration are listed in Table 1. Chlorine content in the dewatered classified MSW was significantly lower than that in the dewatered mixed MSW, attributed to the removal of a large amount of plastics and soluble chloride such as NaCl [13], KCl [14] contained in food waste through dewatering. Although plastics which contain high levels of calories were reduced, the lower heat value (LHV) of the dewatered classified MSW was increased to 5043 kJ/kg, which was higher than that of the comparative mixed MSW and other MSW reported in China [7]. The result indicated that water removal played a significant role in improving heat value of the classified MSW.

3.2. Evaluation of combustion process

Table 2 illustrates the operating conditions for the incineration of both kinds of MSW during the most stable 7 h combustion. The highest furnace temperature was observed during the incineration of the dewatered classified MSW. Although the auxiliary air temperature was relatively lower, the average temperature of the dewatered classified MSW incinerator was 1035.92 °C, which was 32.71 °C higher than that of the dewatered mixed MSW.

On the basis of temperature, pressure, and flow of main-steam produced over the most stable incineration period, total main-steam energy generated by combustion of the dewatered classified MSW was higher than that of the dewatered mixed MSW. Conversely, the total feed water energy of the water supply system over the incineration of the dewatered classified MSW during that period was lower. As a result, net energy produced from the dewatered classified MSW incineration during the same period of time was higher than that of the dewatered mixed MSW incineration. Con-

Table 2
Operating conditions for the incineration of the classified and the mixed MSW

	Classified MSW		Mixed MSW	
	Range	Average	Range	Average
T1 (°C)	969.85–1101.96	1035.92	942.04–1064.26	1003.21
T2 (°C)	249.44–269.14	260.67	271.72–284.27	280.21
T3 (°C)	220.08–238.82	230.79	234.92–247.41	243.56
T4 (°C)	154.21–176.57	162.97	149.16–183.58	161.72
T5 (°C)	395.46–417.56	404.17	399.61–409.36	405.95
P1 (KPa)	3.25–3.51	3.37	3.34–3.41	3.38
F1 (m ³ /h)	9.30–14.81	12.09	10.60–14.69	12.66
T6 (°C)	104.35–119.38	115.52	99.69–121.98	111.57
P2 (Kpa)	5.02–5.72	5.37	5.27–5.86	5.61
F2 (m ³ /h)	3.02–18.81	14.27	6.40–20.00	14.87
Total main-steam energy (kJ)	282,193,436.06		280,372,596.01	
Total feed water energy (kJ)	42,601,842.50		49,123,879.35	
Net power output of steam-turbine generator (Kwh)	13,256.70		12,795.09	

sequently, according to the accumulative net power output of the steam-turbine generator, incineration of the dewatered classified MSW could produce 65.90 Kwh more power in an hour.

3.3. PCDDs/Fs in flue gas before APCD

Table 3 summarizes data for PCDD/F generation and emission from the incineration of both kinds of MSW. Detected before the APCD, the concentration of PCDD/Fs in flue gas generated from the incineration of the classified MSW was about 73.80 ng/Nm³, which was significantly lower than that (132.99 ng/Nm³) in flue gas of the mixed MSW incineration. The ratios of PCDFs/PCDDs were higher than 1 for both flue gases, but the ratio was 3.66 in flue gas of the classified MSW incineration, significantly higher than that in flue gas of the mixed MSW incineration. This indicated that combustion of the classified MSW generated much less PCDDs compared to the mixed MSW. PCDD/F homologue profile of MSW incineration flue gas is shown in Fig. 2(a). The concentrations of PCDFs were larger than those of PCDDs in flue gas generated from the incineration of both kinds of MSW. Among PCDFs, penta-, hexa- and hepta-PCDFs were dominant, and the content of penta-PCDFs in flue gas of the classified MSW incineration amounted to 26.1% of total doxins. Concentrations of PCDDs decreased with the decrease of chlorine number in flue gas from both kinds of MSW incineration.

The international toxic equivalent quantity (I-TEQ) of the flue gas generated from the classified MSW incineration was 9.28 ng I-TEQ/Nm³, which represented only 69.4% of that of the mixed MSW incineration (13.38 ng I-TEQ/Nm³). However, as shown in Fig. 2(b), 2,3,7,8-substituted congener profiles in both flue gases were similar. The I-TEQ of 2,3,4,7,8-PeCDF was the highest in both flue gases, mainly due to its high toxic equivalent factor (TEF) value (0.5). Although the TEF value for 2,3,7,8-TCDD has the maximum of 1.0, this congener could not be detected in either flue gas by HRGC/HRMS due to the detection limit for analysis. Nevertheless, the I-TEQs of the other

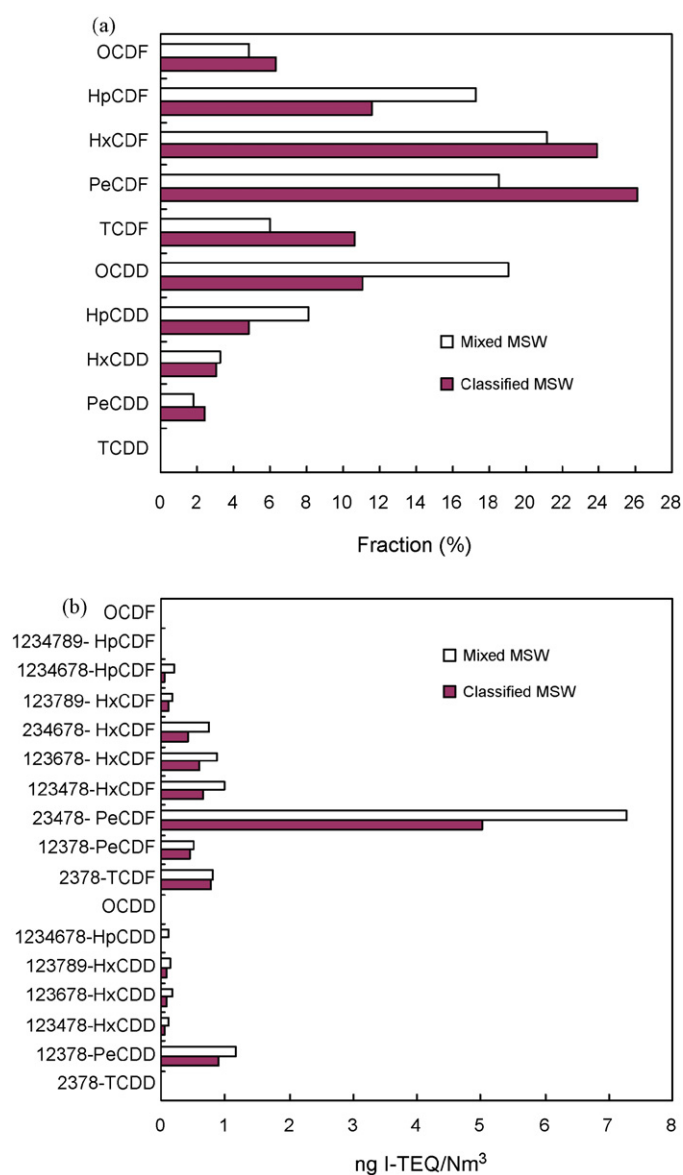


Fig. 2. PCDD/F homologue profile of flue gas generated from combustion of the classified MSW and the mixed MSW.

Table 3
Comparison of PCDDs/Fs in the flue gases of MSW incineration

	Classified MSW		Mixed MSW	
	Before APCD	After APCD	Before APCD	After APCD
Sampling time	11:30–13:20	14:45–17:00	11:50–13:40	15:00–17:00
Volume of flue gas (Nm ³ /h)	49,600	28,300	28,900	59,500
Volume of O ₂ (Vol.%)	6.70	8.60	10.30	9.30
CO (mg/Nm ³)	7.90	8.90	12.30	10.50
I-TEQ (ng/Nm ³)	9.28	0.12	13.38	0.10
PCDDs/Fs (ng/Nm ³)	73.80	1.18	132.99	1.27
PCDDs (ng/Nm ³)	15.85	0.53	42.76	0.79
PCDFs (ng/Nm ³)	57.95	0.65	90.23	0.48
PCDFs/PCDDs	3.66	1.23	2.11	0.61
Activated carbon consumption (kg/h)	4.0		5.0	
Activated carbon absorption efficiency (ng PCDDs/Fs/g activated carbon)	906.78		753.55	

2,3,7,8-substituted congeners in flue gas of the classified MSW incineration were all less than those in flue gas of the mixed MSW incineration.

As described previously, characteristics of feed waste is one of the factors influencing the formation of PCDDs/Fs during MSW incineration. Up to now, many studies on the effect of the total chlorine content in the waste on the formation of PCDDs/Fs have been conducted [8,15]. Some studies found a correlation while others did not [15], but recent research has tended to recognize the correlation between chlorine content in the waste and the formation of PCDDs/Fs [8]. An increased PCDDs/Fs formation rate was noted when the level of chlorine in the waste exceeded 1%, while no correlation existed when the level was below 1% [15]. Wang et al. [8] suggested that the threshold value of chlorine level in the waste was at 0.8–1.1%. However in this paper, combustion of the classified MSW with chlorine content below 0.4% showed a marked decrease of PCDDs/Fs formation in comparison with the mixed MSW, and chlorine content in the waste showed a positive correlation with the formation of PCDDs/Fs.

Besides chlorine content, composition of the flue gas, such as O₂ and CO content, which influences MSW incineration performance, may also affect PCDDs/Fs emission [16]. PCDDs/Fs formation depends on O₂ level [17], and O₂ is an essential parameter controlling the de novo synthesis of PCDDs/Fs [7,18]. PCDDs/Fs formation increases with O₂ concentration between 0% and 10% [19], and a maximum formation was found at O₂ ≥ 5% [18]. Our results showed there was a linear relationship between O₂ and PCDDs/Fs levels. The classified MSW incineration generated lower PCDDs/Fs at relatively lower O₂ level, compared with the mixed MSW incineration. CO, which has been used as an indicator of efficient combustion conditions, is a parameter related to PCDDs/Fs emission in many studies. Results of the classified MSW incineration showed decreased PCDDs/Fs formation at lower CO concentration, which was consistent with data on PCDDs/Fs formation efficiency in some literature [16]. Therefore, the results demonstrated that the established MSW source classified collection system could be conducive to reducing PCDDs/Fs formation in MSW incineration.

3.4. PCDDs/Fs in flue gas treated by APCD

After treatment by the APCD, concentrations of PCDDs/Fs in stack flue gases resulting from classified MSW and mixed MSW incineration decreased dramatically to 1.18 and 1.27 ng/Nm³, respectively (Table 3). Similar PCDDs homologue profiles in APCD treated flue gases of both kinds of MSW incineration were also observed (Fig. 3(a)). However, the PCDFs homologue profiles in stack flue gases were changed after APCD treatment. The total percentage of dioxins as PCDFs in stack flue gas of the classified MSW incineration was close to that of PCDDs (PCDFs/PCDDs = 1.23). In contrast, the fraction of total dioxins as PCDFs in stack flue gas of the mixed MSW incineration was lower than that of PCDDs (PCDFs/PCDDs = 0.61), probably related to the differential retention of dioxin congeners by the absorbent used in APCD.

Concentrations of 2,3,7,8-substituted congeners in both stack flue gases are displayed in Fig. 3(b). Although the total concentration of PCDDs/Fs in stack flue gas of the classified MSW incineration was lower than that of the mixed MSW incineration (Table 3), the calculated I-TEQ was slightly higher due to the high TEF value of 2,3,4,7,8-PeCDF. The I-TEQs of the stack flue gases resulting from the classified MSW and the mixed MSW incineration were 0.12 and 0.10 ng I-TEQ/Nm³, respectively, which were both significantly lower than the standard for PCDD/F emission regulation in China (1.0 ng I-TEQ/Nm³) [20].

3.5. Removal efficiency of PCDDs/Fs

Applying activated carbon to adsorb gaseous PCDDs/Fs has become a common practice for removing PCDDs/Fs from flue gas [21]. Due to the lower content of PCDDs/Fs in flue gas generated from the classified MSW incineration, the quantity of activated carbon injected in the APCD was lessened to 4.0 kg/h (cut down by 20%), as compared with that of the mixed MSW incineration (Table 3). Although the consumption of activated carbon decreased, removal efficiencies of PCDD/F homologues in flue gas generated from the classified MSW incineration all exceeded 97% after treatment by the bag filter, which were higher than those of the corresponding PCDD/F homologues in flue gas resulting from the mixed MSW incineration. In con-

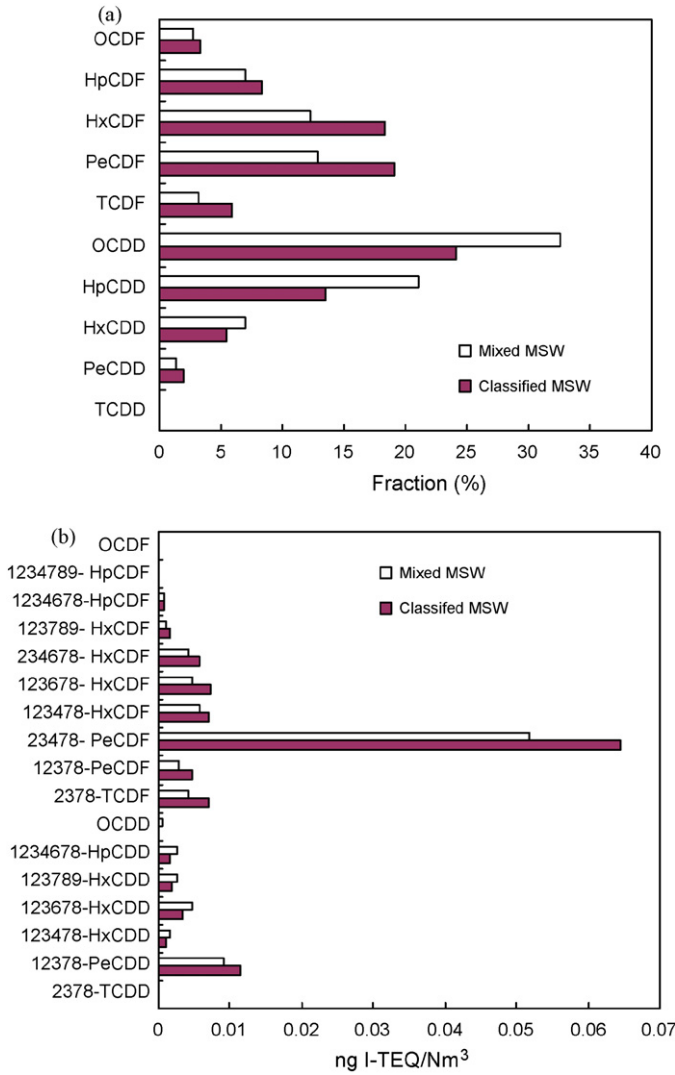


Fig. 3. PCDD/F homologue profile of stack flue gas after treated by APCD.

trast, removal efficiencies of the hexa-, hepta- and octa-PCDDs were lower than those of penta-PCDDs and other PCDFs, as shown in Fig. 4. The calculated adsorption efficiency of activated carbon for PCDD/F removal in flue gases of the classified MSW incineration was 906.78 ng PCDDs/Fs/g activated carbon, which was higher than that of the mixed MSW incineration (Table 3). Additionally, it was found that the adsorption ability of the activated carbon for PCDD/F homologues increased with the increase of chlorination level in PCDDs, but decreased with the increase of chlorination level in PCDFs with the exception of 1,2,3,4,6,7,8-HpCDF and OCDF (Fig. 4). These results indicated that incineration of the classified MSW could enhance the removal efficiency of PCDDs/Fs by APCD and consequently reduce the consumption of activated carbon and lime.

3.6. PCDDs/Fs in fly ash from bag filter

Large amounts of pollutants such as PCDDs/Fs and HMs are transferred into fly ash in the process of fabric filtration coupled with activated carbon injection for adsorption of PCDDs/Fs [1]. Therefore, in China, the fly ash is classified as hazardous waste and requires special treatment [20].

As shown in Fig. 5(a), PCDFs comprised a larger fraction of total dioxins than PCDDs in fly ashes generated by the incineration of both kinds of MSW. The ratios of PCDFs/PCDDs in fly ashes from the classified MSW and the mixed MSW incineration were 2.14 and 2.42, respectively (Table 4), which were close to the values of typical MSW incinerators in China [1,9,22], as well as in some other countries [11,23]. The concentration of the 2,3,7,8-substituted congener in fly ashes is shown in Fig. 5(b). Although the concentration of the most toxic congener, 2,3,7,8-TCDD, in flue gases from the classified MSW and mixed MSW incineration was below the detection limit, it could be enriched in the fly ash and consequently contribute substantially to the I-TEQ. The I-TEQ of fly ash produced by the incineration of the

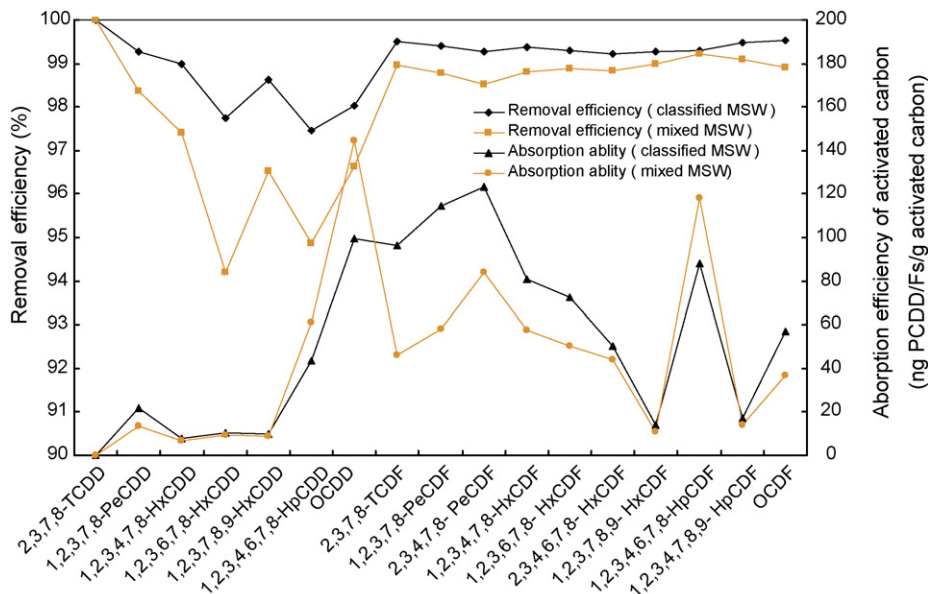


Fig. 4. Comparative removal efficiency of PCDD/F homologue in flue gases after treated by APCD (2,3,7,8-TCDD not be detected).

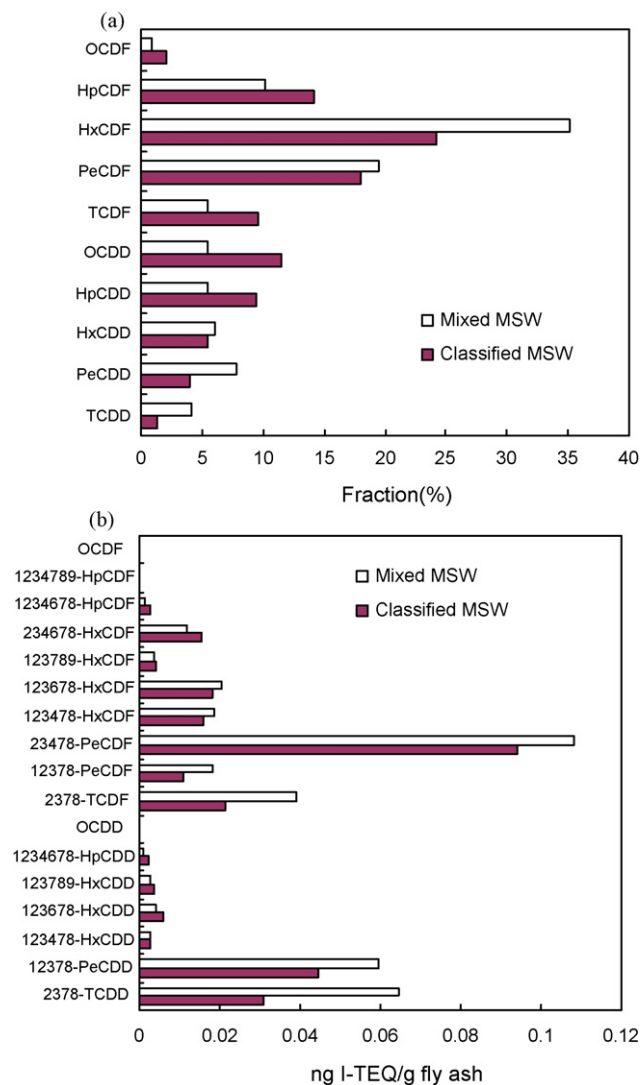


Fig. 5. PCDD/F homologue profile of fly ashes from bag filter.

classified MSW was 0.27 ng I-TEQ/g, which was lower than that of the mixed MSW incineration (0.36 ng I-TEQ/g). The levels of PCDDs/Fs in fly ash of both the classified MSW and the mixed MSW incineration examined herein were lower than those from the stoker and fluidized bed type incinerators in China, and were close to contents of the fly ashes in some developed countries as shown in Table 5.

Dioxin concentrations of fly ash are not mentioned in current Chinese regulations, such as the ‘environmental quality standard for soils’ [27] and the ‘standard for pollution control at secure

Table 5
Concentrations of PCDDs/Fs in fly ashes captured by bag filter from literatures

Country or region	Furnace type ^a	APCD ^b	PCDDs/Fs (ng I-TEQ/g Fly ash)
China	Stoker	DA	1.52 [22]
		(lime) → ACI → FF → stack	
	Stoker	SDA	0.98–1.5 [9]
		(lime) → ACI → FF → stack	
	Stoker	FF (AC) → stack	7.53 [22]
		SDA → ACI → FF → stack	0.73–4.32 [24]
	TIFB	SDA	0.80 [1]
		(lime) → ACI → FF → stack	
	Stoker	DA	0.46 [6]
		(lime) → ACI → FF → stack	
Stoker	DA	2.68 [6]	
	(lime) → ACI → FF → stack		
Stoker	DA → ESP → stack	0.52 [6]	
	CFB	DA	0.90 [6]
CFB	(lime) → ACI → FF → stack		
	DA	0.14 [6]	
Taiwan	Stoker	DA → FF → stack	0.26–2.53 [25]
		FF → stack	0.47–2.3 [11]
Korea	–	ESP or FF → stack	0.13–21 [26]

^a TIFB, twin internal fluidized bed; CFB, circulated fluidized bed.

^b SDA, semidry absorption; DA, dry absorption; FF, fabric filter; ACI, activated carbon injection; AC, activated carbon; ESP, electrostatic precipitator.

landfill sites for hazardous wastes’ [28]. However, the dioxin concentration in the fly ashes generated from the incineration of the classified MSW and the mixed MSW in the experiment both met the environmental quality standards for soil (<1.0 ng I-TEQ/g) specified by the ‘law concerning special measures against dioxin’ in Japan [29].

3.7. Distribution of HMs in residues

MSW incineration residues including bottom ash, heat recovery ash, fly ash, etc. are generated at different points in the process of MSW incineration [4]. Pollutant elements such as As, Cd, Cu, Cr, Ni, Pb, Zn and Hg have been identified in such residues [2]. Levels of HMs are affected by feeding waste composition and combustion history [30], including furnace type, capacity, furnace temperature and so on [31]. Concentrations of HMs in bottom ash, fly ash from boiler, and fly ash from bag filter are shown in Table 6. Concentrations of HMs such as Pb, Cd, Zn, As and Hg in fly ashes generated from the incineration of the classified MSW and the mixed MSW were all significantly higher than those in bottom ashes. In the combustion process, these volatile metals could largely transfer from the feeding waste and become enriched in the fly ash. On the other hand, Cu, Cr, Ni, and Mn mainly existed in bottom ash.

Generally, volatilization of metals increases with furnace temperature. Therefore, volatile metals such as Cd, Pb, Zn, and As are expected to have higher transfer rates to fly ash as furnace temperature increases [30]. Although comparative research was performed in the same incineration facility, owing to the continuously higher temperature in the incinerator furnace during incineration of the classified MSW, Cd, Pb, Cu, Zn, Cr, As and

Table 4
Comparison of PCDDs/Fs in fly ash from bag filter

	Classified MSW	Mixed MSW
I-TEQ (ng/g fly ash)	0.27	0.36
PCDDs/Fs (ng/g fly ash)	2.23	1.54
PCDDs (ng/g fly ash)	0.71	0.45
PCDFs (ng/g fly ash)	1.52	1.09
PCDFs/PCDDs	2.14	2.42

Table 6
Analyses of HMs in bottom ashes and fly ashes (mg/kg)

	Classified MSW			Mixed MSW		
	Bottom ash	Fly ash from boiler	Fly ash from bag filter	Bottom ash	Fly ash from boiler	Fly ash from bag filter
Pb	283	415	1416	321	344	1169
Cd	0.77	6.40	57	0.71	5.70	17
Cu	373	316	261	289	189	160
Zn	1406	2665	2274	1527	3053	2084
Cr	221	212	79	238	186	70
Ni	49	70	24	53	72	40
Mn	768	1286	251	744	1047	253
As	92	73	267	114	64	222
Hg	0.06	0.10	7.70	0.16	0.11	4.80

Hg concentrations in fly ash from the bag filter were all higher than those of the mixed MSW incineration. In addition, concentrations of Mn, Ni and Zn in fly ashes from the boiler were significantly higher than bottom ash and fly ash from the bag filter. Enrichment of heavy metals in fly ash may be advantageous where fly ash is to be treated specially as hazardous waste.

Since bottom ash generated from MSW incineration is identified as non-hazardous waste and widely used as construction materials, lower concentrations of HMs in bottom ash are required for its application in the environment. Compared to the mixed MSW incineration, concentrations of Pb, Zn, Ni, As, Cr, Hg in the bottom ash of the classified MSW incineration were lower, which was probably due to the reduction of metals in the feed waste by source classification.

4. Conclusions

MSW source-classified collection represents an advance in waste management in China and other developing countries. The effect of the newly established MSW source-classified collection on PCDDs/Fs and HMs in flue gas and ash generated from full-scale incinerator in China were investigated in this study. As a result of presorting and dewatering, chlorine level, heavy metal and water content were lower, but heat value was higher in the classified MSW as compared with the mixed MSW. Due to the changes in the characteristics of the feed waste, particularly a lower chlorine level and effects on the operating conditions of the combustion process such as temperature and O₂, PCDDs/Fs in flue gas generated from the classified MSW incineration were significantly lower than those from the mixed MSW incineration. Although the quantity of activated carbon injected in the APCD for the classified MSW incineration was reduced, the final emission of PCDDs/Fs into the environment complied with the 'standard for pollution control on the municipal solid waste incineration' in China, and the level of PCDDs/Fs in fly ash from the bag filter was lower than that from other incinerators in China. These results indicated that the newly established MSW-classified collection method could be conducive to reducing PCDD/F formation and emission in MSW incineration.

Moreover, although comparative research was performed in the same incineration facility, owing to the changes in feed waste and combustion conditions, it was found that levels of Cd, Pb,

Cu, Zn, Cr, As and Hg in fly ash were significantly higher for classified MSW incineration. On the other hand, concentrations of Pb, Zn, Ni, As, Cr, Hg in bottom ash of the classified MSW incineration were relatively lower. These results suggested that MSW source-classified collection enriched HMs in fly ash which then required special treatment as hazardous waste, but reduced HMs in bottom ash which could be used as secondary building materials.

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References

- [1] R.S. Bie, S.Y. Li, H. Wang, Characterization of PCDD/Fs and heavy metals from MSW incineration plant in Harbin, *Waste Manage.* 27 (2007) 1860–1869.
- [2] M. Li, J. Xiang, S. Hu, L.S. Sun, S. Su, P.S. Li, X.X. Sun, Characterization of solid residues from municipal solid incinerator, *Fuel* 83 (2004) 1397–1405.
- [3] Y.H. Chang, W.C. Chen, N.B. Chang, Comparative evaluation of RDF and MSW incineration, *J. Hazard. Mater.* 58 (1998) 33–45.
- [4] J.M. Chimenos, M. Segarra, M.A. Fernandez, F. Espiell, Characterization of the bottom ash in municipal solid waste incinerator, *J. Hazard. Mater. A* 64 (1999) 211–222.
- [5] P.L. S Gu, Current situation and prospect of solid waste treatment in Zhejiang Province, in: The 2nd China–Korea joint Symposium on Incineration/Pyrolysis and environmental Management, Hangzhou, China, 2006.
- [6] T. Chen, et al., Characteristic of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fly ash from incinerators in China, *J. Hazard. Mater.* 150 (2008) 510–514.
- [7] J.H. Yan, T. Chen, X.D. Li, J. Zhang, S.Y. Lu, M.J. Ni, K.F. Cen, Evaluation of PCDD/Fs emission from fluidized bed incinerators co-firing MSW with coal in China, *J. Hazard. Mater. A* 135 (2006) 47–51.
- [8] 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.
- [9] P.J. He, H. Zhang, C.G. Zhang, D.J. Lee, Characteristics of air pollution control residues of MSW incineration plant in Shanghai, *J. Hazard. Mater. B* 116 (2004) 229–237.

- [10] B. Febrellas, P. Sanz, E. Abad, J. Rivera, The Spanish dioxin inventory Part I: incineration as municipal waste management system, *Chemosphere* 43 (2001) 683–688.
- [11] H.B. Chang, Y.T. Chung, Dioxin content in fly ashes of MSW incineration in Taiwan, *Chemosphere* 36 (9) (1998) 1959–1968.
- [12] Ministry of construction of China, Sampling and physical analysis method for MSW, CJ/T 3039-1995, 1995.
- [13] T. Takasuga, T. Makino, K. Tsubota, N. Takeda, Formation of dioxins (PCDDs/PCDFs) by dioxin-free fly ash as a catalyst and relation with several chlorine-sources, *Chemosphere* 40 (9–11) (2000) 1003–1007.
- [14] R. Addink, B.V. Bavel, R. Visser, H. Wever, P. Slot, K. Olie, Surface catalyzed formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans during municipal waste incineration, *Chemosphere* 20 (10–12) (1990) 1929–1934.
- [15] E. Wikstrom, G. Lofvenius, C. Rappe, S. Marklund, Influence of level and form of chlorine on the formation of chlorinated dioxins, dibenzofurans, and benzenes during combustion of an artificial fuel in a laboratory reactor, *Environ. Sci. Technol.* 30 (1996) 1637–1644.
- [16] J.E. Oh, K.T. Lee, J.W. Lee, Y.S. Chang, The evaluation of PCDD/Fs from various incinerators, *Chemosphere* 38 (1999) 2097–2108.
- [17] H.-J. Zhang, et al., Influence of variation in the operating conditions on PCDD/F distribution in a full-scale MSW incinerator, *Chemosphere* 70 (2008) 721–730.
- [18] 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.
- [19] 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.
- [20] State Environmental Protection Administration of China, Standard for pollution control on the municipal solid waste incineration, GB18485-2001, 2001.
- [21] M.B. Chang, J.J. Lin, S.H. Chang, Characterization of dioxin emissions from two municipal solid waste incinerators in Taiwan, *Atmos. Environ.* 36 (2002) 279–286.
- [22] Y.Y. Jin, H.H. Tian, Y.F. Nie, H.M. Yin, Y. Hai, Z.S. Chen, Dioxins contents in fly ash of MSW incinerator in three city, *Environ. Sci.* 24 (3) (2003) 21–25.
- [23] O. Hutzling, H. Fiedler, From source to exposure: some open questions, *Chemosphere* 27 (1–3) (1993) 121–129.
- [24] J.H. Feng, P.J. He, H. Zhang, L.M. Shao, Distribution of dioxin-like compounds in air pollution control residues from municipal solid waste incinerator, *China Environ. Sci.* 25 (6) (2005) 737–741.
- [25] Y.C. Ling, P.C.C. Hou, A Taiwanese study of 2,3,7,8-substituted PCDD/Fs and coplanar PCBs in fly ashes from incinerators, *J. Hazard. Mater.* 58 (1998) 83–91.
- [26] K.J. Shin, Y.S. Chang, Characterization of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls, and heavy metals in fly ash produced from Korean municipal solid waste incinerators, *Chemosphere* 38 (11) (1999) 2655–2666.
- [27] State Environmental Protection Administration of China, Environmental quality standard for soils, GB15618-1995, 1995.
- [28] State Environmental Protection Administration of China, Standard for pollution control at secure landfill sites for hazardous wastes, GB18598-2001, 2001.
- [29] Ministry of the Environment, Informational brochure dioxins 2001, Japan. <http://www.env.go.jp/en/topic/dioxin/brochure2001.pdf>.
- [30] C.H. Jung, T. Matsuto, N. Tanaka, T. Okada, Metal distribution in incineration residues of municipal solid waste (MSW) in Japan, *Waste Manage.* 24 (2004) 381–391.
- [31] F.Y. Chang, M.Y. Wey, Comparison of the characteristics and bottom and fly ashes generated from various incineration processes, *J. Hazard. Mater.* B138 (2006) 594–603.