Journal of Hazardous Materials 161 (2009) 800–807

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Polychlorinated dibenzo-*p*-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries

Jenshi B. Wang[a], Chung-Hsien Hung[b,*], Chung-Hsuang Hung[c], Guo-Ping Chang-Chien[b]

[a] *Department of Chemical Engineering, I-Shou University, 1 Section 1, Syuecheng Road, Dashu, Kaohsiung County 840, Taiwan, ROC*
[b] *Department of Chemical and Materials Engineering, Cheng Shiu University, 840 Chengching Road, Kaohsiung 833, Taiwan, ROC*
[c] *Department of Safety, Health and Environmental Engineering. National Kaohsiung First University of Science and Technology, University Road, Yanchau, Kaohsiung 824, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 7 January 2008
Received in revised form 8 April 2008
Accepted 8 April 2008
Available online 15 April 2008

Keywords:
Dioxin
Metallurgical industry
Congener profile
Emission factor
Industrial park

ABSTRACT

Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from an industrial park operated as Taiwan's center of metallurgical industries were investigated. The characteristics of mean PCDD/F I-TEQ concentrations, congener profiles and emission factors of each source were studied over samples of stack flue gases of individual sources. Different characteristics of congener profiles and large variations of emission factors of secondary aluminum smelters (ALSs) were observed. The mean emission factors of electric arc furnaces were comparable to those for ALSs and much greater than those of municipal solid waste incinerators and sinter plants, but still less than that of clinical waste incinerators. Annual PCDD/F emission contribution of each source was estimated, raising critical concerns over the overall PCDD/F emissions from metallurgical processes. The metallurgical industries altogether contributed ~98.1% of the total annual emissions, while waste incinerators only 1.9%. The contributions by sinter plants and metallurgical industries to the total annual emissions of the Park were much higher than the corresponding national averages of Taiwan. The combined dioxin emissions from the entire metallurgical processes and their controls should be seriously envisaged by industrial parks devoted to metal productions.

1. Introduction

Since polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) were discovered in the stack flue gases and fly ash of municipal solid waste incinerators (MSWIs) in 1977 [1], PCDD/F emissions from various sources have raised serious concerns globally because of their toxicological effects and adverse health implications. PCDD/Fs released to the atmosphere are mainly from anthropogenic activities, particularly from combustion or other thermal processes involving organic matters and chlorine. These include waste incineration, power/energy generation, metallurgical processes and many other chemical–industrial processes.

Among various PCDD/F emission sources, MSWIs have been recognized as the most significant sources of dioxin release to the environment in many industrialized countries. In the UK, the US and Japan, emissions from MSWIs remain as a major source of PCDD/Fs from the industrial sectors, responsible for 30–56, 38 and 87%, respectively, of the total emissions [2–4]. Nevertheless, emissions from other thermal industrial processes have been found to contribute a sizable proportion of dioxin emissions and, hence, have attracted much attention in the past years. According to a report by the Ministry of Environment of Japan, metallurgical processes of electric arc furnaces (EAFs), sinter plants and aluminum smelters (ALSs) also play important roles in PCDD/F emissions, accounting for 6, 3.2 and 0.6%, respectively of the total value [4]. Quaß et al. [5] revealed that on the European scale emissions from sinter plants accounted for 19.6% of total emission, quite closely following the largest emission of 28% from MSWIs. Studies undertaken in the UK reported that the metal sector (sinter plants, iron and steel, and non-ferrous metals) in total contributed about 15–26% of emissions in the late 1990s [2,6].

In this regard, it even deserves more attention toward metallurgical processes in Taiwan. Compared with other countries, MSWIs in Taiwan are larger in size and newer in pollution control technologies, and the enacted emission limit (0.1 ng I-TEQ/N m^3) is among the most stringent in the world. Consequently, the emission contribution from MSWIs is quite low. Lee et al. [7] found that, compared with other emission sources in Taiwan, the total PCDD/Fs emissions from EAFs and secondary ALSs are 27 and 24

* Corresponding author. Tel.: +886 7 7351275; fax: +886 7 7332204.
E-mail address: jurry@csu.edu.tw (C.-H. Hung).

0304-3894/$ – see front matter.
doi:10.1016/j.jhazmat.2008.04.026

Table 1
Basic information of the stationary emission sources in the Industrial Park

Emission sources	Denotation	Feeding rate (T/h)	Auxiliary fuels	APCDs (operating temperature (°C))	Average temperature of stack gas (°C)	Average stack gas flow (N m^3/h)
Large municipal solid waste incinerator	MSWI1	16.4		DS[a] (245), FF[b] (159), ACI[c]	156	119,634
Medium/small airport waste incinerator	MSWI2	1.0		FF[b] (166), ACI[c]	155	5,848
Industrial waste incinerator, steel plant	IWI	4.1	LNG, 450 L/h	FF[b] (180), ACI[c]	163	22,262
Clinical waste incinerator	CWI	0.45	Diesel, 23.5 L/h	DS[a] (150), FF[b] (150), ACI[c]	92	5,160
Coke plant	Coke	219.3	Coke oven gas, 53268 N m^3/h		176	338,235
Secondary aluminum smelters	ALS1	1.6	Light oil, 104 L/h	FF[b] (70–90)	46	82,701
	ALS2	7.1	Heavy oil, 0.68 T/h	FF[b] (40–170)	265	27,380
Electric arc furnace (stainless steel)	EAF1	51.9	Kerosene, 693.8 L/h	FF[b] (65–90)	62	4,014
Electric arc furnaces (carbon steel)	EAF2	89.4		FF[b] (90–102)	79	343,920
	EAF3	86.9		FF[b] (94–105)	73	508,390
	EAF4	82.9		FF[b] (90–101)	89	3,131
	EAF5	24.4		FF[b] (60–70), CO converter	59	2,585
Sinter plants	Sinter1	373.4	Coke breeze, 12.28 T/h	EP[d] (85), SCR[e] (320)	177	502,735
	Sinter2	568.5	Coke breeze, 25.58 T/h	EP[d] (70)	124.	945,353
	Sinter3	713.2	Coke breeze, 30.74 T/h	EP[d] (105), SCR[e] (320)	182	1,308,788
	Sinter4	746.3	Coke breeze, 29.04 T/h	EP[d] (155), SCR[e] (320)	203	1,108,185
Secondary copper smelter	COP	8.4		FF[b] (40–60)	47	40,268

[a] DS is the dry scrubber.
[b] FF is the fabric filter.
[c] ACI is the activated carbon injection.
[d] EP is the electrostatic precipitator.
[e] SCR is the selective catalytic reduction.

times, respectively, higher than those from MSWIs, and are 44 and 40%, respectively, of the emissions from sinter plants. Considering that feeding materials, air pollution control devices (APCDs) and operating conditions involved in metallurgical industries may vary substantially by plants and by countries, more attention should be paid to the emissions from these sources.

The Lin-Hai Industrial Park is located in the Hsiao-Kang District of Kaohsiung, a highly industrialized city in southern Taiwan. The District which covers an area of 39.86 km^2 (about 25.9% of the City of Kaohsiung) is inhabited by approximately 150,000 residents. Since the Park was established in 1980s, it has been planned and operated as the center of metallurgical industries in Taiwan. In view of so many sources of dioxin existing in the densely populated District, the characteristics of I-TEQ and congener profiles of PCDD/F emissions from 17 stationary sources (MSWIs, industrial waste and clinical waste incinerators, coke plant, sinter plants, EAFs, and secondary aluminum and copper smelters) in the Park were studied by analyzing stack flue gases of individual sources as part of a comprehensive monitoring survey in Kaohsiung undertaken by the Taiwan Environmental Protection Agency. The objectives of this study were to present and elucidate information obtained on the emission factors of different sources, and to discuss the annual PCDD/F contributions and raise critical concerns to address the collective PCDD/F emissions from metallurgical processes in an industrial park devoted to metal productions.

2. Experimental

2.1. PCDD/F sampling

Table 1 gives the basic information of the 17 stationary emission sources studied in the Lin-Hai Industrial Park. All these facilities except MSWI1 were operated intermittently. Three stack flue gas samples were taken from each of the facilities except MSWI1, from which five samples were collected. For MSWI1, the sampling was conducted at least 1 month after start-up to avoid memory effect.

The stack flue gas of each selected facility was sampled isokinetically for PCDD/Fs by an accredited laboratory in Taiwan according to the US EPA-modified method 23. The sampling train adopted in this study is comparable to that specified by US EPA-modified method 5. Before sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF. Each sampling was conducted during the batch or continuous operation of the process and lasted for about 3 h. To ensure free contamination of the collected samples, trip blanks and filed blanks were also taken during field sampling. Details are similar to that given in Wang et al. [8].

2.2. Analyses of PCDD/Fs

Analyses of the stack gas samples followed the US EPA-modified method 23. All the chemical analyses were conducted in the Super Micro Mass Research and Technology Center of Cheng Shiu University, currently the only laboratory accredited for PCDD/F analyses in Taiwan. Standard procedures were strictly followed for the analyses. A high-resolution gas chromatograph coupled with a high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/F analyses. The HRGC (Hewlett Packard 6970 Series, CA, USA) was equipped with a DB-5MS fused silica capillary column (60 m, 0.25 mm ID, 0.25 μm film thickness; J&W Scientific, CA, USA) and with a splitless injection. Helium was used as the carrier gas. The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with a resolving

Table 2
Mean PCDD/F concentrations (ng/N m^3) in the stack flue gases of the emission sources

	PCDDs	PCDFs	PCDD/PCDF ratio	Total PCDD/Fs		Total I-TEQ	
				Mean	RSD (%)	Mean	RSD (%)
MSWI1	0.545	0.652	0.861	1.20	14.5	0.0844	45.0
MSWI2	0.340	1.31	0.269	1.65	35.3	0.239	40.2
IWI	0.619	1.11	0.637	1.73	45.5	0.225	64.9
CWI	1.47	7.98	0.190	9.45	16.8	1.64	23.0
Coke	0.0832	0.0808	1.062	0.164	27.1	0.00870	45.9
ALS1	0.139	0.399	0.443	0.538	60.4	0.0568	89.2
ALS2	0.226	0.258	0.902	0.485	37.8	0.0440	46.3
EAF1	0.123	1.84	0.0852	1.96	58.7	0.342	57.3
EAF2	0.870	4.94	0.176	5.81	5.6	0.757	5.09
EAF3	0.521	2.56	0.205	3.08	28.4	0.473	33.5
EAF4	0.254	0.909	0.280	1.16	14.6	0.148	16.9
EAF5	1.63	5.16	0.315	6.80	13.8	0.666	14.3
Sinter1	0.812	4.45	0.813	5.26	54.7	0.657	56.1
Sinter2	0.354	1.64	0.215	1.99	23.9	0.233	28.5
Sinter3	0.878	2.59	0.341	3.47	12.0	0.277	27.0
Sinter4	0.293	0.790	0.251	0.983	20.0	0.137	27.2
COP	1.74	2.33	0.784	4.07	49.9	0.310	52.5

power of 10,000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. The method detection limits of PCDD/Fs for the flue gas samples were found to be between 0.286 and 12.728 pg. The recoveries of PCDD/F surrogate standards ranged from 87 to 105%, meeting the criteria within 70–130%. Details of analytical procedures are given in Wang et al. [8].

3. Results and discussion

3.1. PCDD/F concentrations in stack flue gases of emission sources

In this study, five stack flue gas samples were taken from MSWI1, while three flue gas samplings were conducted for each of the rest batch facilities. As a result, mean PCDD/F concentrations and I-TEQ values in stack flue gases of these emission sources are displayed in Table 2. For these PCDD/F concentrations, the corresponding relative standard deviations (RSDs) were not high because each of the mean PCDD/F concentrations was based on flue gas samples taken for each facility for which no differences in feeding materials and operating conditions were involved.

PCDD/F concentrations obtained in this study for MSWI1, MSWI2 and clinical waste incinerator (CWI) were 0.0844, 0.239 and 1.64 ng I-TEQ/N m^3, respectively, which are quite comparable to those reported by Lee et al. for MSWIs (0.0237–0.105 ng I-TEQ/N m^3) and CWI (0.0403–1.22 ng I-TEQ/N m^3) [9]. Higher concentration of MSWI2 emission reflects the fact that the feed, operating condition and air pollution control devices of this medium/small airport waste incinerator are different from those of large municipal solid waste incinerator of MSWI1, which, due to its elevated capacity, is highly regulated and adopts the best available dioxin removal technologies. The stack flue gas of a steel plant waste incinerator, IWI, was sampled and analyzed, providing a PCDD/F concentration of 0.225 ng I-TEQ/N m^3, which is lower than the emission limit of 0.5 ng I-TEQ/N m^3 regulated for medium/small waste incinerators by Taiwan Environmental Protection Agency.

The concentrations obtained for secondary ALSs (0.044–0.0568 ng I-TEQ/N m^3) were quite low compared with that of 0.02–21.5 ng I-TEQ/N m^3 by Fiedler [10] and that of Lee et al. [7] ranging from 0.041 to 40.1 ng I-TEQ/N m^3. The work of the latter reported a very high RSD of 260%, which was attributed to the wide variations of feeding materials (scrap metals contaminated by PVC plastics and cutting oils), operating conditions of furnaces and APCDs of different plants [7]. As for EAFs studied, their PCDD/F concentrations falling in the range of 0.148–0.757 ng I-TEQ/N m^3 were also parallel to the values of 0.02–0.1 ng I-TEQ/N m^3 obtained by Jager [11] and 0.041–0.83 ng I-TEQ/N m^3 by Lee et al. [7], but much lower than those reported by Fiedler (0.7–9.2 ng I-TEQ/N m^3) [10]. Furthermore, the concentrations of 0.137–0.657 ng I-TEQ/N m^3 for sinter plants were close to those reported by Wang et al. (0.995–3.10 ng I-TEQ/N m^3) [12], and by Anderson and Fisher [13], but were lower than the values of 3–10 ng I-TEQ/N m^3 by Lahl [14] and Jager [11].

3.2. Congener profiles

The congener profiles of the 2,3,7,8-subtituted PCDD/Fs have long been selected as the signatures of emission sources. Fig. 1 displays the congener profiles of the 17 PCDD/Fs detected from stack flue gases of the emission sources studied. Each selected congener was normalized by reference to the total weight of all 2,3,7,8-congners. The "*n*" in the figure stands for the number of stack flue gas samples taken from each source.

Fig. 1 clearly shows that the flue gas of the large-scale MSWI1 was dominated by low toxicity-equivalent OCDD and 1,2,3,4,6,7,8-HpCDD, which accounted for around 27.9 and 12.3%, respectively, of the total concentration of the targeted compounds in MSWI1. These profiles were very different from that of MSWI2, in which 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF were the major congeners. Nevertheless, the congener profile of MSWI1 is similar to those of Lee et al. [15] and US EPA [16] for large-scale MSWIs. In this regard, the profile of the CWI was predominated by PCDFs, mostly 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, which, however, are different from those obtained by Lee et al. [15]. The latter reported that OCDD and 1,2,3,4,6,7,8-HpCDD were among the major congeners. The differences in the characteristics of the profiles may have resulted from variations in the feeding materials between these two CWIs.

As for the secondary aluminum smelters, the major congeners in the stack flue of ALS1 were OCDD, OCDF, 2,3,4,7,8-PeCDF and 2,3,7,8-TeCDF, whereas in ALS2 OCDD, 1,2,3,4,6,7,8-HpCDD were the leading contributors, responsible for 19.7 and 16.9%, respectively, of the total concentration. Different characteristics of these profiles can be ascribed to the variation of involved feeding materials because the feed of ALS1 comprising aluminum scraps, crude and pure ingots, silicon, and copper scraps was more complex than that of ALS2, which only consisted of aluminum scraps and alloying agents. The congener profile of ALS1 is similar to the smelter category of A5, A6 and A7, and that of ALS2 corresponds to the category of A1 and A2 in the work of Lee et al. [7]. In addition, the congener profile of ALS2 is also comparable to those of Aittola et al. [17] and Buekens et al. [18]. According to Lee et al. [7], types of APCD, operating conditions or consumption rates of fuel seem to have very limited effect on the congener profiles of ALSs. Rather, variations of scrap metal feeds might account for the disparity of their profiles.

Fig. 1 also shows that the most abundant congeners from EAF making stainless steel (EAF1) were 2,3,7,8-TeCDF, followed by 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDF, whereas congeners 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF dominated the profiles of the carbon steel making electric arc furnaces (EAF2-5). Different congener profiles were found in either category of steel mills. This may be attributed to the differences in the complex mixture of feeding scrap metals because manufacture of stainless steel requires scraps with less impurity and contamination than that of carbon steel. Nevertheless, congener profiles for EAF2-5 correspond to those obtained by Hofstadler et al. for carbon steel EAFs [19].

Further examination of Fig. 1 also reveals that the profiles for EAF1 and EAF2-5 are parallel, respectively, to those reported by Lee et al. [7].

As illustrated in Fig. 1, 1,2,3,4,6,7,8-HpCDF and 2,3,4,7,8-PeCDF were the major congeners in the stack flue gases of Sinters 1, 2 and 4, while in Sinter3 OCDF, OCDD and 1,2,3,4,6,7,8-HpCDF were the most plentiful ones. These congener profiles of sinter plants are similar to those presented in other work [13]. Finally, the stack flue gas of the secondary copper smelter of the Park (COP) was comprised mainly of the congeners 1,2,3,4,6,7,8-HpCDF and OCDD, while OCDD, OCDF and 1,2,3,4,6,7,8-HpCDF were the most important congeners from the coke plant (Coke).

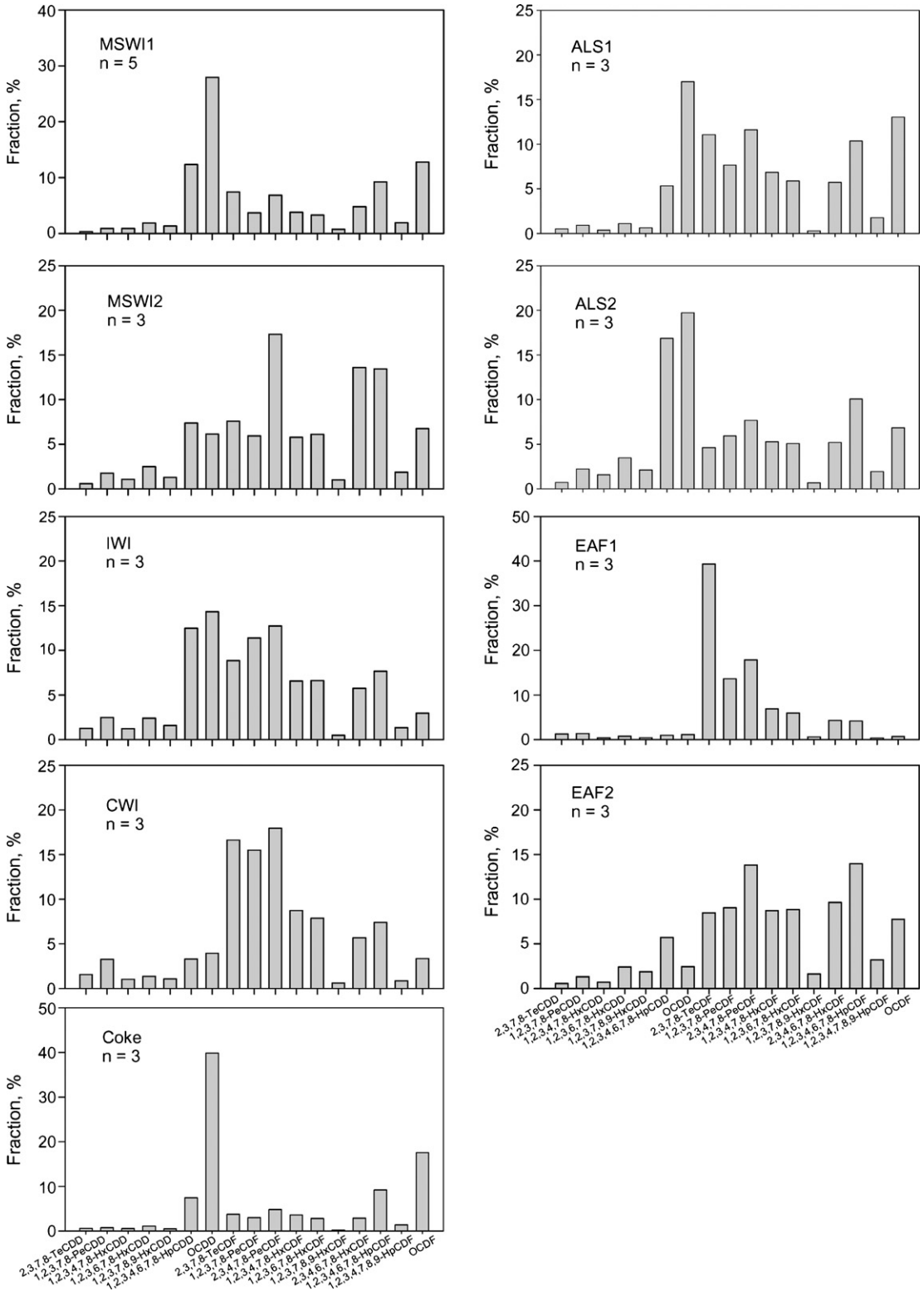

Fig. 1. Congener profiles of stationary emission sources in the Industrial Park.

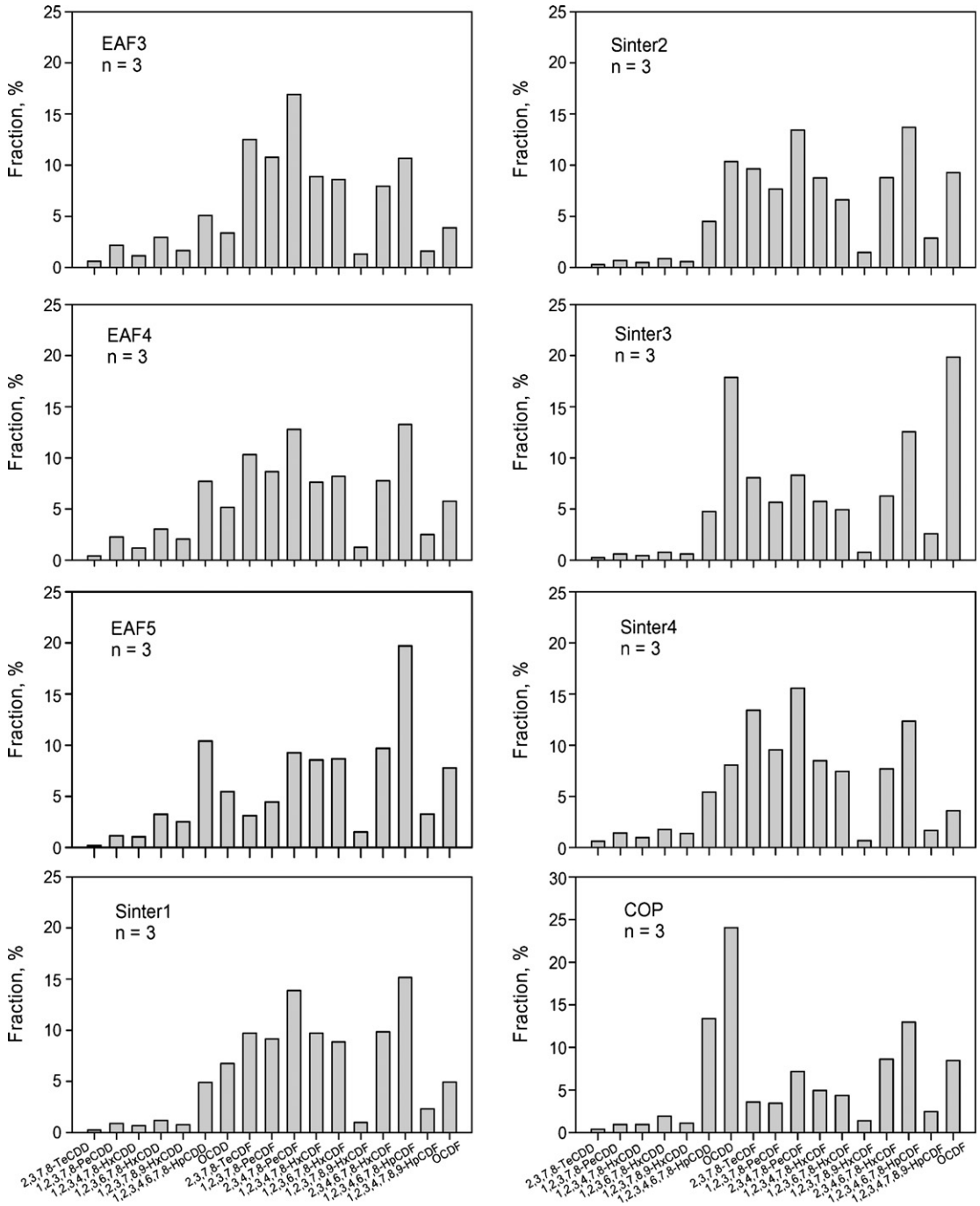

Fig. 1. (*Continued*).

3.3. Emission factors

Table 3 lists the mean emission factors of PCDD/Fs from the stack gases of the emission sources in the Park. These factors are based on the total weights of waste, excluding fuels, for solid waste incinerators, or on the total weights of feedstock, including scraps or iron ore and other additives for the rest of emission sources. It is interesting to note that the mean emission factor of the CWI (16.7 μg I-TEQ/ton waste) was much higher than those of the municipal solid waste incinerators MSWI1 and MSWI2 (1.21, 0.874 μg I-TEQ/ton waste, respectively). This can be attributed to the fact that normally clinical waste incinerators are small and batch-operated with low combustion efficiency and without advanced APCDs, as well as are usually mixed up with PVC in their waste feedstock. The emission factors of CWIs and MSWIs (new plants) in the United Kingdom are 20–200 and 0.8 μg I-TEQ/ton waste, respectively [6] which are either higher than or comparable to our studies. It is of interest also to compare our emission factors of MSWIs (1.21, 0.874 μg I-TEQ/ton waste) with those in the literature. According to Caserini and Monguzzi [20], the 1997 average emission factor from the MSWIs in Lombardy Region, Italy was 22 μg I-TEQ/ton waste, which was 40 times higher than that of 0.6 μg I-TEQ/ton waste if considering the 1998 national legislative establishing 0.1 ng I-TEQ/N m^3 as limit of PCDD/Fs flue gas concentration and a specific flue gas production of about 6 N m^3/kg MSW. Giugliano et al. [21] reported a very low emission factor of 0.17 μg I-TEQ/ton waste for an MSWI (400 ton/day), which was

Table 3
Mean PCDD/F emission factors (μg/ton waste or feedstock) and their corresponding relative standard deviations (RSDs) of the emission sources

	Total PCDD/Fs		Total I-TEQ	
	Mean	RSD (%)	Mean	RSD (%)
MSWI1	17.0	14.4	1.21	45.7
MSWI2	6.02	35.3	0.874	40.4
IWI	6.02	48.3	0.785	67.8
CWI	96.0	7.83	16.7	18.4
Coke	0.253	26.7	0.0134	46.1
ALS1	26.4	49.8	2.72	79.8
ALS2	0.935	36.4	0.0848	44.5
EAF1	20.6	58.7	3.59	57.3
EAF2	23.0	6.20	3.00	5.77
EAF3	17.5	27.8	2.68	32.8
EAF4	10.4	14.6	1.33	16.9
EAF5	77.7	13.8	7.61	14.3
Sinter1	6.95	56.2	0.869	57.7
Sinter2	2.27	7.8	0.265	22.3
Sinter3	6.42	8.72	0.510	23.3
Sinter4	1.26	20.7	0.177	27.2
COP	9.64	48.0	0.735	50.2

operated based on the best control technologies, though. As for the industrial waste incinerator of this research, the emission factor (0.785 μg I-TEQ/ton waste) of IWI was lower than that of 3.83 μg I-TEQ/ton waste obtained by US EPA for hazardous waste incineration [3].

As depicted in Table 3, the emission factors of the two secondary ALS1 and ALS2 were 2.72 and 0.0848 μg I-TEQ/ton feedstock, respectively. The large variation of these emission factors can be ascribed, as elucidated above, to the differences of involved feeding materials of the two smelters. It should be noted that the emission factors of secondary ALSs of this study are lower than or comparable to those reported in the literature. US EPA 2000 report provided emission factors falling in the range of 0.26–36.03 (mean: 21) μg I-TEQ/ton for the'low end' and 'more worst' cases [22]. Umweltbundesamt [23] tested 11 facilities with emission factors ranging from 0.01 to 167 (mean: 42) μg I-TEQ/ton. Among these facilities, three had emission factors exceeding 100 μg I-TEQ/ton feedstock, and two had less than 1 μg I-TEQ/ton feedstock. Quaβ et al. [24] presented 22 μg I-TEQ/ton as the typical emission factor for the European Dioxin Inventory. The wide range of emission factors of this work agree with those found in the literature, pointing out the complexity of feeding materials, and varied operating conditions of furnaces and APCDs employed by secondary aluminum smelters. Thus, it is not feasible to generalize a universal emission factor for ALSs. Moreover, it is known that the high emission factors of some secondary ALSs are due to their low furnace operating temperatures (650–750 °C), which would result in incomplete combustion of impurities in the feedstock.

The emission factors of EAFs of this study ranging from 1.33 to 7.61 μg I-TEQ/ton feedstock are higher than the values of 1.15 and 0.6–1.7 μg I-TEQ/ton feedstock obtained, respectively, by Umweltbundesamt [23] and by Tysklind et al. [25] (batch charging with scrap contaminated with cutting oils or containing PVC plastics), but are lower than the emission factor of 0.7–10 μg I-TEQ/ton feedstock by Eduljee and Dyke for 'no chlorine' and 'high chlorine' operational conditions [6]. Based on these data, 0.6 and 10 μg I-TEQ/ton feedstock may be taken as emission factors representative of 'low emission' and 'high emission', respectively, for EAFs. Furthermore, it is worthwhile to note that the emission factor of the stainless steel EAF1 (3.59 μg I-TEQ/ton feedstock) was only slightly lower than those of the carbon steel EAF2–5 (mean: 3.66 μg I-TEQ/ton feedstock), and the latter were just about lower than that obtained from a local stainless steel EAF of different locality (2.92–10.6, mean: 6.38 μg I-TEQ/ton feedstock) [26]. It reveals that, in general, feeding scraps for EAFs in Taiwan, including the ones making stainless steel, are rather diverse in their sources and compositions, containing high impurities and contaminations. As a result, compared with other PCDD/F sources in the Park, the mean emission factors for EAFs were comparable to that for ALSs and much greater than those for MSWIs and sinter plants, but were still less than that for CWI.

Compared with the data in the literature, the emission factors of sinter plants of this work (0.177–0.869 μg I-TEQ/ton feedstock) are comparable to the 0.547 μg I-TEQ/ton feedstock of LTV Steel (160 ton/h feeding rate, with scrubber as APCD), but lower than the 4.14 μg I-TEQ/ton feedstock of Youngstown Sinter Company (90 ton/h feeding rate, bag house as APCD) [3] and the 1.2–9.0 μg I-TEQ/ton feedstock of the sinter plants in the UK [6].

The emission factor of 0.0134 μg I-TEQ/ton feedstock obtained for the coke plant in the Park is rather low compared with that of 0.23 μg I-TEQ/ton feedstock by Bremmer et al. [27]. The latter reported also a very low emission factor of 0.002 μg I-TEQ/ton feedstock in a case of minimal PCDD/F air emissions for flue gases generated during charging and emptying of coke ovens. As for the secondary copper smelter studied, its emission factor of 0.735 μg I-TEQ/ton feedstock is closer to the 0.005–1.56 μg I-TEQ/ton of a German reverberatory furnace, and lower than the factor of 5.6–110 μg I-TEQ/ton feedstock for shaft furnaces/converters in Germany, but higher than those (0.024 and 0.04 μg I-TEQ/ton feedstock) of two smelter and casting furnaces in Sweden in which relatively clean scarp was used as input [28]. A report by AGES [29] provided an emission factor of 16618 μg I-TEQ/ton feedstock for a facility processing low-purity copper-bearing scrap, telephone switch gear and slags, as well as higher copper content materials.

3.4. Annual PCDD/F contributions of emission sources

Based on statistical data of Taiwan EPA [30] and operational records of each tested facility, as well as the mean emission factors obtained in this study, the annual total emission of PCDD/Fs and percentage contribution of each of the emission sources in the Park were estimated according to the following formula given by US EPA [16], as are listed in Table 4.

$$E_{\text{total}} = \sum \text{EF} \times A$$

where E_{total} is the annual emission from each facility (g I-TEQ/year), EF the mean emission factor of each facility, A the activity measure for the tested facility. Although the contribution of PCDD/Fs from the CWI to the atmosphere was only 11.6% of that from MSWIs, it should be noted that CWIs are normally installed with low stacks so that PCDD/F emissions from CWIs could substantially affect the ambient environment. It is of significance to learn from the table that sinter plants is the leading emission source in the Park, followed by EAFs, contributing ~55.4 and 41.1%, respectively, to the total annual emissions, despite more stringent regulations on dioxin emissions from EAFs and sinter plants were enacted in 2004 and 2005. The metallurgical industry as a whole amounted collectively to ~98.1% of the total annual emissions, while the category of waste incinerators accounted for only 1.9%. The total emission from metallurgical industries was ~61.6 times higher than that from MSWIs (MSWI1 and MSWI2). It deserves to note here that the contributions by sinter plants and metallurgical industries in the Park were 55.4 and 98.1%, respectively, much higher than the national averages of 11.7 and 65.5%, respectively, of Taiwan [31]. These results clearly demonstrate that metallurgical processes are the major PCDD/F emission sources in the Park rather than MSWIs,

Table 4
Annual PCDD/F emissions (g I-TEQ/year) and % contributions by the emission sources in the Park

	Estimated emission	Emission of each category	% Contribution of each category	% Contribution of greater category
Waste incinerators				
MSWI1	0.236	0.241	1.60	1.87
MSWI2	0.00491			
IWI	0.0140	0.0140	0.0928	
CWI	0.0281	0.0281	0.186	
Metallurgical industries				
Coke	0.0890	0.0890	0.590	
ALS1	0.0957	0.101	0.669	
ALS2	0.00518			
EAF1	2.349			
EAF2	0.937			
EAF3	0.950	6.203	41.11	
EAF4	0.677			98.13
EAF5	1.29			
Sinter1	2.79			
Sinter2	1.29	8.36	55.40	
Sinter3	3.13			
Sinter4	1.15			
COP	0.0534	0.0534	0.354	
Total	15.089	15.089	100	100

which are so highly regulated and monitored that their contributions are insignificant. This ranking of emission sources in PCDD/F inventory is quite different from the rest of Taiwan and from those found in other countries. Current regulations in Taiwan on EAFs and sinter plants are 5 and 2 ng-TEQ/N m^3, respectively, but were not in effect before 2004 and 2005. Considering stringent emission limit has already been enforced on large MSWIs (0.1 ng I-TEQ/N m^3 for continuously operating ones), it is imperative for industrial parks as this one clustered with metallurgical industries to enforce a tighter local emission limit on EAFs and sinter plants in order to reduce total PCDD/F emissions further. It becomes apparent that clustering metallurgical facilities in a single industrial park may look good economically, but may lead to excessive dioxin emissions unexpected initially, thereby imposing high health risks to residents.

4. Conclusions

The characteristics of PCDD/Fs emissions from various stationary sources in an industrial park operated as the 'center of metal production' in Taiwan were studied. As a result, information on the mean PCDD/F I-TEQ concentrations in the stack gases, as well as congener profiles and emission factors of each source was determined and presented.

The different characteristics of congener profiles and large variation of emission factors of the secondary ALSs were ascribed to the discrepancies of involved feeding materials to the smelters. The emission factor of PCDD/Fs for the CWI was found to be much greater than those of the municipal solid waste incinerators. While the annual PCDD/F contribution by the CWI was only 11.6% of that by MSWIs, CWIs could adversely affect surroundings since they are usually installed with low stacks. Emission factors obtained from stainless steel EAFs both in the Park and in another location were only comparable to those of carbon steel EAFs. It reveals that feeding scraps for EAFs in Taiwan, including stainless steel ones, are rather diverse in source and composition. Compared with other PCDD/F sources in the Park, the mean emission factors for EAFs were comparable to those for ALSs and much greater than those of MSWIs and sinter plants, but still less than that of CWI.

Sinter plants has been found as the top emission source in the Park, followed by EAFs, contributing ~55.4 and 41.1%, respectively, to the total emissions. The entire metallurgical industry contributed ~98.1% of the total annual emissions, while waste incinerators accounted for only 1.9%. The contributions by sinter plants and metallurgical industries in the Park, i.e., 55.4 and 98.1%, were much higher than the national averages of 11.7 and 65.5%, respectively, of Taiwan. Even though concentrating metallurgical industries in a park may be benefited from business clustering, the resulting collective dioxin emissions and control are among the most important issues that should be seriously addressed. Therefore, industrial parks like this one should either give high priority to enforcing more stringent local emission limits on metallurgical industries or implement a total amount control of dioxin emissions.

References

[1] K. Olie, P.L. Vermeulen, O. Hutzinger, Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands, Chemosphere 6 (1977) 455–459.
[2] R.E. Alcock, R. Gemmill, K.C. Jones, Improvements to the UK PCDD/F and PCB atmospheric emission inventory following an emission measurement programme, Chemosphere 38 (1999) 759–770.
[3] US EPA, Database of sources of environmental releases of dioxin like compounds in the United States, EPA/600/C-01/012, 2001.
[4] Japan Ministry of the Environment, The environmental monitoring report on the persistent organic pollutants (POPs) in Japan, 2002, pp. 40–55.
[5] U. Quaß, M.W. Fermann, G. Bröker, Steps towards a European dioxin emission inventory, Chemosphere 40 (2000) 1125–1129.
[6] G.H. Eduljee, P. Dyke, An updated inventory of potential PCDD and PCDF emission sources in the UK, Sci. Total Environ. 177 (1996) 303–321.
[7] 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.
[8] L.C. Wang, W.J. Lee, W.S. Lee, G.P. Chang-Chien, P.J. Tsai, Characterizing the emission of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from crematories and their impacts to the surrounding environment, Environ. Sci. Technol. 37 (2003) 62–67.
[9] W.S. Lee, G.P. Chang-Chien, L.C. Wang, W.J. Lee, P.J. Tsai, C.K. Chen, Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from the incinerations of both medical and municipal solid wastes, Aerosol Air Qual. Res. 3 (2003) 1–6.
[10] H. Fiedler, Formation and sources of PCDD/PCDF, Organohalog. Comp. 11 (1993) 221–228.
[11] J. Jager, PCDD/F and PCB emission from steel producing, processing and reclamation plants with varying input, Toxicol. Environ. Chem. 40 (1993) 201–211.
[12] 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 gases of sinter plants, Chemosphere 50 (2003) 1123–1129.
[13] D.R. Anderson, R. Fisher, Sources of dioxins in the United Kingdom: the steel industry and other sources, Chemosphere 46 (2002) 371–381.
[14] U. Lahl, Sintering plants of steel industry––the most important thermal PCDD/F source in industrialized regions, Organohalog. Comp. 11 (1993) 311–314.
[15] 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.
[16] US EPA, The inventory of sources of dioxin in the United States, EPA/600/P-98/002Aa, 1998.
[17] J.P. Aittola, J. Paasivirta, A. Vattulainen, S. Sinkkonen, J. Koistinen, J. Tarhanen, Formation of chloroaromatics at a metal reclamation plant and efficiency of stack filter in their removal from emission, Chemosphere 32 (1996) 99–108.
[18] A. Buekens, E. Cornelis, H. Huang, T. Dewettinck, Fingerprints of dioxin from thermal industrial processes, Chemosphere 40 (2000) 1021–1024.
[19] K. Hofstadler, A. Friedacher, W. Gebert, C. Lanzerstorfer, Dioxin at sinter plants and electric arc furnaces—emission profiles and removal efficiency, Organohalog. Comp. 46 (2000) 66–69.
[20] S. Caserini, A.M. Monguzzi, PCDD/Fs emissions inventory in the Lombardy Region: results and uncertainties, Chemosphere 48 (2002) 779–786.
[21] 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.
[22] US EPA, Exposure and human health reassessment of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and related compounds, EPA/600/P-00/001Bb, 2000.
[23] Determination of requirements to limit emissions of dioxins and furans, Report from the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Emission Control Committee, Umweltbundesamt, Berlin, Germany, 1996.
[24] U. Quaβ, M. Fermann, G. Bro¨ker, Identification of relevant industrial sources of dioxins and furans in Europe, Report No. 43, North Rhine-Westphalia: Environment Agency, Dusseldorf, 1997.

[25] M. Tysklind, G. Soderstrom, C. Rappe, PCDD and PCDF emissions from scrap metal melting processes at a steel mill, Chemosphere 19 (1989) 705–710.
[26] Service proposal for dioxin analyses, The Environmental Protection Agency of Kaohsiung County, Taiwan, 2004.
[27] H.J. Bremmer, L.M. Troost, G. Kuipers, J. DeKoning, A.A. Sein, Emissions of dioxins in The Netherlands. National Institute of Public Health and Environmental Protection (RIVM) and Netherlands Organization for Applied Scientific Research (TNO), Report No. 770501018, 1994.
[28] LUA (Landesumweltamt Nordrhein-Westfalen), Identification of relevant industrial sources of dioxins and furans in Europe. Materialien No. 43, Essen, Germany, North Rhine-Westphalia State Environment Agency, ISSN 0947-5206, 1997.
[29] AGES, Applied Geotechnical and Environmental Services Corp., Source sampling report—comprehensive emissions testing; blast furnace, Report No. 42614.01-01, Franklin Smelting & Refining Corp. Valley Forge, PA, AGES, May/June 1992.
[30] Taiwan EPA, http://www.epa.gov.tw/statistics/, 2005.
[31] Taiwan EPA, Project on PCDD/Fs emissions inventory and emissions database in Taiwan, 2003.