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A Taiwanese study of 2,3,7,8-substituted PCDD/DFs and coplanar PCBs in fly ashes from incinerators

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Abstract

Fly ashes from municipal solid waste (MSW), medical waste (MW), and electrical power plant (EPP) incinerators are analyzed for dioxin-like compounds (DLCs), including seventeen 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (2,3,7,8-substituted PCDD/DFs) and three coplanar polychlorinated biphenyls (Co-PCBs) of PCB 77, 126 and 169. The 2,3,7,8-tetradidioxin toxic equivalent (TEQ) values in fly ashes arranged in increasing order is 0.3, 2.1, 13.9 and 29.3 ng/g from EPP, large MSW, MW and small MSW incinerators. The contribution to total TEQ from Co-PCBs ranges from 4 to 25%, indicating that small MSW and MW incinerators are potential Co-PCBs contaminating sources. Fly ashes from small MSW and MW incinerators in Taiwan should be treated as hazardous materials. In the future, priority should be given to the construction of MSW incinerators with large burning capacities. © 1998 Elsevier Science B.V.

Keywords: Fly ashes; Dioxin contamination; Incinerators

1. Introduction

The ROC government in Taiwan plans to develop over 20 waste-to-energy facilities throughout the country to help manage municipal solid waste (MSW) [1]. Currently, there are five large (capacity $\geq$ 300 ton/day) MSW incinerators, 29 small medical waste (MW) incinerators, and few small (capacity $<$ 300 ton/day) MSW incinerators in operations. The problem of dioxin emissions from incinerators has always been a public concern. Studying the performance of different types of incinerators will help address this concern. Recent reports concerning the detection of high levels of polychlorinated

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dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs) in paper clay samples [2], in sediment and fish samples from the Er-Jen river [3,4], as well as in soil and fish samples from a waste pentachlorophenol manufacturing plant [5] make public worry more about dioxin contamination in Taiwan. Thermal reactions have been regarded as one of the four primary sources of PCDD/DFs and usually result in PCDD/DF emissions into the air [6]. These reports already make the construction of new incinerators more difficult. Another controversial issue is associated with the disposal of MSW residues. Currently, these residues are not treated as hazardous waste and are disposed into MSW landfills or dumped into an unknown country site. The leaching or perceived leaching of potentially toxic contaminants into the environment scares the public further.

The combustion of wastes is of special importance and accounts for about 95% of all known dioxin emissions in USA, with municipal and medical waste combustion dominating the combusting sources [7]. Recently, coplanar polychlorinated biphenyls (Co-PCBs) were detected in fly ash and flue gas from MSW incinerators [8,9]. The possible health effect on the residents around the incinerators comes directly from inhalation of air containing dioxin-like compounds (DLCs). Risk analysis is usually based on the measurement of DLCs in total emissions from the incinerators. An International Toxicity Equivalency Factor (I-TEF) method has been developed to simplify risk assessment and regulatory control of dioxin-containing materials. This method is based on in vitro and in vivo tests and relates the toxicity of 210 PCDD/DFs to the most toxic 2,3,7,8-TCDD [10,11]. Based on TCDD-like toxicity, a class of polyhalogenated aromatic hydrocarbons have been recognized as dioxin-like. These include PCDD/DFs, PCBs, diphenyl ethers, terphenyls, quaterphenyls, naphthalenes, azobenzenes, azoxybenzenes. Brominated and chloro/bromo versions of these compounds might be dioxin-like as well. Of the chlorinated compounds, only those processing planar structures exhibit high toxicity. These include seven 2,3,7,8-substituted PCDDs out of the 75 PCDDs, ten 2,3,7,8-substituted PCDFs out of the 135 PCDFs, and 13 coplanar PCBs out of the 209 possible PCBs congeners [12–14].

To our knowledge, this is the first Taiwanese study focusing on the determination of seventeen 2,3,7,8-substituted PCDD/DFs and three most toxic Co-PCBs, i.e. PCB 77, 126 and 169, in fly ashes from different types of incinerators in Taiwan. The aim is to provide technical data as basis for discussing issues such as the possible health impact of incinerator fly ashes, the management and regulation of incinerator fly ashes, and the construction priority of large or small MSW incinerators.

2. Experimental

2.1. Samples

A total of 11 fly ash samples were collected from nine incinerators. Table 1 lists the ash sample and incinerator information. Four different types of incinerators, including large MSW, small MSW, MW, and electrical power plant (EPP) incinerators, were investigated. A system blank sample was included for quality control purpose. The fly ashes consisted of particulate matter carried over from the furnace and removed from the

Table 1
Information concerning ash samples and incinerators

Sample no.	Ash	Incinerator [type]	Capacity	Pollution control device
S1	Fly[a]	A [MSW]	450 t/24 h×2 units	Dry scrubber + fabric filter
S2	Reactive[b]	A [MSW]	450 t/24 h×2 units	Dry scrubber + fabric filter
S3	Fly	A [MSW]	450 t/24 h×2 units	Dry scrubber + fabric filter
S4	Fly	B [MSW]	450 t/24 h×3 units	Dry scrubber + fabric filter
S5	Fly[c]	C [MSW]	300 t/24 h×5 units	Electrostatic precipitators + wet scrubber
S6	Reactive	D [MSW]	300 t/24 h×3 units	Electrostatic precipitators + wet scrubber
S7	Fly	E [MSW]	75 t/24 h×2 units	Semidry scrubber + fabric filter
S8	Fly	F [MSW]	30 t/16 h×1 unit	Semidry scrubber + ESP
S9	Fly[d]	G[e] [MW]	3.6 t/8 h×2 units	Venturi wet scrubber
S10	Fly	H[c] [EPP]	NA	NA
S11	Fly	I[f] [EPP]	NA	NA
S12	System blank			

[a]Particulate matter carried over from the furnace and removed from the flue gas prior to injection sorbents.
[b]Combined materials collected in the air pollution control devices including fly ash, injected sorbents, and flue gas condensate.
[c]Collected just after the incinerator started ignition.
[d]Bottom debris from the wet scrubber tower.
[e]Fed with coal.
[f]Fed with petroleum.
MSW: municipal solid waste.
MW: medical waste.
EPP: electrical power plant.
NA: not available.
ESP: electrostatic precipitator.

flue gas before entering the injection sorbents. The reactive ashes were a mixture of materials collected in the air pollution control devices, i.e. the fabric filter baghouse, and consisted of fly ash, injected sorbents, and flue gas condensate. The samples were collected between August 1994 and June 1995. All samples, except S1 and S2, were collected on different days.

2.2. Analytical procedures

All samples were use as received, except sample S9 which was freeze-dried to remove water content and sieved with a 100-mesh. A 10-g portion of the sample was spiked with internal standards of $^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,7,8-PeCDD, $^{13}C_{12}$-1,2,3,7,8-PeCDF, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-1,2,3,6,7,8-HxCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, $^{13}C_{12}$-1,2,3,6,7,8-HxCDF, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF, $^{13}C_{12}$-2,3,4,6,7,8-HxCDF, $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD, $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF, $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF, $^{13}C_{12}$-OCDD, $^{13}C_{12}$-PCB 77, $^{13}C_{12}$-PCB 126, and $^{13}C_{12}$-PCB 169. The spiked sample was then Soxhlet extracted in 200 ml benzene for 16 h. The extract was concentrated to 2 ml, spiked with clean-up standard of $^{37}Cl_4$-2,3,7,8-TCDD, followed by eluting through a Na_2SO_4/silica

gel/H_2SO_4 silica gel/silica gel/NaOH silica gel/silica gel/$AgNO_3$ silica gel/glass wool clean-up column. Monitoring the color development in the $AgNO_3$ silica gel was mandatory. The eluate was subjected to additional clean-up using another $AgNO_3$ silica gel column if an orange-red color appeared in more than half of the $AgNO_3$ silica gel. Nonplanar PCBs and other interference were collected in the 2% dichloromethane/hexane fraction of a neutral alumina column. Co-PCBs and PCDD/DFs were eluted in the 60% dichloromethane/hexane fraction. Final separation of Co-PCBs and PCDD/DFs was carried out using a carbon (Carbopak B/silica gel) column. Co-PCBs were collected in the hexane fraction; whereas PCDD/DFs were collected in the toluene fraction. The Co-PCBs eluate was concentrated to near dryness, added with 50 μl of recovery standard (dibromo-octachloro-biphenyl). The PCDD/DFs eluate was also concentrated to near dryness, added with 25 μl of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. The spiked concentrates were analyzed using a HP-5890/5971 GC/MS equipped with a J&W DB-5 ms column (60 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm film) for PCDD/DFs and a shorter column (30 m) for Co-PCBs. The 2,3,7,8-tetrachlorodioxin toxic equivalents (TEQ) were calculated using the I-TEF/89 system [15].

3. Results and discussion

3.1. TEQ (ng/g) from 2,3,7,8-substituted PCDD/DFs

The TEQ (ng/g) values from the 2,3,7,8-substituted PCDD/DFs are listed in Table 2. A wide range of concentrations is observed. The TEQ ranges from 0.046 ng/g in sample S11 to 28.917 ng/g in sample S8. The system blank sample possesses the lowest TEQ value (0.0087 ng/g), indicating that the analytical system and method perform well. Among the 11 samples, the TEQ values of fly ashes from large MSW incinerators (S1, S3, S4) and EPP incinerators (S10 and S11) are below the level of concern, i.e. the 1 ng TEQ/g in resident soil recommended by the Center for Disease Control [16]. This level is based on health risk assessments of ingesting soil daily over a lifetime period.

The TEQ values of reactive ashes are 2.526 and 1.592 ng/g in samples S2 and S6, respectively. The average TEQ value ($\sim$ 2.1 ng/g) in reactive ashes is about 5 times that in fly ashes collected at the same time. This might be due to the lower temperatures downstream in incinerating process (the temperatures might be lowered further by the

Table 2
TEQ (ng/g) of 2,3,7,8-substituted PCDD/DFs in ash samples

Analyte	Sample no.											
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
PCDDs	0.252	0.624	0.093	0.069	2.769	0.537	6.705	5.702	3.406	0.422	0.039	0.002
PCDFs	0.456	1.902	0.193	0.190	4.184	1.055	17.090	23.215	9.860	0.150	0.007	0.007
PCDD/DFs[a]	0.708	2.526	0.286	0.259	6.953	1.592	23.795	28.917	13.266	0.572	0.046	0.009

[a] TEQ sum of 2,3,7,8-substituted PCDDs TEQ and PCDFs TEQ.

sorbent injection process) which promotes the conversion of PCDD/DF precursors on the surface of fly ash to form PCDD/DFs. Relatively more lower-chlorine PCDD/DFs might be condensed onto the fly ashes, as the characteristic profiles of 2,3,7,8-substituted PCDD/DF shown in Fig. 1, which consequently increases the TEQ value. High TEQ value (6.953 ng/g) of fly ashes collected from the incinerator just started operating after a maintenance service is observed. This observation indicates that the general practice of monitoring DLC emissions in stack gas when the facility was in appropriate

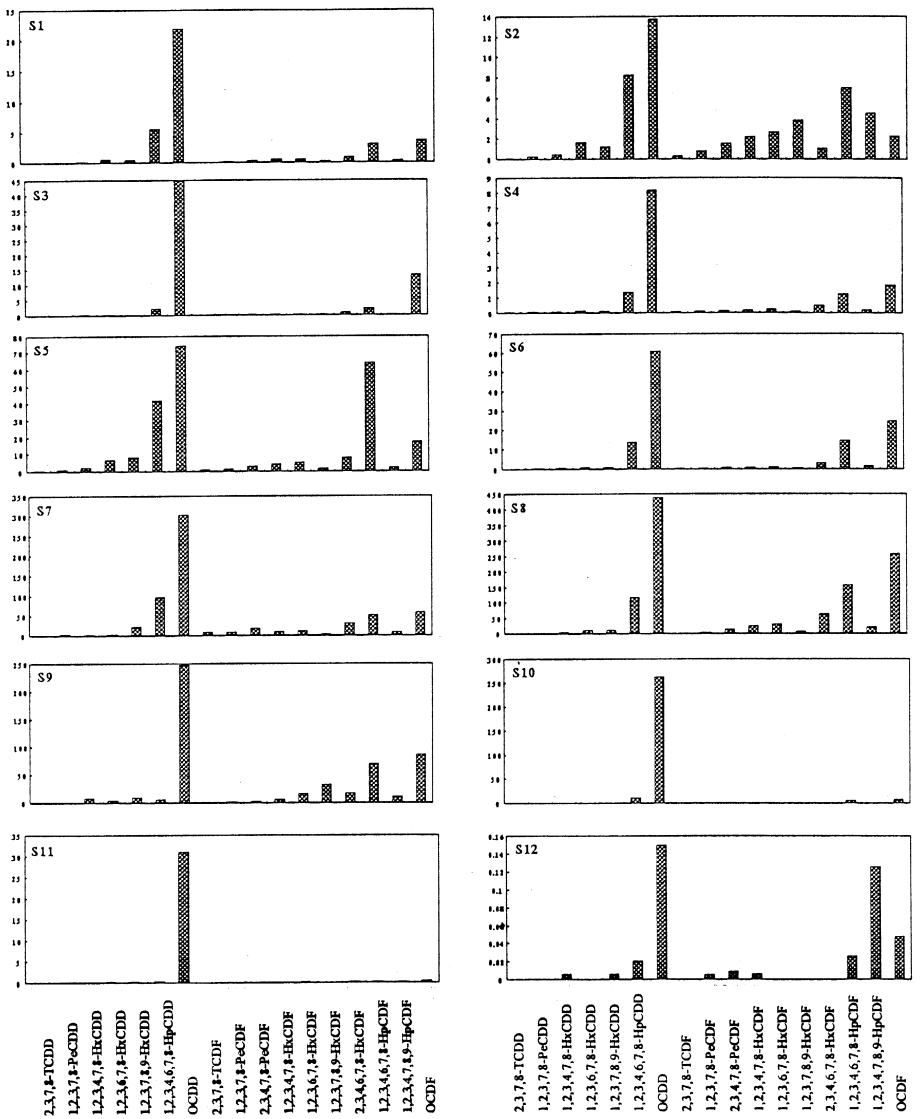

Fig. 1. Characteristic profiles of 2,3,7,8-substituted PCDD/DF congeners in ash samples. The unit in the *y*-axis is ng TEQ/g.

operating conditions might underestimate the total TEQ generated by the facility. For noncontinuous operating incinerators, the extent of TEQ underestimation worsens further.

The TEQ values of fly ashes from small MSW (23.795 ng/g in S7 and 28.917 ng/g in S8) and MW (13.266 ng/g in S9) incinerators far exceed the 1 ng TEQ/g level of concern. The corresponding profiles shown in Fig. 1 are different to those of large MSW incinerators. The characteristic profile of 2,3,7,8-substituted PCDD/DF congeners from the MW (S9 in Fig. 1) is different from those of the small MSW (S7 and S8 in Fig. 1) only in the smaller amount of 1,2,3,4,6,7,8-HpCDD. The lack of a secondary burning chamber and the use of primitive pollution control devices in these small MSW incinerators might be the cause of high TEQ values.

The TEQ values of fly ashes from the coal-fed EPP incinerator (0.572 ng/g in S10) is similar to those found in fly ashes from large MSW incinerators (average 0.418 ng/g for S1, S3, and S4) and is about 2% to that found in fly ashes from small MSW incinerators (average 26.356 ng/g for S7 and S8). This is probably related to the sulfur content in the coal feed. High concentrations of SO_2 in emissions from coal-feed incinerators were regarded to react with Cu(II) catalyst to form $CuSO_4$, which rendered the catalyst less active, and thus decreased the formation of PCDD/DFs [17]. Exceptionally low TEQ value of fly ashes from the petroleum-fed EPP incinerator (0.046 ng/g in S11) was observed. This might be due to the low-chlorine, low-water, and high sulfur content in the petroleum feed. The effect of low-water content in coal- and petroleum-fed is evidenced in the characteristic profiles of 2,3,7,8-substituted PCDD/DF congeners shown in Fig. 1. The amount of OCDD is about twice to that of HpCDD and HxCDD in fly ashes from MSW incinerators. However, the amount of OCDD is 15 and 47 times to that of HpCDD, 133 and 134 times to that of HxCDD in fly ashes from coal-fed and petroleum-fed EPP incinerators, respectively. The amount of PCDDs decreases significantly from high-chlorine towards low-chlorine. This unusual phenomenon might be attributed to the fuel used by these EPP incinerators, in comparison to the MSW incinerators, is relatively simple and contains smaller amount of water. The reduced dechlorination/hydrogenation reaction owing to the lower water content causes smaller amount of OCDD/DF to transform into low-chlorine PCDD/DFs [18,19]. The singly high OCDD in the characteristic profiles of 2,3,7,8-substituted PCDD/DF congeners from these two incinerators (S10 and S11 in Fig. 1) supports this argument. This effect of moisture content on the formation of low-chlorine 2,3,7,8-substituted PCDD/DFs warranted further research because high-water content food residues is dominant in waste from the Taiwanese families. [1]

3.2. TEQ (ng / g) from Co-PCBs

The TEQ (ng/g) values from the three Co-PCBs, i.e., PCB 77, 126 and 169, are listed in Table 3. A wide range of concentrations is also observed. The TEQ ranges from

[1] Waste composition analysis of MSW in Taipei in 1991 as reported by Sinotech Engineering, Taipei, Taiwan.

Table 3
TEQ (ng/g) of Co-PCBs in ash samples

Analyte	Sample No.								
	S1	S2	S4	S7	S8	S9	S10	S11	S12
PCB 77[a]	0.009	0.021	0.005	0.735	0.414	0.119	0.002	0.002	0.000
PCB 126[a]	10.010	37.650	5.740	279.830	272.270	54.530	3.190	1.650	0.340
PCB 169[a]	0.648	2.883	0.361	13.679	25.658	4.436	0.117	0.046	0.000
TEQ of Co-PCB[a]	10.667	40.554	6.106	294.244	298.342	59.085	3.309	1.698	0.340
Total TEQ[b]	0.815	2.932	0.320	26.737	31.900	13.857	0.605	0.063	0.012

[a] $\times 100$.
[b] TEQ sum of seventeen 2,3,7,8-substituted PCDD/DFs TEQ and three Co-PCBs TEQ.

0.0170 ng/g in sample S11 to 2.983 ng/g in sample S8. The system blank sample possesses the lowest TEQ value (0.003 ng/g), indicating that the analytical system and method perform well. The TEQ values in fly ashes in increasing order are from petroleum-fed EPP (0.0170 ng/g in S11), coal-fed EPP (0.033 ng/g in S10), large MSW incinerators (0.006 to 0.041 ng/g in S1 to S4), MW incinerator (0.591 ng/g in S9), and small MSW incinerators (2.942 to 2.983 ng/g in S7 and S8). The highest TEQ value is found of sample S8 which also contains the highest 2,3,7,8-substituted PCDD/DFs. A linear relationship exists between the TEQ value from the 2,3,7,8-substituted PCDD/DFs and the TEQ value from the three Co-PCBs (Fig. 2) with a linear correlation coefficient of 0.9307, indicating that Co-PCBs might be formed by similar reactions as PCDDs and PCDFs [20]. The contribution to total TEQ from the Co-PCBs ranges from 4% to 25% (Fig. 3). The results indicate that these incinerators are potential Co-PCBs contaminating sources.

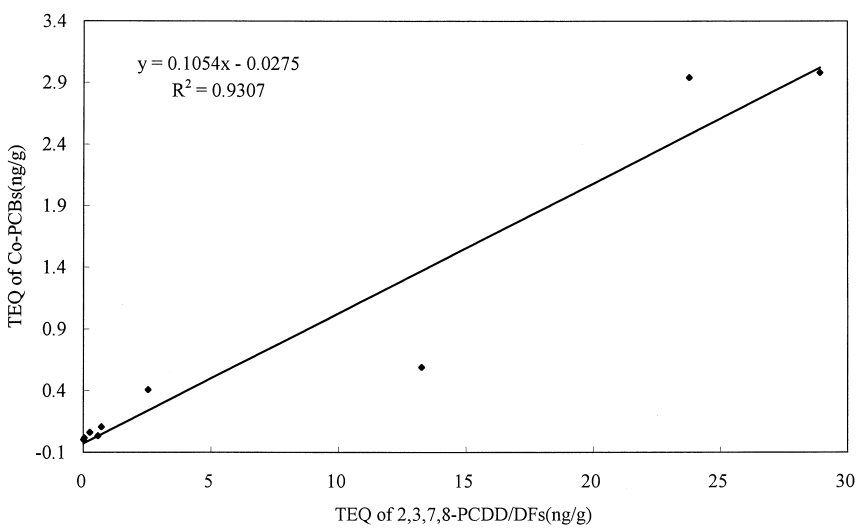

Fig. 2. The relationship between the TEQ of seventeen 2,3,7,8-substituted PCDD/DFs and the TEQ of three coplanar PCBs in ash samples.

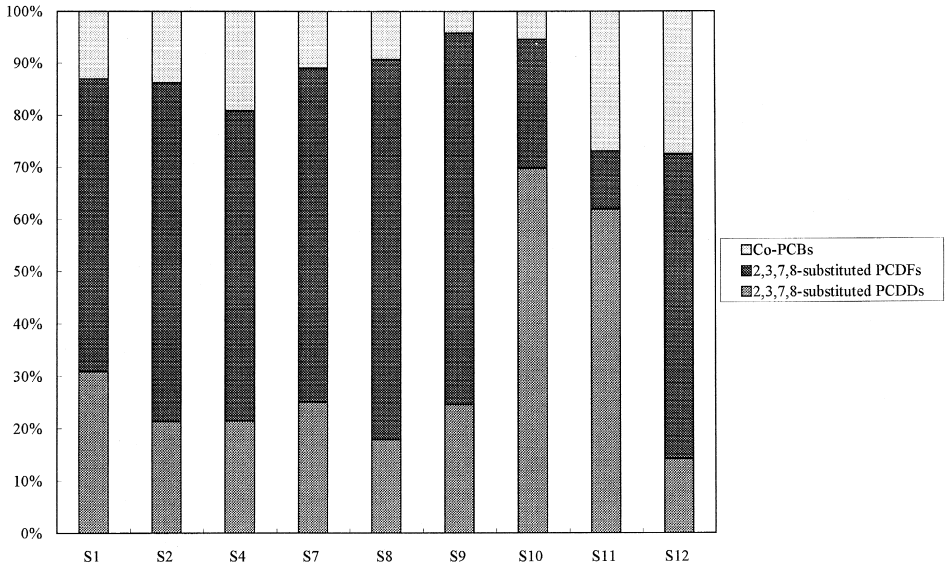

Fig. 3. Relative percent TEQ contribution from seven 2,3,7,8-substituted PCDDs, ten 2,3,7,8-substituted PCDFs, and three coplanar PCBs.

Table 3 indicates that the total TEQ of fly ashes from large MSW incinerators and EPP incinerators are below the 1 ng TEQ/g level of concern. The total TEQ of reactive ashes from large MSW incinerators, fly ashes from small MSW incinerators and MW incinerators far exceeds the 1 ng TEQ/g level of concern. Previous study has shown that close similarities between the profiles of 2,3,7,8-substituted PCDD/DF congeners in whole blood samples from MSW-incinerators', workers, and the profiles in fly ashes might indicate that fly ash was the dominant exposure material for PCDD/DFs at the MSW incinerators [21]. Some of the facilities monitored in this study shipped their fly ashes and/or bottom ashes to MSW landfills for disposal. The ashes were often handled with minimum protection, and could, therefore, constitute a significant occupational hazard to personnel working in these facilities.

4. Conclusion

In order to provide technical data for open discussion of a possible health hazard by fly ashes from different types of incinerators, 11 fly ash samples collected from large and small municipal solid waste (MSW), medical waste (MW), coal-fed and petroleum-fed electrical power plant (EPP) incinerators were analyzed for seventeen 2,3,7,8-substituted PCDD/DFs and three Co-PCBs. The following conclusions and recommendations are based on the TEQ values of fly ashes analyzed in this study.

(1) The TEQ values of fly ashes from small MSW (29.3 ng/g) and MW (13.9 ng/g) incinerators are much higher than those from large MSW (2.1 ng/g) and EPP (0.3

ng/g) incinerators. Based on this finding, high priority should be given to the construction of MSW incinerators with large burning capacities.

(2) The contribution to total TEQ from Co-PCBs ranging from 4% to 25% indicates that 2,3,7,8-substituted PCDD/DFs generate the highest environmental impact. Small MSW and MW incinerators are potential Co-PCBs contaminating sources.

(3) Fly ashes from small MSW and MW incinerators should be treated as hazardous waste. A clear and practical national ash management standard should be established [22]. Adequate occupational safety should be provided for personnel working in these facilities.

(4) The operation of the MSW facilities and the corresponding risk assessment should look into the adverse effect of unusually high dioxin-like compounds (DLCs) emitted during the incinerator start-up period.

(5) A national survey of DLC sources and sinks is warranted to ensure the protection of Taiwan ecosystem and living environment from the threat of DLCs.

Acknowledgements

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