An Overview of PCDD/F Inventories and Emission Factors from Stationary and Mobile Sources: What We Know and What is Missing

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ABSTRACT

This overview attempts to outline what we currently know about the PCDD/F emission inventories and the source categories therein. Besides the best available control techniques, suggestions are offered on how to reduce the PCDD/F emission factors and emission quantity of some important PCDD/F emission sources. The PCDD/F combustion sources can be classified as either stationary or mobile or minimally/uncontrolled combustion sources. The major stationary sources of PCDD/Fs are metal production processes, waste incineration, heat and power plants, and fly ash treatment plant. Crematories, vehicles, residential boilers and stoves are of key concern due to their proximity to residential areas and their relatively lower lying stacks and exhaust gases, which may result in great impact to their surrounding environment.

Moreover, we offered our perspectives on how to improve the quality and representative of the PCDD/F emission factors to attain PCDD/F inventories which correspond more to reality. These points of view include: (1) PCDD/F contributions during start-up procedures of MSWIs should be considered, (2) the sampling times of stack flue gases for EAFs and secondary metal smelters should correspond to whole smelting process stages, (3) longer flue gas sampling time should be executed for power plants, (4) direct exhaust samplings from tailpipes for mobile sources, (5) development of an open burn testing facility that can reflect the real open burning conditions, and (6) long-term sampling techniques like AMESA are suggested to used exclusively for the most contributed PCDD/F stationary sources.

Keywords: PCDD/F inventory; Stationary sources; Mobile sources; Biomass burning; AMESA; Electric arc furnaces.
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INTRODUCTION

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) have been linked to several adverse health risks not only to human beings but also to that of the ecosystem in general (WHO, 1998). These health risks include chloracne, immunotoxicity, endocrine disruptor, and carcinogenicity (Bertazzi et al., 2001; Kogevinas, 2001; Schecter et al., 2006; Yang et al., 2015).

PCDD/Fs are unintentional by-products of combustion processes and many industrial activities, such as waste incineration, metal production activities, power and heating facilities and chemical manufacturing processes (Rappe, 1992; Fiedler, 1996; Hung et al., 2015). There are 210 possible congeners of PCDD/Fs and out of these, only 17 with chlorine atoms attached to the 2, 3, 7 and 8 positions have been shown to be toxic and hence, of major concern (Van den Berg et al., 1998; Schecter et al., 2006). Since PCDD/F emissions are always mixtures of the different congeners, the toxicities of emissions are estimated using toxic equivalence factor (TEF) schemes. Basically, the most toxic congeners, 2, 3, 7, 8-TCDD (Bertazzi et al., 2001; McKay, 2002), is given a TEF of 1 and the rest of the 16 congeners have values relative to 2, 3, 7, 8-TCDD. There are two TEF schemes including International Toxicity Equivalent (I-TEF) and World Health Organization TEF (WHO-TEF). The WHO-TEF has been revised from WHO1998-TEF to WHO2005-TEF by downgrading some of the TEFs and increasing others, but still give higher values than I-TEQ. To get the toxicity equivalence (TEQ), the concentration of the congener is multiplied by its respective TEF value. The TEQ of the mixture is the sum of all the individual TEQs and is given as either PCDD/Fs I-TEQ or PCDD/Fs WHO2005-TEQ depending on the scheme used.

PCDD/Fs are present a comprehensive one and overview of PCDD/F sources and their environmental releases. Many control strategies and policies on PCDD/Fs are closely correlated to PCDD/F inventory, and the government can promulgate relevant PCDD/F regulations and emission standards on the main PCDD/F sources in inventory. The outcomes could be quite apparent, for instance, between reference years 1987 and 2000, there was approximately 89% reduction in the PCDD/F released to the environment of the United States from all known sources combined (US EPA, 2006), and also about 84% reduction in PCDD/F emissions from 327.4 g I-TEQ in 2002 to 52.6 g I-TEQ in 2013 in Taiwan.

PCDD/Fs are semi-volatile compounds, and after being emitted from combustion sources, they are distributed in both gaseous and particle phases in the atmosphere (Li et al., 2008b; Chen et al., 2011a; Kuo et al., 2015). The partitioning between the two phases is highly dependent on their vapor pressure and the ambient temperature, with more molecules volatilizing into the gaseous phase as temperature increases (Fiedler, 1996; Oh et al., 2001). PCDD/Fs are lipophilic persistent organic compounds, which bioaccumulate in the fatty tissues and biomagnify within the food chain (Rolf et al., 1993; Henny et al., 2003). PCDD/Fs also exhibit long range transport properties and have been shown to be present in pristine environments, e.g., Antarctica (Mwangi et al., 2016).

This overview will discuss the major PCDD/F sources as compiled in previous inventory studies (Bawden et al., 2004; Quaß et al., 2004; US EPA, 2006; Taiwan EPA, 2008; Fiedler, 2016). A recent study from Fiedler (2016) reported that the current three sources out of the ten source categories of 86 countries that contribute most to the total PCDD/F release were open burning processes (mean = 45%), waste incineration (13%) and metal production (12%). These sources which contribute the most amount of PCDD/Fs and other sources, which are contribute less, but may possess higher health risk will be discussed in this study for their PCDD/F emission factors and influential factors that affect the emission characteristics. Furthermore, we will offer our perspectives on how to reduce the PCDD/F emission factors and emission quantity as well as how to improve the quality and representative of the PCDD/F emission factors to attain PCDD/F inventories which more correspond to
FORMULATION AND DECOMPOSITION MECHANISMS OF PCDD/Fs

Detailed mechanisms have been addressed in previous studies by (Zhang et al., 2008; Qu et al., 2009; Zhang et al., 2014), therefore here we only briefly describe the important mechanisms that are most related to those in combustion sources, which include De novo synthesis and precursor pathway. Through research work, the pathways for PCDD/F formation have been determined to be either through heterogeneous or homogenous mechanisms (Stanmore, 2004; Altarawneh et al., 2009).

Homogenous pathway occurs in gas phase, where precursors react at a temperature between 500–800°C to form PCDD/Fs. Various PCDD/F congeners, both simple and complex (Jarmohamed and Mulder, 1994; Iino et al., 1999; Tame et al., 2007; Hajizadeh et al., 2011; Cheruiyot et al., 2015), can be suitable precursors, however, monocyclic aromatic compounds e.g., (chloro) phenols and (chloro) benzenes have been shown to be the most direct routes to the formation of PCDD/Fs (Altwicker and Milligan, 1993; Luijk et al., 1994; Altwicker, 1996). The formation reactions from these monocyclic aromatic compounds involve degradation of these precursors and the rearrangement of their structures. The key step is the formation of the phenoxyl radical (Louw and Ahonkhai, 2002; Evans and Dellinger, 2005; Altarawneh et al., 2007). Other important reactions are the self-condensation of the precursors, cyclization of initial intermediates and chlorination/dechlorination reactions (Altarawneh et al., 2009).

On the other hand, heterogeneous precursor mechanisms take place at around 200 to 450°C. The reaction involves the attachment of the precursor on the surface of the catalytic matrix on the fly ash (Briois et al., 2007). The catalyzers are typically the transition metals such as Cu and Fe, which are present in fly ash and APCDs (Lomnicki and Dellinger, 2008; Ngarai et al., 2008). Transitional-metals, especially copper, have been shown to enhance the formation of PCDD/Fs (Luijk et al., 1994; Ryu et al., 2005; Liao et al., 2016).

In De novo synthesis pathway, which is the most widely studied formation mechanism, the maximum formation rate occurs during the temperature window of 200–450°C (Stieglitz, 1998; Stanmore, 2004). The chlorine is either supplied as solid or in gas phase or both (Gullett et al., 1994; Hatanaka et al., 2005; Lu et al., 2007). In the absence of gaseous chlorine, the formation of PCDD/Fs occurs through a series of metal-catalyzed processes. The process takes place in two crucial steps in the post-combustion stage of a plant. Firstly, the incompletely combusted carbon matrix undergoes a series of oxidation reactions to form smaller structures some of which are structurally similar to the precursors. Secondly, the products in the first step are catalyzed by transition metal e.g., Cu and Fe (Gullett et al., 1992). In de novo synthesis, the outputs of PCDFs are about an order of magnitude higher than PCDDs (Cieplik et al., 2006).

MAJOR EMISSION CATEGORIES IN PCDD/F INVENTORIES WORLDWIDE

As a requirement, all parties of the Stockholm Convention are supposed to develop national inventories to estimate releases of unintentional POPs based on the national economic activity (Zhang et al., 2011). Table 1 highlights the important PCDD/Fs emission sources as identified by various countries across the globe. It is evident that the waste incineration, metallurgical processes, power plants and biomass burning including backyard and wood combustion are the major categories of PCDD/F emission sources. These categories combined, contribute about 65.5% of the total annual PCDD/F emission quantity in the EU, 78.7% in USA and even 86.4% in China (Quaß et al., 2004; US EPA, 2006, P.R.C, 2007). Specifically, combustion involving biomass burning, wood burning, and/or backyard burning is the single most significant category in the EU, USA, Brazil and Australia with contributions above 30% of the total PCDD/F emissions, similar to the findings of Fiedler (2016). It can be concluded that industrial sources have been significantly reduced over the years and therefore, non-industrial sources, e.g., biomass open burning, domestic heating, and vehicles are increasingly becoming more important. Thus, in the subsequent sections much focus will be on the individual sources that are significant and representative.

PCDD/F EMISSIONS FROM STATIONARY SOURCES

The main stationary sources of PCDD/Fs majorly include MSWIs, MWIs and HWIs in the waste incineration category; sintering plants, electric arc furnaces (EAFs) and secondary metal smelting plants in the metallurgical facility category; and coal fired power plants and boilers in the power generation category. In this section, these main PCDD/F sources were discussed for their PCDD/F emission factors, and influential factors that affect the emission characteristics.

PCDD/F Emissions from Waste Incinerators

Waste incinerators can be classified according to the type of waste handled i.e., municipal solid waste incinerators (MSWIs), hospital or medical waste incinerators (MWIs), industrial waste incinerators (IWIs), hazardous waste incinerators (HWIs) and so on. Table 2 lists PCDD/F emission factor of various waste incinerators with different APCDs. The emissions of PCDD/Fs from incinerators are dependent on the feeding wastes, operation procedures and the deployed air pollution control devices (APCDs). From the values in Table 2, the emission factors of medical waste incinerators and hazardous waste incinerators were about 1–2 orders higher than those of municipal waste incinerators. This difference can be attributed to the fact that MSWIs are continuous operated, while MWIs and HWIs are commonly intermittently operated/batch operated. For continuous incinerators the feed and bottom ash are periodically fed and removed, respectively. As for the intermittent incinerators, the feed is fed periodically and the ash is removed after burndown and cooling off cycles,
| Country or Region (Reference year) | g I-TEQ year⁻¹ | Major sources | References |
|-----------------------------------|----------------|---------------|------------|
| Japan (2004)                      | 341–363        | Small-scale waste incineration (21.5–26.7%)  | (MoE, 2005) |
|                                   |                | General waste incineration (17.6%)          |            |
|                                   |                | EAFs (17.6%)                                 |            |
|                                   |                | Sintering plants (8.4%)                     |            |
|                                   |                | Zinc recovery plants (2.2%)                 |            |
|                                   |                | Aluminum plants (3.6%)                      |            |
|                                   |                | Other industrial facilities (2.4%)           |            |
|                                   |                | Crematoria (0.63–1.4%)                      |            |
|                                   |                | Subtotal of the above emission sources      |            |
|                                   |                | Percentage a (93.23–99.2%)                  |            |
| Taiwan (2008)                     | 74.7           | Sintering plants (30.7%)                    | (Taiwan EPA, 2008) |
|                                   |                | EAFs (23.7%)                                |            |
|                                   |                | Fossil power plants (Coal = 10.5%, Fuel = 6.4%) |          |
|                                   |                | Secondary ALS (3.5%)                        |            |
|                                   |                | Road transport (3.1%)                       |            |
|                                   |                | MSWIs (2.5%), IWIs (1%), MWIs (0.8%)         |            |
|                                   |                | Ferrous foundries (1.5%)                    |            |
|                                   |                | Subtotal of the above emission sources      |            |
|                                   |                | Percentage a (83.7%)                        |            |
| China (2004)                      | 5042.4         | Sintering plants (30.2)                     | (P.R.C, 2007) |
|                                   |                | MWIs (8.5%)                                 |            |
|                                   |                | Secondary copper smelting (8.0%)            |            |
|                                   |                | Stalk combustion (7.7%)                     |            |
|                                   |                | Cement production (7.2%)                   |            |
|                                   |                | Firewood combustion (5.9%)                  |            |
|                                   |                | Household heating and cooking (5.3%)        |            |
|                                   |                | Fossil fuel power plant (4.9%)              |            |
|                                   |                | Coke production (4.7%)                      |            |
|                                   |                | Iron and steel production and foundries (3.0%) |      |
|                                   |                | Secondary ALS (2.6%)                        |            |
|                                   |                | MSWIs (2.5%)                                |            |
|                                   |                | Heavy oil fired engines (2.3%)              |            |
|                                   |                | Industrial boiler (2.0%)                    |            |
|                                   |                | HWIs (1.1%)                                 |            |
|                                   |                | Subtotal of the above emission sources (4835.66 g I-TEQ) | (95.9%) |
| EU (2005)                         | 1,963–3,752    | Residential combustion (wood = max 25.8%, coal = max 9.0%), | (Quaß et al., 2004) |
|                                   |                | Sintering plants (12.5%), MSWI (11.1%), MWI (4.3%), IWI (1.2%), |          |
|                                   |                | Fires (9.9%), Wood preservation (8.26%), EAFs (4.6%) |            |
|                                   |                | Subtotal of the above emission sources      |            |
|                                   |                | Percentage a (86.7%)                        |            |
| US (2000)                         | 1,314.5        | Backyard burning (36%)                      | (US EPA, 2006) |
|                                   |                | MWI (28.8%)                                |            |
|                                   |                | MSWI (5.8%)                                |            |
|                                   |                | Coal fired utility boilers (5.4%)           |            |
|                                   |                | Diesel heavy-duty trucks (4.7%)             |            |
|                                   |                | Industrial wood combustion (3.2%)           |            |
|                                   |                | Sintering plants (1.9%)                    |            |
|                                   |                | Cement kilns burning hazardous waste (1.3%) |            |
|                                   |                | Cement kilns burning nonhazardous waste (1.3%) |       |
|                                   |                | Residential wood combustion (0.9%)          |            |
Table 1. (continued).

| Country or Region (Reference year) | g I-TEQ year⁻¹ | Major sources | References |
|-----------------------------------|----------------|---------------|------------|
| Subtotal of the above emission sources (1 173.85 g I-TEQ) | Percentage (89.3%) | Biomass burning (48%), Waste burning and accidental fires (17.6%), Zinc production (10%), Sintering plants (6.4%), Iron and steel plants (4.06%), Household heating and cooking with biomass (4.06%), Fossil fuel power plants (2.86%), MWIs (1.3%), Diesel engines (1.1%) | (Bawden et al., 2004) |
| Australia (2002) | 500 |  | |
| Brazil (2008) | 945.41 | Sintering plants (33.4%), Open biomass burning – biomass (25.7%), Waste burning and accidental fires (11.1%), MWIs (5.8%), Iron and steel production (5.0%) | (MMA, 2015) |
| South Africa (2006) | 2,763.13 | Ferrous and non-ferrous metal production (64.8%), Power generation and heating (23.4%), Uncontrolled combustion (7.8%), Production of chemicals and consumer goods (1.6%) waste incineration (1.3%) | (DEA, 2011) |

₄Contribution (%) of the listed emission sources (subtotal) to the total PCDD/F emissions.

after which there is usually a startup operation prior to waste charging. In other words, intermittent stationary plants experience more transient periods than large scale continuous plants. Lee et al. (2003) reported that in terms of the emission factors, the intermittent incinerators were 111 and 214 times higher than those of continuous incinerators in terms of mass and toxicity basis. The observed differences are due to the fact that intermittent incinerators are small scale with lower combustion efficiencies, inefficient pollution control strategies and in some instances, the waste feed has higher chlorine content. For example, the waste feed in the MWIs has high chlorine content of about 1.1–2.1% (Randall, 1994), which may enhance formation of PCDD/Fs and has higher emission factors.

The types and combination of the deployed APCDs are also important factor influencing the PCDD/F emissions from waste incinerators. The MSWIs without activated carbon injection exhibited higher PCDD/F emission factors (1.18 µg I-TEQ ton-waste⁻¹) than those with activated carbon injection (0.711 µg I-TEQ ton-waste⁻¹) in the study of Ni et al. (2009). Wang et al. (2014) also shows that without activated carbon the emission factors were nearly three times higher for HWIs. The combination of dry scrubber (DS), activated carbon injection (ACI) and fabric filter (FF), where the ACI adsorb the gas-phase PCDD/Fs and FF provided particle-phase PCDD/Fs removal, is treated as best available control technology for PCDD/Fs in flue gases, as reported in Lee et al. (2003).

In the study of Wang et al. (2010a), fly ashes in different units of two MSWIs were sampled for POP analyses, and from the PCDD/F trend in the ashes, the economizer had been found the source of PCDD/F formation in the MSWIs, because its operational temperature fall within PCDD/F formation window. Therefore, economizers are encouraged to improve their heat exchange efficiency to shorten the residence time of flue gas in order to effectively reduce PCDD/F formation in the MSWIs.

An important issue concerning PCDD/F emissions from waste incinerators is their start-up procedures. For intermittent incinerators, warm start-up resulted in the PCDD/F concentrations of the first stack flue gas sample 2–3 times higher among three consecutive stack flue gas samples. For continuous MSWIs, the elevated PCDD/F emissions during cold start-up could reach 96.9 ng I-TEQ Nm⁻³, and the PCDD/F emissions contributed by start-up procedures were at least two times larger than that of a whole year’s normal operations for a MSWI with four furnace sets (Wang et al., 2007). During the start-up procedure of the MSWI, two high PCDD/F emission peaks occurred, when the combustion chamber’s temperature passes through PCDD/F formation window and waste was first fed at 850°C (Wang et al., 2007; Guo et al., 2014).
Table 2. PCDD/F emission factors of waste incinerators with different APCDs.

| Waste Incinerator | APCDs | Emission Factors (µg I-TEQ ton-waste⁻¹) | Annotation | References |
|-------------------|-------|----------------------------------------|------------|------------|
| MSWIs             | SDS + FF | 0.169–1.973 (mean = 1.175) | 6 MSWIs. 1 MSWI with extreme value (10.72 µg I-TEQ ton-waste⁻¹) was excluded in mean value determination | (Ni et al., 2009) |
|                   | SDS + AC + FF | 0.226–1.871 (mean = 0.711) | 10 MSWIs. 2 MSWIs with extreme values (4.789 and 5.04 µg I-TEQ ton-waste⁻¹) were excluded in mean value determination | |
|                   | DS + AC + FF | 0.0475–0.187 (mean = 0.104) | 7 MSWIs | (Lee et al., 2003) |
|                   | CY + DSI(AC) + FF | 0.0678 | |
|                   | CY + DS + AC + FF | 0.0642 | |
|                   | ESP(AC) + VS + PBS + SCR | 0.0764 | |
| MWIs              | QC + VS + PBS | 11–40.7 (mean = 26.4) | 3 MWIs, intermittent operation | (Lee et al., 2003) |
|                   | DS + AC + FF | 1.34 | Intermittent operation | (Karademir, 2004) |
|                   | ESP + VS + AC | 0.571 | |
| HWIs              | AC + FF | 4.64 | | (Wang et al., 2014) |
|                   | SDS + FF | 0.489–9.017 (mean = 4.43) | 4 HWIs | |
|                   | SDS + AC + FF | 0.23–3 (mean = 1.563) | 6 HWIs | |
|                   | CY + SDS + AC + FF | 0.463 | Long-term (> 2 years) continuous measurement used to estimate the EF | (Rivera-Austrui et al., 2011) |
|                   | ESP + WS + SCR | 0.25 | |

AC: Activated Carbon; BF: Bag Filter; CY: Cyclone; DS: Dry Scrubber; DSI: Dry Sorbent Injection; ESP: Electrostatic Precipitator; FF: Fabric Filter; PBS: Packed-bed absorber scrubber; QC: Quench Chamber; SCR: Selective Catalytic Reduction; SDS: Semi-Dry Scrubber; VS: Venturi Scrubber.

Furthermore, the elevated PCDD/F emissions during start-up of incinerators can result in de novo based memory effect and adsorptive memory effect (Li et al., 2011; Wu et al., 2014b). The de novo based memory effect caused by start-up procedures resulted from the surfaces of the boilers, heat exchangers, pipes, and APCDs contaminated by soot particles containing high PCDD/F contents as well as hydrocarbons, which promote de novo synthesis of PCDD/F formation (Zimmermann et al., 2001; Weber et al., 2002; Wikström et al., 2004). For the adsorptive memory effect, which occurs in the low temperature, the desorbed PCDD/Fs from the filters of bag filters contaminated by high PCDD/F emissions during start-up, increases the PCDD/F concentrations over a longer period of time (Li et al., 2011). Even two weeks after start-up, the gaseous phase PCDD/F concentration (mean: 0.103 ng I-TEQ Nm⁻³) can be 6.8 times higher than that sampled during normal conditions, while the particulate phase PCDD/F concentrations remained the same level (Li et al., 2011). In some cases, the memory effect caused the PCDD/F concentrations in the stack flue gases higher than those prior to the aged bag filter, rendering a negative PCDD/F removal (Li et al., 2011).

It needs to be mentioned that the high PCDD/F emissions from start-up procedures of incinerators are not considered in the PCDD/F inventories worldwide. Therefore, in order to be representative, it is recommended that the PCDD/F inventories should include PCDD/F contributions by start-up procedures, and studies are encouraged to evaluate the best operations procedures aimed at reducing the high emissions from start-up procedures.

PCDD/F Emissions from Metallurgical Facilities

The metallurgical facilities can be divided into four broad categories comprising of primary and secondary ferrous smelting, as well as primary and secondary nonferrous metal smelting.

According to Table 1, the PCDD/F contribution from metallurgical facilities was about 31.8% of total PCDD/F emissions in Japan (MoE, 2005), 35.7% in Taiwan (Taiwan EPA, 2008), 43.8% in China (P.R.C, 2007), 17.6% in the EU (Quaß et al., 2004), 20.5% in Australia (Bawden et al., 2004), 38.4% in Brazil (MMA, 2015) and 64.8% in South Africa (DEA, 2011). Among the metallurgical facilities, sintering plants, EAFs, aluminum smelters, secondary copper smelters and EAF dust treatment plants were commonly the dominant PCDD/F sources. Therefore, in the following sections the discussion on PCDD/Fs from metallurgical facilities only focus on sintering plants (primary ferrous smelting) and EAFs (secondary ferrous smelting), secondary aluminum smelters, secondary copper smelters and EAF dust treatment plants (secondary nonferrous metal smelting). An important aspect to note is that the units of PCDD/F emission factors...
from metallurgical facilities in a country need to correspond to the units of activities reported in its national statistical reports, therefore, the PCDD/F emission factors may base on either products (µg I-TEQ ton-product–1) or feedstocks (µg I-TEQ ton-feedstock–1).

PCDD/F Emissions from Sintering Plants
Iron ore sintering plants produce a homogenous clinker-like material through an agglomeration process of heterogeneous blends of iron ore, fluxes, fuel (normally coke breeze) and reverted materials. De novo synthesis is proposed as the dominant PCDD/F formation mechanism due to PCDF mean concentrations in the stack flue gas are generally higher than those of PCDD representing over 80% of the total concentration (Wang et al., 2003b; Aries et al., 2006; Sun et al., 2016). Nakano et al. (2005), concluded that the dry zone layer was the primary area of PCDD/F formation in the sinter plant. The temperature range within this layer was between 100 to 1000°C (Arion et al., 2002), with presence of carbonaceous material from the coke and/or soot from the ESP when recycled. There is also the presence of chlorine as alkali chlorides and small amounts of Cu in this region (Suzuki et al., 2004). The raw material can contain substances that have been reported to be essential or facilitate the formation of PCDD/Fs e.g., chlorine, organic compounds and metal catalysts like Cu (Cieplik et al., 2003). However, though the current understanding is that PCDD/Fs are majorly formed within the sinter bed, an analysis of the dust particles in wind boxes revealed that it contains significant amounts of Cl and unburnt carbon (Tsubouchi et al., 2006; Kuo et al., 2011) making it a potential area for PCDD/F formation. The contribution from each region to the total PCDD/Fs emitted is still not fully investigated and understood.

The operating conditions and composition of the raw material are factors affecting PCDD/F formation and emission from sintering plants. The operating conditions include temperature, sinter time, oxygen concentration and combustion efficiency, bed and permeability (Guerriero et al., 2009; Ooi and Lu, 2011; Yu et al., 2012). Water content of 6.5% wt, bed height of 500 mm, suction pressure of 1000 mm H2O and hematite layer hearth were the optimal parameters identified by Chen et al. (2008) that resulted in a 63% reduction in PCDD/F emissions. Table 3 lists emission factors from sintering plants and also shows the influence of APCDs on emission factors. The emission factor when using only electrostatic precipitator (ESP) were in the range of 0.63–5.29 µg I-TEQ ton-product–1, while those with ESP and SCR were ranging from 0.37 to 2.28 µg I-TEQ ton-product–1 (Wang et al., 2010b). The use of SCR in combination with ESP is shown to reduce the PCDD/F emissions by about 50% compared to only using ESP as reported in the studies of Wang et al. (2003b). Thus, while activated carbon injection is the mainstream control technology for waste incinerators, the SCR is usually deployed as PCDD/Fs and/or NOx control measure in sinter plants. Esposito et al. (2014) showed that the activated carbon injection (ACI) was still superior to urea addition in the feed in terms of PCDD/F reduction. However, it needs to be noted that ACI merely transfer PCDD/Fs from gas stream to the collected fly ashes, and in some sintering plants, these fly ashes reverted to feeding raw materials of sintering plants, increasing PCDD/F concentrations in the stack flue gases. Additionally, some studies have shown that coupled deNOx and dioxin destruction SCRs (Wang et al., 2009a), especially V-rich vanadia-tungsta-titania catalysts, are advantageous compared to only deNOx systems in terms of PCDD/F destruction and removal, but are still susceptible to deactivation by high chlorine content in the flue gases (Finocchio et al., 2006). Furthermore, these coupled deNOx and PCDD/F destruction, SCRs can compete with ACI (Finocchio et al., 2006), since the SCR systems destroy PCDD/Fs leading to reduction in PCDD/F mass (Wielgosinski, 2010; Ji et al., 2013).

PCDD/F Emissions from Electric Arc Furnace (EAF)
De novo synthesis is known to dominate in the post-combustion zone of EAFs. EAFs can be classified according to their products. That is carbon steel EAFs and stainless steel EAFs. As seen in Table 4, the emission factors from carbon steel EAFs (mean 1.8 µg I-TEQ ton-feedstock–1) were higher than those of stainless steel EAFs (0.52 µg I-TEQ ton-feedstock–1) (Lee et al., 2005). Similar observations were reported in other studies (Wang et al., 2009a; Wang et al., 2010b). The reason for this is because the production of

| Feeding material and Product | APCDs | Emission factors | Annotation | References |
|-----------------------------|-------|------------------|------------|------------|
| Iron ore, Coal, Lime, Sintered pellets | ESP | 1.92–2.23 µg I-TEQ ton–1 | 3 Sinter plants | (Aries et al., 2006) |
| | ESP | 0.77–0.83 µg I-TEQ ton–1 | 2 Sinter plants | (Zou et al., 2012) |
| | ESP | 3.13 µg I-TEQ ton–1 feedstock | 2 sinter plants | (Wang et al., 2003b) |
| | ESP | 0.63–5.29 µg I-TEQ ton–1 products (mean = 2.96) | 2 sinter plants | (Wang et al., 2010b) |
| | ESP + SCR | 0.664–1.5 µg I-TEQ ton–1 feedstock (mean = 0.97) | 3 Sinter plants, Paddle type deNOx SCR | (Wang et al., 2003b) |
| | ESP + SCR | 0.37–2.28 µg I-TEQ ton–1 products (mean = 1.05) | 3 sinter plants | (Wang et al., 2010b) |

ESP: Electrostatic Precipitator; SCR: Selective Catalytic Reduction.
Table 4. PCDD/F emissions from EAF plants.

| Feeding material                        | Product          | Auxiliary Fuel | APCDs     | Emission Factor | Annotation                  | Reference                  |
|-----------------------------------------|------------------|----------------|-----------|-----------------|-----------------------------|----------------------------|
| Scraps, alloying agents, flux, coke     | Carbon steel     | None           | QT + BF   | 1.6–2 µg I-TEQ ton-feedstock⁻¹ (mean = 1.8) | Operational temperature of the BF was 200°C | (Lee et al., 2005)          |
|                                         | Stainless steel  | None           | QT + BF   | 0.52 µg I-TEQ ton-feedstock⁻¹ | 1.2 samples collected       | (Wang et al., 2010b)        |
|                                         |                  | BF             | BF        | 0.416 µg I-TEQ ton-feedstock⁻¹ | 6 samples collected      | (Chiu et al., 2011)         |
|                                         | Stainless steel  | Kerosene       | BF        | 3.59 µg I-TEQ ton-feedstock⁻¹ |                              | (Wang et al., 2009a)        |
|                                         | Carbon steel     | BF + CO converter | BF        | 1.33–3.00 µg I-TEQ ton-feedstock⁻¹ (mean = 2.33) |                              |                            |
|                                         | Steel scraps     | BF             | -         | 7.61 µg I-TEQ ton-feedstock⁻¹ |                              | (Zou et al., 2012)          |

BF: bag filter; QT: quench tower.
- Information not provided.

stainless steel (the carbon content is less than 0.15%) requires scrap with less impurity and contamination compared to that of carbon steel (the carbon content is between 0.25%–1.4%), whose the feedstock contains more chlorine content than that for stainless steel EAFs (Lee et al., 2005).

Furthermore, the Table 4 provides information on the impact of APCDs on PCDD/F emission from EAFs. A combination of quench tower and bag filter (QT+BF) had lower emissions compared to the case with only bag filters (BF). For example, the emissions from stainless steel EAF with BF (3.59 µg I-TEQ ton-feedstock⁻¹) (Wang et al., 2009a) was approximately 7 times that with QT+BF (0.52 µg I-TEQ ton-feedstock⁻¹) (Lee et al., 2005). This can be attributed to the fact that the quench towers reduced the temperature of the flue gases to below 150°C. In fact, in the study of Lee et al. (2005), due to a quench tower that was not functioning well, the PCDD/F emission factor increased 6 fold from 0.52 µg I-TEQ ton-feedstock⁻¹ to 3.2 µg I-TEQ ton-feedstock⁻¹. This can be supported by the fact that the temperatures in the BF were still 200°C, indicating quenching was not in high efficiency.

PCDD/F Emissions from Secondary Metal Smelting Plants

Secondary metal smelting processes is an important metal recycling industry. Recycling waste copper for example, saves 63–95% energy and reduces 65–92% CO₂ emission compared with copper’s primary production (Hagelüken, 2006). However, these processes cause secondary pollution and in particular emission of PCDD/Fs. Wevers and De Fre (1995) indicated that PCDD/F emission factors from secondary aluminum smelters can be 12 times higher than those of primary aluminum plants, while those of secondary copper smelters can be within 20–78 times higher than those of primary copper smelters. The data from Table 1 indicate that the contribution to the overall inventories by secondary metal smelting plants, including secondary aluminum smelters and secondary copper smelters, was about 10.6% in China (P.R.C, 2007), 3.6% in Japan (MoE, 2005), and 3.5% in Taiwan (Taiwan EPA, 2008).

Table 5 tabulates the emission factors from secondary aluminum and copper smelters. The major driving factor of the diversity in emission from secondary metal smelters is likely to be the feeding raw material. For secondary copper smelters, Hu et al. (2013) showed that pure copper scrap resulted in higher emission factors (102 µg I-TEQ ton-product⁻¹) compared to scraps (30%) and blister copper (50%) (24.8 µg I-TEQ ton-product⁻¹). For secondary aluminum smelters, Li et al. (2007a) reported the emissions from using recycled materials (4.7 µg I-TEQ ton-product⁻¹) and waste aluminum (12.9 µg I-TEQ ton-product⁻¹) were approximately 3 and 8 times higher than those using ingots (1.66 µg I-TEQ ton-product⁻¹) as feeding materials, respectively. Therefore, to reduce PCDD/F formation, pretreatment and precleaning of waste and scrap aluminum can be suggested. Apart from the differences in the composition of feeding materials, other contributing factors to the wide range of emission factors among these metal smelters could be due to the differences in APCDs, auxiliary fuel and type of furnace installed. Therefore, to suggest a universal emission...
Table 5. PCDD/F emissions from secondary ALS and secondary copper smelters.

| Emission source | Feeding raw material | Auxiliary Fuel | Type of furnace | APCDs | Emission Factor | Annotation | Reference |
|-----------------|----------------------|----------------|-----------------|-------|-----------------|------------|-----------|
| Secondary ALSs  | Scraps, alloying agents, Heavy oil ingot | - | BF | 0.63–23 µg I-TEQ ton-feedstock<sup>-1</sup> (mean = 11.43) | 4 secondary ALSs. | (Lee <em>et al.</em>, 2005) |
|                 | -                    | CY + BF | 0.64–36 µg I-TEQ ton-feedstock<sup>-1</sup> (mean = 12.84) | 3 secondary ALSs. | (Zou <em>et al.</em>, 2012) |
|                 | Natural gas          | BF | WS | 147.82 µg I-TEQ ton-product<sup>-1</sup> | High impurity raw materials | (Wang <em>et al.</em>, 2009a) |
| Waste aluminum, Si, ingot | - | CY + PAC + BF | 12.9 µg I-TEQ ton-product<sup>-1</sup> | Representing the low end and worst case scenario | (Li <em>et al.</em>, 2007a) |
| Recycled materials, Si, ingot | - | CY + BF | 1.63 µg I-TEQ ton-product<sup>-1</sup> | | |
| Scrap           | - | BF | 0.0848 µg I-TEQ ton-feedstock<sup>-1</sup> | | |
|                 | - | CY + BF | 4.7 µg I-TEQ ton-product<sup>-1</sup> | | |
|                 | - | BF | 1.69 µg I-TEQ ton-product<sup>-1</sup> | | |
| Scrap           | - | Top-charge melt (low end), Sidewell reverberatory (worst case) | Lime-coated BF | Mean range = 0.26–36 µg I-TEQ ton-feedstock<sup>-1</sup> | | (EPA, 2000) |
|                 | - | BF + CY | 14.80 µg I-TEQ ton-product<sup>-1</sup> | Raw material pre-cleaned and manually selected. One plant used afterburner + BF | (Ba <em>et al.</em>, 2009) |
|                | - | BF | 2.72 µg I-TEQ ton-feedstock<sup>-1</sup> | | |
| Secondary Copper Smelters | - | BF | 102 µg I-TEQ ton-product<sup>-1</sup> | | (Hu <em>et al.</em>, 2013) |
| pure copper scrap | - | BF | 24.8 µg I-TEQ ton-product<sup>-1</sup> | (%) represents the content in the feed. | |
| Copper scrap (30%), blister copper (50%), ACRE (20%) | - | BF | 0.735 µg I-TEQ ton-product<sup>-1</sup> | | (Wang <em>et al.</em>, 2009a) |
| Pure blister copper scraps | - | BF | 5.88 µg I-TEQ ton-product<sup>-1</sup> | Plant fitted with afterburners | (UNEP, 2005) |
| Copper scrap | - | BF | 779 µg I-TEQ ton-feedstock<sup>-1</sup> | | |
| Sludge          | Pulverized coal      | - | BF + CP + WS | 241.72 µg I-TEQ ton-product<sup>-1</sup> | Low input-output productivity | (Zou <em>et al.</em>, 2012) |
| Dried sludge   | Blasted furnace      | - | BF + CP + WS | 2710 µg I-TEQ ton-product<sup>-1</sup> | | |

ACRE: Anode copper remains after electrolysis; BF: bag filter; CY: cyclone; DSC: dust settling chamber; ESP: electrostatic precipitator; PAC: powdered activated carbon; WS: wet scrubber; m = number of facilities.
- information not provided.
factor for secondary metal smelters might be not possible at this stage.

Generally, the PCDD/F emission factors of secondary copper smelters are higher than those of secondary aluminum smelters. From Table 5, Ba et al. (2009) showed that PCDD/F emission factor of secondary copper plants was 14.8 µg I-TEQ tonne-product⁻¹, which was 6 times higher than 2.65 µg I-TEQ tonne-product⁻¹ of secondary aluminum plants. Wevers and De Fre (1995) also reported that PCDD/F emission factor of secondary copper smelters could reach 3 to 13 times higher compared to secondary aluminum smelters. This could be attributed to catalytic nature of copper in the de novo synthesis of PCDD/Fs (Gullett et al., 1992) occurring on the surface of flue particles (Yu et al., 2006). Hung et al. (2015) investigated the characteristics and mechanisms of PCDD/F formation with different feeding materials in secondary copper smelting industry. Their results indicate that PCDD/Fs are significantly formed even with the reaction time less than 0.1 s, especially when the material containing high Cu residues is fed. High copper content (65 ± 2%) in the feeding material did enhance PCDD/F formation rate.

In the secondary copper smelters, the whole process can be divided into three main smelting stages including feeding-fusion, oxidation and deoxidization. According to the study of Hu et al. (2013), about 54–88% of the PCDD/F emissions occur at the feeding-fusion stage. Similar to secondary copper smelters, EAF process constitutes stages of feeding, smelting, oxidation, reduction and steel discharge. Chang et al. (2006) reported that oxidation stage (feeding and oxidation) (0.421–15.9 ng I-TEQ Nm⁻³) had higher PCDD/F concentrations in the stack flue gases than reduction stage (reduction and discharge) (0.261–6.68 ng I-TEQ Nm⁻³). Therefore, since the PCDD/F emission levels in various stages of the EAFs and secondary metal smelters are quite different, the sampling times of stack flue gases for these PCDD/F sources should correspond to one to three whole smelting process stages to be representative of the whole smelting process.

**PCDD/F Emissions from EAF Dust Treatment Plants**

Fly ash treatment plants act as metal recovery facilities to recover the metal in the fly ash from EAFs. Due to high PCDD/F and metal contents (zinc and lead), the EAF fly ash is considered as hazardous waste (Li et al., 2008a). Incomplete destruction of PCDD/Fs in the raw materials or feeding wastes and then surviving in the combustion system is not usually considered as the important route for PCDD/Fs to the atmosphere. But for EAF dust treatment plants; this route could be as important as other PCDD/F formation mechanisms, that is, precursor and de novo synthesis mechanisms.

The Waelz process was developed to refine zinc from iron ore but also used to capture and retain zinc metal as well as to detoxify the EAF dust. In an effort to reduce PCDD/F emissions from Waelz process, Mager et al. (2003) switched from acid mode to base mode operation by changing the flux from SiO₂ to lime and PCDD/F emission factors through stack flue gases reduced from 17–436 µg I-TEQ ton-product⁻¹ to 0.096–0.18 µg I-TEQ ton-product⁻¹. Table 6 lists PCDD/F emission factors of EAF dust treatment plants. Previously, extremely high PCDD/F emissions (145 ng I-TEQ Nm⁻³) from a specific Waelz process plant in Taiwan were linked to the Toxic Duck/Egg event in Changhua, Taiwan in 2004 (Lee et al., 2009). After consequent APCD improvements in this particular Waelz plant, the PCDD/F emission factors through stack flue gases decreased from 560 µg I-TEQ ton-EAF dust⁻¹ (Chí et al., 2006) to 42.5 µg I-TEQ ton-EAF dust⁻¹ by equipping ACI (Li et al., 2007b). Then, after deploying dual bag filter system, the PCDD/F emission factors further reduced to 0.29 µg I-TEQ ton-EAF dust⁻¹ and the PCDD/F concentrations in the stack flue gases were around 0.03 ng I-TEQ Nm⁻³ (Lin et al., 2008).

In addition to Waelz process, the submerged arc furnace (SAF) process has also been utilized in the metallurgical industry to refine, capture and retain metal from ashes. This process is capable of producing pig iron and steel from EAF dust in addition to capturing zinc metal. According to Table 6, the SAF process may have comparatively higher PCDD/F emissions through stack flue gases (1.39 µg I-TEQ ton-EAF dust⁻¹) than Waelz process (0.29 µg I-TEQ ton-EAF dust⁻¹). That is because the PCDD/F I-TEQ removal efficiencies of the APCDs in the SAF process plant (55.1%–64.0%) were much lower than that of the dual bag filter with AC1 (99.3%) in the Waelz process. However, the high PCDD/F removal efficiency only transfers gas phase PCDD/Fs to the fly ash without necessarily destroying them. In fact, the total PCDD/F emission factors of the whole system (ash + stack flue gas) of the Waelz process (840–1120 µg I-TEQ ton-EAF dust⁻¹) were significantly higher than that of SAF process (46.9 µg I-TEQ ton-EAF dust⁻¹) (Xu et al., 2014). This is because, in the SAF process, most of the PCDD/Fs as well as the organic compounds in the pellets, which could play a role in PCDD/F formation, are initially decomposed in the reducing furnace fueled by natural gas, and then further completely destroyed in the SAF. Therefore, SAF process is superior to the Waelz process in reducing PCDD/F formation during thermal treatment of EAF dust (Xu et al., 2014).

**PCDD/F Emissions from Power/Heat Generation**

Power/heat generation systems including fossil fuel (coal and heavy oil) fired power plants, and industrial boilers are also a major source of PCDD/Fs as seen from Table 1. The contribution of the power/heat generation category to the overall PCDD/F inventories in China was about 6.9% (P.R.C, 2007), 5.4% in the US (US EPA, 2006) and 2.86% in Australia (Bawden et al., 2004). The major sources in this category, which will be discussed, are coal-fired power plants, heavy oil-fueled power plants and boilers.

The heavy dependence on coal as a source of energy has made coal-fired power plants as one of the most important PCDD/F sources in the environment. The PCDD/F emissions from coal-fired power plants depend on the type of coal used as well as the APCDs in operation. As seen in Table 7, there exist differences in the emission factors from different power plants (0.001–0.005 µg I-TEQ tonne-coal⁻¹ in Fernández-Martínez et al. (2004), 0.09–0.11 µg I-TEQ tonne-coal⁻¹ in

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**Table 6**

| Process Type          | Emission Factor (µg I-TEQ ton-EAF dust⁻¹) | Percentage Reduction |
|-----------------------|------------------------------------------|----------------------|
| Waelz                 | 0.29                                     | 99.3%                |
| SAF                   | 0.29                                     | 95.5%                |
| Coal-fired Power Plants | 46.9                                    | 99.3%                |
| Heavy oil-fueled Power Plants | 1120                                  | 99.3%                |

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Table 6. PCDD/F emission factors of EAF dust treatment plants.

| Feeding material                                      | Product                | Type of furnace          | APCDs  | Emission Factor | Annotation | Reference                  |
|-------------------------------------------------------|------------------------|--------------------------|--------|-----------------|------------|-----------------------------|
| SiO2 (20%), coke (30%), EAF dust (50%)                | ZnO                    | Waelz rotary kiln        | DSC + VT + CY + BF | 560 µg I-TEQ ton-EAF dust\(^{-1}\) |            | (Chi et al., 2006)          |
| EAF fly ash (74%), coke (13%), sand (13%)             | ZnO                    | Waelz rotary kiln        | DSC + VT + CY + ACI + BF | 42.5 µg I-TEQ ton-EAF dust\(^{-1}\); 40 kg h\(^{-1}\) of ACI was used |            | (Li et al., 2007b)          |
| EAF fly ash (60–70%), coke (10–20%), sand (10–20%)   |                        |                          |        |                 |            | (Lin et al., 2008)          |
| Steel mill flue dust, various zinc-bearing residues,   | Waelz oxide product    | Waelz rotary kiln        | DSC + VT + CY + ACI + DBF | 0.29 µg I-TEQ ton-EAF dust\(^{-1}\); 16 kg h\(^{-1}\) of ACI was used |            | (Mager et al., 2003)        |
| coke, and fluxes                                      |                        |                          |        |                 |            |                             |
| Oxidized iron scraps (11.5%), EAF dusts (64.0%),      | Steel ingots           | Submerged arc furnace (SAF) | GSC + BF | 1.39 µg I-TEQ ton-Waelz Oxide product\(^{-1}\); The emission factor is a sum of emission factors from pelletizer, reducing furnace and SAF subsystems |            | (Xu et al., 2014)           |
| carbon powders (13.2%), binders (1.86%), cokes (3.34%), slagging fluxes (5.98%) |                        |                          |        |                 |            |                             |
| EAF fly ash pellets                                   | Steel ingots           | Submerged arc furnace (SAF) | GSC + BF | 7.97 µg I-TEQ ton-product\(^{-1}\); m = 2, n = 6 |            | (Wang et al., 2010b)        |

ACI: activated carbon injection; BF: bag filter; CY: cyclone; DBF: dual bag filter; DC: dust chamber; GSC: gravity settling chamber; PS: precipitator; SBF: single bag filter; VT: venturi tower; m = number of facilities; n = total number of s
Mokhtar et al. (2014) and 0.147 µg I-TEQ tonne-coal⁻¹ in Lin et al. (2010). Mokhtar et al. (2014) indicated that bituminous coal with high sulfur content resulted in slightly lower PCDD/F emissions compared to sub-bituminous coal. This indicates that the presence of sulfur in coal has contributed to the suppression of PCDD/F emissions from coal fired power plants. Similar to coal combustion, the effect of type of input feed on PCDD/F emissions can be seen in co-combustion power plants whereby Zhang et al. (2013) reported an increase in emission factor with an increase in sewage sludge during co-combustion of coal and sewage sludge. The was because the sewage sludge had higher chlorine (2.98%) content compared to coal (0.17%), therefore with an increase in the fraction of sewage sludge, more chlorine was fed which encouraged PCDD/F formation.

Another important type of power plant in terms of PCDD/F emissions is the heavy oil-fueled power plant. Compared to coal-fired power plants, less research has been conducted on the emission from this particular source. As shown in the Table 7, the emission factors of heavy oil-fueled power plant (0.181 µg I-TEQ tonne-fuel⁻¹) are generally lower than those of coal-fired power plants. Few studies have been done to evaluate the PCDD/F emissions from industrial boilers and small scale boilers. Samaras et al. (2001) evaluated PCDD/F emissions from industrial boilers fueled with biomass, lignite and waste wood blends and the PCDD/F concentrations ranged from 3.0–97.3 pg TEQ Nm⁻³. The highest concentrations (97.3 pg TEQ Nm⁻³) were from wood/lignite blend (80% wood, 20% lignite by weight) and the lowest (3.0 pg TEQ Nm⁻³) was from medium density fiber (MDF)/lignite blend (80% MDF, 20% lignite). This indicates that similar to coal-fired power plants, the type of fuel used is an important factor affecting PCDD/F emissions from boilers. Similarly, the impact of boiler fuel is as seen from Table 7 the emission from wood biomass were in the range of 2–33 µg I-TEQ tonne-wood biomass⁻¹ while those from straw were in the range of 12–13 µg I-TEQ tonne-straw⁻¹ (Kubica et al., 2004).

In the study of PCDD/F output/input ratio related to power plants and boilers, Zhang et al. (2013) found out that PCDD/Fs were destroyed during co-combustion of coal and sewage sludge, since the PCDD/F inputs were in the range of 0.070–0.317 µg I-TEQ tonne-wood biomass⁻¹, while those from straw were in the range of 0.070–0.317 µg I-TEQ tonne-MF⁻¹. On the other hand, Chen et al. (2011b) found out that the output PCDD/F toxicity was about 7 times greater than that contained in the input woodchip feedstock, indicating that PCDD/Fs were formed in the woodchip-fueled boilers rather than destroyed. The formations of PCDD/Fs in the boilers may be as a result of lower efficiency on combustion and heat exchange system, which may increase retention time of flue gases at PCDD/F de novo formation window. Emissions from this particular woodchip-fueled boiler were compounded by the fact that there were no active control devices for gaseous phase PCDD/Fs. There were about 21.4% of total PCDD/F mass and 18.0% of total

### Table 7. PCDD/F emissions from power plants and boilers.

| Facility            | Fuel                  | APCDs                        | Emission Factor           | Annotation | Reference                                      |
|---------------------|-----------------------|-------------------------------|----------------------------|------------|------------------------------------------------|
| Power plants        | Coal                  | SCR + ESP + FGD              | 0.147 µg I-TEQ tonne-coal⁻¹ |            | (Wang et al., 2010b)                           |
|                     | Mixed Fuel (MF)       | SDS + BF                     | 0.034–0.160 µg I-TEQ tonne-MF⁻¹ | Coal co-combustion with sewage sludge | (Zhang et al., 2013) |
|                     | Bituminous coal       | SCR + ESP + FGD              | 0.62 µg I-TEQ tonne-coal⁻¹ |            | (Lin et al., 2007)                             |
|                     | Bituminous, sub-bituminous and lignite coal | -                             | 0.001–0.005 µg I-TEQ tonne-coal⁻¹ |            | (Fernández-Martínez et al., 2004)               |
|                     | coal                  | ESP                           | 0.09–0.11 µg I-TEQ tonne-coal⁻¹ |            | (Mokhtar et al., 2014)                         |
|                     | coal                  | ESP + FGD                    | 0.08 µg I-TEQ tonne-coal⁻¹ |            | (Lin et al., 2010)                             |
|                     | Heavy oil             | ESD                           | 1.75 µg I-TEQ tonne-coal⁻¹ |            | (Wang et al., 2010b)                           |
|                     | Heavy oil             | SCR + ESP + FGD              | 0.181 µg I-TEQ tonne-fuel⁻¹ |            | (Wang et al., 2010b)                           |
|                     | Heavy oil             | ESP                           | 0.188 µg I-TEQ m⁻³ (fuel)  |            | (Wang et al., 2009b)                           |
| Industrial Boiler   | straw                 | -                             | 12–13 µg I-TEQ tonne-straw⁻¹ | Boiler not adopted for biomass combustion | (Kubica et al., 2004) |
|                     | Wood biomass          | -                             | 2–33 µg I-TEQ tonne-wood biomass⁻¹ |            |                                                 |
|                     | Wood Chips            | CY + BF                       | 0.095 µg I-TEQ tonne-woodchip⁻¹ |            | (Chen et al., 2011b)                           |
|                     | Wood Chips            | CY + BF                       | 2.99 µg I-TEQ tonne-woodchip⁻¹ |            | (Wang et al., 2010b)                           |

BF: bag filter, CY: cyclone, ESD: electrostatic dust collectors, FGD: Flue Gas Desulphurization, ESP: Electrostatic Precipitator, SDS: semidry scrubber, SCR: Selective Catalytic Reduction.
PCDD/F toxicity emitted from the stack flue gases of the woodchip-fueled boiler, because only cyclone and bag filter were deployed (Chen et al., 2011b).

These power/heat generation PCDD/F sources have two important issues. Firstly, power plants and boilers have low PCDD/F concentrations in flue gases, for example, 0.002–0.031 ng I-TEQ Nm–3 (Lin et al., 2007) and 0.0119 ng I-TEQ Nm–3 for coal-fired power plants (Mokhtar et al., 2000) and 0.145 ng I-TEQ Nm–3 from woodchip boiler (Wang et al., 2010b). On the other hand, they are characterized by extremely high flow rates of flue gases, 1.80 × 106 Nm3 h–1 and 1.68 × 104 Nm3 h–1 (Wang et al., 2010b). Therefore, it is suggested that during flue gas samplings of power plants for trace pollutants, such as PCDD/Fs and heavy metals, longer time should be executed for flue gas sample collection to enable the collected pollutants amounts to be above the method detection limits (MDLs).

**PCDD/F Emissions from Crematories**

Crematories are characterized by low contributions to the PCDD/F inventories as seen in Table 1, for example, only contributing about 0.63–1.4% in Japan. However, the use of crematories is becoming the mainstream and preferred way of disposing cadavers across the globe. In the U.S., the cremation ratio has increased significantly from 15.2% in 1987 to 25.0% in 2000 (EPA Database, 2001), while in Taiwan, the cremation ratio increased from about 66.9% in 2000 to 95.7% in 2014 (Wang et al., 2003a). In Japan, because of the encouragement of the governmental policy, its current cremation ratio is as high as 99% (Takeda et al., 2000). Crematories usually have poor combustion conditions and low efficient APCDs, resulting in high PCDD/F concentrations in the stack flue gases. Furthermore, due to their proximity to residential areas and their low lying stacks, the PCDD/F emissions from crematories may result in great impact to their surrounding environment (Wang et al., 2003a).

As seen in Table 8, wide range of PCDD/F emission factors can be found in these studies. Obviously, this could be due to the intrinsic differences in the types of combustion chamber, fuel, and air pollution control devices among various crematories. From Table 8, we can see that APCDs have a great impact and potential in reducing the PCDD/F emissions from crematories. For crematories without APCDs, the emission factors were in the range of 2.4–20 µg I-TEQ body–1, while when APCDs, such as bag filters and activated carbon injection, were used, the PCDD/F emissions factors reduced to < 1–6.11 µg I-TEQ body–1 (Bremmer et al., 1994; Xue et al., 2016). Furthermore, equipping crematories with secondary combustion chamber and using natural gas as auxiliary fuel can further reduce PCDD/F emission factors to 0.12–1.83 µg I-TEQ body–1 (Takeda et al., 2001, 2014).

**PCDD/F EMISSIONS FROM MOBILE SOURCES**

Even though the PCDD/F emissions from mobile sources are low compared to stationary combustion sources, their proximity to the human population and living environment makes mobile sources important sources in terms of human exposure. Compared to other regulated pollutants, such as PM, NOx, SOx, there are relatively few PCDD/F studies for

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**Table 8. PCDD/F emission factors of crematories.**

| Crematories                         | Auxiliary Fuel | APCDs | Emission Factor       | Annotation                          | Reference             |
|-------------------------------------|----------------|-------|-----------------------|-------------------------------------|-----------------------|
| **Crematories without APCDs**       | Diesel         | none  | 13.6 µg I-TEQ body–1 | No APCDs employed                   | (Wang et al., 2003a)  |
|                                    |                |       |                       |                                     |                       |
|                                    | -              | none  | 2.4 µg I-TEQ body–1  | “cold” type furnace with direct     | (Bremmer et al., 1994) |
|                                    |                |       |                       | uncooled emissions.                 |                       |
|                                    |                |       | 4.9 µg I-TEQ body–1  | “warm” type with cooling of flue     | (Bremmer et al., 1994) |
|                                    |                |       |                       | gases to 220°C prior to discharge    |                       |
|                                    |                |       | 20 µg body–1         | 11 cremators without post-treatment | (Xue et al., 2016)   |
| **Crematories with APCDs**          | Diesel         | BF    | 6.11 µg I-TEQ body–1 |                                     |                       |
|                                    |                |       |                       |                                     |                       |
|                                    |                | BF    | Less than 1 µg I-TEQ  | both warm and cold types            | (Bremmer et al., 1994) |
|                                    |                |       | body–1               |                                     |                       |
|                                    |                | HE + BF + | 2 µg I-TEQ body–1  | 6 cremators with post-treatment     | (Xue et al., 2016)   |
|                                    |                | WS + ACI |                        | devices in China                    |                       |
| **Crematories with secondary**      | Kerosene, town  | DS    | 1.83 µg I-TEQ body–1 | 17 crematories in Japan              | (Takeda et al., 2001) |
| **combustion**                      | gas, heavy fuel |       | (geometric mean)      |                                     |                       |
| **chamber**                         | oil            |       |                       |                                     |                       |
|                                    | Natural gas    | BF    | 0.00041–16 µg I-TEQ   | 14 crematories in Japan              | (Takeda et al., 2014) |
|                                    | and APCDs      |       | body–1               |                                     |                       |
|                                    |                |       | 0.12 µg I-TEQ body–1  |                                     |                       |

ACI: activated carbon Injection; BF: bag filter; DC: dust collector; HE: heat exchanger; WS: wet scrubber.
- no information on fuel provided by references.
mobile sources, even after engine exhaust was classified as Group 1, carcinogenic to humans, by the International Agency for Research on Cancer (IARC) in 2012. Even fewer PCDD/F studies exist for off-road diesel engines or vehicles, such as farm tractors, heavy forklifts, excavators, etc. Unlike on-road vehicles, the off-road diesel engines or vehicles whose application is in close proximity to humans do not commonly employ aftertreatment and engine innovations to reduce pollutants. Moreover, none or few studies have been carried out to characterize PCDD/F emissions from ships, freighters or airplanes. Therefore, there exists a major research gap in the PCDD/F characteristics in exhaust emitted from off-road vehicles and other non-road modes of transportation.

Many factors, such as fuels, engine types, test modes, after treatment technologies that can affect PCDD/F emissions from vehicles have been discussed in previous study and review articles (Heeb et al., 2007; Chuang et al., 2010, 2011; Chang et al., 2014b; Rey et al., 2014; Mwangi et al., 2015). Here we aim to focus on how to conduct vehicular exhaust samplings to obtain better quality data to estimate PCDD/F emission factors from mobile sources.

Three measurement approaches have been used, including direct measurement involving tailpipe sampling using dynamometers, and on-road tailpipe samplings using actual moving vehicles, as well as indirect measurements in tunnel studies by sampling affected air. Tailpipe PCDD/F samplings using dynamometers further include direct exhaust samplings from tailpipes and use of dilution tunnels suited for PM sampling. One major drawback of dilution tunnel method is that the PCDD/F levels in exhaust of engines are very low and hence the values obtained via this method are usually below detection limit. Otherwise, the tests have to be carried out over 6 hours in order to obtain substantial amounts of samples for PCDD/F analysis (EPA, 2000). In comparison, direct exhaust samplings from tailpipes are only carried out for approximately half hour, and exhaust samples sufficient for PCDD/F analysis can be obtained (Chang et al., 2014b). This really saves money and manpower, especially compared to spending 6 hours on dynamometer test. As for tunnel studies, major disadvantages include uncertainties arising from the possibility of overestimation when aged resuspended particles are collected and also the fact that in the tunnels, the driving conditions are steady state, which rarely involve transient driving cycles and cold engine starts which are representative of urban driving scenarios (EPA, 2000).

Depending on the system in which a country reports its national economic activity and statistics, the units of PCDD/F emission factors of mobile sources for inventory use are usually on the basis of liters of fuel consumed and/or on the basis of number of kilometers covered. PCDD/F emission factors from various studies are presented in Table 9. Heavy duty diesel vehicles have higher PCDD/F emission factors (1690 pg I-TEQ km⁻¹) in comparison to diesel passenger vehicles (80.3 pg I-TEQ km⁻¹) or even sports utility vehicles.

### Table 9. PCDD/F emission factors of mobile sources.

| Engine/vehicle Type | Fuel Type | Test type | Emission factor | Annotation | References |
|---------------------|-----------|-----------|-----------------|------------|------------|
| HDDVs               | Diesel    | Dynamometer | 1690 pg I-TEQ km⁻¹ | Mileage: 5.5 × 10⁷ – 8.7 × 10⁸ | (Chuang et al., 2011) |
|                     |           |           | 7.11–13.6 pg I-TEQ L⁻¹ | m = 4; n = 12 | (Laroo et al., 2012) |
|                     |           |           | 663–1300 pg I-TEQ km⁻¹ | 6-hr dynamometer test at 50 km h⁻¹ | (Lew, 1993, 1996) |
|                     |           | Dynamometer | 30.5 pg I-TEQ L⁻¹ | B2: 2% bio-diesel + 98% diesel; | (Chang et al., 2014b) |
|                     |           | On-road tailpipe sampler | 29–109 pg I-TEQ km⁻¹ | Mileage: 8 × 10⁵ km; | (Ryan and Gullett, 2000) |
|                     |           | Tunnel     | 170 ± 80 pg I-TEQ km⁻¹ | Sampled before the muffler; m = 2 | (Gertler et al., 1998) |
| DPVs                | Diesel    | Dynamometer | 80.3 pg I-TEQ km⁻¹ | Mileage: 7 × 10³ – 12 × 10⁴ | (Chuang et al., 2011) |
|                     |           |           | 23 pg I-TEQ L⁻¹ | m = 4; n = 48 | (Dyke et al., 2007) |
|                     |           |           | 97 pg I-TEQ L⁻¹ | Without DOC | |
| SUVs                | Unleaded gasoline | Dynamometer | 123 pg I-TEQ km⁻¹ | Mileage: 13.9 × 10³ – 12.2 × 10⁶ | (Chuang et al., 2011) |
|                     |           |           | 0.36–0.39 pg I-TEQ km⁻¹ | m = 4; n = 12 | (Marklund et al., 1990) |
|                     |           |           | Sampled before the muffler; m = 2 | |
| Motorcycle          | Standard test gasoline | Dynamometer | 86–114 pg I-TEQ km⁻¹ | 2-stroke engine, Mileage: | (Chuang et al., 2010) |
|                     |           |           | (mean = 96 pg I-TEQ km⁻¹) | 2.8 × 10⁷ – 1.1 × 10⁸ | (m = 6) |
|                     |           |           | 40–138 pg I-TEQ km⁻¹ | 4-stroke engine, Mileage: | (Chuang et al., 2010) |
|                     |           |           | (mean = 81 pg I-TEQ km⁻¹) | 1.7 × 10⁸ – 5.0 × 10⁹ | (m = 6) |

DOC: diesel oxidation catalyst; DPVs: diesel passenger vehicles; HDDVs: heavy duty diesel vehicles; m = number of vehicles samples; n = total number of samples; SUVs: sports utility vehicles.
(123 pg I-TEQ km⁻¹) running on gasoline (Chuang et al., 2011). The PCDD/F emissions factors of motorcycles (86–114 pg I-TEQ km⁻¹) (Chuang et al., 2010) were almost comparable to those of vehicles (Chuang et al., 2011) probably due to lower combustion efficiencies of motorcycles. Unfortunately, there are not as many studies focusing on PCDD/Fs emissions from motorcycles considering that the number of motorcycles in Asia is considerably high, accounting for 75% of the fleet (McDonald et al., 2005).

**PCDD/F EMISSIONS FROM MINIMALLY OR NON-CONTROLLED COMBUSTION SOURCES**

Minimally or non-controlled combustion sources, such as open biomass burning, residential combustion of wastes and backyard waste burning, are arguably among the highest and significant sources of PCDD/Fs. Biomass burning can include either intentional burning of biomass during post-harvest periods or unintentional burning of biomass, like accidental forest fires. The significance of the minimally or non-controlled combustion sources can be seen from Table 1, whereby their contributions to the inventories accounted for 44.7% in the EU (Quaß et al., 2004), 36.9% in the US (US EPA, 2006), 69.66% in Australia (Bawden et al., 2004) and 36.8% in Brazil (MMA, 2015). The concentration of PCDD/Fs in the ambient air of areas with biomass burning activity could have 4–17 times greater than areas with no or minimal biomass burning activity (Shih et al., 2008).

Table 10 lists PCDD/F emission factors from some minimally controlled combustion sources including stoves and residential boilers. A major characteristic of these sources is that, minimally controlled facilities have low combustion efficiencies and poor combustion conditions. Additionally, they lack APCDs to mitigate emissions. As seen in Table 10 major types of fuel used for stoves and residential boilers are coal and wood, which are similar to those of coal fire power plants and industrial boilers reported in Table 5, but their PCDD/F emission factors were five orders higher than those of coal power plants and industrial boilers.

Even though the PCDD/F emissions from minimally or non-controlled combustion sources rank highest, one major issue is that of high uncertainty in terms of emission factor determination. This results from lack of representative tests that can simulate real burning sources or convincing sampling methods for flue gases from field burnings. There are two major methods, which are usually adopted to measure the PCDD/F emission factors of these non-controlled combustion sources. One is indirect measurement by conducting ambient air samplings using high-volume samplers during open burning activity. This emission factor determination involves using CO: CO₂ ratios whereby the elemental carbon and organic carbon are assumed minimal and when the background CO and CO₂ are subtracted from the collected samples, the remaining C represent combusted biomass (Gullett et al., 2001). Thus the emission factors of PCDD/Fs are calculated in terms of PCDD/Fs ng I-TEQ kg-Cburned⁻¹. Another method is to build an open burn testing facility, which equip with stack for direct flue gas measurement, to simulate field burning conditions. These laboratory based modelling facilities like the one used by US EPA (Gullett et al., 2001) or experimental burn tunnels (Black et al., 2012), whereby predetermined mass of biomass are combusted in chambers with enhanced recirculation to mirror open burning and the flue gases collected to determine emission factors on the basis of waste burnt (PCDD/Fs ng-TEQ kg-waste⁻¹).

The disadvantages of indirect measurement by conducting ambient air samplings are the plume may not be caught by ambient air samplers and the results maybe not able to comparable with other studies. However, the open burn testing facility may also have issues on how to reflect the real open burning conditions since the smoke plume in laboratory tests stay at higher temperatures compared to open field (Meyer et al., 2004; Costner, 2005). Open burn testing facility studies usually have higher PCDD/F emission factors compared to field studies (Ivory and Mobbs, 2004; Costner, 2005). That is because in the field the plumes cool faster, heterogeneous reactions to form PCDD/Fs are retarded, while in the open burn testing facility studies, the smoke remains at high temperatures, allowing for more PCDD/F formations (Costner, 2005). Sometimes open fires and barrels are used especially to estimate emissions from backyard burning (Wevers et al., 2004). Also wind tunnel testing, bang box and remote sensing have been employed to estimate emissions of PCDD/Fs (Lemieux et al., 2004).

| Sources       | Type of fuel                                      | Emission Factor                      | Reference               |
|---------------|--------------------------------------------------|--------------------------------------|-------------------------|
| Stoves        | wood (logs, briquettes, chipped wood, pellets), coal (brown coal briquettes, hard coal) and coke | 0.023–4.5 ng TEQ MJ⁻¹ (mean 0.75 ng TEQ MJ⁻¹) | Hübner et al., 2005     |
|               | Pine needles and pine cones                      | 196 ng I-TEQ kg-material burnt⁻¹     | Moltó et al., 2007      |
|               | Coal residential combustion of biofuels          | 3.5–4.9 ng WHO-TEQ kg-fuel⁻¹         | Paradiž et al., 2008    |
| Residential   | wood (logs, briquettes, chipped wood, pellets), coal (brown coal briquettes, hard coal) and coke | 0.002–2.6 ng TEQ MJ⁻¹ (mean 0.38 ng TEQ MJ⁻¹) | Hedman et al., 2006     |
| Boilers       | Lignite, Bituminous coal                         | 3.16–2200 ng I-TEQ GJ⁻¹             | Šyc et al., 2011        |
|               | Beech logs, spruce logs, Different types of boilers remaining combustion of biofuels | 1.2–290 ng WHO-TEQ kg-fuel⁻¹        | Hedman et al., 2006     |
Table 11 lists PCDD/F emission factors of non-controlled combustion sources, which were categorized by the sampling methods and types of wastes. It is clear that the emission factors from open waste burning were very variable and also depended on the type of biomass or waste being combusted. For example, Gullett et al. (2007) reported that the emission factor of burning insulated wire was 11900 ng TEQ kg waste\(^{-1}\), which were 130 times higher than those from circuit boards (92 ng TEQ kg waste\(^{-1}\)). Average values of 25 ng TEQ kg-burned\(^{-1}\) and 15 ng TEQ kg-burned\(^{-1}\) were measured from a forest fire simulation in Oregon and North Carolina, respectively (Gullett and Touati, 2003b). Another study by Gullett and Touati (2003a) measured PCDD/F emissions from wheat and rice straw burning and found them to be 337–602 pg I-TEQ kg\(^{-1}\) for wheat and 537 pg I-TEQ kg\(^{-1}\) for rice straw. Estimating PCDD/F emissions from forest fires has been attempted by some researchers using open burn testing facilities. When evaluating the impact of biomass burning to the environment, Chang et al. (2014a) showed that during rice straw burning periods PCDD/F concentrations measured near the combustion site increased by about 6–20 times. The emission factors calculated in their study were based on burnt carbon method and industrial source complex short-term dispersion model, and ranged from 12.6–14.5 ng I-TEQ kg\(^{-1}\) burned. The values from Chang et al. (2014a), whose measurements were open field test might be in one order range from those of Gullett and Touati (2003a) who conducted simulation using open burning facility. These observations are in contrast with statement from Ivory and Mobbs (2004).

### ADVANCEMENTS TOWARDS REPRESENTATIVE FLUE GAS SAMPLING TECHNIQUES

The regulated methods for sampling PCDD/Fs in stack flue gases, such as US EPA modified Method 23 and EN 1948-1,2,3, are used for manual short-term sampling. Following these standard methods, the sampling time for one stack flue gas sample usually ranges from 3 to 6 hours. PCDD/F concentrations vary depending on the operating conditions. As mentioned earlier, high PCDD/F emissions are observed during transient operations, making the annual emissions, which are calculated from the values obtained during normal operations, to be less representative (Wang et al., 2007; Hung et al., 2016). In other words, the PCDD/F emissions that occur during the time of flue gas sampling are of little relevance to the overall emission levels.

Continuous monitoring and real-time detection could therefore be useful in better understanding of the emission characteristics of PCDD/Fs and also facilitate in the optimal application of APCDs (Gullett et al., 2012). The sampling and analysis of PCDD/Fs is a tedious and time-consuming activity. The real-time measurement of PCDD/Fs is still impossible (Everaert and Baeyens, 2002), even though some semireal-time detection techniques have been proposed, such as Jet-REMPI (Resonance Enhanced Multi-Photon Ionization), REMPI-TOFMS (Resonance Enhanced Multi-Photon Ionization and Time-of-Flight Mass Spectrometry).

| Method | Type of waste | Emission Factor | Reference |
|--------|---------------|----------------|-----------|
| Ambient air field sampling using high-volume samplers | Municipal solid waste | 3.0 to 650 ng TEQ kg-waste\(^{-1}\) (mean 110 ng TEQ kg-waste\(^{-1}\)) | (Zhang et al., 2011) |
| | Household waste | 510–1100 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\) | (Solorzano-Ochoa et al., 2012) |
| | Residential waste | 202-1700 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\) (mean 823 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\)) | (Gullett et al., 2009) |
| | Rice straw | 12.6–14.5 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\) | (Chang et al., 2014a) |
| | Domestic household waste | < 10 to > 6000 ng TEQ kg-waste\(^{-1}\) | (Gullett et al., 2001) |
| | Forest biomass | Mean: 5.8 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\) | (Gullett et al., 2008) |
| | Grass biomass | 0.32 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\) | |
| | Forest biomass | Mean: 25 ng TEQ kg-burned\(^{-1}\) (range: 14–47) (Oregon biomass) | (Gullett and Touati, 2003b) |
| | | Mean: 15 ng TEQ kg-burned\(^{-1}\) (range: 1–56) (North Carolina biomass) | |
| Simulation using Open Burn Testing Facility (OBTF) | Wheat straw | 337 to 602 pg TEQ kg\(^{-1}\) | (Gullett and Touati, 2003a) |
| | Rice straw | 537 pg TEQ kg\(^{-1}\) | (Gullett et al., 2007) |
| | Electronic wastes | 92 ng TEQ kg-waste\(^{-1}\) | |
| | Insulated wire | 11900 ng TEQ kg-waste\(^{-1}\) | |
| | Military waste | 35–780 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\) (mean 270 ng TEQ kg-C\(_{\text{burned}}\)\(^{-1}\)) | (Woodall, 2012) |
| | Biomass burning (straw) | 48.6 ng I-TEQ kg\(^{-1}\) | (Lin et al., 2007) |
| | Biomass burning (wax apples) | 2.69 ng I-TEQ kg\(^{-1}\) | |
| | Ritual paper burning | 1.36 ng I-TEQ kg\(^{-1}\) | |
| | Test carried out using barrels and open fires | Garden waste | 4.5 ng TEQ kg-waste\(^{-1}\) | (Wevers et al., 2004) |
| | Household waste | 35 ng TEQ kg-waste\(^{-1}\) | |
and LI-TOFMS (Laser Ionization and Time-of-Flight Mass Spectrometry) (Lee et al., 2008). In response, there has been an effort in developing continuous monitoring technologies, like AMESA (adsorption method sampling for dioxins) developed for long-term samplings for POPs (Lee et al., 2008; Vicaretti et al., 2013; Wu et al., 2014a). AMESA is a fully automatic long-term sampling system for industrial processes. It is based on isokinetic flue gas sampling and the PCDD/F adsorption takes place on exchange resin-filled cartridges (Lee et al., 2008). AMESA has been tested and is mandatory in some European countries. The advantage of continuous sampling up to one month over short-term is that it is more representative to characterize the emission profile (Rivera-Austrui et al., 2014).

Conversely, it is more challenging to move AMESA from one stack to another compared to manual short-term sampling. Thus in order to make the PCDD/F inventories more conclusive and representative, it is suggested that AMESA be used exclusively for monitoring PCDD/F emissions from the highly contributing stationary sources, such as sinter plants, EAFs, power plants and so on.

CONCLUSIONS

Due to their toxic nature, PCDD/Fs have attracted attention from regulatory bodies and all parties of the Stockholm Convention are supposed to develop national inventories to estimate releases of unintentional POPs based on the national economic activity. The major sources identified by various inventories are the waste incineration, metallurgical processes, power plants and biomass burning including backyard and wood combustion. This overview provides integrative and useful information for the PCDD/F emission and point out several feasible directions for both scientific research and environmental management.

1. PCDD/F emissions from start-up procedures of MSWIs, which can contribute two times larger than that of a whole year’s normal operations, are not considered in the inventories. Furthermore, the start-up procedures may result in de novo and adsorptive based memory effects, which may elevate subsequent PCDD/F emissions. The economizers had been found the source of PCDD/F formation in the MSWIs, because its operational temperature fall within PCDD/F formation window. Therefore, it is encouraged to improve the heat exchange efficiency of economizers in order to shorten the residence time of the flue gas so as to effectively reduce PCDD/F formation in the MSWIs.

2. As for secondary metal smelters, variation in feeding materials and operational conditions make it difficult to obtain universal and representative emission factors and it is suggested that flue gas sampling time should be inclusive of all operational stages in order to obtain conclusive results. On the other hand, pretreatment of scrap metal before feeding into the secondary smelters is proposed as a preventive measure for PCDD/F formation. Quench towers should be a promising device to reduce PCDD/F formations in the post-combustion sections of EAFs.

3. For EAF dust treatment plants, survival of PCDD/Fs in the EAF dust during combustion and then emission to the atmosphere could be an important route compared to other PCDD/F formation mechanisms. SAF process is superior to the Waelz process in reducing PCDD/F formation during thermal treatment of EAF dust because of most PCDD/Fs and organic compounds in the pellets, which could play a role in PCDD/F formation, are initially decomposed in the reducing furnace fueled by natural gas, and then further completely destroyed in the SAF.

4. More research and emission control are needed for sources, which have low PCDD/F emissions, but pose high risk to human beings due to their proximity to human residences. These include crematories, home heating appliances such as boilers and stoves as well as off-road vehicles and motorcycles, which lack regulation in terms of PCDD/F emissions and are operated at low combustion efficiencies with minimal pollution control measures.

5. Long-term sampling methods such as AMESA are advantageous in providing representative sampling results and as such should be widely used in major sources to improve the quality of inventories.

6. Other PCDD/F emission sources such as open burning lack representative tests that simulate real burning conditions. The two existing methods like indirect sampling, which do not give comparable and repeatable results, while simulation methods rarely reflect the real combustion dynamics in the open field. Efforts are required to moderate and reduce variances between field and simulation tests for uncontrolled combustion sources.

7. PCDD/F emissions from minimally or non-controlled combustion sources rank highest, and one major issue is that of high uncertainty in terms of emission factor determination. Efforts to build open burn testing facilities that can reflect the real open burning conditions is needed.

NOMENCLATURE AND ABBREVIATION

- °C: degree Celsius
- AC: activated carbon
- ACI: activated carbon injection
- ALS: aluminum Smelting
- AMESA: adsorption method sampling for dioxins
- APCDs: air pollution control devices
- BFs: bag filters
- BSFC: brake specific fuel consumption
- CFs: catalytic filters
- CO: carbon monoxide
- CO₂: carbon dioxide
- CY: cyclone
- DBF: dual bag filter
- DC: dust chamber
- DEA: Department of Environmental Affairs
- DECS: dioxin emission continuous sampling
- DOC: diesel oxidation catalyst
- DPVs: diesel passenger vehicles
- DS: dry scrubber
- DSC: dust settling chamber
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