



Review

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

Nicholas Kiprotich Cheruiyot<sup>1</sup>, Wen-Jhy Lee<sup>1</sup>, Ping Yan<sup>2\*\*\*</sup>, John Kennedy Mwangi<sup>1\*\*</sup>,  
Lin-Chi Wang<sup>3\*</sup>, Xiang Gao<sup>4</sup>, Neng-Huei Lin<sup>5</sup>, Guo-Ping Chang-Chien<sup>6</sup>

<sup>1</sup> Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan

<sup>2</sup> School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China

<sup>3</sup> Department of Civil Engineering and Geomatics, Cheng Shiu University, Kaohsiung 833, Taiwan

<sup>4</sup> State Key Laboratory of Clean Energy Utilization, Zhenjiang University, Hangzhou 310027, China

<sup>5</sup> Department of Atmospheric Sciences, National Central University, Zhongli 320, Taiwan

<sup>6</sup> Department of Cosmetic and Fashion Styling, Cheng Shiu University, Kaohsiung 833, Taiwan

---

### 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.

---

### CONTENTS

ABSTRACT .....	2965
INTRODUCTION .....	2966
FORMATION AND DECOMPOSITION MECHANISMS OF PCDD/FS .....	2967
MAJOR EMISSION CATEGORIES IN PCDD/F INVENTORIES WORLDWIDE .....	2967
PCDD/F EMISSIONS FROM STATIONARY SOURCES .....	2967

---

\* Corresponding author.

Tel.: +886-7-7351275; Fax: +886-7-7332204

E-mail address: lchwang@csu.edu.tw

\*\* Corresponding author.

Tel.: +886-970-878483

E-mail address: kenjohnmwas@gmail.com

\*\*\* Corresponding author.

E-mail address: y9621227@126.com

PCDD/F Emissions from Waste Incinerators .....	2967
PCDD/F Emissions from Metallurgical Facilities .....	2970
PCDD/F Emissions from Sintering Plants .....	2971
PCDD/F Emissions from Electric Arc Furnace (EAF) .....	2971
PCDD/F Emissions from Secondary Metal Smelting Plants .....	2972
PCDD/F Emissions from EAF Dust Treatment Plants .....	2974
PCDD/F Emissions from Power/Heat Generation .....	2974
PCDD/F Emissions from Crematories .....	2977
PCDD/F EMISSIONS FROM MOBILE SOURCES .....	2977
PCDD/F EMISSIONS FROM MINIMALLY OR NON-CONTROLLED COMBUSTION SOURCES .....	2979
ADVANCEMENTS TOWARDS REPRESENTATIVE FLUE GAS SAMPLING TECHNIQUES .....	2980
CONCLUSIONS .....	2981
NOMENCLATURE AND ABBREVIATION .....	2981
REFERENCES .....	2982

## 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, immunotoxic, 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 congener, 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 WHO<sub>1995</sub>-TEF to WHO<sub>2005</sub>-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 WHO<sub>2005</sub>-TEQ depending on the scheme used.

PCDD/Fs are one of the POPs listed in Annex C of the Stockholm Convention, and there is need to reduce the total releases derived from anthropogenic sources. Stockholm Convention requests countries to develop an action plan, which shall include an evaluation of current and projected releases, including the development and maintenance of PCDD/F inventories and release estimates in order to track the environmental and human exposure to PCDD/Fs (Fiedler, 2016). Therefore, the purpose of PCDD/F inventory is to

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 (Rolff *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 top 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

reality in the future.

## FORMATION 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; Ino *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 phenoxy radical (Louw and Ahonkhah, 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/de chlorination 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, 2003; Nganai *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,

**Table 1.** PCDD/F Emission inventories of various countries/regions.

Country or Region (Reference year)	g I-TEQ year <sup>-1</sup>	Major sources	References
Japan (2004)	341–363	Small-scale waste incineration (21.5–26.7%) IWI (19.3%) 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 <sup>a</sup> (93.23–99.2%)	(MoE, 2005)
Taiwan (2008)	74.7	Sintering plants (30.7%) 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 <sup>a</sup> (83.7%)	(Taiwan EPA, 2008)
China (2004)	5042.4	Sintering plants (30.2) 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) Percentage <sup>a</sup> (95.9%)	(P.R.C, 2007)
EU (2005)	1,963–3,752	Residential combustion (wood = max 25.8%, coal = max 9.0%), 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 <sup>a</sup> (86.7%)	(Quaß et al., 2004)
US (2000)	1,314.5	Backyard burning (36%) 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%)	(US EPA, 2006)

**Table 1.** (continued).

Country or Region (Reference year)	g I-TEQ year <sup>-1</sup>	Major sources	References
Australia (2002)	500	Subtotal of the above emission sources ( 1173.85 g I-TEQ) Percentage <sup>a</sup> (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%) Subtotal of the above emission sources (476.9 g I-TEQ) Percentage <sup>a</sup> (95.38%) 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%) Subtotal of the above emission sources (765.78 g I-TEQ) Percentage <sup>a</sup> (81%)	(Bawden <i>et al.</i> , 2004)
Brazil (2008)	945.41	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%) Subtotal of the above emission sources (2732 g I-TEQ) Percentage <sup>a</sup> (98.9%)	(MMA, 2015)
South Africa (2006)	2,763.13		(DEA, 2011)

<sup>a</sup> Contribution (%) 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<sup>-1</sup>) than those with activated carbon injection (0.711 µg I-TEQ ton-waste<sup>-1</sup>) 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<sup>-3</sup>, 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 ( $\mu\text{g I-TEQ ton-waste}^{-1}$ )	Annotation	References
MSWIs	SDS + FF	0.169–1.973 (mean = 1.175)	6 MSWIs. 1 MSWI with extreme value ( $10.72 \mu\text{g I-TEQ ton-waste}^{-1}$ ) was excluded in mean value determination	(Ni <i>et al.</i> , 2009)
	SDS + AC + FF	0.226–1.871 (mean = 0.711)	10 MSWIs. 2 MSWIs with extreme values ( $4.789$ and $5.04 \mu\text{g I-TEQ ton-waste}^{-1}$ ) were excluded in mean value determination	
	DS + AC + FF	0.0475–0.187 (mean = 0.104)	7 MSWIs	(Lee <i>et al.</i> , 2003)
	CY + DSI(AC) + FF	0.0678		
	CY + DS + AC + FF	0.0642		
MWIs	ESP(AC) + VS + PBS + SCR	0.0764		
	QC + VS + PBS	11–40.7 (mean = 26.4)	3 MWIs, intermittent operation	(Lee <i>et al.</i> , 2003)
	DS + AC + FF	1.34	Intermittent operation	(Karademir, 2004)
	ESP + VS + AC	0.571		(Wang <i>et al.</i> , 2014)
HWIs	AC + FF	4.64		(Wang <i>et al.</i> , 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		
	ESP + WS + SCR	0.25	Long-term (> 2 years) continuous measurement used to estimate the EF.	(Rivera-Austrui <i>et al.</i> , 2011)

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). As 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:  $0.103 \text{ ng I-TEQ Nm}^{-3}$ ) 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 ( $\mu\text{g I-TEQ ton-product}^{-1}$ ) or feedstocks ( $\mu\text{g I-TEQ ton-feedstock}^{-1}$ ).

#### 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 is 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/F 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 H<sub>2</sub>O 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  $\mu\text{g I-TEQ ton-product}^{-1}$ , while those with ESP and SCR were ranging from 0.37 to 2.28  $\mu\text{g I-TEQ ton-product}^{-1}$  (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 NO<sub>x</sub> 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 deNO<sub>x</sub> and dioxin destruction SCR (Wang et al., 2009a), especially V-rich vanadia-tungsta-titania catalysts, are advantageous compared to only deNO<sub>x</sub> 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 deNO<sub>x</sub> and PCDD/F destruction, SCR 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  $\mu\text{g I-TEQ ton-feedstock}^{-1}$ ) were higher than those of stainless steel EAFs (0.52  $\mu\text{g I-TEQ ton-feedstock}^{-1}$ ) (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

**Table 3.** PCDD/F emission of different sinter plants.

Feeding material and	Product	APCDs	Emission factors	Annotation	References
Iron ore, Coal, Lime	Sintered pellets	ESP	1.92–2.23 $\mu\text{g I-TEQ ton}^{-1}$ products (mean = 2.02)	3 Sinter plants	(Aries et al., 2006)
		ESP	0.77–0.83 $\mu\text{g I-TEQ ton}^{-1}$ products	2 Sinter plants	(Zou et al., 2012)
		ESP	3.13 $\mu\text{g I-TEQ ton}^{-1}$ feedstock		(Wang et al., 2003b)
		ESP	0.63–5.29 $\mu\text{g I-TEQ ton}^{-1}$ products (mean = 2.96)	2 sinter plants	(Wang et al., 2010b)
		ESP + SCR	0.664–1.5 $\mu\text{g I-TEQ ton}^{-1}$ feedstock (mean = 0.97)	3 Sinter plants. Paddle type deNO <sub>x</sub> SCR	(Wang et al., 2003b)
		ESP + SCR	0.37–2.28 $\mu\text{g I-TEQ ton}^{-1}$ 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 $\mu\text{g I-TEQ ton-feedstock}^{-1}$ (mean = 1.8)		(Lee <i>et al.</i> , 2005)
	Stainless steel			0.52 $\mu\text{g I-TEQ ton-feedstock}^{-1}$ 3.2 $\mu\text{g I-TEQ ton-feedstock}^{-1}$	Operational temperature of the BF was 200°C	
	Carbon steel	None	QT + BF	0.85–17.73 $\mu\text{g I-TEQ ton-product}^{-1}$ (mean = 5.90)	12 samples collected	(Wang <i>et al.</i> , 2010b)
	Stainless steel			0.19–2.39 $\mu\text{g I-TEQ ton-product}^{-1}$ (mean = 1.29)	6 samples collected	
	-		BF	0.416 $\mu\text{g I-TEQ ton-feedstock}^{-1}$		(Chiu <i>et al.</i> , 2011)
	Stainless steel	Kerosene	BF	3.59 $\mu\text{g I-TEQ ton-feedstock}^{-1}$		(Wang <i>et al.</i> , 2009a)
	Carbon steel		BF	1.33–3.00 $\mu\text{g I-TEQ ton-feedstock}^{-1}$ (mean = 2.33)		
			BF + CO converter	7.61 $\mu\text{g I-TEQ ton-feedstock}^{-1}$		
Steel scraps	-	-	BF	3.16 $\mu\text{g I-TEQ ton-product}^{-1}$		(Zou <i>et al.</i> , 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  $\mu\text{g I-TEQ ton-feedstock}^{-1}$ ) (Wang *et al.*, 2009a) was approximately 7 times that with QT+BF (0.52  $\mu\text{g I-TEQ ton-feedstock}^{-1}$ ) (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  $\mu\text{g I-TEQ ton-feedstock}^{-1}$  to 3.2  $\mu\text{g I-TEQ ton-feedstock}^{-1}$ . 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% CO<sub>2</sub> emission compared with copper's primary production (Hagelüken, 2006). However, these processes cause secondary pollution and in particular emission of PCDD/Fs. The to-be-recycled metals usually consist of other contaminants e.g., plastics, paints and solvents and there is also high presence of chlorine from the use of chloride salts of sodium or potassium as

flux. These contaminants make secondary metal smelting generate more PCDD/Fs than primary smelting plants. 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  $\mu\text{g I-TEQ ton-product}^{-1}$ ) compared to scraps (30%) and blister copper (50%) (24.8  $\mu\text{g I-TEQ ton-product}^{-1}$ ). For secondary aluminum smelters, Li *et al.* (2007a) reported the emissions from using recycled materials (4.7  $\mu\text{g I-TEQ ton-product}^{-1}$ ) and waste aluminum (12.9  $\mu\text{g I-TEQ ton-product}^{-1}$ ) were approximately 3 and 8 times higher than those using ingots (1.66  $\mu\text{g I-TEQ ton-product}^{-1}$ ) 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, ingot	Heavy oil	-	BF	0.63–23 $\mu\text{g I-TEQ ton-feedstock}^{-1}$ (mean = 11.43) 200 $\mu\text{g I-TEQ ton-feedstock}^{-1}$	4 secondary ALSs.	(Lee et al., 2005)
				CY + BF	0.64–36 $\mu\text{g I-TEQ ton-feedstock}^{-1}$ (mean = 12.84)	3 secondary ALSs.	
		Natural gas	-	BF	434.84 $\mu\text{g I-TEQ ton-product}^{-1}$	High impurity raw materials	(Zou et al., 2012)
		Light oil	-	WS	147.82 $\mu\text{g I-TEQ ton-product}^{-1}$		
		Heavy oil	-	BF	2.72 $\mu\text{g I-TEQ ton-feedstock}^{-1}$		(Wang et al., 2009a)
	Waste aluminum, ingot	-	Reverberatory	CY + PAC + BF	0.0848 $\mu\text{g I-TEQ ton-feedstock}^{-1}$		(Li et al., 2007a)
	Recycled materials, ingot	-	Crucible	CY + BF	12.9 $\mu\text{g I-TEQ ton-product}^{-1}$		
	Scrap	-	Reverberatory	CY + BF	1.63 $\mu\text{g I-TEQ ton-product}^{-1}$		
		-	Top-charge melt (low end), Sidewell reverberatory	Lime-coated BF (worst case)	4.7 $\mu\text{g I-TEQ ton-product}^{-1}$		
		-			1.69 $\mu\text{g I-TEQ ton-product}^{-1}$		
		-			Mean range = 0.26–36 $\mu\text{g I-TEQ ton-feedstock}^{-1}$	Representing the low end and worst case scenario	(EPA, 2000)
Secondary Copper Smelters	Scraps	-	-	BF + CY	14.80 $\mu\text{g I-TEQ ton-product}^{-1}$	Raw material pre-cleaned and manually selected. One plant used afterburner + BF	(Ba et al., 2009)
	pure copper scrap	-	-	BF	102 $\mu\text{g I-TEQ ton-product}^{-1}$		(Hu et al., 2013)
	Copper scrap (30%), blister copper (50%), ACRE (20%)	-	-	BF	24.8 $\mu\text{g I-TEQ ton-product}^{-1}$	(%) represents the content in the feed.	
	Pure blister copper	-	-	BF	5.88 $\mu\text{g I-TEQ ton-product}^{-1}$		(UNEP, 2005)
	Scraps	-	Blast furnace	BF	779 $\mu\text{g I-TEQ ton-feedstock}^{-1}$	Plant fitted with afterburners	(Wang et al., 2009a)
	Copper scrap	-	-	BF	0.735 $\mu\text{g I-TEQ ton-product}^{-1}$		(Zou et al., 2012)
	Sludge	Pulverized Coal	Rotary kiln	BF + CP + WS	241.72 $\mu\text{g I-TEQ ton-product}^{-1}$	Low input-output productivity	
	Dried sludge	Coal	Blast furnace	BF + CP + WS	2710 $\mu\text{g I-TEQ ton-product}^{-1}$		

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  $\mu\text{g I-TEQ tonne-product}^{-1}$ , which was 6 times higher than 2.65  $\mu\text{g I-TEQ tonne-product}^{-1}$  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 ( $65 \pm 2\%$ ) 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) ( $0.421\text{--}15.9 \text{ ng I-TEQ Nm}^{-3}$ ) had higher PCDD/F concentrations in the stack flue gases than reduction stage (reduction and discharge) ( $0.261\text{--}6.68 \text{ ng I-TEQ Nm}^{-3}$ ). 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  $\text{SiO}_2$  to lime and PCDD/F emission factors through stack flue gases reduced from 17–436  $\mu\text{g I-TEQ ton-product}^{-1}$  to 0.096–0.18  $\mu\text{g I-TEQ ton-product}^{-1}$ .

Table 6 lists PCDD/F emission factors of EAF dust treatment plants. Previously, extremely high PCDD/F emissions ( $145 \text{ ng I-TEQ Nm}^{-3}$ ) 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  $\mu\text{g I-TEQ ton-EAF dust}^{-1}$  (Chi *et al.*, 2006) to 42.5  $\mu\text{g I-TEQ ton-EAF dust}^{-1}$  by equipping ACI (Li *et al.*, 2007b). Then, after deploying dual bag filter system, the PCDD/F emission factors further reduced to 0.29  $\mu\text{g I-TEQ ton-EAF dust}^{-1}$  and the PCDD/F concentrations in the stack flue gases were around 0.03  $\text{ng I-TEQ Nm}^{-3}$  (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 ( $1.39 \mu\text{g I-TEQ ton-EAF dust}^{-1}$ ) than Waelz process ( $0.29 \mu\text{g I-TEQ ton-EAF dust}^{-1}$ ). 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 ACI (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 ( $840\text{--}1120 \mu\text{g I-TEQ ton-EAF dust}^{-1}$ ) were significantly higher than that of SAF process ( $46.9 \mu\text{g I-TEQ ton-EAF dust}^{-1}$ ) (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/Fs 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 ( $0.001\text{--}0.005 \mu\text{g I-TEQ tonne-coal}^{-1}$  in Fernández-Martínez *et al.* (2004),  $0.09\text{--}0.11 \mu\text{g I-TEQ tonne-coal}^{-1}$  in

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

Feeding material	Product	Type of furnace	APCDS	Emission Factor	Annotation	Reference
SiO <sub>2</sub> (20%), coke (30%), EAF dust (50%)	ZnO	Waelz rotary kiln	DSC + VT + CY + BF	560 µg I-TEQ ton-EAF dust <sup>-1</sup>		(Chi et al., 2006)
EAF fly ash (74%), coke (13%), sand (13%)			DSC + VT + CY + ACI + BF	42.5 µg I-TEQ ton-EAF dust <sup>-1</sup>	40 kg h <sup>-1</sup> of ACI was used	(Li et al., 2007b)
EAF fly ash (60–70%), coke (10–20%), sand (10–20%)			DSC + VT + CY + ACI + DBF	0.29 µg I-TEQ ton-EAF dust <sup>-1</sup>	16 kg h <sup>-1</sup> of ACI was used	(Lin et al., 2008)
Steel mill flue dust, various zinc-bearing residues, coke, and fluxes	Waelz oxide product	Waelz rotary kiln	DS + PS	17–436 µg I-TEQ ton-Waelz Oxide product <sup>-1</sup>	Operated in acid mode by adding SiO <sub>2</sub> as flux	(Mager et al., 2003)
Oxidized iron scraps (1.5%), EAF dusts (64.0%), carbon powders (13.2%), binders (1.86%), cokes (3.34%), slagging fluxes (5.98%)	Steel ingots	Submerged arc furnace (SAF)	GSC + BF	1.39 µg I-TEQ ton-EAF dust <sup>-1</sup>	Operated in base mode by adding Lime as flux	(Xu et al., 2014)
EAF fly ash pellets	Steel ingots	Submerged arc furnace (SAF)	GSC + BF	7.97 µg I-TEQ ton-product <sup>-1</sup>	The emission factor is a sum of emission factors from pelletizer, reducing furnace and SAF subsystems	(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

**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 $\mu\text{g I-TEQ tonne-coal}^{-1}$		(Wang <i>et al.</i> , 2010b)
	Mixed Fuel (MF)	SDS + BF	0.034–0.160 $\mu\text{g I-TEQ tonne-MF}^{-1}$	Coal co-combustion with sewage sludge	(Zhang <i>et al.</i> , 2013)
	Bituminous coal	SCR + ESP + FGD	0.62 $\mu\text{g I-TEQ tonne-coal}^{-1}$		(Lin <i>et al.</i> , 2007)
	Bituminous, sub-bituminous and lignite coal	-	0.001–0.005 $\mu\text{g I-TEQ tonne-coal}^{-1}$		(Fernández-Martínez <i>et al.</i> , 2004)
	coal	ESP	0.09–0.11 $\mu\text{g I-TEQ tonne-coal}^{-1}$		(Mokhtar <i>et al.</i> , 2014)
	coal	ESP + FGD	0.08 $\mu\text{g I-TEQ tonne-coal}^{-1}$		(Lin <i>et al.</i> , 2010)
	coal	ESD	1.75 $\mu\text{g I-TEQ tonne-coal}^{-1}$		(Lin <i>et al.</i> , 2010)
	Heavy oil	SCR + ESP + FGD	0.181 $\mu\text{g I-TEQ tonne-fuel}^{-1}$		(Wang <i>et al.</i> , 2010b)
	Heavy oil	ESP	0.188 $\mu\text{g I-TEQ m}^{-3}$ (fuel)		(Wang <i>et al.</i> , 2009b)
Industrial Boiler	straw	-	12–13 $\mu\text{g I-TEQ tonne-straw}^{-1}$	Boiler not adopted for biomass combustion	(Kubica <i>et al.</i> , 2004)
	Wood biomass	-	2–33 $\mu\text{g I-TEQ tonne-wood biomass}^{-1}$		
	Wood Chips	CY + BF	0.095 $\mu\text{g I-TEQ tonne-woodchip}^{-1}$		(Chen <i>et al.</i> , 2011b)
	Wood Chips	CY + BF	2.99 $\mu\text{g I-TEQ tonne-woodchip}^{-1}$		(Wang <i>et al.</i> , 2010b)

BF: bag filter, CY: cyclone, ESD: electrostatic dust collectors, FGD: Flue Gas Desulphurization, ESP: Electrostatic Precipitator, SDS: semidry scrubber, SCR: Selective Catalytic Reduction.

Mokhtar *et al.* (2014) and 0.147  $\mu\text{g I-TEQ tonne-coal}^{-1}$  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. This 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  $\mu\text{g I-TEQ tonne-fuel}$ , and 0.188  $\mu\text{g I-TEQ m}^{-3}$  (heavy oil)) (Wang *et al.*, 2009b; Wang *et al.*, 2010b) were generally higher 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  $\text{pg TEQ Nm}^{-3}$ . The highest concentrations (97.3  $\text{pg TEQ Nm}^{-3}$ ) were from wood/lignite blend (80% wood, 20% lignite by weight) and the lowest (3.0  $\text{pg TEQ Nm}^{-3}$ ) 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  $\mu\text{g I-TEQ ton-wood biomass}^{-1}$  while those from straw were in the range of 12–13  $\mu\text{g I-TEQ tonne-straw}^{-1}$  (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 1.17–4.69  $\mu\text{g I-TEQ tonne-MF}^{-1}$ , while the output (ashes and flue gases) were in the range of 0.070–0.317  $\mu\text{g I-TEQ tonne-MF}^{-1}$ . On the other hand, Chen *et al.* (2011b) found out that the output PCDD/Fs 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

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<sup>-3</sup> (Lin *et al.*, 2007) and 0.0119 ng I-TEQ Nm<sup>-3</sup> for coal-fired power plants (Mokhtar *et al.*, 2014) and 0.145 ng I-TEQ Nm<sup>-3</sup> from woodchip boiler (Wang *et al.*, 2010b). On the other hand, they are characterized by extremely high flow rates of flue gases, 1.80 × 10<sup>6</sup> Nm<sup>3</sup> h<sup>-1</sup> (Lin *et al.*, 2007), 2.15 × 10<sup>6</sup> Nm<sup>3</sup> h<sup>-1</sup> (Mokhtar *et al.*, 2014), and 1.68 × 10<sup>4</sup> Nm<sup>3</sup> h<sup>-1</sup> (Wang *et al.*, 2010b) for coal-fired power plants, which makes them important PCDD/F contributors. 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<sup>-1</sup>, 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<sup>-1</sup> (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<sup>-1</sup> (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, NO<sub>x</sub>, SO<sub>x</sub>, there are relatively few PCDD/F studies for

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

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

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 re-suspended 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<sup>-1</sup>) in comparison to diesel passenger vehicles (80.3 pg I-TEQ km<sup>-1</sup>) 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 <sup>-1</sup>	Mileage: $5.5 \times 10^3 - 8.7 \times 10^4$ km; m = 4; n = 12	(Chuang <i>et al.</i> , 2011)
			7.11–13.6 pg I-TEQ L <sup>-1</sup>	m = 3, Chlorine (9.8 ppm), sulfur (3900 ppm)	(Laroo <i>et al.</i> , 2012)
			663–1300 pg I-TEQ km <sup>-1</sup>	6-hr dynamometer test at 50 km h <sup>-1</sup>	(Lew, 1993, 1996)
		Dynamometer	30.5 pg I-TEQ L <sup>-1</sup>	B2: 2% bio-diesel + 98% diesel;	(Chang <i>et al.</i> , 2014b)
		On-road tail pipe	29–109 pg I-TEQ km <sup>-1</sup>	Mileage: $8 \times 10^5$ km;	(Ryan and Gullett, 2000)
		Tunnel	170 ± 80 pg I-TEQ km <sup>-1</sup>		(Gertler <i>et al.</i> , 1998)
DPVs	Diesel	Dynamometer	80.3 pg I-TEQ km <sup>-1</sup>	Mileage: $7 \times 10^3 - 12 \times 10^4$ km; m = 4; n = 48	(Chuang <i>et al.</i> , 2011)
			23 pg I-TEQ L <sup>-1</sup>	With DOC	(Dyke <i>et al.</i> , 2007)
			97 pg I-TEQ L <sup>-1</sup>	Without DOC	
SUVs	Unleaded gasoline	Dynamometer	123 pg I-TEQ km <sup>-1</sup>	Mileage: $13.9 \times 10^3 - 12.2 \times 10^4$ km; m = 4; n = 12	(Chuang <i>et al.</i> , 2011)
			0.36–0.39 pg I-TEQ km <sup>-1</sup>	Sampled before the muffler; m = 2	(Marklund <i>et al.</i> , 1990)
Motorcycle	Standard test gasoline	Dynamometer	86–114 pg I-TEQ km <sup>-1</sup>	2-stroke engine, Mileage: $2.8 \times 10^3 - 1.1 \times 10^4$ ; m = 6	(Chuang <i>et al.</i> , 2010)
			(mean = 96 pg I-TEQ km <sup>-1</sup> )	4-stroke engine, Mileage: $1.7 \times 10^4 - 5.0 \times 10^4$ ; m = 6	
			40–138 pg I-TEQ km <sup>-1</sup>		
			(mean = 81 pg I-TEQ km <sup>-1</sup> )		

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<sup>-1</sup>) running on gasoline (Chuang *et al.*, 2011). The PCDD/F emissions factors of motorcycles (86–114 pg I-TEQ km<sup>-1</sup>) (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: CO<sub>2</sub> ratios whereby the elemental carbon and organic carbon are assumed minimal and when the background CO and CO<sub>2</sub> 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-C<sub>burned</sub><sup>-1</sup>. 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<sup>-1</sup>).

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).

**Table 10.** PCDD/F emission factors of some minimally controlled combustion sources.

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 <sup>-1</sup> (mean 0.75 ng TEQ MJ <sup>-1</sup> )	(Hübner <i>et al.</i> , 2005)
	Pine needles and pine cones	196 ng I-TEQ kg-material burnt <sup>-1</sup>	(Moltó <i>et al.</i> , 2007)
Residential Boilers	Coal	Max: 1300 ng TEQ kg-coal <sup>-1</sup>	(Paradiž <i>et al.</i> , 2008)
	residential combustion of biofuels	3.5–4.9 ng WHO-TEQ kg-fuel <sup>-1</sup>	(Hedman <i>et al.</i> , 2006)
	wood (logs, briquettes, chipped wood, pellets), coal (brown coal briquettes, hard coal) and coke	0.002–2.6 ng TEQ MJ <sup>-1</sup> (mean 0.38 ng TEQ MJ <sup>-1</sup> )	(Hübner <i>et al.</i> , 2005)
	Lignite, Bituminous coal	3.16–2200 ng I-TEQ GJ <sup>-1</sup>	(Šyc <i>et al.</i> , 2011)
	Beech logs, spruce logs, Different types of boilers		
	residential combustion of biofuels	1.2–290 ng WHO-TEQ kg-fuel <sup>-1</sup>	(Hedman <i>et al.</i> , 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<sup>-1</sup>, which were 130 times higher than those from circuit boards (92 ng TEQ kg waste<sup>-1</sup>). Average values of 25 ng TEQ kg-burned<sup>-1</sup> and 15 ng TEQ kg-burned<sup>-1</sup> 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<sup>-1</sup> for wheat and 537 pg I-TEQ kg<sup>-1</sup> 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<sup>-1</sup> C<sub>burned</sub>. 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)

**Table 11.** PCDD/F Emission factors of non-controlled combustion sources.

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 <sup>-1</sup> (mean 110 ng TEQ kg-waste <sup>-1</sup> )	(Zhang <i>et al.</i> , 2011)
	Household waste	510–1100 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup>	(Solorzano-Ochoa <i>et al.</i> , 2012)
	Residential waste	202–1700 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup> (mean 823 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup> )	(Gullett <i>et al.</i> , 2009)
Simulation using Open Burn Testing Facility (OBTF)	Rice straw	12.6–14.5 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup>	(Chang <i>et al.</i> , 2014a)
	Domestic household waste	< 10 to > 6000 ng-TEQ kg-waste <sup>-1</sup>	(Gullett <i>et al.</i> , 2001)
	Forest biomass	0.3–26.3 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup> Mean 5.8 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup>	(Gullett <i>et al.</i> , 2008)
	Grass biomass	0.32 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup>	
	Forest biomass	Mean: 25 ng TEQ kg-burned <sup>-1</sup> (range: 14–47) (Oregon biomass) mean: 15 ng TEQ kg-burned <sup>-1</sup> (range: 1–56) (North Carolina biomass)	(Gullett and Touati, 2003b)
	wheat straw	337 to 602 pg TEQ kg <sup>-1</sup>	(Gullett and Touati, 2003a)
	rice straw	537 pg TEQ kg <sup>-1</sup>	(Gullett <i>et al.</i> , 2007)
	electronic wastes	92 ng TEQ kg-waste <sup>-1</sup>	
	insulated wire	11900 ng TEQ kg-waste <sup>-1</sup>	
	Military waste	35–780 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup> (mean 270 ng TEQ kg-C <sub>burned</sub> <sup>-1</sup> )	(Woodall, 2012)
Test carried out using barrels and open fires	Biomass burning (straw)	48.6 ng I-TEQ kg <sup>-1</sup>	(Lin <i>et al.</i> , 2007)
	Biomass burning (wax apples)	2.69 ng I-TEQ kg <sup>-1</sup>	
	Ritual paper burning	1.36 ng I-TEQ kg <sup>-1</sup>	
	Garden waste	4.5 ng TEQ kg-waste <sup>-1</sup>	(Wevers <i>et al.</i> , 2004)
	Household waste	35 ng TEQ kg-waste <sup>-1</sup>	

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
CO <sub>2</sub>	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

DSI	dry sorbent injection
EAFs	electric arc furnace
ESD	electrostatic dust collectors
ESP	electrostatic precipitator
EU	European Union
FF	fabric filter
FGD	flue gas desulphurization
GSC	gravity settling chamber
HCs	hydrocarbons
HDDEs	heavy duty diesel engines
HDDVs	heavy duty diesel vehicles
HE	heat exchanger
HRGC/HRMS	high resolution gas chromatography/ High resolution mass spectrometry
HWIs	hazardous waste incinerators
I-TEQ	International toxic equivalence
LI-TOFMS	laser ionization and time-of-flight mass spectrometry
LLE	liquid-liquid extraction
LODs	limit of detections
LOQ	limit of quantification
MAE	microwave assisted extraction
MDLs	method detection limits
MSPD	matrix solid phase dispersion
MMA	Ministério do Meio Ambiente (Ministry of Environment, Brazil)
MSWIs	municipal solid waste incinerators
MWIs	medical waste incinerators
NO <sub>x</sub>	nitrogen oxides
PAC	powdered activated carbon
PAHs	polycyclic aromatic hydrocarbons
PBS	packed-bed absorber scrubber
PCDD/F	polychlorinated dibenzo- <i>p</i> - dioxins/dibenzofurans
PLE	pressure liquid extraction
PM	particulate Matter
POPs	persistent organic pollutants
QC	quench chamber
QT	quench tower
SAF	submerged arc furnace
SBF	single bag filter
SCR	selective catalytic reduction
SDS	semi-dry scrubber
SO <sub>x</sub>	sulfur oxides
SO <sub>2</sub>	sulfur dioxide
SUVs	sport utility vehicles
TEF	Toxic Equivalent Factor
UNEP	United Nations Environmental Programme
US EPA	United States Environmental Protection Agency
VS	venture scrubber
WHO	World Health Organization
WS	Wet scrubbers

## REFERENCES

Altarawneh, M., Dlugogorski, B.Z., Kennedy, E.M. and Mackie, J.C. (2007). Quantum chemical investigation of

- formation of polychlorodibenzo-*p*-dioxins and dibenzofurans from oxidation and pyrolysis of 2-chlorophenol. *J. Phys. Chem. A* 111: 2563–2573.
- Altarawneh, M., Dlugogorski, B.Z., Kennedy, E.M. and Mackie, J.C. (2009). Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). *Prog. Energy Combust. Sci.* 35: 245–274.
- Altwicker, E. and Milligan, M. (1993). Formation of dioxins: Competing rates between chemically similar precursors and de novo reactions. *Chemosphere* 27: 301–307.
- Altwicker, E.R. (1996). Relative rates of formation of polychlorinated dioxins and furans from precursor and de novo reactions. *Chemosphere* 33: 1897–1904.
- Aries, E., Anderson, D.R., Fisher, R., Fray, T.A. and Hemfrey, D. (2006). PCDD/F and “Dioxin-like” PCB emissions from iron ore sintering plants in the UK. *Chemosphere* 65: 1470–1480.
- Arion, A., Florimond, P., Berho, F., Marliere, E. and Le Louer, P. (2002). Investigation of dioxin formation mechanisms under sintering conditions by use of pilot pot. *Organohalogen Compd.* 56: 127–130.
- Ba, T., Zheng, M., Zhang, B., Liu, W., Xiao, K. and Zhang, L. (2009). Estimation and characterization of PCDD/Fs and dioxin-like PCBs from secondary copper and aluminum metallurgies in China. *Chemosphere* 75: 1173–1178.
- Bawden, K., Ormerod, R., Starke, G. and Zeise, K. (2004). Australian Inventory of Dioxin Emissions, 2004, National Dioxins Program Technical Report No. 3, Australian Government Department of the Environment and Heritage, Canberra.
- Bertazzi, P.A., Consonni, D., Bachetti, S., Rubagotti, M., Baccarelli, A., Zocchetti, C. and Pesatori, A.C. (2001). Health effects of dioxin Exposure: A 20-Year mortality study. *Am. J. Epidemiol.* 153: 1031–1044.
- Black, R., Meyer, C.M., Touati, A., Gullett, B., Fiedler, H. and Mueller, J. (2012). Emission factors for PCDD/PCDF and dl-PCB from open burning of biomass. *Environ. Int.* 38: 62–66.
- Bremmer, H.J.; Troost, L.M.; Kuipers, G.; DeKoning, J.; Sein, A.A. (1994). Emissions of Dioxins in The Netherlands; Report No. 770501018; National Institute of Public Health and Environmental Protection (RIVM) and Netherlands Organization for Applied Scientific Research (TNO).
- Briois, C., Ryan, S., Tabor, D., Touati, A. and Gullett, B.K. (2007). Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from a mixture of chlorophenols over fly ash: influence of water vapor. *Environ. Sci. Technol.* 41: 850–856.
- Chang, M.B., Huang, H.C., Tsai, S.S., Chi, K.H. and Chang-Chien, G.P. (2006). Evaluation of the emission characteristics of PCDD/Fs from electric arc furnaces. *Chemosphere* 62: 1761–1773.
- Chang, S.S., Lee, W.J., Holsen, T.M., Li, H.W., Wang, L.C. and Chang-Chien, G.P. (2014a). Emissions of polychlorinated-*p*-dibenzo dioxin, dibenzofurans (PCDD/Fs) and polybrominated diphenyl ethers (PBDEs)

- from rice straw biomass burning. *Atmos. Environ.* 94: 573–581.
- Chang, Y.C., Lee, W.J., Wang, L.C., Yang, H.H., Cheng, M.T., Lu, J.H., Tsai, Y.I. and Young, L.H. (2014b). Effects of waste cooking oil-based biodiesel on the toxic organic pollutant emissions from a diesel engine. *Appl. Energy* 113: 631–638.
- Chen, T., Li, X., Yan, J., Lu, S. and Cen, K. (2011a). Distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in ambient air of different regions in China. *Atmos. Environ.* 45: 6567–6575.
- Chen, W.S., Shen, Y.H., Hsieh, T.Y., Lin, C.W., Wang, L.C. and Chang-Chien, G.P. (2011b). Fate and distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in a woodchip-fuelled boiler. *Aerosol Air Qual. Res.* 11: 282–289.
- Chen, Y.C., Tsai, P.J. and Mou, J.L. (2008). Determining optimal operation parameters for reducing PCDD/F emissions (I-TEQ values) from the iron ore sintering process by using the Taguchi experimental design. *Environ. Sci. Technol.* 42: 5298–5303.
- Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J., Zhang, R. and Chang-Chien, G.P. (2015). An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air. *Aerosol Air Qual. Res.* 15: 2730–2762.
- Chi, K.H., Chang, S.H. and Chang, M.B. (2006). Characteristics of PCDD/F distributions in vapor and solid phases and emissions from the Waelz process. *Environ. Sci. Technol.* 40: 1770–1775.
- Chiu, J.C., Shen, Y.H., Li, H.W., Lin, L.F., Wang, L.C. and Chang-Chien, G.P. (2011). Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from an electric arc furnace, secondary aluminum smelter, crematory and joss paper incinerators. *Aerosol Air Qual. Res.* 11: 13–20.
- Chuang, S.C., Chen, S.J., Huang, K.L., Chang-Chien, G.P., Wang, L.C. and Huang, Y.C. (2010). Emissions of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran from motorcycles. *Aerosol Air Qual. Res.* 10: 533–539.
- Chuang, S.C., Huang, K.L., Chen, S.J., Wang, L.C., Chang-Chien, G.P. and Tsai, J.H. (2011). PCDD/F emissions from gasoline and diesel fueled vehicles. *Sustainable Environ. Res.* 21: 29–36.
- Cieplik, M.K., Carbonell, J.P., Muñoz, C., Baker, S., Krüger, S., Liljelind, P., Marklund, S. and Louw, R. (2003). On dioxin formation in iron ore sintering. *Environ. Sci. Technol.* 37: 3323–3331.
- Cieplik, M.K., De Jong, V., Bozovič, J., Liljelind, P., Marklund, S. and Louw, R. (2006). Formation of dioxins from combustion micropollutants over MSWI fly ash. *Environ. Sci. Technol.* 40: 1263–1269.
- Costner, P. (2005). *Estimating Releases and Prioritizing Sources in the Context of the Stockholm Convention: Dioxin Emission Factors for Forest Fires, Grassland and Moor Fires, Open Burning of Agricultural Residues, Open Burning of Domestic Waste, Land-fill and Dump Fires, The International POPs Elimination Project, Arnika, Mexico.*
- DEA (Department of Environmental Affairs) (2011). South Africa's National Implementation Plan for the Stockholm Convention on POPs. [https://www.environment.gov.za/sites/default/files/docs/national\\_implementation\\_plaun\\_organic\\_pollutants.pdf](https://www.environment.gov.za/sites/default/files/docs/national_implementation_plaun_organic_pollutants.pdf).
- Dyke, P.H., Sutton, M., Wood, D. and Marshall, J. (2007). Investigations on the effect of chlorine in lubricating oil and the presence of a diesel oxidation catalyst on PCDD/F releases from an internal combustion engine. *Chemosphere* 67: 1275–1286.
- EPA (2000). *Exposure and Human Health Reassessment of 2, 3, 7, 8-Tetrachlorodibenzo-*p*-Dioxin (TCDD) and Related Compounds.* US Environmental Protection Agency, Washington, DC.
- EPA Database (2001). Database of Sources of Environmental Releases of Dioxin-Like Compounds in the United States <https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=20797>.
- Esposito, V., Maffei, A., Bruno, D., Varvaglione, B., Ficocelli, S., Capoccia, C., Spartera, M., Giua, R., Blonda, M. and Assennato, G. (2014). POP emissions from a large sinter plant in Taranto (Italy) over a five-year period following enforcement of new legislation. *Sci. Total Environ.* 491: 118–122.
- Evans, C.S. and Dellinger, B. (2005). Mechanisms of dioxin formation from the high-temperature oxidation of 2-chlorophenol. *Environ. Sci. Technol.* 39: 122–127.
- Everaert, K. and Baeyens, J. (2002). The formation and emission of dioxins in large scale thermal processes. *Chemosphere* 46: 439–448.
- Fernández-Martínez, G., López-Vilarino, J., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., Abad, E. and Rivera, J. (2004). First assessment of dioxin emissions from coal-fired power stations in Spain. *Chemosphere* 57: 67–71.
- Fiedler, H. (1996). Sources of PCDD/PCDF and impact on the environment. *Chemosphere* 32: 55–64.
- Fiedler, H. (2016). Release inventories of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, In *Dioxin and Related Compounds: Special Volume in Honor of Otto Hutzinger*, Alae, M. (Ed.), Springer International Publishing, Cham, pp. 1–27.
- Finocchio, E., Busca, G. and Notaro, M. (2006). A review of catalytic processes for the destruction of PCDD and PCDF from waste gases. *Appl. Catal., B* 62: 12–20.
- Gertler, A.W., Sagebiel, J.C., Dippel, W.A. and Farina, R.J. (1998). Measurements of dioxin and furan emission factors from heavy-duty diesel vehicles. *J. Air Waste Manage. Assoc.* 48: 276–278.
- Guerriero, E., Bianchini, M., Gigliucci, P.F., Guarnieri, A., Mosca, S., Rossetti, G., Varde, M. and Rotatori, M. (2009). Influence of process changes on PCDD/Fs produced in an iron ore sintering plant. *Environ. Eng. Sci.* 26: 71–80.
- Gullett, B. and Touati, A. (2003a). PCDD/F emissions from burning wheat and rice field residue. *Atmos. Environ.* 37: 4893–4899.
- Gullett, B.K. and Touati, A. (2003b). PCDD/F emissions

- from forest fire simulations. *Atmos. Environ.* 37: 803–813.
- Gullett, B., Touati, A. and Oudejans, L. (2008). PCDD/F and aromatic emissions from simulated forest and grassland fires. *Atmos. Environ.* 42: 7997–8006.
- Gullett, B.K., Bruce, K.R., Beach, L.O. and Drago, A.M. (1992). Mechanistic steps in the production of PCDD and PCDF during waste combustion. *Chemosphere* 25: 1387–1392.
- Gullett, B.K., Lemieux, P.M. and Dunn, J.E. (1994). Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran formation during waste combustion. *Environ. Sci. Technol.* 28: 107–118.
- Gullett, B.K., Lemieux, P.M., Lutes, C.C., Winterrowd, C.K. and Winters, D.L. (2001). Emissions of PCDD/F from uncontrolled, domestic waste burning. *Chemosphere* 43: 721–725.
- Gullett, B.K., Linak, W.P., Touati, A., Wasson, S.J., Gatica, S. and King, C.J. (2007). Characterization of air emissions and residual ash from open burning of electronic wastes during simulated rudimentary recycling operations. *J. Mater. Cycles Waste Manage.* 9: 69–79.
- Gullett, B.K., Wyrzykowska, B., Grandesso, E., Touati, A., Tabor, D.G. and Ochoa, G.S.R. (2009). PCDD/F, PBDD/F, and PBDE emissions from open burning of a residential waste dump. *Environ. Sci. Technol.* 44: 394–399.
- Gullett, B.K., Oudejans, L., Tabor, D., Touati, A. and Ryan, S. (2012). Near-real-time combustion monitoring for PCDD/PCDF indicators by GC-REMPI-TOFMS. *Environ. Sci. Technol.* 46: 923–928.
- Guo, C.J., Wang, M.S., Lin, S.L., Mi, H.H., Wang, L.C. and Chang-Chien, G.P. (2014). Emissions of PCDD/Fs and PCBs during the cold start-up of municipal solid waste incinerators. *Aerosol Air Qual. Res.* 14: 1593–U358.
- Hagelüken, C. (2006). Improving metal returns and eco-efficiency in electronics recycling - A holistic approach for interface optimisation between pre-processing and integrated metals smelting and refining. In Proc. 2006 IEEE International Symposium on Electronics and the Environment, May 8–11, 2006, San Francisco, CA, pp. 218–223.
- Hajizadeh, Y., Onwudili, J.A. and Williams, P.T. (2011). PCDD/F formation from oxy-PAH precursors in waste incinerator flyash. *Chemosphere* 85: 1672–1681.
- Hatanaka, T., Kitajima, A. and Takeuchi, M. (2005). Role of chlorine in combustion field in formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans during waste incineration. *Environ. Sci. Technol.* 39: 9452–9456.
- Hedman, B., Näslund, M. and Marklund, S. (2006). Emission of PCDD/F, PCB, and HCB from combustion of firewood and pellets in residential stoves and boilers. *Environ. Sci. Technol.* 40: 4968–4975.
- Heeb, N.V., Zennegg, M., Gujer, E., Honegger, P., Zeyer, K., Gfeller, U., Wichser, A., Kohler, M., Schmid, P. and Emmenegger, L. (2007). Secondary effects of catalytic diesel particulate filters: Copper-induced formation of PCDD/Fs. *Environ. Sci. Technol.* 41: 5789–5794.
- Henny, C.J., Kaiser, J.L., Grove, R.A., Bentley, V.R. and Elliott, J.E. (2003). Biomagnification factors (fish to Osprey eggs from Willamette River, Oregon, U.S.A.) for PCDDs, PCDFs, PCBs and OC pesticides. *Environ. Monit. Assess.* 84: 275–315.
- Hu, J., Zheng, M., Nie, Z., Liu, W., Liu, G., Zhang, B. and Xiao, K. (2013). Polychlorinated dibenzo-*p*-dioxin and dibenzofuran and polychlorinated biphenyl emissions from different smelting stages in secondary copper metallurgy. *Chemosphere* 90: 89–94.
- Hübner, C., Boos, R. and Prey, T. (2005). In-field measurements of PCDD/F emissions from domestic heating appliances for solid fuels. *Chemosphere* 58: 367–372.
- Hung, P.C., Chang, C.C., Chang, S.H. and Chang, M.B. (2015). Characteristics of PCDD/F emissions from secondary copper smelting industry. *Chemosphere* 118: 148–155.
- Hung, P.C., Chang, S.H., Buekens, A. and Chang, M.B. (2016). Continuous sampling of MSWI dioxins. *Chemosphere* 145: 119–124.
- Iino, F., Imagawa, T., Takeuchi, M. and Sadakata, M. (1999). De novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic isomers of polychlorinated naphthalenes. *Environ. Sci. Technol.* 33: 1038–1043.
- Ivory, A. and Mobbs, C. (2004). Dioxin levels in Australia: Key findings of studies. *Organohalogen Compd.* 66: 3446–3451.
- Jarmohamed, W. and Mulder, P. (1994). Oxychlorination and combustion of propene on fly-ash. Formation of chlorinated benzenes, dibenzodioxines and mono- and dibenzofurans. *Chemosphere* 29: 1911–1917.
- Ji, S.S., Li, X.D., Ren, Y., Chen, T., Cen, K.F., Ni, M.J. and Buekens, A. (2013). Low temperature destruction of PCDD/Fs over V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>/TiO<sub>2</sub> catalyst with ozone. *Chemosphere* 92: 265–272.
- Karademir, A. (2004). Health risk assessment of PCDD/F emissions from a hazardous and medical waste incinerator in Turkey. *Environ. Int.* 30: 1027–1038.
- Kogevinas, M. (2001). Human health effects of dioxins: cancer, reproductive and endocrine system effects. *APMIS* 109: S223–S232.
- Kubica, K., Dilara, D.P. and Paradiž B. (2004). Toxic emissions from solid fuel combustion in small residential appliances. *Procc. 6th International Conference on Emission Monitoring CEM-2004*. 9–11, Milano Italy.
- Kuo, Y.C., Chen, Y.C., Yang, C.W., Mou, J.L., Shih, T.S. and Tsai, P.J. (2011). Identification the content of the windbox dust related to the formation of PCDD/Fs during the iron ore sintering process. *Aerosol Air Qual. Res.* 11: 351–359.
- Kuo, Y.C., Chen, Y.C., Lin, M.Y., Young, L.H., Hsu, H.T., Liou, S.H., Wu, T.N., Wang, L.C. and Tsai, P.J. (2015). Ambient air concentrations of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs and their impacts on vegetation and soil. *Int. J. Environ. Sci. Technol.* 12: 2997–3008.
- Laroo, C.A., Schenk, C.R., Sanchez, L.J., McDonald, J.

- and Smith, P.L. (2012). Emissions of PCDD/Fs, PCBs, and PAHs from legacy on-road heavy-duty diesel engines. *Chemosphere* 89: 1287–1294.
- Lee, C.W., Tabor, D.G. and Cowen, K.A. (2008). Environmental Technology Verification (ETV) test of dioxin emission monitors. *J. Mater. Cycles Waste Manage.* 10: 38–45.
- Lee, W.J., Shih, S.I., Li, H.W., Lin, L.F., Yu, K.M., Lu, K., Wang, L.C., Chang-Chien, G.P., Fang, K. and Lin, M. (2009). Assessment of polychlorinated dibenzo-*p*-dioxins and dibenzofurans contribution from different media to surrounding duck farms. *J. Hazard. Mater.* 163: 1185–1193.
- Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Tsai, P.J. and Chen, C.K. (2003). Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from the incinerations of both medical and municipal solid wastes. *Aerosol Air Qual. Res.* 3: 1–6.
- Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Wu, K.Y. and Tsai, P.J. (2005). Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from stack gases of electric arc furnaces and secondary aluminum smelters. *J. Air Waste Manage. Assoc.* 55: 219–226.
- Lemieux, P.M., Lutes, C.C. and Santoianni, D.A. (2004). Emissions of organic air toxics from open burning: a comprehensive review. *Prog. Energy Combust. Sci.* 30: 1–32.
- Lew, G. (1993). Letter to John Schaum Concerning CARB (1987) Draft Report on CDD/CDFs in Vehicle Exhausts. Sacramento, CA. California Air Resources Board, Monitoring and Laboratory Division. Available for Inspection at: US Environmental Protection Agency, Office of Research and Development. National Center for Environmental Assessment, Washington, DC.
- Lew, G. (1996). Letter to G. Schweer (Versar, Inc.) Dated January 11, 1996. Sacramento, CA. State of California Air Resources Board, Engineering and Laboratory Branch. Available for Inspection at: US Environmental Protection Agency, Office of Research and Development. National Center for Environmental Assessment, Washington, DC.
- Li, H.W., Lee, W.J., Huang, K.L. and Chang-Chien, G.P. (2007a). Effect of raw materials on emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from the stack flue gases of secondary aluminum smelters. *J. Hazard. Mater.* 147: 776–784.
- Li, H.W., Wu, Y.L., Lee, W.J. and Chang-Chien, G.P. (2007b). Fate of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in a fly ash treatment plant. *J. Air Waste Manage. Assoc.* 57: 1024–1031.
- Li, H.W., Lee, W.J., Tsai, P.J., Mou, J.L., Chang-Chien, G.P. and Yang, K.T. (2008a). A novel method to enhance polychlorinated dibenzo-*p*-dioxins and dibenzofurans removal by adding bio-solution in EAF dust treatment plant. *J. Hazard. Mater.* 150: 83–91.
- Li, H.W., Wang, L.C., Chen, C.C., Yang, X.Y., Chang-Chien, G.P. and Wu, E.M.Y. (2011). Influence of memory effect caused by aged bag filters on the stack PCDD/F emissions. *J. Hazard. Mater.* 185: 1148–1155.
- Li, Y., Jiang, G., Wang, Y., Cai, Z. and Zhang, Q. (2008b). Concentrations, profiles and gas–particle partitioning of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the ambient air of Beijing, China. *Atmos. Environ.* 42: 2037–2047.
- Liao, J., Buekens, A., Olie, K., Yang, J., Chen, T. and Li, X. (2016). Iron and copper catalysis of PCDD/F formation. *Environ. Sci. Pollut. Res.* 23: 2415–2425.
- Lin, L.F., Lee, W.J., Li, H.W., Wang, M.S. and Chang-Chien, G.P. (2007). Characterization and inventory of PCDD/F emissions from coal-fired power plants and other sources in Taiwan. *Chemosphere* 68: 1642–1649.
- Lin, W.Y., Wang, L.C., Wang, Y.F., Li, H.W. and Chang-Chien, G.P. (2008). Removal characteristics of PCDD/Fs by the dual bag filter system of a fly ash treatment plant. *J. Hazard. Mater.* 153: 1015–1022.
- Lin, W.Y., Wu, Y.L., Tu, L.K., Wang, L.C. and Lu, X. (2010). The emission and distribution of PCDD/Fs in municipal solid waste incinerators and coal-fired power plant. *Aerosol Air Qual. Res.* 10: 519–532.
- Lomnicki, S. and Dellinger, B. (2003). A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on CuO/silica surface. *J. Phys. Chem. A* 107: 4387–4395.
- Louw, R. and Ahonkhai, S.I. (2002). Radical/radical vs radical/molecule reactions in the formation of PCDD/Fs from (chloro) phenols in incinerators. *Chemosphere* 46: 1273–1278.
- Lu, S.Y., Yan, J.H., Li, X.D., Ni, M.J., Cen, K.F. and Dai, H.F. (2007). Effects of inorganic chlorine source on dioxin formation using fly ash from a fluidized bed incinerator. *J. Environ. Sci.* 19: 756–761.
- Luijk, R., Akkerman, D.M., Slot, P., Olie, K. and Kapteijn, F. (1994). Mechanism of formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the catalyzed combustion of carbon. *Environ. Sci. Technol.* 28: 312–321.
- Mager, K., Meurer, U. and Wirling, J. (2003). Minimizing dioxin and furan emissions during zinc dust recycle by the Waelz process. *JOM* 55: 20–25.
- Marklund, S., Andersson, R., Tysklind, M., Rappe, C., Egeback, K.E., Björkman, E. and Grigoriadis, V. (1990). Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. *Chemosphere* 20: 553–561.
- McDonald, J., Menter, J., Armstrong, J. and Shah, J. (2005). Evaluation of emissions from Asian 2-stroke motorcycles. *SAE Technical Paper* 20056624.
- McKay, G. (2002). Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review. *Chem. Eng. J.* 86: 343–368.
- Meyer, C., Beer, T., Müller, J., Gillett, R., Weeks, I., Powell, J., Tolhurst, K., McCaw, L., Cook, G. and Marney, D. (2004). Dioxins Emissions from Bushfires in Australia, Technical Report No. 1, Australian Government Department of the Environment and Heritage, Canberra.
- MMA (2015). National Implementation Plan Brazil: Convention Stockholm, Ministry of Environment, Brazil.
- MoE (2005). Dioxin Emission Inventory of Japan from 1997 through 2004, Ministry of Environment, Japan, <http://www.env.go.jp/en/press/2005/1125a.html>.

- Mokhtar, M.M., Taib, R.M. and Hassim, M.H. (2014). Measurement of PCDD/Fs emissions from a coal-fired power plant in Malaysia and establishment of emission factors. *Atmos. Pollut. Res.* 5: 388–397.
- Moltó, J., Gálvez, A., Fuentes, M., Fullana, A. and Font, R. (2007). Emission of PCDD/Fs from combustion of pine needles and pine cones in a residential stove. *Organohalogen Compd.* 69: 1578–1581.
- Mwangi, J.K., Lee, W.J., Chang, Y.C., Chen, C.Y. and Wang, L.C. (2015). An overview: Energy saving and pollution reduction by using green fuel blends in diesel engines. *Appl. Energy* 159: 214–236.
- Mwangi, J.K., Lee, W.J., Wang, L.C., Sung, P.J., Fang, L.S., Lee, Y.Y. and Chang-Chien, G.P. (2016). Persistent organic pollutants in the Antarctic coastal environment and their bioaccumulation in penguins. *Environ Pollut.* 2016: 924–934.
- Nakano, M., Hosotani, Y. and Kasai, E. (2005). Observation of behavior of dioxins and some relating elements in iron ore sintering bed by quenching pot test. *ISIJ Int.* 45: 609–617.
- Nganai, S., Lomnicki, S. and Dellinger, B. (2008). Ferric oxide mediated formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. Technol.* 43: 368–373.
- Ni, Y., Zhang, H., Fan, S., Zhang, X., Zhang, Q. and Chen, J. (2009). Emissions of PCDD/Fs from municipal solid waste incinerators in China. *Chemosphere* 75: 1153–1158.
- Oh, J.E., Choi, J.S. and Chang, Y.S. (2001). Gas/particle partitioning of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in atmosphere; evaluation of predicting models. *Atmos. Environ.* 35: 4125–4134.
- Ooi, T.C. and Lu, L. (2011). Formation and mitigation of PCDD/Fs in iron ore sintering. *Chemosphere* 85: 291–299.
- Paradiž, B., Dilara, P., Horák, J., De Santi, G., Christoph, E. and Umlauf, G. (2008). An integrated approach to assess the PCDD/F emissions of the coal fired stoves combining emission measurements and ambient air levels modelling. *Chemosphere* 73: S94–S100.
- P.R.C (2007). The People's Republic of China National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants.
- Qu, X., Wang, H., Zhang, Q., Shi, X., Xu, F. and Wang, W. (2009). Mechanistic and kinetic studies on the homogeneous gas-phase formation of PCDD/Fs from 2, 4, 5-trichlorophenol. *Environ. Sci. Technol.* 43: 4068–4075.
- Quaß, U., Fermann, M. and Bröker, G. (2004). The European dioxin air emission inventory project—final results. *Chemosphere* 54: 1319–1327.
- Randall, D. (1994). *An Evaluation of the Cost of Incinerating Wastes Containing PVC*. Vol. 31. Amer Society of Mechanical.
- Rappe, C. (1992). Sources of PCDDs and PCDFs. Introduction. Reactions, levels, patterns, profiles and trends. *Chemosphere* 25: 41–44.
- Rey, M., Font, R. and Aracil, I. (2014). PCDD/F emissions from light-duty diesel vehicles operated under highway conditions and a diesel-engine based power generator. *J. Hazard. Mater.* 278: 116–123.
- Rivera-Austrui, J., Borrajo, M.A., Martinez, K., Adrados, M.A., Abalos, M., Van Bavel, B., Rivera, J. and Abad, E. (2011). Assessment of polychlorinated dibenzo-*p*-dioxin and dibenzofuran emissions from a hazardous waste incineration plant using long-term sampling equipment. *Chemosphere* 82: 1343–1349.
- Rivera-Austrui, J., Martínez, K., Marco-Almagro, L., Abalos, M. and Abad, E. (2014). Long-term sampling of dioxin-like substances from a clinker kiln stack using alternative fuels. *Sci. Total Environ.* 485: 528–533.
- Rolff, C., Broman, D., Näf, C. and Zebühr, Y. (1993). Potential biomagnification of PCDD/Fs - new possibilities for quantitative assessment using stable isotope trophic position. *Chemosphere* 27: 461–468.
- Ryan, J.V. and Gullett, B.K. (2000). On-road emission sampling of a heavy-duty diesel vehicle for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* 34: 4483–4489.
- Ryu, J.Y., Mulholland, J.A., Takeuchi, M., Kim, D.H. and Hatanaka, T. (2005). CuCl<sub>2</sub>-catalyzed PCDD/F formation and congener patterns from phenols. *Chemosphere* 61: 1312–1326.
- Samaras, P., Skodras, G., Sakellaropoulos, G., Blumenstock, M., Schramm, K.W. and Kettrup, A. (2001). Toxic emissions during co-combustion of biomass-waste wood-lignite blends in an industrial boiler. *Chemosphere* 43: 751–755.
- Schechter, A., Birnbaum, L., Ryan, J.J. and Constable, J.D. (2006). Dioxins: An overview. *Environ. Res.* 101: 419–428.
- Shih, S.I., Lee, W.J., Lin, L.F., Huang, J.Y., Su, J.W. and Chang-Chien, G.P. (2008). Significance of biomass open burning on the levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the ambient air. *J. Hazard. Mater.* 153: 276–284.
- Solorzano-Ochoa, G., David, A., Maiz-Laralde, P., Gullett, B.K., Tabor, D.G., Touati, A., Wyrzykowska-Ceradini, B., Fiedler, H., Abel, T. and Carroll, W.F. (2012). Open burning of household waste: Effect of experimental condition on combustion quality and emission of PCDD, PCDF and PCB. *Chemosphere* 87: 1003–1008.
- Stanmore, B.R. (2004). The formation of dioxins in combustion systems. *Combust. Flame* 136: 398–427.
- Stieglitz, L. (1998). Selected topics on the de novo synthesis of PCDD/PCDF on fly ash. *Environ. Eng. Sci.* 15: 5–18.
- Sun, Y., Liu, L., Fu, X., Zhu, T., Buekens, A., Yang, X. and Wang, Q. (2016). Mechanism of unintentionally produced persistent organic pollutant formation in iron ore sintering. *J. Hazard. Mater.* 306: 41–49.
- Suzuki, K., Kasai, E., Aono, T., Yamazaki, H. and Kawamoto, K. (2004). De novo formation characteristics of dioxins in the dry zone of an iron ore sintering bed. *Chemosphere* 54: 97–104.
- Šyc, M., Horák, J., Hopan, F.e., Krpec, K., Tomšej, T.s., Ocelka, T.s. and Pekárek, V. (2011). Effect of fuels and domestic heating appliance types on emission factors of selected organic pollutants. *Environ. Sci. Technol.* 45:

- 9427–9434.
- Taiwan EPA (2008). The Project of Emission Investigation and Draft Control Strategy of Air Toxic Pollutants (Dioxins and Heavy Metals) from the Stationary Sources. Taiwan EPA.
- Takeda, N., Takaoka, M., Fujiwara, T., Takeyama, H. and Eguchi, S. (2000). PCDDs/DFs emissions from crematories in Japan. *Chemosphere* 40: 575–586.
- Takeda, N., Takaoka, M., Fujiwara, T., Takeyama, H. and Eguchi, S. (2001). Measures to prevent emissions of PCDDs/DFs and co-planar PCBs from crematories in Japan. *Chemosphere* 43: 763–771.
- Takeda, N., Takaoka, M., Oshita, K. and Eguchi, S. (2014). PCDD/DF and co-planar PCB emissions from crematories in Japan. *Chemosphere* 98: 91–98.
- Tame, N.W., Dlugogorski, B.Z. and Kennedy, E.M. (2007). Formation of dioxins and furans during combustion of treated wood. *Prog. Energy Combust. Sci.* 33: 384–408.
- Tsubouchi, N., Kuzuhara, S., Kasai, E., Hashimoto, H. and Ohtsuka, Y. (2006). Properties of dust particles sampled from windboxes of an iron ore sintering plant: surface structures of unburned carbon. *ISIJ Int.* 46: 1020–1026.
- UNEP (2005). Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases. Geneva, Switzerland, United Nations Environment Programme Chemicals.
- US EPA (2006). An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000, Assessment, N.C.f.E. (Ed.), Washington, DC.
- Van den Berg, M., Birnbaum, L., Bosveld, A., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R. and Kennedy, S.W. (1998). Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* 106: 775–792.
- Vicaretti, M., D'Emilia, G., Mosca, S., Guerriero, E. and Rotatori, M. (2013). Evaluation of the measurement uncertainty in automated long-term sampling of PCDD/PCDFs. *Environ. Sci. Pollut. Res.* 20: 8535–8545.
- Wang, J.B., Hung, C.H., Hung, C.H. and Chang-Chien, G.P. (2009a). Polychlorinated dibenzo-*p*-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries. *J. Hazard. Mater.* 161: 800–807.
- Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003a). Characterizing the emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from crematories and their impacts to the surrounding environment. *Environ. Sci. Technol.* 37: 62–67.
- Wang, L.C., Lee, W.J., Tsai, P.J., Lee, W.S. and Chang-Chien, G.P. (2003b). Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from stack flue gases of sinter plants. *Chemosphere* 50: 1123–1129.
- Wang, L.C., Hsi, H.C., Chang, J.E., Yang, X.Y., Chang-Chien, G.P. and Lee, W.S. (2007). Influence of start-up on PCDD/F emission of incinerators. *Chemosphere* 67: 1346–1353.
- Wang, L.C., Lee, W.J., Lee, W.S. and Chang-Chien, G.P. (2010a). Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources. *Environ. Pollut.* 158: 3108–3115.
- Wang, L.C., Wang, Y.F., Hsi, H.C. and Chang-Chien, G.P. (2010b). Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes. *Environ. Sci. Technol.* 44: 1240–1246.
- Wang, Q., Jin, Y., Li, X., Chen, J., Lu, S., Chen, T., Yan, J., Zhou, M. and Wang, H. (2014). PCDD/F emissions from hazardous waste incinerators in China. *Aerosol Air Qual. Res.* 14: 1152–1159.
- Wang, Y.F., Chao, H.R., Wu, C.H., Wang, L.C., Chang-Chien, G.P., Yang, H.H., Lin, D.Y. and Tsou, T.C. (2009b). Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from a heavy oil-fueled power plant in northern Taiwan. *J. Hazard. Mater.* 163: 266–272.
- Weber, R., Sakurai, T., Ueno, S. and Nishino, J. (2002). Correlation of PCDD/PCDF and CO values in a MSW incinerator—indication of memory effects in the high temperature/cooling section. *Chemosphere* 49: 127–134.
- Wevers, M. and De Fre, R. (1995). Estimated evolution of dioxin emissions in Belgium from 1985 to 1995. *Organohalogen Compd.* 24: 105–108.
- Wevers, M., De Fre, R. and Desmedt, M. (2004). Effect of backyard burning on dioxin deposition and air concentrations. *Chemosphere* 54: 1351–1356.
- WHO (1998). Assessment of the Health Risk of Dioxins: Reevaluation of the Tolerable Daily Intake TDI. May, Geneva, Switzerland. pp. 25–29.
- Wielgosinski, G. (2010). The possibilities of reduction of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans emission. *Int. J. Chem. Eng.* 2010: 392175.
- Wikström, E., Ryan, S., Touati, A. and Gullett, B.K. (2004). In situ formed soot deposit as a carbon source for polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Sci. Technol.* 38: 2097–2101.
- Wu, E.M.Y., Wang, L.C., Lin, S.L. and Chang-Chien, G.P. (2014a). Validation and characterization of persistent organic pollutant emissions from stack flue gases of an electric arc furnace by using a long-term sampling system (AMESA®). *Aerosol Air Qual. Res.* 14: 185–196.
- Wu, J.L., Lin, T.C., Wang, L.C. and Chang-Chien, G.P. (2014b). Memory effects of polychlorinated dibenzo-*p*-dioxin and furan emissions in a laboratory waste incinerator. *Aerosol Air Qual. Res.* 14: 1168–1178.
- Xu, F.Q., Huang, S.B., Liao, W.T., Wang, L.C., Chang, Y.C. and Chang-Chien, G.P. (2014). Submerged arc furnace process superior to the Waelz process in reducing PCDD/F emission during thermal treatment of electric arc furnace dust. *Sci. Total Environ.* 466: 598–603.
- Xue, Y., Tian, H., Yan, J., Xiong, C., Pan, T., Nie, L., Wu, X., Li, J., Wang, W., Gao, J., Zhu, C. and Wang, K. (2016). Present and future emissions of HAPs from crematories in China. *Atmos. Environ.* 124: 28–36.
- Yang, C.Y., Chiou, S.L., Wang, J.D. and Guo, Y.L. (2015). Health related quality of life and polychlorinated biphenyls and dibenzofurans exposure: 30 years follow-up of Yucheng cohort. *Environ. Res.* 137: 59–64.

- Yu, B.W., Jin, G.Z., Moon, Y.H., Kim, M.K., Kyoung, J.D. and Chang, Y.S. (2006). Emission of PCDD/Fs and dioxin-like PCBs from metallurgy industries in S. Korea. *Chemosphere* 62: 494–501.
- Yu, Y., Zheng, M., Li, X. and He, X. (2012). Operating condition influences on PCDD/Fs emissions from sinter pot tests with hot flue gas recycling. *J. Environ. Sci.* 24: 875–881.
- Zhang, G., Hai, J., Ren, M., Zhang, S., Cheng, J. and Yang, Z. (2013). Emission, mass balance, and distribution characteristics of PCDD/Fs and heavy metals during cocombustion of sewage sludge and coal in power plants. *Environ. Sci. Technol.* 47: 2123–2130.
- Zhang, Q., Li, S., Qu, X., Shi, X. and Wang, W. (2008). A quantum mechanical study on the formation of PCDD/Fs from 2-chlorophenol as precursor. *Environ. Sci. Technol.* 42: 7301–7308.
- Zhang, T., Fiedler, H., Yu, G., Ochoa, G.S., Carroll, W.F., Gullett, B.K., Marklund, S. and Touati, A. (2011). Emissions of unintentional persistent organic pollutants from open burning of municipal solid waste from developing countries. *Chemosphere* 84: 994–1001.
- Zhang, Y., Zhang, D., Gao, J., Zhan, J. and Liu, C. (2014). New understanding of the formation of PCDD/Fs from chlorophenol precursors: A mechanistic and kinetic study. *J. Phys. Chem. A* 118: 449–456.
- Zimmermann, R., Blumenstock, M., Heger, H., Schramm, K. and Kettrup, A. (2001). Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: Delayed emission effects. *Environ. Sci. Technol.* 35: 1019–1030.
- Zou, C., Han, J. and Fu, H. (2012). Emissions of PCDD/Fs from steel and secondary nonferrous productions. *Proc. Environ. Sci.* 16: 279–288.

Received for review, October 14, 2016

Revised, November 19, 2016

Accepted, November 19, 2016