



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[®])

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ABSTRACT

A long-term sampling system, called the Adsorption Method for Sampling of Dioxins and Furans (AMESA), was used for long-term sampling (up to 168 hours) of an electric arc furnace (EAF) to obtain the representative flue gas samples. In order to have a comprehensive view of the emissions of persistent organic pollutants (POPs) from EAFs, six POPs, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDEs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs), were investigated. Tests showed the breakthroughs of PBDD/Fs and PBDEs are much larger (8.9%–43%), while the others are less than 3%. A significant increase in breakthrough with the increase in halogen numbers is observed, because highly halogen-substituted POPs tend to partition to the particulate-phase. Except for PCBs and PCDEs, whose percentages of the POPs in the rinses to the total POPs collected from the long-term samples (cartridges + rinses) are less than 7%, those of the other POPs are all greater than 30%. Therefore, the solvents from the rinses of the sampling probe and other components need to be combined with an XAD-2 cartridge for analyses. The PCBs and PBDEs are the most abundant pollutants in the stack flue gases of the EAF, and their mass concentrations are one to three orders higher than those of the other POPs. With regard to POPs with dioxin-like toxicity, the percentages of the contributed toxicities by PCDD/Fs, PCBs and PBDD/Fs are 87.1%, 11.7% and 1.2%. The close association that PBDEs and PBDD/Fs have with the concentrations and congener profiles is not present for PCDEs and PCDD/Fs, suggesting the need for further studies of the formation mechanisms of these analogues.

Keywords: PCDD/Fs; PCDEs; PBDEs; PBDD/Fs; AMESA.

INTRODUCTION

Electric arc furnaces (EAFs) are used to produce carbon and steel alloys, primarily from melting iron and steel scraps, and play an important role in iron/steel making. A typical EAF includes the stages of feeding, smelting, oxidation, reduction and steel discharge. The melting of scrap ferrous material contaminated with varying amounts of chlorinated compounds (i.e., PVC plastics, cutting oils, coatings and

paints) provides conditions favorable to the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Wang *et al.*, 2003b; Lee *et al.*, 2005). EAFs have been reported as one of the major PCDD/F emission sources (European Commission, 2000; Lee *et al.*, 2004). Together with sinter plants (Wang *et al.*, 2003c), they contribute 99% of the aggregate PCDD/F health risk to residents in densely populated areas of a city in southern Taiwan (Kao *et al.*, 2007).

In addition to PCDD/Fs, EAFs have also been recognized as an important emitter of polybrominated diphenyl ethers (PBDEs) (Odabasi *et al.*, 2009; Wang *et al.*, 2010b, 2011a, c) and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) (Wang *et al.*, 2008, 2010c). PBDEs and PBDD/Fs are emitted from EAFs when they are not completely

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destroyed in the feeding scraps, and are also formed during the combustion process. This suggests that it is necessary to further characterize the other analogues that are contained in the emissions of EAFs, such as polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs) and polychlorinated diphenyl ethers (PCDEs). Except for PCDEs, the various pollutants noted above, such as PCDD/Fs, PBDD/Fs, PCBs, PBBs and PBDEs, all appear on the list of persistent organic pollutants (POPs) in the Stockholm Convention. These POPs are bio-accumulative, toxic, and susceptible to long-range transport (LRT) (Wania, 2003; Wang *et al.*, 2011b). For example, PBDEs can have various harmful effects on humans, such as developmental neurotoxicity, hepatotoxicity, embryotoxicity, and decreased reproductive success (Chao *et al.*, 2010, 2011; Shy *et al.*, 2012).

PCDEs are a group of halogenated aromatic compounds, which are structurally similar to PCBs and PCDFs. The difference in the chemical structures of PCDEs and PBDEs, which have been extensively used as brominated flame retardants (BFRs) in a large variety of consumer products, is that bromine substitutions are all replaced by chlorine. Similar to their analogues, PCDEs with lipophilic and persistent properties tend to bioaccumulate and biomagnify in food webs (Domingo, 2006). Some PCDEs may have biochemical and toxic effects similar to those of PCBs and PCDD/Fs (Becker *et al.*, 1991). Furthermore, PCDEs may be converted to or form toxic PCDD/Fs by photolysis or pyrolysis (Norström *et al.*, 1976; Lindahl *et al.*, 1980; Liu *et al.*, 2010), and have been observed in the flue gas and fly ash of waste incinerators (Kurz and Ballschmiter, 1995; Nakao *et al.*, 2006). Nevertheless, in terms of being a product of incomplete combustion, PCDEs have attracted little attention compared to related combustion-originated POPs, such as PCDD/Fs (Wang *et al.*, 2007; Lin *et al.*, 2008; Li *et al.*, 2011), PCBs (Chang *et al.*, 2014), PBDD/Fs and PBDEs (Wang *et al.*, 2010a, c).

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, with the time for one stack flue gas sample usually ranging from three to six hours. Therefore, the PCDD/F emissions that occur during the sampling time are of little relevance to the overall emission level, especially for EAFs that have significant variations in the properties of the raw feeding scraps (Lee *et al.*, 2005). Another issue is that some POPs, such as PBDD/Fs and PBBs, have very low concentrations in the stack flue gases of combustion sources, and several stack flue gas samples are thus usually combined into one for the PBDD/F measurement in order to meet their detection limits (Wang and Chang-Chien, 2007; Wang *et al.*, 2010c).

To solve the representative issue resulting from spot PCDD/F measurements using manual short-term sampling, which occur for only a few hours each year, three long-term sampling systems and two semi-real-time continuous monitoring systems have been developed (Mayer *et al.*, 2000; Lee *et al.*, 2008; Vicaretti *et al.*, 2012). One of these is the Adsorption Method for Sampling of Dioxins and Furans (AMESA), which is a fully automatic long-term sampling system for industrial processes based on isokinetic

flue gas sampling and the PCDD/F adsorption that occurs on an exchangeable resin-filled cartridge (Lee *et al.*, 2008). This system has been tested, undergoing certification procedures (Mayer *et al.*, 2000; Idczak *et al.*, 2003; Lee *et al.*, 2008; Vicaretti *et al.*, 2012), and is obligatory for incinerator plants in Belgium, France and the Lombardy region of Italy (Rivera-Austrui *et al.*, 2012). The European Committee for Standardization (CEN) is currently developing a standard for long-term sampling of PCDD/Fs and dioxin-like PCBs (pr EN 1948–5). While AMESA has been widely installed in incinerators, especially in Europe, and some related studies with regard to PCDD/Fs and PCBs have been reported (Mayer *et al.*, 2000; Idczak *et al.*, 2003; Lee *et al.*, 2008; Vicaretti *et al.*, 2012), few works have discussed its application with regard to EAFs or for sampling other POPs, such as PCDEs, PBDD/Fs, PBBs and PBDEs.

In this study, AMESA was used for long-term sampling (up to 168 hours) of an EAF to obtain the representative POP flue gas samples. In order to have a comprehensive view of the POP emissions from EAFs, six POPs, including three chlorinated ones (PCDD/Fs, PCBs and PCDEs) and three brominated analogues (PBDD/Fs, PBBs and PBDEs) were investigated. Breakthrough tests of XAD-2 cartridges and rinses of the sampling probe were conducted to evaluate the feasibility of the long-term POP sampling of EAF by AMESA. Furthermore, the concentrations, emission factors and congener profiles of the six POPs were compared with each other to clarify which one is the most influential atmospheric pollutant, as well as the similarities or differences among their formation mechanisms.

MATERIALS AND METHODS

Basic Details of the Investigated EAF and AMESA

The EAF investigated in this study is operated intermittently, with scrap (104 tonnes/hr), alloying agents (1.1 tonnes/hr), flux (2.1 tonnes/hr) and coke (1.8 tonnes/hr) used as its raw feeding materials, and bag filters as its air pollution control devices (APCDs). It can produce carbon steel as a rate of 100 tonnes/hr.

The operation of AMESA complies with the cooled probe method of EN-1948. The flue gas is isokinetically sampled by using a titanium probe to cool the temperature of flue gas down to less than 50°C, before it is introduced into the XAD-2 cartridge. Fifty grams of XAD-2 resin were filled into the cartridge, which is greater than that used in the manual short-term sampling method. Instead of using filters to collect particles, quartz wool is placed in the front of XAD-2 cartridge. AMESA can thus collect flue gases for up to four weeks at a time. In this study, an additional XAD-2 cartridge is mounted in series to check the breakthrough of the POPs.

Sampling Procedures

A total of six stack flue gas samples were collected from the EAF by using AMESA, and were performed by an accredited laboratory in Taiwan. Prior to sampling, XAD-2 resin was spiked with isotopically labeled PCDD/F surrogate standards. The AMESA system was manually started and

stopped to be consistent with the batch time of processes. Each stack gas sample accumulated ~168 hour sampling time (about a week and half of sampling). The sampled flue gas volumes were normalized to the dry conditions of 760 mmHg and 273 K, and denoted as Nm³.

The sampling probe and other components of the sample train were rinsed after each sampling. The nozzle, probe and probe lines were brushed while rinsing three times with acetone, three times with methylene chloride and then three times with toluene. The rinsate were collected and analyzed for POPs. To ensure that the collected samples were free of contamination, one field blank were also taken during field sampling.

Analytical Procedures

In contrast to other POPs, there is little data associated with PCDEs emitted from combustion sources and in the environment, because native and mass-labeled PCDEs have not been commercially available until recently (Domingo, 2006). In this study, each sample was analyzed for seventeen 2,3,7,8-substituted PCDD/F, twelve dioxin-like PCB, six PCDE, twelve 2,3,7,8-substituted PBDD/F, five PBBs and fourteen PBDE congeners. Internal standards were spiked into the samples before Soxhlet extraction with toluene, and were used to monitor the extraction and cleanup procedures. After the sample was extracted in a Soxhlet extractor with toluene for 24 hours, the extracts were concentrated, and then treated with concentrated sulfuric acid, and this was followed by a series of sample cleanup and fractionation procedures, including a multi-layered silica column, alumina column and an activated carbon column. During the alumina column cleanup, non-planar PCBs and PBBs were eluted with 15 mL hexane, and were then further eluted with 25 mL DCM/hexane (1/24, v/v) for activated carbon column use. The activated carbon column was sequentially eluted with 5 mL toluene/methanol/ethyl acetate/hexane (1/1/2/16, v/v) for PCDE, PBDEs, planar PCBs and PBBs, which was further followed by 40 mL of toluene for PCDD/Fs and PBDD/Fs. Before instrument analyses, the planar and non-planar PCBs/PBBs eluates were mixed together, representing the PCB and PBB samples. The eluate was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further concentrated to near dryness, using a stream of nitrogen. 10 µL of the standard solution for recovery checking was added to the sample extract immediately prior to injection to minimize the possibility of loss. The detailed analytical procedures are given in our previous works (Wang *et al.*, 2010a, b, c; Chang *et al.*, 2013; Chang *et al.*, 2014).

Instrumental Analysis

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for the POP analyses. The HRGC (Hewlett–Packard 6970 Series gas, CA) was equipped with a silica capillary column (J&W Scientific, CA) and a splitless injector, while the HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The selected ion monitoring (SIM) mode was used with a resolving power

of 10,000. The electron energy and source temperature were specified at 35 eV and 250°C, respectively. The detailed instrumental analysis parameters of PCDD/Fs, PCBs, PBDD/Fs, PBBs and PBDEs are given in our previous works (Wang *et al.*, 2010a, b, c; Chang *et al.*, 2014). The instrumental parameters of the PCDEs analyses are the same as those of the PCDD/Fs.

Quality Assurance and Quality Control (QA/QC)

Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including ³⁷Cl₄-2,3,7,8-TCDD, ¹³C₁₂-1,2,3,4,7,8-HxCDD, ¹³C₁₂-2,3,4,7,8-PeCDF, ¹³C₁₂-1,2,3,4,7,8-HxCDF and ¹³C₁₂-1,2,3,4,7,8,9-HpCDF. The recoveries of precision and recovery (PAR), surrogate, and internal labeled standards of POPs all met the relevant standards. Field and laboratory blanks were carried for each batch of sampling and analyses. The total amounts of PCDD/Fs and PBDEs in the field and laboratory blanks were all < 0.1% and 0.3% of the real stack flue gas samples. As for the other POPs, the blanks were all below the detection limits. Furthermore, breakthrough tests of XAD-2 cartridges and determination of the accumulated POP levels onto the surface of the sampling probe were conducted. The detailed results are discussed in the following section.

RESULTS AND DISCUSSION

Breakthrough Tests

Two XAD-2 cartridges are mounted in series and analyzed individually to evaluate the POP breakthrough for the long-term sampling of the EAF by AMESA. The breakthrough of POPs is calculated as follows.

$$\text{Breakthrough (\%)} = B/(A + B) \times 100\%, \quad (1)$$

where A is the mass (toxicity) adsorbed by the first XAD-2 cartridge, and B is the mass (toxicity) adsorbed by the second XAD-2 cartridge.

The results of chlorinated and brominated POPs breakthroughs are listed in Tables 1 and 2, respectively. Less than 3% breakthroughs are found for the mass and toxicity of PCDD/Fs, PCBs, PCDEs and PBBs. The breakthroughs are lowest for PCBs (only 0.0533% for mass and 0.236% for toxicity). However, for PBDD/Fs and PBDEs, their breakthroughs are much larger, and are 43.4% and 14.9% for PBDD/Fs mass and toxicity, and 8.91% for PBDEs mass. As for the individual congeners of these POPs, there was a significant increase in breakthrough with the increase in halogen numbers for the PCDD/Fs, PCBs, PBDD/Fs and PBDEs.

We know that as the halogen numbers of POPs increase, their boiling points rise and vapor pressures drop (Gajewicz *et al.*, 2010). In order to clarify the relation between the breakthrough and halogen numbers, the breakthrough and the subcooled liquid vapor pressure (P_L) of these POPs, which is an important property affecting the gas-particle partition of POPs in the environment, are analyzed by Pearson correlation analyses. We find that the logarithms

Table 1. Breakthrough tests of PCDD/Fs, PCBs and PCDEs of AMESA.

PCDD/Fs	Mean (%) (n = 6)	RSD (%)	PCBs (n = 6)	Mean (%) (%)	RSD (%)	PCDEs (n = 6)	Mean (%) (%)	RSD (%)
2,3,7,8-TeCDD	0.692	109	PCB-77(4Cl)	0.0575	48.8	CDE-28(3Cl)	1.10	139.2
1,2,3,7,8-PeCDD	0.920	46.0	PCB-81(4Cl)	0.0646	45.4	CDE-77(4Cl)	0.100	223.6
1,2,3,4,7,8-HxCDD	2.85	48.4	PCB-105(5Cl)	0.0829	47.4	CDE-99(5Cl)	0.100	143.8
1,2,3,6,7,8-HxCDD	2.80	18.8	PCB-114(5Cl)	0.0409	50.8	CDE-141(6Cl)	0	-
1,2,3,7,8,9-HxCDD	3.57	10.6	PCB-118(5Cl)	0.0370	44.5	CDE-180(7Cl)	0	-
1,2,3,4,6,7,8-HpCDD	8.80	38.0	PCB-123(5Cl)	0.0419	53.8	CDE-209(10Cl)	-	-
OCDD	31.1	54.8	PCB-126(5Cl)	0.221	43.3	Total mass	0.4	182.2
2,3,7,8-TeCDF	0.368	20.3	PCB-156(6Cl)	0.115	54.5			
1,2,3,7,8-PeCDF	0.775	16.5	PCB-157(6Cl)	0.150	42.0			
2,3,4,7,8-PeCDF	0.964	16.1	PCB-167(6Cl)	0.0937	47.8			
1,2,3,4,7,8-HxCDF	1.82	27.9	PCB-169(6Cl)	1.34	61.3			
1,2,3,6,7,8-HxCDF	1.81	28.6	PCB-189(7Cl)	0.558	34.1			
2,3,4,6,7,8-HxCDF	2.52	22.5	Total mass	0.0533	35.8			
1,2,3,7,8,9-HxCDF	3.98	38.1	Total WHO-TEQ	0.236	43.5			
1,2,3,4,6,7,8-HpCDF	4.93	26.2						
1,2,3,4,7,8,9-HpCDF	5.54	27.3						
OCDF	16.2	41.3						
PCDDs	8.19	55.1						
PCDFs	1.44	30.8						
Total mass	2.10	41.0						
PCDDs I-TEQ	1.06	47.7						
PCDFs I-TEQ	0.949	14.4						
Total I-TEQ	0.966	17.9						

Table 2. Breakthrough tests of PBDD/Fs, PBBs and PBDEs of AMESA.

PBDD/Fs	Mean (%) (n = 6)	RSD (%)	PBBs	Mean (%) (n = 6)	RSD (%)	PBDEs	Mean (%) (n = 6)	RSD (%)
2,3,7,8-TeBDD	-	-	PBB-15(2Br)	0.3	124.2	BDE-28(3Br)	0.248	115
1,2,3,7,8-PeBDD	-	-	PBB-52(4Br)	0.0	-	BDE-47(4Br)	0.750	92.8
1,2,3,4/6,7,8-HxBDD	-	-	PBB-153(6Br)	1.5	86.3	BDE-100(5Br)	1.13	86.9
1,2,3,7,8,9-HxBDD	-	-	PBB-180(7Br)	0.0	-	BDE-99(5Br)	1.47	87.4
1,2,3,4,6,7,8-HpBDD	-	-	PBB-194(8Br)	0.0	-	BDE-154(6Br)	2.16	71.5
OBDD	-	-	Total mass	0.7	95.8	BDE-153(6Br)	5.83	48.4
2,3,7,8-TeBDF	0	-				BDE-183(7Br)	18.8	44.1
1,2,3,7,8-PeBDF	0	-				BDE-197(8Br)	22.0	40.6
2,3,4,7,8-PeBDF	0	-				BDE-203(8Br)	26.2	51.0
1,2,3,4,7,8-HxBDF	5.20	107				BDE-196(8Br)	30.0	54.9
1,2,3,4,6,7,8-HpBDF	20.3	43.5				BDE-208(9Br)	41.7	47.4
OBDF	51.8	47.6				BDE-207(9Br)	37.1	52.8
PBDDs	-	-				BDE-206(9Br)	40.6	62.9
PBDFs	43.4	58.1				BDE-209(10Br)	41.3	62.7
Total mass	43.4	58.1				Total mass	8.91	129
PBDDs TEQ	-	-						
PBDFs TEQ	14.9	71.8						
Total TEQ	14.9	71.8						

of the breakthroughs for these POPs are significantly and negatively correlated with the logarithm of P_L ($r = -0.904$, $p < 0.0001$) (see Fig. 1). This strong negative correlation implies that the highly halogen-substituted POPs with lower P_L tend to partition to the particulate-phase, resulting in their greater breakthrough in the AMESA. This is because AMESA uses quartz wool instead of filters to collect particles,

and a higher percentage of the smaller particles emitted from the stack flue gases pass through the first cartridge to the second one.

Rinse of the Sampling Probe

The operation of AMESA complies with the cooled probe method of EN-1948, and thus the particulate- and gaseous-

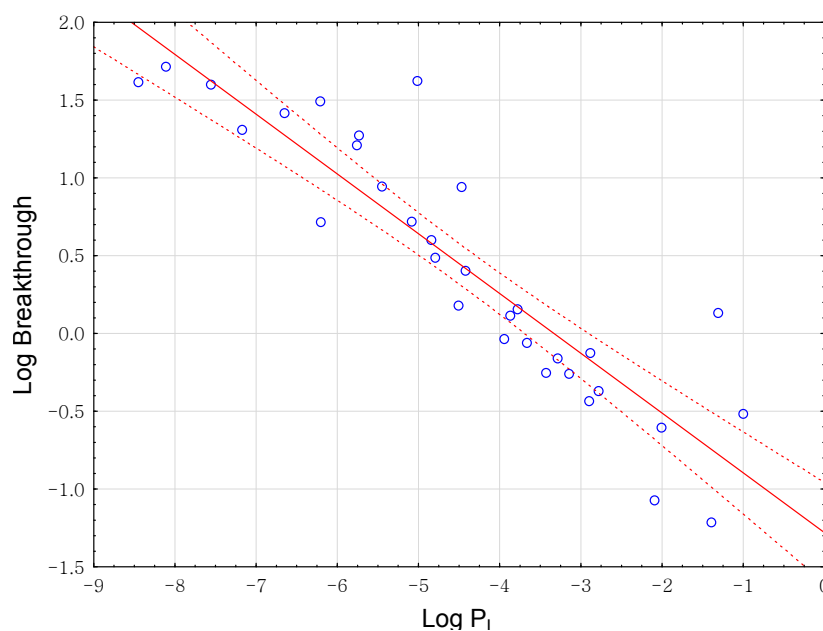


Fig. 1. Relation between the logarithms of the breakthroughs and the logarithm of P_L among the investigated POPs.

phase POPs in the flue gas will adhere and condense onto the surface of the sampling probe and other components of the sample train. To evaluate their accumulated POP levels, four rinses of the sampling probe and other components of the sample train were performed after each sampling, and then individually analyzed for POPs.

The percentages of the POPs in each rinse to the corresponding total POPs collected from long-term sampling (cartridges + rinses) are listed in Table S1 of the supporting information. The amount of POPs in the first rinse of the sampling probe and other components of the sample train are one to three orders higher than those in the second one. Except for the first rinse, the POPs in the subsequent rinse of the sampling probe and other components contributed less than 3% of the total POPs. The results show that the rinse procedures adopted in this study are effective with regard to the removal of POPs from the surface of the sampling probe and other components after long long-term sampling by AMESA.

Table 3 lists the percentages of the POPs in the whole four rinses to the total POPs collected from long-term sampling (cartridges + rinses). The percentages of the rinses based on total mass are 58.0% for PCDD/Fs, 2.6% for PCBs, 2.9% for PCDEs, 55.1% for PBDD/Fs, 31.6% for PBBs and 32.1% for PBDEs, while those based on total toxicity are 40.8% for PCDD/Fs, 7.0% for PCBs and 49.8% for PBDD/Fs. Except for PCBs and PCDEs whose total percentages are less than 7%, those of the other POPs are all greater than 30%.

A significant trend seen in these figures is that the percentages increased along with the increase in halogen numbers for these six POPs. That is attributed to the fact that the highly halogen-substituted POPs in the gaseous phase more easily condense onto the surface of the sampling probe than the lower halogen-substituted ones. Furthermore, the particles that adhere onto the surface of the sampling probe contain more highly halogen-substituted POPs. Therefore,

it is crucial to carefully perform the cleaning procedures, and the solvents from the rinses of the sampling probe and other components need to be combined with XAD-2 cartridges for analyses to obtain the real POP concentrations in the stack flue gases. Although performing rinses could remove most POPs which are adherent to the surface of the sampling probe and components, residues might cause memory effects if the next sampling is a short-term one, because the difference between the sampling volumes of the flue gases could reach about 200-fold.

Concentrations and Congener Profiles of POPs in the Stack Flue Gases

The POP concentrations in the stack flue gases of the EAFs are listed in Table 4. The mass concentrations are 0.439 ng/Nm³ for PCDD/Fs, 7.53 ng/Nm³ for PCBs, 0.0115 ng/Nm³ for PCDEs, 0.163 ng/Nm³ for PBDD/Fs, 0.145 ng/Nm³ for PBBs and 8.03 ng/Nm³ for PBDEs. The PCBs and PBDEs are the most abundant pollutants, and their mass concentrations are one to three orders higher than those of the other POPs. Regarding POPs with dioxin-like toxicity, the toxicity concentrations are 0.0601 ng I-TEQ/Nm³ for PCDD/Fs, 0.00804 ng WHO-TEQ/Nm³ for PCBs and 0.000869 ng TEQ/Nm³ for PBDD/Fs, and the sum of the dioxin-like toxicity concentrations of these three POPs is 0.0690 ng TEQ/Nm³. The toxicities contributed by PCDD/Fs, PCBs and PBDD/Fs are 87.1%, 11.7% and 1.2%, respectively.

Table 5 lists the POP concentrations in the stack flue gases/exhausts of various emission sources, such as incinerators (Kim et al., 2004; Wang et al., 2010a), sinter plants (Kuo et al., 2012; Wang et al., 2003c), EAFs (Lee et al., 2005; Wang et al., 2010c;), power plants (Dyke et al., 2003; Hutson et al., 2009;) and diesel engines (Wang et al., 2010b). As yet, no data regarding PCDEs and PBBs in flue gases emitted from combustion facilities have been reported in the literature.

Table 4. POP concentrations in the stack flue gases of the EAFs.

	POPs	Mean (n = 6)	RSD (%)
PCDD/Fs	mass (ng/Nm ³)	0.439	54.9
	I-TEQ (ng I-TEQ/Nm ³)	0.0601	55.4
PCBs	mass (ng/Nm ³)	7.53	26.3
	WHO-TEQ (ng WHO-TEQ/Nm ³)	0.00804	54.8
PCDEs	Mass (ng/Nm ³)	0.0115	47.7
PBDD/Fs	mass (ng/Nm ³)	0.163	140
	TEQ (ng TEQ/Nm ³)	0.000869	102
PBBs	mass (ng/Nm ³)	0.145	90.5
PBDEs	mass (ng/Nm ³)	8.03	25.7

Table 5. Concentrations of the POPs in the stack flue gases/exhaust of different emission sources.

POPs	Emission sources	Concentrations	Reference
PCDD/Fs	Municipal solid waste incinerators (MSWIs)	0.0725–0.118 ng I-TEQ/Nm ³	(Wang <i>et al.</i> , 2010a)
	Sinter plants	0.357 ng I-TEQ/Nm ³	(Kuo <i>et al.</i> , 2012)
	Power plants	0.0024–0.0203 ng I-TEQ/Nm ³	(Hutson <i>et al.</i> , 2009)
	Diesel engine	0.00972 ng I-TEQ/Nm ³	(Chang <i>et al.</i> , 2014)
	EAFs	0.28 ng I-TEQ/Nm ³	(Lee <i>et al.</i> , 2005)
	EAFs	0.172 ng I-TEQ/Nm ³	(Wang <i>et al.</i> , 2010c)
	EAF dust treatment plant	0.0107–0.0143 ng I-TEQ/Nm ³	(Xu <i>et al.</i> , 2014)
PCBs	MSWIs	0.022–0.061 ng WHO-TEQ/Nm ³	(Kim <i>et al.</i> , 2004)
	Power plants	0.010–0.011 ng WHO-TEQ/Nm ³	(Dyke <i>et al.</i> , 2003)
	Secondary aluminum and copper metallurgies	0.019–0.023 ng WHO-TEQ/Nm ³	(Ba <i>et al.</i> , 2009)
	Diesel engine	0.00115 ng WHO-TEQ/Nm ³	(Chang <i>et al.</i> , 2014)
PBDD/Fs	MSWIs	0.0653–0.0881 ng TEQ/Nm ³	(Wang <i>et al.</i> , 2010a)
	Power plants	0.0085–0.0414 ng TEQ/Nm ³	(Hutson <i>et al.</i> , 2009)
	EAFs	0.00188 ng TEQ/Nm ³	(Wang <i>et al.</i> , 2010c)
	Sinter plants	0.00416 ng TEQ/Nm ³	
	Diesel engine	0.00240 ng TEQ/Nm ³	(Chang <i>et al.</i> , 2014)
PBDEs	MSWIs	109–26.1 ng/Nm ³	(Wang <i>et al.</i> , 2010a)
	Sinter plants	22.2 ng/Nm ³	
	EAFs	19.4 ng/Nm ³	
	Secondary aluminum smelters	33.5 ng/Nm ³	(Wang <i>et al.</i> , 2010b)
	Power plants	29.1–46.7 ng/Nm ³	
	Diesel engine (NEDC test)	41.3 ng/Nm ³	
	Diesel engine	29.1 ng/Nm ³	(Chang <i>et al.</i> , 2014)

Compared to the results in previous studies of EAFs (Wang *et al.*, 2010b, c; Lee *et al.*, 2005), the concentrations of PCDD/Fs, PBDD/Fs and PBDEs obtained in this work are lower, but still within one order. Generally, the PCDD/F and PCB concentrations in the flue gases of stationary sources are higher than those in the exhausts of diesel engines or vehicles, although diesel engines seem to emit higher or at least similar levels of PBDD/F and PBDE concentrations (Wang *et al.*, 2010b) than stationary sources.

The congener profiles of these POPs in the stack flue gases of the EAF are shown in Fig. 2. The congener profiles of PCDD/Fs, PBDD/Fs and PBDEs obtained from this study are consistent with the results of previous works (Hofstadler *et al.*, 2000; Wang *et al.*, 2003c; Lee *et al.*, 2004, 2005; Wang *et al.*, 2010c). The PBDE congeners in the stack flue gases leaned more to the low to medium brominated congeners, namely BDE-28, -47, -100 and -99. These abundant low to

medium brominated congeners may be attributed to the thermal desorption of the commercial penta-BDE mixtures, which were impurities in the feeding scrap (Wang *et al.*, 2010c). Among the highly brominated-substituted congeners, BDE-209 was the most abundant. BDE-209 could be formed through combustion processes, which is similar to that of sinter plants (Wang *et al.*, 2010c), and from the undestroyed BDE-209 in the feeding scrap.

The PBDD/F congener profile was dominated by 1,2,3,4,6,7,8-HpBDF and OBDF (highly brominated PBDF congeners), while the others were all quite minor or below the detection limits. Among the highly brominated congeners, the congener profiles of PBDEs showed a similar pattern to those of the PBDFs. In addition, the much higher concentration of PBDEs than PBDD/Fs also reveals that highly brominated PBDEs were available as precursors of highly brominated PBDFs (Chang *et al.*, 2014).

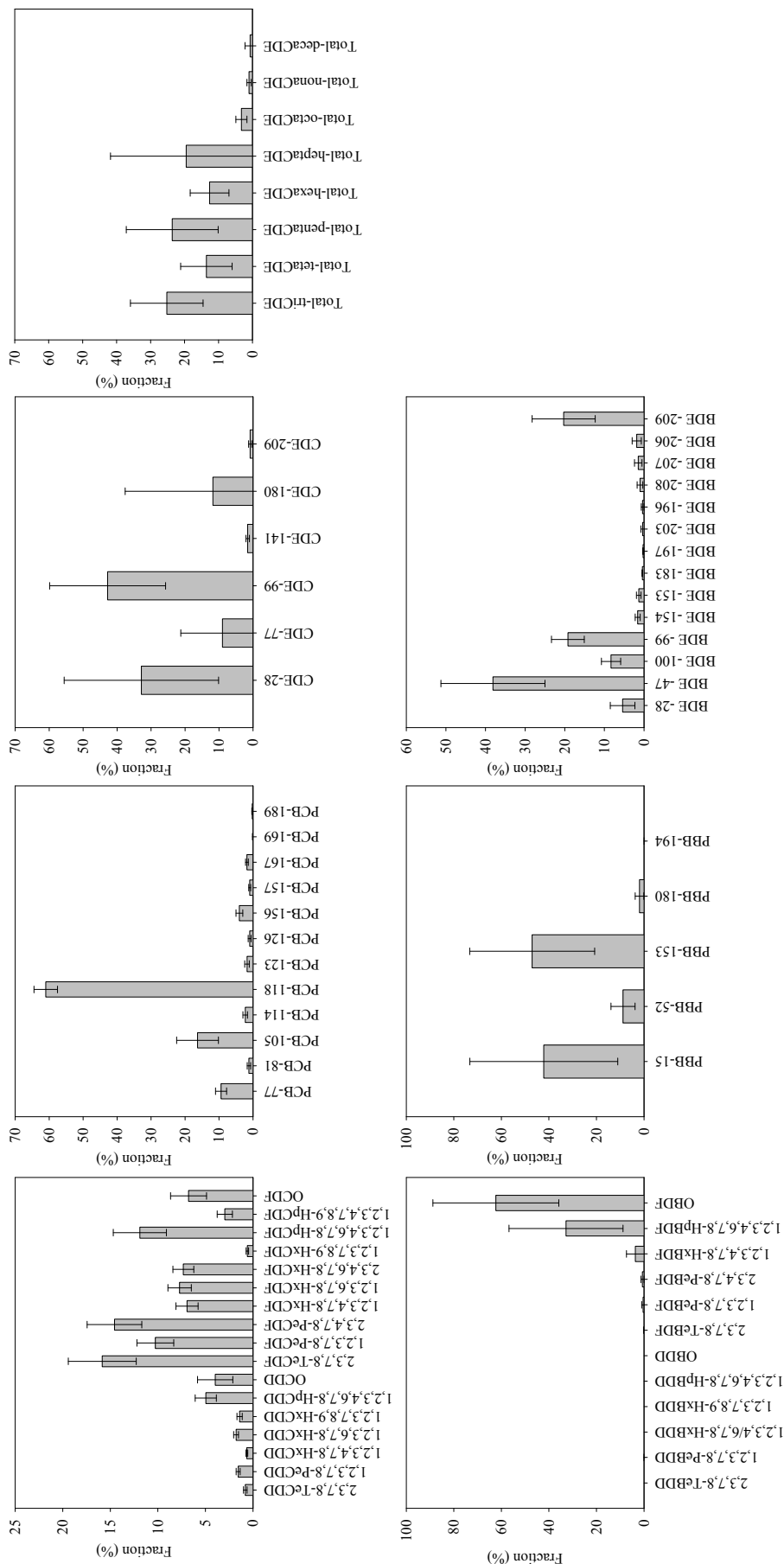


Fig. 2. Congener profiles of these POPs in the stack flue gases of the EAF.

Table 6. Emission factors of the POPs from stack flue gases of EAFs.

POPs	Emission factors	Country	Reference
PCDD/Fs	3.098 µg I-TEQ/tonne-product	Portugal	(Antunes <i>et al.</i> , 2012)
	1.15 µg I-TEQ/tonne-product	Italy	(Caserini and Monguzzi, 2002)
	1.8 µg I-TEQ/tonne-product	Taiwan	(Lee <i>et al.</i> , 2005)
	2.13 µg I-TEQ/tonne-feedstock	Taiwan	(Wang <i>et al.</i> , 2010b)
	0.177 µg I-TEQ/tonne-feedstock	Taiwan	This study
PCBs	0.0617-0.0867 µg WHO-TEQ/tonne-product	China	(Liu <i>et al.</i> , 2012)
	0.659 I-TEQ/tonne-product	Portugal	(Antunes <i>et al.</i> , 2012)
	0.0232 µg WHO-TEQ/tonne-feedstock	Taiwan	This study
PCDEs	0.0343 µg/tonne-feedstock (six congeners)	Taiwan	This study
	0.268 µg/tonne-feedstock (Total PCDEs)		
PBDD/Fs	0.0799 µg TEQ/tonne-product	Taiwan	(Wang <i>et al.</i> , 2010c)
	0.00247 µg TEQ/tonne-feedstock	Taiwan	This study
PBBs	0.416 µg/tonne-feedstock	Taiwan	This study
PBDEs	212 µg/tonne-product	Turkey	(Odabasi <i>et al.</i> , 2009)
	296 µg/tonne-product	Taiwan	(Wang <i>et al.</i> , 2010c)
	215 µg/tonne-feedstock	Taiwan	(Wang <i>et al.</i> , 2010b)
	24.0 µg/tonne-feedstock	Taiwan	This study

The PCDD/F congener profile dominated by 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF (lower chlorinated-substituted PCDFs) was very different to the corresponding PBDD/F congener profiles. De novo synthesis of PCDD/Fs is known to dominate in the post-combustion zone of EAFs (Lee *et al.*, 2005; Wang *et al.*, 2010c), and therefore, for PBDD/Fs, formation from PBDE precursors is much more significant than that from de novo synthesis.

For the PCBs, the dominant congeners in the stack flue gases were in the order of PCB-118, -105, and -77, showing that tetra- and penta-CBs were the major PCB homologues. This assembled to the results found for the PCDF homologue. Although PBBs, like PCBs, were also dominant in lower halogenated-substituted congeners, the bromination pattern was different from that seen for PBDD/Fs.

The PCDE congener profile is dominated by CDEs-28 and -99, the lower chlorinated-substituted congeners. The homologue profile clearly shows that the formation of PCDEs is favorable to the lower chlorinated ones, while the highly chlorinated ones remain minor components. Similar phenomena occurred with regard to PCDFs of the EAF, which had higher fractions of the lower chlorinated congeners compared to other combustion sources, such as vehicles (Chang *et al.*, 2014), incinerators (Wang and Chang-Chien, 2007) and crematories (Wang *et al.*, 2003a). We speculate that Fe₂O₃, which should be abundant in fly ashes of EAFs, may shift the formation of PCDEs towards the lower chlorinated congeners (Liu *et al.*, 2013). The close association between PBDEs and PBDD/Fs does not exist for PCDEs and PCDD/Fs. Furthermore, the formation mechanisms between PBDEs and PCDEs, as well as those between PBDD/Fs and PCDD/Fs, are not very similar, suggesting the need for further studies on the relationships among the formation mechanisms of these analogues.

The congener profiles of PBDD/Fs and PBDEs, especially for PBDD/Fs, which were more dominated by the highly halogen-substituted congeners than other POPs, resulted in their breakthroughs much larger than those of other POPs.

Emission Factors of the POPs

Table 6 lists the POP emission factors of EAFs obtained from this study and from elsewhere. The emission factors are calculated based on the total weights of steel production or feedstock, including scraps, alloying agents, flux and coke. For the same measurement, the obtained emission factors based on the product will be 10%–15% higher than those based on the feedstock, because the transformation rate of feedstock to produced steel is commonly around 90% or lower.

The emission factors of the investigated EAF in this study are 0.177 µg I-TEQ/tonne-feedstock for PCDD/Fs, 0.0232 µg WHO-TEQ/tonne-feedstock for PCBs, 0.0343 µg/tonne-feedstock for PCDEs, 0.00247 µg TEQ/tonne-feedstock for PBDD/Fs, 0.416 µg/tonne-feedstock for PBBs and 24.0 µg/tonne-feedstock for PBDEs, which are all one order lower than those reported in other studies. The much higher sampling time of AMESA should include more high emission events, which will then cause higher emission factors. Therefore, we think that the lower emission factors obtained in this study should be attributed to the influence of feeding materials and the operating condition of EAFs (Lee *et al.*, 2005; Wang *et al.*, 2010a, c), not the samplings by AMESA.

CONCLUSIONS

The PBDD/F congener profile was dominated by 1,2,3,4,6,7,8-HpBDF and OBDF (highly brominated PBDF congeners), while the others were all quite minor components or below the detection limits. Among the highly brominated congeners, the congener profiles of PBDEs showed a similar pattern to those of the PBDFs. The PCDD/F congener profile, which was dominated by lower chlorinated-substituted PCDFs, was very different to the corresponding PBDD/F congener profiles. De novo synthesis of PCDD/Fs is known to dominate in the post-combustion zone of EAFs, and therefore the formation of PBDD/Fs from PBDE precursors

is much more significant than that from de novo synthesis. The logarithms of the breakthroughs of these POPs are significantly and negatively correlated with the logarithm of P_L ($r = -0.904$, $p < 0.0001$). This strong negative correlation implies that the highly halogen-substituted POPs with lower P_L tend to partition to the particulate-phase, resulting in their greater breakthrough in the AMESA. Therefore, PBDD/Fs had much higher breakthroughs than the other POPs.

The emission factors of the investigated EAF in this study are one order lower than those from other studies. This should be attributed to the influence of feeding materials and the operating condition of the EAFs, not samplings by AMESA, because the much higher sampling time of AMESA should include more high emission events.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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SUPPLEMENTARY MATERIALS

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[®])

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Table S1. Mean percentage (%) of the POPs in each rinse to the corresponding total POPs collected from long-term samplings (cartridges + rinses).

POPs		Rinse 1		Rinse 2		Rinse 3		Rinse 4	
		mean (n = 6)	SD	mean (n = 6)	SD	mean (n = 6)	SD	mean (n = 6)	SD
PCDD/Fs	mass	57.0	5.92	0.541	0.649	0.225	0.135	0.230	0.189
	I-TEQ	40.7	7.13	0.0371	0.0225	0.0257	0.0197	0.0544	0.0622
PCBs	mass	2.54	1.11	0.0133	0.0154	0.0154	0.0146	0.00959	0.0123
	WHO-TEQ	6.94	2.99	0.0147	0.0314	0.0293	0.0406	0.0381	0.0541
PCDEs	mass	2.28	0.911	0.637	1.27	0.0315	0.0631	ND	ND
PBDD/Fs	mass	50.9	20.9	2.23	2.45	1.09	1.08	0.837	1.17
	TEQ	48.4	24.9	0.619	0.748	0.286	0.299	0.390	0.544
PBBs	mass	28.8	12.5	0.933	0.569	1.00	0.736	0.853	0.566
PBDEs	mass	30.0	9.52	0.884	0.563	0.560	0.299	0.656	0.386