

# Concentration and congener patterns of polychlorinated biphenyls in industrial and municipal waste incinerator flue gas, Korea

Sun-Kyoung Shin<sup>a</sup>, Kyoung-Soo Kim<sup>b,\*</sup>, Jae-Cheon You<sup>c</sup>,  
Byung-Joo Song<sup>d</sup>, Jong-Guk Kim<sup>b,d</sup>

<sup>a</sup> National Institute of Environmental Research, Kyungseo-dong, Seo-gu, Incheon 404-170, Korea

<sup>b</sup> Center for Chemical Safety Management, Chonbuk National University, 664-14 Duckjin-dong, Chonju 561-756, Korea

<sup>c</sup> Analytical Research Center, Environmental Management Corporation, Kyungseo-dong, Seo-gu, Incheon 404-708, Korea

<sup>d</sup> Department of Environmental Engineering, Chonbuk National University, 664-14 Duckjin-dong, Chonju 561-756, Korea

Received 25 November 2004; received in revised form 10 October 2005; accepted 11 October 2005

Available online 1 December 2005

## Abstract

In the present study, individual PCB congeners were determined in the flue gases of 10 industrial and 5 municipal solid waste incinerators using HRGC/HRMS. The total PCBs concentration of all congeners (168 tetra to deca-chlorinated congeners) ranged from 26 to 343 ng/Nm<sup>3</sup>, and from 36 to 1095 ng/Nm<sup>3</sup> in industrial waste incinerators (IWI) and municipal solid waste incinerators (MSWI), respectively. The total TEQ concentrations of PCBs, calculated using WHO-TEF values, varied from 0.001 to 0.55 ng-TEQ/Nm<sup>3</sup> and from 0.001 to 8.29 ng-TEQ/Nm<sup>3</sup> in the industrial waste incinerators and municipal solid waste incinerators, respectively. In all samples, the contribution of PCB 126 to total TEQ of PCBs was higher than 87%. The homologue pattern of PCBs in the incinerator flue gas samples was generally dominated by tetra- and penta-CBs. The distribution of other homologues was less than 15% in most of the incinerators. The fraction of co-PCBs against to total PCBs ranged from 1% to 19% and from 2% to 31% in IWI and MSWI flue gas samples. Results of the present study reveal that the presence of non-ortho PCB congeners in the flue gas originated from the combustion process.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** PCBs; Incinerators; Flue gas; Korea

## 1. Introduction

The major environmental sources of polychlorinated biphenyls (PCBs) to the air are from (i) volatilization from commercial PCB formulations and (ii) emission from combustion processes [1]. Today solid waste management is a challenging problem in developing countries, due to insufficient land to dump solid waste, and to the contamination of land by leaching. Difficulties arise in the separation of waste materials prior to landfill also presents a problem to waste management. Rapid and multi fold industrial growth also results in an increase in the volume of industrial wastes, which causes a problem for disposal. Hence, many countries choose incineration to dispose solid waste. In Korea, the incineration ratio of municipal waste and specific waste (a harmful waste as like waste oil, waste

acid/alkali, waste asbestos, ash, etc.) was 14.5% and 16.7% in 2003, respectively [2]. The present capacity of available landfill is about 15 years from now (nationwide average). Consequently, the option of incineration will have to be utilized significantly more in the future.

During incineration waste material is burned at high temperatures and converted into ash, unburned solids, carbon dioxide, oxygen, oxides of nitrogen, sulfur dioxide, ammonia and water [3]. A major concern regarding the operation of incinerators is the problem of air pollution. Although the major air pollutants, such as fly ash, and acidic gases, are removed by bag filters or scrubbers, the complete removal of all micro level toxic gaseous pollutants, such as dioxins and dioxin-like PCBs, is not achieved. A remarkably high concentration of PCBs in the flue gas of municipal solid waste incinerators and industrial waste incinerators, after conventional air pollution control measures, was reported in both Japan and Korea [4,5,6]. Incineration-pyrolysis is also used for the destruction of PCB compounds at higher temperatures. The pyroplasma system uses a plasma torch to

\* Corresponding author. Tel.: +82 63 270 2448; fax: +82 63 270 2449.  
E-mail address: skysil99@empal.com (K.-S. Kim).

induce temperatures up to 15,000 °C and pyrolyse the organic liquid. The resultant products are carbon mono-oxide, nitrogen, hydrogen and some low molecular-weight-hydrocarbons [7]. In Japan, 5300 tonnes of waste liquid PCBs, namely, Kanechlors, were thermally destroyed in 1988 [8]. The incinerator fly ash was studied to ascertain whether dioxins and PCBs were destroyed or dechlorinated in an oxygen deficient condition between 340 and 380 °C [9,10]. Hence, the incineration process has potential to both produce and destroy PCBs. In Korea, the production and use of PCBs were banned in 1996, and commercial products (transformer and electric capacitor) of PCBs have been consigned and treated in countries abroad. At present, the treatment of PCB waste using incineration is prohibited.

The polychlorinated biphenyls are a class of 209 chemical compounds having the formula  $C_{12}H_{10-n}Cl_n$ , where  $n = 1 - 10$ ; i.e. monochlorobiphenyl (1CB) though decachlorobiphenyl (10CB). Among the PCB congeners, only 20 can attain lack of substitution in the ortho-position, which leads to coplanar configuration. The coplanar PCBs (non- and mono-ortho-substituted) have a high toxicity, similar to that of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Hence, these compounds are referred to as ‘dioxin-like PCBs’ [11]. Generally, the PCB toxicity is expressed as toxic equivalents (TEQ), the TEQ was calculated using World Health Organization (WHO)—Toxic equivalency factor (TEF). In present, 12 coplanar PCB congeners are assigned with a TEF.

Previously, it was thought that the major source for PCBs in the environment was from PCB formulations, the result of a wide usage in capacitors, transformers, dye, solvents and plasticizers. Hence, incineration emission has not been considered as a main source for PCBs. Though several reports are available for PCDD/Fs emission from incinerators, little information is available on detailed congener patterns of PCBs. Presently in Korea, dioxin released from a municipal solid waste incinerator (MSWI) newly constructed after 1997 (above 50 tonnes/day), has been regulated at 0.1 ng-TEQ/m<sup>3</sup>. However, there is no regulation for PCBs emissions from incinerators. Only a few reports are available on PCB emissions in the industrial waste incinerator (IWI) and MSWI [5,6]. Therefore, we are forced to investigate IWIs and MSWIs in the country. For this purpose, we have selected incinerators other than previously studied. In the present investigation, we have determined PCB congeners from tetra-CBs to deca-CBs in 10 industrial waste incinerators and 5 municipal waste incinerator flue gases. The results were compared with previous reports on incinerator emissions and PCB formulations.

## 2. Experimental

### 2.1. Sample collection

All the stacks were located in various areas of South Korea. The operating conditions are provided in Table 1. The stack gas samples were collected following Korean Standard Method between December 2001 and March 2002. The volume of samples collected was between 3.0 and 4.0 Nm<sup>3</sup> (about 15 L/min)

and the concentration of individual PCBs was corrected by an oxygen compensation factor according to the following formula [4]. In Korea, all data are compensated by 12% oxygen concentration because of the difference of oxygen concentration in flue gas as incinerators. Particle phase was collected using a thimble filter and the gas phase was collected using gas adsorbent (XAD-2) and diethylene glycol [5]. The particle and gas phase were combined and analyzed.

$$\text{PCB concentration (ng/Nm}^3\text{)} \\ \times \left[ \frac{21 - 12}{21 - \text{measured oxygen concentration}} \right]$$

### 2.2. Extraction, purification and analysis

Sample extraction and purification methods were performed according to the US EPA Method 1613 [12] and 1668 [13]. The dust filter was digested with 2 M HCl before Soxhlet extraction with toluene. Diethylene glycol, water, rinse solution and the water phase from acid treatment of the dust filter were combined and liquid–liquid extracted with toluene. The detailed procedure is shown in Fig. 1. Prior to extraction, the samples were spiked with a mixture of <sup>13</sup>C-labeled PCB containing at least one congener for each homologue group of PCBs besides dioxin-like PCB congeners. The MBP-MXP (contain 12 PCB congeners), MBP-MXK (contain 10 PCB congeners) and WP-LCS (contain 12 co-PCB congeners) of Wellington laboratories were used as <sup>13</sup>C-labeled PCB internal standards. The flue gas extracts were cleaned up using a sulfuric acid-treated silica column (sulfuric acid 44%, w/w) with 150 mL of distilled *n*-hexane, and followed by an activated carbon (Kanto Chemical Co.) column. Other PCBs were collected in the 25% dichloromethane/hexane fraction (30 mL); whereas PCB-77, 81, 126, 169 congeners and PCDD/DFs were collected in the distilled toluene fraction (250 mL). The PCBs eluate was dried into the glass insert, added with 25 μL of recovery standard (<sup>13</sup>C-1,2,3,4-TCDD and <sup>13</sup>C-1,2,3,7,8,9-HxCDD). PCBs were analyzed using a high-resolution gas chromatography (HRGC) equipped with a high-resolution mass spectrometer (HRMS) (Agilent HP6890 and

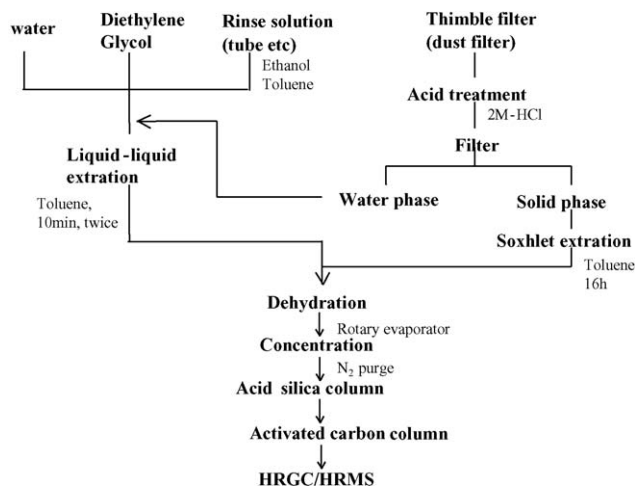


Fig. 1. Cleanup procedure for flue gas samples.

Table 1  
Operating conditions of industrial waste incinerators and municipal solid waste incinerators

Incinerator number	Incinerator Type	Sampling period (Year and month)	Capacity (Tonnes/h)	Sampling Volume (Nm <sup>3</sup> )	Oxygen concentration (%)	Mode of Operation	Furnace temperature (°C)	Stack gas temperature (°C)	Type of waste material	Air pollution control measures <sup>a</sup>
IWI-1	Stocker	2001 (December)	1.600	3.3872	13.1	Continuous	919	30	General IWI	MC-Scrubber
IWI-2	Stocker	2002 (January)	1.250	3.3298	15.9	Continuous	–	–	General IWI	Cyclone1-Cyclone2-scrubber
IWI-3	Melting furnaces	2001 (December)	0.437	3.5653	12.6	Continuous	–	–	General IWI	EP-scrubber-adsorption
IWI-4	Downward combustion	2001 (December)	0.450	3.7086	16.1	Batch	970	47	General IWI	MC-scrubber-cyclone
IWI-5	Fluidized bed	2001 (December)	2.080	3.1361	11.5	Continuous	870	40	Wastewater sludge	Cyclone-EP-S/C
IWI-6	Combustion bed	2001 (December)	0.285	3.3144	15.8	Batch	850	105	Waste tire	Cyclone-B/F-scrubber
IWI-7	Fixed grate stoker	2002 (March)	0.210	3.4944	13.9	Batch	–	56	Infectious waste	Scrubber
IWI-8	Combustion bed	2002 (March)	0.400	3.4014	13.8	Semi-Continuous	900	46	Waste oil and organic solvent	Cyclone-scrubber
IWI-9	Fixed grate stoker	2001 (December)	2.500	3.1011	13.3	Continuous	880	57	Specific IWI	Cyclone-ventury S/C-Packed tower-rotary S/C BF
IWI-10	Fluidized bed	2002 (February)	2.700	3.177	10.5	Continuous	880	178	Sludge	BF
MSWI-1	Traveling grate stoker	2002 (January)	1.000	3.9528	14.8	Semi-Continuous	890	109	MSWI	Cyclone-SDA-BF
MSWI-2	Traveling grate stoker	2002 (March)	1.500	3.6235	16.2	Continuous	872	125	MSWI	SDA-BF
MSWI-3	Traveling grate stoker	2002 (January)	2.083	3.0805	12.3	Continuous	871	145	MSWI	SDA-BF
MSWI-4	Fixed grate stoker	2002 (February)	0.650	3.1488	15.1	Semi-Continuous	640	135	MSWI	Cyclone-SDA-BF
MSWI-5	Combustion bed	2002 (January)	1.200	3.1307	16.1	Continuous	1040	91	MSWI	SDA-BF

<sup>a</sup> MC, multi cyclone; S/C, spray cooling tower; SDA, spray dryer absorber; EP, electrostatic precipitator.

Micromass Autospec Ultima). The detected peaks were identified referring to reports [14,15,16]. The concentration of peaks was determined by isotope dilution quantification. The average recoveries of spiked PCBs ranged from 50% to 80%, except from mono-CBs to tri-CBs (below 50%). Consequently, congeners of these homologues (from mono- to tri-CBs) are not used data analysis. Blank levels of individual PCB congeners were negligible compared to the samples and no blank correction was performed in this study.

### 3. Results and discussion

#### 3.1. PCB concentrations in flue gases

PCB concentrations in the flue gas of IWI (IWI-1 to IWI-10) and MSWI (MSWI-1 to MSWI-5) are presented in Table 2. In the present study the IUPAC numbering system was used for individual PCBs [17]. The total PCB concentration in flue gas of IWI incinerators showed a highest value of 343.47 ng/Nm<sup>3</sup> in IWI-1 and a lowest value of 26.11 ng/Nm<sup>3</sup> in IWI-6. Among the MSWI, the highest value of 1095.12 ng/Nm<sup>3</sup> is measured in MSWI-5 and the lowest concentration of 35.81 ng/Nm<sup>3</sup> is measured in MSWI-1. In some Asian countries (like Korea and Japan), the concentration of PCBs (from tetra- to deca-CBs) in stack gas samples ranged from 16.14 to 6905 ng/Nm<sup>3</sup> [6] and from 13.91 to 7029 ng/Nm<sup>3</sup> [4]. The observed total PCB (from tetra- to deca-CBs) concentration in present study is lower than the flue gas level of incinerators reported by previous investigations [4,6].

The concentration of WHO-TEQ in the IWI ranged from 0.001 (IWI-3) to 0.55 ng TEQ/Nm<sup>3</sup> (IWI-1). In the MSWI, it

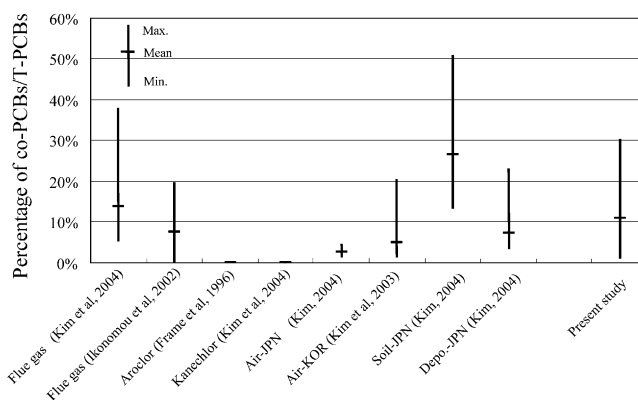


Fig. 2. The fraction of co-PCB against t-PCB (4CB-10CB) in flue gas, PCB commercial products and Air samples (JPN, KOR and Depo means Japan, Korea and Deposition, respectively).

ranged from 0.006 (MSWI-3) to 8.29 ng TEQ/Nm<sup>3</sup> (MSWI-5). The mean TEQ concentration of fifteen incinerators was 0.69 ng TEQ/Nm<sup>3</sup>. The WHO-TEQ values in comparison with previous studies are presented in Table 3. TEQ levels observed in the incinerators were lower than those given in the report of Kim et al. [4] in Japan and higher than the levels reported by Sakai et al. [18] in Japan. However, they are comparable to the levels reported by Chang et al. [5] in Korea. The observed concentrations of TEQ were higher than the report of Luthardt et al. [19] in Germany (the individual dioxin-like PCB congener concentrations were not reported by the author). The fraction of co-PCB against t-PCB (4CB-10CB) was higher than the PCB commercial products [4,20], air [21] and deposition samples [22] as shown in Fig. 2. Soil media showed the highest values

Table 2  
Concentration of individual PCB congeners (ng/Nm<sup>3</sup>) in the flue gas sample of IWIs and MSWIs in Korea

IUPAC no.	Industrial waste incinerator (IWIs)										Municipal solid waste incinerators (MSWIs)				
	IWI-1	IWI-2	IWI-3	IWI-4	IWI-5	IWI-6	IWI-7	IWI-8	IWI-9	IWI-10	MSWI-1	MSWI-2	MSWI-3	MSWI-4	MSWI-5
81	7.12	2.81	0.01	1.20	0.11	0.03	1.22	0.55	0.56	1.82	0.31	0.25	0.05	6.59	19.53
77	8.36	2.29	0.03	2.65	0.23	0.11	2.59	1.43	1.20	7.54	1.68	0.57	0.09	11.14	66.19
123	2.05	1.31	0.04	0.22	0.05	0.02	0.43	0.22	0.17	0.27	0.09	0.07	0.03	1.84	3.69
118	7.29	4.46	0.13	0.75	0.30	0.16	1.66	0.88	0.71	1.15	0.43	0.37	0.17	7.89	19.99
114	4.03	2.34	0.04	0.29	0.08	0.02	0.49	0.22	0.27	0.30	0.12	0.08	0.02	4.00	4.45
105	4.96	1.77	0.04	0.51	0.14	0.05	0.92	0.66	0.52	0.93	0.27	0.22	0.07	4.90	25.21
126	5.23	1.31	0.01	2.76	0.07	0.03	1.57	0.64	0.59	1.37	0.47	0.24	0.06	5.48	77.10
167	0.61	0.46	0.00	0.12	0.01	0.00	0.17	0.12	0.09	0.14	0.04	0.03	0.00	0.50	3.21
156	1.32	0.67	0.01	0.18	0.01	0.01	0.30	0.18	0.18	0.19	0.09	0.06	0.01	1.15	9.47
157	0.80	0.25	0.00	0.10	0.01	0.00	0.14	0.16	0.09	0.19	0.04	0.04	0.00	0.61	5.73
169	2.11	0.57	0.01	2.46	0.03	0.03	0.65	0.18	0.20	0.52	0.16	0.10	0.05	1.89	55.34
189	3.07	1.37	0.01	0.46	0.02	0.01	0.56	0.22	0.38	0.32	0.18	0.12	0.06	2.18	44.10
4CB	194.78	76.26	30.73	43.02	33.48	21.62	58.02	27.13	41.53	50.10	24.24	37.40	30.12	203.70	294.74
5CB	82.30	37.43	3.40	11.87	5.40	3.54	16.52	8.75	9.43	13.13	7.06	6.36	4.47	89.09	271.79
6CB	15.22	7.67	0.44	4.42	0.52	0.51	3.46	1.65	2.02	4.18	1.60	1.40	0.43	15.51	121.23
7CB	25.96	14.05	0.32	3.12	0.49	0.33	4.05	3.73	3.76	6.29	1.54	1.54	0.63	20.94	200.68
8CB	12.51	8.61	0.10	1.46	0.12	0.07	2.76	0.91	1.00	1.98	0.63	0.64	0.15	8.51	116.80
9CB	9.22	7.70	0.01	1.34	0.05	0.03	3.71	0.93	1.07	2.60	0.50	0.53	0.11	5.70	74.48
10CB	3.49	3.74	0.01	0.80	0.04	0.01	0.58	0.19	0.44	0.90	0.23	0.23	0.06	1.77	15.39
Co-PCBs	46.95	19.62	0.34	11.69	1.04	0.49	10.70	5.46	4.94	14.74	3.90	2.12	0.61	48.19	334.00
Total PCBs	343.47	155.46	35.03	66.04	40.11	26.11	89.11	43.30	59.23	79.17	35.81	48.10	35.96	345.23	1095.12
TEQ PCBs	0.550	0.140	0.001	0.302	0.008	0.004	0.164	0.067	0.062	0.143	0.049	0.025	0.006	0.573	8.291

Table 3  
Concentration of Co-PCBs (dioxin like PCBs) in the incinerator stack emissions (ng/Nm<sup>3</sup>) in comparison to the previous study

Co-PCB congeners	(A) Sakai et al., 2001 (n = 1)	(B) Chang et al., 1999 (n = 11)			(c) Kim et al., 2004 (n = 9)			(D) Present study (n = 15)			WHO-TEF
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
PCB-81	0.04	0.02	33.06	3.80	0.09	44.84	7.57	0.01	35.87	4.45	0.0001
PCB-77	0.68	0.03	45.62	5.90	0.23	255.82	33.57	0.04	121.56	11.60	0.0001
PCB-123	<0.02 <sup>a</sup>	0.01	10.95	1.28	0.03	14.84	3.10	0.03	6.77	1.09	0.0001
PCB-118	0.11	0.00	29.90	4.03	0.19	54.76	13.04	0.14	36.71	4.90	0.0001
PCB-114	<0.02 <sup>a</sup>	0.01	14.44	1.65	0.05	15.97	3.34	0.02	8.17	1.70	0.0005
PCB-105	0.61	NR	NR	NR	0.11	161.51	27.45	0.05	46.31	4.54	0.0001
PCB-126	0.03	0.04	60.69	8.66	0.19	430.83	62.68	0.01	141.61	11.29	0.1
PCB-167	<0.02 <sup>a</sup>	0.00	13.13	1.58	0.04	23.65	5.14	0.00	5.90	0.61	0.00001
PCB-156	0.02	0.00	32.12	4.35	0.08	72.55	14.85	0.01	17.39	1.56	0.0005
PCB-157	<0.02 <sup>a</sup>	0.01	23.12	3.27	0.07	105.18	21.17	0.00	10.53	0.92	0.0005
PCB-169	<0.02 <sup>a</sup>	0.03	23.26	3.43	0.17	103.33	20.22	0.01	101.65	7.65	0.01
PCB-189	<0.02 <sup>a</sup>	0.01	30.76	4.43	0.15	100.46	20.51	0.01	81.00	6.23	0.0001
Sum Co-PCBs	1.49	0.16	317.05	42.38	1.40	1383.75	232.63	0.33	613.47	56.52	
TEQ (ng/Nm <sup>3</sup> )	0.00			0.91			6.50			1.21	

n, number of stacks investigated; NR, values not reported; A: Japan, B: Korea, C: Japan, D: present study in Korea.

<sup>a</sup> Values less than the detection limit are considered as 0 for the calculation of TEQ.

among samples, which indicates that the soil is a reservoir of co-PCB. The main source of co-PCB entering the environment is considered to be the incinerators.

### 3.2. Homologue and congener distribution in flue gases

Among dioxin-like PCBs, PCB-77 (8 samples) and PCB-118 (5 samples) showed the highest values in most of the samples, while PCB-126 showed the highest value in IWI-4 and MSWI-5. However, the predominant average dioxin-like PCBs in the incinerators were in the order of PCB-77, PCB-118, PCB-126, PCB-81, PCB-105, PCB-169, PCB-189, PCB-114, PCB-123, PCB-156, PCB-157 and PCB-167.

In terms of the distribution of individual co-PCBs to the PCB-TEQ in the flue gas of IWI and MSWI, the results clearly indicate that PCB-126 contributes between 88% and 96% TEQ value in all incinerators, followed by PCB-169, of which the concentration ranged from 2.66% and 9.62%. This is due to the higher

TEF value for PCB-126 than the one for other congeners. The contributions of all other dioxin-like toxic congeners to the total TEQ was less than 1.3% in all incinerators. The observed result supports the findings of Lopez Garcia et al. [23], that PCB-126 is the most important PCB congener in the combustion process in view of toxicity.

Fig. 3 compares the distribution of dioxin like PCBs in the incinerator flue gas with commercial PCB formulations (Aroclor 1242, 1254 and 1260). The dioxin like non-ortho compounds, such as PCB-81, PCB-77, PCB-126 and 169 were more present in the flue gases of this study than in commercial PCB mixtures. In Aroclor samples, PCB-81, and PCB-126 were almost absent in all formulations and PCB-169 was present only in Aroclor 1260 (6.4%). This observation agrees with the review of Alcock et al. [24] that the presence of non-ortho PCBs in the municipal waste incinerator flue gas may be due to the combustion process itself and does not solely come from the commercial PCB mixtures. Brown et al. [1] also concluded that the environmental burden of PCB congeners originated from non-Aroclor sources.

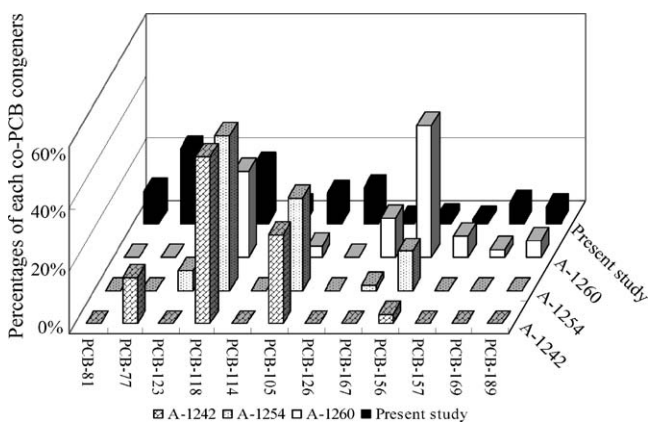


Fig. 3. Distribution of dioxin like PCBs in the incinerator flue gas in composition with Aroclor commercial formulations (Aroclor 1242, 1254, 1260 (Schulz et al. 1999)), \* average value calculated from 15 incinerator flue gas in the present study).

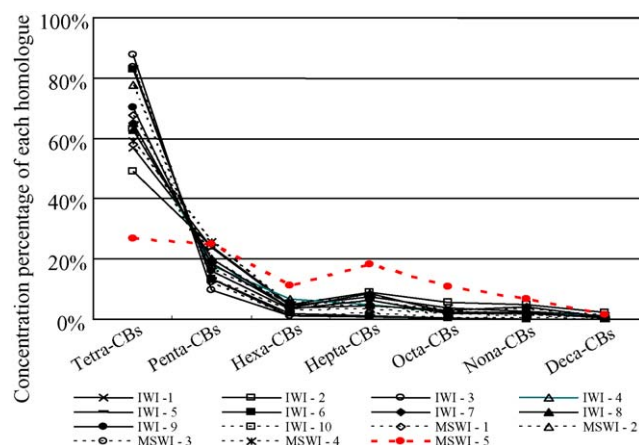


Fig. 4. Distribution of PCB homologue groups in the flue gas of IWI and MSWI.



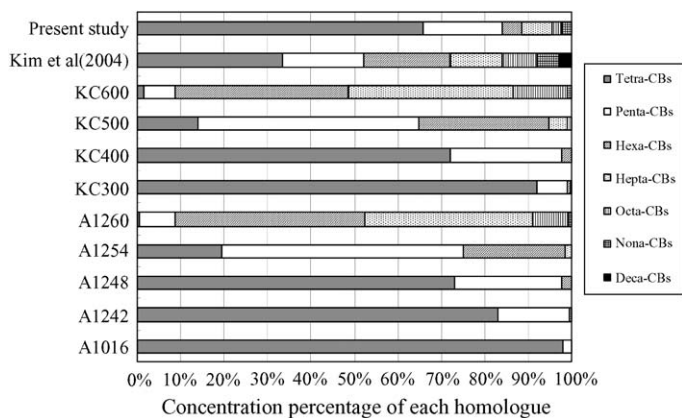


Fig. 5. Homologue distribution of PCBs in the flue gas in comparison to the commercial formulation (Source: Aroclors-A1016, A1242, A1248, A1245, A1260 (Frame et al. 1996); Clophen—A30, A40, A50, A60 (Schulz et al. 1999), Kanechlor—KC-300, KC-400, KC-500, KC-600 and incinerator flue gas (average value of 10 samples) (Kim et al. 2004), The value of present study is an average of 10 IWIs and 5 MSWIs).

Fig. 4 shows the homologue distribution of PCBs in the incinerator flue gas samples. The PCBs concentration was normalized as the sum of  $\Sigma[\text{PCB}] = 100\%$ . The contribution of PCB homologue group was not similar in all flue gas samples. However, the average value calculated in all flue gas samples showed the following order. Concentrations of tetra CBs ( $67 \pm 16\%$ ) were the highest, followed by penta-CBs ( $18 \pm 5\%$ ), hepta-CBs ( $6 \pm 4\%$ ) and hexa-CBs ( $4 \pm 3\%$ ). The total concentration of all other CBs, i.e from octa-CBs to deca-CBs was less than 10% in most of the samples, except IWI-2 (13%) and MSWI-5 (19%), which showed 13% and 19%, respectively. The result reveals that stack gas samples were predominated by low chlorinated PCBs. The observed results are in agreement with the results reported by Chang et al. [5]. Fig. 5 showed the homologue distribution of PCBs in the incinerator flue gas sample compared to commercial PCB formulations such as Aroclor, Kanechlor and the incinerator flue gas sample from the previous study [4,20]. The incinerator flue gas sample does not resemble the pattern of any of the commercial PCB formulations; however, it showed the contribution of low chlorinated PCBs (tetra and penta-CBs) is higher than high-chlorinated PCBs when compared to the observations of Kim et al. [4] in flue gas samples.

### 3.3. Relationship between PCB concentration and dioxin concentration

In this study, the relationship between PCB concentration and PCDD/DFs concentration was estimated using regression analysis (Fig. 6). The concentration of PCDD/DFs in flue gas samples was obtained by Environmental Management Corporation (EMC), Korea. The MSWI-5 sample is clearly an outlier because it has a much higher concentration than the other samples. Thus, regression analysis was conducted on all other samples except for the MSWI-5 sample. The coefficient of determination and  $p$ -value in 95% of the confidence level was 0.6 and 0.0012, respectively, which is statistically significant. Chang

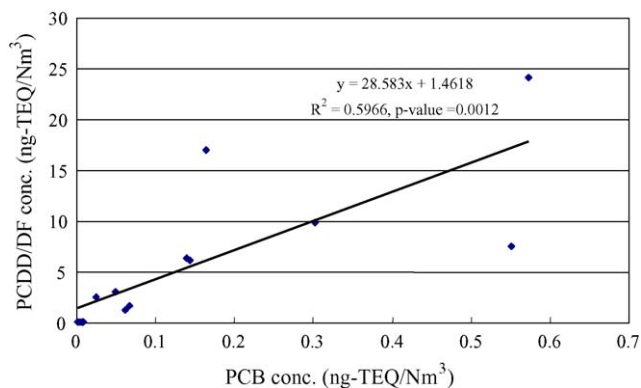


Fig. 6. The relationship between PCB concentration and PCDD/DFs concentration.

et al. [5] reported that the relationship between the total TEQ amount of PCBs and that of PCDD/DFs was weak among stack gas samples. However, Ling and Hou [25] observed that a linear relationship existed between the TEQ value of PCDD/DFs and three co-PCBs with a coefficient of determination of 0.93. The agreement of PCDD/DFs with PCBs can be explained by the precursor character of PCBs with respect to PCDFs [26], which indicates that co-PCBs might be formed by similar reactions as PCDDs and PCDFs [27]. The contribution to total TEQ (PCBs plus PCDD/DFs) concentration from the PCBs ranged from 0.9% to 7.4%. This result indicates that these incinerators act as a source of PCB contamination, in addition to PCB commercial products.

## 4. Conclusion

The concentrations of all PCB congeners in the flue gas sample of 10 IWIs and 5 MSWIs were determined. The distribution of dioxin-like congener patterns was compared to PCB commercial formulations and flue gas sample of previous studies. PCB-126 contributed the highest TEQ value, which was about 86% to 96% in the flue gas samples. The lower chlorinated PCBs were more dominant in the flue gas emission than in the higher chlorinated compound. The homologue pattern of PCBs in the flue gas was different from the commercial PCB formulations. The findings of the present study support previous literature, which suggests that non-ortho PCBs are generated during the combustion process. Finally, a good relationship between TEQ concentration of PCBs and PCDD/DFs was shown.

## Acknowledgment

This paper was supported by research funds of Chonbuk National University.

## References

- [1] J.F. Brown, G.M. Frame II, D.R. Olson, J.L. Webb, The sources of coplanar PCBs, *Organohalogen compd.* 26 (1995) 427–430.
- [2] Environment of Ministry, Korea, The situation of production and management of waste, December 2004.

- [3] D.A. Vaughan, P.D. Miller, W.K. Boyd, Resource Recovery through Incineration, The American Society of Mechanical Engineers, New York, 1974.
- [4] K.S. Kim, Y. Hirai, M. Kato, K. Urano, S. Masunaga, Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor), *Chemosphere* 55 (2004) 539–553.
- [5] Y.S. Chang, S.-B. Kong, M.G. Ikonou, PCBs contributions to the total TEQ released from Korean municipal and industrial waste incinerators, *Chemosphere* 39 (1999) 2629–2640.
- [6] M.G. Ikonou, P. Sather, J.-E. Oh, W.-Y. Choi, Y.-S. Chang, PCB levels and congener patterns from Korean municipal waste incinerator stack emissions, *Chemosphere* 49 (2002) 205–216.
- [7] L.J. Amend, P.B. Lederman, Critical evaluation of PCB remediation technology, *Environ. Prog.* 11 (1992) 173–177.
- [8] M. Hiraoka, Environmental conservation and the control of hazardous compounds, *Nippon Kagaku Kaishi* 5 (1991) 559–573 (in Japanese).
- [9] J. Stach, V. Pekarek, R. Grabic, M. Lojkasek, V. Pacakova, Dechlorination of polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans on fly ash, *Chemosphere* 41 (2000) 1881–1887.
- [10] R. Weber, T. Takasuga, K. Nagai, H. Shiraishi, T. Sakurai, T. Matuda, M. Hiraoka, Dechlorination and destruction of PCDD, PCDF and PCB on selected fly ash from municipal waste incineration, *Chemosphere* 46 (2002) 1255–1262.
- [11] U.G. Ahlborg, A. Hanberg, Toxic equivalency factors for dioxin like PCBs, *Environ. Sci. Pollut. Res. Int.* 1 (1994) 67–68.
- [12] US EPA Method 1613, Revision B: Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, 1994.
- [13] US EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, 1999.
- [14] T. Takasuga, T. Inoue, E. Ohi, All congener specific analytical method for polychlorinated biphenyls (PCBs) with various chromatographic clean-up and HRGC/HRMS, *J. Environ. Chem.* 53 (1995) 647–675.
- [15] T.H. Mikael, H. Peter, P.N. Krishna, Gas-chromatographic properties of the 209 PCB congeners on con-polar, chiral, and liquid-crystal columns, *Organohalogen Compd.* 35 (1998) 111–114.
- [16] K. Mimura, M. Tamura, K. Haraguchi, Y. Masuda, Analysis of 209 PCB congeners by high separation gas chromatography/low resolution mass spectrometer, *Fukuoka ISHi.* 5 (1999) 192–201 (in Japanese).
- [17] K. Ballschmiter, M. Zell, Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography: Composition of technical Aroclor and Clophen-PCB mixtures, *Fresenius' Zeitschrift für Analytische Chemie* 302 (1980) 20–31.
- [18] S.-I. Sakai, K. Hayakawa, H. Takatsuki, I. Kawakami, Dioxin-like PCBs released from waste incineration and their deposition flux, *Environ. Sci. Technol.* 35 (2001) 3601–3607.
- [19] P. Luthardt, J. Mayer, J. Fuchs, Total TEQ emissions (PCDD/F and PCB) from industrial sources, *Chemosphere* 46 (2002) 1303–1308.
- [20] G.M. Frame, J.W. Cochran, S.S. Boewadt, Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis, *J. High Res. Chromatogr.* 19 (1996) 657–668.
- [21] K.S. Kim, B.J. Song, J.G. Kim, Analysis of all PCB congeners in air samples by HRGC/HRMS, *Analyt. Sci. Technol.* 16 (2003) 309–319 (in Korean).
- [22] K.S. Kim, Study on the behavior and mass balance of PCBs in ambient air, Yokohama National University, A thesis for a doctorate 2004 (chapter 2).
- [23] A. Lopez Garcia, A.C. Den Boer, A.P.J.M. De Jong, Determination of non- and mono-ortho polychlorinated biphenyls in background ambient air, *Environ. Sci. Technol.* 30 (1996) 1032–1037.
- [24] R.E. Alcock, P.A. Behnisch, K.C. Jones, H. Hagenmaier, Dioxin-like PCBs in the environment—human exposure and the significance of sources, *Chemosphere* 37 (1998) 1452–1457.
- [25] Y.-C. Ling, P.C.C. Hou, A Taiwanese study of 2,3,7,8-substituted PCDD/DFs and coplanar PCBs in fly ashes from incinerators, *J. Hazardous Mater.* 58 (1998) 83–91.
- [26] M. Blumenstock, R. Zimmermann, L.-W. Schraumn, A. Kaune, B. Henkelmann, A. Ketrup, Presence of polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDFs), biphenyls (PCB), chlorinated benzenes (PCBz) and polycyclic aromatic hydrocarbons (PAH) under various combustion conditions in a post combustion chamber, *Organohalogen Compd.* 36 (1998) 59–63.
- [27] M.H. Schoonenboom, P.C. Tromp, K. Olie, The formation of coplanar PCBs, PCDDs and PCDFs in a fly ash model system, *Chemosphere* 30 (1995) 1341–1349.