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Emission Characteristics of Polychlorinated Dibenzo-p-Dioxins/Dibenzofurans (PCDD/DFs) in Commercial Bio-SRF and SRF Incineration Plants

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Abstract: Incineration plants using solid refused fuel (SRF) should control their air pollution materials to minimize environmental impact. This study evaluated the emission of polychlorinated dibenzo-p-dioxin/dibenzofurans (PCDD/DFs) congener patterns in seven commercial incineration plants in Korea using SRF and biomass SRF (bio-SRF). We examined the reduction rate differences of PCDD/DFs, depending on the air pollutant control device. All seven incineration plants sufficiently managed their dioxin emissions. However, both SRF and bio-SRF incineration plants showed active chlorination reactions and resulted in a large amount of highly chlorinated dioxins. The average dioxin concentration was 0.02 ng international toxic equivalency quantity (I-TEQ)/Sm^3. Ratios of 1,2,3,4,6,7,8-HpCDF and 1,2,3,7,8-PeCDF were high in the waste heat boilers of both SRF and bio-SRF incineration plants. The octachlorinated dibenzofuran (OCDF) ratio was only high in the SRF incineration plants. Octachlorodibenzo-p-dioxin (OCDD) and OCDF exhibited high dioxin ratios. SRF incineration plants had a low ratio of OCDF to 1,2,3,4,6,7,8-HpCDF. In addition, the reduction rate of PCDD/DFs was substantially high after treatment with the air pollutant control device.

Keywords: solid refused fuel; polychlorinated dibenzo-p-dioxins; polychlorinated dibenzofurans; waste heat boiler; stack

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1. Introduction

Waste resources with high heating values, such as plastic film, paper, and synthetic waste resins can be separated and converted into combustible materials [1,2] and used as fuels for boilers and combustion facilities [3]. Solid refused fuel (SRF) is normally derived from the daily waste of the residential sector, synthetic waste resins and rubber waste of the industrial sector, and biomass waste. Many incineration plants in Korea use SRF, which have been manufactured in domestic areas and imported from foreign countries depending on the quality standards prescribed in the Act on the Promotion of Saving and Recycling of Resources, an ordinance of the Ministry of Environment. The SRF supplied in Korea in December 2019 was 1.6 million tons of SRF and 2.7 million tons of biomass SRF (bio-SRF). Currently, SRF manufacturing facilities of 263 and SRF combustion facilities of 157 were in operation [4].

Thermal treating facilities, which intend to use SRF as a feedstock, should be designed to satisfy government regulation criteria and manage their air pollutant emissions. In particular, the harmfulness of dioxins is widely known [5,6]. Dioxins are slowly metabolized and eliminated and then tend to bioaccumulate due to lipophilic characteristics [5]. In particular, the half-life of tetrachlorodibenzo-p-dioxin (TCDD) is estimated to be in the range of seven to eight years in the human body. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are classified as dioxins [7–10]. Each PCDD/DFs can include chlorine atoms up to eight in different places on the molecule [11]. These characteristics result in different types of molecules, such as congeners. PCDDs have 75 congeners, and PCDFs have 135 congeners [12]. The Wastes Control Act in Korea requires the measurement of the dioxin concentrations in urban daily waste incineration plants twice a year, particularly those of 17 chlorine substituents at positions 2,3, 7, and 8, which are known to be toxic congeners.

In Korea, the congener concentration of PCDD/DFs emission according to waste incineration plant capacity and feedstock type was investigated [13]. The previous results indicated that octachlorodibenzo-p-dioxin (OCDD) occurred most frequently among the congeners in large daily waste incineration plants, and the concentrations of 1,2,3,4,6,7,8-HpCDD, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and octachlorinated dibenzofuran (OCDF) were high. On the other hand, OCDD concentrations were lower in small to mid-sized daily and industrial waste incineration plants than in large ones, and PCDF concentrations, including 1,2,3,4,6,7,8-HpCDF and OCDF, were high. These results indicated that the PCDD/DFs emission characteristics varied depending on the incineration plant's capacity and feedstock type. However, PCDD/DFs reduction rate between waste heat boiler (WHB) and a stack of commercial incineration plants was rarely investigated depending on the type of air pollutant control device and feedstock.

In this study, the dioxin emission factors and characteristics were investigated from commercial incineration plants. First, this study determined incineration plants using SRF and bio-SRF, which operate in normal conditions to assess the air pollutant emission characteristics, including oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), and sulfur oxides (SO_x) from WHB and plant stack. Second, the differences in the PCDD/DFs congener pattern in emission were investigated. In addition, the differences in the PCDD/DFs reduction rates were examined depending on the incineration plant process.

2. Experimental Section

2.1. Incineration Plants

The incineration plants were chosen for three plants using bio-SRF and four plants using SRF in normal operation conditions, as verified by the stack emission management system of the National Institute of Environmental Research (NIER) in Table 1. The bio-SRF incineration plants have fluidized incinerators, and the SRF incineration plants have two stoker incinerators and two fluidized incinerators in this study. Those continuously operated on all days, and the downstream process was varied depending on waste characteristics and operation conditions, which contained selective non-catalytic reduction (SNCR) system, selective catalytic reduction (SCR) system, semi-dry reactor (SDR), dry reactor (DR), bag filter (B/F), activated carbon (AC), and dry venturi to control acid gas and dioxin emissions.

Table 1. Outline of incineration plants for PCDD/DFs analysis.

Fuel Type	Plant	Capacity	Feedstocks	Incinerator	Air Pollutant Control Device
Bio-SRF	Bio-1	31.1 ton/h	Fluff	Fluidized bed	SNCR-SDR-B/F-SCR
	Bio-2	45.8 ton/h	Fluff + Pellet	Fluidized bed	SNCR-DR-B/F-SCR
	Bio-3	24.5 ton/h	Fluff	Fluidized bed	SNCR-DR-AC-B/F
SRF	SRF-1	2 ton/h	Fluff + Pellet	Stoker	SNCR-SDR-DR-B/F-SCR
	SRF-2	3.8 ton/h	Fluff	Stoker	SNCR-SDR-B/F-SCR
	SRF-3	6.7 ton/h	Pellet	Fluidized bed	SNCR-DR-B/F-AC
	SRF-4	5.8 ton/h	Fluff	Fluidized bed	SNCR-SDR-AC-Dry Venturi-B/F

2.2. Materials and Methods

2.2.1. Sampling Method

To measure the combustion gas such as CO, CO_2, NO_x, and SO_x, automated measuring method-electrochemistry of air pollutant test standard (EPA Method 10, JIS K 0151, EPA Method 7E, and JIS B 7981) was adopted. The combustion gas was measured from WHB and stack at a flow rate of 2.7 L/min for 2 h (WHB) and 4 h (stack). In the case of dioxin measurement, it was carried out by the persistent organic pollutant test standard (EPA Method 23) for 2 h (WHB) and 4 h (stack). The schematic diagram of the stack sampler is shown in Figure 1.

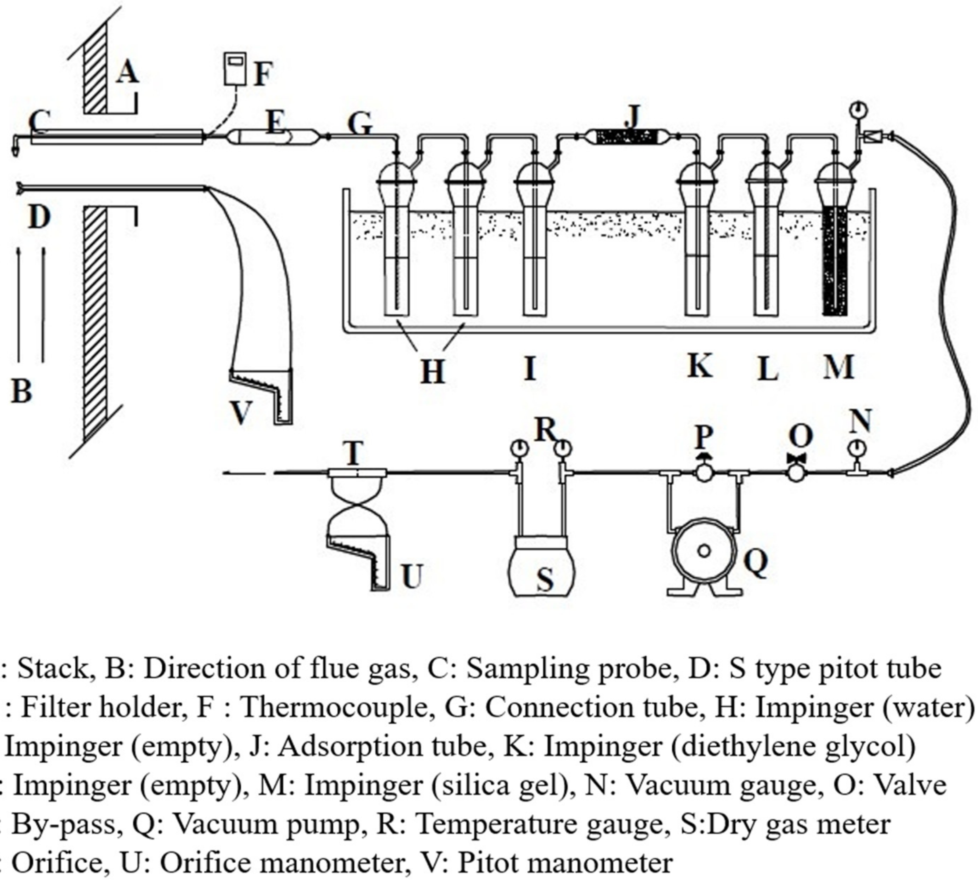

Figure 1. Schematic diagram of stack sampler.

We first measured the PCDD/DFs concentrations and congener patterns from the WHBs and stacks of the selected plants. We also diluted the gas phase samples emitted from the incineration plants by one-half and analyzed them using a high-resolution gas chromatograph (Agilent 6890)/high-resolution mass spectrometer (Jeol JMS-700D) (HRGC/HRMS) based on the persistent organic pollutant test standard (EPA Method 1613).

2.2.2. Processing for PCDD/DFs Analysis

To purify the samples during preprocessing, we utilized purification standards and applied sulfuric acid treatment, if necessary, and a multi-layer silica gel column and alumina column (dichloromethane in hexane). The multi-layer silica gel column was filled with 3 g of 2% KOH, 3 g of 44% H_2SO_4, and 12 g of 10% $AgNO_3$ using silica gel activated at 160 °C for 16 h. In the case of the alumina column, it was filled with 6 g of neutral alumina pretreated at 600 °C for 24 h. The procedure to analyze PCDD/DFs is illustrated in Figure 2.

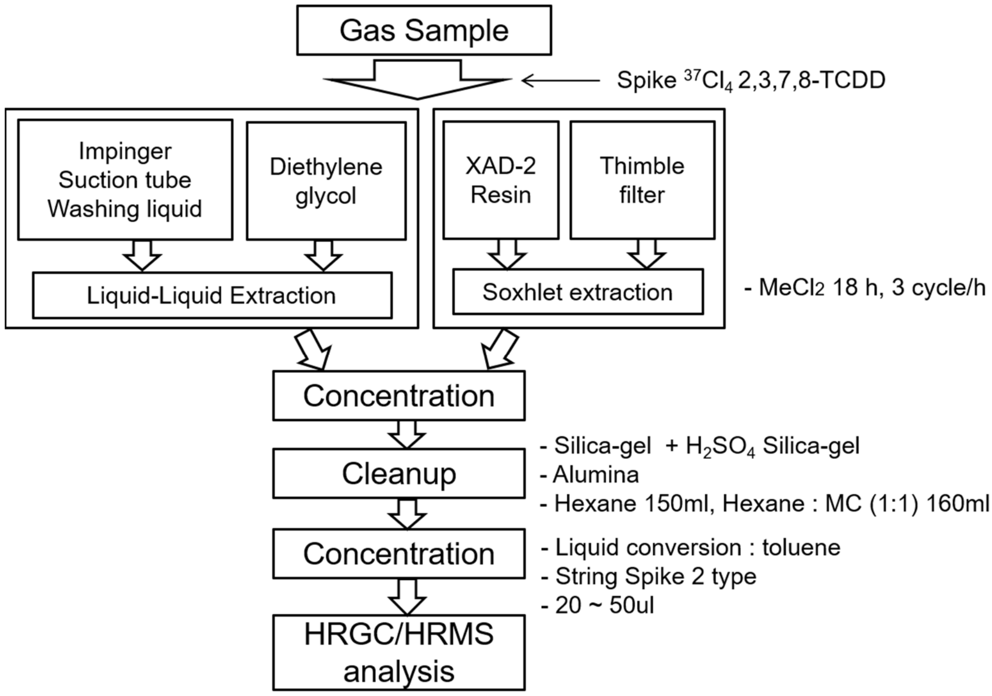

Figure 2. Experimental procedure for PCDD/DFs analysis.

The experimental values and sample concentration for PCDD/DFs analysis were calculated as follows:

$$E_V = S_A / I_A \times I_Q / R_F \quad (1)$$

$$S_C = E_V \times D_R / S_E \quad (2)$$

where,

E_V: Experimental values (pg)
S_A: Value of the sample peak area
I_A: Internal standard peak area
I_Q: Internal standard quantity
R_F: Relative response factor
S_C: Sample concentration (pg/Sm^3)
D_R: Dilution rate
S_E: Amount of sample extracted (Sm^3)

The internal standard and HRGC/HRMS analytical conditions are listed in Tables 2 and 3, respectively. And the average method detection limit of congeners was 0.053 pg/Sm^3.

Table 2. Internal standard materials for PCDD/DFs analysis.

Addition Point	PCDD	PCDF
Before pretreatment	$^{37}Cl_4$-2,3,7,8-TCDD	
After the extraction	$^{13}C_{12}$-2,3,7,8-TCDD $^{13}C_{12}$-1,2,3,7,8-PeCDD $^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,6,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD $^{13}C_{12}$-OCDD	$^{13}C_{12}$-2,3,7,8-TCDF $^{13}C_{12}$-1,2,3,7,8-PeCDF $^{13}C_{12}$-2,3,4,7,8-PeCDF $^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,6,7,8-HxCDF $^{13}C_{12}$-2,3,4,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF
Before HRGC/HRMS analysis	$^{13}C_{12}$-1,2,3,4-TCDD $^{13}C_{12}$-1,2,3,7,8,9-HxCDD	

Table 3. HRGC/HRMS analytical conditions.

Instrument	Condition	
HRGC	Capillary column	SP-2331 (60 m × 0.32 mm × 0.20 μm)
	Oven temp.	120 °C (1 min)→20 °C/min→220 °C→2 °C/min→265 °C (20 min)
	Inlet temp.	260 °C
	Injection mode	Splitless (injection volume 1 μL)
	Carrier gas	He (99.9999%)
	Flow rate	1 mL/min
HRMS	Ionization	EI mode (electron ionization)
	Measuring	SIM mode (selected ion monitoring)
	Chamber Temp	270 °C
	Interface Temp	260 °C
	Ionization Energy	38 eV
	Ionizing current	600~700 μA

3. Results

3.1. Emission Characteristics of Air Pollutants

To verify the air pollutant characteristics of plants, we first examined the O_2, CO, CO_2, NO_x, and SO_x concentrations from WHB and stack in accordance with the dioxin sampling (Table 4).

Table 4. Concentration of air pollutant materials in WHB and stack.

		O_2 [%]		CO [ppm (12)]		CO_2 [%]		NO_x [ppm (12)]		SO_x [ppm (12)]	
		WHB	Stack	WHB	Stack	WHB	Stack	WHB	Stack	WHB	Stack
National regulation		-	-	-	50	-	50	-	70	-	30
Bio-SRF	Bio-1	4.9	6.3	1.1	0.9	11.9	10.8	47.5	18.6	0.0	0.0
	Bio-2	3.5	3.6	4.9	4.8	13.0	12.7	10.1	9.9	0.0	0.0
	Bio-3	4.6	5.3	2.4	2.4	12.2	11.5	21.8	21.7	0.0	0.0
SRF	SRF-1	12.0	13.0	15.6	15.0	6.6	5.8	13.3	13.1	0.1	0.0
	SRF-2	10.5	11.2	16.5	16.3	7.8	7.2	50.2	1.6	0.5	0.3
	SRF-3	6.2	7.3	0.3	0.3	11.0	10.0	26.2	26.0	0.1	0.1
	SRF-4	8.8	9.6	3.5	3.4	9.0	8.3	14.9	14.6	0.1	0.1
Average		7.21	8.04	6.33	6.16	10.21	9.47	26.29	15.07	0.11	0.07

- ( ): Standard concentration at 12 vol.% O_2.

The O_2 concentrations of the plants were 7.2% on average in the WHB and 8.0% in the stacks. The most effective and stable range of O_2 concentrations to control air pollutants in emissions such as CO is approximately in the range of 7–9% [14]. Bio-2,3 and SRF-3 plants exhibited O_2 concentrations below the stable range during operation. In addition, in the plants using bio-SRF, the O_2 and CO concentrations were proportionally inversed. In the plants using SRF, the CO concentrations were the lowest in SRF-3; the O_2 concentrations were approximately in the range of 6–7%. SRF-1 and SRF-2 exhibited higher O_2 and CO concentrations than those of the other plants. However, both plants demonstrated lower CO_2 concentrations than those of the other plants. In this study, CO concentrations were high when O_2 concentrations were greater than 7–9%, while the CO_2 concentrations were low when the O_2 concentrations were greater than 7–9%. The primary cause of CO is due to incomplete combustion. When the O_2 concentration is above 7–9% in flue gas during combustion, incomplete combustion behavior occurs more frequently in the plants. The NO_x generation depends on fuel and thermal NO_x. Fuel NO_x is generated when a large quantity of nitrogen is included in feedstock, and nitrogen compounds produced from the fuel during combustion react with the O_2, resulting in Fuel NO_x. Thermal NO_x is generated when O_2 in the air oxidizes nitrogen during the high-temperature combustion reaction.

SO_x is predominately generated by the sulfur component, including in fuel [15]. The sulfur content of the SRF used in the plants is approximately 0.06 wt.%, which results in a small amount of SO_x emission [16].

3.2. Concentration and Congener Pattern of Dioxin Emission in Incineration Plants

Table 5 indicates the toxic equivalents of PCDD/DFs in the plant WHBs and stacks. According to the Persistent Organic Pollutants Control Act [17], if the capacity is larger than 2 ton/h, the limit of dioxin emission is 0.1 ng international toxic equivalency quantity (I-TEQ)/Sm^3. The results indicate that the concentration of PCDF is higher than PCDD in both the WHB and stack. In particular, the SRF-2 plant approximately presented 9.47 ng I-TEQ/Sm^3 of PCDD/DFs in WHB, which was higher than that of the other plants. On the other hand, the air pollutant control device of the SRF-2 plant showed a good reduction performance of PCDD/DFs emissions, which was approximately 2.6% of the emission limit. The average PCDD/DFs concentrations from WHB and stack of seven incineration plants were approximately 1.74 and 0.02 ng I-TEQ/Sm^3.

Table 5. PCDD/DFs concentration in WHB and stack (I-TEQ/Sm^3).

		WHB			Stack		
		PCDD	PCDF	PCDD/DFs	PCDD	PCDF	PCDD/DFs
Bio-SRF	Bio-1	0.1132	0.2895	0.4027	0.0055	0.0135	0.0190
	Bio-2	0.0051	0.0167	0.0218	-	0.0004	0.0004
	Bio-3	0.0815	0.1356	0.2171	0.0013	0.0039	0.0052
SRF	SRF-1	0.0593	0.8798	0.9391	0.0051	0.0582	0.0633
	SRF-2	0.8013	8.6662	9.4675	0.0001	0.0025	0.0026
	SRF-3	0.0565	0.2824	0.3389	0.0001	0.0013	0.0014
	SRF-4	0.0960	0.7132	0.8092	0.0227	0.0282	0.0509
Average		0.1733	1.5691	1.7423	0.0050	0.0154	0.0204

We compared the results of the PCDD/DFs congener pattern in WHB and a stack of three bio-SRF incineration plants (Bio-1, Bio-2, and Bio-3) in Figures 3–5. One nanogram of $^{37}Cl_4$-2,3,7,8-TCDD was used as the internal standard for sampling, and the average recovery rate of the reference material was 84.40%.

In the identification of the congener pattern in the WHB and stack of bio-SRF incineration plants, we found that 1,2,3,4,6,7,8-HpCDF exhibited the highest ratio (approximately 21%) in the WHB and the high ratio in the stack at Bio-1. In the case of 2,3,7,8-TCDF, it was shown in the third-highest ratio in WHB but a low ratio in the stack. In addition, Bio-2 showed the highest ratio of 1,2,3,4,6,7,8-HpCDF (approximately 21%) in the WHB. 1,2,3,7,8-PeCDF, 2,3,7,8-TCDF, and OCDD demonstrated high ratios in all bio-SRF incineration plants. In particular, the highest ratio of OCDD was displayed in the stack of Bio-1 and Bio-2. In Bio-3, the ratio of 2,3,7,8-TCDF was the highest in the WHB. The analysis concentration of 2,3,7,8-TCDF from the WHBs of Bio-1 and Bio-3 was similar. However, the ratios were different because the total congener emissions of the PCDD/DFs were higher in Bio-1.

Overall, the ratio of 1,2,3,4,6,7,8-HpCDF was high in all Bio-1, Bio-2, and Bio-3 stacks, and the ratio of OCDF was approximately 15% higher in Bio-3 than that in the other incineration plants. Both Bio-1 and Bio-2 have the same air pollutant control device, while Bio-3 does not install the SCR. An air pollutant control device might influence the ratio of OCDF. After the SCR treatment, the ratio of OCDF decreased [18]. 1,2,3,4,6,7,8-HpCDF is generated when the chlorine in the ninth position of the OCDF is removed [19], and it is more stable than other congeners [20]. Therefore, the ratio of 1,2,3,4,6,7,8-HpCDF is high because the chlorination reaction is active, and the OCDF likely transforms into 1,2,3,4,6,7,8-HpCDF with large quantities of highly chlorinated dioxins.

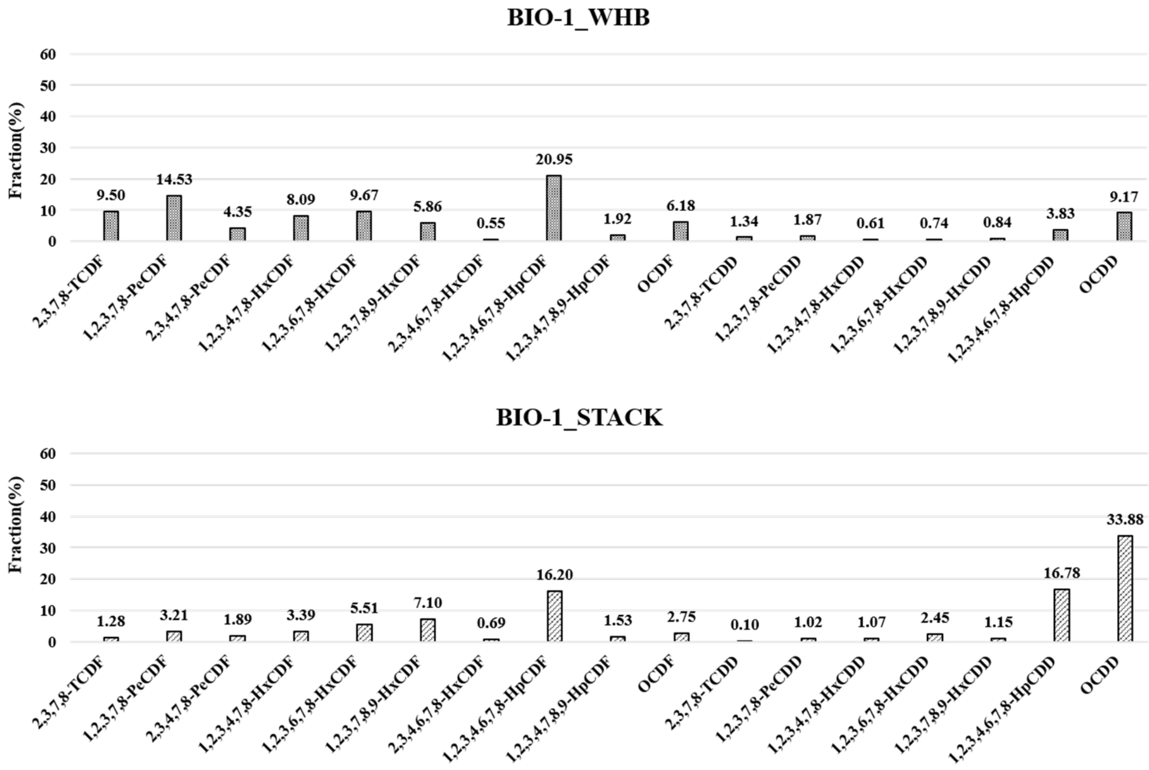

Figure 3. PCDD/DFs congener pattern in Bio-1 incineration plant.

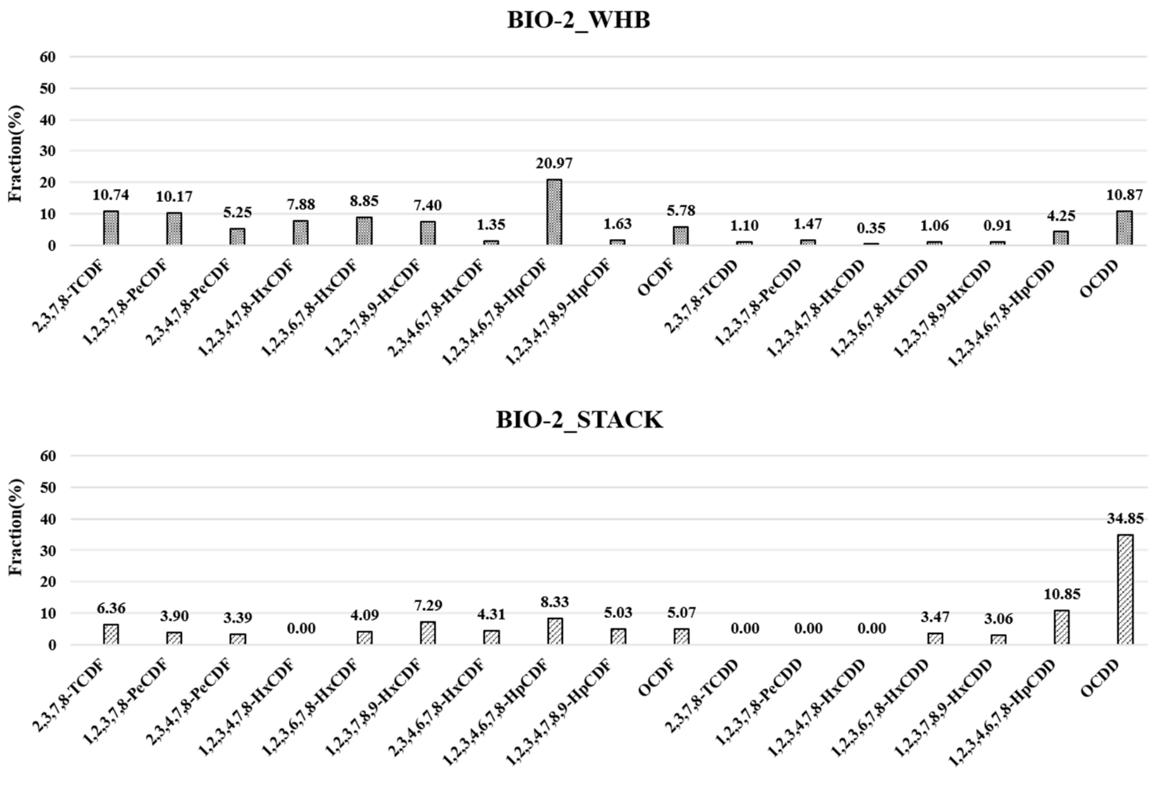

Figure 4. PCDD/DFs congener pattern in Bio-2 incineration plant.

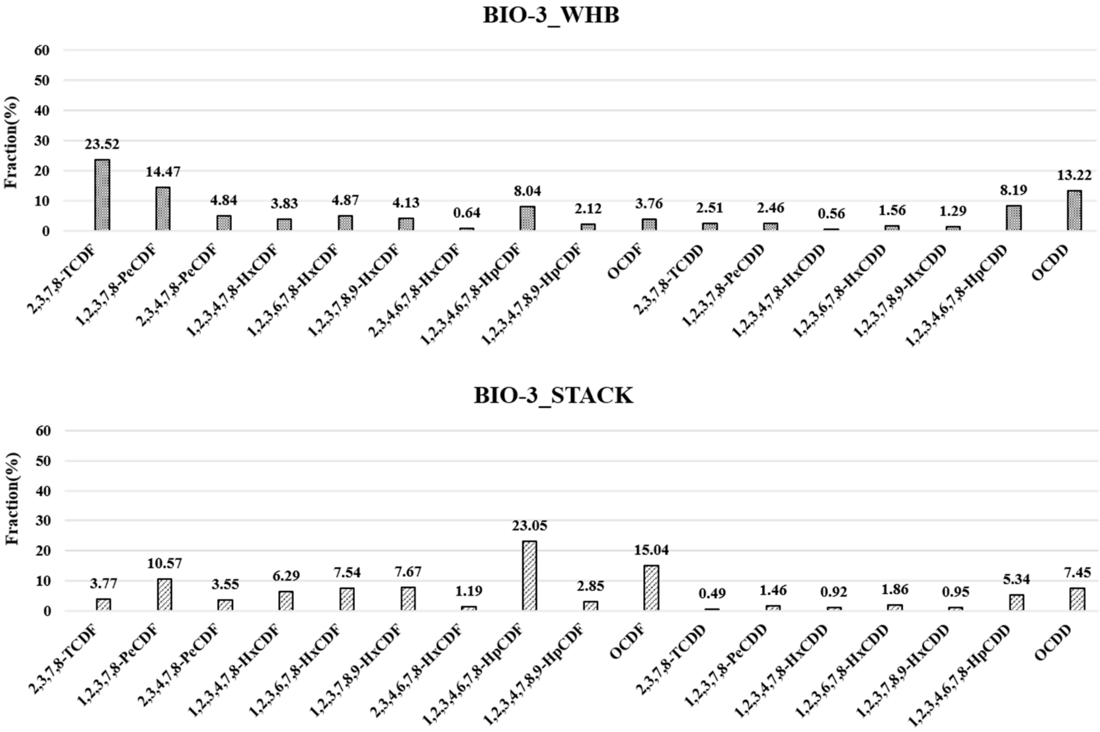

Figure 5. PCDD/DFs congener pattern in Bio-3 incineration plant.

In addition, PCDD/DFs congener pattern in WHB and stack of four SRF incineration plants (SRF-1, SRF-2, SRF-3, and SRF-4) was compared in Figures 6–9. One nanogram of $^{37}Cl_4$-2,3,7,8-TCDD was used as the internal standard for sampling, and the average recovery rate of the reference material was 89.25%. SRF incineration plants, which installed the SCR, indicated high ratios of 1,2,3,4,6,7,8-HpCDF, and OCDF in the stack.

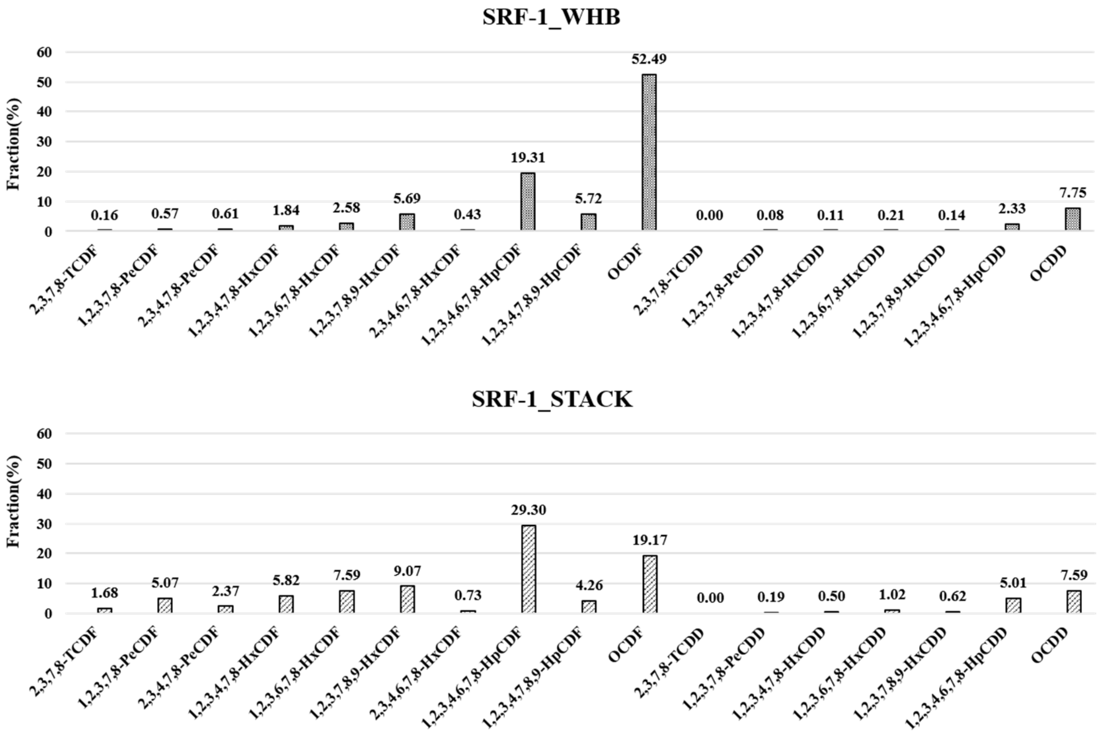

Figure 6. PCDD/DFs congener pattern in an SRF-1 incineration plant.

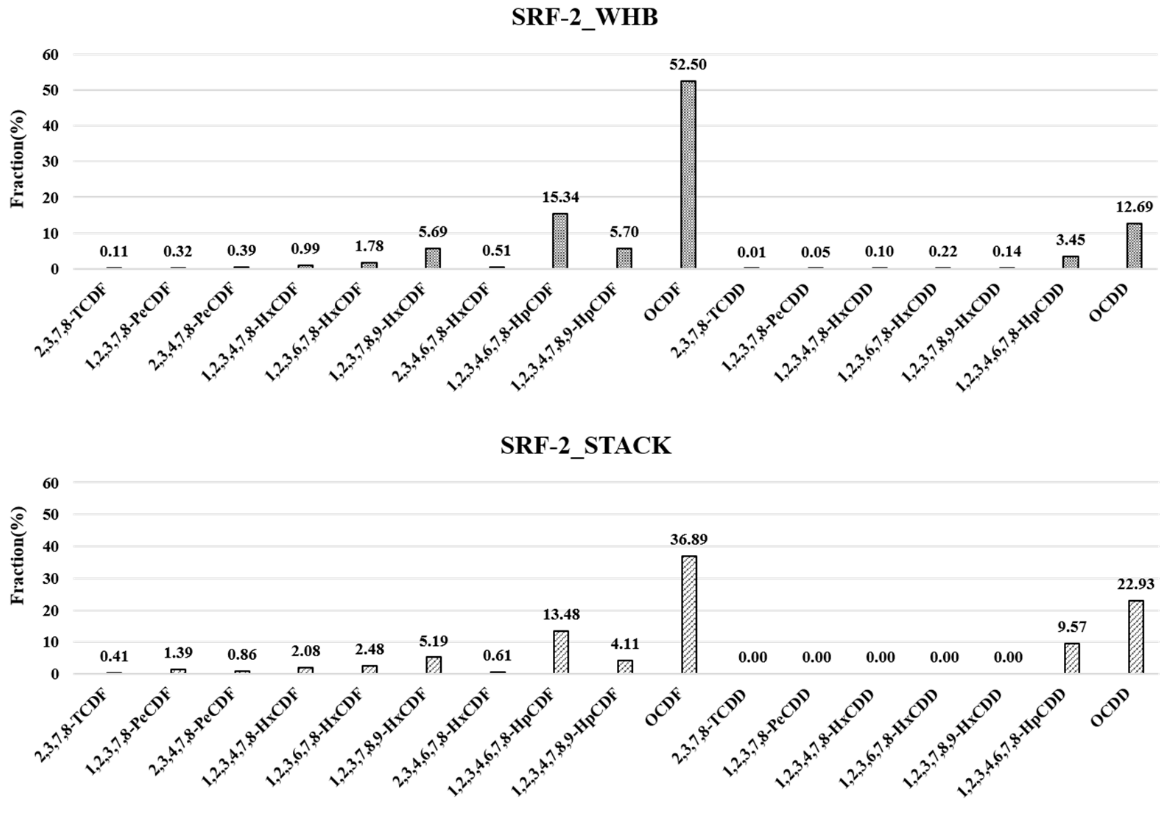

Figure 7. PCDD/DFs congener pattern in an SRF-2 incineration plant.

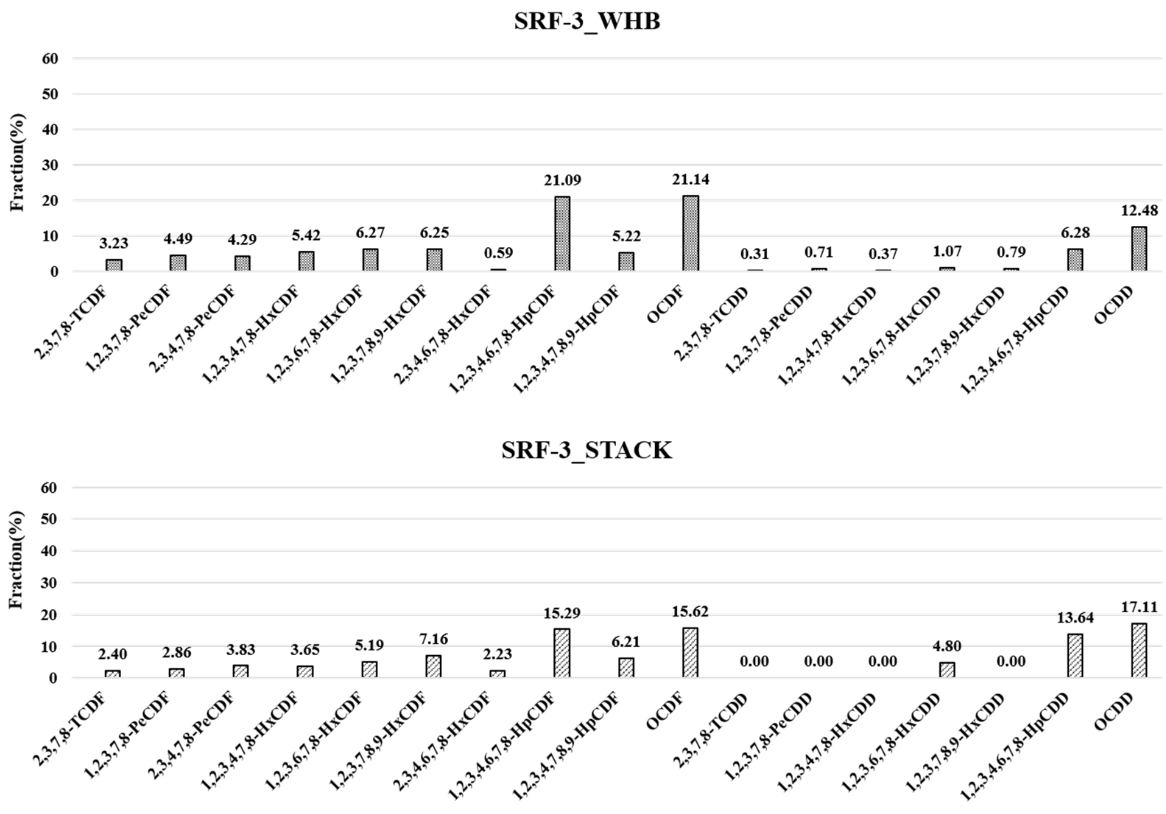

Figure 8. PCDD/DFs congener pattern in an SRF-3 incineration plant.

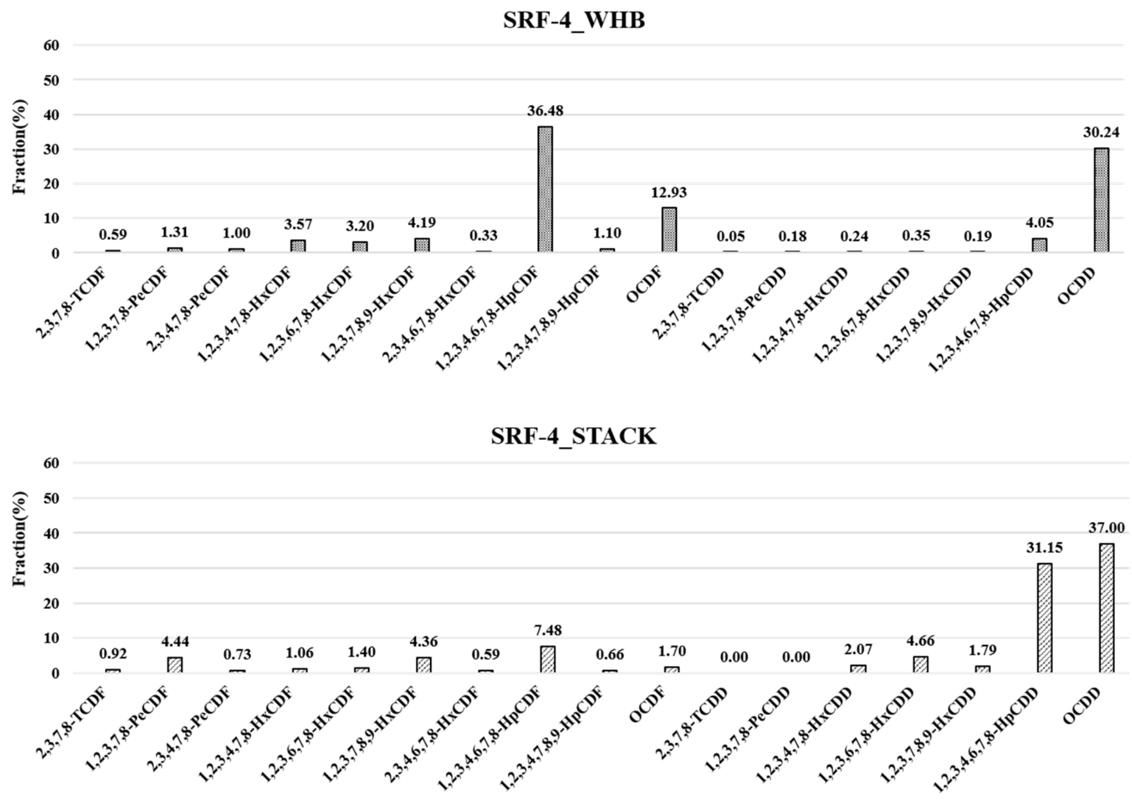

Figure 9. PCDD/DFs congener pattern in an SRF-4 incineration plant.

3.3. Reduction Rate of PCDD/DFs Congener Concentration in WHB and Stack

The reduction rate of each congener between the WHB and stack of Bio-2 and Bio-3 incineration plants presented more than 85% in all congener concentrations of PCDD/DFs in Table 6. In contrast, in the case of Bio-1, the reduction rates of 1,2,3,6,7,8-HxCDD (approximately 71%), 1,2,3,4,6,7,8-HpCDD (approximately 61%), and OCDD (approximately 67%) were lower than those of the other plants. The difference in the arrangement of the air pollutant control device was that the Bio-1 incineration plant contains an SDR, and Bio-2 and 3 incineration plants contain a DR. Resultingly, using a liquid alkali reactant, unlike using a DR powder reactant, may affect the reduction rates of 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD. PCDFs had high reduction rates overall, but SRF-4 exhibited low reduction rates of 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, and 1,2,3,4,6,7,8-HpCDD. SRF-4 incineration plant involves dry venturi without the SCR in the process.

Table 6. Reduction rate of PCDD/DFs concentration between WHB and stack.

Congener	PCDD/DFs Reduction Rate (%)						
	Bio-1	**Bio-2**	**Bio-3**	**SRF-1**	**SRF-2**	**SRF-3**	**SRF-4**
2,3,7,8-TCDF	98.82	97.95	99.43	74.96	99.92	99.66	91.74
1,2,3,7,8-PeCDF	98.05	98.68	97.41	79.29	99.91	99.71	82.04
2,3,4,7,8-PeCDF	96.17	97.77	97.39	90.89	99.96	99.59	96.13
1,2,3,4,7,8-HxCDF	96.31	100	94.17	92.61	99.96	99.69	98.43
1,2,3,6,7,8-HxCDF	94.97	98.40	94.50	93.12	99.97	99.62	97.68
1,2,3,7,8,9-HxCDF	89.32	96.60	93.41	96.27	99.98	99.48	94.49
2,3,4,6,7,8-HxCDF	88.95	88.95	93.43	96.02	99.98	98.26	90.40
1,2,3,4,6,7,8-HpCDF	93.18	98.63	89.82	96.46	99.98	99.67	98.91
1,2,3,4,7,8,9-HpCDF	92.95	89.33	95.23	98.26	99.99	99.46	96.79
OCDF	96.07	96.96	85.81	99.15	99.99	99.66	99.31

Table 6. *Cont.*

Congener	PCDD/DFs Reduction Rate (%)						
	Bio-1	**Bio-2**	**Bio-3**	**SRF-1**	**SRF-2**	**SRF-3**	**SRF-4**
2,3,7,8-TCDD	99.33	100	99.31	100	100	100	100
1,2,3,7,8-PeCDD	95.20	100	97.89	94.17	100	100	100
1,2,3,4,7,8-HxCDD	84.68	100	94.12	89.69	100	100	54.76
1,2,3,6,7,8-HxCDD	70.71	88.73	95.78	88.51	100	97.95	30.47
1,2,3,7,8,9-HxCDD	88.02	88.42	97.38	89.32	100	100	49.76
1,2,3,4,6,7,8-HpCDD	61.33	91.17	97.68	94.98	99.94	99.01	59.19
OCDD	67.41	88.91	98.00	97.71	99.96	99.38	93.52

Note: TCDF, Tetrachlorodibenzofuran; PeCDF, Pentachlorodibenzofuran; HxCDF, Hexachlorodibenzofuran; HpCDF, Heptachlorodibenzofuran; OCDF, Octachlorodibenzofuran; TCDD, Tetrachlorodibenzo-p-dioxin; PeCDD, Pentachlorodibenzo-p-dioxin; HxCDD, Hexachlorodibenzo-p-dioxin; HpCDD, Heptachlorodibenzo-p-dioxin; OCDD, Octachlorodibenzo-p-dioxin.

4. Conclusions

In this study, flue gas samples were collected and measured from WHB and a stack of three bio-SRF incineration plants and four SRF incineration plants to analyze the characteristics of PCDD/DFs congeners in Korea. The average PCDD/DFs concentration from the stack of the seven plants was 0.02 ng I-TEQ/Sm^3, indicating that all plants satisfied the emission limit and presented approximately 1–60% of that of the emission limit. However, the seven incineration plants exhibited the highest concentration to OCDF, 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,4,6,7,8-HpCDF. In the WHB, the ratio of 1,2,3,4,6,7,8-HpCDF and 1,2,3,7,8-PeCDF were high in both bio-SRF and SRF incineration plants, while the OCDF ratio was only high in SRF incineration plants. OCDD and OCDF were presented as high dioxin concentrations. 1,2,3,4,6,7,8-HpCDF may originate from OCDF, and both bio-SRF and SRF incineration plants exhibited high concentrations of increased chlorinated dioxin, which depends on active chlorination reaction and large quantities of highly chlorinated dioxin. In addition, the PCDD/DFs reduction rate indicated the different trends according to the arrangement of the air pollutant control device.

Therefore, further detailed research should be required to investigate optimized operational conditions such as an incinerator, catalyst, and gas cleaning system related to decomposing certain congeners, which influence high I-TEQ contribution in the commercial-scale thermal process.

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