CHARACTERIZATION OF PCDDs/DFs, PCBs and PAHs CONTAINING WASTE IN KOREA

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are persistent organic pollutants (POP) which can induce various adverse health effects. The Stockholm Convention defines the need to eliminate POP production and emissions. PCDDs and PCDFs mainly emitted from municipal solid waste incinerator (MSWI), commonly known as PCDDs and PCDFs have caused much public concern owing to their high toxicity and potential carcinogenic and mutagenic effects (Huang et al., 1995; Gang et al., 2012; Renbo et al., 2012). In Korea, PCDDs/Fs in the flue gas emitted from waste incinerator facilities arose as an environmental issue in the 1990s, which led to the enactment of the Waste Control Act of 1997 that stipulated the maximum release limit and strengthened management for PCDDs/Fs. Based on the PCDDs/Fs monitoring project, the background level was evaluated and the maximum release limit for PCDDs/Fs in each industry was prescribed in the POPs Control Act. The act also stipulated the treatment criteria of waste such as dust and sludge. The regulation standard of PCDDs/Fs set using I-TEF instead of WHO-TEF (MoE, 2009), therefore two results represented in the report.

Recently, the Korean Waste Catalogue (KWC) and hazardous waste list are prepared for the classification of all wastes and hazardous wastes and are designed to form a consistent waste classification system. Therefore, the waste streams are surveying from 2008 to 2012 by basis of European Waste Catalogue (EWC) by comparing the Korean Waste streams and 633 waste samples collected to evaluate the hazardous or not (EU, 2007 & 2012). In this research, eighteen compounds, including non organic compounds (Hg, Cu, Pb, Cd, Cr^{6+} (contained total Cr), As, CN, Ni, Zn, Ba, Be, Sb, Se, V, Zn) and organic compounds (7 kinds of PCBs, 7 kinds of PAHs, 17 kinds of PCDD/Fs) were quantified. From this study, the forty-three waste samples of potential PCDDs/Fs discharging process were analyzed the 17 congeners to confirm the PCDDs/Fs containing waste or not. Also, the classification system of hazardous waste is designed to ease the work of classifying waste and hazardous waste and understanding the legislation associated with the classification of waste and hazardous waste.

In this research, the congener profiles of PCDD/Fs were presented and compared among the collected wastes such as fly ashes, bottom ashes etc. Also, the PCDDs/Fs containing waste lists were evaluated using the collected 43 samples. Twenty waste samples for PCBs (IUPAC No. 28, 52, 101, 118, 138, 153, 180) congeners and 173 waste samples for PAHs (phenanthrene, anthrancene, fluoranthene, benzo(a)anthracene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene) also analyzed to evaluate the hazardous substance containing tendency. The PCBs and PAHs concentration also measured (NIER, 2008~2011).

Materials and methods

All samplings, as well as complex chemical analyzes were carried out by National Institute of Environmental Research (NIER), Ministry of Environment. Each sample was spiked with a mixture of ^{13}C-labeled PCDD/Fs internal standards. Then the spiked samples were extracted for 24 h with 250 mL toluene. Prior to clean-up process, they were treated with conc-H_2SO_4 and NaOH repeatedly until transparent. The clean-up procedure was performed with two columns: multi-layer silica gel and basic alumina column. Prior to HRGC/HRMS analysis, ^{13}C-labeled PCDD/Fs recovery standard mixture was spiked. Instrumental analysis were performed by HRGC/HRMS on a 6890 series gas chromatograph (Agilent, USA) coupled to a high resolution mass

spectrometer (Waters, AutoSpec Ultima). One uL of sample was injected by an auto-sampler in splitless mode. The mass spectrometer was operated in the selected ion monitoring (SIM) mode using a positive electron impact (EI+) source at a resolving power of 10000 (10% valley definition). The source temperature was 270 ºC. Helium at a constant flow rate of 1.2 mL/min was the carrier gas. Chromatographic separation was achieved with a DB-5MS fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 um film thickness). The detailed quantitative determination of PCDD/Fs was referred to Korean official method of POPs. In Korea, the PCDDs/PCDFs concentration calculated I-TEQ and WHO-TEF because the regulation standard still applied the I-TEF. PCBs congeners and PAHs also analyzed using the GC/MS.

Results and discussion

Concentration levels of PCDDs/Fs: Forty-three samples were collected and analyzed as shown in Table 1. Table 1 lists the PCDD/F concentrations measured in fly ashes, bottom ashes, adsorbent, slag, sludge and so on in terms of total values and I-TEQ, respectively. Five fly ash samples ranged 0.074 to 4.325 ng I-TEQ/kg, and sixteen dust samples ranged 0.000 to 11.514 ng I-TEQ/kg. The highest PCDDs/DFs concentration of dust measured in the solid wastes from gas treatment containing dangerous substances. Also, three adsorbent samples ranged 0.001 to 1.224 ng I-TEQ/kg, and nine bottom ash samples ranged 0.001~1.193 ng I-TEQ/kg in the waste discharging process.

Table 1. PCDDs/DFs concentration of industrial waste

EWC code	European waste catalogue and hazardous waste list	Waste kinds in Korean	PCDDs/Fs	
			I-TEQ ng/g	who-TEQ ng/g
03 01 04	sawdust, shavings, cuttings, wood, particle board and veneer containing dangerous substances	bottom ash cinder fly ash	0.002 ~ 4.325 (n=5)	-
06 04 04 06 09 03	wastes containing mercury calcium-based reaction wastes containing or contaminated with dangerous substances	dust bottom ash sludge	0.003 ~ 1.193 (n=3)	-
07 01 07 07 01 09 07 02 09 07 03 11 07 04 09 07 05 07 07 05 09 07 05 13 07 06 09 07 07 07 07 07 09 07 07 11	halogenated still bottoms and reaction residues halogenated filter cakes and spent absorbents sludges from on-site effluent treatment containing dangerous substances halogenated filter cakes and spent absorbents halogenated still bottoms and reaction residues halogenated filter cakes and spent absorbents solid wastes containing dangerous substances sludges from on-site effluent treatment containing dangerous substances	sediment wipe sludge adsorbent medicines dust slag	0.001~ 1.224 (n=12)	-
10 01 04 10 02 07 10 02 13 10 03 19 10 03 21 10 03 23 10 06 03	oil fly ash and boiler dust solid wastes from gas treatment containing dangerous substances sludges and filter cakes from gas treatment containing dangerous substances flue-gas dust containing dangerous substances other particulates and dust (including ball-mill dust) containing dangerous substances solid wastes from gas treatment containing dangerous substances flue-gas dust	dust bottom ash	0.000 ~ 11.735 (n=11)	0.000 ~ 10.733
11 01 98	other wastes containing dangerous substances	dust	1.856 (n=1)	1.765
12 01 20	spent grinding bodies and grinding materials containing dangerous substances	dust	0.386 (n=1)	0.384

19 01 07 19 01 11 19 01 13 19 01 15 19 01 17 19 11 07	solid wastes from gas treatment bottom ash and slag containing dangerous substances fly ash containing dangerous substances boiler dust containing dangerous substances pyrolysis wastes containing dangerous substances wastes from flue-gas cleaning	bottom ash fly ash dust	0.001~ 0.855 (n=10)	0.002~ 0.785

Characteristics of PCDD/F congener distribution: The congener profile of PCDD/Fs is often referred to as fingerprint. Fingerprinting of PCDDs has been extensively employed in source identification and transformation studies. Figure 1 showed average congener-specific 2, 3, 7, 8-PCDD/PCDF distributions in fly ash, bottom ash, dust and adsorbent samples. In concentration units, it can be observed that as the chlorinated-level increases, the concentration of the 2, 3, 7, 8-PCDD congener increases, but the concentration of the 2, 3, 7, 8,-PCDF congener presents irregularities. For PCDFs 2, 3, 4, 7, 8-PeCDF, 1, 2, 3, 6, 7, 8-HxCDF and 1, 2, 3, 4, 6, 7, 8-HpCDF are the major congeners. These profiles are in accordance with emission patterns previously reported for MSWI. As shown in Figure, remarkable differences could be found compared with those output profiles between adsorbent and ash. In adsorbent, the 2, 3, 4, 7, 8-TxCDF is major congener as shown in Figure 1. The other types of wastes congener profile also observed depending on the waste kinds.

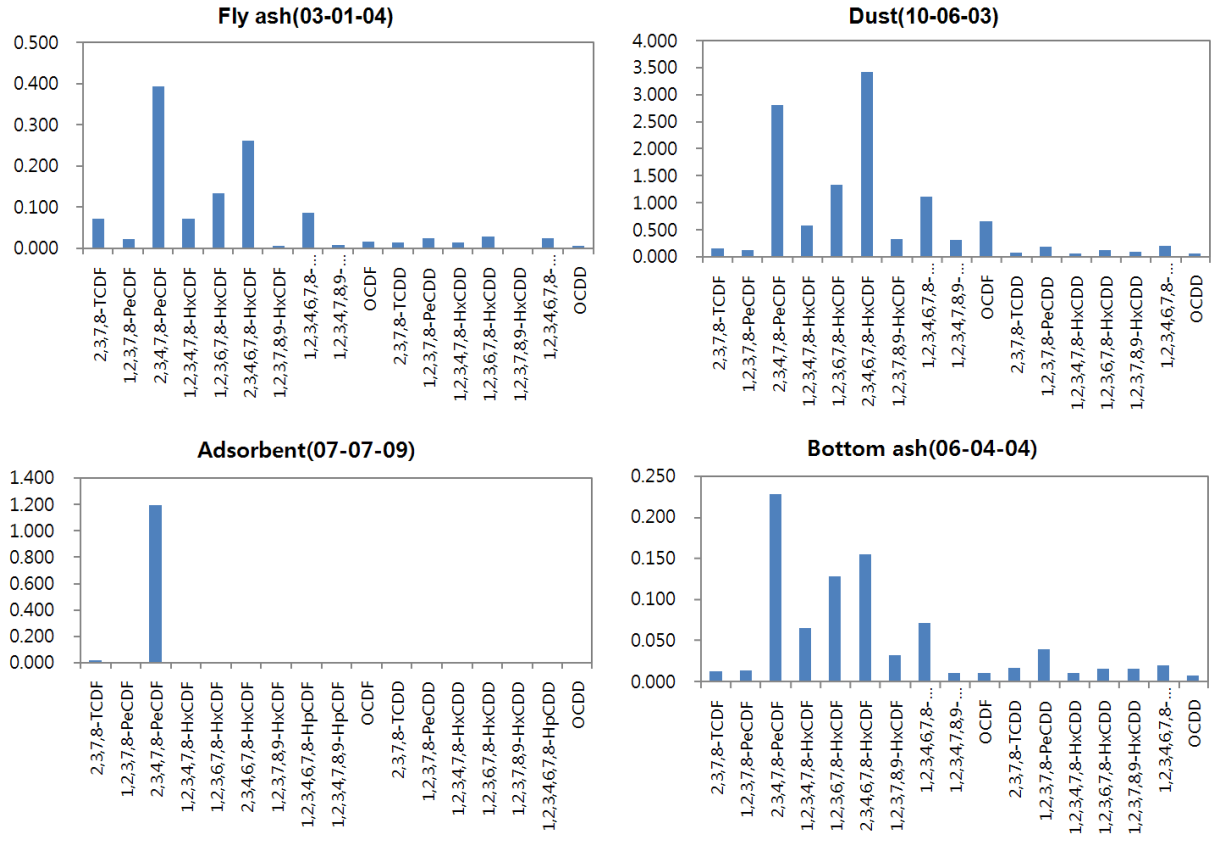

Figure 1. Congener profiles of 2,3,7,8-chlorinated substituted PCDD/Fs containing wastes (ng I-TEQ/kg)

Characteristics of PCBs and PAHs congener distribution: Nineteen waste samples for PCBs (IUPAC No. 28, 52, 101, 118, 138, 153, 180) congeners and 173 waste samples for PAHs (phenanthrene, anthrancene, fluoranthene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene) analyzed to

evaluate the hazardous substance containing tendency. Seven kinds of PCBs congeners and PAHs compounds were selected based on the Korean Ocean Pollutant Management Law (MoE, 2009). The potential PCBs containing waste samples were collected such as waste thermal (heat transfer) fluids, fluff-light fraction from shredding and so on (EWC 10, 11 and 12). Also, the potential PAHs containing wastes were collected EWC 2, 3, 6, 7, 8, 10, 11 and 19. The 7 kinds of PCBs isomers detected in the range of ND to 62 mg/kg and the highest concentration detected in the wastes from wood processing and the production of panels and furniture as shown in Table 2 (EWC 03 01 04). The detected isomer order was IUPAC No. 52 > 118 > 153 > 28 > 138 > 101 > 180. Also, PAHs detected in the range of ND to 3931 mg/kg and the highest level detected in the filter cake frpm gas treatment of incineration & pyrolsis waste.

Table 2. PCBs concentration of industrial waste

EWC code	Sample	28	52	101	118	138	153	180	Total PCBs
03 01 04	Ash	7.1210	2.8152	8.8760	1.7177	8.8043	3.9652	2.7485	36.0479
03 01 04	Fly ash	0.0414	9.2868	3.7794	0.3561	4.3590	2.0125	0.8437	20.6789
03 01 04	Fly ash	5.3769	2.6254	36.0542	3.0335	10.3840	4.6117	0.0000	62.0857
06 04 04	Dust	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0002
06 04 04	Bottom ash	0.0000	0.0000	0.0000	0.0019	0.0005	0.0011	0.0021	0.0056
06 09 03	Sludge	0.0000	0.0000	0.0004	0.0005	0.0020	0.0001	0.0007	0.0036
06 13 01	chemicals	0.0001	0.0000	0.0000	0.0001	0.0002	0.0000	0.0001	0.0005
07 02 09	Oil wiper	0.0090	0.0220	0.0360	0.0380	0.0130	0.0260	0.0050	0.1490
07 02 09	Oil wiper	0.0010	0.0010	0.0020	0.0020	0.0020	0.0010	0.0000	0.0090
11 01 98	Oil	0.0108	0.0444	0.0190	0.0178	0.0700	0.0000	0.0000	0.0231
12 01 06	Oil	0.0155	0.0349	0.0217	0.0193	0.1243	0.0000	0.0000	0.2157
12 01 09	Oil	0.0255	0.0634	0.0167	0.0169	0.0363	0.0159	0.0448	0.2194
12 01 09	Oil	0.0715	0.3129	0.3142	0.1223	0.5496	0.2747	0.6022	2.2473
12 01 10	Oil	0.0697	0.3421	0.1408	0.0633	0.6475	0.0000	0.0000	1.2633
12 01 10	Oil	0.0128	0.0541	0.0217	0.0379	0.0953	0.0000	0.0000	0.2216
12 03 01	Oil	0.0097	0.0423	0.0182	0.0168	0.0937	0.0000	0.0000	0.1805
19 02 07	Oil	0.0487	0.2975	0.0653	0.0595	0.0700	0.0000	0.0000	0.5410
19 08 10	Oil	0.0325	0.1849	0.0721	0.0595	0.3773	0.0000	0.0000	0.7263
19 08 10	Oil	0.0800	0.3536	0.1113	0.1133	0.4247	0.0000	0.0000	1.0828

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