

“Dioxin Releases in Waste Incinerations and Thermal Processes”

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Abstract The releases of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from waste incinerators and thermal processes were investigated. The characteristics of mean PCDD/Fs I-TEQ concentrations and congener profiles were studied over the samples of water, soil, fly ash and bottom ash of individual source. The TEQ value for fly ash ranges from 0.013 to 17.01 pg-TEQ/g. Moreover, the TEQ value for bottom ash was 12.06 pg-TEQ/g and the TEQ values for the water samples were found to be in a consistent range from 0.41–0.56 ng-TEQ/L. In almost all the analyzed matrices the congener OCDD/OCDF was found in highest concentration raising the critical concerns over the overall PCDD/Fs emissions from incinerations and thermal processes.

Keywords Dioxins · Furans · Persistent organic pollutants · High temperature processes

Monitoring of dioxin and furan (Polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCDD/Fs) levels and congener distribution patterns in various environmental samples has attracted much attention from environmental researchers (Fabrellas et al. 2004). The main pathway of PCDD/Fs in the environment is via the combustion processes (Stanmore 2004). However the compounds are also released to the environment during metal-processing operations and

production processes involving elemental chlorine (Everaert and Baeyens 2002; Yu et al. 2006). PCDD/Fs are transported via incinerator emission to environmental media such as air, soil and water, and then expose into the media such as drinking water, food and vegetation (McKay 2002). The usual temperature range, at which incinerator operate is 1000–1100°C. Dioxins are also produced when chlorinated plastics are burnt (UNEP Toolkit, 2005; Conesa et al. 2005).

For effective reduction of environmental loading and human exposure to PCDD/Fs, the total emissions of these compounds from various sources must be determined. (Everaert and Baeyens 2002; Yu et al. 2006; Chen 2004).

Materials and Methods

Samples of different matrices viz., wastewater, fly ash, bottom ash and soil were collected from each identified sources.

Fly ash, bottom ash and soil were collected from the residues obtained from air pollution control systems (APCs) and landfill sites. Wastewater samples were collected from the outlet system where water is drained out after used for wet scrubbers, for maintaining temperature in flue gas etc.

1. Fly ash-1 and 2. Fly ash-2: from hazardous waste incineration (HWI), 3. Fly ash-3: ferrous and non-ferrous plant, 4. Fly ash-4: thermal power plant, 5. Bottom ash-1: medical waste incineration, 6. Water-1 and 7. Water-2: medical waste incineration (MWI), 8. Water-3: pulp and paper industry, 9. Soil-1: pulp and paper industry, 10. Soil-2: cement industry.

Solid samples were extracted by using soxhlet extraction system and wastewater samples collected from the incinerators were extracted through liquid-liquid extraction. The procedures followed the US EPA methods 8280 and 8290

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(US EPA methods 8280 and 8290, 1996 1994). The extracted samples were further cleaned up and prepared as given in the method. The $^{13}\text{C}_{12}$ -labelled standard mixture of 17 compounds was used during the whole procedure.

The extracted samples were further concentrated in rotavapor and then in turbovapor to a final volume of 0.5 ml. They were finally analyzed in HRGC/HRMS.

Results and Discussion

The individual concentrations of the 17 congeners of dioxins and furans in fly ash and bottom ash have been highlighted in Table 1.

In the given Table 1, OCDD was found to be highest with a concentration of 100 pg/g in Fly ash-1, which is a sample from hazardous waste incineration (HWI) plant. 1,2,3,4,6,7,8-HpCDF got the lowest concentration in Fly ash-4 with 0.9 pg/g, which is a sample from thermal power plant. However regarding the bottom ash, concentration of the congeners were found to be in higher range starting from 10 pg/g to 260 pg/g with 1,2,3,4,7,8-HxCDF being the lowest and OCDD being the highest.

In water, PCDD/Fs are normally released in cases where wet scrubbers are used for flue gas treatment and where

discharged ashes are cooled down with water. And again it has been clearly found that most of the sampling sites installed wet scrubber as the main APCs for stack purification, which again contributes to the positive possibility of release in wastewater. Highest concentration of individual congener in water has been obtained as OCDF with 39.68 ng/L. The concentration found in this matrix ranges from 0.02 ng/L of 2,3,7,8-TeCCD; 1,2,3,6,7,8-HxCDD and 2,3,7,8-TeCDF to 39.68 ng/L of OCDF.

The highest concentration in soil samples accounts for OCDD with 48 ng/g. The lowest value in soil sample was found to be 0.001 ng/g of 1,2,3,7,8-PeCDF (Table 2).

Conclusion

The present analysis covered the levels of PCDD/Fs in four different environmental matrices and from a variety of sources, which involves thermal treatment processes at high temperature. It can be concluded on the basis of the result obtained that untreated residue must have been directly placed onto or mixed with soil of Soil-1 sampling site, which is from medical waste incineration (Fig. 1).

The TEQ value for fly ash ranges from 0.013 to 17.01 pg-TEQ/g. In particular, the Fly ash-1 and 2 from

Table 1 Concentrations of PCDD/Fs and WHO-TEQ in fly ash and bottom ash

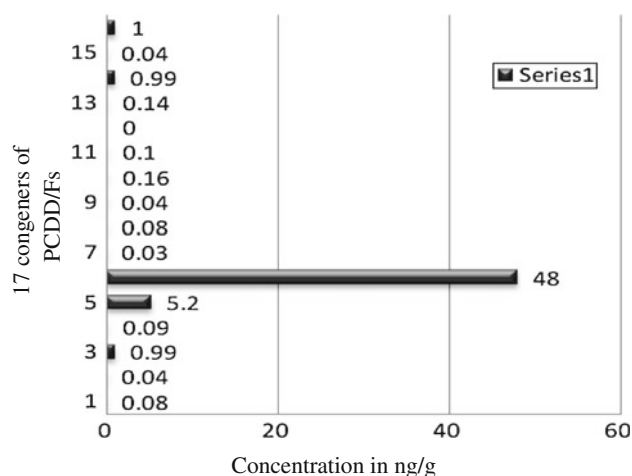
Compounds	Fly ash (pg/g)				Bottom ash (pg/g)
	Fly ash-1	Fly ash-2	Fly ash-3	Fly ash-4	Bottom ash-1
2,3,7,8-TeCDD	–	1.6	–	–	–
1,2,3,7,8-PeCDD	9.6	3.0	–	–	–
1,2,3,4,7,8-HxCDD	–	–	–	–	–
1,2,3,6,7,8-HxCDD	–	1.7	–	–	–
1,2,3,7,8,9-HxCDD	–	1.8	–	–	–
1,2,3,4,6,7,8-HpCDD	27	8.6	–	–	100
OCDD	100	22	4.8	6.2	260
2,3,7,8-TeCDF	12	2.0	–	–	27
1,2,3,7,8-PeCDF	–	2.6	–	–	16
2,3,4,7,8-PeCDF	12	2.3	–	–	18
1,2,3,4,7,8-HxCDF	10	3.8	–	–	10
1,2,3,6,7,8-HxCDF	11	3.1	–	–	12
1,2,3,7,8,9-HxCDF	–	–	–	–	–
2,3,4,6,7,8-HxCDF	–	2.4	–	–	–
1,2,3,4,6,7,8-HpCDF	22	17	1.2	0.9	22
1,2,3,4,7,8,9-HpCDF	–	–	–	–	–
OCDF	–	32	10	6.7	–
Total PCDD	136.6	38.7	4.8	6.2	360
Total PCDF	66	65.2	11.2	7.6	105
WHO-TEQ*	17.01	7.12	0.016	0.013	12.06

*Toxicity Equivalent Quotient derived from Toxicity Equivalent Factor given by World Health Organization, 2006

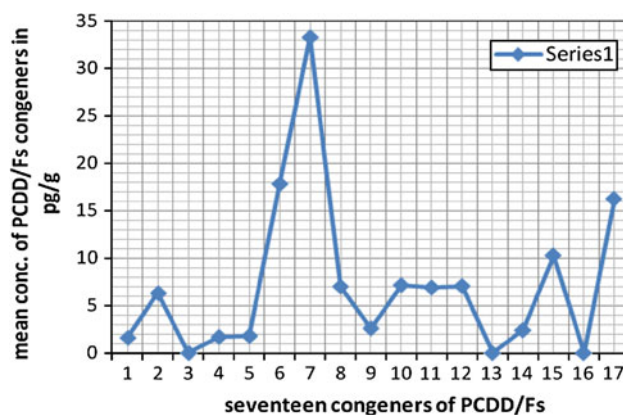
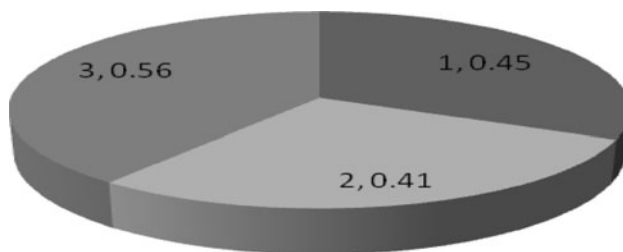
Table 2 Concentrations of PCDD/Fs and WHO-TEQ in water, soil and air

Compounds	Water (ng/L)			Soil (ng/g)	
	Water-1	Water-2	Water-3	Soil-1	Soil-2
2,3,7,8-TeCDD	0.02	0.03	0.04	0.007	0.002
1,2,3,7,8-PeCDD	0.19	–	0.19	0.08	0.002
1,2,3,4,7,8-HxCDD	0.03	0.19	0.17	0.04	–
1,2,3,6,7,8-HxCDD	0.02	2.01	0.18	0.99	–
1,2,3,7,8,9-HxCDD	0.03	0.19	0.45	0.09	–
1,2,3,4,6,7,8-HpCDD	1.04	–	0.28	5.20	0.005
OCDD	–	5.03	2.04	48.00	0.27
2,3,7,8-TeCDF	0.02	0.05	0.08	0.03	0.002
1,2,3,7,8-PeCDF	0.06	–	0.15	0.08	0.001
2,3,4,7,8-PeCDF	0.41	0.13	–	0.04	–
1,2,3,4,7,8-HxCDF	0.31	–	0.18	0.16	0.003
1,2,3,6,7,8-HxCDF	–	–	–	0.10	0.002
1,2,3,7,8,9-HxCDF	–	0.52	–	–	–
2,3,4,6,7,8-HxCDF	0.27	0.27	0.24	0.14	–
1,2,3,4,6,7,8-HpCDF	3.75	1.80	0.32	0.99	0.35
1,2,3,4,7,8,9-HpCDF	3.18	–	16.71	0.04	0.06
OCDF	2.14	3.83	39.68	1.00	3.60
Total PCDD	1.33	7.45	3.35	54.41	0.28
Total PCDF	10.14	6.60	51.36	2.58	3.99
WHO-TEQ*	0.45	0.41	0.56	0.34	0.01

*Toxicity Equivalent Quotient derived from toxicity equivalent factor given by world health organization, 2006

**Fig. 1** Spatial distribution of PCDD/Fs in Soil-1 of a medical waste incineration

HWI were among the strong emitter of PCDD/Fs congener (Fig. 2). Moreover, the TEQ value for Bottom ash-1 (MWI) was 12.06 pg-TEQ/g. The high concentration of PCDD/Fs reported from these sources proves the idea of medical waste incinerator to be one of the main high emitter of these toxic congeners.

**Fig. 2** Mean concentration of PCDD/Fs in fly ash samples of four sampling sites**Fig. 3** Total WHO-TEQ values of water samples in ng-TEQ/L

Besides the TEQ values of the water samples, they were found to be in a consistent range of 0.45, 0.41 and 0.56 ng-TEQ/L (Fig. 3).

From the whole study it can be observed that the operation of incinerators and other thermal processes have directly influenced the observed congener profile of toxic persistent pollutants with respect to different sampling sites.

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