EMISSION LEVELS OF POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS (PCDDs/PCDFs) FROM WASTE INCINERATORS IN INDIA

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Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are recognized as persistent organic pollutants (POPs) and included in priority list for action under Stockholm Convention. Waste incinerators are prime sources for influx of PCDDs/PCDFs into the environment. In recent years studies have been continuously carried out world-wide on the emissions of these pollutants from incinerators in India also, studies are being undertaken on assessment of the levels of PCDDs/PCDFs in biological matrices and ambient air particulate matter including emissions from waste incinerators in India. The emission levels of total dioxin/furan in this study have been found as 498.40, 139.23 and 195.34 pg I-TEQ/m^3 respectively from biomedical waste, industrial process waste, and hazardous waste incinerator. The detected congener pattern shows that high chlorinated dioxins are dominant in all the samples while low chlorinated furans are higher in biomedical waste incinerator except hepta and octa furans in hazardous waste incinerator. Congener pattern and group homolog profile is also presented.

Introduction

Persistent organic pollutants (POPs) harm human health and environment. These are produced and released to the environment predominantly as a result of human activities. The Stockholm convention is intended to reduce and eliminate POPs, starting with an initial list of twelve of the most notorious, the "dirty dozen". Among the list of POPs there are four groups of substance that are produced unintentionally; polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). The last two groups are simply known as dioxins are ubiquitous in different environmental compartments with enhanced chronic toxicity. The level of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been recognized and intensely studied world-wide over the past 25 years. While many regulatory efforts have been undertaken, further interest has led in recent years to studying and quantifying potential dioxin and furan emissions from incinerators, because incinerators are important pathway for the loading of PCDDs/PCDFs to the environmental sinks.

Central Pollution Control Board (CPCB) the apex body under Ministry of Environment & Forests of India for control of pollution established National Reference Trace Organics Laboratory to enable itself for monitoring of the POPs compounds to fulfill the national obligations to implement the Stockholm Convention in India. Although some reports on PCDDs/PCDFs levels in biological matrices[1,2,3] are available from India, but the data on environmental levels of PCDDs/PCDFs in ambient air is limited[4] and there is no study reported on PCDDs/PCDFs emission level from waste incinerators. Therefore, Central Pollution Control Board (CPCB) initiated the monitoring of 17 congeners of PCDDs/PCDFs in ambient air, some of the prominent stationary emission sources and other environmental matrices like industrial solid wastes, sewage treatment plant sludge and solids from contaminated sites to assess levels of these compounds. CPCB is regularly monitoring PCDDs/PCDFs level in ambient air but

source sampling is recently started after acquiring the stack sampling kit for dioxin/furans. This study reports concentrations of PCDDs/PCDFs from waste incinerators from India for the first time.

Materials and Methods

Solvent and Chemicals

Chemicals (sodium sulfate, silver nitrate, potassium hydroxide) and solvents (acetone, dichloromethane, n-hexane, and toluene) were procured from Merck India and silica gel and aluminum oxide were from Supelco. The 17 congener's dioxin/furan standards solutions in nonane (CS-1 to CS-5 from Wellington Laboratories Inc. as per EN: 1948) were used for instrument calibration, quantification, recovery and quality control.

Table 1: Emission levels of PCDDs / PCDFs (pg I-TEQ/m^3) from different incinerator sources in India

Congeners	Sources*		
	B	**P**	**H****
2,3,7,8-TCDD	86.42	19.97	10.15
1,2,3,7,8-PeCDD	66.06	15.46	17.06
1,2,3,4,7,8-HxCDD	3.28	0.96	2.84
1,2,3,6,7,8-HxCDD	13.10	3.86	5.69
1,2,3,7,8,9-HxCDD	10.04	2.96	3.90
1,2,3,4,6,7,8-HpCDD	5.98	2.51	3.24
OCDD	0.54	0.30	1.17
2,3,7,8-TCDF	41.20	14.69	5.64
1,2,3,7,8-PeCDF	21.45	5.53	2.96
2,3,4,7,8-PeCDF	182.88	52.78	63.53
1,2,3,4,7,8-HxCDF	22.02	6.26	14.46
1,2,3,6,7,8-HxCDF	22.98	6.79	14.91
1,2,3,7,8,9-HxCDF	15.88	4.90	26.20
2,3,4,6,7,8-HxCDF	3.68	1.29	10.29
1,2,3,4,6,7,8-HpCDF	2.43	0.98	11.21
1,2,3,4,7,8,9-HpCDF	0.43	0.16	0.99
OCDF	0.05	0.02	1.08
Total	**498.40**	**139.23**	**195.34**

*-B=Biomedical waste Incinerator, P=Industrial process waste Incinerator, H=Hazardous waste incinerator, **-Average of two samples

Sampling

The sampling was carried out from three stationary emission sources covering biomedical waste, industrial process waste and hazardous waste incinerators. Isokinetic sampling was performed and approximately 5 m^3 flue gas sample from each incinerator was collected as per EPA method 23 using stack sampling kit (Westech Instruments Services, U.K., model XC-572 WTS). The particulate phase of the sample was collected on glass fiber filter paper and vapor phase was adsorbed on XAD-2 (Supelpack-2 amberlite resin from Supelco).

Sample Extraction and Cleanup

Sample extraction and cleanup was performed as per EN 1948. The pollutants were extracted from filter papers and XAD by Soxhlet with toluene for 24 hour and rinsate of sampling probe and liners of kit with dichloromethane, the extracts were combined and concentrated to near 5 ml using Rotary Vacuum Evaporator (Eyela, Japan). The extracts were primarily cleaned by multilayer silica column and finally by alumina column.

Instrumental Analysis

Identification and quantification of PCDDs/PCDFs were performed on HRGC-HRMS (JEOL JMS 800D) at resolution higher than 10000 and operated at positive electron ionization mode and data acquired for selected ions monitoring (SIM) mode with two mass fragments of each target compound and two mass fragments of $^{13}C_{12}$- isotope labeled compounds. Separation of compounds was achieved using capillary column (DB dioxin of J&W 60m x 25mm ID x 0.25µm film), and identified with respect to labeled compounds and quantified using relative response factors derived from five level calibration using standard solutions (as per EN 1948). The temperature program of

gas chromatograph was as follows: from 150^0C (2 min) to 190^0C at a rate of 20^0C min^{-1}, then finally to 280^0C at the rate of 3^0C min^{-1} and held for 23 min.

Analytical Quality Control

Quality assurance and quality control were conducted with method blank and recovery of target analytes by spiking three $^{13}C_{12}$- labeled standards before sampling and 13 $^{13}C_{12}$- labeled standards before extraction. Syringe standards (two $^{13}C_{12}$- labeled) were added before final make up of sample extract (25 µl) as recovery standards (as per EN 1948) quantification of labeled compounds and calculating their recovery rates. The rates of recovery of labeled compounds range in 69-140% for all the samples. The toxic equivalent factors (TEFs) presented by International system[5] were used to calculate the International Toxic Equivalent quantities (I-TEQ) of PCDDs/PCDFs.

Results and Discussions

The levels of PCDDs/PCDFs detected in flue gas of incinerators of this study are presented in terms of pg I-TEQ/m^3 in Table 1. The total concentration of 17 PCDDs/PCDFs congeners is higher in biomedical waste incinerator (498.40 pg I-TEQ/m^3) followed by Hazardous waste (195.34 pg I-TEQ/m^3) and industrial process waste incinerator (139.23 pg I-TEQ/m^3). The measured levels are in the same order of magnitude as literature data on measured concentration in other study[6].

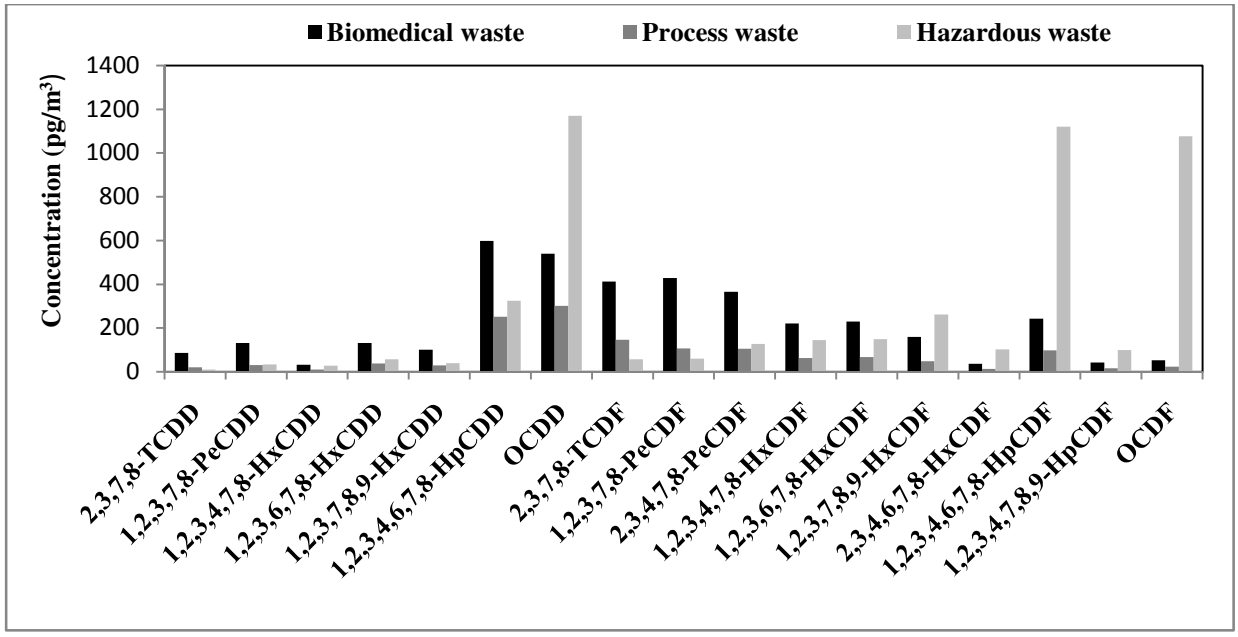

Figure 1: Congener pattern of PCDDs/PCDFs in three different types of incinerator sources in India

The congener pattern of PCDDs/PCDFs in flue gas from different incinerators is presented in Figure 1. In biomedical waste incinerator the 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF congeners are the main contributors to total dioxin/furan concentration, while OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF are important contributor in hazardous waste incinerator. The 1,2,3,4,6,7,8-HpCDD, OCDD are relatively larger contributor in the total concentration as observed in industrial process waste incinerator.

The homolog profiles of PCDDs/PCDFs (Figure 2) in flue gas clearly showed the similarities exhibited in different incinerators except hazardous waste incinerator where HpCDF and OCDF are higher than other two incinerators.

The data revealed that the concentration of total PCDDs/ in flue gas of studied incinerators is higher than regulatory limit (100 pg I-TEQ/m3). This study provides the preliminary information on the current status of PCDDs/PCDFs levels in flue gas of selected incinerators in India. Further regular work on dioxins/furans in incinerators is needed.

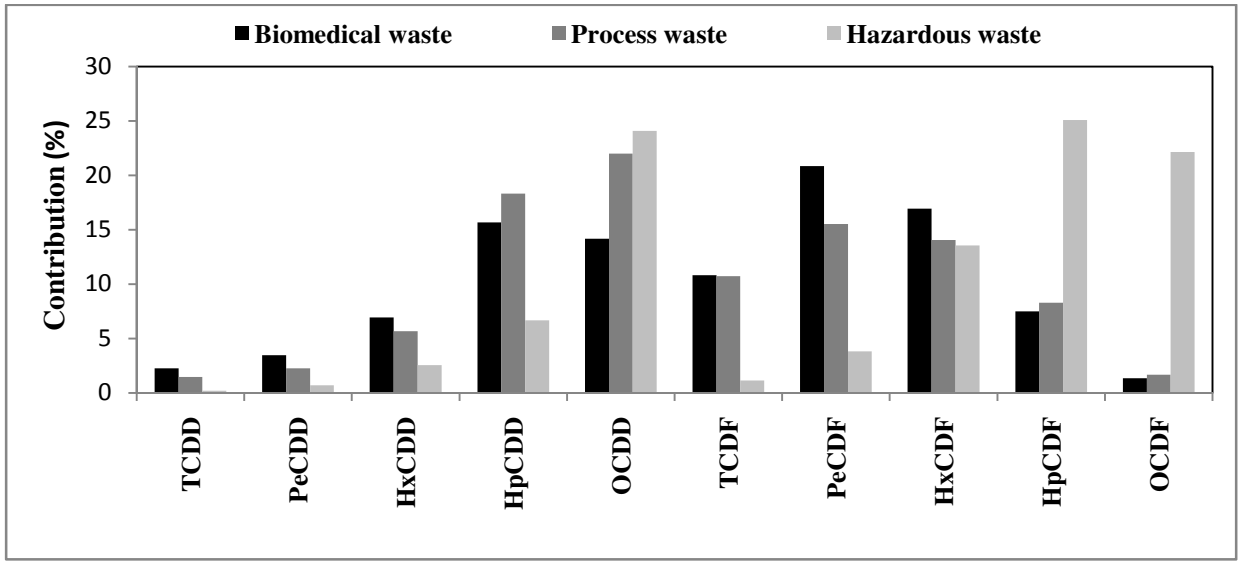

Figure 2: Group Homolog profile of total PCDDs/PCDFs in three different type incinerator sources in India

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