

AIR BORNE PARTICULATE BOUND POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS (PCDDs/Fs) LEVELS IN DELHI, INDIA

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Abstract

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofuran (PCDFs) are globally wide spread, and persistent environmental pollutants. The four sampling locations namely ITO (n=13), Siri Fort (n=12), Janakpuri (n=7) and Shahdara (n=9) have been selected for monitoring of PCDDs/Fs in air borne particulates in ambient air at Delhi. ITO is busy traffic intersection with two nearby Coal based and Gas based thermal power plants, Siri Fort and Janakpuri are the residential sites while Shahdara an Industrial site. The identification and quantification of PCDDs/Fs were performed by HRGC-HRMS (JEOL JMS-800D, Japan) coupled to auto sampler using a positive electron ionization (EI⁺) source operated in Selective Ion Monitoring (SIM) mode at 10000 or better resolution. The average deposition of total 2,3,7,8-substituted PCDDs/Fs congeners were found as 0.971 pg I-TEQ/m³ at ITO monitoring site, 0.570 pg I-TEQ/m³ at Siri Fort, 0.631 pg I-TEQ/m³ at Janakpuri and 1.250 pg I-TEQ/m³ at Shahdara industrial site.

Introduction

Researchers have studied levels of dioxin and furans in biological tissues, foods and ambient environment from India^{1, 2} but data on PCDD/Fs in environmental samples specifically in air borne particulate matter (total suspended and inhalable respiratory suspended particulate) of ambient air is limited. Central Pollution Control Board (CPCB) is a statutory body under Ministry of Environment & Forests, Govt. of India and is responsible at national level for inventory of sources of Persistent Organic Pollutants (POPs) and estimating their potential releases into the environment. CPCB has recently developed a National Reference Trace Organic Laboratory in its Head Office in Delhi for assessment of POPs including dioxin-furan in various environmental matrices. The finding of levels of PCDDs and PCDFs in respiratory fraction of suspended particulate matter (PM₁₀) monitored in Delhi were presented in Dioxin 2007 Conference³ at Tokyo, Japan.

After having developed its analytical facilities the similar samples of PM₁₀ monitored at four sites of Delhi, between January to July 2008 were analysed at National Reference Trace Organics Laboratory, adopting international protocols. This present paper reports the observed levels of 17 dioxin furan congeners (2,3,7,8 substituted) and comparison of there levels with those observed earlier as well as reported in other previous studies elsewhere.

Materials and Methods

Ambient Air Sampling

The Four sampling sites namely ITO, Siri Fort, Janakpuri and Shahdara were selected for the monitoring of PCDDs/Fs in Respirable Suspended Particulate Matter. ITO, site is a busy traffic intersection with two nearby thermal power plants i.e. one coal based and another gas based; Siri Fort and Janakpuri sites are residential sites while Shahdara an Industrial site. These four locations are also the part of Nation wide monitoring network under National Ambient Air Monitoring Programme (NAMP). The Respirable fraction of ambient air particulate matter (PM₁₀) was collected on EPA glass fibre filter papers using respirable dust sampler (RDS, APM-460, Dx of Envirotech India). 24 hourly (6 AM – 6 AM) sampling of ambient air was carried out at an interval of 8 hour for collection of Respirable fraction of Ambient air particulates (PM₁₀). The samples were collected at average sampling flow rate of 1.0 m³/min. After collection of samples filter papers were wrapped in aluminum foil and transferred to the laboratory for processing.

Chemicals and Solvents

Toluene, acetone, dichloromethane and n-hexane for organic trace analysis and chemicals (sodium sulfate, silver nitrate and potassium hydroxide) were purchased from Merck (India). Silica gel and aluminum oxide were from Sigma-Aldrich (Germany). EN 1948 the dioxin/furan standards solutions in nonane (CS-1 to CS-5, Cambridge Isotope Laboratories (CIL), Inc USA) were used for instrument (High Resolution Gas Chromatograph-High Resolution Mass Spectrometer) calibration, quantification, recovery and quality control.

Extraction and Cleanup

Exposed filter papers were shredded into small pieces and spiked with the 13 2,3,7,8 substituted PCDD and PCDF as $^{13}\text{C}_{12}$ -labeled quantification standards. The organic contaminants were extracted from the filter papers using Soxhlet with toluene continuously for 24 hour. Extracts were concentrated to near 5 ml volume using Rotary Vacuum Evaporator (Eyela, Japan) at 40°C.

The primary cleanup of the extract was done on multilayered column (35 mm id x 300 mm l). The column packing with the absorbents was in following sequence: 2.0 g activated silica, 5.0 g basic silica, 1.0 g activated silica, 10 g acid silica, 1.0 g activated silica, 5.0 g silver nitrate coated silica and followed by 5.0 g sodium sulphate. The column was prewashed with 120 ml n-hexane and analyte were eluted with 250 ml n-hexane. Elute were concentrated to near 2.0 ml volume in rotavapor. Final cleanup of elute was performed on aluminum oxide column (22 mm id x 250 mm l) using 25 g aluminum oxide (basic) and 10 g sodium sulphate. Analyte were eluted as F1: 60 ml n-hexane, F2: 90 ml toluene and F3: 200 ml of n-hexane-dichloromethane (1:1 v/v). Fraction F1 & F2 discarded as they contain unwanted analyte but F3 fraction was retained and concentrated to near 1.0 ml volume for dioxin/furan analysis. The concentrate was dried under gentle blow of purified nitrogen. 25 μl of syringe spiked standard (1,2,3,4 substituted TCDD and 1,2,3,7,8,9 HxCDD as $^{13}\text{C}_{12}$ -labeled recovery standards) in nonane was added and sealed for instrumental analysis.

Instrumental Analysis

Identification and quantification of PCDDs/Fs were performed by HRGC-HRMS (JEOL JMS-800D, Japan) coupled to auto sampler using a positive electron ionization (EI^+) source operated in Selective Ion Monitoring (SIM) mode at 10000 or better resolution. Chromatographic separation was performed on a 60 m x 0.25 mm ID x 0.25 μm (DB-5) capillary column with helium as carrier gas. Quantification of each congener was performed by direct comparison of peak areas of mass fragmentograms for the (M^{+2}) $^+$ -ion of the native compound and the M^{+2} $^+$ -ion of the corresponding $^{13}\text{C}_{12}$ -labeled standard (isotopic dilution method). Relative response factors (RRF) for the individual isomers were obtained by analyzing CS-1 to CS-5 standard solution mixtures. The recoveries of labeled standards were calculated using a mixture of two labeled PCDDs added before the HRGC-HRMS analysis.

TEQ values have been calculated by multiplying the concentration of individual PCDD/PCDF congener with the corresponding toxicity equivalency factor (TEF). PCDD/PCDF TEQ values have been calculated in two different ways: considering the WHO-TEFs results in PCDD/PCDF WHO-TEQ, considering the NATO/CCMS⁷ TEFs (NATO) results in pg I-TEQ/m³.

Results and Discussion

Levels of PCDDs/ PCDFs detected in air borne particulates of Delhi are presented in Table 1. I-TEQ (1998) levels calculated in terms of pg/m³ are reported in same Table. It is worth mentioning here that data presented is for particle bound PCDDs/Fs only as vapour phase PCDD/Fs could not be sampled due to limitations of availability of PUF samplers and hence the data does not represent as Total PCDDs/Fs. The congeners profile of 17 congeners of PCDDs/Fs are presented in the figure 1.

The average deposition of total 2,3,7,8-substituted PCDDs/Fs congeners were found as 0.971 pg I-TEQ/m³ at ITO monitoring locations for 13 number of samples, 0.570 pg I-TEQ/m³ at Siri Fort residential sites for 12 number of samples, 0.631 pg-I-TEQ/m³ at Janakpuri residential sites for 7 number of samples and 1.250 pg I-TEQ/m³ at Shahdara industrial site for 9 samples. The average concentration of PCDDs/Fs was found highest at Shahdara site, as it is surrounded by number of Industries. PCDDs/Fs concentrations at ITO

monitoring site was also high as it is one of the major traffic intersection, the vehicle exhaust might be an important source for PCDDs/Fs deposition. The deposition of PCDDs/Fs is comparatively less at Siri Fort and Janakpuri than ITO and Shahdara, as these stations are the residential.

The total PCDDs load of seven 2,3,7,8 – substituted congeners was observed as 0.145 pg I-TEQ/m³ at traffic intersection station, 0.309 pg I-TEQ/m³ at Industrial site while, 0.148 & 0.228 pg I-TEQ/m³ at residential sites. The total PCDFs load of ten 2,3,7,8 – substituted congeners was observed as 0.836 pg I-TEQ/m³ at traffic intersection site, 0.950 pg I-TEQ/m³ at Industrial site, 0.427 & 0.413 pg I-TEQ/m³ at residential sites.

Table-1: PCDDs/Fs levels in Respirable fraction of ambient particulate matter (PM₁₀) collected from different Ambient Air sites

17 Congener of PCDDs/Fs	Average PCDDs/PCDFs levels in Respirable fraction of Ambient Particulate Matter - pg I-TEQ/ m ³			
	ITO (Traffic Intersection)	Shahdara (Industrial)	Siri Fort (Residential)	Janakpuri (Residential)
	n=13	n=9	n=12	n=7
2,3,7,8-TCDD	0.020	0.049	0.031	0.045
1,2,3,7,8-PeCDD	0.058	0.120	0.064	0.116
1,2,3,4,7,8-HxCDD	0.009	0.023	0.013	0.015
1,2,3,6,7,8-HxCDD	0.022	0.047	0.016	0.020
1,2,3,7,8,9-HxCDD	0.015	0.040	0.017	0.022
1,2,3,4,6,7,8-HpCDD	0.017	0.026	0.006	0.008
OCDD	0.004	0.004	0.001	0.002
2,3,7,8-TCDF	0.045	0.023	0.010	0.013
1,2,3,7,8-PeCDF	0.026	0.025	0.042	0.016
2,3,4,7,8-PeCDF	0.437	0.377	0.217	0.196
1,2,3,4,7,8-HxCDF	0.093	0.125	0.036	0.044
1,2,3,6,7,8-HxCDF	0.085	0.115	0.029	0.044
1,2,3,7,8,9-HxCDF	0.087	0.143	0.044	0.046
2,3,4,6,7,8-HxCDF	0.025	0.062	0.028	0.034
1,2,3,4,6,7,8-HpCDF	0.032	0.061	0.012	0.015
1,2,3,4,7,8,9-HpCDF	0.004	0.014	0.008	0.004
OCDF	0.002	0.005	0.001	0.001
Σ PCDDs	0.145	0.309	0.148	0.228
Σ PCDFs	0.836	0.950	0.427	0.413
PCDDs/PCDFs Ratio	0.173	0.325	0.347	0.552
Total PCDDs/Fs	0.971	1.259	0.575	0.641

Note: n=the number of sampling days as 24 hour basis

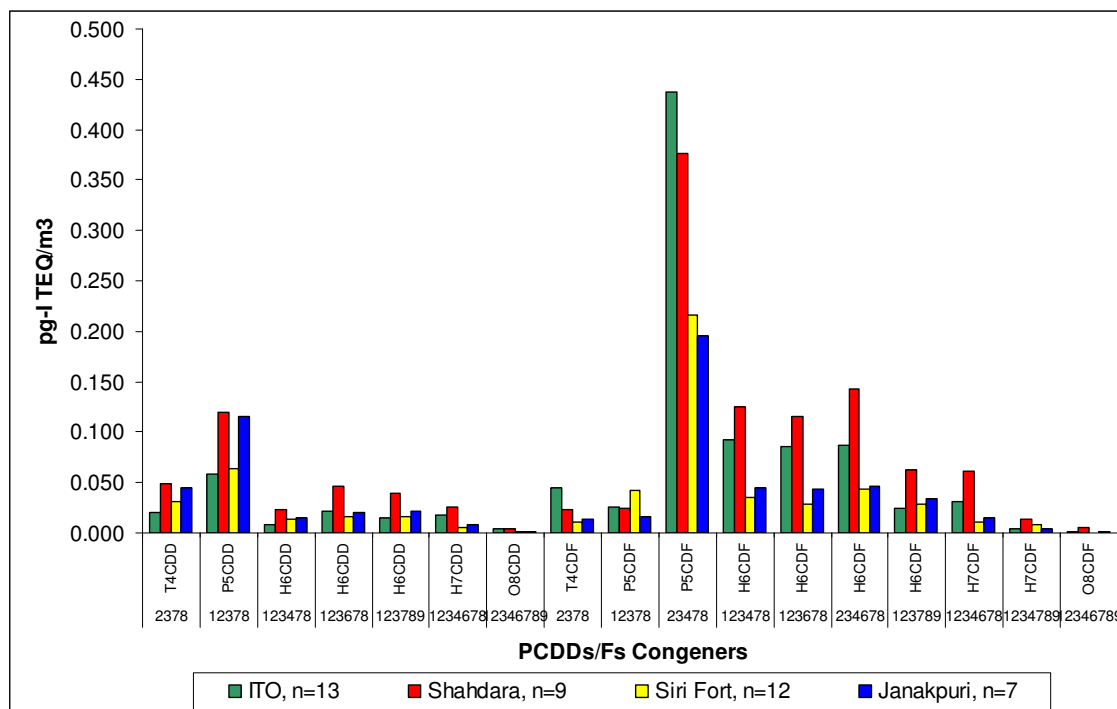


Figure 1: Bar Plot of Levels of 2, 3, 7, 8-substituted PCDDs/Fs (pg I-TEQ/m³) in Respirable fraction of Ambient Particulates (PM₁₀) at various sites in Delhi, India

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