

INHALATION OF POLYCHLORINATED DIBENZO-*P*-DIOXINS/FURANS (PCDDs/PCDFs) FROM AMBIENT AIR FROM NEW DELHI, INDIA

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are primarily formed from inefficient combustion and also by unintentional by-products¹. Further, PCDD/Fs are resistance in environment and found everywhere in the world. Therefore, Stockholm Convention listed PCDD/Fs among persistent organic pollutants (POPs). Due to their resistance to chemical, physical and biological degradation, PCDD/Fs have been transported world-wide, affecting regions far from their original sources and found in all environmental media of the earth².

PCDD/Fs adsorbed to dust particles in atmosphere and most of PCDD/Fs are found in the particulate phase³. Gas-phase PCDD/Fs are believed to be depleted due to degradation reactions in the atmosphere. Particle properties play an important role in the transport of particle-bound PCDD/Fs away from sources⁴. Compared with the larger particles the inhalable <PM₁₀ could remain longer in the air and therefore, cause greater concern for human health⁵. In this particular context, the levels of PCDDs/Fs in <PM₁₀ have been recognized and intensely increased.

There are very few studies have been conducted in India with regard to occurrence and distribution of PCDDs/Fs compounds and have been reported in different matrices including humans⁶⁻¹¹. On 17th May 2004 Stockholm Convention on POPs entered into force with the intention of reducing and eliminating these pollutants. As a part to the Convention India is obligated to abide the objectives of the treaty with the purpose to reduce and eliminate the use of POPs, and encouraged a supportive research on POPs. Consequently, The Central Pollution Control Board (CPCB) a statutory body under Ministry of Environment & Forest, Government of India is inventorying the sources of POPs with a view to quantify and estimate their potential release into the environment. The national implementation plan (NIP) has already been developed. Consequently, in this study we report distribution and inhalation risk assessment of PCDDs/Fs in New Delhi, India for the first time.

Materials and Methods

New Delhi is the administrative capital city of India with population ~20 million and situated between the geographical coordinates of 28° 36' 36" N to 77° 13' 48" E. There are specified industrial zones with more than 8000 small to medium industries for food, textile, chemical, paint, dyes metallic and non-metallic etc.¹², which contribute significant total suspended particulates in to the environment.

The monitoring locations of NAMP (National Ambient Air Monitoring Programme) in New Delhi had been used for Ambient Air Sampling in this study. Air borne particulate matter (PM₁₀) was monitored and sampled at six different locations in New Delhi on EPA glass filter papers during March 2007 using respirable suspended particulate matter sampler (modified high volume sampler with cyclone for particle size cut off). Twenty four hour samples (6 AM to 6 AM) were collected operating the instrument at an average ambient air flow 1.0 m³ min⁻¹.

Sample extraction and cleanup was performed as per standard procedure³. Particularly, extraction, cleanup and analysis was performed in the Fraunhofer Institute for Process Engineering and Packaging (IVV), Friesing, Germany. The exposed filter papers with particulate matter were spiked with the 2,3,7,8 substituted PCDDs and PCDFs as ¹³C₁₂ labeled quantification standards. The pollutants were extracted from the filter papers by Soxhlet with toluene for 24 hour. Extracts were concentrated to near 5 ml using Buchi Rotary Vacuum Evaporator. The extracts

were cleaned after EN 1948 through two steps: first by modified multi-layer silica gel column and second alumina column chromatography. The final concentrate was dried under gentle stream of high purity nitrogen. Before analysis $^{13}\text{C}_{12}$ 1,2,3,4-TCDD added as recovery standard.

Identification and quantification of PCDDs/Fs were performed in the laboratory of Bavarian Environmental Agency, Augsburg, Germany by HRGC-HRMS with Thermo, Finnigan MAT 95 coupled to auto sampler using a positive electron ionization (EI^+) source operating Selective Ion mode (SIM) at a >10,000 resolution (10% valley definition). Chromatographic separation was performed on weakly polar 60 m \times 0.25 ID \times 0.25 μm (DB-XLB) capillary columns. Quantification of each congener was performed by direct comparison of peak areas of mass fragment grams for the (M+2) $^+$ -ion of the native compound and the (M+2) $^+$ -ion of the corresponding $^{13}\text{C}_{12}$ -labeled standard (isotope dilution method). For congeners with a concentration below the limit of quantification (LOQ), signal to noise value of 10:1 of the mass used for quantification.

Analytical quality assurance and quality control procedures were conducted using method blank and recovery of target analytes by spiking $^{13}\text{C}_{12}$ -labeled standards (Wellington Laboratories Inc, Guelph Ontario, Canada). Recovery rates of $^{13}\text{C}_{12}$ -labeled internal standards were within the acceptable 50-130% ranges set by the EN 1948 methods. Toxic equivalent quantities (TEQ) were calculated by multiplying the concentration of individual PCDD/PCDF congener with the corresponding toxicity equivalent factors (TEFs) proposed by international system¹⁴. The results were presented as fg m^{-3} and their toxic equivalent in fg I-TEQ m^{-3} .

Results and Discussions:

Concentrations of 17 individual PCDD/PCDFs congeners and their I-TEQs in particulate matter (PM_{10}) of New Delhi are presented in Table 1 (total) and Figure 1 (individual), respectively. $\Sigma\text{PCDD/PCDFs}$ in ambient air from New Delhi ranged from 1720-9010 fg m^{-3} with a mean of 5559 fg m^{-3} , and their TEQ values ranged from 67 to 460 fg I-TEQ m^{-3} with an average of 239 fg I-TEQ m^{-3} (Table 1, Figure 2), which were considerably lower than the ambient air standard of 0.6 pg I-TEQ m^{-3} proposed by Japan and 1.0 pg I-TEQ m^{-3} by State of Connecticut, USA. According to Lohmann and Jones⁴, PCDD/Fs concentrations for the total sum of TEQ are typically as follows: remote <10 fg I-TEQ m^{-3} ; rural ~20-50 fg I-TEQ m^{-3} ; and urban/industrial ~100-400 fg I-TEQ m^{-3} . The ratio of $\Sigma\text{PCDD/F}$ was from 0.66 to 1.77 with an average of 1.10 (Table 1).

Table 1: Concentration and TEQ of PCDD/Fs in ambient air particles (PM_{10}) at New Delhi.

Congeners	Sampling locations						All locations		
	DA1	DA 2	DA 3	DA 4	DA 5	DA 6	Range	Mean	%
	fg m^{-3}								
ΣPCDDs	4012	1090	3500	1100	3570	2280	1090-4012	2592	47
ΣPCDFs	4290	800	4670	620	5440	1980	620-5440	2967	53
PCDDs/PCDFs ratio	0.94	1.36	0.75	1.77	0.66	1.15	0.66-1.77	1.10	-
$\Sigma\text{PCDDs/Fs}$	8302	1890	8170	1720	9010	4260	1720-9010	5559	-
	fg I-TEQ m^{-3}								
$\Sigma\text{PCDDs/Fs}$	400	83	272	67	460	151	67-460	239	-

The dominant congeners were OCDD (31%), 1,2,3,4,6,7,8-HpCDF (19%), OCDF (13%) and 1,2,3,4,6,7,8-HpCDD (12%) and all these together accounted for more than 75% of total PCDD/Fs concentration (Figure 1). The homolog pattern for $\Sigma\text{PCDDs/Fs}$ I-TEQ were in the order of OCDD (31%) > HCDF (21%) > HxCDF (13%) = OCDF (13%) \geq HCDF (12%) and other individual congeners have <5% contribution (Figure 2). High chlorinated congeners of PCDD (OCDD and HCDD) and PCDF (HxCDF, HCDF and OCDF) contributed respectively, with 43% and 47% for the $\Sigma\text{PCDD/F}$ I-TEQ (Figure 3).

In addition to the observation from the PCDDs/Fs ratio, the TEQs for PCDFs were 2-3 times higher than those of PCDDs. The characteristics of the profiles and $\Sigma\text{PCDD/F}$ ratios suggest the reaction processes driven from precursors as well as by *de novo* synthesis during combustions. The homologue profiles at sampling locations DA1, DA3 and DA5 were enriched by PCDFs, and can be classified as “source” profiles. Particularly, the pattern indicate

that the source for the homologues at these locations were not far away. Therefore, these results indicates that *de novo* synthesis probably be the main formation mechanism for the sources of the PCDD/Fs in the ambient air of New Delhi, India, which could be influenced by anthropogenic activities mainly by combustion sources such as small

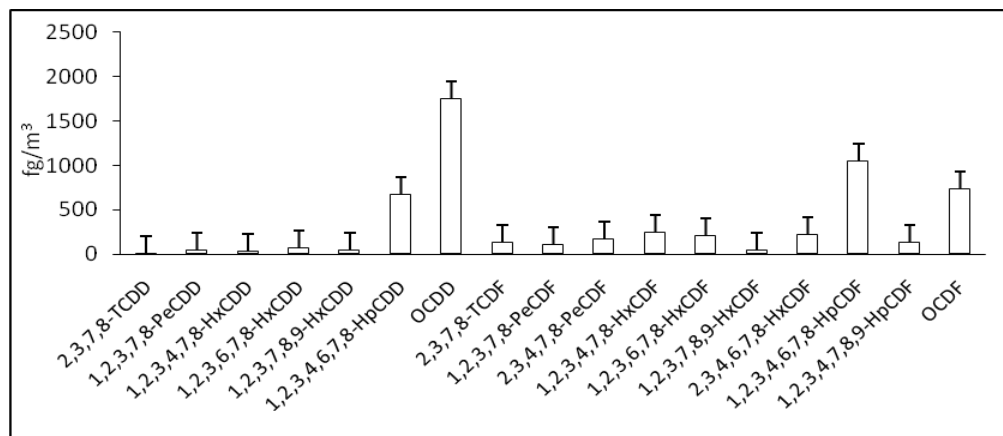


Figure 1: Concentration profiles of PCDDs/Fs congener in ambient air (PM_{10}) at New Delhi.

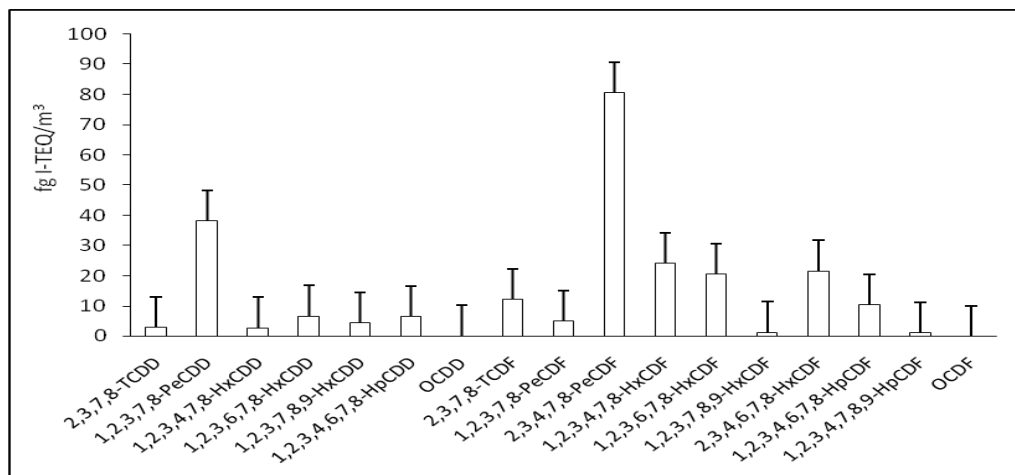


Figure 2: TEQ profiles of PCDDs/Fs congener in ambient air (PM_{10})

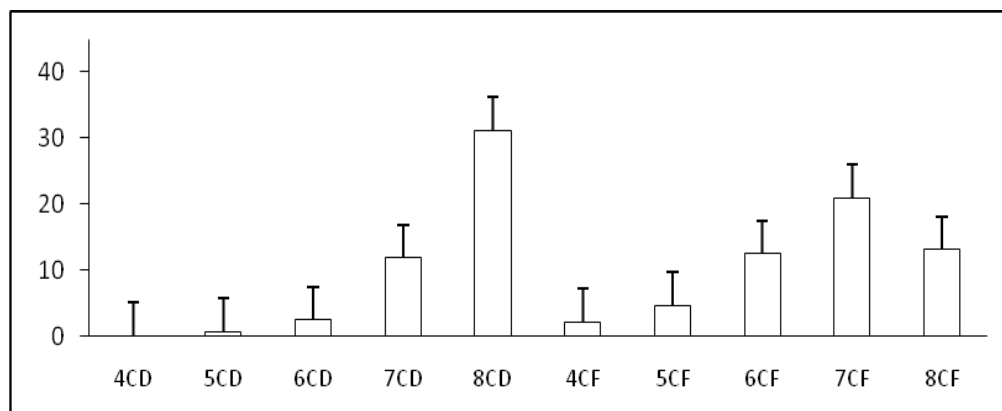


Figure 3: Percent of native PCDD/Fs homologues in ambient air (PM_{10}) at New Delhi.

diffuse combustion sources, e.g., traffic sources, domestic burning of fossil fuels, non-industrial combustion sources and also uncontrolled open mass burning cannot be ignored.

Table 2: Rough assessment of inhalation risk ($pg\ I\text{-}TEQ\ kg^{-1}\ day^{-1}$) of PCDD/Fs in New Delhi.

Locations	Concentration		PCDD/Fs inhalation	
	Air phase	($pg\ I\text{-}TEQ\ m^{-3}$)	Adult	Children
DA1	Particle phase	0.400	0.114	0.178
	Particle + gas phase*	0.571	0.163	0.254
DA2	Particle phase	0.083	0.024	0.037
	Particle + gas phase*	0.119	0.034	0.053
DA3	Particle phase	0.272	0.078	0.121
	Particle + gas phase*	0.389	0.111	0.172
DA4	Particle phase	0.067	0.019	0.029
	Particle + gas phase*	0.096	0.027	0.043
DA5	Particle phase	0.460	0.131	0.204
	Particle + gas phase*	0.657	0.188	0.292
DA6	Particle phase	0.151	0.043	0.067
	Particle + gas phase*	0.216	0.062	0.096
All locations	Particle phase	0.239	0.068	0.106
	Particle + gas phase*	0.341	0.098	0.152

*Gaseous PCDD/Fs are conservatively estimated as 30% of the total PCDD/Fs.

Diet ingestion, inhalation and dermal contact are the main pathways of direct exposure to toxic pollutants. Ambient and indoor air is potential sources of inhalation exposure to toxic substances. Dioxins are associated strongly with carcinogenesis. To ensure public safety, the tolerable daily intake (TDI) of dioxins has been set by various international agencies. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) recommended a TDI for dioxin as $1.0\ pg\ I\text{-}TEQ\ kg^{-1}\ d^{-1}$ and a warning value of $4.0\ pg\ I\text{-}TEQ\ kg^{-1}\ d^{-1}$ or $70\ pg\ to\ 280\ pg\ day^{-1}$ for 70 kg adult. The USEPA recommends that the daily inhalation exposure to dioxins should be not more than $1.0\ pg\ WHO_{98}\text{-}TEQ\ kg^{-1}\ d^{-1}$. The ATSDR assessed the non-cancer risks from dioxin exposure by setting minimal risk levels (MRLs) at $1\ pg\ kg^{-1}\ d^{-1}$. Scientific Committee for Food (SCF) of European Commission fixed a tolerable weekly intake (TWI) of $14\ pg\ WHO\text{-}TEQ/kg$ body weight for dioxins and 12 dioxin-like PCBs. In 1999, Japan established the TDI of dioxins at $4\ pg\ \text{-}TEQ\ kg^{-1}\ d^{-1}$. Daily dioxins inhalation exposure doses in New Delhi for adults and children are computed by the following equation¹⁵.

$$ED_{Inh} = (IR \times Conc_{air} \times EF)/BW$$

Where ED_{inh} is the inhalation exposure dose in $pg\ I\text{-}TEQ\ kg^{-1}\ day^{-1}$; IR is inhalation rate ($20\ m^3\ day^{-1}$ for adults and $12\ m^3\ day^{-1}$ for children); $Conc_{air}$ is the average air concentration of dioxin in $pg\ I\text{-}TEQ\ m^{-3}$; EF is exposure factor and conservatively used as 1 for this study, representing a daily exposure to the PCDD/Fs; BW is the body weight (70 kg for adults and 27 kg for children).

In this study, the gaseous PCDD/Fs were not determined. For the calculation of total TEQ concentration we conservatively used the values of 70% PCDD/Fs in particle and 30% PCDD/Fs in gaseous phase. The total TEQ values thus calculated was $341\ fg\ I\text{-}TEQ\ m^{-3}$. Table 2 showed that residents in New Delhi are seems to have low health risk from exposure to PCDD/Fs with calculated Inhalation of $0.098\ pg\ I\text{-}TEQ\ kg^{-1}\ day^{-1}$ for adult and $0.152\ pg\ TEQ\ kg^{-1}\ day^{-1}$ for children. However, the most significant uptake route of dioxins and furans is via diet. Almost 95% of total daily intake (TDI) is taken up by the food contamination. The inhalation intake doses have been reported contributing approximately 1-2% to the total daily intake¹⁶. For lack of data about PCDD/Fs diet exposure we cannot give precise total daily PCDD/Fs intake. However, according to our results of inhalations, we can tentatively conclude that the TDIs of PCDD/Fs for the residents of New Delhi, India are low at present.

Acknowledgements:

The authors express their sincere gratitude to the Member Secretary and Chairman of Central Pollution Control Board, Ministry of Environment & Forest Government of India for support to conduct the study. Authors namely, BK, SKS and RBL were highly thankful to ASEM-GTZ, Germany for sponsoring training programme at Fraunhofer-Institute for Process Engineering and Packaging, Freising, Germany and Bavarian Environment Agency, Augsburg, Germany. The assistance received from various officials of these agencies is gratefully acknowledged

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