

# PCDDs/Fs IN AMBIENT AIR AND HEALTH RISK FOR HUMAN POPULATION AT NORTH EAST COAST OF INDIA

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## Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs) are halogenated compounds. Due to their persistence and semi-volatility, they can be transported over long distances on a global scale. PCDD/DFs adsorbed to dust particles in the atmosphere<sup>1</sup> and, inhalable PM<sub>10</sub> particles could remain longer in the air and therefore cause greater concern for human health<sup>2</sup>.

Quite few studies have been conducted in India on PCDDs/Fs in atmospheric air<sup>3-7</sup>. This study was undertaken to determine the concentrations of particle bound PCDDs/DFs in rural ambient air at North East coast of India.

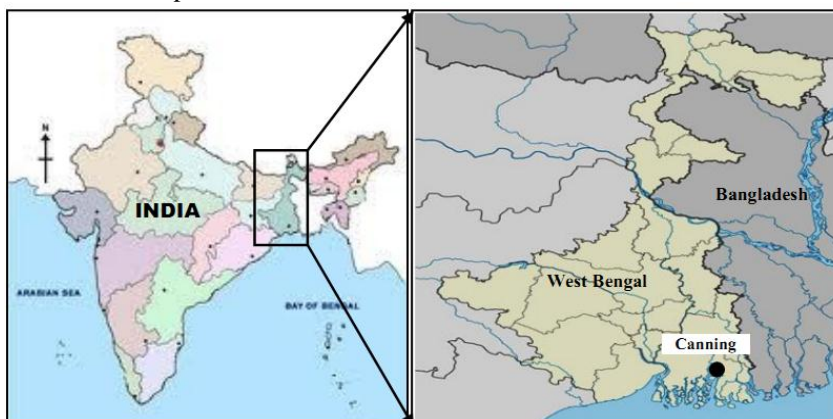


Figure 1: Map showing study location.

## Materials and Methods

### Study location and sampling

The sampling site is located at geographical coordinates of 22°19'N 88°40'E, near the north eastern coast of Bay of Bengal (Figure 1). Location is the closest gateway to Sundarbans mangrove ecosystem before the Bangladesh Border. Location lies on south of the Tropic of Cancer and has an average elevation of 4 meters (13 feet). Due to its proximity to the sea, annual ambient temperature is equable and varied between 9-29°C during September to March and, 37-42°C during April to August. Annual rainfall and humidity remain more or less uniform throughout the year with 1920 mm and about 82%, respectively. The wind directions during winter are N to NE and in summer S to SW<sup>8</sup>.

Sampling was carried out for six months during April-September 2009 in the first and second week of the each month. The air particulates (PM<sub>10</sub>) was collected on EPA glass fiber filter papers using respirable dust sampler (modified high volume sampler with cyclone for particle size cut off) (Envirotech India Ltd) for 24 hour (three eight hourly samples combined). After collection of sample filter papers were wrapped in aluminum foil and transferred to the laboratory for processing.

### Extraction and cleanup

EN 1948 methods were followed for sample extraction, cleanup and quantification<sup>9</sup>. The filter papers with air particulates were spiked with 2,3,7,8 substituted PCDD/DFs as <sup>13</sup>C<sub>12</sub>-labeled quantification standards and Soxhlet

extracted using with toluene for 24 hours. The extracts were concentrated using Rotary Vacuum Evaporator (Eyela Japan) at 40<sup>0</sup>C and followed by cleanup. Primarily extracts were clean with multi-layer silica gel column and fractionation of analytes was carried with alumina column chromatography.

#### Instrumental Analysis

Reference standard solutions of 17 PCDD/DFs congeners in nonane (CS1 to CS5 extraction spike solutions and syringe spike solutions as per EN 1948) used for instrument calibration, quantification, recovery and quality control were purchased from Wellington Laboratories Inc., Canada. HRGC coupled with a HRMS (JEOL JMS 800D, Japan) was used for identification and quantifications. The instrument was operated at high resolution (>10,000) with positive electron ionization (EI<sup>+</sup>) mode. Source and data acquired for selective ions monitoring (SIM) mode with two mass fragments of each target compound and two mass fragments of <sup>13</sup>C<sub>12</sub>-labeled isotope compounds. Verification of the resolution in the working mass range was obtained by measuring perfluorokerosene (PFK) reference peaks. Chromatographic separations were performed on a 60m × 0.25 mm ID × 0.25 μm capillary column (DB column, J&W) using helium as carrier gas. Quantification of each congener was performed by comparison of peak areas of the native compound and the corresponding <sup>13</sup>C<sub>12</sub>-labeled standard compounds (isotope dilution method). The relative response factors (RRFs) for the individual compounds were obtained by analyzing CS-1 to CS-2 standard solution mixtures using five level calibration curves<sup>9</sup>. The gas chromatograph was operated with following temperature programming: 150<sup>0</sup>C for 2 min and ramped to 190<sup>0</sup>C at the rate of 20<sup>0</sup>C min<sup>-1</sup> and then finally increased at the rate of 3<sup>0</sup>C min<sup>-1</sup> to 280<sup>0</sup>C and held for 23 min.

Analytical quality assurance and quality control procedures were conducted using method blank and recovery of target analytes by spiking <sup>13</sup>C<sub>12</sub>-labeled standards before sample extraction. In general the laboratory method blanks meet the requirements of the analytical method. Syringe standards (<sup>13</sup>C<sub>12</sub>-labeled) were added before final sample extract volume (25 μl) as recovery standards. Recovery rates of <sup>13</sup>C<sub>12</sub>-labeled internal standards determined against external standards calculated and found with the range in 74-123% for all the samples fall within the acceptable range of 50-130%<sup>9</sup>. 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 system<sup>10</sup>. The results were presented as fg m<sup>-3</sup> and their toxic equivalent in fg I-TEQ m<sup>-3</sup>.

### Result and Discussions

#### Concentrations of PCDD/Fs

The TEQ concentrations of PCDD/PCDFs in ambient air of NE coast, India ranged between 1.0 to 62.6 fg I-TEQ m<sup>-3</sup> with an average of 17.1 fg I-TEQ m<sup>-3</sup> (Fig.1). Observed values were lower than the ambient air standard of Japan (0.6 pg I-TEQ m<sup>-3</sup>) and State of Connecticut in USA (1.0 pg I-TEQ m<sup>-3</sup>). Lohmann and Jones<sup>2</sup> reported PCDDs/Fs concentrations for remote (<10 fg I-TEQ m<sup>-3</sup>) and rural (~20-50 fg I-TEQ m<sup>-3</sup>) areas worldwide. Thus, concentrations at Canning are comparable to those found in remote and rural areas.

The dominant congeners were OCDD (46%) OCDF (14%) 1,2,3,4,6,7,8-HpCDF (11%) and 1,2,3,4,6,7,8-HpCDD (10%) and accounted more than 80% of total native PCDD/PCDFs concentration (Table 1) and these are all highly chlorinated PCDD/Fs. 2,3,7,8-TCDD (29%) and 2,3,4,7,8-PeCDF (27%) congeners represent the higher This feature was also found in the air of other cities in the world<sup>2</sup>. The percent contributions of individual homolog for ΣPCDDs/Fs I-TEQ were in the order of TCDD (29%) > PeCDF (28%) > HxCDF (16%) > PeCDD (13%) and other individual congeners have <5% contribution. The OCDD and OCDF congeners contribute with <1% to the ΣTEQ (Figure 2).

Under warmer weather conditions, PCDD/DFs can undergo photochemical transformation with dechlorination process leading to more toxic congeners (if octa- and hepta-chlorinated congeners degrade to tetra- and penta-chlorinated and finally to non-toxic compounds with only three or less chlorine atoms)<sup>1</sup>. The studied area is located under the Tropic of Cancer line with strong ultraviolet radiation, warmer and highly humid environment in most times. Therefore, our results suggested that the transformation from high chlorinated PCDD/DFs into low chlorinated under such conditions may be significant. Under this study during sampling period the concentration of low chlorinated PCDD/DFs were comparatively high than higher chlorinated PCDD/DFs. Total concentrations during summer (May-July) are lower than those other months. Therefore this study clearly provides clues to link with pollution sources which reflected that PCDD/DFs concentrations could be highly influenced by anthropogenic activities all the way of combustion sources such as small diffuse combustion sources.

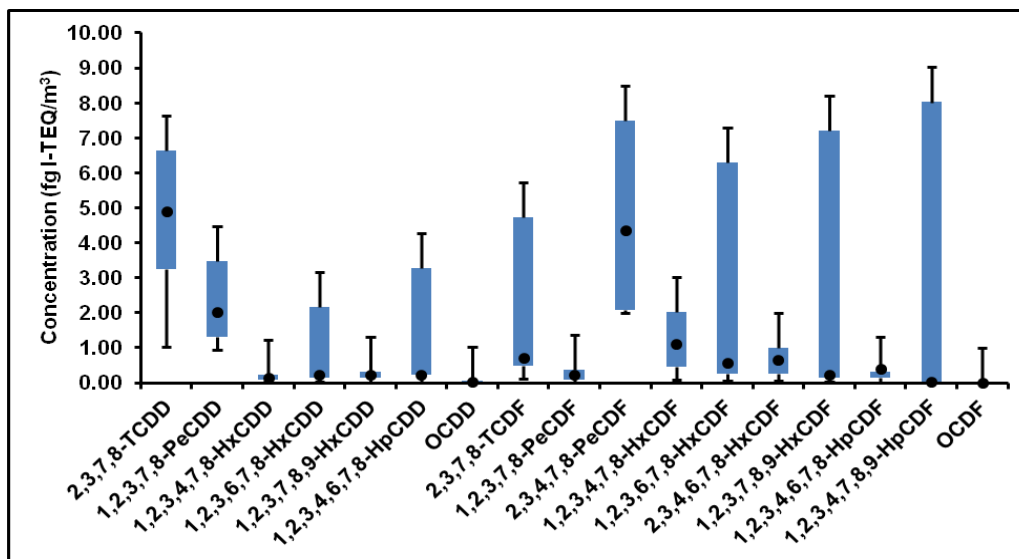


Fig. 1. Box and Whisker Plot of 17 PCDDs/Fs congeners in air particles at NE coast, India

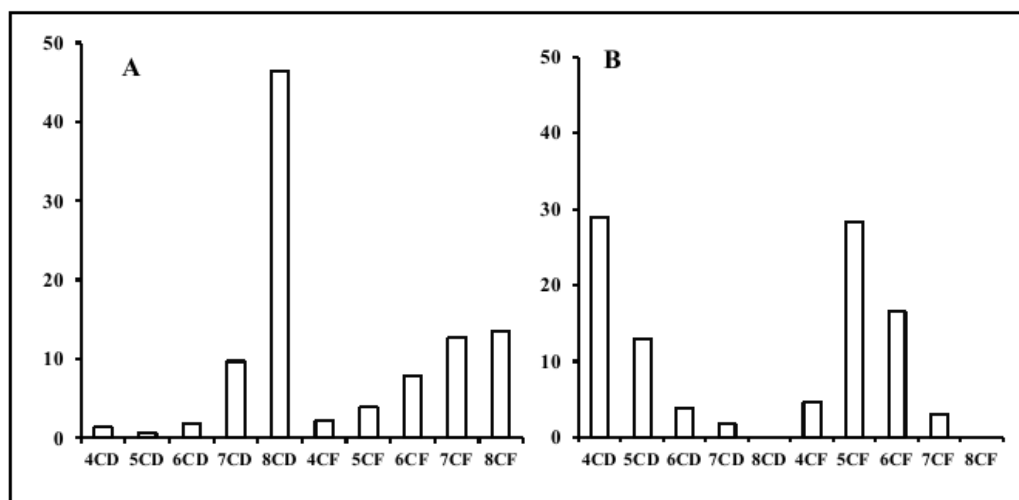


Fig. 2: Percent abundances of the ambient air (PM<sub>10</sub>) PCDD/Fs homologues at Canning, India: (A) native PCDD/Fs; (B) PCDD/Fs I-TEQ.

#### Inhalation risk assessment

To ensure public safety as far as possible the tolerable daily intake (TDI) of dioxins has been set by international agencies. The JECFA and USEPA recommended a TDI for dioxin of 1.0 pg I-TEQ kg<sup>-1</sup>d<sup>-1</sup>. European Commission fixed a tolerable weekly intake (TWI) of 14 pg WHO-TEQ/kg body weight for total dioxins. Government of Japan established the TDI of dioxins at 4 pg-TEQ kg<sup>-1</sup>d<sup>-1</sup>. Daily dioxins inhalation exposure doses for adults and children are computed by the equation after ATSDR<sup>11</sup>.

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

Where ED<sub>inh</sub> is the inhalation exposure dose in pg I-TEQ kg<sup>-1</sup> day<sup>-1</sup>; IR is inhalation rate (20 m<sup>3</sup> day<sup>-1</sup> for adults and 12 m<sup>3</sup> day<sup>-1</sup> for children); Conc<sub>air</sub> is the average air concentration of dioxin in pg I-TEQ m<sup>-3</sup>; EF is exposure factor and conservatively used as 1, representing a daily exposure to the PCDD/Fs; BW is the body weight (adult, 70 kg; children, 27 kg).

**Table 2:** Roughly Assessment of inhalation risk of PCDD/Fs for Canning, India

Ambient air phase	Concentration	$\Sigma$ PCDD/Fs inhalation (pg I-TEQ kg <sup>-1</sup> day <sup>-1</sup> )	
	(pg I-TEQ m <sup>-3</sup> )	Adult	Children
Particle phase	0.017	4.89 x 10 <sup>-3</sup>	7.60 x 10 <sup>-3</sup>
Particle + gas phase*	0.024	6.98 x 10 <sup>-3</sup>	10.86 x 10 <sup>-3</sup>

\*Gaseous PCDD/Fs are conservatively estimated as 30% of the  $\Sigma$ PCDD/Fs

In our study the gaseous PCDD/Fs were not determined. Previous studies carried out in Asian countries indicate that the range of relative particle-bound PCDD/Fs concentration is wider<sup>12</sup> i.e. from 36.4% to 71.5%. 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 24.43 fg I-TEQ m<sup>-3</sup> (Table 3). Then it was concluded that population in this area have low risk of exposure to PCDD/Fs through Inhalation of 4.89 x10<sup>-3</sup>-6.98x10<sup>-3</sup> pg I-TEQ kg<sup>-1</sup>day<sup>-1</sup> for adult and 7.60 x10<sup>-3</sup>-10.86x10<sup>-3</sup> pg TEQ kg<sup>-1</sup>day<sup>-1</sup> for children. However, diet is the most significant uptake route of dioxins and furans and about 95% of total daily intake (TDI) is taken up by the food contamination and inhalation intake has been reported approximately 1-2% to the total daily intake. So, due to lack of data about PCDD/F diet exposure, this study cannot give precise total daily intake of dioxins, However from our results of Inhalations we can conclude that the TDIs for the human population in coast of Bengal, India were very low.

#### Acknowledgement

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