LEVELS OF POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS (PCDDs/Fs) IN AIRBORNE PARTICULATE MATTER COLLECTED IN DELHI, INDIA

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Abstract

Rapid growth of the Indian cities will lead to an urban population of over 500 million in 20 years. Amongst others this implies a risk to human health and sustainable development and environment. Data on environmental levels of PCDDs/Fs in India is limited. Therefore, a dioxin laboratory was installed in Delhi, India, to fill this data gap in the near future. During training of the officials, data of PCDDs/Fs levels in Indian airborne particulate matter were produced in German laboratories. The levels range from 563 to 3592 pg WHO-TEQ/g and from 654 to 3765 pg I-TEQ/g. The detected congener pattern may be due to unorganized metal scrap recycling and uncontrolled municipal waste burning

Introduction

Rapid growth of the Indian cities will lead to an urban population of over 500 million in 20 years. This implies huge challenges for the urban development which includes issues like uncontrolled industrialization and urbanization, risk to human health and sustainable development and environment. Stockholm convention, 2001 have made efforts to eliminate and /or reduce the emissions and discharges of 12 toxics organic chemicals, also called as the "12 DIRTIES" and the chemicals are classified as persistent organic pollutants (POPs). Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzo-*p*-furans (PCDFs) were also included as POPs, with enhanced chronic toxicity.

PCDDs and PCDFs are not created intentionally but produced by human activities and natural processes. Municipal and industrial incinerators, pulp and paper bleaching, certain herbicide production are to be known as major source of dioxin to the environment.

Although some data on PCDDs/Fs levels in fish and other food products[1,2] is available for Indian subcontinent, but data on environmental levels of PCDDs/Fs is limited and there may be few studies in past for measurement of PCDDs/Fs in urban Indian cities. Utilization of wood as fuel and combustion of municipal waste, and metal scrap recycling may be the possible sources of PCDDs/Fs to the environment.

ASEM (Advisory Services in Environment Management) the executing arm of the German agency for Technical Cooperation (GTZ) in India provided assistance in development of infrastructural facilities for monitoring of dioxin-furan at national level at the headquarters of Central Pollution Control Board (CPCB) at Delhi, India. The infrastructure facilities and instrumentation (JEOL JMS 800D HRGC-HRMS) have been fully established and these are functional recently for wide scale assessment of POPslevels in the country.

This present communication deals with PCDDs/Fs levels in Delhi airborne particulate matter, which has been processed and analyzed at German laboratory during the training of CPCB officials.

Method and Materials

Ambient Air Sampling

The ambient air sampling locations were covered as traffic, industrial and residential from the National Ambient Air Quality Monitoring Network in Delhi. Air borne particulate matter (PM_{10}) was monitored and sampled at six different locations representing residential industrial and traffic intersections in Delhi on EPA glass fibre filter papers during March 2007 using respirable dust sampler (RDS APM 460 Dx, Envirotech, India). 24 hourly samples (6AM to 6AM) were collected operating the instrument at an average ambient air flow 1.0 m^3/min.

ITO traffic intersection is a busy crossing with two thermal power plants (one coal based and other gas based) in vicinity at Delhi has been sampled three fold in different week days were, wrapped in aluminum foil and were shipped to Germany in paper bags.

Chemicals and Solvents

Solvents (acetone, dichloromethane, n-hexane, and cyclohexane) for organic trace analysis and chemicals (sodium sulfate, silver nitrate, potassium hydroxide, aluminum oxide) were purchased by *Lfu* and *IVV* (Germany) from Merck (Darmstadt, Germany). EPA 1613 the dioxin/furan standards solutions in nonane (CS-1 to CS-5, Wellington Laboratories Inc. Guelph, Ontario, Canada) were used for instrument calibration, quantification, recovery and quality control.

Extraction and Cleanup

Sample extraction and cleanup was performed in the analytical laboratory for dioxin and furan of the *Fraunhofer Institute* for Process Engineering and Packaging (*IVV*) in Friesing, Germany. Filter papers with particulate matter were spiked with the 17 2,3,7,8 substituted PCDD and PCDF as $^{13}C_{12}$ 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 primarily cleaned by modified silica column and alumina. Before analysis $^{13}C_{12}$ 1,2,3,4 TCDD added as recovery standard. Two method blank samples were carried out in analogy and to check any cross contamination or loss of the pollutant.

Instrumental Analysis

Identification and quantification of PCDDs/Fs were performed in a laboratory at Bavarian Environmental Agency, Augsburg, Germany by HRGC-HRMS (Thermo, Finnigan MAT 95) coupled to auto sampler using a positive electron ionization (EI+) source operating Selective Ion mode (SIM) at a 10000 resolution (10% valley definition).

Chromatographic separation was performed on a weakly polar 60 m x 0.25 ID x 0.25 um (DB-XLB) capillary column. 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 $^{13}C_{12}$-labeled standard (isotopic 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), these LOQ values are given as "<" in Table 1.

Results and Discussion

PCDDs/Fs levels detected in particulate matter of Indian urban air samples are presented in terms of pg/g in Table 1.I-TEQ and WHO-TEQ levels are also reported in terms of pg/m^3, however, it has to be stated, that these values reflect particle bound PCDDs/Fs only and are not considered as total PCDDs/Fs data.

Table1: Levels of PCDDs/Fs in Indian airborne particulate matter

Sampling date (March 2007)	**2/3**	**4/5**	**21/22**	**8/9**	**14/15**	**20/21**	**22/23**	**21/22**
Sampling site*	**ITO (T)**	**ITO (T)**	**ITO (T)**	**R-1**	**I-1**	**R-2**	**R-3**	**I-2**
					pg/g			
2,3,7,8-TCDD	31	11	<9	12	<29	39	39	29
1,2,3,7,8-PeCDD	622	176	<121	80	706	131	309	166
1,2,3,4,7,8-HxCDD	475	76	376	48	609	42	225	148
1,2,3,6,7,8-HxCDD	1160	159	681	138	1335	152	503	431
1,2,3,7,8,9-HxCDD	725	187	472	56	1041	132	304	250
1,2,3,4,6,7,8-HpCDD	9528	2176	5574	794	14382	3210	4684	4521
OCDD	23159	5840	16386	7904	34346	9409	10030	11159
2,3,7,8-TCDF	1817	623	614	870	1606	929	777	696
1,2,3,7,8-PeCDF	1802	471	546	526	1204	534	895	435
2,3,4,7,8-PeCDF	3030	654	1101	568	2311	643	1445	745
1,2,3,4,7,8-HxCDF	3952	734	1943	546	4495	778	2186	990
1,2,3,6,7,8-HxCDF	3251	619	1499	489	3499	594	2093	840
1,2,3,7,8,9-HxCDF	221	<73	<219	<63	<476	<102	154	<105
2,3,4,6,7,8-HxCDF	3598	643	1739	400	4414	402	1832	1226
1,2,3,4,6,7,8-HpCDF	14955	2711	7540	1802	26595	2037	8719	5045
1,2,3,4,7,8,9-HpCDF	1790	293	1009	178	2972	295	1099	648
OCDF	9629	1339	4759	1293	23163	1013	5424	3747
Total	**79745**	**16712**	**44239**	**15702**	**122677**	**20340**	**40719**	**31079**
I-TEQ (1998)	**3762**	**812**	**1472**	**654**	**3765**	**822**	**1929**	**1082**
WHO-TEQ (2005)	**3408**	**755**	**1227**	**563**	**3592**	**740**	**1766**	**997**
					pg/m^3			
I-TEQ (1998)	**0.652**	**0.125**	**0.281**	**0.079**	**0.250**	**0.063**	**0.429**	**0.143**
WHO-TEQ (2005)	**0.593**	**0.118**	**0.234**	**0.068**	**0.241**	**0.056**	**0.393**	**0.130**

***- T= (Traffic intersection), R= (Residential), I= (Industrial)**

PCDDs/Fs levels in the samples ranged from 563 to 3592 pg WHO-TEQ/g and 654 to 3765 pg I-TEQ/g or from 0.056 to 0.593 pg WHO-TEQ/m^3 and 0.063 to 0.652 pg I-TEQ/m^3. The measured levels are in the same order of magnitude as literature data on urban ambient air concentration measured in Europe, US and Japan in the 1990ies[3], Spain[4], South Africa[5].

With respect to the traffic dominated sampling site at ITO traffic junction, a significant influence of the week day is visible, since increasing levels were obtained for Sunday to Monday (4th/5th March 2007), Wednesday to Thursday (21st /22nd March 2007) and Friday to Saturday (2nd /3rd March 2007), However, an additional influence of precipitation cannot be excluded and in this context a further in-depth study of PCDDs/Fs in particulate matter is prepared and to be undertaken at Central Pollution Control Board at Delhi.

The congener patterns of 2,3,7,8-substituted PCDDs/Fs of three different sampling sites (traffic, residential and industrial) are presented in Fig 1. There is no significant difference between the sampling sites. The dominance of higher chlorinated dioxins and furans is typical for particle bound PCDDs/Fs. With respect to lower chlorinated PCDDs/Fs, PCDFs exceed the PCDDs levels significantly, which may be attributable to fossil fuels sources as expected for urban locations.

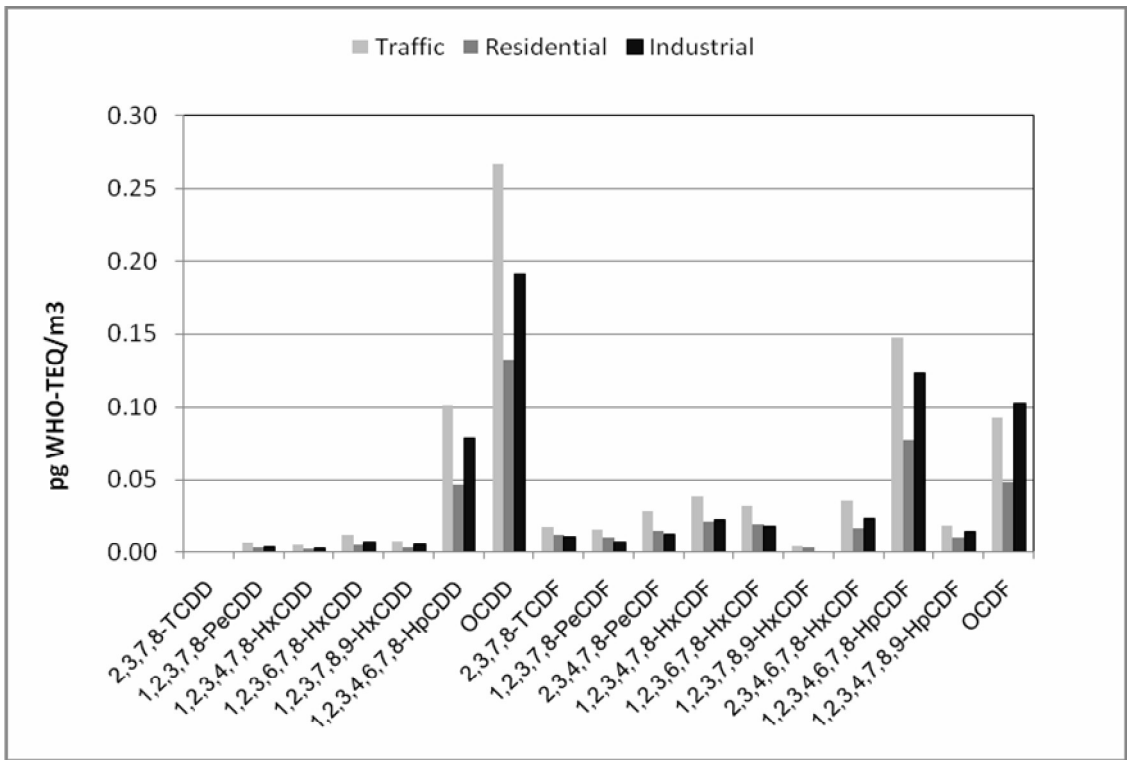

Fig.1: Congener pattern of 2,3,7,8-sustituted PCDDs/Fs in airborne particulate matter at Delhi, India

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References

1 Min NH, Min TB, Watanabe M, Kunisue T, Monirith I, Tanabe S, Sakai S, Subramanian A, Sasikumar K, Viet PH, Tuyen BC, Tana TS Prudente MS. *Environ Sci Technol* 2003; 37:1493
2 IPEN 2005: *http://www.toxiclink.org*
3 Lohamann R, Jones KC. *The science of the Total Environment* 1998;219:53
4 Abad E, Caixach J, Rivera J Gustems L, Massague G, Puig O. *Science of The Total Environment* 2004;334:279
5 Batterman S, Chernayak S, Gounden Y, Matoonae M *Organohalgen Compounds* 2006; 68:1111