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Contamination by Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Dibenzo*p*-furans (PCDFs) in Selected Solid Wastes: An Implication of Potential Sources of Pollution

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ABSTRACT

In this study seventeen congeners of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans (PCDDs/Fs) in selected solid wastes analyzed by HRGC-HRMS applying the isotopic dilution technique. Recovery rates of spiked ¹³C₁₂-labeled standard compounds were calculated and found within the accepted ranges for all the samples. The observed concentration of 17 PCDDs/Fs was 13763.00 pg g⁻¹, 256.66 pg g⁻¹, 1857.63 pg g⁻¹ and 9.64 pg g⁻¹ dw, in sewage sludge, paper mill sludge, industrial contaminated soil and flyash, respectively. The 2,3,7,8-TeCDD substituted toxic equivalent (I-TEQ) was 77.068 pg I-TEQ g⁻¹, 11.319 pg I-TEQ g⁻¹, 96.316 pg I-TEQ g⁻¹ and 0.401 pg I-TEQ g⁻¹, respectively. OCDD, Hep-CDD, OCDF, Hep-CDF and TCDF were the dominant congeners. In this study, the ratio of $\sum PCDD/\sum PCDF$ was 10.39, 4.91, 4.28 and 3.97 for sewage sludge, paper mill sludge, soil and flyash, respectively which indicates that PCDD/Fs sources in the studied samples were contaminated significantly with the mechanism of the precursor formation routes. The concentration levels observed in this study were lower than recommended guideline values.

Key Words: PCDDs/Fs, sludge, contaminated soil, flyash, HRGC-HRMS.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-*p*-furans (PCDFs) are listed by Stockholm Convention as one of 12 persistent organic pollutants (POPs). These compounds primarily formed from inefficient combustion processes such as biomass combustion in incineration plants, sintering plants, cement kiln plants and unintentional by-products from the synthesis of various chlorinated products [1-2]. Once emitted, these substances show a strong tendency to bind to particulate material and can transported to other environmental compartments [3-4]. Due to their resistance to chemical, physical and biological degradation they have been transported world-wide, affecting regions far from their original sources and ubiquitously found in all environmental media of the earth [5].

TeCDD (2, 3, 7, 8 tetrachorinated-dibenzo-*p*-dioxin) is the most toxic congener of this group has high metabolism transformation resistance in the body. All the substituent with 2, 3, 7, 8 position are characterized by increased toxicity. Only 2, 3, 7, 8 TeCDD is supposed to cause the human cancerogenity. These compounds have a wide range of acute and chronic health effects, including cancer, neurological damage, reproductive disorders, immune suppression, birth defects, and are also suspected endocrine disruptors [6]. In 1997, the International Agency for

Research on Cancer (IARC) [7] declared the 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) as a "known human carcinogen".

Even, air represents the dominant medium of global transport of organic pollutants and the site of important degradation loss, soil and sediment are important reservoirs of organic pollutants globally. Vegetation acts as an efficient scavenging medium from the atmosphere and as a major vector of terrestrial food chain [8-9].

Being lipophilic compounds, PCDD/F adsorb to the organic carbon of the soil, and due to the low mobility and high persistence, these contaminants accumulate in the soil and sludge. Fly ashes from coal burning plants were found to be potential source of PCDDs/Fs. The presence, movement and behavior of these compounds in soil/sludge have been intensely studied world-wide [10-12]. Solid waste from municipal and industrial wastewater treatment processes may act as sources of pollution due to high affinities of organic pollutants for the organic matter rich media. Sludge-treated soil have received an increasing level of research attention in the past 25 years [13]. Contamination of Pulp and paper mill effluents and sludge with polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs) has been reported, where, chlorine is used for bleaching process with thermal activities [14-15].

Quite few studies have been conducted in India and reported for occurrence and distribution of PCDDs/Fs compounds in different matrices such as soil and sediments [15-16], biological samples [17-18], human milk [19-20] and atmospheric air [21-24]. This study was undertaken to assess the concentrations of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-*p*-furans (PCDDs/Fs) in selected samples of contaminated soil, sewage sludge, pulp & paper mill sludge and flyash from thermal power plant.

MATERIALS AND METHODS

Chemicals and Solvents

Solvents (acetone, methanol, dichloromethane, toluene, n-hexane) for organic trace analysis, and chemicals (sodium sulphate, potassium hydroxide, silver nitrate, sulfuric acid) were purchased from Merck India. For the manual cleanup silica (70-210 mesh), and alumina both from Supelco (USA) were employed as adsorbents in glass columns at atmospheric pressure. Standard reference solutions of 17 dioxin/furans congeners in nonane (CS1 to CS5, extraction spike solutions and syringe spike solutions after EN 1948) [25] used for instrument calibration, quantification, recovery and quality control were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada).

Description of Samples

Samples of each sample origin were collected from different locations in India. Approximately 500 grams of sample was collected in replicates, and after removing pebbles and wood sticks and other materials the replicate samples were mixed thoroughly to ensure that the sample collected was truly representative of each location. Then, subsamples was subsequently taken and transferred to clean wide mouth amber glass bottle. After proper labeling the sample bottles sealed with PTFE caps were transported to laboratory and kept at -4^{0} C until further chemical treatment. Sample origins were selected as:

Sample	Sample origin description
Contaminated soil	Treatment, storage and disposal facility (TSDF) of hazardous waste
Sewage sludge	Sewage treatment plant (STP)
Paper mill sludge	Pulp and paper mill
Flyash	Coal fired thermal power plant

Sample Extraction and Cleanup

Standard methods after EN 1948 [25] were followed for sample extraction and cleanup. About 2 g of sample was extracted by Soxhlet with toluene for 24 hours. The extracts were concentrated to near 5 ml using vacuum rotary evaporator (Eyela, Japan) at 40° C. The final extracts were treated with sulphuric acid before the cleanup. The cleanup process was based on the sequential use of open chromatographic multilayer silica and basic alumina columns. In brief cleanup of the extracts started using multilayred column (30x300 mm) packed with absorbent in following order from bottom to up: 2.0 g activated silica, 5.0 g KOH silica, 1.0 g activated silica, 10.0 g sulfuric impregnated silica; 5.0 g silver nitrate coated silica and followed by 5.0 g sodium sulphate. After loading the concentrated sample extracts with three washings on to the column, the analytes were eluted with 150 ml n-hexane and concentrated to near 2.0 ml with a rotavapor. The final cleanup of the concentrated elute was performed on

aluminum oxide column (22x250 mm) using 25 g activated aluminum oxide (basic) and 10 g sodium sulphate. The elutions of the analytes were carried out as fraction1: 60 ml n-hexane, fraction 2: 120 ml of 2% dichloromethane in n-hexane and fraction 3: 200 ml of dichloromethane/n-hexane (1:1 v/v). Fraction 1 & 2 was discarded as they contain unwanted analytes but fraction 3 which contained PCDDs/Fs was retained and concentrated to near 1.0 ml. The concentrated extracts finally dried under a gentle stream of purified nitrogen. 25 μ l of 1,2,3,4-substituted TCDD and 1,2,3,7,8,9-HxCDD as ¹³C₁₂-labeled syringe spiked recovery standard in nonane was added and the vials were sealed for instrumental analysis.

Instrumental Analysis

Purified extracts were analysed by HRGC-HRMS on a GC 6890 series gas chromatograph (Agilent) equipped with a autosampler and coupled to an mass spectrometer (JEOL, JMS 800D, Japan), using positive electron ionization (EI+) source and operating in the SIM mode at high resolution (>10,000). Verification of the resolution in the working mass range was obtained by measuring perfluorokerosene (PFK) reference peaks. Chromatographic separations were achieved with a DB-dioxin (J&W, USA) fused silica capillary column (60 m x 0.25 mm ID x 0.25 μ m film thickness) with helium as a carrier gas in splitless injection mode (1µl). The temperature program was: 150 $^{\circ}$ C hold for 2 min and ramped to 190 $^{\circ}$ C at a rate of 20 $^{\circ}$ C min⁻¹, and then finally increased to 280 $^{\circ}$ C (at the rate 3 $^{\circ}$ C min⁻¹) and held for 23 min.

Quantification of each congener was carried out by isotopic dilution method using comparison of peak areas of the native compound and the corresponding ${}^{13}C_{12}$ -labeled standard compounds. The relative response factors (RRFs) for the individual compounds were obtained by analyzing CS-1 to CS-5 standard solution mixtures using five level calibration curves [25].

Analytical Quality Control

Analytical quality assurance and quality control procedures were conducted using method blank and recovery of target analytes by spiking ${}^{13}C_{12}$ -labeled standards before sample extraction. Syringe standards (${}^{13}C_{12}$ -labeled) were added before final sample extract volume (25 µl) as recovery standards. Recovery rates of labeled compounds were calculated and found within the range of 50-97 percent for all the samples. Toxic equivalent quantities (TEQ) were calculated by multiplying the concentration of individual PCDD/PCDF congener with the corresponding toxicity equivalent factors (TEFs) presented by international system [26]. The moisture contents of the samples calculated gravimetrically to report dry weight basis. The results were presented as pg g⁻¹ and pg I-TEQ g⁻¹ dw.

Congeners	Sewage sludge	Paper mill sludge	Soil	Flyash
2,3,7,8-TCDD	1.18	3.04	12.35	0.12
1,2,3,7,8-PeCDD	9.79	3.76	44.14	0.09
1,2,3,4,7,8-HxCDD	2.42	0.59	20.39	0.05
1,2,3,6,7,8-HxCDD	26.53	2.00	34.89	0.20
1,2,3,7,8,9-HxCDD	9.34	1.93	13.87	0.11
1,2,3,4,6,7,8-HpCDD	1273.16	21.38	445.73	1.72
OCDD	11231.72	180.56	934.48	5.40
2,3,7,8-TCDF	222.03	20.95	93.43	0.09
1,2,3,7,8-PeCDF	49.83	2.64	40.10	0.10
2,3,4,7,8-PeCDF	25.70	2.15	24.50	0.14
1,2,3,4,7,8-HxCDF	49.23	2.04	20.04	0.13
1,2,3,6,7,8-HxCDF	11.74	0.98	8.18	0.14
1,2,3,7,8,9-HxCDF	14.05	0.94	9.24	0.12
2,3,4,6,7,8-HxCDF	2.64	1.02	4.73	0.12
1,2,3,4,6,7,8-HpCDF	291.73	3.81	43.39	0.57
1,2,3,4,7,8,9-HpCDF	13.60	0.00	10.28	0.08
OCDF	528.31	8.88	97.90	0.45
∑PCDDs/Fs	13763.00	256.66	1857.63	9.64
∑PCDDs	12554.14	213.26	1505.84	7.70
∑PCDFs	1208.86	43.41	351.79	1.94
D/F ratio	10.39	4.91	4.28	3.97

Table 1: PCDDs/Fs concentrations (pg g⁻¹) in Solid Wastes

RESULTS AND DISCUSSION

PCDDs/PCDFs Concentrations

The concentrations of PCDD/PCDFs and their I-TEQs in selected solid wastes are presented in **Table 1 and Table 2**, respectively. We report the concentrations of all 2, 3, 7, 8-substituted PCDD/PCDF congeners, the dioxin, furan and total International-TEQ values. A series of PCDDs and PCDFs were identified in studied samples. The seven 2, 3, 7, 8-substituted PCDDs and the ten 2, 3, 7, 8-substituted PCDFs were normalized by multiplying their measured concentrations by the appropriate I-TEFs. The sum of these products yields the I-TEQ values which express these analyte concentrations as a single number, equivalent to that of a toxicity derived exclusively from 2,3,7,8-TCDD.

The concentration of 17 PCDDs/Fs was observed as 13763.00 pg g⁻¹, 256.66 pg g⁻¹, 1857.63 pg g⁻¹ and 9.64 pg g⁻¹, in sewage sludge, paper mill sludge, contaminated soil and flyash, respectively. The 2,3,7,8-TeCDD substituted toxic equivalent (I-TEQ) was 77.068 pg I-TEQ g⁻¹, 11.319 pg I-TEQ g⁻¹, 96.316 pg I-TEQ g⁻¹ and 0.401 pg I-TEQ g⁻¹, respectively.

Table 2: Toxic Equivalency	(TEQ) of PCDDs/Fs (pg	I-TEQ g ⁻¹) in Solid Wastes
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Congeners	Sewage sludge	Paper mill sludge	Soil	Flyash
2,3,7,8-TCDD	1.18	3.04	12.35	0.12
1,2,3,7,8-PeCDD	9.79	3.76	44.14	0.09
1,2,3,4,7,8-HxCDD	0.24	0.06	2.04	0.01
1,2,3,6,7,8-HxCDD	2.65	0.20	3.49	0.02
1,2,3,7,8,9-HxCDD	0.93	0.19	1.39	0.01
1,2,3,4,6,7,8-HpCDD	12.73	0.21	4.46	0.02
OCDD	1.12	0.02	0.09	< 0.01
2,3,7,8-TCDF	22.20	2.09	9.34	0.01
1,2,3,7,8-PeCDF	2.49	0.13	2.00	0.01
2,3,4,7,8-PeCDF	12.85	1.07	12.25	0.07
1,2,3,4,7,8-HxCDF	4.92	0.20	2.00	0.01
1,2,3,6,7,8-HxCDF	1.17	0.10	0.82	0.01
1,2,3,7,8,9-HxCDF	1.40	0.09	0.92	0.01
2,3,4,6,7,8-HxCDF	0.26	0.10	0.47	0.01
1,2,3,4,6,7,8-HpCDF	2.92	0.04	0.43	0.01
1,2,3,4,7,8,9-HpCDF	0.14	< 0.01	0.10	< 0.01
OCDF	0.05	< 0.01	0.01	< 0.01
Σ PCDDs/Fs	77.068	11.319	96.316	0.401



Figure 1: Percent of native PCDDs/Fs group homolog in solid wastes

The finding of this study was compared with the similar study from other countries. The results of this study for PCDDs/Fs in soils were in agreement with the observations reported in soils from Taizhou area, China [11] and South Africa [27]. PCDDs/Fs in studied soil samples were lower than reported in contaminated soil from Barcelona, Spain [28], Pyuongtak, Korea [2], European Union member countries [27] and Guiyu, China [29]. However, the concentrations of PCDDs/Fs in contaminated soil analyzed in this study were higher than those PCDDs/Fs in soils from South Korea [30], Switzerland [31] and Zhejiang Province, China [32]. PCDD/Fs in flyash of power plant were reported similar to our results by Eljarrat et al., [33]. However, high level of TEQ for PCDD/Fs reported in fly ash samples collected from Mauritius [34] and China [35]. The PCDD/Fs I-TEQ in sludge from this study was comparable with those published in literature [36-37]. However, lower than those PCDDs/Fs in sewage sludge from Catalonia, Spain [33] and Beijing, China [38], but higher than those PCDDs/Fs in sewage sludge from Beijing [35] and Australian sewage sludge [10].

Congener and group homolog of PCDDs/Fs

The concentrations of individual congeners were dominated by OCDD; 1, 2, 3, 4, 6, 7, 8-Hep-CDD; OCDF; 1, 2, 3, 4, 6, 7, 8-Hp-CDF and TCDF (**Figure 1**). Considering homologous groups an increase in the PCDDs concentrations was observed as chlorination level increased (Low chlorinated < High chlorinated). Group homolog of OCDD (50-82%) and Hep-CDD (8-24%) contributed predominantly for native concentration of total PCDDs/Fs. This has been reported by other workers [11,36] that the homologue group pattern of the PCDDs/Fs in sewage sludges is dominated by the Hep-CDD and OCDD. This homologue distribution indicated that soil-bound PCDD/Fs in this region are highly chlorinated, suggesting that the less chlorinated homologues may have undergone much faster degradation than the highly chlorinated ones and/or that the highly chlorinated homologues may be the dominant ones produced in the sources of the pollution [39]. These results imply that OCDD is more persistent in the environment than OCDF, 1,2,3,4,6,7,8-HepCDD, and 1,2,3,4,6,7,8-HepCDF.The contribution of each congener to the TEQ was calculated using the International toxicity equivalent factors (I-TEFs) and the analyzed concentrations in all the samples shown in Table 2. As low chlorinated congener of PCDDs and PCDFs assigned with comparatively high TEF values, thus significantly increasing the total PCDD/F I-TEQ value.



As shown in **Figure 2**, group homolog of TCDD (2-29%), PeCDD (13-46%), TCDF (2-29%), and PeCDF (11-20%) were the main contributors for \sum PCDDs/Fs I-TEQ in selected solid samples. Similar to our study contamination of sludges by lower chlorinated PCDDs/Fs were reported [40].

PCDDs/Fs formed at high temperature either by the "de novo" formation or by precursor formation. In general, the ratio of $\sum PCDD/\sum PCDF$ was previously reported to be a good indicator for possible formation processes or emission sources of the PCDD/Fs. The ratio of $\sum PCDD/\sum PCDF$ from chemical reactions formation is greater than 1, (preferable with PCDD formations) while *de novo* synthesis during combustion processes normally shows a ratio of $\sum PCDD/\sum PCDF$ less than 1 (preferable with PCDF formations) [34,41]. In this study, the ratio of $\sum PCDD/\sum PCDF$

was calculated, and the values were 10.39, 4.91, 4.28 and 3.97 for sewage sludge, paper mill sludge, soil and flyash, respectively. Generally, sewage sludge samples are characterized by ratio of more than 1 (>1) [42]. It indicates that PCDD/Fs sources in the studied samples are significantly formed by the mechanism of the precursor routes.

Comparison with Environmental guidelines

The results obtained from this study for selected solid waste was compared with, standards for maximum concentration of PCDDs/Fs in soil and sludge stipulated by various other countries (**Table 3**). There are no common international guidelines for PCDD/Fs in soils and sludge. The established guidelines vary among different country. In general, the guideline levels for soils and sewage sludge tend to be lower than the levels for soils of industrial areas [13,43-45]. The Indian government has not yet established a guideline on PCDD/F contaminated soils and solid wastes for evaluating their environmental risks. In recent years, many countries have used the following guidelines [46]. Soils containing PCDD/Fs at 5 pg I-TEQ g⁻¹ or lower should be safe for all agricultural purposes. Soils with 5–40 pg I-TEQ g⁻¹ are not restricted for cultivation of foodstuffs, but these soils should be avoided for agricultural uses if the PCDD/F levels in foodstuffs found bioconcentrated. Soils with I-TEQ greater than 40 pg I-TEQ g⁻¹ should not be used for growing plants that accumulate PCDD/Fs. Zhang et al. [46] also recommended that remediation actions be required in playgrounds, residential and industrial areas if soil contains TEQ > 100 pg I-TEQ g⁻¹, not 10,000 pg I-TEQ g⁻¹, respectively. **Table 3** shows that the PCDDs/Fs in studied soil, sludge and flyash were lower than guideline values recommended by various environmental agencies.

CONCLUSION

This study was focused on PCDDs/Fs assessment in selected solid wastes such as sewage sludge, industrial sludge, industrial contaminated soil and flyash. The study concluded that solid wastes are potential sources of pollution. Samples show the presence of PCDDs/Fs which is matter of concern for risk assessment of these pollutants during the safe disposal of the wastes. Further intensive study with more samples is needed to verify origin of these toxic pollutants.

Country	Agric. soil	Ind. soil	General soil	Sewage sludge	Ref.	
EU countries	-	-	-	100	[13]	
Italy	-	5000	-	-	[42]	
Netherland	-	1000	-	-	[43]	
Germany	5-40	10,000	-	100	[13,44]	
Sweden	10	250	-	-	[44]	
Finland	500	10,000	-	-	[44]	
Japan	-	-	1,000	-	[45]	
ΠĒΔ	_	_	_	300	[47]	

Table 3: Standards for maximum concentration of PCDD/Fs in soil and sewage sludge (pg I-TEQ g⁻¹ dw)

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