Dioxins and furans in industries and processes using chlorine base chemicals

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Abstract

The study aimed to measure 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), dioxins congeners and precursors in industries and related processes involving chlorine base material . The representative samples were collected from pulp and paper mill, plastic and PVC, chloro-organic and chlorine base industries, thermal power plants, brick kilns, crematorium and incinerators and land fills. 2,3,7,8-TCDD was found only in 7% of the total 85 samples analysed. The highest level of 0.27 ng g^{-1} of 2,3,7,8-TCDD was found in the ash collected from hospital-waste incinerator. 2,3,7,8-TCDD ranged from BDL to 0.2 ngL^{-1} / ng g^{-1} in the effluent and sludge samples collected from pulp and paper mills, plastic and PVC and chlor-organic industries. Tri, tetra and hexachlorodibenzo-p-dioxins (tri, tetra and hexa-TCDDs) and octachlorodibenzofuran (OCDF) were found in the effluent and sludge samples. Tri, hexa and hepta polychlorinated biphenyls (PCBs) and tri and penta chlorophenols (TCP & PCPs) and others were also found in the samples.

1 Introduction

Dioxins and Furans are created inadvertently by a host of industrial activities in which chlorine based compounds are exposed to high temperature in the presence of organic material. There considerable evidences that dioxins are spread over the entire globe in all media in soil, air and water [1-2]. The sources of environmental contamination of these compounds include municipal waste, hospital waste, automobiles operation, fossil fuel combustion and contaminated commercial products. These are formed as a result of natural processes, and also as by-products in the manufacture of specific chlorinated chemicals [3-5]. There are 75 positional dioxins and 135 furans. The exposure to these contaminants results in adverse health effects in human and experimental animals like liver necrosis, and neurobehavioral changes, skin lesions, reproductive and endocrine dysfunction. The most toxic isomer is 2,3,7,8- tetrachlorodibenzo-p-dioxin (2,3,7,8–TCDD). WHO has set a tolerable daily intake of 1-4 pg of dioxin/kgbw/day.

Inefficient incineration may allow some combustible material to remain unburnt. The usual temperature range, at which municipal incinerators operate, is 1000-1100^{O}C. The main combustible components being fed into a municipal incinerator include different types of papers, newspaper, magazine paper, corrugated box board, textile fabric, wood, leather and plastic rubber. Dioxins are also produced when chlorinated plastics are burnt. In pulp and paper mills chemical bleaching with chlorine may produce dioxins and furans. Although many analytical techniques have been described for the analysis of PCDD, the most specific method uses GC-MS/MS[6]

2 Material and Methods

EPA 1613 [7] method was used for the analysis of dioxins and furans. The Varian CP-3800 Gas Chromatograph / Mass Spectrometer with Data System (GC/MS/DS) equipped with temperature programming, and required accessories, including syringes, gases, and a capillary column was used. A fused silica capillary column (60 m x 0.32 mm ID) coated with BP-5, 1.0 μm film thickness has been used to isolate and confirmation of dioxins and furans.

2.1 Sampling sites

The following sampling sites of industrial combustion and related processes involving chlorine base materials were selected

- Industries : Pulp and paper Mills, Plastic and PVC Industries, Chloro-organics and chlorine base Industries, Coal combustion processes, Hospital waste incinerator and Thermal Power Plant
- Others : Crematorium, Brick Kiln and Landfill Sites

Samples of different matrices were collected from each identified industry viz. source water, effluent, sludge soil and final product. In case of incinerator, crematorium and brick kilns bottom and fly ash samples were collected for analysis. The soil samples were collected from abandoned landfill sites.

3 Results and Discussion

3.1 Pulp and Paper Mills

Pulp and paper mills using either chlorine or chlorine dioxide for bleaching were identified and sampled. . The mill using chlorine for bleaching process has shown 2,3,7,8-TCDD, dioxin congeners and precursors contamination. In Paper Mill effluent PPM-1 (1st set), 0.12 ngL^{-1} of 2,3,7,8-TCDD was detected. In PPM-1 (2nd set), 0.06 and 0.10 ngL^{-1} of 2,3,7,8-TCDD were detected in secondary treated and primary clarifier effluent respectively (Table-1). 2,2,3,4,4',5-hexaPCB was found in the final effluent (Table-1). Naphthalene, biphenyl, and 3,3'-dimethyl biphenyl were found in the final effluent. In the sludge sample acetamide, thioxanthene and phenanthrene were only detected (Table-1).0.01ng g^{-1} of 2,3,7,8-TCDD was found in the bleached pulp sample of PPM-2. In PPM-4, the effluent sample showed the presence of 1,3,6,8-TCDD and 2,4,5-trichlorobiphenyl.Dioxin contamination was not found in the samples of sludge from primary clarifier, agriculture soil, writing paper, and pulp mill effluent. In PPM-5, in treated effluent, sludge treated and soil sample from high rate transpiration system (HRTS), the dioxin contamination was below detection limit. In paper mill (PPM-6), the samples of effluents from bleached plant, sludge and ash from boiler, the dioxin contamination was below detectable limit. In PPM-7, the samples of effluent before treatment showed the presence of 1,3,6,8- TCDD and 2,4,5-tri-chlorobiphenyl , but in the sludge sample, 2,5-biphenyl furan was found (Table 1) .

Table 1: Dioxins and furans in Pulp and paper mills

Industry	Sample set	2,3,7,8-TCDD Conc. (ng g^{-1} or ngL^{-1})	Dioxins & furan congeners	Other aromatic hydrocarbons
PPM-1 (1st set)	Final effluent	0.12	Benz(b)benzo (3,4)cyclobuta (1,2-e)dioxin	2,2'3,4,4',5-HxPCB,
	Waste from pulp industry	ND	ND	Acetamide, thioxanthene and phenanthrene
PPM-1 (2nd set)	Secondary treated effluent	0.06	ND	Naphthalene
	Primary clarifier effluent	0.10	ND	Biphenyl, 3,3' dimethyl biphenyl
PPM-2	Final treated effluent	ND	ND	Anthracene, Endosulfan
	Bleached pulp	0.01	ND	Endosulfan
PPM-3	Secondary sludge from ETP	ND	2,5-Diphenyl Furan	ND
PPM-4	Effluent before treatment	ND	1,3,6,8-TCDD	2,4,5-trichlorobiphenyl
PPM-5	Raw effluent at inlet to clarification	BDL	ND	ND
	Final treated effluent	BDL	ND	ND
PPM-6	Bleached plant effluent	BDL	ND	ND
	Final treated effluent	BDL	ND	ND
PPM-7	Effluent before treatment	BDL	1,3,6,8-TCDD	2,4,5-trichlorobiphenyl
	Final treated effluent	BDL	ND	ND
	ETP Secondary sludge	BDL	2,5-Diphenyl Furan	ND

3.2 Chloro-organic and Chlorine Base Industries

Samples were collected from two chlor-alkali plants and four of the industries producing chlorine base products like trimethylacetyl chloride, nitrophenol, hydrochloric acid (HCl), sodium hypochlorite, chlorine, chlorosalicyclic acid, chloralhydrate, chlorobenzenes. 2,3,7,8-TCDD was below detectable level in all the samples analysed. 1,2,4-TriCDD, 2,3,3'4,5,5',6-heptachlorobiphenyl and tri and pentachlorophenol congeners were found in the effluent sample.

3.3 Plastic and PVC Industries

Samples were collected from the industries using vinyl chloride monomer (VCM), polyvinylchloride (PVC), ethylene dichloride (EDC) and chlorine as their raw materials. In PVC-1, 0.12 ngL^{-1} of 2,3,7,8-TCDD concentration was found in the final treated effluent. In PVC-3, the 2,3,7,8-TCDD concentration was 0.15 ngL^{-1} and 0.2 ngL^{-1} in effluent before treatment and final treated effluent respectively (Table-2). In PVC-2, 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin, trichlorobiphenyl, 2,3,4,5-tetrachlorophenol and trichloronapthalene were found in effluent before treatment (after super decanter) (Table-2). In PVC-3, carbazole and anthracene were identified in effluent before treatment from vinyl chloride monomer plant of the industry (Table-2). In PVC-3, 1,1-biphenyl, benzofuran, p,p'-DDE and benzo(∝)pyrine were identified in the effluent before treatment from suspended PVC plant. Anthracene, isobenzofuran, naphthalene, o',p'-DDE and phenanthrene were found in effluent before treatment from emulsion of PVC plant. 3,3,4,4-tetrachlorobiphenyl and p,p'-DDE were found in the final treated effluent (Table-2). Octachlorodibenzofuran (OCDF), hexachlorobenzene, endosulphan and 4-methyl dibenzofuran were found in the sludge sample (Table-2).

Table 2: Dioxins and furans in plastic and PVC industries

Industry	Sample set	2,3,7,8-TCDD conc. (ng g^{-1} or ngL^{-1})	Dioxins & furan congeners	Other aromatic hydrocarbons
PVC-1	Final treated effluent	0.12	1,2,3,4-TCDD	ND
PVC-2	Effluent before treatment (after super decanter)	ND	1,2,3,4,7,8-HxCDD	Trichloro bihenyl, 2,3,4,5-TCP, Trichloronapthalene
PVC-3	Effluent before treatment from vinyl chloride monomer plant	ND	ND	Carbazole, Anthracene
	Effluent before treatment from suspended PVC plant	0.15	ND	1,1-biphenyl, benzofuran, p,p'-DDE, benzo(∝)pyrene
	Final Treated Effluent	0.2	ND	3,3,4,4-tetrachloro biphenyl, p,p'-DDE
	Oxycatalyst sludge	ND	Octachlorodibenzofuran	Hexachlorobenzene, Endosulphan, 4-methyldibenzofuran

ND: Not detectable

3.4 Others Sites

In the ash sample collected from hospital waste incinerator, the concentration of 2,3,7,8-TCDD was found to be 0.27 ng g^{-1}. Bibenzyl and endosulfan were found in the sample (Table-3). In ash collected from thermal power plant incinerator, crematoria and brick kilns, the concentration of 2,3,7,8-TCDD was below detectable level.

Table 3: Dioxins and furans in incinerators and processes exposed to high temperatures

Sample	2,3,7,8-TCDD Conc. (ng g^{-1} or ngL^{-1})	Dioxins & Furan Congeners	Other aromatic hydrocarbons
Hospital Incinerator ash	0.27	ND	Bibenzyl, Endosulfan,
Thermal Power plant ash	ND	ND	ND
Crematoria ash	ND	ND	Phenanthrene
Brick Kilns	ND	ND	ND

ND: Not detectable

The study showed that pulp and paper mills using chlorine for bleaching indicated the presence of 2,3,7,8-TCDD compared to the industries using chlorine dioxide. ND to 0.12 ngL^{-1} of 2,3,7,8-TCDD was detected in the effluent and bleached pulp of paper mill using chlorine for bleaching. It can thus be concluded that pulp and paper mills can reduce dioxin formation by substituting chlorine with chlorine dioxide. PVC industries using VCM, PVC, EDC as raw material showed the presence of 2,3,7,8-TCDD, 1,2,3,4-TCDD, 1,2,3,4,7,8-hexaCDD and OCDF in effluent and sludge samples. 2,3,7,8-TCDD contamination was detected in the ash sample collected from hospital waste incinerator, which indicates that the hospital waste was undergoing incomplete combustion.

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