

Dioxin (PCDDs) and Furan (PCDFs)

**- Critical Persistent
Organic Pollutants (POPs)**



**CENTRAL POLLUTION CONTROL BOARD
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EDITORIAL

Polychlorinated dibenzo-para-dioxin (PCDDs) and Polychlorinated dibenzofuran (PCDFs) are chlorinated aromatic compounds having tremendous toxic effects, carcinogenicity and persistence in the environment; hence these Persistent Organic Pollutants (POPs) are real threats to the environment and existence of mankind.

In view of their hydrophobic and lipophilic properties, strategic minimization of their formation is the immediate need through process control, abatement and development of awareness leading to their reduction and elimination. In recent years, various regulations have been introduced in the country to deal with such hazardous and persistent organic pollutants under Environment (Protection) Act, 1986. The Stockholm Convention on Persistent Organic Pollutants deals with dioxin and furan sources and steps to be taken to reduce emission of these extremely toxic substances by adopting Best Available Technology (BAT).

Recognizing the need for awareness and strategic management of these persistent organic pollutants, an attempt has been made to highlight various technical aspects and environmental implications of dioxin and furan in the present issue of 'Parivesh' Newsletter. The efforts made by my colleagues Sh. Abhijit Pathak, Mrs. Kavita Yadav, Sh. Sanjay Kumar, Dr. C. S. Sharma, Dr. S. D. Makhijani and Dr. B. Sengupta for compiling and collating information for this issue are appreciated. We hope that the information contained in the newsletter will be useful to all the stake holders.

(V. Rajagopalan)
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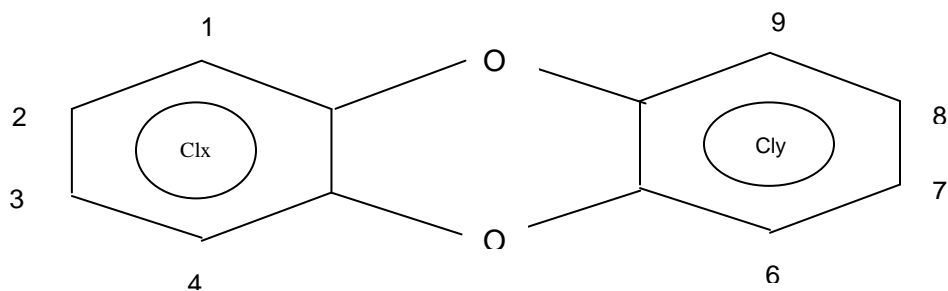
CONTENTS

	<u>Page No.</u>
1.0 Introduction	1
2.0 Physico-chemical Properties of Dioxin and Furan	3
3.0 Sources of Dioxin and Furan in Environment and their Pollution Potential	5
4.0 Toxicity of Dioxin and Furan	12
• Pathways of Human Exposure	13
• Effects on Human Health	13
5.0 Environmental Transformations of Dioxin and Furan	14
• Abiotic Transformations	14
• Bio-Transformation and Bio-Degradation	14
• Bio-Accumulation	14
6.0 Dioxin and Furan contamination in Environment – Global Status	15
• Dioxin in Air environment	16
• Dioxin in Aquatic environment	17
• Dioxin in Soil and Sediments	17
• Dioxin in Plant Tissues (Vegetation)	19
• Dioxin in Tissues of Fishes and Aquatic Organisms	19
• Dioxin in Tissues of Terrestrial Organisms	19
• Dioxin in Human Tissues	20
7.0 Dioxin in Indian Environment	20
8.0 Episodal Pollution related with Dioxin and Furan	22
• Yusho Accident, Japan, 1968	22
• Yu-Cheng Accident, Taiwan, 1980	22
• Seveso Accident, Italy, 1976	22
• Contamination of Poultry Food with PCDDs, USA, 1997	23
• Contamination of Soil with 'Agent Orange', Vietnam	23
9.0 Environmental Standards for Dioxin and Furan	23
10.0 Environmental Monitoring Techniques for Dioxin and Furan	25
11.0 Dioxin and Furan - Emission Control from Critical Processes	31
• Dioxin Emission Control at Incinerators	31
• Dioxin Emission Control at Chemical Waste Treatment Processes	32
• Dioxin Emission Control at Cement Kilns	33
12.0 Global Developments against Persistent Organic Pollutants (POPs)	33
References / Further Readings	34

1.0 INTRODUCTION

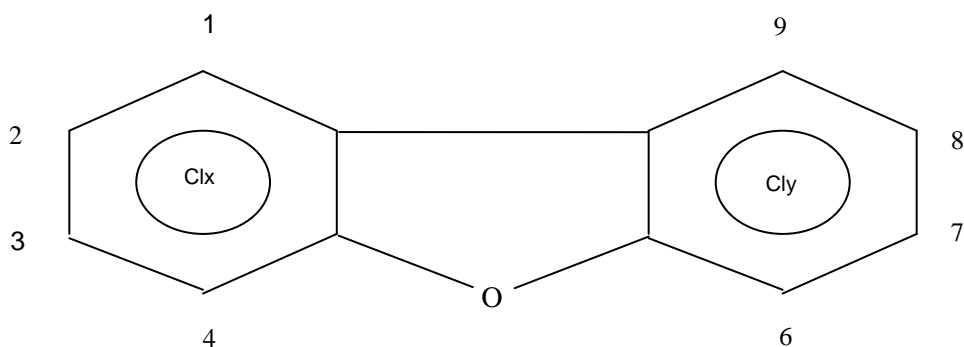
The polychlorinated dibenzo-para-dioxin (PCDDs) and polychlorinated dibenzo-furan (PCDFs) are two series of tri-cyclic chlorinated aromatic compounds having different levels of chlorine substitution in their parent molecules. These compounds do not occur naturally, nor they are produced intentionally. In fact these are the byproducts of industrial and pollution control related operations, barring few catastrophic or accidental origins like volcanoes, forest fires and accidental fires etc.

The PCDDs and PCDFs have oxygenated tri-cyclic molecules (Fig. 1 & 2). Structurally two oxygen atoms bind two benzene rings at 5th and 10th position in dibenzo para-dioxin to form tri-cyclic structure, whereas, in dibenzo-furan, one oxygen atom binds a biphenyl molecule to become tri-cyclic. There are eight substitution positions of chlorine in both Dioxin and Furan parent molecule, resulting into 75 PCDDs and 135 PCDFs positional isomers respectively, substituted with 1-8 chlorine atoms.



$x + y = 1$ to 8 (*Clx* and *Cly* are numbers of chlorine atoms attached to two different benzene rings)

Fig. 1 : Structure of Polychlorinated dibenzo-para dioxin (PCDDs)



$x + y = 1$ to 8 (*Clx* and *Cly* are numbers of chlorine atoms attached to two different benzene rings)

Fig. 2 : Structure of Polychlorinated dibenzo furan (PCDFs)

Certain dioxin and furan are also reported to contain bromine in place of chlorine and even have combined substitution with bromine and chlorine atoms. The inventory of PCDDs and PCDFs isomers according to their level of chlorine substitution are presented in Table 1.

Table 1: Isomers of Dioxin (PCDDs) and Furan (PCDFs)

No. of Chlorine atoms in molecule	Dioxin (PCDDs)	No. of Isomers		Furan (PCDFs)	No. of Isomers	
		Total	Toxic		Total	Toxic
1	Mono - chloro dibenzo-para dioxin	2	-	Mono - chloro dibenzo furan	4	-
2	Di - chloro dibenzo-para dioxin	10	-	Di - chloro dibenzo furan	16	-
3	Tri - chloro dibenzo-para dioxin	14	-	Tri - chloro dibenzo furan	28	-
4	Tetra - chloro dibenzo-para dioxin	22	5	Tetra - chloro dibenzo furan	38	8
5	Penta - chloro dibenzo-para dioxin	14	7	Penta - chloro dibenzo furan	28	14
6	Hexa - chloro dibenzo-para dioxin	10	7	Hexa - chloro dibenzo furan	16	12
7	Hepta - chloro dibenzo-para dioxin	2	1	Hepta - chloro dibenzo furan	4	2
8	Octa - chloro dibenzo-para dioxin	1	-	Octa - chloro dibenzo furan	1	-
Total PCDDs		75	20	Total PCDFs	135	36

PCDDs and PCDFs are serious threat to public health due to their high persistence in the environment. The most toxic and extensively studied representative of the dioxin, 2,3,7,8 tetra-chloro dibenzo para-dioxin (2,3,7,8 TCDD) has been identified as class-I carcinogen, meaning “known human carcinogen”. These compounds have extraordinary toxic properties and are teratogenic, mutagenic and carcinogenic (IARC, 1978). Besides cancer causing effects, exposure to dioxin can also cause severe reproductive abnormalities, developmental problems, immune system damage and interference with regulatory hormonal functions. There exist no safe level of exposure to dioxin.

2.0 PHYSICO-CHEMICAL PROPERTIES OF DIOXIN AND FURAN

Dioxin (PCDDs) and Furan (PCDFs) are structurally related halogenated aryl hydrocarbons exhibiting some common properties. These are non-polar, poorly water-soluble, lipophilic compounds (having affinity to lipids or fats) generally resistant to chemical breakdown through acid-base reaction, oxidation-reduction and even hydrolysis. The degree of lipophilicity and stability of PCDDs and PCDFs also increases with degree of chlorine substitution in their parent molecule. These compounds are not occurring naturally and even their synthesis and isolation in the laboratory are difficult. Taylor *et al.* (1985) was succeeded to synthesize and isolate all the 22 isomers of Tetra-chlorinated dibenzo-para dioxin (TCDDs). Methods of synthesis and melting points of Dioxin are presented in Table 2.

Table 2: Synthesis methods and melting points of some PCDDs

Dioxin Isomers	Methods of Synthesis	Melting point (°C)
1 – chloro dibenzo-para dioxin	Reaction between Chatecol + Chlorobenzene	80 – 90
2 – chloro dibenzo-para dioxin		80 – 89
1,3 –di- chloro dibenzo-para dioxin		113.5 – 114.5
2,3 – di-chloro dibenzo-para dioxin		163 – 164
2,3,7 – tri-chloro dibenzo-para dioxin		157 – 158
1,3,7,8 – Tetra-chloro dibenzo-para dioxin		193.5 – 195
2,7 – di-chloro dibenzo-para dioxin	Pyrolysis of Chloro-phenols	209 – 210
2,3,7,8 – tetra-chloro dibenzo-para dioxin		305 – 306
2,3,6,8 – tetra-chloro dibenzo-para dioxin		219 – 219.5
1,2,4,6,7,9 –hexa-chloro dibenzo-para dioxin		238 – 240
Octa-chloro dibenzopara dioxin		330
2,8 – di-chloro dibenzo-para dioxin	Cyclization of Chloro-phenoxy-phenol	150.5 – 151
1,2,4 – tri-chloro dibenzo-para dioxin	Reaction between Chatecol + Chloro-nitrobenzene	128 – 129
1,2,3,4 – tetra-chloro dibenzo-para dioxin		188 – 190
2,3,7,8 – tetra-chloro dibenzo-para dioxin	Chlorination of chloro-dibenzo dioxin	305 – 307
1,2,3,4,7 – penta-chloro dibenzo-para dioxin		195 – 196
1,2,3,4,7,8 – hexa-chloro dibenzo-para dioxin		275

Source: ICPS/Environment Health criteria – 88; World Health Organization

Water solubility of dioxin isomers varied widely. The most toxic and extensively studied dioxin 2,3,7,8 – TCDD (2,3,7,8 – tetra-chloro dibenzo-para dioxin) has lipophilic characteristic but hydrophobic in nature having little water solubility, while high solubility in most of the organic solvents (Table 4). The water solubility characteristics of important dioxin is presented in Table 3.

Table 3: Solubility of selected Dioxin (PCDDs) in water

Dioxin isomers	Solubility in water (gram per litre)	
	At 20 °C Temperature	At 40 °C Temperature
1,3,6,8 – Tetra-chloro dibenzo-para dioxin	$(3.2 \pm 0.2) * 10^{-7}$	$(4.4 \pm 0.4) * 10^{-7}$
1,2,3,7 – Tetra-chloro dibenzo-para dioxin	$(4.3 \pm 0.1) * 10^{-7}$	$(12.7 \pm 0.8) * 10^{-7}$
1,2,3,4,7 – Penta-chloro dibenzo-para dioxin	$(1.2 \pm 0.1) * 10^{-7}$	$(4.6 \pm 0.1) * 10^{-7}$
1,2,3,4,7,8 – Hexa-chloro dibenzo-para dioxin	$(4.4 \pm 0.1) * 10^{-9}$	$(19.0 \pm 0.1) * 10^{-9}$
1,2,3,4,6,8 – Hexa-chloro dibenzo-para dioxin	$(2.4 \pm 0.3) * 10^{-9}$	$(6.3 \pm 0.2) * 10^{-9}$
Octa - chloro dibenzo-para dioxin	$(0.4 \pm 0.1) * 10^{-9}$	$(2.0 \pm 0.2) * 10^{-9}$

Source: ICPS/Environment Health criteria – 88; World Health Organization

Table 4: Solubility of 2,3,7,8 TCDD in various organic solvents

Organic Solvents	Solubility of 2, 3, 7, 8 TCDD	
	(Gram per litre)	(Gram per Kg)
O – Di-chloro benzene	1.8	1.4
Chlorobenzene	0.8	0.72
Perchloroethylene	0.68	0.48
Chloroform	0.55	0.37
Benzene	0.47	-
Acetone	0.09	-
Dimethyl sulphoxide	<0.1	< 0.1
Methanol	0.01	0.01

Source: ICPS/Environment Health criteria – 88; World Health Organization

3.0 SOURCES OF DIOXIN AND FURAN IN ENVIRONMENT AND THEIR POLLUTION POTENTIAL

Dioxin (PCDDs) and Furan (PCDFs) are not produced commercially, as there are no known technical uses of these compounds. These are undesirable by-products of chemical manufacturing processes such as - chlorinated phenols and their derivatives, chlorinated di-phenyl ethers, poly-chlorinated bi-phenyls (PCBs) and other industrial processes involving chlorine such as pulp and paper industries. Waste incineration and other combustion processes are also known to generate dioxin and furan. The possible contamination of the environment through these sources is presented in Fig. 3.

- ***Synthesis of Dioxin for Research***

Most of the individual Dioxin (PCDDs) and Furan (PCDFs) have been successfully synthesized for research purposes (Table 2) and characterized by High Resolution Gas Chromatography – High Resolution Mass Spectroscopy (HRGC-HRMS), Ultraviolet Spectroscopy (UV-Spectroscopy), Infra-red Spectroscopy (IR-Spectroscopy), X-Ray analysis and also by Nuclear Magnetic Resonance (NMR) techniques.

- ***By-Products of Industrial Processes***

Dioxin and Furan are formed as by-products during the manufacturing of chlorinated phenols, chlorinated di-phenyl ether and hexachlorobenzene. The generation of PCDDs and PCDFs during production of various chlorinated organic compounds is presented below.

- ***During Manufacture of 2,4,5 Tri-Chloro Phenol***

2,3,7,8 TCDD may be formed alongwith the commercial manufacturing of 2,4,5 tri-chloro phenol from 1,2,4,5 tetra- chloro benzene. In industrial process, this substitution reaction takes place at 180 °C temperature with methanol as solvent. Generally the pressure in this reaction rises to about 7 Kpa. As the reaction is exothermic, the temperature of reaction mixture may go up further under pressure and unwanted TCDDs are formed when the temperature reaches 230 °C – 240 °C. Few industries use ethylene glycol as solvent to avoid high pressure, but this operation needs special precautions as the production of ethylene oxide may spontaneously raise the temperature above 180 °C and the reaction proceeds rapidly in uncontrolled manner to generate relatively more TCDDs. Solvent recovery process removes TCDD from the product but it goes into bottom residues.

➤ ***During Manufacture of other Chlorinated Products***

During the manufacturing of 2,4 di-chloro-, 2,4,6 tri-chloro-, 2,3,4,6 tetra-chloro and pentachlorophenols, TCDDs and TCDFs are formed as by-products. Generally commercial production is practiced both by chlorination of phenol using various catalyst or through alkaline hydrolyses of appropriate chloro-benzenes to produce chloro-phenols during which PCDDs and PCDFs are produced.

➤ ***During Commercial Production of Chlorinated Di-Phenyl Ether***

PCDDs and PCDFs are formed simultaneously with the commercial production of chlorinated di-phenyl ether and hexachlorobenzene.

➤ ***Contamination of Commercial Products with Dioxin***

Production equipments are often used for manufacturing of different chemicals or batch. If the equipments are not cleaned properly, there are the chances of contamination of products with residual dioxin. For instance the manufacturing equipment is used for production of 2,4,5 Tri-chloro-phenoxy acetic acid (2,4,5-T) during first batch and subsequently the same equipment is used again for production of 2,4 di-chloro phenoxy acetic ester (2,4-D) without thorough cleaning, there are significant chances of contamination of 2,4-D with 2,3,7,8 TCDD.

Table 5 (a): Contamination of Commercial Products with Dioxin

Commercial Products	Dioxin contamination
Agent Orange	The herbicide may get 2,3,7,8-TCDD contamination during its formulation as a mixture of butyl ester of 2,4,5-Trichlorophenol and 2,4 -D.
Hexachlorophene	The bactericide, an intermediate product of 2,4,5 T production from 2,4,5 Trichloro phenols
Chlorophenols	Extensively used as insecticides, fungicides, mold inhibitors, antiseptic and disinfectant. Tri-chloro-, Tetra-chloro- and Penta-chloro-phenols and their salts are used for wood preservation. Penta chlorophenol is used as fungicide during paper and pulp manufacturing process and for several other purposes like in cutting oils and fluids, leather tanning, glue manufacturing, paints, and outdoor textiles. Chlorophenols may contain PCDDs and PCDFs besides other contaminants as by-product.
Polychlorinated biphenyls (PCBs)	Polychlorinated biphenyls (PCBs) commercial preparation may be contaminated with PCDFs as byproduct.
Chlorophenyl Ether	Commercially available compounds used as herbicide, di-phenyl ethers like 1,3,5 trichloro-2-(4-triphenoxy) benzene (CNP), 2,4 dichloro-1-(4-nitrophenoxy) benzene (NIP) and 2,4 dichloro-1-(3-methoxy-4-nitrophenoxy) benzene(X-52) are reported to have PCDDs and PCDFs contamination.

Commercial Products	Dioxin contamination
Hexa-chlorobenzene	It is used to control wheat bunt, and fungal growth reported to have OCDD, HCDFs and OCDF contamination.
Rice Oil	Rice oil was reported as contaminated with PCBs, PCDFs and Poly chlorinated terphenyls (PCTs) in Japan and Taiwan during 1968 and 1979 respectively.

Table 5 (b): Commercial Products suspected with Dioxin contamination

Common / Commercial Name	IUPAC Name
2,4,5-T	2,4,5-Trichloro-phenoxy acetic acid
2,4,5-T esters	n-Butyl or butoxy-ethyl or iso-octyl esters of 2,4,5-Trichloro-phenoxy acetic acid
2,4,5-T salts	Dimetyl-amine salts of 2,4,5-Trichloro-phenoxy acetic acid
Fenoprop	Esters of 2-(2,4,5-Trichloro-phenoxy) proanoic acid
Erbon	Ethyl esters of 2-(2,4,5-Trichloro-phenoxy) –2,2-dichloro-propanoic acid
2,4,5-Trichlorophenol	2,4,5-Trichlorophenol
Fenochlorphos	O, O –Dimethyl-O-2,4,5-trichlorophenoxy- phosphono-thioate
Trichlornate	O-Ethyl-O-2,4,5-trichloro phenyl ethyl phosphono thioate.
Hexachlorophene/Isobac 20	2,2'-Methylene-bis-(3,4,6-trichlorophenol)

Source: ICPS / Environment Health Criteria – 88; World Health Organization

- **Chemical Accidents**

Any accidents in chemical processing industries dealing with Chlorine and organics together can cause emissions of Dioxin and Furan.

- **Thermal Degradation of Commercial Products**

The pyrolysis of commercial PCBs, even in sealed quartz ampoules in presence of air have been reported to yield about 30 major and more than 30 minor PCDFs. Thus uncontrolled burning of PCBs would be an important source of Furan (PCDFs). Significant amount of Dioxin and Furan may be

Dioxin and Furan Sources in Environment

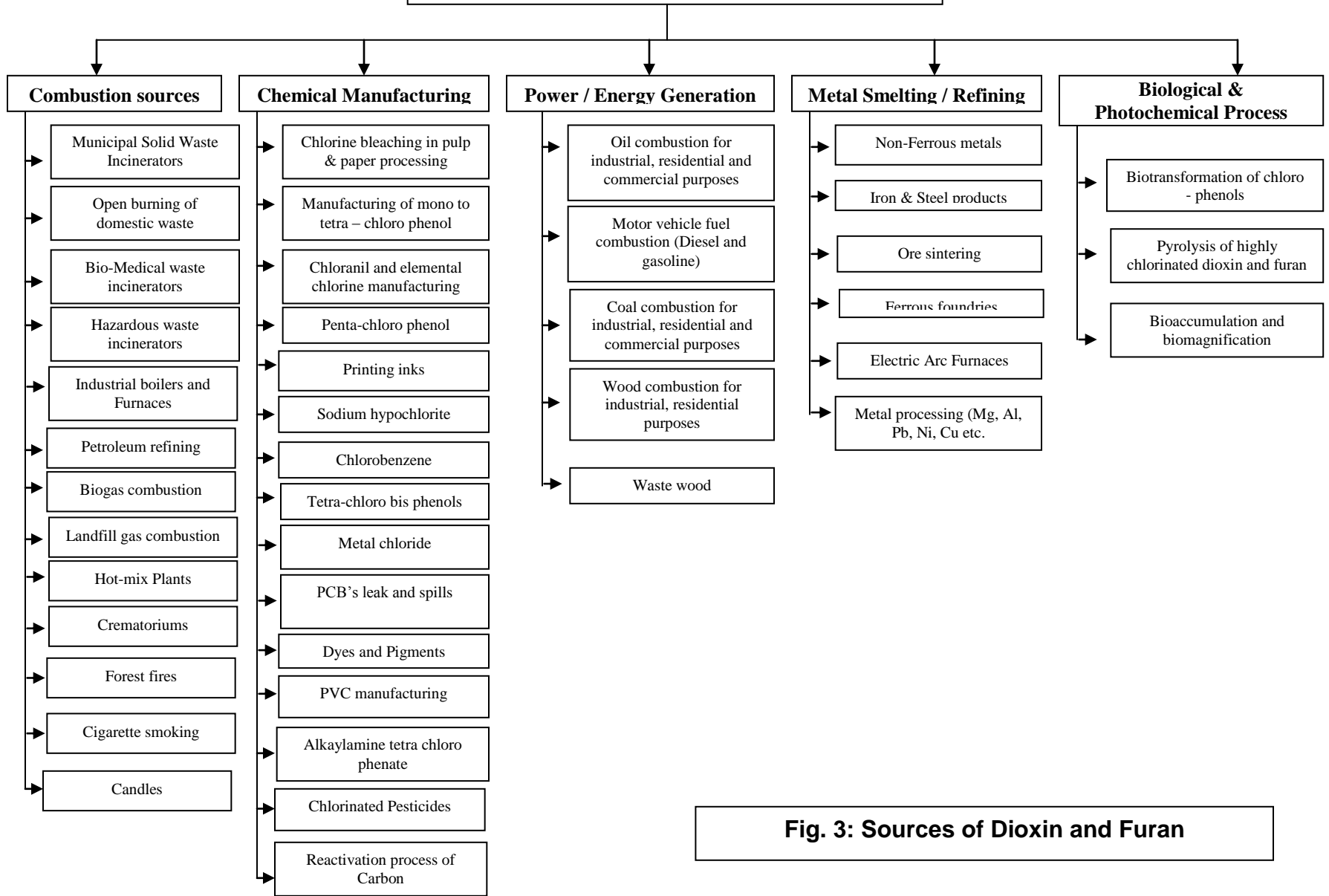


Fig. 3: Sources of Dioxin and Furan

formed due to pyrolysis of chlorobenzene and polychlorinated bi-phenyl ethers. Conversion of PVC (Polyvinyl Chloride) to Dioxin (PCDDs) and Furan (PCDFs) has also been reported. Burning of PVC can lead to Hexa- and Hepta-chlorinated congeners of Dioxin and Furan (Tetra- to Hepta- i.e. 4 to 7 chlorine substituted congeners).

- ***Disposal of Industrial / Municipal Solid Waste***

Improper disposal of industrial waste such as waste oil sludge may contaminate soil and sediments. Waste oil refinery produces sticky sludge having various toxic organic constituents including PCBs, PCDDs and PCDFs. Similarly chlorinated organic compounds including Dioxin and Furan are reportedly found in fly ash and bottom ash. These compounds are formed due to incomplete thermal reaction, poor combustion and thorough sublimation particularly in air pollution control system (APCS) of solid waste incinerator.

- ***Incineration of Sewage Sludge / Municipal Solid Waste / Hospital Waste***

Dewatered sludge of STP and CETP (with domestic sewage), if incinerated may produce dioxin and furan. The emission of PCDDs and PCDFs are however lower than incineration of Municipal Solid Waste. Incomplete combustion of hospital wastes containing halogenated organics can produce high levels of PCDDs and PCDFs in fly ash and bottom ash.

- ***Metal Treatment and Processing Industries***

Industries involving high temperature processes like copper smelting and electric arc furnaces in steel processing also have emission of PCDDs and PCDFs.

- ***Exhaust Emission of Leaded Gasoline driven Vehicles***

The cars using leaded gasoline (0.15g/l) with dichloro-ethane scavenger was reported to have 30 – 540 pg/Kg of TCDDs equivalent in their exhaust on average. The dichloro-ethane is assumed as the precursor for Dioxin (PCDDs) and Furan (PCDFs) formation.

- ***Fires, Accidents, Coal and Wood Burning***

Dielectric fluids in the transformer oil mainly contain PCBs and chlorinated benzenes. Any fire accident in these electrical items may produce emissions of PCDFs and PCDDs. PCBs are precursor of PCDFs formation at high temperature combustion, whereas chlorinated benzenes are responsible for dioxin emission.

It has also been reported that low levels of PCDDs and PCDFs are emitted during coal and wood burning. Although dioxin and furan concentrations are very low but large quantity of flue gas during coal and wood burning contribute large dioxin emissions.

- ***Pulp and Paper Industries***

In Pulp and Paper industries, the bleaching of pulp is undertaken by chlorine and chlorinated compounds, which react with phenols available in pulp forming PCDDs and PCDFs during high pressure and temperature digestion. Pentachlorophenol is used in paper industries as fungicide, which may also be converted to dioxin.

- ***Asphalt Mixing (Hot-Mix Plants)***

During melting and mixing of asphalt, PCDDs and PCDFs are formed and emitted to the environment. The road construction activities are contributing extensive dioxin emission through hot mix plants.

- ***Photochemical Processes***

Photochemical de-chlorination of higher PCDDs and PCDFs may results into lower chlorinated isomers. For example - Octa CDD and Octa CDF may be converted into Hepta-, Hexa-, Penta- and even Tetra – isomers, which are more toxic than their parent congener.

Source-wise Pollution Potential of Dioxin and Furan in Developed Countries

The Environment Protection Agency (EPA) United States of America has compiled an inventory of pollution potential of dioxin and furan from various sources in United States of America during 1995. Source wise toxic potential of dioxin and furan in USA based on EPA inventory is presented in Table 6, which indicated that municipal waste incineration was liable to generate maximum emission of dioxin and furan in ambient air.

Table 6: Pollution Potential of Sources of Dioxin and Furan in United States of America

Sources	Mean Dioxin & Furan contribution gm TEQ per year
Air	
Municipal waste incineration	1100.0
Secondary copper smelting	541.0
Medical waste incinerator	477.0
Forest fire	208.0
Cement Kiln (Hazardous waste burning)	153.0
Coal combustion	72.8
Wood combustion (Residential)	62.8
Wood combustion (Industrial)	29.1
Vehicle fuel combustion (diesel)	33.5
Cement Kiln (Non hazardous waste burning)	17.8
Secondary aluminum smelting	17.0
Oil combustion industries	9.3.0
Sewage sludge incineration	6.0
Hazardous waste incineration	5.7
Vehicle fuel combustion (Unleaded gasoline)	6.3
Kraft recovery boilers	2.3
Secondary lead smelter	1.63
Tobacco / Cigarette smoking	0.81
Boilers and industrial furnaces	0.38
Crematoria	0.24
Sub total – 27,44.66	
Products	
Pentachloro phenol treated wood	25000.0
Bleached chemical wood pulp and paper	24.1
Dioxazine dyes and pigments	0.36
2,4 – dichloro phenoxy acetic acid	18.4
Non incinerated municipal waste	7.0
Sub total – 25,049.86	
Land Environment	
Non incinerated municipal sludge	207
Bleached chemical wood pulp and paper mill	1.4
Sub total – 208.40	
Aquatic Environment	
Bleached chemical wood pulp and paper mill	19.5
Sub total – 19.50	
Total – 28,014.42	

Source: United States Environment Protection Agency (1995)

The pollution potential of dioxin and furan from identified sources was estimated as 28014.42 gm TEQ/year during 1995 in United States of America. Implementation of strong strategies to reduce dioxin thereafter resulted in downward trend of pollution from PCDDs & PCDFs.

Japan has also brought down their dioxin pollution potential to 2260 – 2440 gm TEQ/year during 1999 against 6300 gm TEQ/year during 1977. Germany has reportedly reduced their potential to 291 gm TEQ/year during 1994 – 1995 from 1210 gm TEQ/year as estimated during 1989 – 1990. According to most recent data, it is reported that about 12900 gm TEQ/year PCDDs and PCDFs are added to global environment together by sixteen developed and most industrialized countries. (Source: Environmental Science and Pollution Research; Vol. 8, No. 3, 2001).

4.0 TOXICITY OF DIOXIN AND FURAN

All the isomers of dioxin and dioxin like compounds are toxic but their toxicity potential varies widely among their different congeners and positional isomers. Only 7 out of 75 isomers of dioxin and 10 out of 135 isomers of furan exhibit critical toxic effects because of their chemical nature and property.

2,3,7,8 TCDD, the most toxic compound has been utilized as a prototype for investigating the toxicity, carcinogenicity and reaction mechanism. It is a microcrystalline solid, insoluble in water, sparingly soluble in other solvents and thermally very stable. Thermal decomposition can only occur at above 750 °C. It undergoes substitution reactions and de-chlorination as well. The International Toxicity Equivalency Factors (I-TEF) for various congeners of Dioxin and Furan are depicted in Table 7.

Table 7: International Toxicity Equivalency Factors (I-TEF) for Dioxin and Furan

Toxic Isomer of Dioxin	I-TEF	Toxic Isomer of Furan	I-TEF	
Tetra-chloro members (4 Chlorine substitution)	1.0	Tetra-chloro members (4 Chlorine substitution)	0.1	
2,3,7,8 TCDD		2,3,7,8 TCDF		
Penta-chloro members (5 Chlorine substitution)	0.5	Penta-chloro members (5 Chlorine substitution)	0.5	
1,2,3,7,8 PCDD		2,3,4,7,8 PCDF		0.5
		1,2,3,7,8 PCDF		0.05
Hexa-chloro members (6 Chlorine substitution)	0.1	Hexa-chloro members (6 Chlorine substitution)	0.1	
1,2,3,4,7,8 HCDD		1,2,3,4,7,8 HCDF		
1,2,3,6,7,8 HCDD		1,2,3,6,7,8 HCDF		0.1
1,2,3,7,8,9 HCDD		1,2,3,7,8,9 HCDF		0.1
		2,3,4,6,7,8 HCDF		0.1
Hepta-chloro members (7 Chlorine substitution)	0.01	Hepta-chloro members (7 Chlorine substitution)	0.01	
1,2,3,4,6,7,8 HCDD		1,2,3,4,6,7,8 HCDF		0.01
		1,2,3,4,7,8,9 HCDF		0.01
Octa-chloro members (8 Chlorine substitution)	0.001	Octa-chloro members (8 Chlorine substitution)	0.001	
OCDD		OCDF		

Source: NATO-CCMS, 1998

- **Pathways of Human Exposure**

Dioxin are released into the ambient environment either directly along with emissions or indirectly through volatilization from land, water and resuspension of particulates. The atmospheric temperature and vapor pressure of each compound in ambient condition will govern the congeners speciation of Dioxin (PCDDs) and Furan (PCDFs).

The food has been identified as the major route of human exposure to Dioxin (PCDDs) and Furan (PCDFs) in European countries. Some segment of population such as nursing babies and people, who takes high animal fat or contaminated food because of their proximity to dioxin releasing sites, are exposed to high levels of dioxin / furan than average. Food having animal origin contributes about 90% of daily intake of dioxin among European population. Dietary intake may contribute to the extent of 90 – 98% of the total daily intake of dioxin by population in advanced countries.

Average daily intake of dioxin in European population was estimated as 0.9 – 3.0 pg/Kg of body weight assuming 70 Kg as average body weight. Due to lipophilic properties of dioxin, these accumulate mostly in fat tissues of fish, meat and dairy products. Consequently, may enter in human system, when people consume these contaminated foods and undergoes bio-magnification during repeated exposure. The degree of bio-magnification was estimated as 10,000 times higher than the concentration of dioxin in surrounding environment. Traces of Dioxin (PCDDs) and Furan (PCDFs) have also been reported in human adipose tissues, blood and milk among the population from various advanced countries.

- **Effects on Human Health**

Short-term exposure to high levels of dioxin may result in skin lesions, such as chlorance, patchy darkening of the skin, altered liver functions etc. in human beings. Chronic exposure may result in various types of cancer, porphyria – a disorder in enzyme synthesis (Kociba *et al.* 1976,1978) and Sweeny *et al.* (1984). A specific type of human porphyria known as 'Porphyria Cutanea Tarda (PCT)', which is marked by discolouration and increased fragility of the skin may occur on chronic exposure.

Dioxin (PCDDs) generally causes immune system toxicity as well as gastro-intestinal ulcers in human beings. Industrial exposure to dioxin may lead to neuro-toxic effects involving polyneuropathy of lower extremities. Inhalation of high levels of dioxin not only chokes the lungs but also enter into the blood stream. The liver is affected to such an extent that it leads to increased susceptibility to cancer. Dioxin exposure may result in increase in serum cholesterol and tri-glycerides concentrations, which ultimately changes blood lipids and liver function indicators.

Many scientists believe that dioxin exposure is responsible for developing breast cancer in women and reduced sperm count in men. Organic chemicals like PCBs, PCDDs, PCDFs, OCPs are known as “Gender bender”. Long-term exposure is linked to impairment of immune system, nervous system, endocrine system and reproductive functions. Long-term exposure even to low concentration of dioxin alters the reproductive functions including infertility, miscarriage, spontaneous abortion, congenital anomalies, and neonatal developmental abnormalities. Dioxin released during spraying of phenoxy herbicide results in soft tissue sarcomas, malignant lymphoma and tumors of all organs.

5.0 ENVIRONMENTAL TRANSFORMATION OF DIOXIN AND FURAN

Dioxin and Furan have potential to transform to other toxic organic pollutants through various transformation processes and routes, some of which are as below:

- ***Abiotic Transformations***

The Dioxin and Furan are chemically quite stable, however these compounds may undergo photochemical degradation. TCDDs seem to be stable to photochemical degradation (Crosby *et al.* 1971) and its half-life is reported as 10-12 years in soil (Young *et al.* 1983). The photochemical degradation of PCDDs is reportedly enhanced in the presence of “hydrogen donor”, like methanol etc. An increase in substituted chlorine levels in PCDDs molecule can be correlated with decrease in rate of photochemical degradation. The predominant PCDDs and PCDFs remain adsorbed on the particles and sediment; further ultraviolet radiation does not penetrate much into the water bodies. Therefore, the scope of photolytic decomposition of PCDDs and PCDFs in environment is very limited.

- ***Bio-transformation and Bio-degradation***

The most toxic congener of dioxin, 2,3,7,8 TCDD is very stable to bio-degradation. It is resistant to many microbial strains capable to degrade persistent pesticides. The half-life of 2,3,7,8 TCDD in lake waters and sediments has been estimated as 550-590 days. Several other isomers of dioxin have been reported to metabolize to their mono- and di-hydroxy derivatives. These transformed derivatives are more susceptible to ingestion and accumulation in fat tissues.

- ***Bio-accumulation***

Bioaccumulation of 2,3,7,8 TCDD in various biotic tissues have been studied in various biotic organisms. Mosquito larvae (*Aedes egypti*) have

been found to accumulate 9000 times higher concentration of Dioxin than available in surrounding aquatic environment. Brine shrimp (*Artemia salina*) had found accumulated 1570 times higher concentration than its surrounding experimental lake water.

The bioaccumulation for 2,3,7,8 TCDD in freshwater aquatic organisms as studied by USEPA and the bioaccumulation factors derived during the study are presented in Table 8.

Table 8: Bioaccumulation Factors (USEPA Study) for 2,3,7,8 TCDD in Freshwater Aquatic Organisms

Organism / Species	Tissue / body part	Exposure Duration (days)	Bioaccumulation factor
Alga (<i>Oedogonium cardiacum</i>)	Whole body	33	3094 ^b
Alga (<i>Oedogonium cardiacum</i>)	Whole body	32	2075 ^c
Snail (<i>Physa sp.</i>)	Whole body	33	5471 ^b
Snail (<i>Physa sp.</i>)	Whole body	32	3095 ^c 3731
Cladoceran (<i>Daphnia magna</i>)	Whole body	30	7070 ^c 7125
Cladoceran (<i>Daphnia magna</i>)	Whole body	32	3895 ^b
Catfish (<i>Italurus punctatus</i>)	Whole body	28	4875
Mosquito fish (<i>Gambusia affinis</i>)	Whole body	14	4850 ^c 4875

Notes: ^b – Arithmetic mean of several values reported. ^c – Tissue concentrations at equilibrium

6.0 DIOXIN AND FURAN CONTAMINATION IN ENVIRONMENT - GLOBAL STATUS

Dioxin (PCDDs) and furan (PCDFs) are released into the environment either directly alongwith emissions or indirectly through volatilization from land, water or by suspension of particles contaminated with PCDDs and PCDFs. The prevailing temperature and vapour pressure of each congener decides the speciation and its persistent form. More chlorinated compounds tend to adsorb on particulates and thus protected from chemical and photo-degradation. These proportions may account for their relative abundance in the environment. Air borne dioxin may be dispersed to long distances, downwind from the source and get deposited on soil, water, plants and animal tissues and may also enter the food chain. Being highly persistent, dioxin and furan leaves their imprint in environmental matrices like soil, sediment, vegetation and biota. The data pertaining to environmental levels of dioxin and furan in various environmental matrices is limited, however efforts have been made to compile global levels based on various research studies worldwide.

- **Dioxin in Air Environment**

PCDDs and PCDFs are transported and dispersed from stationary and area sources through air route. Stack and fugitive emissions from Chemical processing units, Power plants, Incinerators are the potential point sources. Whereas, waste disposal sites and automobile exhaust may be considered as important area and line sources respectively.

Owing to the difficult sampling and analytical problems in determining sub-micro level (Sub ppt) of dioxin and furan, there are only few studies and reporting on levels of PCDDs and PCDFs in air environment. According to the study by Rappe and Kjiller (1996) on dioxin at different locations in Guthenberg, Sweden, PCDDs were found more than 40 times of background concentration adjacent to dumpsite and metal refining units, while approximately 10 times at traffic tunnels (Table 9).

Table 9: Environmental Levels of PCDDs and PCDFs in Ambient air (picogram/m³) at Guthenberg (Sweden)

Monitoring sites	Tetra - Isomers		Penta- Isomers		Hexa - Isomers		Hepta - Isomers		Octa - Isomers		Total	
	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs
Urban Area	0.10	0.36	0.07	0.51	0.74	0.18	0.60	0.10	0.37	0.10	1.88	1.25
Traffic tunnel	0.22	6.2	1.3	4.1	2.7	1.1	3.4	1.20	6.4	1.0	14.02	13.6
Downwind of MSW incinerator	0.21	4.9	2.4	5.0	5.3	2.2	5.3	2.0	7.40	0.78	20.61	14.88
Vicinity of dump site and metal refinery	1.5	3.3	5.0	10.0	24.0	9.5	15.0	5.0	40.0	7.0	85.5	34.8
Street when clean air blowing	0.15	0.32	0.2	0.47	0.1	0.18	0.38	0.10	0.29	0.15	1.12	1.22
Street at inversion	0.35	2.0	0.84	2.5	0.52	0.80	2.90	1.1	1.90	0.48	6.51	6.88
Rural research station (during wind blowing from sea)	0.009	0.054	0.031	0.085	0.032	0.07	0.14	0.12	0.064	0.10	0.276	0.429
Rural research station (during wind blowing from city)	0.13	0.49	0.28	0.60	0.19	0.31	1.0	0.50	0.54	0.44	2.54	2.34

1gm = 10¹² Picogram.

Source: Rappe & Kjiller (1996)

Heister et al. (1995) presented annual mean of PCDD/PCDF in ambient air of four cities (Koln, Duisburg, Essen and Dortmund) in North-Rhine Westfalia and observed decreasing trend from 46 to 69% (0.22 pg/m³ to 0.14 pg/m³ at Dortmund and 0.13 pg/m³ to 0.04 pg/m³ at Koln) during 1988 and 1994 respectively. The decline in concentrations of Dioxin was due to strategic reduction in source emissions like prohibition of halogenated scavengers in petrol, a ban on PCBs and upgrading or shutdown of 12 out of 26 Municipal Solid Waste incinerators in the region.

- **Dioxin in Aquatic Environment**

The water solubility of PCDDs and PCDFs is very rare. The water solubility of highly toxic isomer 2,3,7,8 TCDD is very less. It is more likely that PCDDs and PCDFs are present in adsorbed state in the aquatic environment. Surface runoff from agricultural land with contaminated pesticides; herbicides and insecticides could be the main contributor for PCDDs and PCDFs contamination in water. Effluent from pulp and paper industries, fly-ash pond overflow of power plants, electrical equipments repairing sites, car sheds, garages, lubricating oil-processing industries may add PCDDs and PCDFs contamination to aquatic environment.

Due to hydrophobic properties and scarce water solubility dioxin and furan remain adsorbed on the surface of suspended particles, which settle fast to bottom substrate. It has been reported that OCDD (Octa chlorinated di-benzo para dioxin) is the most frequently observed isomer in surface water. The study undertaken for Canadian surface water, the levels of PCDDs and PCDFs have been found 1.1 pg/l. Gotz (1986) reported PCDDs and PCDFs in oily leachates from sanitary landfill in Germany. Tetra- to Hexa- chlorinated congeners of both PCDDs and PCDFs were found abundant in the leachate water (Table 10).

Table 10: PCDDs and PCDFs Levels in Leachate from Sanitary landfill in Federal Republic of Germany

PCDD Isomers	Concentrations (ng/l)	PCDF Isomers	Concentrations (ng/l)
2,3,7,8-TCDD	60	2,3,7,8-TCDF	9
1,2,3,7,8-PCDD	28	1,2,3,7,8-PCDF	322
1,2,3,4,7,8-HCDD	476	2,3,4,7,8-PCDF	261
1,2,3,6,7,8-HCDD	1440	1,2,3,4,7,8-HCDF	748
1,2,3,7,8,9-HCDD	310	1,2,3,6,7,8-HCDF	336
		1,2,3,7,8,9-HCDF	558
		2,3,4,6,7,8-HCDF	114

Source: Gotz (1986)

- **Dioxin in Soil and Sediments**

Contamination of soil and sediments by PCDDs and PCDFs may occur due to transportation of these toxic chemicals through different routes as below:

- Precipitation of air borne particulate matter along with adsorbed molecules of PCDDs and PCDFs in water bodies.
- Erosion of contaminated soil with surface and storm water runoff.
- Suspension of contaminated airborne dust due to wind effect.
- Direct volatilization.

- Contamination to surface water via erosion of soil.
- Contamination to ground water through percolation.
- Contamination to food chain via bio-accumulation and bio-magnification.

Diffused combustion sources are major contributor of PCDDs and PCDFs in soil environment. Rappe & Kjeller (1986) studied Dioxin and Furan in soil samples from various parts of Europe covering rural and industrial areas. The isomeric pattern of tetra- and penta-CDFs was found similar to those found in air environment. Decrease in levels with the increase in distance from the city was also established (Table 11).

Table 11: PCDDs and PCDFs in soil samples (picogram/gm) in European countries

PCDD & PCDF Isomers	Remote rural site	Rural site I	Rural site II	Industrial site I	Industrial site II
Dioxin (PCDDs)					
Tetra – chlorinated Isomer	< 2.0	< 2.1	3.2	55.5	11.2
Penta – chlorinated Isomer	<2.0	<2.0	4.6	200.0	450.0
Hexa – chlorinated Isomer	<2.0	<2.0	4.7	200.0	330.0
Hepta – chlorinated Isomer	10.0	10.0	1.7	370.0	1600.0
Octa – chlorinated Isomer	---	---	14.0	140.0	180.0
Furan (PCDFs)					
Tetra – chlorinated Isomer	9.3	7.7	11.0	320.0	370.0
Penta – chlorinated Isomer	14.0	13.0	6.7	200.0	450.0
Hexa – chlorinated Isomer	16.0	12.0	11.0	170.0	1900.0
Hepta – chlorinated Isomer	22.0	14.0	18	260.0	4500.0
Octa – chlorinated Isomer	--	--	5.7	68.0	71.0

Czuczwa & Hiles (1986) have identified PCDDs and PCDFs in sediment samples. In rural and urban areas, their concentration varied widely from 100 ng/kg to 100 ng/gm.

Soil and sediments play a unique role for chronological study of persistent pollutants. Different studies on core samples, identified by carbon dating to represent the 1860 to 1990 generation sediment collected from different lakes in America and Europe revealed that PCDDs and PCDFs were present during 1860 (sediment of Green lake) in very low concentration (below 10 ng/kg). However, the levels of PCDDs and PCDFs started increasing during 1920-1930s and attained maximum during 1970s (750 ng/kg) and started declining (375 ng/kg) thereafter. Although the trend was almost same in advanced countries, the peak time was differing and may be correlated with the industrialization in the respective countries (Smith *et al.* 1993).

- ***Dioxin in Plant tissues (Vegetation)***

Very few studies have been reported for contamination of vegetation with dioxin and furan. Laboratory scale studies confirmed TCDD contamination of leaves through transpiration. However, study on vegetation after industrial accident in Seveso, Italy suggested that the contamination in vegetation occurred due to deposited dust rather than through plant's uptake. On the other hand Vegetation may effectively scavenge PCDDs and PCDFs from the atmosphere by retaining vapour phase on waxy cuticle and trapping aerosol-bound PCDDs / PCDFs brought in contact with leaves through dry or wet deposition (McLachlan, 1996).

- ***Dioxin in Tissues of Fishes and Aquatic Organisms***

It has been established that fish and other aquatic organisms of the water bodies situated in the vicinity of related industrial units or at impact point of users, where chlorinated organics and precursor of PCDDs and PCDFs are used, accumulate PCDDs and PCDFs in their body tissues. The concentrations 4.0 – 695 ng/Kg of TCDD had been reported in edible parts of channel catfishes, yellow perch and suckerfish from Saginaw Bay, Michigan, USA (1992). The bottom feeder fishes were found to accumulate more dioxin and furan because of their association with adsorbed contaminants. In most aquatic organisms 2,3,7,8 – substituted PCDD and PCDF congeners were found.

Varofjord, in Sweden has a potential source of PCDDs and PCDFs pollution due to effluent discharge of pulp and paper industries. The effluent discharge was found responsible for contaminating hepato-pancreas of crab, observing 990 pg/gm PCDDs and 1660 pg/gm of PCDFs.

- ***Dioxin in Tissues of Terrestrial Organisms***

The studies in contaminated fields in Florida, USA, had shown that beach mice (*Peromyscus polinotus*) contained 540 – 1300 ng/Kg TCDD in liver. The visceral mass of the reptile (*Cnemidophorus sexlineatus*) had also been found contaminated with 360 ng/Kg TCDD, whereas the trunk of the same reptile was containing 370 ng/Kg TCDD (Young *et al.* 1976).

In another study, body tissue of horse grazing near wire reclamation incinerator had been found contaminated with 165 ng/Kg TCDFs in fat and 57 ng/Kg TCDFs in liver. Other unspecified TCDDs were reported as 45 ng/Kg in fatty tissues and less than 6 ng/Kg in liver (Hryhorczuk, 1981).

- **Dioxin in Human Tissues**

There are scanty information available about dioxin contamination of human tissues, may be because of complications in sample collection and ultra trace analysis of PCDDs and PCDFs. The levels of PCDDs and PCDFs in human adipose tissues based on the studies undertaken worldwide are presented in Table 12. It is evident from the table that the contamination level of human tissues with PCDDs and PCDFs are almost in the same range in industrially developed countries

Table 12: TCDDs and TCDFs in human adipose tissue (ng/Kg wet tissue) in various advanced countries 1989

PCDD & PCDF Isomers	Sewden (31) ^S	USA (8) ^S	Canada (46) ^S	Japan (13) ^S	North Vietnam (9) ^S	South Vietnam (15) ^S	Federal Republic of Germany (4) ^S
PCDDs (Poly chlorinated di-benzo para dioxin)							
2,3,7,8 - TCDD	3.0 (31) ^P	7.2 (8) ^P	6.4 (25) ^P	9.0 (12) ^P	<2	28.0 (12) ^P	150.0 (4) ^P
1,2,3,7,8 - PCDD	10.0 (31) ^P	11.1 (8) ^P	10.0 (46) ^P	15.0 (13) ^P	<2	15.0 (14) ^P	19.2 (4) ^P
1,2,3,6,7,8 - HCDD	15.0 (31) ^P	96 (8) ^P	81.0 (46) ^P	70.0 (12) ^P	11.0 (6) ^P	100.0 (15) ^P	77.0 (4) ^P
1,2,3,7,8,9 - HCDD	4.0 (31) ^P	NA (8) ^P	NA	12.0 (10) ^P	NA	NA	9.4 (4) ^P
1,2,3,4,6,7,8 - HCDD	97.0 (31) ^P	164 (8) ^P	135 (46) ^P	77.0 (12) ^P	28.0 (6) ^P	178.0 (15) ^P	56.0 (4) ^P
Octa – CDD	414.0 (31) ^P	707 (8) ^P	830 (46) ^P	230.0 (12) ^P	104.0 (8) ^P	1256.0 (15) ^P	267.0 (4) ^P
PCDFs (Poly chlorinated di-benzo furan)							
2,3,7,8 - TCDF	3.9 (31) ^P	NA	NA	9.0 (13) ^P	NA	NA	0.9 (4) ^P
1,2,3,7,8 – PCDF	54.0 (31) ^P	14.3 (8) ^P	15.0 (46) ^P	25.0 (13) ^P	13.0 (7) ^P	21.0 (15) ^P	44 (4) ^P
1,2,3,4,7,8 – HCDF	6.0 (31) ^P	NA	NA	15.0 (11) ^P	NA	NA	10 (4) ^P
1,2,3,6,7,8 – HCDF	5.0 (31) ^P	31.3 (8) ^P	16.0 (34) ^P	14.0 (11) ^P	13.0 (7) ^P	58.0 (15) ^P	6.7 (4) ^P
2,3,4,6,7,8 – HCDF	2.0 (31) ^P	NA	NA	8.0 (3) ^P	NA	NA	3.8 (4) ^P
1,2,3,4,6,7,8 – HCDF	11.0 (31) ^P	16.5 (8) ^P	30.0 (44) ^P	NA	7.0 (3) ^P	29.0 (15) ^P	19.5 (4) ^P
Octa – CDF	4.0 (31) ^P	NA	NA	NA	NA	NA	1.0 (4) ^P

Notes: ()^S indicates Total number of samples ; ()^P indicates number of positive samples; NA – Data not available

7.0 DIOXIN IN INDIAN ENVIRONMENT

The contamination of PCDDs and PCDFs in human tissues, fishes, meat, and wildlife collected from India has been first reported in the research paper entitled “ Polychlorinated Dibenzop-dioxin, Dibenzofuran and Polychlorinated Biphenyls in Human tissues, Meat, Fish and Wildlife samples from India” Environ. Sci. Technol. 2001, 35, 3448 – 3455. The Dioxin and Furan as reported in the study have been analyzed at an Environmental laboratory at Japan. The following are the salient findings of the study.

- According to the study report, 2,3,7,8 – substituted PCDDs and PCDFs (most toxic isomers) have been found in human fat tissues in the concentration ranging between 170 – 1300 pg/gm of fat weight.
- The levels of PCDD and PCDF in Indian fishes, meat and wildlife samples have been found in the order: Country chicken < Fat bodies of Goat / lamb < Fishes < River Dolphins < Predatory birds. The carnivorous creatures have been found more susceptible to the presence of dioxin.
- Liver of the spotted owl (a predatory bird) contained highest concentration of PCDD and PCDF (3300 pg/gm of fat weight).
- Fishes contained the highest concentration of total PCDDs / PCDFs (130 pg/gm of fat weight). Concentrations of Dioxin (PCDDs) were 2 – 8 times higher than the Furan (PCDFs). Hepta-chloro and Octa-chloro dibenzo-para dioxin were accounting for 77 – 100 % of total PCDDs concentration in fishes.
- Concentrations of PCDDs and PCDFs in meat products were, on average, 2 – 5 times less than those found in fishes.
- The liver tissue of dolphins contained approximately three fold higher concentrations of PCDDs and PCDFs than those of fishes. The tissues of male dolphins had less dioxin contamination than female.
- Concentrations of PCDDs and PCDFs in human tissues ranged from 170 pg/gm – 1300 pg/gm of fat weight (mean 540 pg/gm of fat weight). Concentrations of PCDDs (520 pg/gm of fat weight) in human tissues were almost 17 times higher than that of PCDFs (30 pg/gm of fat weight).
- Presence of 2,3,7,8–TCDF in environmental matrices suggests pulp and paper mill related sources, while OCDF and Hepta-CDF are indicative of sources originating from Chlor-Alkali process.

It is unfortunate that there are scanty infrastructure facilities for Dioxin and Furan measurement in the country. There exist no laboratory, which have complete and adequate infrastructure to undertake ultra trace dioxin measurement in various environmental matrices, hence, it is very difficult to cross check or validate the findings of above referred studies. Considering immense need of Dioxin measurement in environmental matrices Central Pollution Control Board is presently undertaking development of infrastructure for dioxin measurement. The Ministry of Environment and Forests, Govt. of India has also sanctioned the project to Regional Research Laboratory CSIR, Trivandram to develop infrastructure for sampling and analysis of dioxin and furan in environmental samples.

8.0 EPISODAL POLLUTION RELATED WITH DIOXIN AND FURAN

There had been several devastating episodes related with PCDDs and PCDFs. Specific few are presented below:

- ***Yusho Accident, Japan, 1968***

In 1968, more than 1500 people in southwest Japan were intoxicated through consumption of commercial rice oil accidentally contaminated with PCBs, PCDFs and Poly chlorinated terphenyls (PCTs). 5 mg/Kg PCDFs was found in three contaminated rice oil samples. More than 40 congeners of TCDFs were identified in these samples by Buser *et al.* (1978). 10 – 15 % of the total amount of PCDF was identified as the most toxic congener 2,3,7,8 – TCDF by Masude *et al.* (1985).

Yusho patients reported symptoms of hyperkeratosis, i.e. dilation of follicles and accumulation of melanin in basal cells of epidermis. Oedema of the arms and legs, respiratory trouble and chronic bronchitis were common symptoms amongst the affected people.

- ***Yu-Cheng Accident, Taiwan, 1980***

The accident similar to Yusho Accident, occurred in Taiwan during 1979. The number of affected persons reached to 1843 nos. by the year-end. The accident cause was again the consumption of contaminated rice bran oil. The mean total consumption of PCDFs among the Yusho and Yu-cheng patients has been estimated as 3.3 – 3.8 mg/person.

The prominent symptoms and disorders found in the patients were heavy pigmentation of conjunctiva, pigmentation on skin and nails, swelling of eyelids, eye irritation and watering, headache, nausea and numbness of limbs. The blood disorder included decreased haemoglobin, erythrocytes, gamma immunoglobulin and very high WBC count.

- ***Seveso Accident, Italy, 1976***

There had been an explosion in the industrial unit at Seveso, Italy manufacturing 2,4,5 – trichloro phenoxy acetic acid, a herbicide during July, 1976. The white cloud of poisonous gas containing TCDD came out and engulfed nearby town of Seveso. The air and soil got heavily contaminated with toxic dioxin. After three weeks, Government of Italy evacuated 800 peoples from the worst affected areas. Dioxin pollution continued to spread and the particulates were deposited in wide spread areas. As an immediate effect, about 25% population had suffered from skin diseases and some of them complained for liver malfunctioning. About 10% of the babies born after the

accident were prematurely delivered and found deformed. The affected area of Seveso was studied by several researchers to identify chronic effects and environmental impacts of TCDD pollution.

- ***Contamination of Poultry Food With PCDDs, USA, 1997***

The dioxin pollution of poultry food occurred during 1997 in Southern parts of USA. Chicken, eggs and catfishes were found intoxicated, when a contaminated ingredient ('bentonite clay' sometimes called 'Ball clay') was used to manufacture animal food. The regulatory authorities in USA eventually identified the origin of contaminated clay to a bentonite mine.

- ***Contamination of Soil With 'Agent Orange', Vietnam***

The herbicide 'Agent Orange' was frequently used in Vietnam. Dioxin content in 'Agent Orange' varied widely from 0.1 ppm to over 60 ppm. This dioxin-contaminated herbicide diluted with kerosene, was sprayed over forested area for destroying forests during Vietnam warfare. There had been repeated claims of adverse health effects due to exposure to 'Agent Orange' by the Vietnam veterans exposed with the spray.

9.0 ENVIRONMENTAL STANDARDS FOR DIOXIN AND FURAN

The United States Environment Protection Agency (USEPA) was the first environmental organization; which had promulgated the Maximum Achievable Control Technology (MACT) Standards during September 1999 for hazardous waste combustors including hazardous waste incinerator, cement kilns, and lightweight aggregate kilns. Pollutants regulated through MACT Standards included dioxin and furan, mercury, total chlorine (Cl_2 and HCl), semi-volatile metals including lead and cadmium, low volatility metals such as arsenic, beryllium, and chromium, particulate matter, carbon monoxide and hydrocarbons. Due to legal hurdles, interim standards were promulgated in February 2002. United States Environment Protection Agency, will be notifying final MACT standard by June 2005. Meanwhile directions have been issued to the concerned parties in United States of America to comply with the interim standards by 30th September 2003. The interim standards promulgated by USEPA are presented below (Table 13). The environmental standards for Dioxin adopted by various agencies worldwide are compiled in Table 14.

Table 13: Interim MACT Standards for Combustors in United States of America (USEPA; Sept. 1999)

Pollutants	Interim MACT Standards		
	Incinerators	Lightweight aggregate Kilns	Cement Kilns
Dioxin and Furan (ng TEQ/dscm)	0.20	0.20 ^a	0.20 or 0.40 ^b
Mercury (µg/ dscm)	45	120	120
Semi Volatile Metals (µg/dscm)	120	43	180
Low Volatile Metals (µg/dscm)	97	110	54
HCl / Cl ₂ (ppm _v dry)	21	600	86
Particulate Matter mg/dscm	34	57	0.15
Opacity (%)	---	---	20
Hydrocarbons or Carbon monoxide (ppm _v dry)	10 or 100	20 or 100	20 ^c or 100
Hydrocarbons (ppm _v dry) ^d	---	---	50
Hydrocarbons or Carbon monoxide (ppm _v dry) ^e	---	---	10 or 100

- Notes:**
- i) 'dscm' is dry standard cubic meter
 - ii) ^a If the temperature of flue gas at the exit of last combustion chamber by rapid quench or heat recovery to less than 204.4°C (400°F).
 - iii) ^b If the gas temperature at the inlet of the dry particulate control device is maintained below 204.4°C (400°F).
 - iv) ^c for kilns without by-pass
 - v) ^d Main stack standard for kiln with by-pass
 - vi) ^e By-pass duct and stack standard for kiln with by-pass

Table 14: International Environmental Standards for Dioxin and Furan

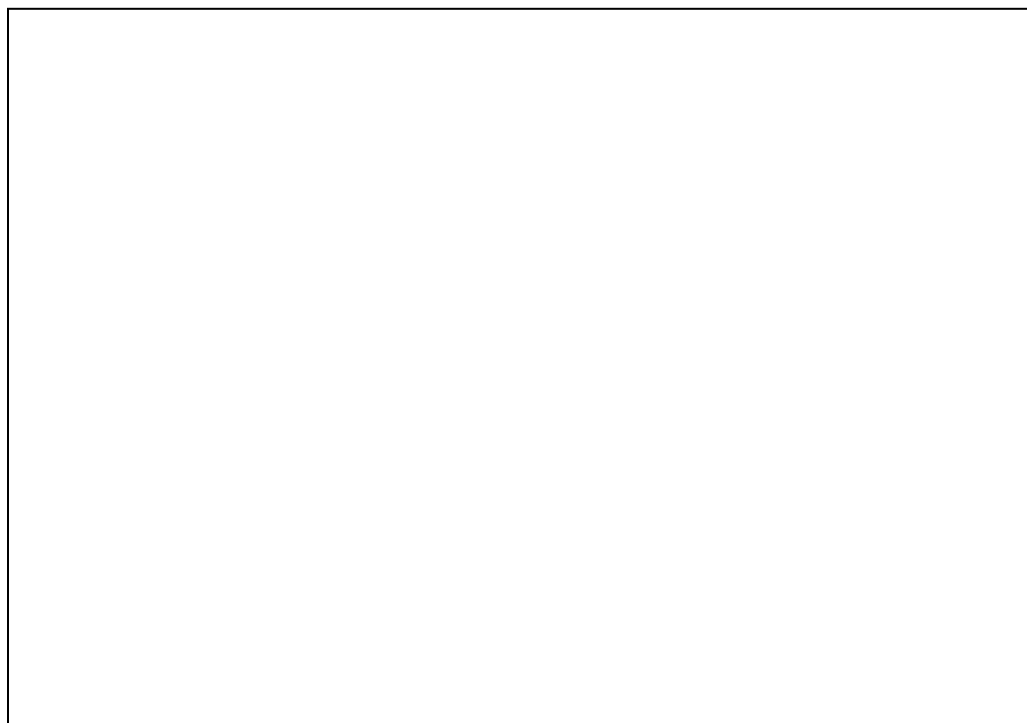
Country	Sources	Standards for Dioxin and Furan
Hong Kong	Municipal Solid Waste Incinerator	13 ng/ m ³ (Total mass)
	Chemical Waste Treatment	0.1 ng I-TEQ / m ³
United States of America (USA)	Municipal Solid Waste Incinerator (more than 35 Tonnes / day)	13 ng/ m ³ (Total mass) about 0.1 to 0.3 ng I-TEQ / m ³
	Hazardous waste incinerator	0.2 ng I-TEQ / m ³
European Union	Waste Incinerators	0.1 ng I-TEQ / m ³
Japan	• Capacity more than 4 Tonnes / hour	0.1 ng I-TEQ / m ³
	• Capacity from 2 to 4 Tonnes / hour	1.0 ng I-TEQ / m ³
	• Capacity less than 2 Tonnes / hour	5.0 ng I-TEQ / m ³
Canada	All New incinerators	0.08 ng I-TEQ / m ³

10.0 ENVIRONMENTAL MONITORING TECHNIQUES FOR DIOXIN AND FURAN

Monitoring of PCDDs and PCDFs in various environmental matrices viz. water, soil, sediment and biological matter involve typical and complicated sampling, ultra clean extraction, clean up facilities and sophisticated analytical procedure. Monitoring of air for PCDDs and PCDFs (both source and ambient) require intricate, comprehensive sampling procedure for both volatile as well as particulate dioxin and furan. The analytical methodologies involved have to pass through similar sample preparation and clean up as used for other organics.

- ***Ambient Air Monitoring***

For ambient air monitoring, specially designed High Volume samplers (HVS) having mass flow controller and cyclone separator are used. These HVS can accommodate both normal size filter paper and a PUF (Poly Urethane Foam) filter fitted at the trunk. High Volume Sampler instruments available in Indian market will require intricate modifications to suit sampling of dioxin and furan from ambient air. 'Anderson' make Hi-Vol sampler or Dicotomous sampler available in international market are suitable for ambient dioxin monitoring.



High Resolution Gas Chromatograph – High Resolution Mass Spectrometer (HRGC – HRMS)

- **Stack/Source Monitoring**

For source emission monitoring of dioxin and furan, an intricate flue gas sampling train and procedures are required to be adopted. The integrated stack gas sample is iso-kinetically withdrawn from selected traverse points along the stack cross-section. Semi-volatile organic compounds associated with particulate matter are collected in the front-half components of the sampling train. Semi-volatile organic compounds not collected by high efficiency glass or quartz fiber are adsorbed on porous, polymeric resin, Amberlite XAD-2. The borosilicate or quartz liner, encased in a stainless steel tube is required to perform stack monitoring. This stainless steel tube is capable of maintaining the exit gas temperature at $120 \pm 14^\circ\text{C}$ or at required temperature necessary to prevent condensation during sampling. The internationally accepted flue gas source emission sampling train used for monitoring of source emission of Dioxin, Furan and other semi-volatile is diagrammatically depicted in Fig 4.

- **Sampling and Analysis of Dioxin and Furan**

Liquid samples should be collected in narrow-mouth amber glass bottles. The level of the liquid in bottle should be marked just after collection to allow for assessment of possible loss during shipment. Liquid samples should be processed as a whole, no sub-sampling is recommended.

Representative **Solid samples** should be collected in wide-mouth amber glass bottles. Care should be taken to exclude as much water as possible.

Fish / vegetables / other biota should be wrapped in clean aluminum foil and frozen.

Special type amber glass bottles with teflon line lid, already cleaned and screened for possible contamination should be used for PCDDs & PCDFs.

Air samples (filter papers, Thimbles, PUFs and XAD-2 Adsorbent) should be wrapped with aluminum foil and kept in dark cool place at $1 - 5^\circ\text{C}$.

All the samples (except tissues) must be maintained at $1 - 5^\circ\text{C}$ in dark from the time of collection till extraction. Tissue samples should be kept frozen during shipment. Recommended sample size, volume of final extract and achievable Method Detection Limits (MDL) for various matrices are presented in Table 15. Typical flow sheets for sample processing and clean up are depicted in Fig. 5, 6 and 7.

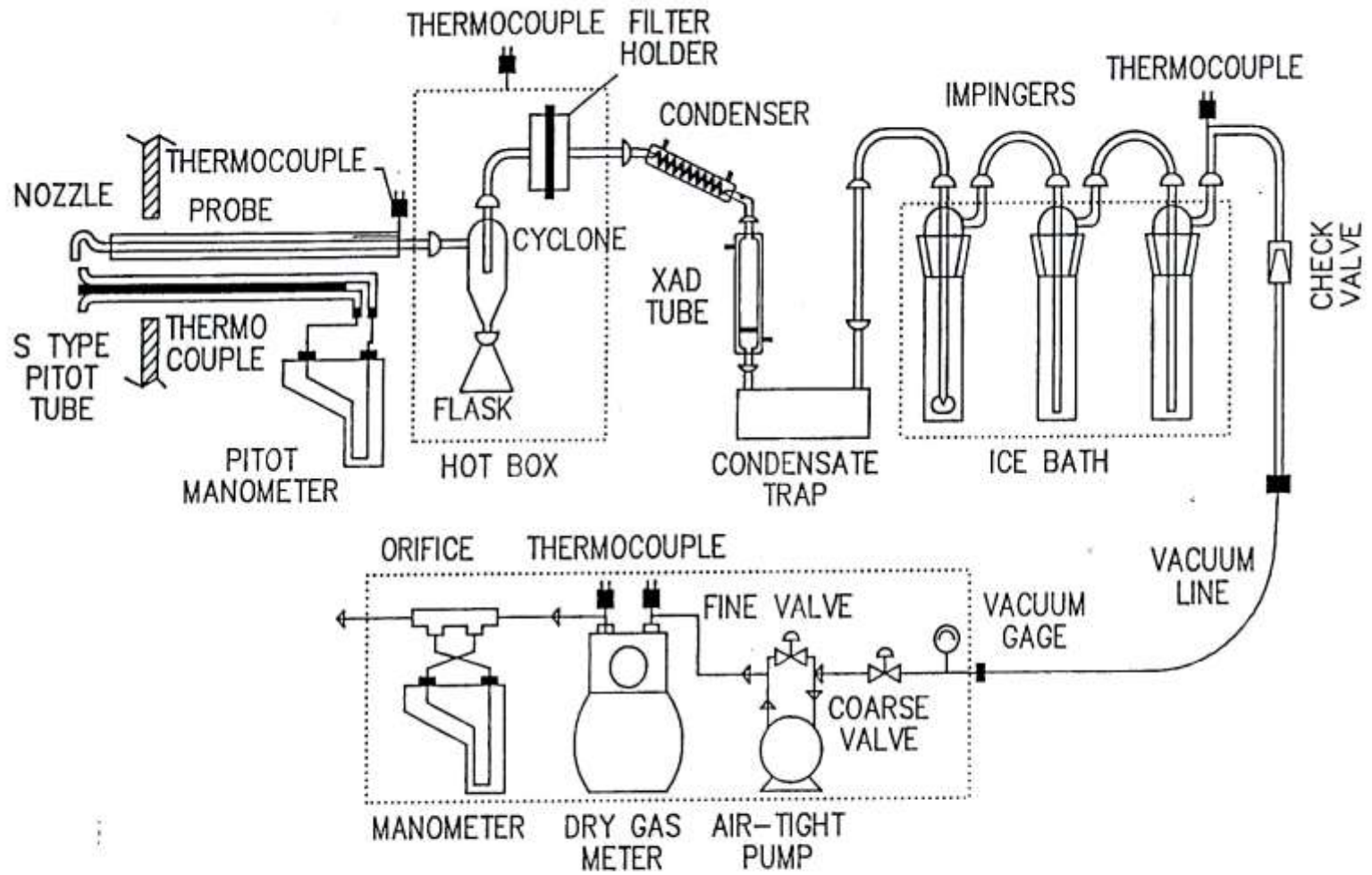


Fig 4 Typical Fluegas Sampling Train for Monitoring of Source Emissions of Dioxin and Furan

Fig. 6: Solid sample / Filter paper / Thimble / PUF / Adsorbent extraction flow sheet

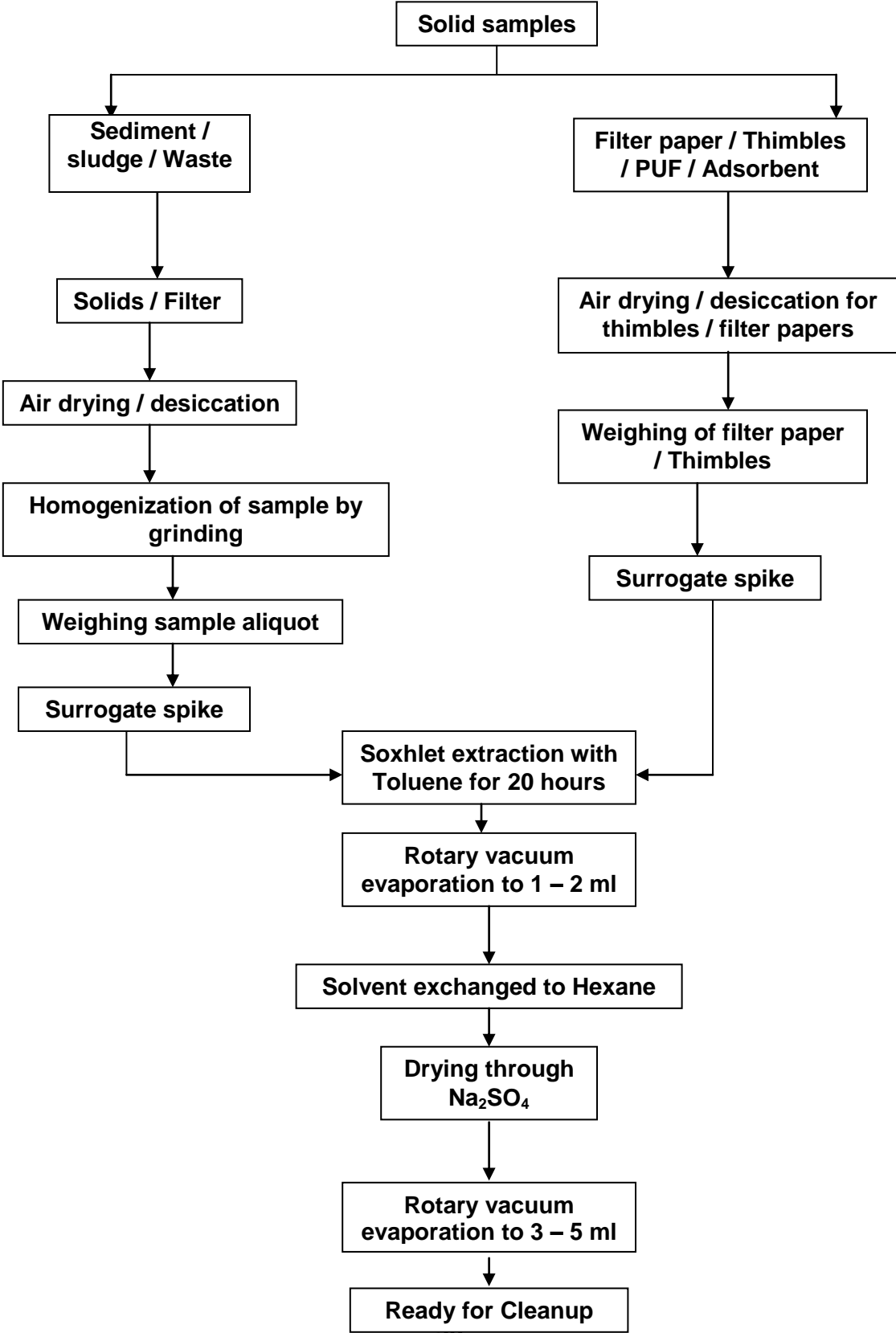


Fig. 7: Liquid samples / Solid sample / Filter paper / Thimble / PUF / Adsorbent Extracts Cleanup flow sheet

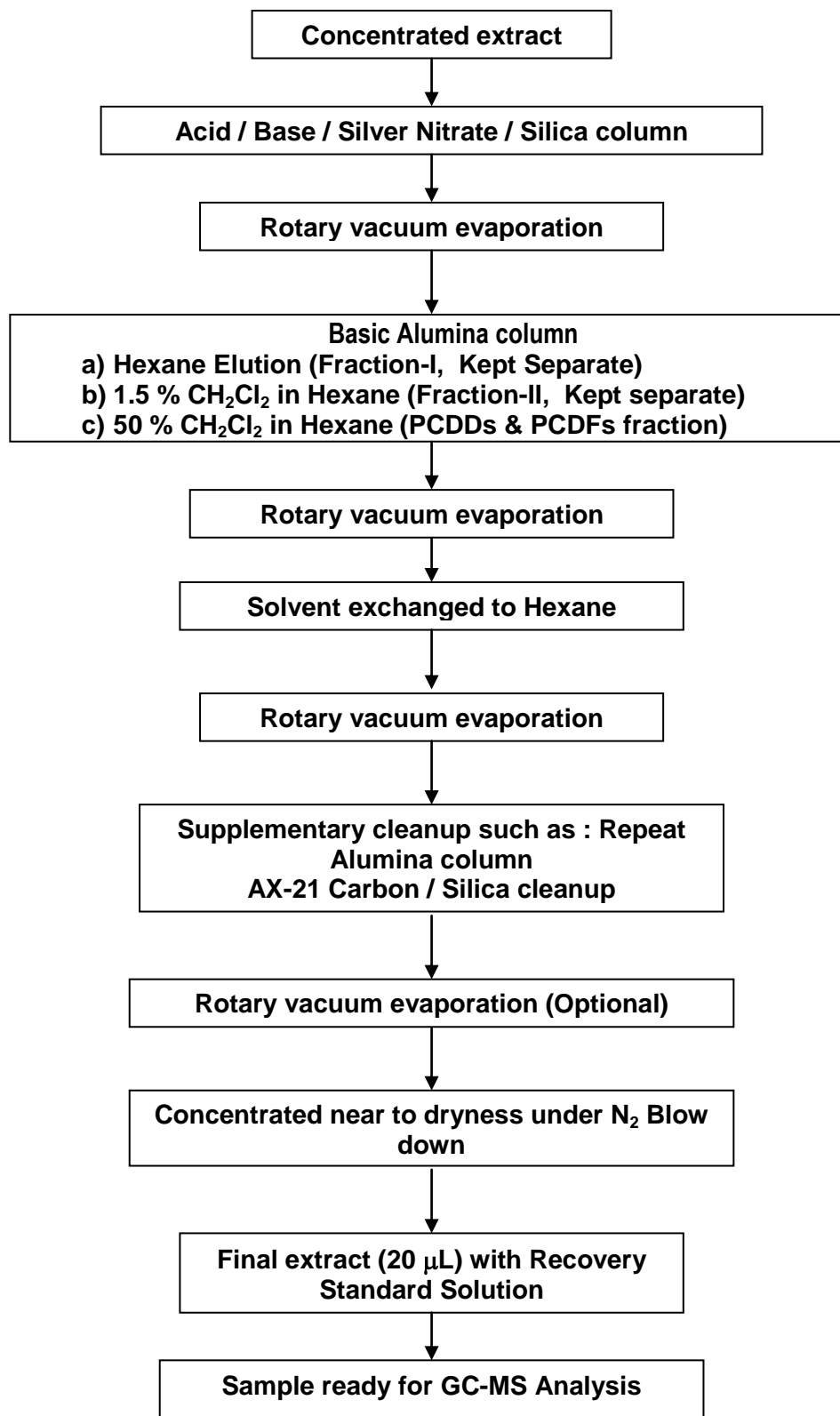


Table 15: Sample Size and Detection Limits of Dioxin and Furan

	Tissue	Sediment, Soil, Sludge, Ash	Pulp & Paper mill effluent	Pulp	Drinking water	Oil	Ambient air
Sample size	10 g (wet)	5 g (dry)	1 L	12 g (dry)	12 L	1 g	1000 m ³
Final Volume of extract	20µL	20µL	20µL	20µL	20µL	20µL	20µL
Target Detection Limits	LRMS (HRMS) pg/g	LRMS (HRMS) pg/g	LRMS (HRMS) pg/L	LRMS (HRMS) pg/g	LRMS (HRMS) pg/L	LRMS (HRMS) pg/g	LRMS (HRMS) pg/ m ³
T ₄ CDD/F	2 (0.5)	12 (1)	60 (5)	5 (0.4)	5 (0.4)	60 (5)	0.06 (0.005)
P ₅ CDD/F	5 (1)	24 (2)	120 (10)	10 (0.8)	10 (0.8)	120 (10)	0.12 (0.01)
H ₆ CDD/F	10 (1)	24 (2)	120 (10)	10 (0.8)	10 (0.8)	120 (10)	0.12 (0.01)
H ₇ CDD/F	15 (1.5)	36 (3)	180 (15)	15 (1.2)	15 (1.2)	180 (15)	0.18 (0.015)
OCDD/F	20 (2)	48 (4)	240 (20)	20 (1.6)	20 (1.6)	240 (20)	0.24 (0.02)

Source: Environment Canada, Report EPS 1/RM/23

11.0 DIOXIN AND FURAN – EMISSION CONTROL FROM CRITICAL PROCESSES

Combustion processes are the main source of dioxin and furan emissions globally. Out of the known sources of Dioxin contamination, more than 95% emissions derive from combustion processes. Dioxin and furan are formed from the thermal breakdown of organic materials combined with transitional metals and chlorinated compounds. It is also known that dioxin are chemically formed at temperature above 200°C but completely destroyed at 800°C. Reformation of dioxin occurs, when the temperature lies between 200°C to 400°C. Chlorine availability and process temperature are the two important factors responsible for dioxin formation.

- ***Dioxin Emission Control at Incinerators***

Modern incinerator plants can be designed and operated to achieve nearly complete destruction of the combustible portion of the waste with very low emission under normal operating conditions. Following are the practical measures to be adopted to reduce emission of dioxin and furan from municipal solid waste / Hazardous waste incinerators.

- Proper segregation of waste. PVC in garbage affects the amount of dioxin formation.
- Chlorine input has a definite role in formation of dioxin and furan therefore, minimization of Chlorine input is required.
- Avoid combustion of wet garbage, as the wet garbage produce more dioxin.
- Good combustion chamber design to optimize the supply of air for achieving more complete destruction of waste.
- The flue gas resulting from the combustion process is raised to a temperature to 850°C for at least 2 seconds in municipal waste incinerator or to a temperature of 1100°C for at least 2 seconds for hazardous waste incinerators for destruction of dioxin in the flue gas.
- Quick cooling of flue gas to minimize dioxin reformation between 200°C to 400°C.
- Regular cleaning of boiler tubes to prevent build up of fly ash, which can serve as a catalyst for dioxin reformation.
- Facilities for injection of activated carbon by powered injection system, which is operated in parallel with the alarm warning system to capture any dioxin, if reformed, for treatment.
- Regular monitoring of combustion products including dioxin emissions.
- Suspension of waste feeding operation to allow urgent trouble shooting and problem-fixing, when abnormal monitoring readings of air emissions or incinerator temperature is detected.

- ***Dioxin Emission Control at Chemical Waste Treatment***

Following measures are recommended to control dioxin emissions from chemical waste treatment.

- Rotary kiln should operate at temperature more than 1000°C.
- The secondary chamber operating at 1100°C to 1250°C should be capable to retain the flue gas for at least 2 seconds.
- The temperature at exit of waste heat boiler to be maintained about 400°C.
- Efficient functioning of wet scrubber to remove hydrogen chloride from flue gas.

- The flue gas has to be abruptly cooled (quenching) to temperature below 200°C to reduce dioxin reformation.
- Daily manual checking of activated carbon injection system, which is operated in parallel with the alarm warning system.
- A fabric filter system to contain the fly ash emission alongwith flue gas.

- ***Dioxin Emission Control at Cement Kilns***

Cement kilns are potential dioxin emission source. Naturally occurring precursors of dioxin in raw materials for cement industries are responsible for highly toxic emissions of dioxin and furan from Cement kilns.

- Change of raw materials has been the successful remedy to prevent dioxin and furan emissions from some plants, but it is not universally acceptable since proposed alternates are also not free from dioxin precursor.
- Temperature control at the inlet of Air Pollution Control Devices (APCD) may be an alternative to prevent dioxin emissions. There is an inverse exponential between dioxin emission and APCD inlet temperature. Proper design and maintenance can lower the temperature of flue gas. Additional water spraying and air quenching may be installed for further control of temperature to prevent reformation of dioxin.
- Recently few other control options for dioxin have been established but these are too expensive and problematic to implement. Gore bags (Remedia catalytic filter system) actually destroy the dioxin as the exhaust gases are simultaneously cleaned of particulates. This system is reportedly reducing considerable dioxin emissions (more than 90%).

12.0 GLOBAL DEVELOPMENTS AGAINST PERSISTENT ORGANIC POLLUTANTS (POPs)

Persistent Organic Pollutants (POPs) are defined as organic substances, which possess toxic characteristics, persistent, bio-accumulative characteristics, prone to long-range trans-boundary atmospheric transport and depositions; and are likely to cause significant adverse human health or environmental effects near to and distant from their sources. Dioxin (PCDDs) and Furan (PCDFs) have been identified as Persistent Organic Pollutants (POPs). The UN-ECE Protocol on POPs drafted in March 1998 has identified 16 most hazardous and persistent chemicals, which included Dioxin (PCDDs) and Furan (PCDFs) apart

from 14 other highly persistent organic compounds. In the adopted Protocol PCDDs and PCDFs are included in Annexure III along with PAHs and HCBs.

Several Countries with Economic Transition (CET) like Ukraine, Poland, Czech Republic, Slovakia, Hungary, Croatia and Slovenia have agreed to reduce their total annual emissions of identified POP substances (Listed in Annexure III of Protocol) by taking effective measures appropriate in circumstances from the level of emission in a reference year set in accordance. Dioxin, furan PAHs and HCBs emission reduction should be below the levels of 1990 or an alternative year between 1985 and 1995, which is more convenient for Countries in Economic Transition (CET).

India has become a part of Global Action against hazardous wastes, being one of the signatory of Basel Convention, Stockholm Conference. Regional Workshops under the United Nations Environment Programme regarding Status of Persistent Organic Pollutants (POPs) in South Asian countries has recently been organized by Industrial Toxicological Research Centre (ITRC), Lucknow. There is strong need for development of infrastructure facilities for extensive measurement of POP's, road map for research, development of treatment technology, development of monitoring techniques and environmental standards in the country to deal with the critical persistent organic pollutants (POPs) and Hazardous Air Pollutants (HAPs). These critical pollutants have to be delimited, reduced and phased out strategically to provide better environmental quality for future generation.

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