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DIOXINS AND FURANS : A BRIEF OVERVIEW

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Toxic organic pollutants are entering into the environment due to advancement in technology. These organic pollutants may be agrochemicals, Industrial by-products, Dyes, paints etc. These toxic organic pollutants are produced intentionally or unintentionally and entering into the environment due to their persistent, long range transport property, bioaccumulative nature. Chlorinated aromatic compounds named as polychlorodibenzo-p-dioxins and polychlorodibenzofurans are persistent organic pollutants which are mainly produced unintentionally by the incineration of hazardous waste, municipal waste, pharmaceutical waste etc. These are persistent in nature due to their high melting point and low vapour pressure. As a consequence of this, accumulation or adsorption takes place in organic matter, in sediments, suspended solids, fly ash, soot and fatty tissues of organisms and enters in human tissues and wildlife also. Mainly 17 congeners with chlorine are reported to have potential health effects. 2, 3, 7, 8-TCDD is considered to be an extremely toxic compound considered as carcinogenic in nature. Seventeen dioxin congeners have been identified as having significant toxicity and have been assigned the Toxic Equivalent Factors (TEF). So, different sources, standards, toxicity and impact on human health will be discussed in my paper.

Keywords : Persistent Organic Pollutants (POPs), Polychlorinated dibenzodioxins (PCDD) and Polychlorinated dibenzofurans (PCDF).

INTRODUCTION

Persistent Organic Pollutants (POPs) are as the name suggests, persist in the environment for very long period in the environment due to their slow degradation [1]. These bioaccumulate in soil, water or air [2, 3]. Even when released in relatively small quantities they degrade very slowly [1].

There are number of POPs. Some are used intentionally like various agrochemicals, dyes etc. and some are produced unintentionally like Dioxins and Furans [1]. These POPs enter into the environment from various sources like household furnaces, various agricultural sprays, incinerators, medical waste, combustion of fossil fuels etc. [3-7]. These pollutants are highly toxic in nature and affecting the health of human beings and animals. Human beings are getting exposed to these toxic pollutants occupationally, orally, by direct contact, through respiration or accidentally. The two unintentionally produced dioxins and Furans are

polychlhorinated biphenyl compounds. Polychlorinated dibenzodioxins (PCDD) Polychlorinated dibenzofurans (PCDF) are commonly regarded as highly toxic compounds and causing various ill-effects on human health. There are 75 PCDDs, and seven of them are specifically very toxic in nature. There are 135 congeners (derivatives differing only in the number and location of chlorine atoms) [8]. The structures of PCDD and PCDF are:

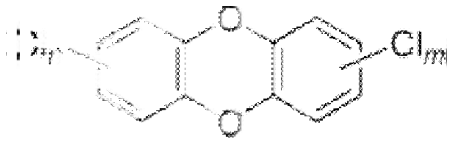

Fig. 1. Polychlorinated dibenzo-p-dioxins (PCDD). [2]

Fig. 2. Polychlorinated dibenzofurans (PCDF). [2]

PCDD and PCDF are the subject of recent, often heated debate because some of these compounds are very toxic *e.g*. 2, 3, 7, 8-tetrachlorodibenzodioxins (2, 3, 7, 8-TCDD) has been found to be acnegenic to humans, carcinogenic to rats etc.[9]

I. HISTORY and STOCKHOLM CONVENTION

Various organic chemicals were produced commercially before and during the World War II. William Perkin synthesized coloured substance from coal tar which can be used in dying the clothes. First chemical industry was also set up by Perkin in 1857. Afterwards a number of chemical industries were set up and producing various organic chemicals like agrochemicals, pharmaceuticals, paints, dyes, plastics etc. [10]. After the World War II, the various ill effects are being noticed due to these toxic organic chemicals and it was found that this is due to the persistent nature of chemicals so they had been given the name Persistent Organic Pollutants (POPs) [11].

Convention on Long-Range Transboundary Air Pollution (CLRTAP) integrated POPs into its agenda, creating a CRTAP POPs agreement that covers "Dirty Dozen" regulated under the Stockholm convention. The Chemistry, sources and toxicity of these twelve POPs was assessed by the working group. The 'Dirty Dozen includes Aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, dioxins, endrin, furans, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls and toxaphene. The foundation of Stockholm Convention was laid down in 2001 when 91 countries and EU signed the convention in Stockholm, Sweden. The convention entered into force on 17th May 2004 [12]. Afterwards a number of meetings were held and last 7th meeting was held in Geneva from 4-15 May 2015 on the theme "From science to action, working for a safer tomorrow". Currently some more chemicals like Dicofol, short chain chlorinated paraffins etc. are under review.

II. Sources of PCDD & PCDF

Dioxins and furans are unintentionally produced during most forms of combustions like

(i) Burning of municipal waste

(ii) Medical wastes

(iii) backyard burning of trash

(iv) Industrial processes.

Also can be found as trace contaminants in certain herbicides, wood preservatives, and in PCB mixtures [1, 13]

An issue of particular concern is the exposure of the human foetus and newborn infants to POPs through placental blood, breast milk and baby food as high levels of these contaminants have been reported in these substances [14].

More recently, PCDD and PCDF have been discharged as an effluent from the various combustion process i.e. incineration of various wastes. In particular dioxins and furans have been found in fly ash and flue gas of municipal incinerators [9]. PCDD and PCDF are also released as by-products of combustion processes of various hazardous wastes. Most coal fired thermal plants are also releasing Dioxins and Furans by burning compounds containing chlorine atoms e.g. sodium chloride.

The Government of India stated in the Manual of Municipal Solid Waste Management 2016 that the urban growth is very fast in India. The ratio of people residing in urban areas has increased from 27.8 % in 2001 to 31.80% in 2011 and it is supposed to reach 50 % by 2030. It is estimated that municipal solid waste generated from urban areas is about 150,000 tonnes per day. The per capita waste generated in major cities ranges from 0.20 to 0.60 kg per capita. The municipal solid waste consist about 40-60% organic fraction, 30-40% ash and fine earth, 3-6% paper and less than 1% of plastic, glass and metals each [15] . A study carried out by CPCB in 59 cities shows that Ludhiana, with highest population growth in the state, ranks 12th in the country in terms of waste generation. With increase in population, urbanization, consumerism, etc. the generation of solid waste is increasing considerably, As per Punjab Pollution Control Board (PPCB), All the 137 Municipal Bodies (including towns and cantonments) are collectively generating 2944.4 tons/day of municipal solid waste per day is generated by all the Municipal Bodies out of which 73% is being generated in 5 Municipal Corporations (i.e. Ludhiana, Jalandhar, Amritsar, Bathinda and Patiala) alone [16]. Electronic waste or e-waste includes used T.Vs, computers, mobile phones, electronic devices, etc. With increase in production and use of electronic goods, the generation of e-waste is also increasing [17].

Table 1. Toxic elements of a computer [6]

Components of PCs	**Toxic constituents**
Printed circuit boards	Lead and cadmium
Cathode Ray Tubes (CRTs)	Lead oxide and cadmium
Switches and flat-screen monitors	Mercury
Computer batteries	Cadmium
Capacitors and transformers	Poly Chlorinated Biphenyls (PCBs)
Printed circuit boards, plastic casing cable	Brominated Flame Retardants (BFRs)
Cable insulation	Poly Vinyl Chloride (PVC), releaseshighly toxicdioxins and furans when burned to retrieve copperfrom the wires

So with growth of population and technology, use of electronic products is increasing indirectly there is increase in e-waste by which more amounts of dioxins and furans are entering into the environment.

Table 2. State wise Incineration Facilities for Management of Hazardous Waste. [18]

S.No.	Name of State/UT	Nos. of Common Incinerator	Nos. of Captive Incinerator
1	Andhra Pradesh	2	26
2	Gujarat	4	35
3	Himachal Pradesh	-	7
4	Karnataka	3	7
5	Kerala	1	1
6	Madhya Pradesh	-	7
7	Maharashtra	2	-
8	Punjab	-	17
9	Pondicherry	-	1
10	Rajasthan	-	5
11	Uttar Pradesh	1	13
12	West Bengal	1	4
13	Damman, Diu, Dadra& Nagar haveli	-	4
Total 12 states and 1 UT		14	127

III Emissions

Table 3. Dioxin Emission data for Common and Captive Incinerators[18]

S.No.	Name of Unit	EmissionngTEQ/Nm^3
Common Incinerators		
1	Bharuch Enviro Infrastructure ltd. Ankaleshwar	0.0255
2	Mumbai Waste Management ltd. Taloja	8.621
3	Gujarat Enviro Protection &Infra.ltd. Surat	0.0352
Drug Manufacturing Units		
1	M/s Ranbaxy Laboratories Ltd, Tonsa	0.1965
2	M/s Lupin limited, Ankleshwar, Gujarat	0.0156
3	M/s NatcoPharma Ltd, Mekaguda,	AP 0.1866
Dyes and Dye Intermediates Manufacturing units		
1	Color Synth Industries (P) ltd. Surat Gujarat	0.0203
2	Atul Ltd., Atul Gujarat	0.0684
3	Metrochem Industries (P) ltd., Baroda	0.051
Pesticides Manufacturing Units		
1	PI Industries ltd., Panoli	0.0195
2	Bayer Crop Science, Thane	0.50
3	Syngenta India ltd., Goa	0.38
Basic Organic Chemicals manufacturing Units		
1	Jubilant Organosys ltd., Gajraula. UP	0.029

2	ChemplastSanmar ltd., Tamil Nadu	1.36
3	Gwalior Chemical Industries ltd., Nagada	6.4717

On an average a hospital bed generates 1 kg of waste per day, out of which 10-15 percent is infectious, 5 percent is hazardous and rest is general waste. As per PPCB the total bed capacity in the state is approximately 35000. Hence, according to Toxics Link a total of approximately 35000 kg/day of waste is being generated from these institutions, if the occupancy of the beds is 100%. Out of total waste generated by these HCEs 4478 kg/day (approx. 12.9%) of infectious biomedical waste is being collected and treated [18].

Incineration is a common method of disposal of infectious wastes and body parts. However, high temperature burning can cause air pollution by release of dioxins and furan (especially while incinerating plastics used in medical equipments). So due to the commercialization and modern living standards a huge amount of waste is entering into the environment and unintentionally dioxins and furans [18]

All groups of dioxin-like compounds are persistent in the environment. Neither soil microbes nor animals are able to break down effectively the PCDD/Fs with lateral chlorines (positions 2, 3, 7, and 8). This causes very slow elimination. Lipophilicity (tendency to seek for fat-like environments) and very poor water solubility make these compounds move from water environment to living organisms having lipid cell structures. This is called bioaccumulation. Due to persistent nature and bioaccumulation the unintentionally produced chemicals are affecting the trophic levels of pyramid. Bioaccumulation is followed by biomagnification. Lipid soluble compounds are first accumulated to microscopic organisms such as phytoplankton (plankton of plant character, e.g. algae). Phytoplankton is consumed by animal plankton, this by invertebrates such as insects, these by small fish, and further by large fish and seals. At every stage or trophic level the concentration is higher, because the persistent chemicals are not "burned off" when the higher organism uses the fat of the prey organism to produce energy [8].

Given the lipophilic characteristics of POPs, it is expected that POPs will accumulate in adipose tissues. For example, PCDD/DF levels were 312 pg/g of fat in samples taken near a municipal dumping site in Southern India. This level was significantly higher than levels of 2-3 pg/g of fat lipid reported from countries around the world [14]. Dioxins are very less soluble in water so Kidneys are not able to secrete them and slowly their concentrations increases in the human body. Same happens in case of animals.

IV. Standards and Toxicity levels

The standard prescribed for the emission of total dioxins and furans is 0.1 ng TEQ/Nm^3 WHO has specified a standard for Total Daily Intake (TDI) of 1-4 pg TEQ/kg body weight/day. Considering average body weight of 60 kg and air intake of 20 m^3/day (with 5% inhalation contribution), the allowable concentration levels were calculated to be 0.15 – 0.60 pg TEQ/m^3in ambient air [18].

Dioxins and Dioxins like compounds form a broad class of compounds. The toxicity of different congeners of PCDD and PCDF can be calculated by comparing their toxicity with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) because TCDD is most toxic of all the congeners. Other dioxin congeners (or mixtures thereof) are given a toxicity rating from 0 to 1, where TCDD = 1. This toxicity rating is called the Toxic Equivalency Factor, or TEF [18] 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 [19].TEF values exist for seven congeners of PCDD(varies from 1-0.001) and ten congeners of PCDF(varies from 0.1-0.001) [18].

From June 29-July 3, 1998, the United Nations Environment Program (UNEP), together with other relevant international organizations, convened the first session of the Intergovernmental Negotiating Committee (INC-1) in Montreal, Canada. John Buccini from Canada was elected as Chairman of the INC process. With 100 countries represented, INC-1 initiated work on the mandate to prepare a legally-binding instrument for implementing international action by the year 2000 on an initial list of twelve POPs: aldrin, chlordane, DDT, dieldrin, dioxins, endrin, furans, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls (PCBs), and toxaphene. They fall into three categories: pesticides, industrial by-products, and unintended by-products of combustion and industrial processes [20]

V. Effects on human health

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) [19].

Dioxins and Furans entered into the human body by various modes like breathing air, contaminated food and water and soil. People working in or near to the incinerators of solid and hazardous waste, cement kiln or coal fired thermal power plant are generally exposed with dioxins and furans. Even people burning household waste or burning wood can be exposed with these toxic chemicals.

Short term exposure to high levels of dioxin may result in chloracne and other related skin disorders. It also causes immune system toxicity, gastrointestinal ulcers, and also may lead to neuro-toxic effects. It may cause choking of lungs and increases susceptibility to cancer. 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 [19].

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 [19].

2, 3, 7, 8-TCDD is carcinogenic to humans.Other PCDDs are not classifiable as to their carcinogenicity to humans. PCDFs are not classifiable as to their carcinogenicity to humans. [21].

Conclusions

The study reveals that the main sources of Dioxins and Furans in India are Incinerators where solid waste undergoes combustion. These toxic compounds are entering into the environment Due to lack of infrastructure and Laboratories which can detect the trace amount of PCDD and PCDFs. There is need to modify incinerator plants to reduce emissions of such toxic chemicals. Best ways to achieve goals are : reduce solid waste, effective segregation of waste, proper design of incinerators, manufacturing incinerators away from populated areas, regular maintenance and organising training and management programme. So lot of work is needed to do to reduce/prevent the emission of such toxic chemicals.

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