Dioxins

Toxics Link
Factsheet
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What are Dioxins

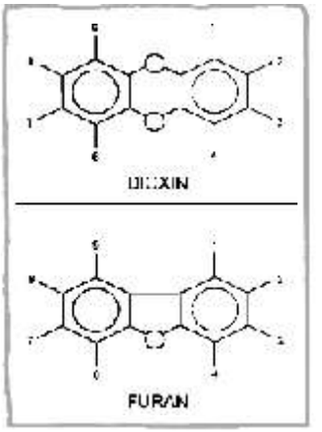
Dioxins are the part of original "dirty dozen" list of persistent organic pollutants (POPs) which have been banned under Stockholm Convention. These chemicals are unintentional by-products of certain industrial activities and incomplete combustion. Dioxins have also been found in automobile exhaust, tobacco smoke and wood and coal smoke.

Dioxins are polychlorinated aromatic compounds with similar chemical, physical properties and structures. They are not naturally existing chemicals. They are not produced intentionally or deliberately, but are formed as a by-product of chemical processes. These include the manufacturing of chemicals, pesticides, steel and paints, pulp and paper bleaching, exhaust emissions and incineration. For example, when chlorinated waste is burned in an uncontrolled way in an incinerator, the emissions into the air contain dioxins. There is a continuing debate about whether dioxins are produced from non-anthropogenic sources. It is possible that some natural processes produce very small quantities but this would be a very minor contribution to the total emissions to the environment.

The name 'dioxins' is often used for the family of structurally and chemically related polychlorinated dibenzo para dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), also known as furans. There are over 5,000 halo-genated dioxins but most studies have concentrated on just seventeen chlorinated dioxins. The most toxic of these is 2,3,7,8-tetrachlorodibenzo-p-dioxin, abbreviated as 2,3,7,8- TCDD. It is measured in parts per trillion (ppt).

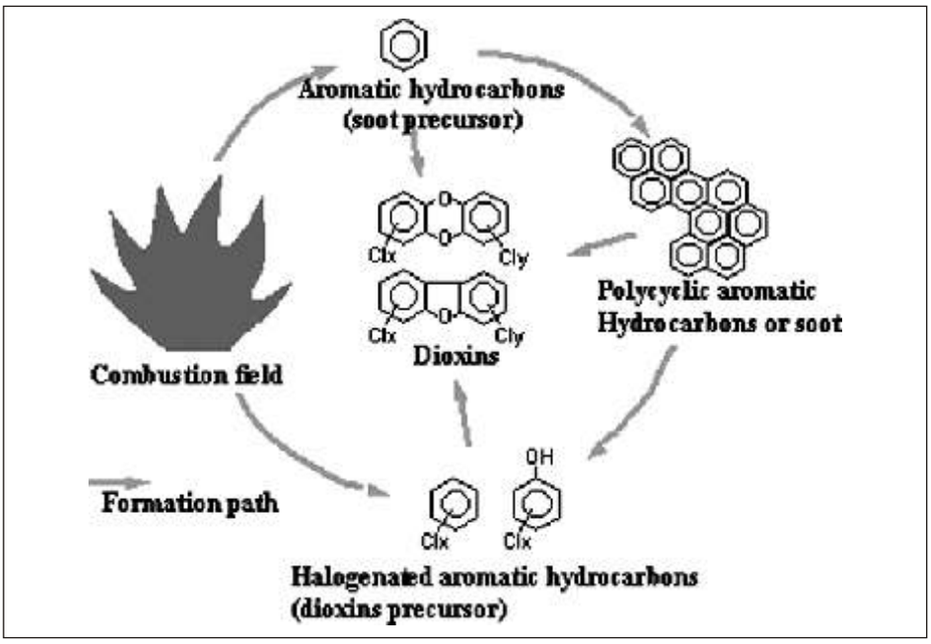
Characteristics of Dioxins

Physical properties: In the pure form dioxins are crystals or colourless solids.



AT A GLANCE

- **Dioxin sources include, agricultural and backyard burning of household wastes, incinerators, atmosphere, sewage sludge, pesticides, fertilizers etc.**
- **Besides cancer human exposure to dioxins can cause a number of serious diseases, disruptions and disorders of liver, thymus, spleen, endocrine gland, skin etc. In extreme cases death is also not rare.**
- **Livestock can also get affected by dioxin exposure leading to health hazards for them.**
- **Unfortunately, India does not have any standards for dioxin in food products. India lacks environment standards for dioxin too**



Generally present, as mixtures containing a number of individual components 2,3,7,8-TCDD is odourless. The odours of the other dioxins are not known. As mentioned above all compounds in the dioxin family have varying degrees of toxicity in comparison to the most toxic 2,3,7,8-TCDD. Melting point of dioxin is 305-306 (°C) and thermal decomposition happens at 700 (°C). Other compounds in these families have differing properties, depending on the number and position of chlorine atoms in the molecule.

Chemical properties: In general the compounds have low water solubility and low vapour pressure. Many are very stable and tend to bioaccumulate. Dioxins are highly soluble in fat. This means that they bind to sediment and organic matter in the environment and are absorbed in animal and human fatty tissue. In addition they are not biodegradable so they are persistent and bioaccumulate in the food chain. When released into the air, they settle down locally. When released into lakes or rivers, most dioxins accumulate in the sediment. In soil, dioxins attach to soil particles and remain so for long periods before they can be re-released into the environment. Burning household trash in yard can contaminate soil with dioxins.

What are PCBs

PCBs, or polychlorinated biphenyls are another group of chemicals. They are chlorinated aromatic hydrocarbons, which are synthesized by direct chlorinating of biphenyls. Technical PCB mixtures are still widespread and present today, such as in transformers, building materials, lubricants, coatings, plasti-cizers and inks. Some of the PCB compounds have toxicological properties that are similar to dioxins and are therefore often termed "dioxin-like" PCBs.

Sources

Dioxins are formed as unwanted by-products from a number of human activities including certain industrial processes (e.g., production of chemicals and combustion processes). Accidents at chemical factories have been shown to result in high emissions and contamination of local areas. Other dioxin sources include domestic heaters, agricultural and backyard burning of household wastes. In terms of dioxins release into the environment, waste incinerators (solid waste and hospital waste) are often the worst culprits, due to incomplete burning and large amounts of waste incinerated.

Sources of dioxins in soil include deposition from atmospheric dioxins, application of contaminated sewage sludge to farm land, flooding of pastures with contaminated sludge, and prior use of contaminated pesticides and fertilizers.

Dioxins are poorly soluble in water; however, they are adsorbed onto mineral and organic particles suspended in water. The surfaces of oceans, lakes and rivers are exposed to aerial deposition of these compounds, which are consequently concentrated along the aquatic food chain. The entry of waste water or contaminated effluents from certain processes, such as chlorine bleaching of paper or pulp or metallurgical processes, can lead to contamination of water and sediment of coastal ocean areas, lakes and rivers.

Current sources of dioxins entering the food chain include new emissions and remobilisation of deposits or reservoirs in the environment. New emissions are mainly via air.

Routes of exposure to dioxins

Food of animal origin is the predominant route of human exposure to dioxins due to the deposition of these substances in the lipid component of animal- derived foods. In lactating animals dioxins are excreted partly with milk fat, and in laying hens they are concentrated in fat content of the yolk in laid eggs.

Approximately 80-90 %, or more, of the total exposure in the human general population is via fats in fish, meat, eggs, milk and dairy products. In 2005, International POPs elimination network (IPEN) conducted a study to determine dioxin levels in eggs. It found high levels of dioxins and PCBs contamination in free-chicken eggs from 20 locations in 17 countries. Levels of dioxins in animal fat may be related to contamination of the local environment and to contamination of feed or, to certain production processes (e.g., artificial drying, smoking). Infants are exposed through the assumption of contaminated breast milk.

Occupational exposure is an issue for some in the chemical industry, or in agriculture sector, e.g. through application of chemicals, notably herbicides.

Due to the omnipresence of dioxins, all people have background exposure and a certain level of dioxins in the body, leading to the so-called body burden. Due to the high toxic potential of this class of compounds, efforts need to be undertaken to reduce current background exposure.

Animal exposure to dioxin contamination by feed may originate from many different sources. Dioxins may be inherent to a product (e.g. clay minerals, recuperated copper sulphate, zinc oxide, food by-products and fish by-products such as fish meal and fish oils), can be formed during heat processing (e.g. lime in citrus pulp, directly dried bakery waste), or may arise through the use of treated wood in animal production, the grass meal or grass meal pellets produced from grass dried directly fed flue gases from (e.g. coal-fired heating plants) and pasture placed near polluting plants (e.g. coal-fired heating plants).

The uptake of dioxins by fish occurs via gills and diet. Fish accumulate dioxins in their fatty tissue and liver. Bottom dwelling/bottom feeding fish species are more exposed to contaminated sediments than pelagic fish species. However, these levels are not always higher than those in pelagic fish depending on the size, diet and physiological characteristics of the fish. In general, fish show an age-dependent accumulation of dioxins.

Health effects

Dioxins are known to cause a wide variety of toxic effects and to be carcinogenic in humans and animals. Endocrine, reproductive and developmental effects are among the most sensitive to dioxin exposure. In general, toxic exposure to dioxins has been known to cause disorders of liver, thymus and spleen, endocrine disruption, skin lesions and in extreme cases, death. The most sensitive effects, observed in multiple species, appear to be developmental, including effects on the developing immune, nervous, and reproductive systems. Health effects can be observed for years after the initial exposure. Intoxications can be acute or chronic depending on the toxic dose ingested and the time of exposure.

Differences in species sensitivity for dioxins exist and have been suggested to be a result of either different body fat compositions by species or of differences in metabolism. In spite of the differences in the amount of chemical required to elicit a toxic response, once toxicosis is induced, the toxic effects observed in different animal species are very similar.

Effects on human beings

Short-term exposure of humans to high levels of dioxins may result in skin lesions, such as chloracne and patchy darkening of the skin, and altered liver function. Long-term exposure is linked to impairment of the immune system, the developing nervous system, the endocrine system and reproductive functions. Chronic exposure of animals to dioxins has resulted in several types of cancer. TCDD was evaluated by the WHO's International Agency for Research on Cancer (IARC) in 1997. Based on animal data and on human epidemiological data, TCDD was classified by IARC as a "known human carcinogen". There is however, continuing debate about whether TCDD affects genetic material and whether there is a level of exposure below, which cancer risk would be negligible. Experimental data indicate that endocrine and reproductive effects should be among the most sensitive effects in both animals and humans.

Effects in animal species

In poultry, several clinical signs have been described after dioxins exposure through ingestion of contaminated feed during the Belgian dioxin crisis in 1999. The symptoms included a decrease in egg production and hatching. Furthermore, the chicken edema disease was observed with symptoms of hydropericardium, edema and ascitis leading to a high mortality rate.

In cattle weight loss and emaciation, with food intake remaining at normal level, have been associated with dioxin intoxication. Furthermore, drop in milk production and pathologies in kidneys, spleen and skin can be observed. In dairy cows, hypofertility has been associated

with grazing in a highly contaminated industrial area in Italy.

In experimental animals dioxins have a broad spectrum of hepaptoxic, immunotoxic, carcinogenetic, teratogenetic effects and causes developmental, reproductive and dermal toxicity. Endometritis has been linked to chronic exposure to dioxins in primates and rodents. In an incident where a horse arena became contaminated, horses showed signs of intoxication such as chronic weight loss, hair loss, skin disorders, colic, dark urine, conjunctivitis, joint stiffness, and laminitis. In dogs and cats weight loss and pathologies in liver and kidneys as well as skin lesions have been observed.

Prevention and control of dioxin exposure

Source-directed measures are essential for a further reduction of dioxin contamination. These measures should be directed towards reducing the formation of dioxin during thermal processes and destruction techniques, minimizing releases from existing equipment, preventing accidents and having a better control over the disposal of dioxins containing oils and wastes.

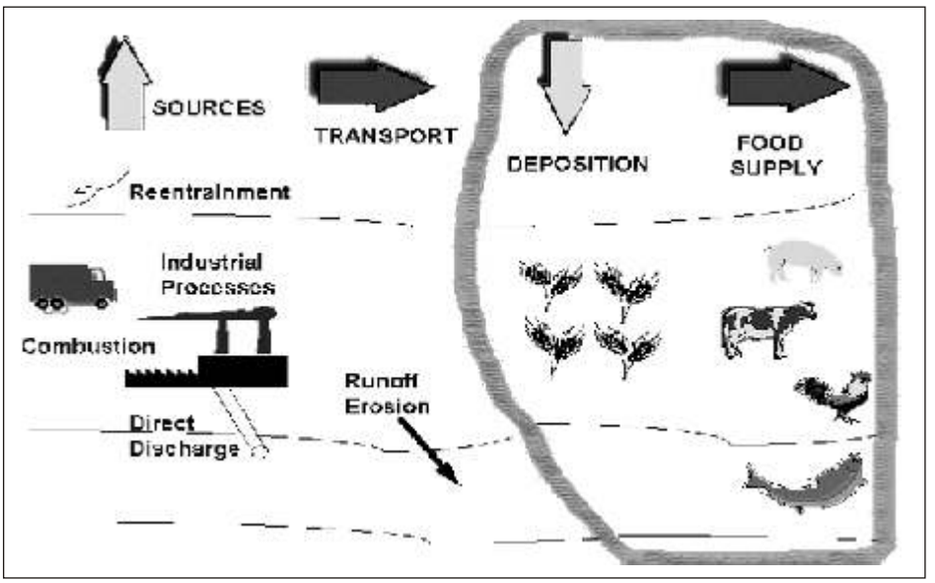
As more than 80%-90% of human exposure to dioxins in the general population is through food supply, (mainly meat and dairy products, fish and shellfish), protecting the food supply from dioxins contamination is critical. Measures to reduce dioxins

contamination entering in the food chain should aim at preventing or reducing contamination of environment (air, soil and water) and animal feed (for convenience herein after, the term feed is intended to include also feed ingredients); at preventing or reducing the formation of dioxins during food and feed processing; and at applying good agricultural and hygienic practices during primary production, processing, distribution and sale of food and feed.

Contaminated animal feed above background levels should be identified and, where necessary, excluded from entering in the food chain. To reduce dioxins contamination in the environment, national authorities should avoid incineration; stop uncontrolled burning of wastes, including the burning of landfill sites or backyard burning; and prevent the use of PCB treated wood, or oil, for domestic heaters.

Areas with unacceptable dioxins contamination in the soil, water and air should be identified and controlled. If necessary, agricultural production should be avoided or restricted.

It is the role of government and producers to monitor the safety of food and feed supply and to take action to protect public and animal health. Food contamination monitoring systems must be in place to ensure that guideline levels / maximum levels are not exceeded. When incidents of contamination are suspected, countries should have contingency plans to identify, detain and dispose of contaminated food and feed. The exposed population should be examined in terms of exposure (e.g. measuring the contaminants in blood or human milk) and effects (e.g. clinical surveillance to detect signs of ill health).



Recommended specific measures to prevent and control contamination of food and animal feed

In order to reduce the contamination of food, control measures to reduce the dioxins at the feed level should be considered. These measures may involve developing good agricultural practice, good animal feeding practice and good manufacturing practice.

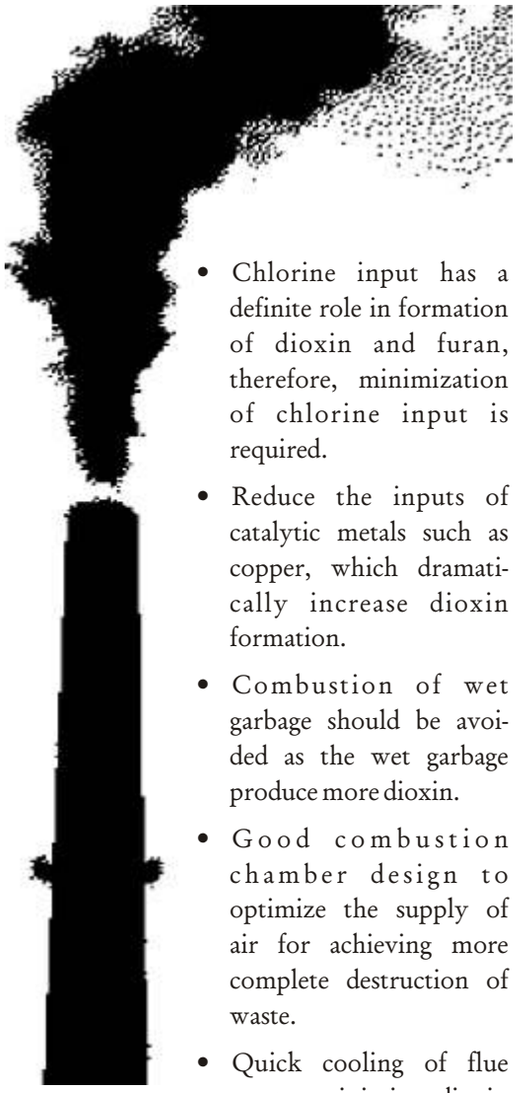
Measures include:

- Set standards for dioxins in soil and water and recommendation for specific agricultural use (e.g., limitation of grazing or use of appropriate agricultural techniques);
- When the standard is exceeded, government should decide whether and under what circumstances the food should be distributed
- Avoid areas with increased dioxin contamination due to local emission, accidents or illegal disposal of contaminated materials used for grazing or for the production of feed crops. If possible, contaminated soil should be treated and detoxified or removed and stored under environmentally sound conditions;
- Avoid spreading of sewage sludge contaminated with dioxins on pasture and grazing areas. Sewage sludge used in agriculture should be monitored for compliance with the guideline levels, as necessary for dioxins. Additionally, sewage sludge should be treated, as necessary, to render it inert or to detoxify it;
- Prevent contaminated animal derived feed from entering the food chain; animal derived feed should be monitored, as necessary, for dioxins;
- Monitor compliance with standards and minimize or decontaminate non-complying feed;
- Identify possibly contaminated feed and control critical feed manufacturing processes (e.g., artificial drying by direct heating);
- Similar control measures, where applicable, should be considered for reducing dioxins in food.

Dioxin Emission Control at Incinerators

Some of the measures for controlling Dioxin emission at incinerators are following:

- 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.
- Reduce the inputs of catalytic metals such as copper, which dramatically increase dioxin formation.
- Combustion of wet garbage should be avoided as the wet garbage produce more dioxin.
- Good combustion chamber design to optimize the supply of air for achieving more complete destruction of waste.
- Quick cooling of flue gas to minimise dioxin formation between 200 to 4000C. Regular monitoring of combustion products including dioxin emissions.

Dioxin Emission Control at Chemical Waste Treatment

Some of the important measures recommended to control dioxin emission at chemical waste treatment are stated below:

- Using non-combustion alternatives to incineration whenever possible.
- Incinerators (rotary kilns for hazardous wastes) should operate at temperature more than 10000C and higher if PCB contaminated waste is being incinerated.
- Waste heat boiler should not be used on chemical waste incinerators and flue gasses should be rapidly quenched to below 2000C .
- Efficient functioning of wet scrubber to remove hydrogen chloride from flue gas.

Dioxin Emission Control at Cement Kilns

Cement kilns are potential dioxin emission source. Waste burned in kilns and, occasionally naturally occurring precursors of dioxins in raw materials can generate high levels of emissions of dioxins from cement kilns in certain circumstances. Methods to reduce this risk include:

- Avoiding any chlorinated or halozgenated inputs
- Minimizing metal inputs to kilns
- Changing 'hot sided' electrostatic precipitators to bag filters
- Change of raw materials and other inputs for reduced dioxin and furan emissions.

Methods of analysis

The method of choice for the combined confirmation of dioxins is gas chromatography high-resolution mass spectrometry (GC/HR-MS) after extensive sample clean-up. This expensive and time-consuming technique is only applied by a relatively small number of laboratories. Thus, there will be a delay of several days between an incident and the results of the analysis.

Dioxin-like PCBs can also be determined by gas chromatography with other low-resolution mass spectrometry instruments. For screening purposes of mixtures of dioxins including dioxin-like PCBs, less expensive and more rapid bio-assays such as the Calux-assay are applied. Although these bio-assays are successfully applied in various laboratories, there is still a need for improvement with regards to robustness and selectivity, although knowledge of the degree toxic effects of the mixture, which is measured by the bioassay, is an important tool for risk management measures.

As analysis of dioxins by GCMS are quite expensive in comparison to determination of other chemical contaminants, periodic tests should be performed to the extent feasible at least by industrial feed and food manufacturers including both incoming raw materials and final products and data should be kept. As many combustion processes, particularly those burning mixed wastes, have very variable emissions it is not normally possible to reduce the frequency of sampling based on previous results nor to rely on data from industry results within the same sector.

Continuous sampling for dioxins is available and should be used for any new large-scale facility.

Environmental Standards for Dioxin

Whilst environmental standards for dioxin adopted by various agencies worldwide vary the emission standards in the European Union (0.1 ng l-TEQ/ m3 should normally be used for new facilities.

Codex Alimentarius has recommended code of practices for the prevention and reduction of dioxin and dioxin like PCB contamination in food and feeds (CAC/RCP 62-2006).

European union in year 2002 decided to set legally binding limits on dioxins in food and animal feeds. EU's overall plan is to reduce human daily intake of dioxins to <2 picograms per kilogram of body weight, a value established by EU's Scientific Committee on Food. The EU established a regulation on feedstuffs that limited dioxins in animal products including eggs and egg products to 0.75 pg WHO-TEQ/g of fat. The same regulation limits dioxins in animal fat (including egg fat) to 2.0 pg WHO-TEQ/g of fat.

Dioxin and Women

Dioxin is particularly worrisome for women, who can accumulate it in their bodies for years and then pass it on to their children or nursing infants. Dioxin can pass through the placental barriers to foetus and also through breast milk to infants. In one of the recent study reported in Chemosphere (Dioxins in adipose tissue of women in Soutehrn Spain by Lopez-Espinosa MJ, Kiviranta H, Araque P, Ruokojarvi P, Molina-Molina JM, Fernandez MF, Vartiainen T, Olea N. Chemosphere. 2008, 73, 6, 967-971) authors quantified seventeen polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in adipose tissue samples of non-occupationally exposed women living in Southern Spain. Geometric mean levels of sum

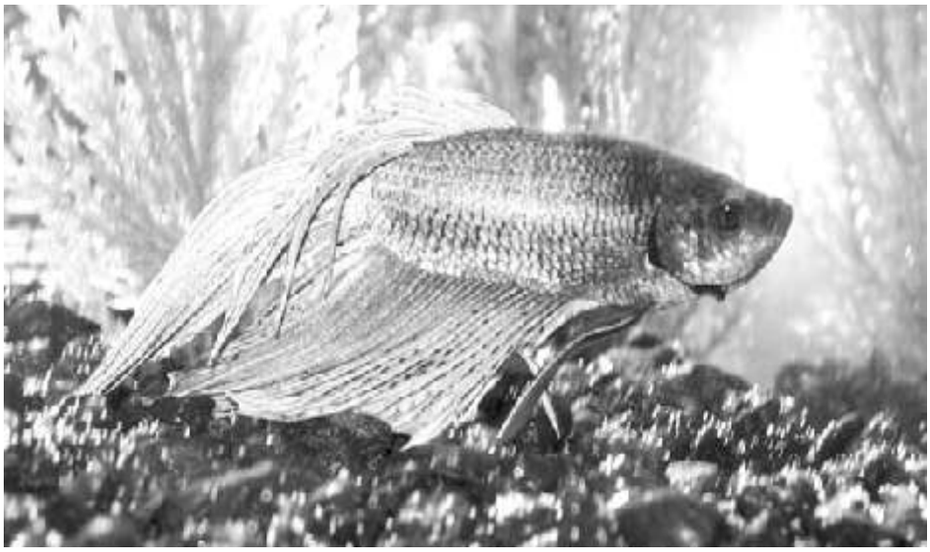
of congeners and WHO (PCDD/F)-TEQ (2005) were 410 and 17.9pgg(-1) fat, respectively. Among PCDDs, octachlorodibenzo-p-dioxin (OCDD) showed the highest concentration with a mean value of 265pgg (-1) fat, followed by 1,2,3,6,7,8-HxCDD (49.3pgg (-1) fat) and 1,2,3,4,6,7,8-HpCDD (45.2pgg(-1) fat). These three congeners were responsible for around 90% of the sum of all PCDD/F congeners in adipose tissue. The geometric mean 2,3,7,8-TCDD value was 1.87pgg (-1) fat. 2,3,4,7,8-PeCDF (8.43pgg (-1) fat) showed the highest concentration among the PCDFs, followed by 1,2,3,4,7,8-HxCDF (4.17pgg (-1) fat) and 1,2,3,6,7,8-HxCDF (3.28pgg (-1) fat), and these three congeners were responsible for 4% of the sum of all studied PCDD/F congeners in adipose tissue and 76% of the sum of ten PCDFs. 1,2,3,7,8,9-HxCDF was the only congener not quantified in any sample, while 1,2,3,4,7,8,9-HpCDF, 1,2,3,7,8-PeCDF, OCDF and 2,3,7,8-TCDF were found in 5, 16, 16 and 19 samples, respectively. All other congeners were quantifiable in all 20 samples. Congeners contributing most to the WHO (PCDD/F)-TEQ (2005) were 1,2,3,7,8-PeCDD (31.6%), 1,2,3,6,7,8-HxCDD (28.3%) and 2,3,4,7,8-PeCDF (14.6%). The body burden of log-transformed WHO (PCDD/F)-TEQ (2005) levels increased with age ($B = 0.02$; 95% $CI = 0.01, 0.03$; $p = 0.02$). Authors further point out that although these adipose tissue PCDD/F levels are similar to previously published findings in Spain and other European countries, further research is needed to determine trends in the exposure of women to these chemical residues.

Dioxin and India

In one of the important studies done by IPEN in year 2005 to determine levels of dioxins in egg samples, it collected samples from 17 countries and 20 locations. It also collected 10 egg samples from two locations in India, viz., Lucknow and Kerala. The results found egg samples to be contaminated with dioxins exceeding the EU standards.

Another study reported in Environ. Sci.Technol. (Polychlorinated Dibenzo-p-Dioxins, Dibenzofurans, and Polychlorinated Biphenyls in Human Tissues, Meat, Fish, and Wildlife Samples from India. Kumar KS, Kannan K, Paramasivan ON, Sundaram VPS, Nakanishi J and Masunaga S. 2001. 35, 17, 3448 -3455) measured concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and non- and mono-ortho-substituted polychlorinated biphenyls (dioxin-like PCBs) in tissues of humans, fishes, chicken, lamb, goat, predatory birds, and Ganges River dolphins collected from various locations in India. PCDDs/DFs were found in most of the samples analyzed with the liver of spotted owlet containing the highest concentration of

3300 pg/g, fat wt. 2,3,7,8-Substituted PCDDs and PCDFs were found in human fat tissues at concentrations ranging from 170 to 1300 pg/g, fat wt. Concentrations of PCDDs were generally greater than those of PCDFs in human tissues, fish, animal fat, and dolphin. Among fish, meat, and wildlife samples analyzed, concentrations of PCDDs/DFs were found in the following order: country chicken < goat/lamb fat < fishes < river dolphins < predatory birds. Hepta-CDDs and OCDD were the major PCDD homologues found in humans, fishes, meat products,



and dolphins. 2,3,7,8-Tetrachlorodibenzo-p-dioxin equivalents of PCDDs/DFs were greater than those of PCBs in selected fish, dolphin, and human samples.

Last year EU food safety experts issued a alert on high levels of dioxins in gum shipments from an India supplier. This has had an impact on guar gum exports as India accounts for 80% of world trade in guar gum, a food additive extracted from the guar bean. Swiss company Unipektin AG, which supplied guar gum products to EU markets, recalled several batches of food additives containing guar gum sent by India Glycols on July 30, 2007.

It is unfortunate that India does not have any standard for dioxin in food products. India also lacks environmental standards for dioxins. As a signatory to Stockholm Convention, India is mandated to prepare a national implementation plan (NIP). An Inception Workshop for the development of a National Implementation Plan of Stockholm convention on Persistent Organic Pollutants (POP) was held on 6th may 2008 according to Press In formation Bureau, Government of India. It was to be the first step to prepare implementation mechanism in India.

GEF has sanctioned US $ 3,074,700 for India's National Implementation Plan (NIP). According to National Institute for Interdisciplinary Science & Technology (NIST) earlier Regional Research Laboratory sources, Trivandrum, the project "Development of NIP in India as first step to implementing Stockholm Convention on PoPs" is of two years duration. The Project documents have been signed on 8th November, 2007 by GEF Operation Focal Points in India.

Four premier Institutions are jointly working on this project. The Hindustan Insecticides Ltd., New Delhi, would undertake project activities related to Pesticides including DDT; the Central Power Research Institute (CPRI), Bangalore would cover the PCBs; the National Environment Engineering Research Institute (NEERI), Nagpur of the CSIR would cover POPs Stockpiles and Wastes; the unintentionally produced POPs, Dioxins and Furans would be jointly undertaken National Institute for Interdisciplinary Science & Technology (NIST), Trivandrum , the Central Pollution Control Board (CPCB), New Delhi and the NEERI, Nagpur. As usual NGOs were again sidelined.

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