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Dioxins in the Environment: A Critical Review

By

K.I. Idehen[*], G. Obi[**]

Abstract
The objective of this paper is to review the health effects and environmental risks of dioxins, which are persistent organic pollutants (POPs) present in the environment occurring naturally and as by-products of combustion and of various industrial processes. The review explains in plain terms the nature of dioxins, how they are generated, highlighting particularly the environmental implications of constant exposure to these harmful substances and introducing pollution prevention/management strategies that will help promote public awareness.

Introduction

The term "dioxins" denotes a family of polychlorinated biphenyls (PCBs) that contain carbon, hydrogen and chlorine. They are POPs which can travel long distances from the emission source and bioaccumulate in food-chains[1]. PCBs are two – or three – ringed structures that can be chlorinated to varying degrees. They can have up to 10 chlorine atoms substituting for hydrogen atoms. PCBs are not natural substances but are globally manufactured and their release into the environment occurs from the disposal of large – scale equipment and waste. The degree of chlorination of dioxins released to the environment through incineration is determined by the source material and the amount of chlorine available. Several hundreds of these compounds exist and are members of three closely related families: the chlorinated dibenzo-p-dioxins (CDDs), chlorinated dibenzofurans (CDFs) and certain polychlorinated biphenyls (PCBs). The general structure of a dioxin molecule is two rings of 6 carbon atoms (benzene rings, shown as hexagons in Fig. 1) bound by oxygen atom(s) (shown as O in Fig. 1) with chlorine or hydrogen atoms attached (the numbered positions in Fig. 1). The degree of toxicity of dioxins varies from compound to compound. Among all dioxins, the tetrachlorinated dibenzo-p-dioxin with chlorine atoms attached in the 2, 3, 7 and 8 positions (2,3,7,8-TCDD) is known to possess the highest toxic potency.

* Department of Petroleum and Natural Gas Processing, Petroleum Training Institute, Effurun, Delta State, Nigeria
**Department of Chemistry, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria
[1] WHO (2002). Polychlorinated dibenzodioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls. In: Safety evaluation of certain food additives and contaminants. Geneva, World Health Organization (WHO food additives series, No. 48; http://www.inchem.org/documents/jecfa/jecmono/v48je20.htm)

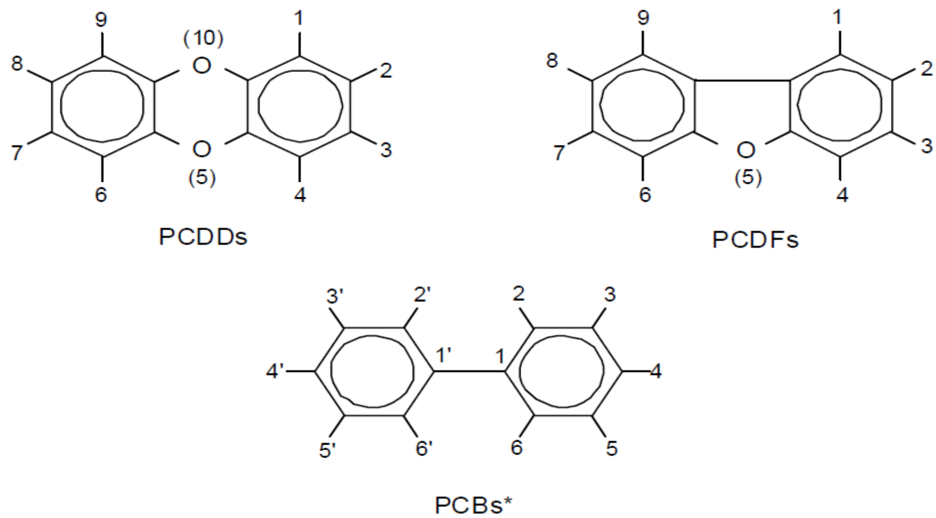

Fig. 1. Chemical Structure of Dioxins

Dioxin[2] is a by-product of the manufacture, moulding, or burning of organic chemicals and plastics that contain chlorine. It is the most unpleasant, most toxic man-made organic chemical. Unfortunately, dioxin has entered our food supply, primarily in meat, fish and milk. Dioxins in general are colourless solids with properties of very low water solubility and low vapour pressure. On the other hand, dioxins characteristically exhibit a high degree of solubility in fats and oils. They are generally stable, not reacting easily with other chemical substances, acids and alkalis, but are thought to gradually decompose in the presence of solar ultraviolet light. The main source of dioxins at present is waste incineration, with most being generated in combustion processes and released to the ambient air without being fully captured by waste-gas treatment equipment. Other sources exist, such as emissions from electric steelmaking furnaces, cigarette smoke, and automobile exhaust. Some reports[3] indicate that dioxins may have accumulated in sediment in the environment due to the past use of PCBs and some types of agricultural chemicals, which contained dioxins as impurities. Many humans harbour traces of dioxins and related compounds as a result of exposure to pesticides in their diet or air-borne dioxins released by certain type of waste incineration. Dioxin has been a little-known threat for many years near factories that produce PVC plastic or chlorinated pesticides and herbicides, and where those pesticides and herbicides have been heavily used, such as on farms, near electric and railway lines. It has also been a hazard downstream of paper mills (where chlorine bleach combines with natural organics in wood pulp). In the last 20 years, household, industrial trash and medical waste are burnt in huge mass-burn incinerators. Dioxin, formed during burning, is carried for hundreds of miles on tiny specks of fly-ash from the incinerators. It settles on crops, which are eaten by cows, steers, pigs, and chickens. It contaminates lakes, streams, and the ocean. Like the pesticides such as DDT (dichlorodiphenyltrichloroethane), dioxin accumulates in the fat cells of the animals, and re-appears in meat and milk. A typical hamburger today has as much as 100 picograms of dioxin in it.[3]

[2]Steenland K. Bertazzi, P.A. Maccarelli, A. & Kogevinas, M. 2004. 'Dioxin Revisited: Developments Since the 1997 IARC Classification of Dioxin as a Human Carcinogen', Environmental Health Perspectives, 112(13), 1265-1268.
[3] Pekkanen, J., Pearce, N. 2001. "Environmental epidemiology: challenges and opportunities". *Environmental Health Perspectives*, 109, pp. 1-5

Dioxins in the environment: An Unprecedented Threat

Dioxins are harmful because it has been found that they are highly active at extremely low levels[4, 5]. Dioxin is a powerful hormone-disrupting chemical. By binding to a cell's hormone receptor, it literally modifies the functioning and genetic mechanism of the cell, causing a wide range of side effects, from cancer to reduced immunity to nervous system disorders to miscarriages and birth deformity.[6] It is well known that dioxin exhibits serious health effects when it reaches as little as a few parts per trillion in body fat; a picogram (one millionth of a millionth of a gram) has 1.8 billion molecules of dioxin, each of which has the capability of disrupting a cell. Because it literally changes the functioning of the cells, the effects can be very obvious or very subtle. There is no "threshold" dose - the tiniest amount can cause damage, and the human body has no defence against it. Over the past decade, government and industry have worked to dramatically reduce dioxin emissions. Dioxin levels in Northern Ireland and the UK have been declining for the last 30 years due to reductions in man-made sources. However, because dioxins are extremely persistent compounds, even if all current human-generated dioxins could somehow be eliminated, low levels of naturally produced dioxins and the 'reservoir' of dioxins created from natural events and industrial activities in the past will remain. Dioxins have low volatility and low water solubility. They tend to adhere to particles in the air; on plants and soil; and in sediment in waterways. They can be deposited on plants and taken up by animals when these are eaten. Actual plant uptake of dioxins from soil is minimal because dioxins become strongly bound to soil, which greatly reduces their bioavailability. When dioxins are released into water, they tend to settle into sediments where they can be further transported or ingested by fish and other aquatic organisms. When released into the air, some dioxins may be transported over long distances. Dioxins may be concentrated in the food chain so that animals have higher concentrations than plants, water, soil, or sediments. Within animals and humans, dioxins tend to accumulate in fat. Approximately 95 % of human exposure is estimated to occur through the diet with the consumption of fats and fatty foods being the main sources e.g. meat, dairy products, fish and shellfish.

Current levels and sources of dioxins in the environment

The current levels of dioxins have been estimated to be in the region of 270 g I-TEQ. Table 1 shows the concentration range of sources of dioxins.

Dioxin levels in the environment have been declining for the last 30 years due to reductions in man-made sources[6]. Dioxin emissions have fallen by over 70 % in the last 15 years[6]. However, dioxins break down so slowly that some of the dioxins from past releases will still be in the environment many years from now.

[4] Whitlock, J.P. 1998, 'Genetic and molecular aspects of 2,3,7,8 – tetrachlorodibenzo-p-dioxin action. Ann. Rev. Pharmacol. 30, 251 – 277.

[5] Clark, G., Trotscher, A., Bell, D. & Lucier, G. 1992, 'Integrated approach for evaluating species and interindividual differences in responsiveness to dioxins and structural analogs'. Environmental perspectives 98, 125 – 132.

[6] Schecter, A. *et al*. 1994. Chlorinated dioxins and dibenzofurans in human tissue from general populations: a selective review. Environmental Health Perspectives 102, 159 – 171.

Table 1 Estimate of UK dioxin emissions by activity in 2005 (Sources: Detailed Emissions Data Warehouse, National Atmospheric Emissions Inventory)

S/N	Top 20 activities	Overall emissions from these activities (grams of International Toxic Equivalent – g I-TEQ)
1	Accidental fires	58
2	Small scale waste burning	52
3	Agricultural waste burning (farmers burning material on their farms)	35
4	Sinter production (iron)	29
6	Other industrial combustion (coal, untreated & treated wood, lubricant, gas oil, fuel oil)	12
5	Crematoria	11
7	Electric arc furnaces	8
8	Bonfire night	7
9	Agriculture straw burning	7
10	Natural fires (forest and moorland)	6
11	Primary aluminium production	6
12	Domestic combustion (wood/coal/solid smokeless fuel/ anthracite)	4
13	Shipping (coastal and international)	3
14	Accidental vehicle fires	3
15	Power stations (municipal solid waste)*	2.3
16	Power stations (coal)	1.5
17	Road Transport (cars)	2
18	Refineries combustion (fuel oil)	2
19	Foundries (castings)	2
20	Secondary lead production	2

Dioxins that remain in the environment from past releases are sometimes called "reservoir sources" of dioxins. Because of natural processes, dioxin levels in the environment will never go to zero. For developing and economy in transition countries the monitoring of dioxin emissions has been a particular challenge and currently not feasible in almost all developing countries due to the lack of analytical capacity.[7] However, studies[7] to determine the levels PCDD/Fs and PFASs in sewage sludge from industrial, municipal, and hospital wastewater treatment plants in Nigeria show that the levels in the Nigerian sludge were in the range of the emission factors from the UNEP Dioxin Toolkit. The domestic sludges, dairy sludge and sludge from the hospital were between 6 to 23 ng TEQ/kg d.m. and therefore in the range of the emission factor (EF) of domestic sludge (4 pg

[7] Sindiku, O., Orata, F., Haglund, P., Weber, R. and Osibanjo, O. 2014. PCDD/F and Per- & Polyfluoroalkyl substances contamination in selected sewage sludges in Nigeria. 34th International Symposium of Halogenated Persistent Organic Pollutants, Madrid, Spain

TEQ/kg d.m.) and sludge with urban and industrial inputs (EF 20 ng TEQ/kg d.m.). The industrial sludge with 48.2 ng TEQ/kg d.m. was between the EF for urban and industrial inputs and sludge with toolkit EF for specific industrial inputs (200 ng TEQ/kg d.m.). This indicates that these two PFOS alternatives are present only in minor concentrations in releases from the Nigerian society and is therefore currently not used in significant amounts in the country.

Clean up and safe disposal of industrial waste containing PCBs and PCDFs (or likely to generate PCDDs) should be put in place and developing international programmes for disposal to aid countries without suitable waste management facilities is recommended.