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REVIEW PAPER

DIOXIN-LIKE COMPOUNDS (DLCS) IN THE ENVIRONMENT AND THEIR IMPACT ON HUMAN HEALTH*

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Abstract

Dioxins such as polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs) are commonly regarded as one of the most dangerous chemical pollutants for the environment and human health alike due to their toxicological properties, persistence and potential to bioconcentrate. Their uptake by the organism takes place mainly through the oral route, and to a lesser degree through the respiratory and dermal routes. Numerous epidemiological studies show that those compounds have the ability of long-term accumulation in the organism, causing the disruption of homeostatic mechanisms and the deterioration of immune resistance. Short-term exposure to dioxins manifests in skin changes and chloracne. Long-term subjection to dioxins causes disorders in the functioning of the endocrine system, immune system, nervous system, reproductive system and affects the course of pregnancy and fetal development. The primary sources of dioxin pollution in the environment are the processes of burning waste of the industrial, municipal and healthcare kind. Another

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significant source of pollution is the industrial sector, including steelworks and non-ferrous metal smelters, as well as secondary raw material processing plants and landfills of municipal and industrial waste. According to various scientific research sources, approximately 95% of the daily dioxin intake enters human organisms with food, which makes it the primary source of human exposure to this particular group of environmental pollutants. This paper presents information regarding dioxins, chloroorganic compounds commonly encountered in the environment. Among this numerous group of chemical compounds, there are ones that exhibit heavily toxic properties for the environment and the living organisms that inhabit it.

Keywords: polychlorinated dibenzo-p-dioxins, dibenzofurans, polychlorinated biphenyls, spread of pollution, environment, health.

INTRODUCTION

On the one hand, the development of civilization over the last centuries has contributed to the steady improvement of peoples' living conditions; on the other hand, it has brought about irreversible changes in the natural environment. In recent years, environmental transformations, which occur due to natural causes as well as human interference, have increased in intensity, affecting the environment to a larger extent. These include mainly pollution with industrial and municipal waste, which is the cause of contamination of oceanic, deep, surface, ground and atmospheric waters. This is confirmed by each and every recent scientific publication and research-based report, becoming an issue of concern for wide social groups in all the countries of the world. Therefore, environmental protection is recognized as one of the main and urgent tasks for modern society.

Various contaminants synthesized during production processes have a detrimental effect on organisms living in many different environmental habitats. Pollution poses a threat to entire ecosystems and to human health, hence it is an understandable reason for societal fears and concerns. Dioxins are types of harmful chemical compounds which are widespread in nature. They are by-products of various technological processes and the burning of organic substances, especially those whose structure includes atoms of chlorine. What separates them from other chloroorganic substances is that they have never been produced on an industrial scale and no practical application has been found for them. They have been introduced to the environment as unintentional trace impurities.

Protection of societal health against the harmful effects of dioxins is one of the priorities of research carried out by scientific research centres around the world. Although over the last few years, the emission of those compounds to the environment has been reduced, it has to be noted that they still constitute a threat to human health due to the persistent nature of the pollution and their ability to accumulate in the subsequent levels of the trophic pyramid.

DIOXIN-LIKE COMPOUNDS – SOURCES OF EXPOSURE AND PROPERTIES

Dioxin-like compounds are a group of chemicals consisting of PCDDs, PCDFs and PCBs (Struciński et al. 2011).

PCDDs, PCDFs, PCBs belong to a group of chemical compounds referred to as Persistent Organic Pollutants (POPs), which are characterized by their toxicity, potential to bioconcentrate and persistency in the environment (Ukalska-Jaruga et al. 2015).

Research indicates the possibility of DLC synthesis through enzymatic processes occurring in sludge as well as during the storage of waste in landfills. They are difficult to remove through the process of biodegradation (Gworek et al. 2013, Chmielewski et al. 2020).

'Dioxins' is a commonly used term which most often refers to the collective understanding of an entire group of chemical compounds, divided into PCDDs, PCDFs and PCBs. It is a group of aromatic chloroorganic compounds (Sarnowska, Gach 2017). Dioxins as a group include polychlorinated and polybrominated dibenzodioxins (PCDDs and PBDDs) as well as polychlorinated and polybrominated dibenzofurans (PCDFs and PBDFs). There are 75 congeners of dioxins and 135 congeners of dibenzofurans (Chmielewski et al. 2020*a*).

A diagram illustrating the structure of dioxin precursors and the polychlorinated derivative is presented in Figure 1 (Chmielewski et al. 2020*a*).

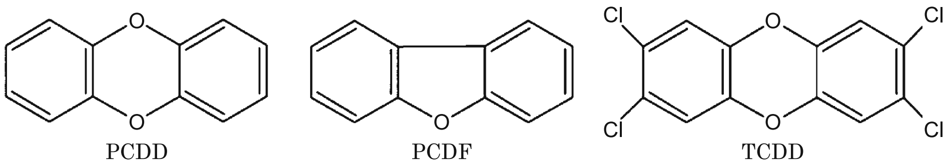

Fig. 1. Diagram of the structure of PCDD/F precursors and a polychlorinated derivative

Generally, dioxins have never been intentionally produced by man, although the source of over 95% of dioxins in the environment is industrial, mainly the metal industry and burning of waste. However, the burning of waste, be it post-industrial or municipal, in much of the world takes place outdoors or in technologically outdated incineration plants without any purification processes. The ever so familiar reports of smog and the causes of its generation that are published systematically are also concerned with the release of dioxins, which are created in the process of burning trash in domestic furnaces or those which originate from car exhaust. This is because the waste subjected to burning also contains large amounts of chloroorganic plant protection products and fungicides, whose contents include chlorophenols. They are a source of dioxins and other chemical pollution which end up mainly in the atmosphere, but also in groundwater and soil. The ash generated in the combustion processes falls to the ground and becomes a primary source of dioxins in agricultural goods and in organisms of livestock thereafter. While modern incinerators may be equipped with purification systems that effectively remove dioxins, they are not in common use due to the high costs of such machinery (Brzeski 2011, Anger et al. 2013, Zhou, Liu 2018).

Other sources of dioxin emission include steelwork plants, secondary raw material processing plants or the incinerators of medical and hazardous waste. Processes involved in waste treatment constitute a significant source of their emission to the environment. Those compounds are also generated in the process of pulp and paper production. Dioxins are released throughout the thermal reactions that the intermediate product is subjected to in the production of paper and pulp (Zhou et al. 2015, Xing et al. 2019, Zhan et al. 2019, Chmielewski et al. 2020*b*).

Dioxins are also found in sludge and the soil surrounding landfills of chemical plants. The presence of dioxins was also noted in composts made from municipal waste (Gworek et al. 2018, Chmielewski et al. 2020).

Dioxins are also released to the environment as a result of fires, volcanic eruptions, recycling of computer hardware, landfill storage of plastic treated with direct sunlight, ecological disasters or treatment of medical and hazardous waste (Pham et al. 2019, Chmielewski et al. 2020, 2020*b*,*c*).

Studies show that with the industrial development, there has been an anthropogenic increase of dioxin emission into the environment (Wong 2020). Those compounds have toxic properties as far as humans and animals are concerned, therefore it is a necessity to monitor the spread of such pollution in the environment (Dawid et al. 2016, Coudon et al. 2018, Salian et al. 2019).

Dusts are the primary carriers of POPs. This allows for them to be transmitted at long distances and what comes with it, they may be a threat to the health regardless of the source of emission (Niemirycz, Kobusińska 2020).

Significant attempts at reducing the emission of these harmful compounds were made in Europe after the enormous ecological disaster that took place in Seveso in 1976. An accident in the industrial plants manufacturing ICMESA plant protection products in Seveso near Milan caused the leakage of over 6 tons of chemicals (mostly dioxins) into the atmosphere, which then fell across the area of approximately 18 km^2. In the days following the Seveso disaster, 3300 dead animals were found, mostly rabbits and poultry. Around 37 thousand people suffered from light poisoning, over 1600 people suffered from more acute poisoning, while 447 people experienced skin changes or chloracne (Eskenazi et al. 2018).

Table 1 lists sources of PCDDs in the environment (Chmielewski et al. 2020*a*), while Table 2 details the occurrence PCBs in the environment (Stec et al. 2012), and Table 3 presents the emission of PCDDs/Fs in Poland, in selected years (Bebkiewicz et al. 2020).

Table 1

Sources of dioxins in the environment

Source	Form of pollution
Burning of waste	gases, fly ash
Cars	leaded petrol – addition of so-called scavengers – 1,2-dichloroethane, 1,2-dibromoethane
Metal industry	metal reclamation, melting of scrap and secondary raw material
Pulp and paper industry	bleaching with chlorine, sulphite pulp
Chemical industry	production and usage of pentachlorophenol (PCP), chlorobenzene, chlorination of organic compounds, processes where chlorine is used as an intermediate product even if the end-product does not contain chlorine, inorganic processes where chlorine is used e.g., extraction of magnesium from its ores, processes where chlorinated solvents are used
Accidents, failures, disasters	chemical industry failures, fires, volcanic eruptions, explosions

Table 2

Occurrence of polychlorinated biphenyls (PCBs) in the environment

Environment	Concentration (ng m^{-3})
Air	0.1-20
Water	0.001-30000
Sediment	1.0-1000
Organism	Concentration (mg kg^{-1})
Plankton	0.01-20
Invertebrate	0.01-10
Fish	0.01-25
Bird's eggs	0.1-500
Human body	0.1-10

DIOXINS IN FOOD

Important and worrying information about the presence of dioxins in food became the subject of public knowledge and concern in 1999 as a result of the so-called Dioxin affair that took place in Belgium. Livestock was given 500 t of feed containing polychlorinated biphenyls and dioxins and, as a result, an increased concentration of these substances in chicken meat, eggs and derivative products was noted. Subsequently, around 30% of those contaminants ended up consumed as food by almost 10 million Belgian citizens. The concentration of dioxins in poultry meat that was exported to Poland, amongst other countries, was at the level of 0.1 to 5 picograms g^{-1} expressed in WHO toxic equivalents (TEQ) – Covaci et al. (2008).

The degree of PCDDs/Fs and PCBs concentration in the examined food samples is expressed using Toxic Equivalents (TEQs), which are the sum of

Table 3

Emission of polychlorinated dioxins and furans (PCDDs/Fs) in Poland in select years

Source of emission according to NFR classification	1990	2005	2010	2017	2018
	g I-TEQ	g I-TEQ	g I-TEQ	g I-TEQ	G I-TEQ
Overall	387.22	368.50	386.11	305.76	316.07
1. Energy	260.11	258.79	290.03	233.73	229.07
A. Fuel combustion	255.98	256.16	286.95	230.76	226.08
1. Energy Industries	11.71	8.93	11.89	10.82	10.97
2. Manufacturing and construction industries	1.90	3.43	3.56	5.27	5.04
3. Transport	2.67	7.15	9.97	9.54	9.46
4. Other sectors	239.71	236.65	261.54	205.13	200.61
B. Volatile emission from fuels	4.13	2.62	3.08	2.97	3.00
1. Volatile emission from solid fuels	4.05	2.52	2.95	2.83	2.84
2. Volatile emission from natural gas and petroleum systems	0.07	0.10	0.13	0.14	0.15
2. Industrial processes	13.59	10.52	11.06	13.84	14.37
A. Mineral products	0.21	0.38	0.48	0.62	0.61
B. Chemical industry	0.00	0.00	0.00	0.00	0.00
C. Metal production	12.02	7.79	8.21	10.44	11.06
D. Use of solvents and other products	0.00	0.00	0.00	0.00	0.00
G. – L. Others	1.36	2.35	2.37	2.79	2.70
3. Agriculture	0.02	0.01	0.00	0.00	0.01
B. Natural fertilizers	0.00	0.00	0.00	0.00	0.00
D. Agricultural soils	0.00	0.00	0.00	0.00	0.00
F. Plant residue combustion	0.02	0.01	0.00	0.00	0.01
A. Solid waste landfills	0.00	0.00	0.00	0.00	0.00
C. Waste incineration and open burning of waste	54.05	36.41	29.17	10.88	10.53
D. Waste management	0.00	0.00	0.00	0.00	0.00
E. Other	59.45	62.76	55.85	47.30	62.09

concentration products of particular congeners and their Toxicity Equivalency Factors (TEF).

The values of toxic equivalency factors for dioxins are regulated in the Commission Regulation (EU) No 277/2012 of 28 March 2012 (Commission Regulation 2012).

According to various sources, nowadays around 90-98% of dioxins reach the human body with food, e.g., through drinking milk (35.1%) or consuming meat, poultry and eggs (58.8%). Fish and processed fish goods usually have a higher dioxin compound group contamination compared to meat. Where fish were caught has an effect on their level of dioxin contamination (Strucinski et al. 2011, Piskorska-Pliszczynska, Warenik-Bany 2013, Piskorska-Pliszczyńska et al. 2013, Malisch, Kotz 2014, Huang et al. 2016, Chmielewski 2020*a*).

The concentration of dioxins in food products differs across countries. It is mostly due to the differences in the tradition and culture of food, the place of origin of a given product and the sensitivity of the analysis method. The products that are subject to the largest cross-country difference in dioxin concentration in the European context are fish and processed fish goods as well as milk and dairy products. Those differences are equal from 12% to 80% and from 6% to 51% of the Allowable Daily Intake (ADI) respectively. Significant concentrations of dioxins are also observed in beef and pork meat (Strucinski 2011, Horst, Lahrssen-Wiederholt 2013, Chmielewski et al. 2020*a*, Mikołajczyk et al. 2020).

The problem of dioxin presence in eggs designated for consumption is well documented in subject literature, from the addition of dioxins to animal feed to the result of consuming feed with dioxins from the soil (Hoang et al. 2014, Squadrone et al. 2015, Adamse et al. 2015, Hoogenboom et al. 2016, Polder et al. 2016, Piskorska-Pliszczyńska et al. 2019).

It is important to note that plants cultured without protection, especially in areas suffering from industrial contamination, livestock farmed near industrial plants and free-living animals are all exposed to the fallout of hazardous dusts from the air which contain dioxins, and are, as an effect, subject to contamination (Grassi et al. 2010, Desiato et al. 2014, Zacs, Bartkevics 2014, Pemberthy et al. 2016, Ochwanowska et al. 2019).

EFFECTS OF DIOXINS ON ORGANISMS

Dioxins are widely regarded as health-threatening substances due to their toxicological properties, as well as the ability of long-term accumulation in the organism they exhibit. People are exposed to PCDDs, PCDFs and PCBs mainly through inhaled air (8%), through the skin (2%), and most importantly due to the consumption of contaminated water and food, approximately 90% (Chmielewski 2020*a*). Afterwards, dioxins spread to the liver and the adipose tissue, where they are accumulated because of the lipids of the blood plasma, merging with the aryl hydrocarbon receptor – AhR (Kołłątaj et al. 2017, Zouboulis 2020). However, it is important to keep in mind that the human bodies are not equally susceptible to PCDD, PCDF and PCB exposure, nor are they equally sensitive to their activity. It is the result of the individuality of eating habits (contaminated foods) or profession-related exposure (employees of the plant protection product facilities or hazardous waste incinerators). The group most vulnerable to dioxins are the developing fetuses and newborn children, especially those exposed to high dioxin concentrations in the breast milk (Baccarelli et al. 2008, Marinković et al. 2010, Kim et al. 2015).

The toxic impact of these compounds accumulated in the human body and their effect on its health concern mostly the disruption of the balance of the endocrine system (Eskenazi et al. 2018).

As regards dioxins and PCBs, the SCF adopted on 30 May 2001 an opinion on dioxins and dioxin-like PCBs in food, updating its opinion of 22 November 2000 fixing a tolerable weekly intake (TWI) of 14 pg World Health Organisation toxic equivalent (WHO-TEQ) kg^{-1} bw for dioxins and dioxin-like PCBs (Commission Regulation 2006).

The chemical structure of dioxins which resembles that of steroid hormones makes male and female gonads, the thyroid gland and other organs where these kinds of hormones are produced the target areas of the detrimental activity of dioxins (Eskenazi et al. 2018, Samer et al. 2020, Warner et al. 2020). For example, polychlorinated biphenyls usually reduce the concentration of thyroid hormones as a result of a direct attack on the thyroid gland, causing its hypertrophy and hyperplasia. Moreover, they can also have a negative effect on the excretion of hormones from the pituitary gland and the hypothalamus, causing disorders such as hypothyroidism (Benson et al. 2018, Eskenazi et al. 2018, Samer et al. 2020).

Other researchers also observed in their studies that adults who consumed fish contaminated with polychlorinated biphenyls suffered from impaired memory and the slowing down of learning processes (Schantz et al. 2001).

Research carried out over the recent years shows that POPs have a definite negative impact on reproductive processes, the course of pregnancy and the development of the fetus (Eskenazi et al. 2018, Chmielewski 2020*d*).

The conducted research shows that exposing people to dioxins increases the risk of developing disorders of the cardiovascular system. Dioxins may in fact cause atherosclerosis, hypertension and other cardiovascular diseases (Pavuk et al. 2019, Chmielewski 2020*a*, Donat-Vargas et al. 2020).

Numerous studies conclude that increased doses of TCDD cause an increased incidence of morbidity as far as various cancers are concerned, e.g., cancers of the tongue, the hard palate, the lungs, the liver and the thyroid (Kogevinas 2011, Chmielewski 2020*e*, Samer et al. 2020).

A characteristic symptom of dioxin infection is the occurrence of chloracne on the skin. This illness is characterized by disorders of the structure and activity of the sebaceous glands, which causes the formation of cysts and blackheads on the skin of the face, the chest and the back. According to research, the toxic effect of dioxins on the skin causes the hyperplasia of the epidermis cells and hair follicles. Furthermore, skin changes are usually accompanied by conjunctivitis, excessive growth of body hair and often brown discoloration of the nails. One of the most prominent examples of dioxin poisoning is that of the president of Ukraine, Viktor Yushchenko (Sorg et al. 2009, Chmielewski 2020f, Zouboulis 2020).

Dioxins have the ability to concentrate in living organisms, and their half-life in an abiotic environment amounts to an average of 30-100 years

(Gworek et al. 2013). Therefore, mothers may transfer some amounts of the substances they were earlier exposed to over to their children (Desiato et al. 2014, Warner et al. 2014).

CONCLUSIONS

Foods of animal origin are the primary source of dioxin exposure for humans, and it is a crucial issue for public health.

Long-term exposure of an organism to dioxins causes damage to internal organs, the occurrence of painful allergic rashes, mutagenic, teratogenic and proven cancerogenic activity and finally disorders in the functioning of the nervous, endocrine, immunological and reproductive systems.

The threat of dioxin exposure occurs every time large quantities of these substances spread into the environment as a result of unintentional human activity. With this context in mind, the importance of constantly educating people about the causes of environmental pollution and the effect it has on the environment and living organisms, in particular humans cannot be overestimated.

The issue of dioxins in our environment has not been entirely solved. The burning of waste has not ceased. It is impossible to withdraw chloroorganic compounds and chlorine from industrial production. Those processes can only be subjected to control to prevent dioxins from spreading into the environment. In reality, the number of dioxins continues to increase. In one way or another, they are accumulated in hazardous waste landfills, as ashes, oily waste, etc., or processed waste. The level of dioxin concentration in the natural environment is much higher than it was thousands of years before. However, our knowledge of the risks involved in the production and utilization of these compounds is vast enough to facilitate the further reduction of possible negative health effects on a larger scale.

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