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Dioxins and furans: A review from chemical and environmental perspectives

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ABSTRACT

Persistent organic pollutants (POPs) in the environment have generated great interest within the scientific community due to their toxic effect to animal, human health, and the environment. This review encompasses the historical presence of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the world-wide environment. Information on exposure indicated that the main route of exposure of dioxins/furans to humans is through ingestion, which is discussed in this paper. In addition, we present a thorough assessment of sampling, methods for extraction, and analysis as well as the photodegradation of dioxins under various conditions. In general, extraction methods including USEPA 8290 are the most used with high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) preferred as a detection tool. Moreover, a detailed compilation of studies of the PCDD/F concentrations and environmental sources from major industrial regions in several countries are presented. In summary, the major sources of dioxins in the worldwide environment include combustion and industrial sources with major challenges related to the lack of data availability in the Middle East especially with the current Warfare conflicts in the region.

1. Background

Persistent organic pollutants (POPs) are harmful organic compounds that are resistant to biological, chemical, and photolytic degradation. They are persistent in the environment especially in soils, sediments, and air for several decades [1]. Because of their toxicity and persistency, they pose a significant threat to animal, human health, and the environment since they accumulate in the fatty tissues of humans and animals [2,3]. In humans, POPs have been linked with behavioral, reproductive, developmental, endocrine, neurologic, and immunologic adverse health effects [4,5]. While in animals, they have caused diseases and abnormalities in a number of wildlife species including certain kinds of birds, fish, and mammals. They are a global concern due to their transportation over long distances from the point of production or release since they can evaporate from the soils and travel through the air and condense in colder regions.

According to researchers POPs are just a subset of more dangerous materials such as persistent, bio accumulative and toxic ((PBT)) chemicals including pesticides and organic compounds such as γ-hexachlorocyclohexane, 1,1,1-trichloro-2,2-diethane, polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalene, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), as well as groups of brominated flame retardants such as polybrominated biphenyls (PBBs) [6,7]. The quantity of the POPs in the atmosphere increases due to the massive disposal of some of the PBTs and PAHs, pollution from the combustions of fossil fuels, pesticides [8]. A vital challenge is to cut back the quantity of POPs contamination and it's unfolding through organic phenomenon. The data obtained for the concentration of POPs in the food chain, is necessary to support the implementation of policies and processes to reduce the amounts of POPs within these chains [9,10]. The Stockholm treaty on POPs was instituted to control the concentration levels of POPs within the general population, as a result, "the dirty dozen" was created. In specific, 12 different types of POPs including aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, dichlorodiphenyl Trichloroethane (DDT), polychlorinated biphenyls, polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs), were identified in order to be eliminated and controlled by 150 countries [11].

PCDDs and PCDFs are generally classified as toxic and carcinogenic unintentional by-products that are present in small amounts in the environment. The major issue with PCDDs/Fs is their extreme persistency in the environment, which is toxic to living organisms and can potentially cause cancer. There are three main categories for dioxins and furans: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs). PCDDs and PCDFs are released as byproducts of anthropogenic activities, or processes such as forest fires [12]. They are byproducts of the synthesis or combustion of chlorine based compounds that include some of the most toxic chemical substrates. This group of

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compounds include 210 possible congeners and at least seventeen have been identify as toxic with wide ranging toxicity from which 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), was identified as the most toxic compound [1,13]. Humans are normally exposed to dioxins and furans through contaminated food products which are often affected through the accumulation of these chemicals in the food chain and in high fat foods, such as eggs, dairy products, animal fats, and fish [11,14–19]. In order to obtain the toxicity of these compounds in vivo and in vitro data involving processes such as uptake, tissue distribution, metabolism, receptor binding, and activation was obtained in relative to the most toxic congener 2,3,7,8-TCDD. To express concentrations of the most toxic PCDDs/Fs and dioxin-like PCBS in relation to their toxicity toxic equivalency factors (TEFs) have been used and determined by the comparison of its toxic or biological endpoints to those of the 2,3,7,8-TCDD. TEFs for 17 PCDD/F congeners are then used to estimate the overall dioxin-like toxic equivalency (TEQ) found in samples, with 2,3,7,8-TCDD having a reference TEF of unity. TEFs are used as a consistent method to report the toxicities of varying mixtures of dioxin-like compounds. They have been developed to facilitate comparative risk assessment and regulatory control of exposure to these mixtures [20–22].

The goal of this review article is to access the current status of the analysis of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in the global environment using some of the main countries as examples. In addition, we will briefly explore and discuss the most common techniques for the extraction, clean-up and instrumental determination of this compounds in different matrixes, as well as the common techniques for their removal and/or degradation. For simplicity purposes, PCDDs, PCDFs and DL-PCBs will be often referred as dioxins throughout the paper.

2. Common sources of PCDDs, PCDFs and DL-PCBs

Studies have shown that concentrations of dioxins and furans were low in the early 1900s, and showed signs of increase during the 1920s to the 1970s [18,23]. This indicates that they are mainly formed due to anthropogenic sources, as summarized in Fig. 1. In specific, any process involving organic chlorine or inorganic chlorides presents a significant source of dioxins and furans. Conical municipal waste combustion in new found land, waste incineration, coastal pulp mill boilers burning salt laden wood, residential wood combustion, iron sintering and electrical arc furnace steel manufacturing are the major sources of dioxins emissions as generate 80% of the total national emissions that had a total of 198 g TEQ/year according to the 1997 national inventory [24]. Steel manufacturing and iron sintering processes were found to be among the major sources of dioxins and furans emissions despite the fact that low levels of chloride may enter the combustion processes. In addition, extensive studies on municipal solid waste, medical waste, sewage sludge, and hazardous waste incinerations showed that low levels of dioxins emissions, can be achieved from even trace quantities of organic and inorganic chlorides. An example of this common source, is the municipal solid waste in Canada, containing seven solid waste treatment facilities having a capacity of 25 t/day and they handled 3% of the [25,26].

Waste incineration is responsible for 37.6% of the total dioxin emissions from anthropogenic sources with a 74.5 g TEQ/year [2,24]. Moreover, it was reported that wood can absorb significant amounts of sodium chloride when stored in the marine waters along the west coasts of Canada. Under certain combustion conditions, the burning of salt laden wood waste in pulp mill power boilers leads to the formation and emission of dioxins and furans. The formation of these compounds is favored under poor combustion conditions as the gas phase precursors formation such as chlorophenols and polycyclic aromatic hydrocarbons will be favored [26,27]. Thus, dioxins and furans can be formed through adsorption/desorption on ash particles. A total of 7.9 g TEQ/year of dioxins and furans emissions were resulting from coastal power boilers burning salt-laden hog fuel which is equivalent to 4% of the total anthropogenic emissions [24]. These emissions are regulated according to Canada wide-standards to be reduced, in 2006, to 0.5 ng TEQ/m^3 for existing reboilers and 0.1 ng TEQ/m^3 for new reboilers [28]. Other main sources around the world will be discussed in section 3 of this paper.

Finally, dioxins are also formed in pulp and paper mills effluent discharge as a result chlorine bleaching. Since the emissions of dioxins and furans from pulp and paper mills is under the legal limit of quantifications, a total emission of 2 g TEQ/year has resulted from all pulp and paper mills in Canada [24]. Their presence could be detected in air, water, and soil. It is shown that 90% of human exposure to dioxins is attributed to food consumption, hence, creating various adverse health effects in human and animals. Dioxins vary in their toxicity that depends mainly on the type of dioxin, frequency and duration of the exposure [3,24,29,30]. Pentachlorophenol (from the textile industry) has been suggested as the major source of PCDD/F in sewage sludge. For this reason, countries such as Germany, banned the use of the chemical resulting in a significant reduction of PCDD/F levels in sewage sludge [31].

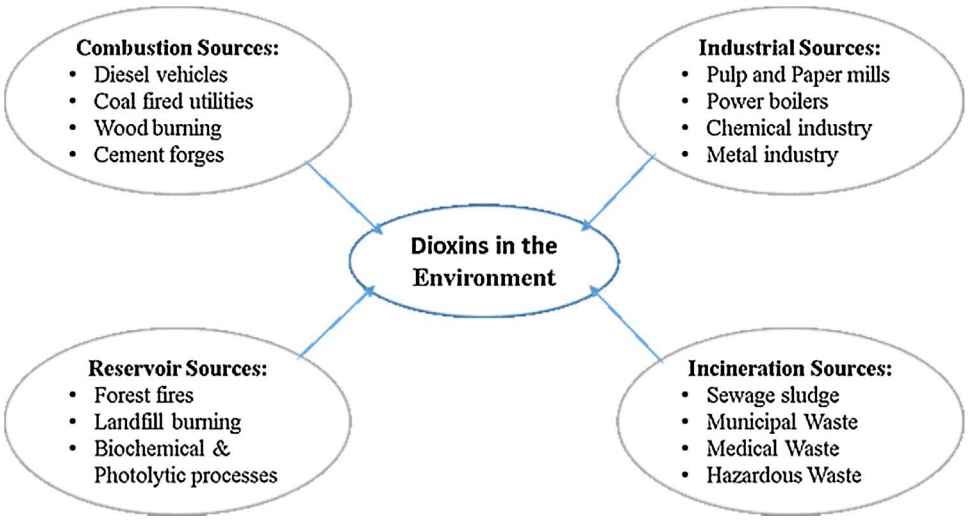

Fig. 1. Major Dioxins Sources in the Environment.