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Degradation Pathways of Persistent Organic Pollutants (POPs) in the Environment

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Abstract

Persistent organic pollutants (POPs) are resistant to most of the known environmental degradation processes. Because of their persistence, POPs bioaccumulate in animal tissues and biomagnify along food chains and food webs with potential adverse impacts on human and wildlife health and the environment. Although POPs are resistant to most of the environmental degradation processes, there are some environmental processes mostly microbial degradation that can degrade POPs to other forms that are not necessarily simpler and less toxic. The Stockholm Convention on Persistent Organic Pollutants adopted in 2001 was meant to restrict the production and use of these toxic chemicals in the environment.

Keywords: degradation, POPs, bioaccumulation, biomagnification, Stockholm convention

1. Introduction

Persistent organic pollutants (POPs) are toxic organic compounds that are resistant to most of the degradation processes in the environment, and therefore they tend to persist in the environment, thus bioaccumulating in organisms and biomagnifying along the food chains and food webs in ecosystems. POPs pose a risk of causing adverse effects to human and wildlife health in particular and the environment in general. POPs include a wide class of chemical species with different physicochemical properties and toxicologies. The priority list of POPs consists of pesticides such as dichloro diphenyl trichloroethane (DDT), hexachloro-cyclohexanes (HCHs), and hexachlorobenzenes (HCBs), industrial chemicals such as polychlorinated biphenyls (PCBs), and unintentional by-products of industrial processes such as

polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) and polycyclic aromatic hydrocarbons (PAHs). The first priority list of POPs consisted of 12 compounds commonly referred as the dirty dozen by the Stockholm Convention that was adopted in 2001.

Over the last decade, the priority list of POPs has been updated to include such compounds like brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), listed under the Stockholm Convention in 2017 [1], and hexabromocyclododecanes (HBCDDs), currently under consideration for listing. A further group of recently recognized halogenated POPs are the perfluorinated alkyl substances, of which perfluorooctane sulfonate (PFOS), its salts, and perfluorooctane sulfonyl fluoride were also added to the Stockholm list in 2017. Other compounds in the new list include endosulfan, lindane, pentachlorobenzene, chlordecone, and hexabromocyclododecane (HBCD).

POPs have a tendency to persist in the environment for long periods, are capable of long-range transport, bioaccumulate in human and animal tissue and biomagnify in food chains and food webs, and have potential significant adverse impacts on human health and the environment. Exposure to POPs can cause serious health problems including certain cancers, birth defects, dysfunctional immune and reproductive systems, greater susceptibility to disease, and even diminished intelligence. Of all known POPs so far, the organochlorine compounds, including polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs), have received the most attention due to their persistence in the environment, bioaccumulation, biomagnification, and hazard effects to biota.

2. Sources of POPs in the environment

There are many ways that release POPs to the environment. POPs such as pesticides are released, as a result of plant protection efforts. The main sources of pesticide pollution include



Figure 1. Emission of dioxins from industrial wastes. Source: Marie Sedillo et al. 2010.

their use, transportation, storage, and disposal of obsolete pesticides. Some other chemicals [polychlorinated biphenyls (PCBs), pentachlorophenol] are used as oils, as dielectric and cooling fluids in capacitors and transformers, for wood preservation, etc., and are released into the environment as a result of spills and evaporation. A number of substances like dioxins/furans, polycyclic aromatic hydrocarbons (PAHs), and hexachlorobenzene are by-products of many industrial processes, mainly, thermal (fuel combustion and waste incineration, ferrous industry, coke and aluminum production, road transport, chemical synthesis of chlorinated substances, etc.) and are emitted directly into the air (**Figure 1**) [2].

3. Why are POPs resistant to most of the environmental degradation processes?

In the initial list of the Stockholm Convention, POPs are typically polyhalogenated organic compounds which exhibit high lipid solubility. For this reason, they bioaccumulate in fatty tissues of animals. Halogenated compounds also exhibit great stability reflecting the nonreactivity of C-Cl bonds toward hydrolysis and photolytic degradation in the environment. The high electronegativity of halogens compared to carbon gives the carbon-halogen bond a significant polarity/dipole moment. The electron density is concentrated around the halogen, leaving the carbon relatively electron poor. This introduces ionic character to the bond through partial charges ($C^{\delta+}Cl^{\delta-}$). The partial charges on the chlorine and carbon exert electrostatic attraction between them, contributing to the unusual bond strength of the carbon-halogen bonds. The carbon-halogen bonds are known to be “the strongest in organic chemistry,” because halogen forms the strongest single bond to carbon [3, 4]. The bond also strengthens and shortens as more halogens are added to the same carbon on a chemical compound.

The stability and lipophilicity of persistent organic compounds often correlate with their halogen content; thus, polyhalogenated organic compounds are of particular concern. They exert their negative effects on the environment through two processes, long-range transport, which allows them to travel far from their source, and bioaccumulation, which reconcentrates these chemical compounds to potentially dangerous levels in animal tissues [5].

4. Health effects of POPs

POP exposure may cause developmental defects, chronic illnesses, and death. Some are carcinogens, possibly including breast cancer. Many POPs are capable of endocrine disruption within the reproductive system, the central nervous system, or the immune system. People and animals are exposed to POPs mostly through their diet, occupationally, or while growing in the womb [6]. For humans not exposed to POPs through accidental or occupational means, over 90% of exposure comes from animal food products due to bioaccumulation in fat tissues and bioaccumulation through the food chain. In general, POP serum levels increase with age and tend to be higher in females than males [7].

4.1. Effect on endocrine disruption

Exogenous substance/mixture that alters the function(s) of the hormonal system and consequently causes adverse effects in an intact organism or its progeny or its subpopulation is called endocrine disruptors. The majority of POPs are known to disrupt the normal functioning of the endocrine system. Low-level exposure to POPs during critical developmental periods of the fetus, newborn, and child can have a lasting effect throughout its lifespan. A 2002 study [8] synthesizes data on endocrine disruption and health complications from exposure to POPs during critical developmental stages in an organism's lifespan. The study aimed to answer the question whether or not chronic, low-level exposure to POPs can have a health impact on the endocrine system and development of organisms from different species. The study found that exposure of POPs during a critical developmental time frame can produce a permanent change in the organism's path of development. Exposure of POPs during non-critical developmental time frames may not lead to detectable diseases and health complications later in their life. In wildlife, the critical development time frames are in utero, in ovo, and during reproductive periods. In humans, the critical development time frame is during fetal development [9].

4.2. Effect on the reproductive system

The same study in 2002 with evidence of a link from POPs to endocrine disruption also linked low-dose exposure of POPs to reproductive health effects. The study stated that POP exposure can lead to negative health effects especially in the male reproductive system, such as decreased sperm quality and quantity, altered sex ratio, and early puberty onset. For females exposed to POPs, altered reproductive tissues and pregnancy outcomes as well as endometriosis have been reported [9, 10].

4.3. Effect on gestational weight gain and newborn head circumference

A Greek study in 2014 investigated the link between maternal weight gain during pregnancy exposure and PCB level in their newborn infants, their birth weight, gestational age, and head circumference. The lower the birth weight and head circumference of the infants was, the higher POPs levels during prenatal development had been, but only if mothers had either excessive or inadequate weight gain during pregnancy. No correlation between POP exposure and gestational age was found [11]. A 2013 case-control study conducted in 2009 in Indian mothers and their offspring showed prenatal exposure of three types of organochlorine pesticides (HCH, DDT and DDE) impaired the growth of the fetus, reduced the birth weight, head circumference and chest circumference [12].

5. Environmental effects of POPs

POPs can travel long distances in the environment by air or in water so that they are found in ecosystems in which they have never been used and far from their source. Animals of the Canadian Arctic have significant levels of PCBs, organochlorine pesticides (like DDT), and metals, and this poses a health risk to the human population that relies on these animals as a food source. The long-range transport of POPs leads to global pollution (**Figure 2**) [13].

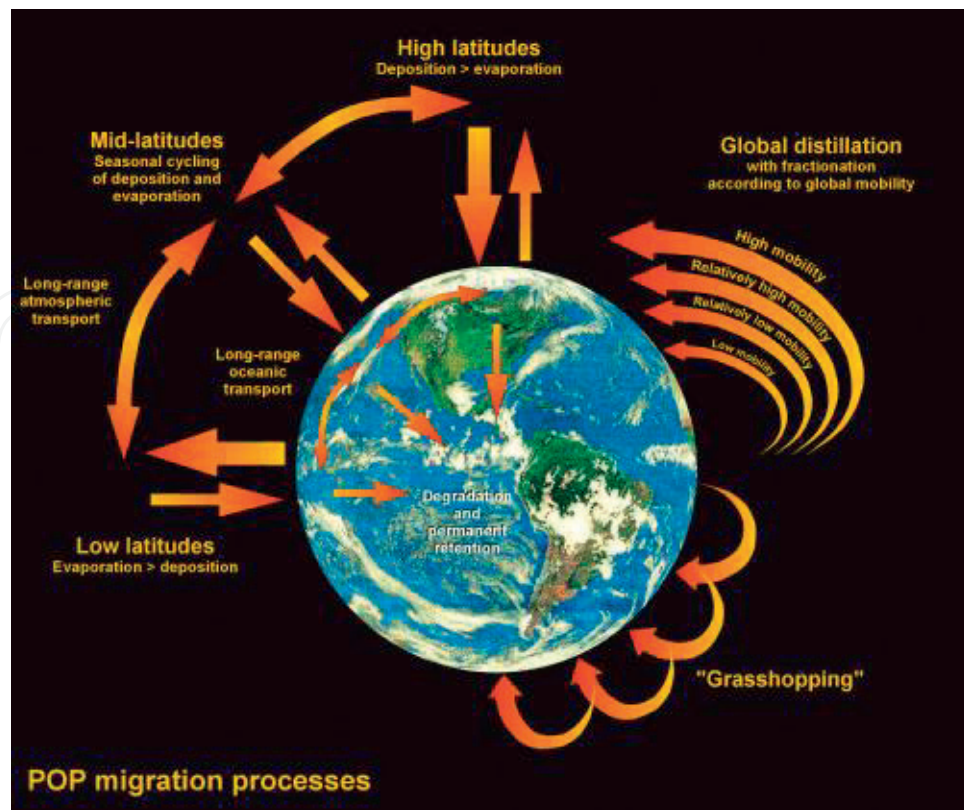


Figure 2. Transboundary movement of POPs. (Source: Ref. [13]).

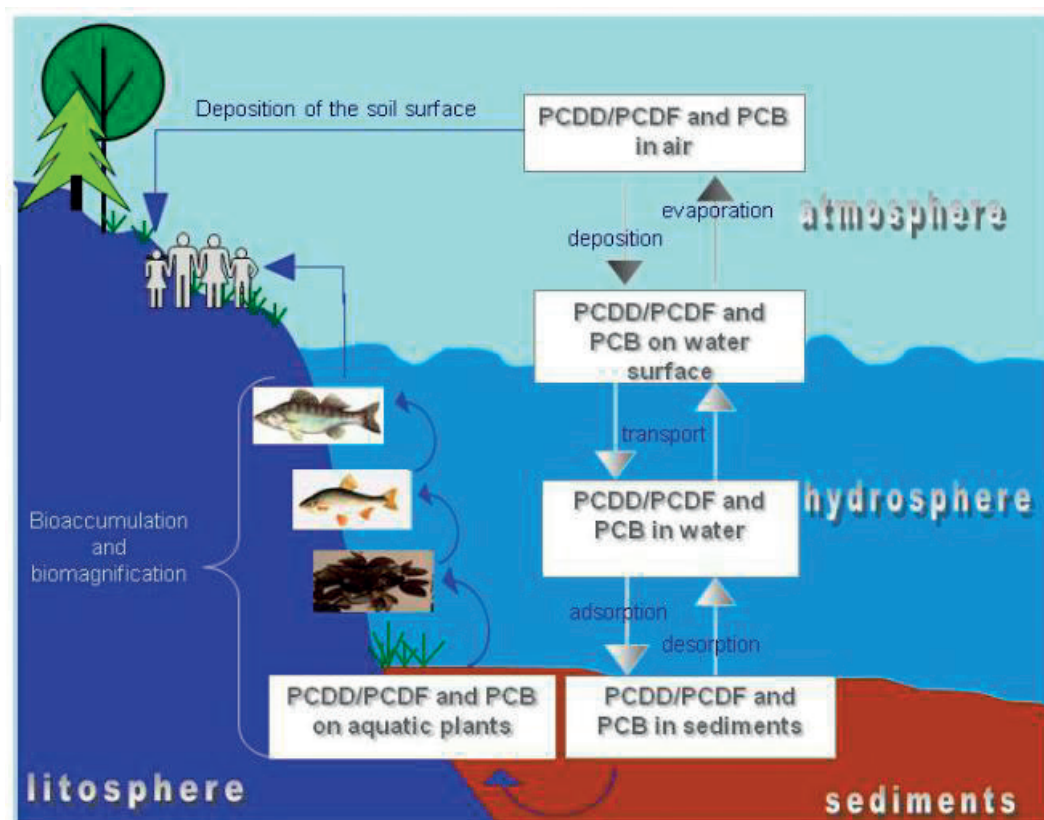


Figure 3. Transport and circulation of PCDDs/PCDFs and PCBs in the environment. (Source: Ref. [14]).

The slow decomposition of PCDDs/PCDFs and PCBs in the environment and the hazards they pose for living organisms make them large-scale environmental degraders, especially because their toxicity can be further enhanced by their ability to accumulate in the soil and sediments and their bioaccumulation and biomagnification within aquatic and land food chains (**Figure 3**) [14].

6. Degradation pathways of POPs in the environment

Despite the fact POPs are resistant to most of the degradation processes in the environment, some molecular alterations are possible in the environment that does not necessarily lead to simpler and less toxic compounds. Some of POP metabolites are equally complex and even more toxic than the parent molecules. Most of the degradation processes of POPs in the environment are assisted by microorganisms. Nevertheless, the half-lives of biodegradation processes of POPs are significantly long, thus accounting for their persistency in the environment. Some representative examples of POP degradations are as presented below.

6.1. Degradation of heptachlor

Heptachlor is known to undergo oxidative dechlorinating in the soil to form 1-hydroxychlor-dene and by the influence of soil microorganisms to form heptachlor epoxide with a half-life of up to 112 days [15] as shown in **Scheme 1**.

6.2. Degradation of DDT

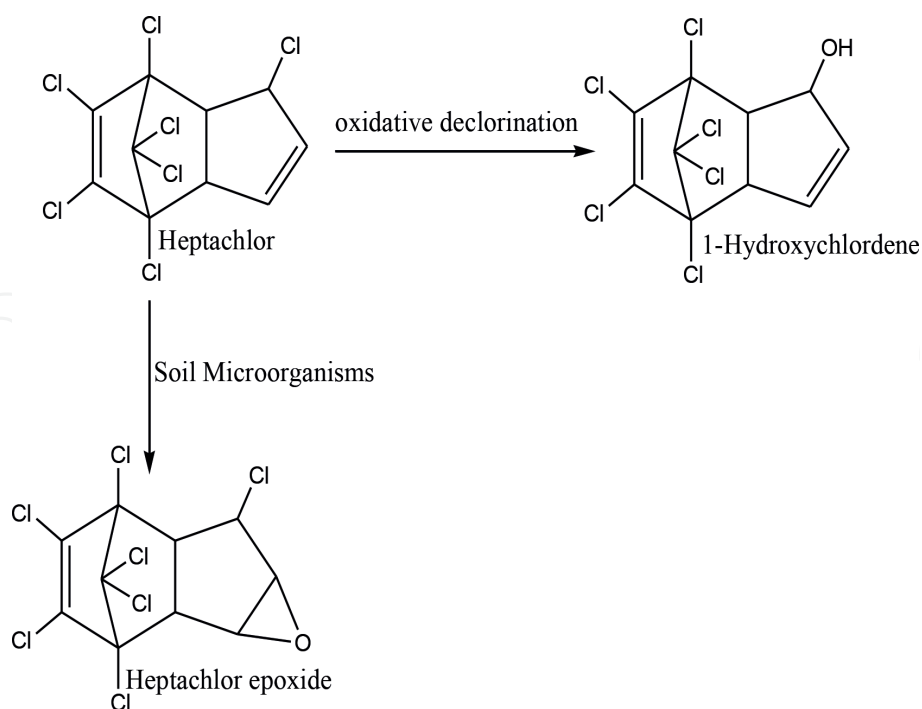
p,p'-DDT can be broken down in the soil by *Enterobacter aerogenes* microorganisms in the presence of UV light and/or iron catalyst to reduced dehydrochlorinated compounds, DDE, and DDD as well as oxidized derivatives which ultimately form *p,p'*-dichlorobenzophenone (**Scheme 2**). *o,p'*-DDT degrades in the same way as *p,p'*-DDT [16].

6.3. Degradation of endosulfan

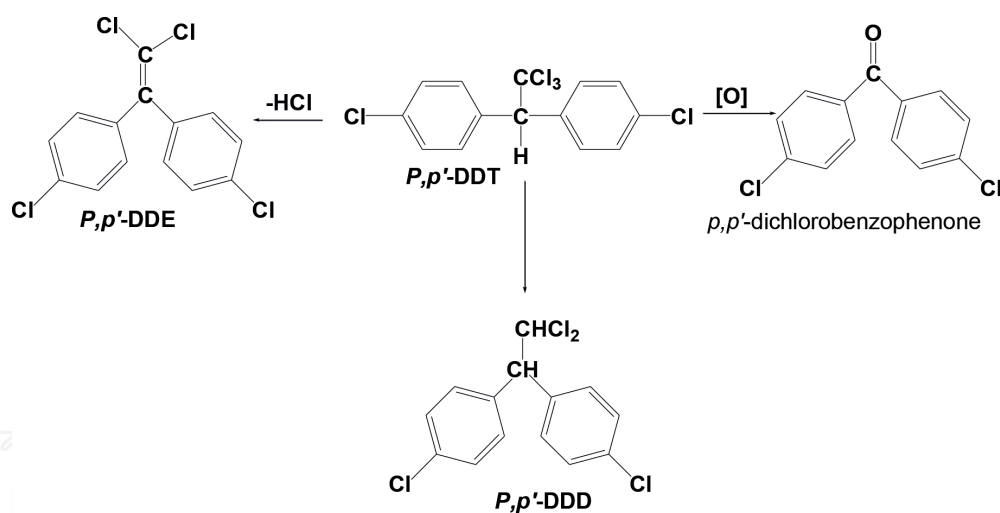
The technical grade of endosulfan consists of two isomers, alpha and beta in the ratio of 70:30. In the environment, endosulfan is photolytically degraded to yield endosulfan sulfate in soil and endosulfan diol in aquatic environment. Endosulfan sulfate is equally toxic as the parent molecule (**Scheme 3**) [16].

6.4. Degradation of hexachlorobenzene

In anaerobic condition, biodegradation of HCB in an arable soil takes place with several dechlorination steps, indicating the following main HCB transformation pathways: HCB → pentachlorobenzene (QCB) → 1,2,3,5-tetrachlorobenzene (TeCB) → 1,3,5-TCB → 1,3-dichlorobenzene (DCB), with 1,3,5-TCB as the main intermediate dechlorination product [17] (**Scheme 4**).



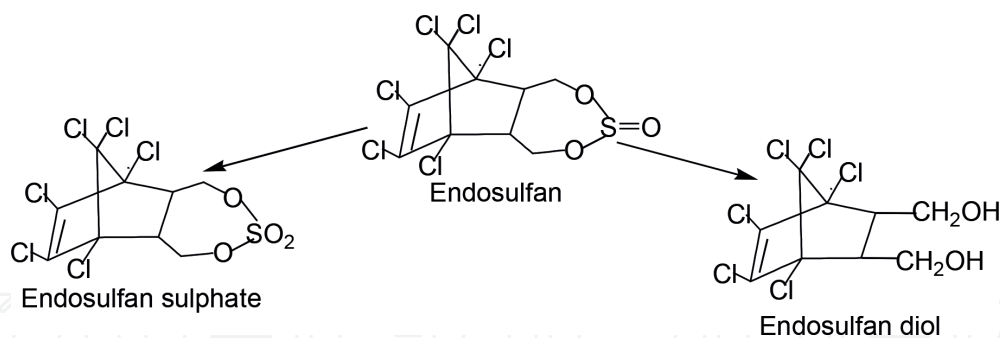
Scheme 1. Degradation pathways of heptachlor in the soil.



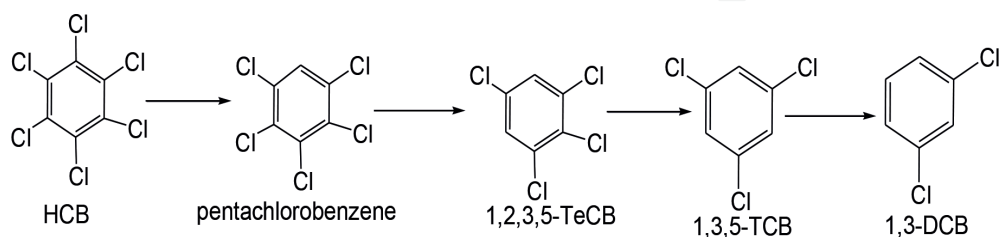
Scheme 2. Degradation of *p,p'*-DDT in the environment.

6.5. Degradation of aldrin/dieldrin

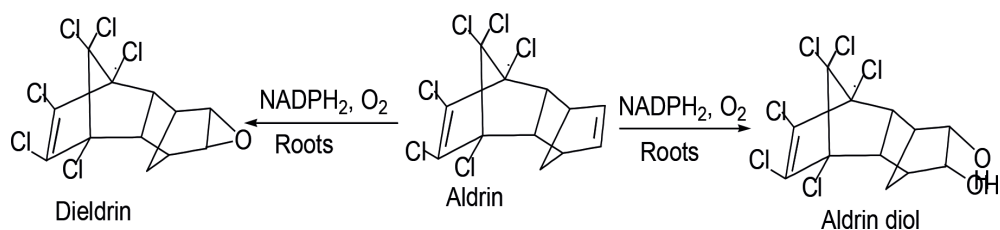
The NADPH₂-dependent enzymatic oxidation of aldrin to dieldrin and aldrin to aldrin-diol by two enzyme systems is present in excised roots. The enzymatic oxidation of aldrin in plants is known to be more species specific than the oxidation by microorganisms [10] (Scheme 5).



Scheme 3. Degradation of endosulfan in the environment.



Scheme 4. Degradation of hexachlorobenzene.



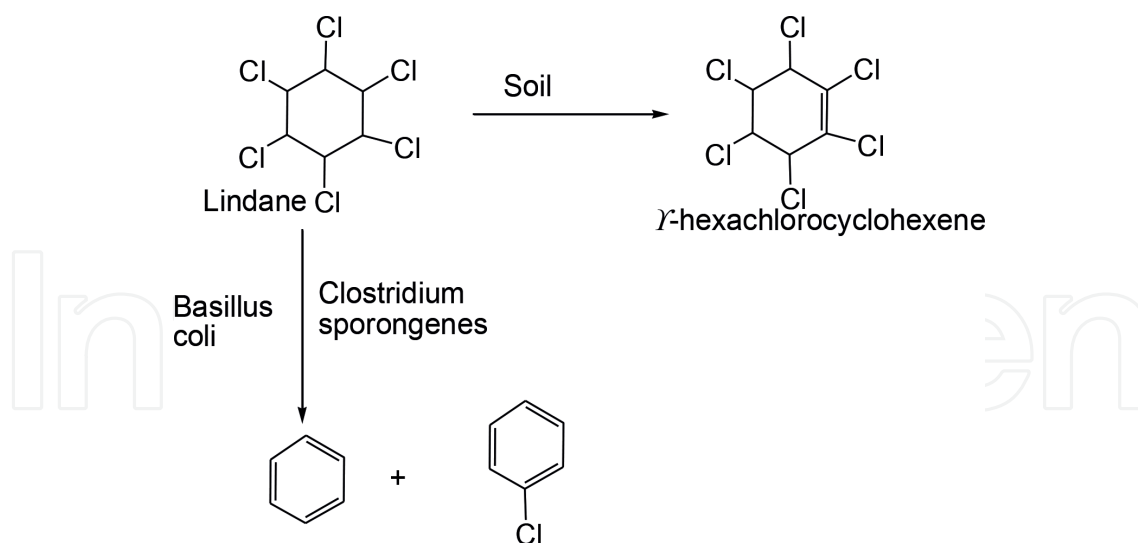
Scheme 5. Degradation of aldrin in the environment.

6.6. Degradation of lindane

Dehydrohalogenation of lindane to γ -hexachlorocyclohexane takes place in moist soil and is attributed to the soil microorganisms such as *Bacillus coli* and *Clostridium sporogenes*. Also these bacteria produced trace amount of benzene and monochlorobenzene from lindane (**Scheme 6**) [18].

6.7. Degradation of PCBs

Various microorganisms are involved in a two-stage process of degradation of PCBs, which happens in aerobic and anaerobic environments. Degrading PCBs is similar to the degradation of biphenyl. However, the chlorines on PCBs prevent them from being utilized as a substrate of biphenyl degradation. Due to high chemical stability, PCBs cannot be used as energy sources. However, due to the chlorination, PCBs can be used as electron acceptors in anaerobic respiration to store energy, which is also the first stage of the degradation pathway, reductive dechlorination. Once the PCBs are dechlorinated to a certain degree, usually lower than five chlorines presenting in the structure and one aromatic ring has no chlorine, they can



Scheme 6. Degradation of lindane in the environment.

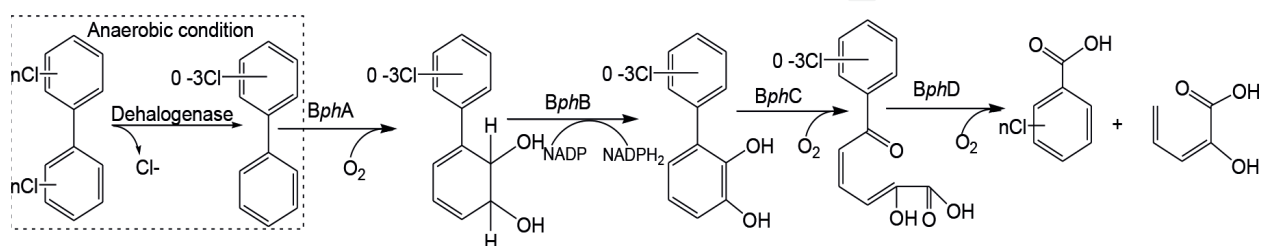
undergo the biphenyl degradation pathway (BP pathway) to be degraded to accessible carbon or CO_2 in the aerobic environment. BP pathway is a pathway that utilizes series of enzymes (BphA, B, C, D, E, F, G) to convert biphenyl to TCA cycle intermediates (pyruvate and Acyl-CoA) and benzoate. However, there are few microorganisms that can dechlorinate substrate under natural conditions. Even with selective media, the accumulation of PCB-dechlorinating microorganisms is still slow, which is one reason for the slow degradation rate. As a result, PCBs usually go through a co-metabolism pathway that involves different microorganism species [7, 14, 17, 25] (**Scheme 7**).

6.8. Degradation of dioxins by reductive dehalogenation

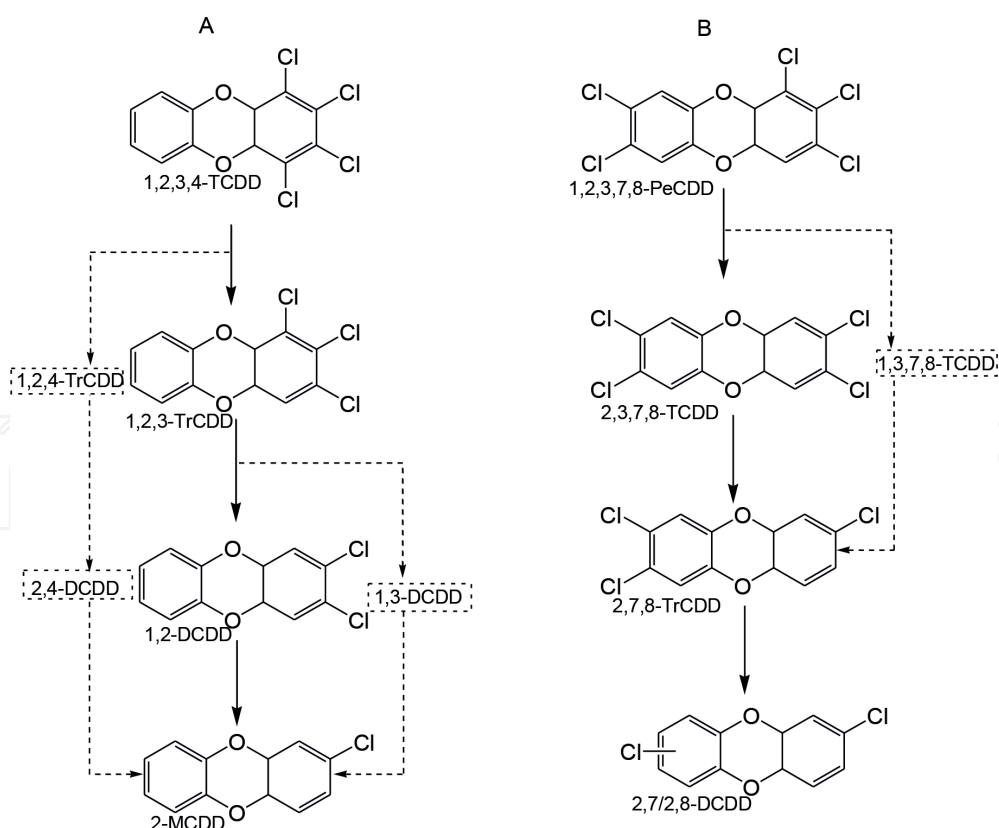
It has been well reported that several species of strictly or facultatively anaerobic bacteria are capable of de-halogenating chlorinated aliphatic and aromatic compounds. Some of these dehalogenation processes have been shown to couple to ATP synthesis via a chemiosmotic mechanism. The reductive dehalogenation linked to energy conservation is called “halorespiration” or “dehalorespiration.” For example, a sulfate-reducing bacterium, *Desulfomonile tiedjei* strain DCB-1, has been shown to conserve energy for growth from reductive dehalogenation of 3-chlorobenzoate by an uncharacterized chemiosmotic process. Bacterial dehalorespiration with tri- or tetrachlorinated benzene as a terminal electron acceptor is also known to take place. Gibbs free energy of formation of various PCDDs/PCDFs and redox potentials for PCDD/PCDF substrate/product couples indicate that the reductive dehalogenation of PCDDs/PCDFs is an exergonic reaction, and this implies that microorganisms acquire energy via anaerobic electron transport with PCDDs/PCDFs as terminal electron acceptors.

Despite its physiological and ecological importance, the biological reductive dehalogenation of PCDDs/PCDFs as well as of PCBs has been studied much less than the aerobic biodegradation of dioxin-related compounds. This biological reaction has so far been studied mostly in sediments, sludge, and soils containing anaerobic microbial consortia. Earlier work related to this subject showed changes in PCDD-/PCDF-congener distribution patterns and the resultant

accumulation of less-chlorinated forms in sediments. More intensive studies on microbial dehalogenation of PCDDs/PCDFs in the environment started appearing in the past decade. Microbial dehalogenation of PCDDs/PCDFs takes place by removal mainly at positions 1, 4, 6, and/or 9 and led to much more toxic congeners, including 2,3,7,8-TCDD, in some cases. The maximum yield of cell protein coincided with the production of less-chlorinated DD isomers, where no methanogenic activity was detected. Experiments with sediment microcosms spiked with the much less toxic congener 1,2,3,4-TCDD revealed that reductive dehalogenation occurred at the lateral positions with 1,2,4-TrCDD as the main intermediate, leading to 2-MCDD as the final end product. The available information indicates that MCDDs/MCDFs are not dehalogenated further [14, 19–21] (**Scheme 8**).



Scheme 7. Degradation of PCBs in the environment.



Scheme 8. Possible degradation pathways of reductive dechlorination of 1,2,3,4-TCDD (A) and 1,2,3,7,8-PeCDD (B) by *Dehalococcoides* sp. strain CBDB1.

7. What can be done to control or remove POPs in the environment?

The Stockholm Convention on POPs clearly provides suggestive solutions by restricting the production and use of POPs in the environment. The Convention requires that production and use of POPs be stopped and their stockpiles destroyed so that the resulting products are no longer POP. Article 6 of the Convention addresses the identification and management of POP waste. The Convention requires that such wastes be managed in a safe, efficient, and environmentally sound manner and that the disposal be done such that the POP content be destroyed or irreversibly transformed so it is no longer a POP.

Stockpiles of POPs are well documented worldwide, which include obsolete pesticides, PCBs discarded from use (PCB oils and liquids), and heavily contaminated soil (e.g., soil surrounding landfills and deep wells containing POPs). To eliminate these stockpiles of POPs from the environment, two basic POP destruction technologies are suggested, namely, combustion technology and non-combustion technology.

The combustion technologies (hazardous waste incinerators, rotary kilns, furnaces, boilers, IR incinerators, etc.) are usually believed to be the most economically appropriate way for concentrated POP waste treatment. This is why in industrialized nations POP wastes are routinely burnt in incinerators, and for most countries combustion technologies still remain the most economically acceptable way to treat POP waste on the macroscale. Modern waste incinerators are designed to satisfy the required emissions levels.

Over the last 15 years, a number of non-combustion technologies have been demonstrated to effectively treat POP wastes in countries such as Canada, the USA, Australia, and Japan. Some methods, particularly for PCBs, are outlined by the UNEP. However, even developed non-combustion technologies can hardly be competitive with incineration. Other non-combustion technologies lack in research or technical development, and most of them have a scarce commercial operation history.

Current studies aimed at minimizing POPs in the environment are investigating their behavior in photocatalytic oxidation reactions. POPs that are found in humans and in aquatic environments the most are the main subjects of these experiments. Aromatic and aliphatic degradation products have been identified in these reactions. Photochemical degradation is negligible compared to photocatalytic degradation. A method of removal of POPs from marine environments that has been explored is adsorption. It occurs when an absorbable solute comes into contact with a solid with a porous surface structure. Current efforts are more focused on banning the use and production of POPs worldwide rather than the removal of POPs [20, 22–24].

8. Conclusion

POPs pose one of the most challenging problems in environmental science and technology. Their fate, transport, and biodegradation in the environment occur via complex networks,

involving complicated interactions with other contaminants and with slow biodegradation and various physiological, chemical, and biological processes. Those processes can be used and modified in order to diminish their environmental concentration. There are more promising results of such activities performed by various researchers worldwide. Nevertheless, the still existing challenge is to develop a bioremediation strategy that involves and integrates different types of solutions, on the scale of the whole ecosystem, in order to optimize the effectiveness of pollutant removal from the environment. For POP stockpiles, the combustion technologies remain by far the most effective and economic method of removing them from the environment.

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