

PERSISTENT ORGANIC POLLUTANTS IN ENVIRONMENT AND THEIR HEALTH HAZARDS

Ram Chandra* and Shalini Chaudhary

Department of Environmental Microbiology, School for Environmental Sciences, Babasaheb Bhimrao Ambedkar University (A Central university), Vidya Vihar, Raebareli Road, Lucknow, India.

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Abstract: This review article provides an overview of the exposure of persistent organic pollutants (POPs) in the environment and their fate of transport. The purpose of this paper is to address the health and environmental problems related to synthetic toxic POPs of increasing concern at the local, national, and global level and their relationship between environmental pollution and health problems affecting human and non-human species. We report scientific studies on climate change related effect on POP environmental behavior in order to feature how climate change is influencing POP fate and transport. In this review paper, we report the track of POP regulation efforts driven towards decreasing POPs environmental concentration through reducing or banning on POPs emission in the environment. Our final aim is to identify how POP related regulation may take into account climate change in managing current or future POP sources.

Keywords: Persistent Organic Pollutant; Health Hazards; Regulation and Guideline.

INTRODUCTION

During the last half of the 20th century, the global environment has become contaminated with a number of persistent, fat-soluble chemical contaminants, commonly referred to as the persistent organic pollutant (POPs). Contamination of the global environment with a complex mixture of POPs has resulted from deliberate discharges and applications as well as from the inadvertent formation of byproducts of incomplete combustion or industrial processes. The POPs are a group of chemical compounds originate from different anthropogenic activity but have some common characteristics like semi-volatility, lipophilicity, bioaccumulation that is in large quantity resist photolytic, biological and chemical degradation over a reasonable period of time. They persist in the environment for a long time, being also able to longrange transport and to have potential significant impacts on human health and the environment ^[1]. It is halogenated and characterized by low water solubility and high lipid solubility, due to this if these compounds have been continuously used in large quantities leading to bioaccumulation and biomagnifications in fatty tissues across the globe, including remote areas such as the Antarctica. In order to concentrate in organisms in the environment, POPs must also possess a property that results in their movement into organisms. This property is called lipophilicity or a tendency to preferentially dissolve in fats and lipids, rather than water. This tendency is leading to POPs to pass readily through the phospholipids structure of biological membrane and accumulate in fat deposits. Lipophilicity also results in biomagnifications through the food chain ^[2]. POPs are readily absorbed in fatty tissue, where concentrations can become magnified by up to 70,000 times the background levels^[3].

The importance of persistent environmental chemicals like pesticides was first identified by Rachel Carson an American courageous woman and scientist in the early 1960s with the publication of her seminal work in her classic book "Silent Spring" [4]. POP substances often have three common characteristics: (i) one or more cyclical ring structures of either aromatic or aliphatic nature, (ii) a lack of polar functional groups, and (iii) a variable amount of halogen usually chlorine. Certain key properties of chemicals control their fate in the environment and if these properties are known, then environmental chemists can make predictions about their fate and behavior. These properties include aqueous solubility, vapor pressure, partition coefficients between water: solid and air: solid or liquid, and half-lives in air, soil and water.

POPs are also noted for their semi-volatility, this property may permit these compounds to occur either in the vapor phase or adsorbed on atmospheric particles, thereby facilitating their long range transport through the atmosphere before being deposited. Thus POPs can be found all over the world. Wania 1999 described the concentrations of POPs have been higher in remote regions than in source regions. Due to semi volatility these substances may volatilize from hot regions but will condense and tend to remain in colder regions. Therefore, these are highly halogenated, molecular weight of 200 to 500 and a vapor pressure lower than 1000 Pascal $^{\left[2\right] }$. The scale of atmospheric transport of POPs depends on the meteorological conditions ^[5]. The transfer of chemicals from land surface to atmosphere consists of two steps at first it Change from liquid or solid state to vapors and then

*Corresponding Author:

Prof. Ram Chandra,

Head, Department of Environmental Microbiology, Babasaheb Bhimrao Ambedkar University (A Central University), Vidya Vihar Raebareli Road, Lucknow-25, U.P., India.



subsequent dispersed by turbulent mixing ^[6-7]. POPs can undertake several cycles of deposition and reemission before reaching their final destination because several physico-chemical properties governing the environmental fate of POPs are temperature dependent ^[1].

POPs are substances that produce very adverse effects on both the ecosystem and human health due to their very high toxicity, their prolonged persistence in contaminated ecosystems, their extremely limited biodegradability and also their deep penetration in even the remotest areas such as the Arctic. POP exposure can cause death and illness including disruption of the endocrine, reproduction, immune system, neurobehavioral disorder and cancer possibly including breast cancer. These pollutants are accumulated in animal fats, so minimizing consumption of animal fats may reduce the risk of diabetes^[8].

Some POPs are highly toxic and have a wide range of chronic effects, including endocrine disruption, mutagenicity and carcinogenicity ^[9-10]. Specific effects of POPs include cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system by altering the hormonal system. Their ecotoxicity has been highlighted in aquatic [11] and terrestrial ecosystems ^[12-13]. Furthermore, POPs are chemically stable and not easily degraded in the environment. A large amount of waste discharge from eight largest industries such as oil, cement, leather, textile, steel, pulp paper, tannery and distillery industries discharging variety of gaseous, liquid and solid waste into the environment which persist in the environment. These POP containing effluent cause considerable damage to the receiving water. However, the knowledge of persistent organic pollutant in environment is insufficient for its monitoring because it persists in complex form and analysis through conventional method is not so easy. Therefore, presently no proper research work has been done related their mechanism of action for adverse effect on human health.

Till date there is lack of information in research papers regarding the systematic classification and major human health hazards cause by POPs. Therefore, our objective in this paper is to provide a brief overview of POPs, their harmful effect on biota and their microbial degradation. We also describe some guideline for the control of POPs on worldwide.

Categories of pops and their characteristics:

POP are highly toxic synthetic organic chemicals fall in to two categories according to their existence i.e. intentionally and unintentionally persistent organic pollutant.

Intentionally Persistent Organic Pollutant:

These compounds are produced intentionally as commercial products by different chemical reactions including chlorine. These are organic molecules with high lipophilicity, high neurotoxicity and are called as organochlorine compounds (OCs). This category is also classified into two types based on their use i.e. pesticides & industrial product.

Pesticides: It contains the large part of the POP up to 70%. The persistence of pesticides in the environment depends upon their chemical and physical properties, type of the soil, its moisture content, temperature, physical properties of the soil, composition of the soil micro flora and the plant species present in soil. Various categories of pesticides are mentioned in table 1.

Iddle.1 : List of pesticides	Tab	le.1:	List	of	pesticides
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Organophosphate	Carbamates	Organochlorine insecticides	Pyrethroides
Organophosphate Parathion Malathion Methyl Parathion Chlorpyrifos Diazinon Dichlorvos Phosmet Fenitrothion Tetrachlorvinphos Azinphos Methyl	Carbamates Aldicarb Carbofuran Carbaryl Ethienocarb Fenobucarb Oxamyl Methomyl	Organochlorine insecticides DDT Chlordane Mirex HCB, Endrin Aldrin, Dieldrin Toxaphene Heptachlor Hexachlorobene (HCB)	Pyrethroides Allethrin, Bifenthrin, Cyfluthrin, Cyplermethrin, Cyphenothrin, Deltamethrin, Esfenvalerate, Etofenprox Fenpropathrin, Fenvalerate Flucythrinate, Imiprothrin,
			Metofluthrin, Permethrin, Prallethrin, Resmethrin, Silafluofen, Sumithrin, tau-Fluvalinate, Tefluthrin, Tetramethrin, Tralomethrin

Table.2: List of Industrial POP product from different sources

S. No.	Industrial product	Source
1.	Polychlorinated biphenyls (PCBs)	Transformer, capacitor, elect
		ricmotors
2.	Hexachlorobenzene (HCB)	Agriculture
3.	Chlordecone	Agricultural insecticide
4.	Pentachlorobenzene	Industrial
5.	Hexabromobiphenyl	Flame retardant
6.	Hexabromodiphenyl ether	Flame retardant
7.	Heptabromodiphenyl ether	Flame retardant
8.	Tetrabromodiphenyl ether	Flame retardant
9.	Pentabromodiphenyl ether	Flame retardant
10.	Polychlorinated biphenyls (PCB)	Industrial
11.	Alpha hexachlorocyclohexane,	Insecticide
12.	Beta hexachlorocyclohexane,	Insecticide
13.	Lindane	Agricultural insecticide
14.	Perfluorooctane sulfonic acid	Industrial
15.	Perfluorooctane sulfonyl fluoride	Industrial

Industrial Product: POPs are also produced for use in industrial processes, such as coolants for electrical transformers. This group includes polychlorinated biphenyls (PCBs) and hexachloro benzene. This category of POPs is shown in table 2.

Unintended Byproducts: They were produced as unwanted by-products of combustion or burning of chlorine containing compound. They are divided into three types: polycyclic aromatic hydrocarbons (PAHs), dioxin and furan compounds. The most common list of unintentionally POPs is given in table 3.

Table.3: List of Uninte	entional byproduct
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Unintentional products
Polychlorinated dibenzo-p-dioxins (PCDDs)
Polychlorinated dibenzofurans (PCDFs)
Polycyclic aromatic hydrocarbons (PAHs)
Octachlorstyrene
Brominated dioxin
Bromochlorodioxin
Pentachloro biphenyl
Polychlorinated diphenyl ethers (PCDEs)

Toxicological properties of pops and related health hazards:

The toxicological properties of these compounds are very low solubility, high lipid solubility leading to their bioaccumulation in tissues^[14]. They are entering in the body through food and then transfer to all trophic level of ecosystem. The ecotoxicological effect of POPs has been identified as hormones disrupters which can alter normal function of endocrine and reproduction systems in humans and wild life. In humans it causes hormone disrupters, which can alter the normal function of endocrine and reproductive system. These are able to stay in the environment for decades causing problems such as cancer, birth defects, and learning disabilities, immunological, behavioral, neurological and reproductive discrepancies in human^[15]. Some POP have also reduced immunity in infants and increase infection, developmental abnormalities neurological impairment, cancer and tumor. Some POP have also being considered as important health hazards in the etiology of human breast cancer by some authors ^[16].

Exposure of POP in humans is carried out through the food chain and the developing child is serving caused by POP because they are more susceptible to infected by these POP. Their developing cells are sensitive to contaminates and are more likely to be affected by exposure of POP. Some studies have shown that children exposed to POPs during infancy had remarkably lower scores in assessment determining intelligence ^[17]. At young stage of human POP can have following serious consequence side effect such as birth defects, certain cancer and tumor at multiple sites, immune system disorder, and reproductive problems reduced ability towards off diseases, stunted growth and permanent impairment of brain function, POP are a suspected carcinogen, causes endometriosis, increase incidence of diabetes and neurobehavioral impairment including learning disorder, reduced performance on standard test and changes in temperament ^[18].

In wild life, it causes egg shell aberration in birds to extinction of certain bird species ^[19-21]; other serious effects include cancers, twisted spines and skeletal deformations, and death of beluga whales. In Florida's Lake Apoka, stunted penis, hormone disruption and reproductive failure have been found among alligators reproductive development, disrupted deformity, immunotoxicity, hormonal deficiencies, to overall population decimation have been reported [3,21,22,23]. The Stockholm convention identified the 12 most dangerous POPs, collectively referred as Dirty Dozen which is presented in table 4 including their uses, halflife and their causing effects in the environment ^[24].

Microbial degradation of pops:

A large number of bacterial and fungal species possess the capability to degrade persistent organic pollutants. Biodegradation is catalyzed reduction of complex chemical compounds based on two processes i.e. growth and co-metabolism. In the case of growth, organic pollutants are used as a sole source of carbon and energy. The second possibility is co metabolism, the cellular uptake of compounds, manipulation of substrate for ring fission, ring cleavage, conversion of cleaved product into standard metabolites and utilization of metabolites.

Biodegradation generally depends on many factors. These factors include the structure of the compound, substituent's position in the molecule, and solubility of the compound and concentration of the pollutant. Environmental and soil condition like organic carbon content also influenced degradation rate of POPs. Addition of organic substrate and nutrients to contaminated soil could enhanced microbial and degradation activity ^[25]. Microorganisms have very large enzymatic facilities due to their genetic flexibility, short reproduction cycle and high adaptive potential. The degradation of the POPs has been monitored by HPLC/DAD/FLD.

Class	Chemical	Uses	Half-Life in Soil (Years)	Adverse Health Effects
	Aldrin	Insecticide	N/A	Carcinogenic, malaise, dizziness and nausea
	Chlordane	Insect and termite control	1	Carcinogenic
	DDT	Insecticide	10-15	Cancer of liver, immune system suppression
	Dieldrin	Insecticide	5	Liver and biliary cancer
Agricultural and	Endrin	Insecticide, rodenticide	Up to 12	Cancers
Chemicals: Pesticides	Heptachlor	Insect and termite control	Up to 2	Cancers, mutations, stillbirths, birth defects, liver disease
	Hexachloro- benzene (HCB)	Fungicide	2.7-22.9	Cancers, mutations, birth benzene (HCB) defects, fetal and embryo toxicity, nervous disorder, liver disease
	Mirex termiticide	Insecticide	Up to 10	Acute toxicity, termiticide possible cancers
	Toxaphene	Insecticide	3 months to 12	Carcinogenic, chromosome aberrations, liver and kidney problems
Industrial Chemicals	Polychlorinated biphenyls	Industry manufacture co- planar	10 days to 1.5 years	Cancers mutations, births defects, fetal and embryo toxicity, neurological disorder and liver damage
	Dioxin	By-product	10-12	Peripheral neuropathis, fatigue, depression, liver disease, embryo toxicity
	Furan	By-product	10-12	Peripheral neuropathis, embryo toxicity, liver problems

Biodegradation of chlorinated compounds is highly affected by the degree of chlorination and presence of other functional groups. Higher chlorinated congeners are only susceptible to anaerobic biotransformation, whereas lower congeners are only susceptible to aerobic biodegradation. Complete biodegradation of the higher chlorinated congeners requires a sequence of anaerobic and aerobic conditions.

A majority of microorganisms are able to metabolized aldrin to dieldrin by epoxidation^[26]. Dieldrin is highly persistent (5 years) in soil and residues ^[2]. Dieldrin could be further hydrolyzed by several bacteria and fungi strains, which convert dieldrin to water-soluble and solvent-soluble metabolites and to CO₂ ^[27]. Miles et al. (1969) have shown that soil microorganisms metabolize heptachlor to many different products by many independent metabolic pathways^[28]. The insecticide endosulfan is structurally similar to chlordane and dieldrin. The degradation time of endosulfan and its metabolites could exceed 6 months in some acidic soil [29]. Beta-endosulfan has a longer half-life and is slowly converted to alphaendosulfan. It was reported that mixed soil microbial culture was able to interconvert α and β isomers and consequently further metabolism.

Hexachlorobenzene (HCB) is a fungicide that was first introduced in 1945 for seed treatment and is also a by-product of the industrial chemicals. Volatilization is important process of HCB losses from soil. Estimated half lives in soil under aerobic and anaerobic degradation range from 2.7 to 22.9 years ^[2].

Chlorophenols have been introduced into the environment through their use as biocides in wood preservation. Wide spectrum of indigenous soil microorganisms is able to metabolize chlorophenols and utilize it as a carbon source ^[30]. Chlorphenols are degradable under both aerobic and anaerobic conditions.

Other POP compounds are releases from the world's largest polluting industries such as pulp paper and distillery industries waste which are recalcitrant to degradation. These Recalcitrant wastes including phenolic substances, fatty acids, resin acids, chlorolignin, molasses, dyes, pesticides, explosives, heavy metals, poly alcohols, dioxin and furan derivatives.

There is not much information about soil microbial degradation of other POPs. These candidate and new POPs chemicals are often very stable and no longer used. In case of brominated diphhenyl ethers (BDE), OctaBDE is not readily biodegradable in standard tests and is not expected to degrade rapidly under anaerobic conditions ^[31]. More highly brominated congeners have been found to degrade anaerobically in sewage sludge, although at a very slow rate ^[32]. Lower brominated diphenyl ethers are usually more toxic and much more bioaccumulative.

Perfluorochemicals (PFCs) are non-polar, highly fluorinated compounds that are chemically and biologically inert. They are used in surface treatments to provide soil and stain resistant coatings, in paper treatments to provide oil, grease, and water resistance. PFOS (perflorooctane sulfonate) and its salts are highly persistent in the environment and do not appear to degrade ^[33].

In pulp paper industry varius types of persistent organic pollutants are releases in which PAH is one of

them. PAH-degrading populations in soil are probably mostly not growing and degradation of PAHs is a complex process involving assimilation as well as cometabolisms by many bacterial species. It has been observed that PAH degradation in soil is dominated by bacterial strains belonging to a very limited number of taxonomic groups such as Sphingomonas, Burkholderia, Pseudomonas and Mycobacterium ^[34]. PAHs degrading bacteria are able to produce bio-surfactants that increased dissolution of PAHS and facilitate their [35] bioavailability and then biodegradation Biodegradation of PAHs by isolated strains of white-rot fungi was also reported [36]

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are produced unintentionally due to incomplete combustion, during manufacturing of other chlorinated compounds, and in the chlorine bleaching of wood-pulp. They are also toxic, persistent and bio-accumulating manmade compounds.

Regulation and guideline for control of pops in environment:

To protect the environment from the adverse effects of POPs, many nations worldwide have enacted legislation to regulate various types of POPs as well as to mitigate the adverse effects of pollution. There are three main POPs initiatives exist i.e. the Aarhus Protocol and the Stockholm Convention and Persistent Organic Pollutants Review Committee. The aim of these initiatives is to control, reduce or eliminate POPs in to the environment.

The Aarhus Protocol: The 1998 Aarhus Protocol on POPs Convention on Long-range Transboundary Air Pollution (LRTAP) and the aim is to eliminate or restrict the production and use of selected POPs. The LRTAP Convention adopted the Protocol on POPs on 24 June 1998 in Aarhus (Denmark). There are about 42 members of this protocol, which covers both eastern and Western Europe, besides Canada and the US. It focused on a list of 16 substances that have been find out according to agreed risk criteria; many substances on the list are chlororganic pesticides. The ultimate objective is to eliminate any discharges, emissions and losses of POPs. The Protocol bans the production and use of some products i.e. aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene. It focuses on a list of 16 substances (eleven pesticides, two industrial chemicals and three by-products/contaminants). Chemicals present in these Arhus Protocols are listed in table 5.

 Table.5:
 List of persistent organic pollutants found in the Aarhus Protocol

Prior POPs according to the UN-ECE			
Organochlorine pesticides	Aldrin		
	DDT and metabolites		
	Dieldrin		
	Endrin		
	Heptachlor		
	Chlordane		
	Mirex		
	Toxaphene		
	Chlordecone		
	Lindane (gama HCH)		
Industrial products	Hexachlorobenzene (HCB)		
·	Polychlorinated biphenyls (PCBs)		
	Hexabromobiphenyl (HBB)		
	Polychlorinated dibenzo- dioxins		
Industrial byproducts	(PCDDs)		
	Polychlorinated dibenzo-furans(PCDFs)		
	Polycyclic aromatic hydrocarbons		

The Stockholm Convention: The Stockholm Convention on POPs was adopted on 22 May 2001, focusing on 12 substances and entered into force on 17 May 2004. The Convention was further amended in 2009 to include nine new substances. The Stockholm Convention generally includes the same substances as the POPs Protocol of the LRTAP Convention but not all. It does not include PAHs and HCB.

The Stockholm Convention is a global treaty to protect human health and the environment from POPs. It focuses on eliminating or reducing releases of 12 POPs, the so-called "Dirty Dozen". Chemicals included to this convention must provide evidence of persistence in water, soil or sediment. In implementing the Convention, Governments will take measures to eliminate or reduce the release of these 12 "Dirty Dozen" POPs into the environment.

There are many chemicals with POP-like characteristics that are currently not listed in the Stockholm Convention or Arhus protocol. In 2005, five candidate chemicals are nominated to the POPs Review Committee for inclusion in the Convention. Norway nominated pentabromodiphenyl ether (a brominated flame retardant); the European Union nominated chlordecone (pesticide) and hexabromobiphenyl (flame retardant); Sweden nominated perfluorooctansulfonate (PFOS); and Mexico nominated Lindane. In November 2005, the Committee concluded that all chemicals are classifiable as POPs. The evaluation proceeded to the second stage of constructing and evaluating a risk profile for each substance. World Wildlife Fund (WWF) released a list of 20 chemicals that it recommends be added to the treaty mentioned in table 6.

Table.6: List of twenty additional persistent organic pollutants proposed by WWF^[27]

New POPs candidates (According to WWF)			
Pesticides (insecticides, Biocides, fungicides)	Chlordecone Dicofol Endosulfan Hexachlorobutadiene (HCBD) Hexachlorocyclohexane (HCH) (includes lindane) Methoxychlor Pentachlorophenol (PCP) (organometals)		
Brominated flame retardants	Hexabromocyclododecane (HBCD) Hexabromobiphenyl (HxBB) Polybrominated diphenyl ethers (PBDEs) (okta-BDE, penta-BDE, deca-BDE)		
Perfluorochemicals	Perfluorooctane sulfonate (PFOS) Perfluorooctanoic acid and its salts (PFOA)		
Other chlorinated chemicals	Chlorobenzene (penta-CB, tetra-CB) Short-chain chlorinated paraffins (SCCPs) Polychlorinated naphthalenes (PCNs)		
Unintentionally produced	Octachlorostyrene (OCS) Polycyclic aromatic hydrocarbons (PAHs) Brominated dioxins and bromo-chlorodioxins		

Therefore the main objective of the POPs convention is to control, reduce or eliminate discharges, emissions and losses of specific POPs to the environment. Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that will be banned.

CONCLUSION

POPs are toxic substances released into the environment through a variety of human activities. They tend to concentrate in colder climates and have adverse effects on the health of ecosystems, wildlife and people. They tend to bioaccumulation in the food chain of ecosystems as they have a low volatility and water solubility. Generally, biomagnifications of POPs through aquatic-based food chains is greater than terrestrial-based food chains, as in the terrestrial ecosystem bioaccumulation is restricted by lower bioavailability, longer food chains and a comparatively lower fat content of organisms ^[37]. There is no proper documents and information available in this crucial area regarding their health hazards. Thus more emphasis has to be concentrated on classification and characterization of different POP. Their toxicological properties and health hazards; their life cycle and detail guideline for its disposal in environment.

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