



## Persistent organic pollutants in water resources: Fate, occurrence, characterization and risk analysis



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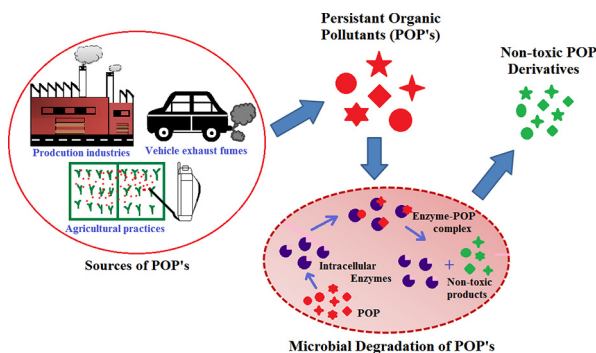
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### HIGHLIGHTS

- Persistent organic pollutants (POPs) are the prominent toxic contaminants exist in environmental sources.
- Agricultural and industrial practices are the primary sources for persistent organic pollutants.
- The review involves the fate, persistence and occurrence of POPs.
- The study inculcates the importance of microbial degradation to a greater extent.
- Biological remediation of POPs is well discussed.
- Future aspects of POP elimination through biological methods is emphasized.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Persistent organic pollutants (POPs) are organic chemicals that can persist in the environment for a longer period due to their non-biodegradability. The pervasive and bio-accumulative behavior of POPs makes them highly toxic to the environmental species including plants, animals, and humans. The present review specifies the POP along with their fate, persistence, occurrence, and risk analysis towards humans. The different biological POPs degradation methods, especially the microbial degradation using bacteria, fungi, algae, and actinomycetes, and their mechanisms were described. Moreover, the source, transport of POPs to the environmental sources, and the toxic nature of POPs were discussed in detail. Agricultural and industrial activities are distinguished as the primary source of these toxic compounds, which are delivered to air, soil, and water, affecting on the social and economic advancement of society at a worldwide scale. This review also demonstrated the microbial degradation of POPs and outlines the potential for an eco-accommodating and cost-effective approach for the biological remediation of POPs using microbes. The direction for future research in eliminating POPs from the environmental sources through various microbial processes was emphasized.

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## 1. Introduction

Demand for a pollution-free environment is the need for the hour. The necessity to protect the natural environment has been raising over the past decades leading to the establishment of novel and effective chemical as well as physico-chemical treatment methodologies (Yu et al., 2019; Bhavya et al., 2021). Comparison of environmentally friendly techniques to remove POPs from the environment was shown in Table 1. Since the II world war, researchers have noticed several contaminants that expose toxic behavior and are bio-accumulative, prone to long-distance towards the atmospheric region of boundary deposition/ migration, even persistent in the natural environment. They are also aggravated to produce serious health issues on human beings, fauna, flora and to marine ecosystem adjacent to as well as relatively distant from its point of source emission. Such toxic pollutants are so-called defined as persistent organic pollutants, (POPs) (Girones et al., 2021; Negrete-Bolagay et al., 2021). Compared to other chemicals, these are much more toxic despite being present in lower concentrations. Moreover, continuous exposure to such components enhances the risk effect. By definition, these are persistent/recalcitrant which is connected to their chemical stability (Gaur et al., 2018; de Andrade et al., 2021). These are much resistant to chemical, biological and photolytic decomposition (Kosek and Ruman, 2021). The persisting nature of a chemical component relies on the ability with which it can be broken down and deteriorated to less toxic components. Such behavioral features enable them to get accumulated within the biota over a longer duration of time hence symbolizing a longer duration exposure hazard (Yen et al., 2014; Singh and Chandra, 2019; Xiang et al., 2022). POPs can extend

their availability all around the universe even in the Arctic/Antarctic continent since they can be transported to longer kilometers even with much higher stability (Kosek and Ruman, 2021; Kosek et al., 2019a, 2019b; Ruman et al., 2021). These can be available in gaseous form and thereby stick to the solid material surface or with water sediment zones. They can also reach the ground either through rainfall or land deposition of industrial/agricultural fly ashes (Methneni et al., 2021).

The major sources of POPs are owing to anthropogenic activities and hence can be made available in the natural environment via several mechanisms (Nguyen et al., 2020a, 2020b). They can come into contact with the ecosystem through industrial effluent disposal, agricultural runoff, drainage leakages, urban runoff, landfilling leachate mixing, and huge atmospheric deposition (Lorenzo et al., 2018; Hidayati et al., 2021). Environmental pollution by organic insecticides is traditionally found in agricultural farms and conventional rice paddy regions. The residual % of most organic insecticides present in water sources or land sediments are diagnosed to be much higher in particle concentration at agriculture-based sectors compared to other regions which do not initiate farming activities (Wan et al., 2015; Liber et al., 2019). Usage of household insecticides, vector control agents, and pest management devices are a few of the various sources of POPs contamination. Anyhow, these data have not been much collected and hence result in a broader gap in detecting the actual fate and occurrence of POPs dissemination in sectors apart from agriculture-based localities (Passuello et al., 2010; Sharma et al., 2014). These are typically fat-dissolving and water-repelling substances i.e. lipophilic/hydrophobic. In aquatic environments and land textures, they divide extremely to solids, preferentially to organic content leaving the aqueous

**Table 1**  
Comparison of environmentally friendly techniques to remove POPs from the environment.

SNo	Treatment techniques	Merits	Demerits	References
1	Advanced oxidation system	<ul style="list-style-type: none"> <li>✓ Effective removal</li> <li>✓ Rapid reaction rates</li> <li>✓ No sludge formation</li> </ul>	<ul style="list-style-type: none"> <li>✓ Corrosion</li> <li>✓ High installation and operational cost</li> <li>✓ Complex chemistry</li> </ul>	He et al., 2021
2	Photocatalysis	<ul style="list-style-type: none"> <li>✓ Highly efficient</li> <li>✓ Low cost</li> <li>✓ Ecofriendly</li> </ul>	<ul style="list-style-type: none"> <li>✓ Lack of solar sensitivity</li> </ul>	Nguyen et al., 2020
3	Adsorption	<ul style="list-style-type: none"> <li>✓ High potential</li> <li>✓ Less energy</li> <li>✓ Easy operation</li> <li>✓ Separate different chemical compounds</li> </ul>	<ul style="list-style-type: none"> <li>✓ High cost of adsorbent</li> <li>✓ Desorption study</li> <li>✓ Weak selectivity</li> </ul>	Titchou et al., 2021
4	Electrocoagulation	<ul style="list-style-type: none"> <li>✓ Less expensive</li> <li>✓ Easily dewatered</li> <li>✓ Non-hazardous</li> <li>✓ Less maintenance</li> </ul>	<ul style="list-style-type: none"> <li>✓ Requires pH adjustment</li> <li>✓ High operational cost</li> <li>✓ Corrode over time</li> </ul>	Babu et al., 2020
5	Fenton oxidation	<ul style="list-style-type: none"> <li>✓ Less treatment time</li> <li>✓ High efficiency</li> <li>✓ Non-toxic</li> <li>✓ Environmental friendly</li> <li>✓ Easy handling</li> </ul>	<ul style="list-style-type: none"> <li>✓ Large quantity of oxidant is needed</li> <li>✓ Oxidant handling problem</li> <li>✓ Less economic</li> </ul>	Venny et al., 2012
6	Electrokinetic remediation	<ul style="list-style-type: none"> <li>✓ Cost effectiveness</li> <li>✓ Wide range application</li> <li>✓ Non-toxic</li> <li>✓ Strong controllability</li> <li>✓ Environmental friendly</li> </ul>	<ul style="list-style-type: none"> <li>✓ Time consuming process</li> <li>✓ Non-targeted contaminants</li> <li>✓ Degradation of electrolyte</li> </ul>	Chen et al., 2021
7	Ultrasonication	<ul style="list-style-type: none"> <li>✓ High potential</li> <li>✓ Economical</li> <li>✓ Environmental friendly</li> <li>✓ Greater accuracy</li> <li>✓ Easy operation</li> </ul>	<ul style="list-style-type: none"> <li>✓ limited range of detection</li> <li>✓ Not work in vacuum</li> <li>✓ More sound waves</li> </ul>	Shrestha et al., 2009
8	Nanotechnology	<ul style="list-style-type: none"> <li>✓ Weight decreases</li> <li>✓ Less power consumption</li> <li>✓ More efficient</li> <li>✓ Faster and accurate</li> </ul>	<ul style="list-style-type: none"> <li>✓ Employment reduces</li> <li>✓ High installation cost</li> </ul>	Abdek-Fatah, 2018
9	Membrane Bioreactor	<ul style="list-style-type: none"> <li>✓ High degradation efficiency</li> <li>✓ Short hydraulic retention times</li> <li>✓ Less sludge production</li> <li>✓ High volumetric loading rates</li> </ul>	<ul style="list-style-type: none"> <li>✓ Surface fouling</li> <li>✓ Process complexity</li> <li>✓ High installation and operational cost</li> <li>✓ Channel clogging</li> </ul>	Bouju et al., 2008
10	Multifunctional materials for thermal degradation	<ul style="list-style-type: none"> <li>✓ High catalytic activity</li> <li>✓ Thermal stability</li> <li>✓ Cost effective</li> <li>✓ Easy operation</li> </ul>	<ul style="list-style-type: none"> <li>✓ Depends on surface area and particle size, phase composition</li> </ul>	Sun et al., 2020

solution phase. They may also divide into organelle lipids compared to their entry in milieu cells and hence stored in biological tissues containing fatty matter. Such property confers its persistent nature onto the chemical component avail in biota owing to slower metabolism and thereby they can accumulate in larger traces along the food-chains (Islam et al., 2018; Weber et al., 2019).

Most importantly, they have the tough propensity to make an entry to the gaseous phase under ambient temperature levels. Therefore, they may easily volatilize from soil structures, vegetative matter and from water sources, thus transferred into the dry/wet atmospheric zones and also owing to their resistive power to breakdown chemical reactions in the surrounding air, so that it can travel to longer distances before getting re-deposited (Shen et al., 2021; Chinnadurai et al., 2022). The cyclic process of volatilization/deposition can be repeated more times and as a consequence, these could agglomerate in a remote area that is farther from where they are being discharged or used (Kosek et al., 2018). In the natural atmosphere itself, they can partition betwixt aerosols and particulate matter depending on the maintained temperature conditions and physico-chemical characteristics of the constituent chemical (Gomez-Gutierrez et al., 2007; Sanganyado et al., 2021). In an outlook, the mutual combination of its stability and definite propensity to appear as a gas under the influence of proper environmental standards configures that these are easily subjected to longer-range atmospheric deposition and transport (Rodriguez et al., 2021). The carbon and halogen bonding is much stable and water-resistant, and maximum, if the number of halogen molecules, higher is the resisting ability to undergo bio/photolytic degradation. In technical view, the stable nature rendered by halogens is a recommended feature. The fire resistive nature of Poly-chlorinated biphenyls, for example, is improved by the addition of chlorine, whereas in the case of 4-Chlorophenyl ethane, it confirms long-lasting impacts on insecticides. In addition, the bonding betwixt carbon and fluorine covalent linkages of PFC components is the actual cause for their environmental persistence. This review highlights the fate, occurrence, transport, classification, characterization, and impacts on various parameters associated with humans, biota and animals.

## 2. Persistent organic pollutants

Persistent organic pollutants are present in the ecosystem for a longer period and can move to long distances when released from various sources. These compounds interfere with the food chain by exposing to animals owing to their bioaccumulation property (Ge et al., 2021). It causes health impacts to living beings in present condition and also in future. Stockholm Convention addresses the persistent organic pollutants and came into force in 2004. The main aim is to secure the ecosystem and human welfare from the adverse effects due to exposure to these organic pollutants. Initially, 12 were listed as POPs and now 9 have been added to it. Stockholm Convention focuses on eliminating POPs from the environment (Fernandes et al., 2019; Wu et al., 2020). The disposal should be in such a way that these pollutants are destroyed or modified irreversibly such that it does not possess the characteristic feature of persistent organic pollutants (Xie et al., 2021). Persistent organic pollutants can be located in regions where they are not present or produced also and cause serious effects to the entire community. These pollutants get changed to the gaseous state under ideal temperatures and other conditions and start to vaporize from soil and water into the ecosystem withstanding the breakdown reactions occurring in the atmosphere and thus travel over long distances and get deposited (Bajaj and Singh, 2015; Chan et al., 2022). Thus the characteristics of persistent organic pollutants can be summarized as the ability to resist biodegradation, toxic to humans and the environment, deposition in aquatic as well as terrestrial regions, ability to remain in fat-rich tissues and possessing ability to travel long distances (Abromaitis et al., 2016; Karthigadevi et al., 2021).

The 1998 Aarhus protocol on persistent organic pollutants (POPs) listed out 16 different substances comprised of 11 pesticides, 2 industrial chemicals and 3 by-products and have been signed out according to agreed risk criteria. The major objective of this protocol is to eliminate the losses,

discharges and emissions of POPs in the environment. This protocol also bans the production and use of various toxic chemicals including aldrin, chlordecone, chlordane, endrin, dieldrin, mirex, toxaphene and hexabromobiphenyl. Moreover, dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs), heptachlor and hexachlorobenzene are a few more chemicals that were listed for elimination at a later stage. This protocol also takes responsibility to reduce emissions of various POPs including dioxins, furans, hexachlorobenzene (HCB), polycyclic aromatic hydrocarbons (PAHs) below their levels as mentioned in 1990. Also, it fixes certain specific limit values for municipal, medical and hazardous wastes incineration. In 2001 a treaty negotiated was conducted under the auspices of the United Nations Environment Programme (UNEP) where the Stockholm Convention on Persistent Organic Pollutants was adopted and developed a new profile with specific guidelines based on the 1998 Aarhus protocol to global level to reduce the level of POPs in environmental sources. In 2009, Parties to the Protocol on POPs adopted decisions 2009/1 and 2009/2 to amend the 1998 Aarhus protocol to include 7 new chemicals along with 11 chemicals (POPs) such as pentabromodiphenyl ether, octabromodiphenyl ether, hexachlorobutadiene, pentachlorobenzene, polychlorinated naphthalenes, short-chain chlorinated paraffin and perfluorooctane sulfonates. Besides, the parties revised the previous obligations for heptachlor, DDT, hexachlorobenzene and PCBs and also revised the emission limit values for waste incineration. The parties also provide flexibilities to a few countries regarding the time frames for the application of ELVs and best available technologies (BATs) for the protocol ratification and implementation in their economies transition. At last, the Parties adopted decisions 2009/3 and 2009/4 to upgrade guidance on BAT to control emissions of POPs in annex V and was included in the guidance document as contained in annex VII. The amendments to Annex V and VII entered into force for most of the parties on 13 December 2010. In the recent decades, different POPs detection methods in various food materials were developed such as Electron capture detector, Mass spectrometry (MS) with various ionization and monitoring modes including negative chemical ionization mode, electron ionization mode, selected monitoring mode, time-of-flight TOF-MS, high-resolution mass spectrometry (HRMS), etc. (Guo et al., 2019).

## 3. Fate and persistence

Certain key parameters of these chemicals decide their fate in the natural environment and if these features are broken out, environmental analysts/researchers can tend to render predictions about their structural fate and appropriate behavior (Adithya et al., 2021; Cao et al., 2021). Such characteristics involve aqueous solubility, total vapor pressure, associating partition coefficients which exist between water and solid and air with solid/liquid, their half-life periods in air, water and soil. Such properties have been consolidated for various POPs available in several databases, eg. The United States Environmental agency for Protection (US EPA), Dutch AQUAPOL system avail from either direct measurement those are calculated in laboratory/field or based on theoretical knowledge. Anyhow, these databases have more variations in the data being reported and obviously, their quality/features confer uncertainty onto POPs' precise nature and hence, this information is continually collected, revised and greatly improved (Ilyina et al., 2006; Chaves et al., 2013).

Given an accurate rate of emergence of a chemical into the surroundings, concentrations in water, air and soil are influenced by different chemical characteristics such as persistence as well as properties of the environmental component. Persistent chemical substances can last longer in the surrounding environment (Wania and Mackay, 1999; Katsoyiannis and Samara, 2005). There are two aspects to describe such a statement. If POP emissions are more/less uniform over a sufficient period, concentrations will rise to a steady rate, such that the releases are well balanced by their cumulative losses. For several extreme POPs, even decades are long. At steady conditions, the quantities constituted within the surroundings are inversely proportional to the rate constant parameter of total transformation which is, in turn, proportional to overall half-life/ overall residence

time (Choo et al., 2020; Wang et al., 2020a, 2020b). The rate constant parameter of overall transformation in the surrounding part is an aggregate composite of rate constant parameters available for water, air and soil and its weightage been dependent on the relative quantity of chemical component which is dispersed into such media (Bogdal et al., 2013; Wang et al., 2020a, 2020b). After a certain period, if emissions reduce to zero, the number of chemicals present in the ecosystem will deduce exponentially. The sequestration rate is represented by the wholesome transformation kinetic constant present in the environment. During the initial stages, this can be the rate constant under steady conditions. As removal continues, the relative quantities of chemical components in water, air and soil may normally change (Wang et al., 2012; Liu et al., 2017). This variation may be enhanced if transformation rate differences are much great, the slow velocity of intermediate-mass diffusion and determining masses are available in a slower compartment. Consequently, the appropriate transformation constant will also reduce with time. Usually, the period for complete sequestration will be a bit longer than that is evaluated on the basic feature that the overall rate parameter under the initial stages is in steady-state.

#### 4. Occurrence

There are many categories involved in POPs. Among them, the most important are chlorinated/ brominated aromatic compounds such as polychlorinated di-benzo-para-dioxins (PCDDs), poly chlorinated biphenyls (PCBs) and furans, poly-brominated diphenyl ethers (PBDEs) and various organo-halo pesticides (eg. chlordane, toxaphene, DDT and its metabolites) (Hao et al., 2014; Lu et al., 2021). Few are sudden by-products emerging from combustion or during the industrial synthesis of certain chemicals (furans/PCDDs) which are not manufactured deliberately. Most of them have been obtained for industrial purposes (PBDEs, PCBs, chlorinated paraffins) or even as agro-based chemical substances (Lindane, DDT, chlordane). Few components of polar natured POPs are phenols/phenolic compounds and chlorinated phenols. (eg. poly-ethoxylated phenol alkanes which are used as non-ionic surfactants).

##### 4.1. Sources and nature of emission

Fire forms the first and foremost source of POPs which includes natural, unconventional and planned combustion of flora. They are highly recalcitrant in all constituents of the natural environment. The major sources of persistent organic pollutants (POPs) were depicted in Fig. 1.

POPs enter into atmospheric air from several industrial discharges such as power plants, incinerating and other heating stations, landfill transport, volatilization caused by water/soil regions, household furnace equipment and agricultural sprayer consumptions (Bidleman et al., 2012; Vasseghian et al., 2021). Excessive POP sources involve unpremeditated emission occurring through chemical amenities, aggregated combustion pathways that arise from forest fires as well as toxic waste decomposition comprising more PCBs and also incineration consequences. Such category of wastes can develop in various zones and eventual halt through diversified arrangements such as obsolescent oil consumption, destruction of native buildings, fixing/repair of tools, evaporation, cement production, complete burning of faunal wastes, coal combustion, lixiviation action of dumping wastes along with reprocessing actions, therapeutic wastes, municipal waste incineration, industrial plants comprising of chloro alkali, organochlorine pesticides, aluminium secondary process plants, furnace/foundry coke manufacturing processes, hazardous plastic/ other waste available in landfills, sewage sludge accumulation along with fly-ash storage (Ooi et al., 2011; Liu et al., 2016; Cheruiyot et al., 2020).

Various elements, oils, liquefied fuels, soil, fats, ash and sediment in the aquatic ecosystem emanate from the waste effluents through manufacturing processes or POP excessive consumption, by overflowing through fields/roads and also from huge atmospheric deposition (Segui et al., 2013; Tkaczyk et al., 2020). Seas, as well as oceans, act as prevalent reservoirs wherein POPs tend to receive from water sediments via large atmospheric deposition and also occur unintentionally. They are accumulated

in the water sediments on the deep beds of seas, oceans, rivers and larger lakes, in which they are precisely discharged after a particular time and thereafter withdraw into the ambient air (Llado et al., 2021). The toxicity and persistence of these lethal compounds pose a serious threat worldwide. This is due to the continuous application of chemical pesticides, the production of organochlorine and other carcinogenic compounds. The pesticides produced contain chlordane, Aldrin and DDT compounds which are banned by a few countries too (Dinc et al., 2021).

##### 4.2. Transport of POPs

POPs are abundant in water, air, sediments, soils and their exposure to humans with the influence of normal conditions, they may be volatile to some margin. In specific, toxic pollutants of lesser volatility do not exist longer in the ambient environment, but are strongly adsorbed onto the surface of airborne particulates and then reach the ground surface. Anyhow, more evaporative POPs exist in the atmosphere for more than weeks before reaching the earth's crust. This implies that the winds can lift them to more than 1000's kilometers which is far away from their point of emission. In certain events, the POPs concentration present in sediments and water of Arctic/Antarctic may be greater than anywhere (Kosek and Ruman, 2021; Kosek et al., 2019a, 2019b; Ruman et al., 2021). This mechanism finds to be related to the reduction of component volatility at mild temperatures whereas pollutants that volatilize at high-temperature latitudes are transported by moving winds to ice pole regions in which they concentrate and condensate. Universally, such a process is said to be global distillation (Kallenborn et al., 2015).

A new mechanism of environmental transfer was observed recently concerning water diffusion in poly-fluorinated compounds. PFCs containing negative charges such as carboxylates, phosphates and sulfonates are known as anionic perfluorinated acid compounds, which involve the most common per fluoro octanoic acid and fluoro octane-sulfonate. They possess extremely higher aqueous solubility, lower pKa ranges and hence are dissociated at recognized pH values (Ruman et al., 2021). Owing to the lesser vapor pressure of their ions, they may be sarcastically abundant in water or bound to particulates, soils and sediments. There are two principal hypotheses proposed on the global transportation mechanism of PFCs. At first, the volatile and neutral precursor components can undergo atmospheric transport at longer distances and deteriorate in remote sectors (Kosek et al., 2019a, 2019b). The second one predicts that ionic PFCs might be transferred due to oceanic currents directly or else due to sea spray. Among the PFCs, the most studied compounds are PFOA and PFOS, while numerous hundreds can be classified into ionic/neutral.

##### 4.3. Classification of POPs

The POPs are classified into three types. They are intentionally obtained, unintentionally produced and new species. Based on Stockholm Convention associated with (UNEP) United Nations Environmental Programme held in 2001, several legislative policies described by nearly 92 republic nations approved the convention on such POPs to reduce and completely eradicate the release of 12 distinguished POP substances. These are defined as legacy POPs or the dirty dozen POPs (Kosek et al., 2019a, 2019b; Kosek et al., 2018). Despite recognizing certain additional contaminants, the focus is on such 12 unique POPs to have key concerns on them. These constitute 10 pollutants produced unintentionally which are aldrin, chlordane, dieldrin, DDT, mirex, heptachlor, hexachlorobenzene, toxaphene along polychlorinated biphenyl compounds (Kozak et al., 2017). Few more contaminants such as polychlorinated dibenzo-p-dioxins along with furans (PCDD/Fs), several chloro organic pesticides such as DDT, its metabolites such as chlordane, toxaphene, polybrominated diphenyl ethers (PBDEs) and biphenyl components are generated unintentionally. Some are eventual by-products obtained via combustion activities or through industrial manufacture of certain chemicals that were not obtained deliberately. Much of them were produced for industrial usages (chlorinated paraffins, Poly-chlorinated bi-phenyls (PCBs) and PBDEs or



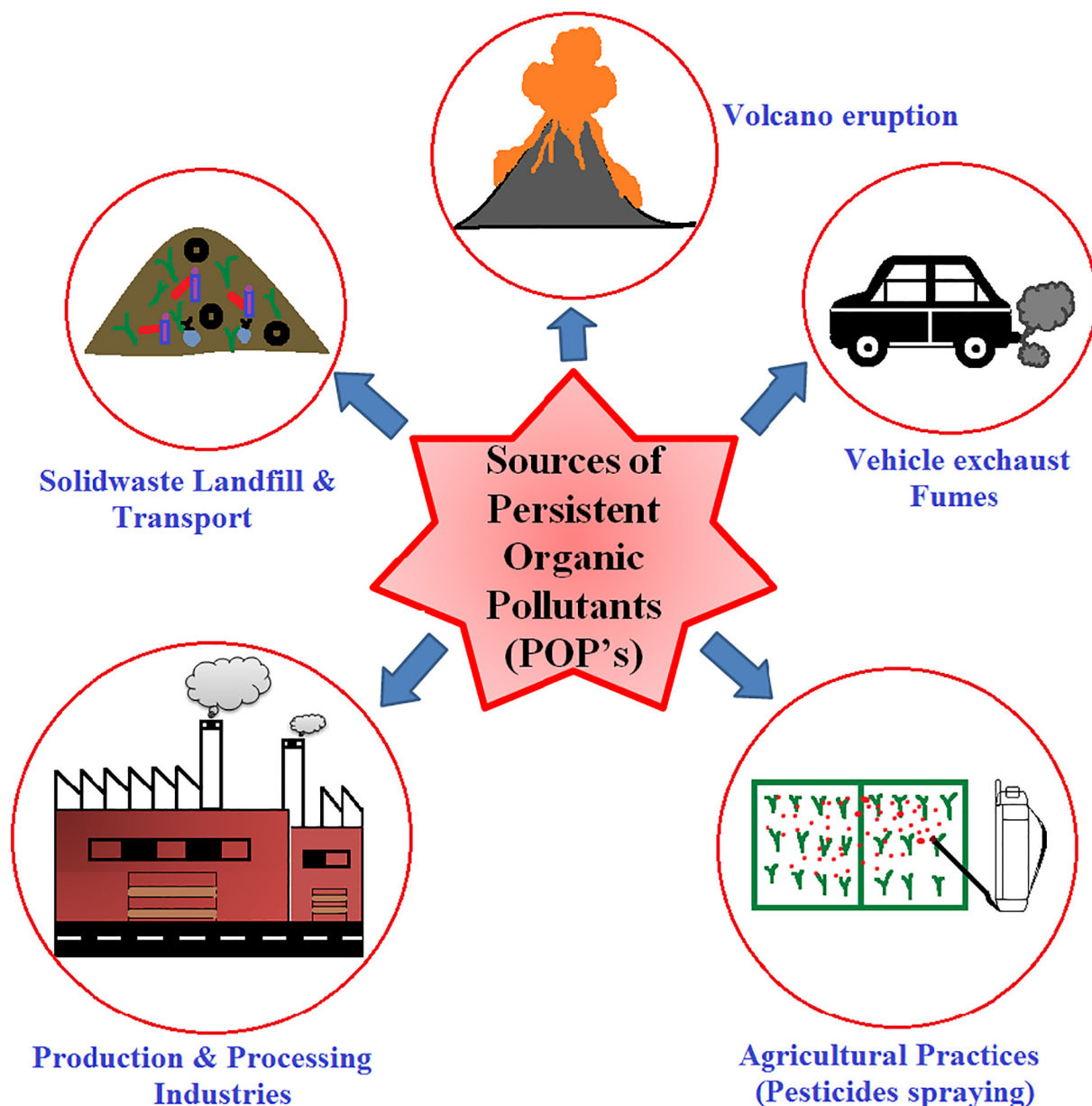


Fig. 1. Major Sources of Persistent organic pollutants (POP's).

via agro-based chemicals (Lindane, DDT, chlordane). A few examples of polar POPs include poly-ethoxylated alkyl and chlorinated phenols (Wania and Mackay, 1996). Even poly-aromatic compounds are recommended as POPs only. Combustion and terrific burning of various organic pollutants tend to emerge these contaminants unintentionally. Perhaps, their abundance is related to human activities, pollution problems in river sources due to PAHs are much more common in denser industrial regions (Kosek et al., 2019a, 2019b). Fig. 2 portrayed different classes and examples of persistent organic pollutants (POPs).

Persistent organic pollutants were widely utilized during the industrial revolution period and most of these compounds were found to be useful in controlling pests and other diseases though they have a severe impact on humans and other living beings in the ecosystem. A wide range of substances that are included in POPs include deliberately produced chemical compounds once utilized in agricultural fields, manufacturing processes, control of diseases and any industrial processes. Those chemicals are produced unintentionally due to the burning of medical waste, smoke releasing industrial processes or incineration (Kosek and Ruman, 2021; Kosek et al., 2018). POPs that are frequently utilized include (i) aldrin: insecticide

utilized for protecting crops against insects and pests (Kosek et al., 2019a, 2019b). This compound is a mutagen as well as a carcinogen. This causes nausea, vomiting, headaches, dizziness, etc. (ii) DDT: a synthetic pesticide and toxic compound that is banned in most countries due to high bioaccumulation in humans and aquatic life forms (Ruman et al., 2021). (iii) chlordane: pesticide used to control termites in the agricultural field and causes damage to digestive system and nerves. (iv) endrin: an insecticidal compound that can bioaccumulate in fat-rich tissues and cause poisoning especially in children. (v) dieldrin: accumulates as it interferes with the food chain (Koziol et al., 2020). It is banned in most countries as it causes damage to the nervous and reproductive system, breast cancer and Parkinson's disease. (vi) mirex: insecticide used for controlling ants and other insects. It can also be transferred from the placenta of the mother to the growing fetus and even through breast milk. It poses long-term effects on living beings and the ecosystem. (vii) hexachlorobenzene: compound used for treating seeds and may cause skin lesions, liver diseases, thyroid damage and results in the death of aquatic organisms (Kosek and Ruman, 2021; Kosek et al., 2019a, 2019b). (viii) polychlorinated biphenyls: mainly used as coolants, pesticides, paints, hydraulic press, etc. This compound was banned in the

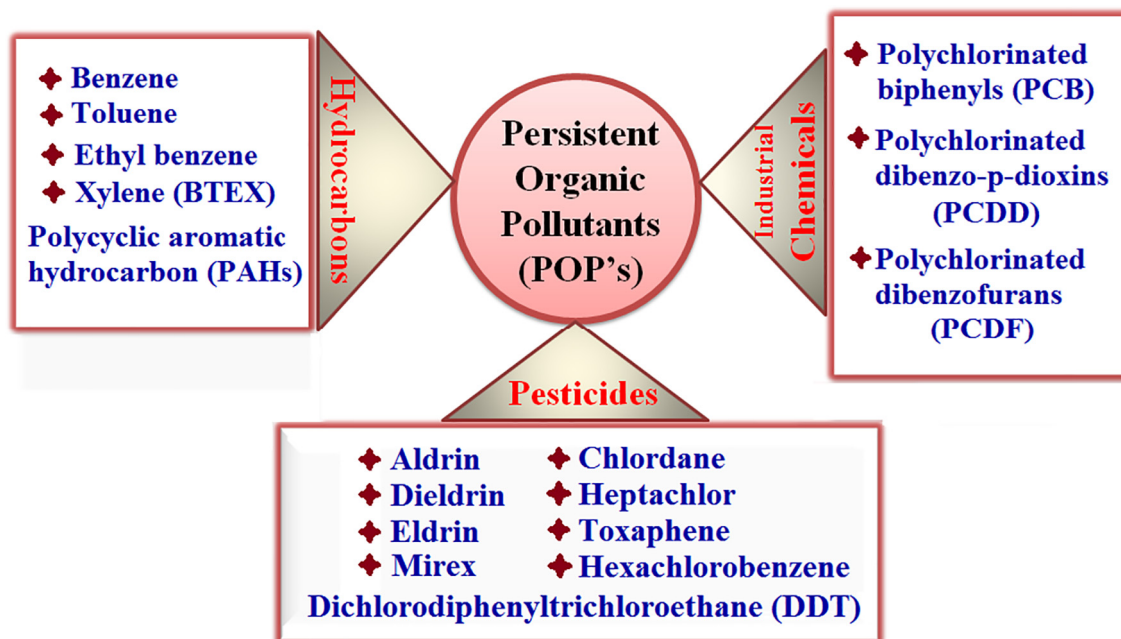


Fig. 2. Classification of persistent organic pollutants (POP's).

year 1970 but still, it exists in the environment due to hyper accumulation and transporting property (Ruman et al., 2021). It causes damage to the stomach, liver, reproductive system, immune system, etc. (ix) taxophene: a highly toxic insecticide that enters the human food chain causing kidney, lung and nervous system damage. (x) polychlorinated dibenzofurans: these compounds are produced due to incomplete combustion at high temperatures. They stay in the ecosystem for a longer period and are considered human carcinogenic compounds.

#### 4.4. Dosage level and toxic nature of POPs

POPs can cause attention owing to their extreme toxicity and are more-over predominant in environmental systems, even at distant geographical localities. The potential impacts of such POPs in the natural ecosystem have triggered more worry in present decades, which has thereby led to the evaluation and sanctioning of these toxic components consumption in various states (Wania and Mackay, 1999). A lump sum of various organic substances pollutes the water sources, which forms as a most important concern that was being provided as great attention on organochlorine pesticide compounds and PCBs. The tremendous growth of such organic components in the water resources in the environment is extremely commendable owing to their extraneous persistence along with maximum resistance to natural degradation (Kozioł et al., 2020).

The public attention towards the toxicity of POPs has been recorded recently since many numbers of such chemical components are recommended as hormone damaging disrupters, which may lead to malfunctioning of reproductive organs/endocrine systems both in humans and animals (Nguyen et al., 2020a, 2020b). Such chemicals expose toxic ill-effects to our environment and any of them possesses beneficial impacts. When these are introduced in the ecosystem, they keep on existing in the same environment for many years creating severe difficulties such as birth defects, learning inefficiencies, carcinogenic diseases, neurological, behavioral, immunological, reproductive and genetic disorders in human systems and wildlife species (Segui et al., 2013).

#### 5. Characterization of POPs

POPs are in general chemically stable. Anyhow, strong consideration must be given to some compounds such as HCB, which is more volatile and hence those sample solutions are probably lost during a few operations

of drying and evaporation. Other than phthalate esters, there exists little chance of possible contamination in a normal experimental situation. Owing to its volatile nature, received samples must be stored under careful conditions and pre-treated in distinct places much distant from the place in which standard samples were made and stored. Environmental analysts have now been indefinitely sensitive and various analytical techniques were prescribed for their disposal (Kosek and Ruman, 2021). To validate this fact, PCDD/Fs are liberated into the ambient environment in traces, their national standard emission in Indian continents is approximately 0.8 Kg  $\Sigma$ TEQ for an annual time. If such components were spread uniformly throughout the Indian continent (volume of 20 m<sup>3</sup>), air concentrations may be of the range of fg/m<sup>3</sup>. Nowadays, the gas chromatography technique merged with mass spectrometry (HRGC-HRMS) under high-resolution methods enables the tracing of few fg available on the column. Similarly, if an air concentration of greater than 500 m<sup>3</sup> is considered, a large group of components can be traced out (Zhang et al., 2015). Sensing at such levels can also lead to issues since such samples can be easily contaminated owing to glassware residues, solvent solutions, or ambient air that comes into contact with that of the solution sample. Modern procedures for detection greatly benefit from the utilization of <sup>13</sup>C along with deuterated analog components of POPs, thereby enabling possible accurate and sensitive methods of quantitation via isotope dilution method and mass spectrometry techniques (Yen et al., 2014).

Owing to the maximized sensitivity of electron acquisition and mass spectrometry detectors, POPs can also be routinely traced in the complete array of the environmental system, even at low concentrations (Xiao and Kondo, 2019a, 2019b). Moreover, they are seemed to be ubiquitous in the complex/modern ecosystem in several regions which are faraway eliminated from sources too. Anyhow, detection limits are to be prioritized with an aspect to concentration emitted along with POP persistence. In another way, tracing does not signify that there exists POPs influence. At first, instrument producers have found prompt ways to merge high pressure liquid chromatographic technique with mass spectrometry, exploring the utilization of highly sensitive analysis of many polar and water-soluble categories of chemicals for further research. The second point is that POPs sampling/analysis is much time consuming and expensive when compared to several other toxicants (Xiang et al., 2022). This has made a focus to huge efforts by few researchers into the development and successful validation of theoretical models to evaluate the residue concentrations, fate and their behavioral nature.

## 6. Risk assessment

### 6.1. Impact of POPs

The adverse relationship between the hazardous action of chemical substances on biota and the distinguished effects demonstrated at various levels of a population parameter is one among the centralized focus of eco-toxicology right now (Kozek et al., 2019). To evaluate the deleterious effects of chemical-based pollution, the prescribed mechanisms involve within a habitat to replace or to enlarge the toxic consequences on its associated members ought to be identified. How does the localized population-level response relies on the several priorities of the different biotic organisms that correspond to toxic stress? Such practical priorities involved in the specific lifetime of a species may be accounted to growth reproduction or survival, which are impacted in various pathways utilizing toxicant exposure. The prominent impacts of POPs on biotic species can be described in two primary actions (Weber et al., 2019). At first, in laboratory premises and monitored exposure levels of biotic species to single matrices, mixtures or congenial extracts and thereafter followed by expressing substance mass/mol fractions in the ambient environments with its adverse impacts on birds, animals, mammals and fish's characteristics population. These two approaches possess various application sectors. Extensive field study/research can combine the detailed understanding of the effect of multi-sized environmental pollution on exposed biotic species but are associated in nature. Both in-vitro and in-vivo laboratory exposures may develop specific responses correlated with toxicant exposure, and thereby estimate their dose-response behavioral relationships (Wang et al., 2012). A biotic organism's responsive action takes into consideration, a sequence of definite events starting from the molecular interaction of a foreign component with an extremely endogenous substance. Such an interactive mechanism starts its impact by assuming a source of a disturbance at molecular ranges. Whenever the biotic species' capacity to counteract becomes overloaded, the impact can even be extended up-to-the cellular regions (Wang et al., 2020a). The excessive pressure at these regions consequences in tissue as well as entire organism disturbance. Moreover, such impact may be transmitted through the whole body of an organism, and simultaneously from the individual organism to the widespread population. Both laboratory and field level research is mandatory for analyzing the hazardous nature of chemical substances (Wang et al., 2020b). To interconnect the above fields, the action of the mechanism of such chemical substances is elaborated and discussed here.

### 6.2. Various mechanisms of hazardous action

Mechanism of action involving the production of oxygen-reactive chemical components. In 2013, the International Cancer Research Agency (IARC) proclaimed the carcinogenic intensity of PCBs. Less chlorinated along with more chlorinated PCBs of non-dioxin (NDLPCB) were involved with inflammatory responsiveness due to chronic conditions. These can influence the formation of inflammatory components, whereas DLPCBs may influence such chemical reactions (Wan et al., 2015). As a whole, less chlorinated PCB components are much metabolized in more reactive electrophilic substances, which may be mutagenic and genotoxic. More chlorinated PCB components are feebly metabolized through the induction of xenobiotic enzymes and can formulate oxygen reactive molecules, lipid peroxidation, alkylating and oxidative DNA components. For such reason, PCBs are categorized as carcinogenic by IARC for human beings.

#### 6.2.1. Interactive action with aryl-hydrocarbon (Ah) receptor

The action of mechanism for chemical species involves the molecular interaction among the various congeners of PCDF/PCDD and 12 dioxins alike action associating PCBs agglomerated to cytosolic receptor component Ah, which is much distributed among the molecular species. When a ligand molecule possesses a planar geometry, it binds to the above-mentioned receptor involved with several affinities producing a complex media that get translocated along with the cell nuclei, in which it strongly binds to

particular DNA patterns and also influences certain variations in gene arrangement (Tkaczyk et al., 2020). Various DNA patterns of such type may be existing in animals, and hence it could impact many gene arrangements. The most hazardous congener involved among the defined compounds is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Hence the toxic potential fractions of other components are represented as TCDD toxicity and represented as Toxicity equivalence parameters/factors (TEFs). In the current trend, the impacts obtained due to such interaction mechanism appears to be much more correlated owing to the impact of 12 dioxin which is similar to action PCBs when compared to PCDFs and PCDDs, since the concentrations of latter components reduced to almost 2 magnitude orders in the past 20 years (Shen et al., 2021). Anyhow, such an action mechanism did not involve unsubstituted polycyclic moieties (PAHs), chlorinated naphthalenes and hexachlorobenzene owing to its weak/moderate affinity towards the Ah-receptor. An important category of synthetic dioxin chemical species was not included from the toxicity equivalent methodology and they are a mixed class of chloro/bromodibenzo-p-dioxins and dibenzofurans. Such components can be more/less intense compared to their chlorinated compounds, anyhow their relevance to toxicity, which is determined based on sample concentrations prescribed in biotic part, it finds to be unpredictable (Sharma et al., 2014).

#### 6.2.2. Peroxisome proliferation

Poly-fluoro chloro compounds (PFCs) are in general, correlated to a hypothesis-based action, which accounts for the induction mechanism of peroxisome proliferators, in specific notable activation mechanism rendered by peroxisome proliferator enhanced receptor, a member species in receptor accompanying nuclear superfamily, impacts the target gene expression accomplished in cell proliferation as well as variation, along with inflammation and immune responses. Yet another action mechanism involves the disruption of lipid metabolism as well as transport in which the abovementioned PFCs can be responsible for peroxisome proliferation (Sharma et al., 2014).

#### 6.2.3. Influence of $Ca^{2+}$ 'adenosine phosphatase enzyme

The action mechanism elicited owing to thinning of DDE shell finds to be accounted with definite inhibition caused by  $Ca^{2+}$  Adenosine Phosphatase enzyme agglomerated in the gland comprising the shell. Such action pathways determined in the lab in-vivo conditions can be accountable for various impacts noticed in the working field which constitutes the reduction in breeding nature of various predator and piscivorous bird species (Segui et al., 2013). Such impacts may be still under extreme concern in developing nations at least since, by the year 2006, the World health organization prompted the usage of DDT to prevent the indefinite spread of Malarial disease (banned in the year 1972).

#### 6.2.4. Endocrine-disrupting action

Certain chemical components either of natural/anthropogenic origin were identified to be endocrine disruptors. They may affect the endocrine glands of various organisms either by direct/indirect mode of interaction (Sanganyado et al., 2021). The components responsible for such action were certain old POPs, which include the DDT along with its derivatives, PCDDs, PCBs, and also PCDFs. Considering the DDT isomer compounds, ortho and Para DDT ranks to be the most effective molecular species containing estrogenic mechanism, whereas a mechanism of anti-estrogenic impact has been recorded for Para-dichloro-diphenyl-dichloro ethylene (DDE). In vitro mechanism involves the affinity shown by chlorinated biphenyl constituent mixtures due to estrogenic action, whereas the in-vivo mechanism of mammals rendered the uterotrophic impact (Sakakibara et al., 2011). In specific, TCDD forms to be an exogenous agonist component for aryl-hydrocarbon receptor species, which, after activation enhances the degradation rate of estrogen receptors, thereby inducing the metabolic action of estradiol enzymes and also provides inhibition to gene expression control carried out by growth factors or estradiol promoters.



### 6.3. Peroxisome impact on mammals

Among the variety of mammals, the available information on the POP exposure rate has been recorded for marine/terrestrial habitats. Certain studies provide a clear demonstration of the influencing action of lipids involved in such a mammalian's vulnerability. The dominant impact ascertained in wild species was the effect of mortality which is exhibited among the migratory species underexposure of DDE. The starvation phenomenon was forced to activate the lipid mobilization for meeting energy demands, which is one among the typical conditions of such migrating species (Wan et al., 2015). Before performing experiments on the environmental species, low DDE residue levels were noticed. After forced exercise, the species died owing to a gradual increment in concentrations of brain DDE. Organo halogen constituents and their related impacts are of serious concern among the polar bears available from hotspot regions. It is being identified that polar bear species may adhere to exposure-related impacts which might have been obtained due to reproductive impairment found in female species, reduced survival of young cubs, or else incremented mortality rate found among reproductive female species. In specific, these impacts could be accounted to the definite exposure of HBCD, PBDEs and PFCs. Different persistent organic pollutants (POPs), sources of exposure, toxicological mechanism and their impacts on human health were summarized in Table 2.

## 7. Microbial degradation of persistent organic pollutants

Microbial degradation involves destruction by bacteria, fungi, algae, actinomycetes and yeasts that require three important elements: an efficient microbe, nutrient for microbial community and foodstuff so-called the bioremediation triangle. The general mechanism of microbial degradation of persistent organic pollutants (POPs) was illustrated in Fig. 3. Microbes intake food even from the polluted environmental conditions by consuming all the contaminants and pollutants as carbon sources and absorbing the nutrients for their growth and development even in such contaminated or harsh conditions (Purnomo et al., 2017; Ito, 2021). The microbes obtain their energy by breaking down the chemical bonds and transferring the electrons that are away from the contaminants. The process through which electron transport takes place is called the oxidation-reduction reaction. Through these reactions, the lethal nature of the contaminants gets changed or reduced. The chemical compound that takes up an electron gets reduced while the pollutant that drops an electron gets oxidized. During these reactions, energy is being released that is utilized by the microbes with the carbon sources for enhancing the microbial community so that contaminant degradation takes place at a faster rate (Wang et al., 2020a, 2020b). The microbes accept electrons using molecular oxygen. Other compounds such as carbon dioxide, nitrate, iron and sulfate also serve as suitable elements for electron acceptors. Microbial remediation can be performed using in situ practices. It is a cheap, reliable technique and involves employing microbes at the site of contamination. It is used for cleaning aquatic systems and soils that are polluted with both organic and inorganic pollutants like heavy metals, hydrocarbons and chemical solvents. An aerating system is provided at the site for stimulating microbes to degrade organic pollutants in unsubmerged regions termed as bioventing or sometimes in submerged soil and water (Kosek and Ruman, 2021). In situ method is highly suitable for controlling polluted ecosystems and increases the chemostatic and catabolic abilities of microbes. Chemostasis raises the bioavailability of contaminants to the microbial community for faster removal and efficient outcomes (Wu et al., 2021). This process involves the removal of polluted water and soil from the region of pollution from where it is taken to another place for increasing contaminant degradation by microbes by supplying adequate nutrients and other growth factors. Bioreactors are used for increasing the rate of breakdown reactions of contaminants into products by the bio-stimulation process. The continuous release and discharge of these POPs from agricultural and industrial sectors into the environmental flora and fauna results in deterioration of the ecosystem (Ritter et al., 1995; Wania and Mackay, 1996). Owing to its toxic

nature and high exposure, POPs are considered to be one of the major contaminants in the environment. Conventional methodologies used for removing and degrading these POPs include chemical reduction, landfilling, stabilization, solidification, incineration and solvent extraction. These conventional techniques are not being applied due to their high cost, maintenance of expensive instruments, manpower and requirement of chemical range, these methods are considered not be effective for complete degradation or removal of POPs. Microbial degradation stands as a better alternative to overcome these drawbacks of conventional techniques (Weber et al., 2011). It serves as an efficient, cost-effective and sustainable method for bioremediation purposes since it involves the utilization of microorganisms such as bacteria, fungi, yeasts, algae, etc. The benefits of microbial degradation techniques are more compared to conventional methods. Microbes possess the capability to make use of metals, pesticides, hydrocarbons, minerals, etc. by transforming them into less toxic forms by modifying their chemical and physical characteristics for their nutrition and growth. The inbuilt resistant mechanism and enzymatic reactions produced by microbes convert the contaminants into less toxic forms (Pariathamby and Kee, 2016). Few enzymes that are produced by microbes reported to be beneficial against pollutant degradation are manganese peroxidase, lignin peroxidase, oxidoreductase, laccase, hydrolases, etc. by catalyzing various reactions such as dechlorination, aromatic compounds, ring cleavage, hydrolysis, the addition of functional groups, etc. The list of microorganisms utilized for various persistent organic pollutants (POPs) degradation and their efficiencies were listed in Table 3.

### 7.1. Bacterial degradation of POPs

Bacteria are widely distributed in the ecosystem and are considered an important agent for bioremediation especially for detoxification and degradation of many organic pollutants like POPs and other xenobiotic substances from polluted regions using both in situ and ex situ methods (Miraji et al., 2021). Bacterial degradation of POPs is a viable detoxification method for the transformation and mineralization of lethal organic contaminants into a less toxic form. This method of using the bacteria community is feasible that utilizes adaptability and flexibility of bacteria to withstand highly polluted conditions and degrade the carcinogenic contaminants. The degradation by bacteria occurs through the aerobic or anaerobic process and breakdown the contaminants into outcomes such as methane, carbon dioxide and biomass. Aerobic degradation is performed using bacteria such as *Escherichia*, *Bacillus*, *Pseudomonas* and *Micrococcus*. These microbes grow and survive in presence of oxygen make use of molecular oxygen as an electron acceptor and convert the toxic pollutants into less toxic carbon dioxide. The anaerobic process is done using anaerobic microbes such as *Methanospirillum*, *Desulfovibrio*, *Desulfotomaculum*, *Methanococcus*, etc. These microbes react with the functional groups present in the pollutants resulting in the removal of electrons and breakdown or degradation of contaminants finally production of inorganic salts and methane occurs. Anaerobic degradation of POPs involves the methanogenic and methanotrophic bacteria as methane gas is produced as a by-product of anaerobic digestion. The methane gas produced is being utilized by methanotrophs for metabolic activities and finally results in the production of carbon dioxide as an end product (Akram et al., 2019). The Methanogenesis process is a condition during which the bacteria utilize oxygen and transform into carbon dioxide. Methane monooxygenase enzyme is produced by methanotrophs that react with methane gas and aids in the degradation of chlorinated hydrocarbons. Nitrifying and denitrifying bacteria, ferric ion reducers and sulphate reducers are also used in anaerobic and aerobic degradation processes.

### 7.2. Degradation of POPs by fungi

Fungi are eukaryotic microbes possessing the ability to grow and survive by utilizing the organic and inorganic substrates present in the surroundings. Fungi can efficiently degrade lignin and cellulose, a long chain of organic pollutants that are not easily degradable. Fungi have gained



**Table 2**

Different persistent organic pollutants (POPs), sources of exposure, toxicological mechanism and their impacts on human health.

S. No.	Persistent organic pollutants (POP's)-References	Sources of exposure		Health impacts	Toxicological mechanism of POPs
		Products	Route		
1	Aldrin (Wania and Mackay, 1996; Kusvuran and Erbatur, 2004) (Fitzgerald and Wikoff, 2014a, 2014b)	Dairy products Animal meat	Oral Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Central Nervous system disorder</li> <li>&gt; Liver damage</li> <li>&gt; Tremors</li> <li>&gt; Gastrointestinal track disorder</li> </ul>	Soil insecticide – Accumulate in living organisms
2	Chlordane (Baghour, 2019)	Meat Egg Milk Fruits Vegetables	Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Gastrointestinal distress</li> <li>&gt; Neurological disorders</li> <li>&gt; Tremors</li> <li>&gt; Convulsion</li> <li>&gt; Damage in Nervous system</li> </ul>	Water contamination - Accumulates in the liver and kidney, altering the action of signaling components and endogenous hormones.
3	Chlordecone (Cheruiyot et al., 2020) (Wania and Mackay, 1996; Crabit et al., 2016)	Fruits Vegetables	Ingestion of contaminated food Dermal	<ul style="list-style-type: none"> <li>&gt; Liver damage</li> <li>&gt; Affects nervous system</li> <li>&gt; Toxic effect on reproductive system</li> </ul>	Water and soil contamination – Rivers, drinking and coastal ecosystem. Accumulates in lipid tissue
4	Dieldrin (Birolli et al., 2015a, 2015b; Koziol et al., 2020; Chinnadurai et al., 2022)	Contaminated foods Fruits Vegetables	Dermal Ingestion	<ul style="list-style-type: none"> <li>&gt; Malaise</li> <li>&gt; Headache</li> <li>&gt; Gastrointestinal track disorder</li> </ul>	Water, Soil and air contamination – Soil insecticide – Bioaccumulates in human through the food chain
5	Dichlorodiphenyltrichloroethane (DDT) (Umulisa et al., 2020; Dinc et al., 2021)	Meat Fish Dairy products	Oral/Ingestion Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Tremors</li> <li>&gt; Seizures</li> <li>&gt; Shakiness</li> <li>&gt; Liver damage</li> <li>&gt; Reproductive diseases</li> <li>&gt; Neurological diseases</li> <li>&gt; Childhood diabetes</li> <li>&gt; Cancer</li> </ul>	Water and soil contamination – Accumulate in food chain because of vapor pressure and less aqueous solubility
6	Endrin (Kosek et al., 2018; Xiao and Kondo, 2019a, 2019b; Cheruiyot et al., 2020)	Fish Grains Vegetables	Oral/Ingestion Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Nervousness</li> <li>&gt; Dizziness</li> <li>&gt; Convulsions</li> <li>&gt; Twitching facial muscles</li> <li>&gt; Jerking of legs and arms</li> </ul>	Soil contamination – Persistent in soil due to its lipophilicity and chemical stability
7	Endosulfan (Fernandes et al., 2019; Sathishkumar et al., 2021)	Fruits Vegetables	Oral Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Tremors</li> <li>&gt; Hyperactivity</li> <li>&gt; Diarrhoea</li> <li>&gt; Rashes</li> <li>&gt; Skin irritation</li> <li>&gt; Delays in sexual maturity</li> <li>&gt; Impaired consciousness</li> <li>&gt; Brain damage</li> </ul>	Water and soil contamination – Persistence in nature due to biomagnification and bioaccumulation in food chain
8	Hexachlorobenzene (HCB) (Wania and Mackay, 1996; Fitzgerald and Wikoff, 2014a, 2014b; Starek-Swiechowicz et al., 2017)	Fatty foods Fish Wildfowl	Oral Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Skin sores</li> <li>&gt; Bone damage</li> <li>&gt; Liver damage</li> <li>&gt; Thyroid</li> <li>&gt; Kidneys damage</li> <li>&gt; Nervous system disorders</li> <li>&gt; Reproductive system damage</li> </ul>	Soil contamination – Slow biodegradation and bioaccumulation in food chain and detected in food, milk, blood, animal feed and adipose tissue.
9	Mirex (Kallenborn et al., 2015; Gagol et al., 2020)	Fish Animal meat Contaminated foods	Inhalation Oral Dermal	<ul style="list-style-type: none"> <li>&gt; Thyroid</li> <li>&gt; Gastrointestinal track disorders</li> <li>&gt; Liver damage</li> <li>&gt; Kidneys damage</li> <li>&gt; Nervous system damage</li> </ul>	Water and soil contamination – Accumulate in food chain, ability to travel long distance
10	Polychlorinated biphenyls (PCBs) (Gaur et al., 2018; Li et al., 2019)	Fish Meat Poultry Dairy products Drinking water	Oral Ingestion Inhalation Dermal	<ul style="list-style-type: none"> <li>&gt; Effects on Immune system</li> <li>&gt; Reproductive system damage</li> <li>&gt; Damage in endocrine system</li> <li>&gt; Nervous system disorders</li> <li>&gt; Brain Cancer</li> <li>&gt; Gastrointestinal track cancer</li> <li>&gt; Breast cancer</li> </ul>	Water and soil contamination – Lipophilic and persistent in nature, accumulate through the food chain, stored in marine reservoir
11	Polychlorinated Dibenzo-p-dioxins (PCDDs) (Fitzgerald and Wikoff, 2014a, 2014b; Gonzalez and Domingo, 2021)	Fish Drinking water	Dermal Oral Inhalation Ingestion	<ul style="list-style-type: none"> <li>&gt; Chloracne</li> <li>&gt; Hyperpigmentation</li> <li>&gt; Weight loss</li> <li>&gt; Liver damage</li> <li>&gt; Affects lipid metabolism</li> <li>&gt; Depression of immune system</li> </ul>	Water contamination – Accumulate in food chain and enters the human body through dietary intake
12	Pentachlorobenzene (PCBz) (Carrizo et al., 2008; Fitzgerald and Wikoff, 2014a, 2014b)	Animal meat Poultry	Oral Inhalation	<ul style="list-style-type: none"> <li>&gt; Liver damage</li> <li>&gt; Neurological disorders</li> <li>&gt; Immunological toxicity</li> </ul>	Water and soil environment – Atmospheric deposition, lipophilic and persistent in nature, accumulates in food chain
13	Toxaphene (Fitzgerald and Wikoff, 2014a, 2014b; Singh et al., 2019)	Fish Sea foods	Oral Inhalation Ingestion	<ul style="list-style-type: none"> <li>&gt; Reversible respiratory toxicity</li> <li>&gt; Liver damage</li> <li>&gt; Kidneys damage</li> <li>&gt; Spleen damage</li> <li>&gt; Affects thyroid glands</li> </ul>	Soil contamination – Environmental exposures, transmitted through ingestion of contaminated foods,

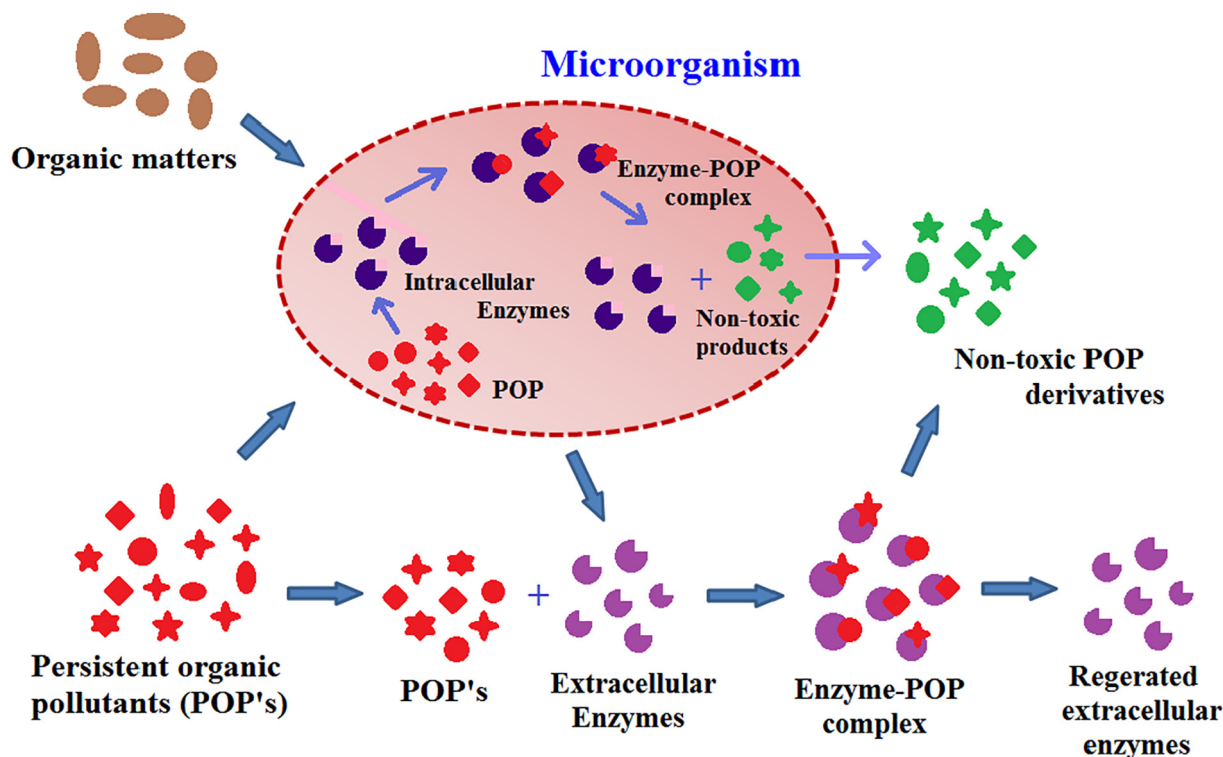


Fig. 3. General mechanism for microbial degradation of persistent organic pollutants.

interest in recent years in the degradation of those long-chain pollutants (Munschy et al., 2020). Fungi also possess the ability to reduce the toxic nature of contaminants such as oils, dyes, petroleum, leather, pesticides, PCBs, etc. Mycoremediation is a process through which fungal species are utilized for the degradation of pollutants. This technology is considered to be the efficient, cheap and eco-friendly approach for the removal and breakdown of pollutants. Specific fungal species such as white rot fungi can be utilized for the degradation of POPs through intracellular and extracellular enzymes such as lipases, versatile peroxidase, laccases, cytochrome P450, etc. These enzymes possess a high oxidative potential and the capability to oxidize huge substances into value-added products (Nantaba et al., 2020). White rot fungi have the efficiency to reduce lignin, PCBs, polysaccharides, etc. through enzymatic transformation into a simpler form. *Phanerochaete chrysosporium* is an example of white-rot fungal species reported to reduce

benzopyrene and fluorine enzymatically (Uhlik et al., 2014; Abdek-Fatah, 2018; Pisa et al., 2020). Other fungal species such as *Trametes Versicolor*, *Aspergillus*, *Pleurotus ostreatus*, etc. have been reported to be effective for remediation of atrazine, starch, imazalil, keratin, pectins and many other compounds through oxidation and reduction processes. The lignocellulosic waste materials are degraded using ligninolytic enzymes. These enzymes are also used for the degradation of toxic pollutants and xenobiotic compounds, dye decolorization and conversion of high molecular weight to low molecular weight compounds.

### 7.3. Algal degradation of POPs

Phycoremediation is a process in which algal species are utilized for degrading POPs such as xenobiotics, pesticides, recalcitrant, heavy metals

**Table 3**  
Different microorganisms employed for various POPs degradation and their efficiencies.

S. No.	Microorganism used		POPs	Biodegradation		References
	Type	Name		Incubation (Day)	Efficiency (%)	
1	Fungi	<i>Phlebia acanthocystis</i>	Endrin	20	80	(Xiao and Kondo, 2019a, 2019b)
2	Fungi	<i>Penicillium miczynskii</i> CBMAI 930	Dieldrin	14	90	(Biolli et al., 2015a, 2015b)
3	Fungi	<i>Pleurotus ostreatus</i>	Dieldrin	14	18	(Purnomo et al., 2017)
4	Bacteria & Fungi	<i>Pseudomonas aeruginosa</i> <i>Pleurotus eryngii</i>	Dichloro-diphenyl-trichloroethane (DDT)	7	82	(Maulianawati et al., 2021)
5	Fungi	<i>Pleurotus ostreatus</i>	Heptachlor & Heptachlor epoxide	14	31	(Purnomo et al., 2013)
6	Bacteria	<i>Pseudonocardia</i> sp. strain KSF27	Aldrin trans-diol Dieldrin	10	99 & 86	(Sakakibara et al., 2011)
7	Bacteria	<i>Pseudomonas</i> sp.	Phenanthrene Pyrene	2.5	100 & 50	(Feng et al., 2014)
8	Bacteria	<i>Stenotrophomonas</i> sp.	Dichloro-diphenyl-trichloroethane (DDT) & Hexachlorobenzene (HCB)	10	26.7 & 34.9	(Lovecka et al., 2015)
9	Bacteria	<i>Bacillus cereus</i>	Dichloro-diphenyl-trichloroethane (DDT) & Hexachlorocyclohexane (HCH)	10	36.6 & 21.3	(Lovecka et al., 2015)
10	Bacteria	<i>Cyanobacterium Anabaena</i> PD-1	Dioxin-like Polychlorinated biphenyls (PCBs)	25	68.4	(Zhang et al., 2015)
11	Bacteria	<i>Cyanobacterium Anabaena</i> PD-1	Aroclor 1254	25	84.4	(Zhang et al., 2015)
12	Bacteria	<i>Terrabacter</i> sp. DBF63	Dioxin (28-DCDF)	7	90	(Habe et al., 2002)
13	Bacteria	<i>Sphingomonas</i> sp. HL7	Dioxin (28-DCDF)	0.3	97.5	(Fukuda et al., 2002)
14	Bacteria	<i>Dehalococcoides</i> sp. CBDB1	(1,2,4-Tetrachlorodibenzo-p-dioxin (TCDD))	84	55	(Bunge et al., 2003)
15	Bacteria	<i>Sphingomonas wittichii</i> RW1	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HCDD)	5	10	(Nam et al., 2006)

and other compounds from soil and wastewater. This method has been gaining importance in recent years owing to its benefits in metabolism, surviving capabilities under stress conditions also. Algae, cyanobacteria and protozoa are widely utilized for the degradation of compounds such as hydrocarbons, pesticides, aromatic compounds, etc. few examples of algal species used for POP degradation include *Dermarestia*, *Fucus*, *Rhodococcus*, *Ascomyllum nodosum*, etc. These species have been analyzed and found effective for bioremediation purposes (Baghour, 2019). The hydrocarbon-degrading enzymes produced by these algae help in the degradation of hydrocarbons. Phycoremediation serves as a better method for detoxification of harmful toxic POPs and transforms them into a less toxic form. The chlorophyll pigments present in algae and cyanobacteria make them best suited for the photosynthetic process. This significant property plays a major role in the degradation of organic contaminants (Chekroun et al., 2014). The degradation mechanism followed by algae for pollutant destruction has three phases. In phase 1, processes such as oxidation, reduction, hydrolysis reactions and addition of functional groups transform xenobiotics or recalcitrant compounds into water-soluble substances. Large polar groups are added to xenobiotic compounds in phase 2 and are followed by phase 3 where the xenobiotics are segregated into vacuoles and cell walls (Oh et al., 2000). Algae also produce a few important enzymes similar to bacteria and fungi that are effective in the degradation of POPs.

#### 7.4. POPs degradation by Actinomycetes

Actinomycetes are gram-positive bacteria having potential in detoxification and degradation of various pollutants such as aromatic compounds, hydrocarbons, etc. It is also efficient against other toxic pesticidal contaminants such as organochlorides, organophosphates and carbamates. Actinomycetes also aid in the degradation of complex polymer compounds and plays important role in the remediation of an aquatic and terrestrial ecosystem by recycling toxic contaminated pollutants (Takagi, 2020). Actinomycetes also produce enzymes for the degradation process such as cellulose and hemicellulose degrading enzymes and peroxidase enzymes (Wang et al., 2010). These enzymes are suitable for lignin solubilization and reduction of polysaccharides into simple sugars. Recently petroleum hydrocarbons are a major source of soil contamination due to their frequent usage in industries and households (Pisa et al., 2020). *Streptomyces flora* was found to be suitable for degradation and biotransformation of chlorinated hydrocarbons. Actinomycetes genus including *Clavibacter*, *Mycobacterium*, *Rhodococcus*, *Streptomyces*, *Arthrobacter*, etc. was found to be suited better for pesticide remediation through the process of co-metabolism (Uhlík et al., 2014). These 9 actinomycetes community utilizes pesticide compounds as substrates for an energy source for their growth and metabolism. Actinomycetes degrade POPs such as aldrin, polychlorinated phenols and DDT and detoxify them aerobically and anaerobically. Cytochrome P450 is an enzyme mainly involved in the degradation mechanism. One example is *Mycobacterium chlorophenolicum* was studied and showed PCP degradation through enzyme action of microbes. It can easily survive and grow even at a high concentration of PCP (Polder et al., 2014). It consumes PCPs as a source of carbon energy for its development. Actinomycetes are considered to be a powerful tool for detoxification and degradation of POPs anyhow more research and advancement technologies are required for enhancing the organism to degrade at a faster rate.

### 8. Advanced POPs treatment technologies

#### 8.1. Hydrodynamic cavitation

Hydrodynamic cavitation (HC) can be generated by flow and pressure variation of liquid which enables the degradation of various toxic organic pollutants including POPs, polycyclic aromatic hydrocarbons (PAHs), etc. HC transpires the liquid to pass through a constriction device such as convergent and divergent nozzle, orifice plate, venturi, etc. that generates numerous cavities, then the produced cavities were allowed to collapse violently and recovered due to the reduction of pressure through forming

strong mechanical waves and high-speed micro jets. The bubble dynamic and chemical reactions in various phases strongly depended on the geometrical and operational parameters of the HC process. The intensity of cavitation depends on the intensity of turbulence and the number of cavities generated during the process. Nuclei generation is the foremost initial step in the hydrodynamic cavitation where initiation of cavitation was taken place that strongly depends on the concentration of dissolved gases and suspended particles in the liquid phase. During hydrodynamic cavitation, different highly reactive free radicals were generated and also several additional radicals were generated through recombination of ions and generation of new radical species or by sifting of free oxidizing revolutionaries in responses with inorganic particles, coming about either in improvement or in crumbling of the corruption productivity of the objective natural foreign substances (Yi et al., 2018; Gagol et al., 2020; Wang et al., 2021). The major advantages of hydrodynamic cavitation processes are; it enhances the chemical reaction, homogenizes the suspended particles in the colloidal liquids and destruction and degradation of POPs.

#### 8.2. Advanced oxidation processes

Advanced oxidation processes (AOPs) are fluid stage oxidation frameworks that create exceptionally reactive hydroxyl (OH) extremists as the transcendent species with high capacities for degradation of POPs. The OH extremists guarantee the viable corruption of dissolvable natural pollutants into simpler biodegradable structures. Reaction time, water turbidity, solution pH, amount of the organic compound vulnerable to degradation and the presence of OH radical scavengers are the major factors that affect the degradation efficiency of OH radicals. The diverse production of reactive hydroxyl radicals is the major individuality of AOPs compared with other conventional approaches. In AOPs, the produced reactive OH radicals non-specifically react with the organic pollutants and hastily oxidize them from the environmental sources. Ozone is the most commonly utilized chemical in AOPs and in some cases, their combinations like  $O_3/H_2O_2$ ,  $O_3/UV$  or  $O_3/Fe_2O_3$  are also used for effective degradation of POPs through AOPs. Though Ozone provides an excellent result in POPs degradation through AOPs, their toxicity, high treatment and maintenance cost are the major disadvantages of the process. Moreover, degradation of POPs using ozone was ineffective when wastewater contains high COD, high BOD, high TOC level and high soluble solids (SS) contents (Bethi et al., 2016; Badmus et al., 2018). The major advantages of AOPs are they completely remove the POPs from wastewater and other environmental sources unlike accumulating and transferring them into another phase as like conventional methods. Other advantages of AOPs are rapid removal rates, no secondary metabolites generation during the treatment, mineralization of organic chemicals, no sludge generation, etc. High capital and maintenance cost is the major disadvantages of AOPs for POPs removal.

#### 8.3. Nano-treatment methods

In recent times, conventional technologies were failed to achieve effective POPs degradation when the POPs concentration in the environmental sources or wastewater was lower (minor dose level). But nanotechnology-based approaches effectively remove those toxic POPs even at their lower concentrations due to the excellent physiochemical properties of the nanomaterials employed for the process. Adsorption and photocatalysis, ozonation and membrane separation are the most commonly utilized efficient methods for POPs removal and degradation at their minor dose levels in the wastewater. Though the nanomaterials have excellent magnetic and physiochemical properties, the selection of suitable nanomaterial is mandatory to achieve the complete removal of POPs from the medium. Moreover, the nano-composites and the combination of nanomaterials with biological agents such as plants and microorganisms result in the complete removal of toxic pollutants like POPs from the environmental source (Karthigadevi et al., 2021). High POPs removal capability, high nanomaterial regeneration capability, high potency of action, high target specificity and selectivity, low toxicity and less accumulation in tissues are the major benefits of

nano-treatment methods for POPs. The major limitation of the nanotechnology-based POPs removal method is difficult to scale up for industrial wastewater treatment.

## 9. Conclusion and future perspective

The contamination caused by POPs is spread worldwide as these compounds are chemically stable, transportable and capable to bioaccumulate in environmental species. Human anthropogenic activities, different pesticides and other chemical production industries are the major causes for the environmental pollution by POPs. Due to the potential bioaccumulation capability, POPs get accumulated on the human adipose tissue and cause harmful effects to them. Therefore, the elimination of POPs from environmental sources is mandatory to reduce their toxic effects on humans, plants and animals. Since, microbial degradation is an effective alternative method for POPs reduction, the effectiveness of the bioremediation was depending on several factors including survival conditions, substrate availability for microbial growth and development and potentiality of microorganisms. Likewise, the identification of new POPs that are deposited on the environmental sources is a difficult task to reduce their toxicity. Therefore, future studies should be focused on the development of effective techniques to identify the new POPs and also to optimize the factors which influence POPs bioremediation. In general, the study related to POP degradation and detoxification is not comprehensive and requires more research to be conducted in this field. After proper identification of degradation techniques, their impacts on living beings and the environment must be studied in detail and analyzed completely before implementing those technologies.

## CRedit authorship contribution statement

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T. Krithiga<sup>b</sup> – Grammar checking  
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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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