Persistent Organic Pollutants- A Silent Threat to the Agro-ecosystem and Surrounding Environment

ABSTRACT

Persistent organic pollutants (POPs) are a class of hazardous, bio-accumulative, biomagnified, and extremely persistent chemicals with plausible extended off-site mobility in the environment or agro-ecosystem. These constitute a wide variety of chemicals, their sources may be either natural or anthropogenic. These are contaminants of emerging concerns for researchers as well as environmentalists. These contaminants are supposed to cause toxicity in terms of their carcinogenic, genotoxic, neurotoxic, and endocrine disruptors nature. Therefore, it is very important to discuss various kinds of POPs present in the environment and their detection methods. Various extraction and analytical techniques have been strategized to determine the POPs in soil and food samples either quantitatively or qualitatively. The literature lacks a comprehensive review over various POPs present in the environment, different techniques of their extraction and analysis, along with their toxicity in agro-ecosystem. The present review is expected to fulfills this gap by considering all the necessary aspects discussed above.

Keywords: Persistent organic pollutants, Agro-ecosystem, Pollutants, Carcinogenic, extraction techniques

1. Introduction

With the rapid urbanization and industrialization, a plethora of environmental contamination issues have been unveiled and have become increasingly serious around the world [1,2]. A variety of pollutants present in the environment and identified by the scientific community are considered highly toxic to living bodies and environment. Some of these are resistant to environmental degradation (physical, biochemical and biological phenomena) and can exist for a very long time [3]. Persistent organic pollutants (POPs) are the pollutants that are existing in our environment for an extended period of time. POPs include polychlorinated biphenyls (PCBs), polychlorinated dioxins and dibenzofurans (PCDFs- as a single entry), organochlorine insecticides, polycyclic aromatic hydrocarbons (PAHs), and many more. These pollutants have been present for a long time and travel from one location to another. They have also been reported in places where they have never been used, like the earth's polar regions [4].

Many reports are available in the literature which justified that POPs can disrupt the endocrine system and are often called as endocrine disruptors. Different hazardous outcomes have been observed such as population declines, reproductive impairment, embryonic deformities, and metabolic and behavioral changes in various species including eagles, alligators, and cormorants during exposure to

POPs. Therefore, there is a big challenge for the scientific community to successfully detect POPs in agro-ecosystem and environmental samples, so that better strategies could be designed to remove them from the environment. Hence, the present review will focus all types of POPs observed till date, their toxicity behaviors, extraction techniques and the methods of their analysis.

2. Persistent organic pollutants

Various pollutants are constantly contaminating the earth's ecosystem and primarily agro-ecosystem. POPs have drawn significant attention over the past several decades. These are mainly featured by their abilities to resist degradation, persist longer and bioaccumulate These molecules travel great distances, withstand degradation, and bioaccumulate. owing to their unique chemical structures and physicochemical properties. Twelve POPs (commonly called the original ‘dirty dozens’ or ‘legacy POPs’) were initially identified during the Stockholm Convention and proposed ban on their usage or source [5]. Later, certain non-chlorinated compounds were also added to the list such as perfluorooctanesulfonate (PFOS), per and poly-fluoroalkyl substances (PFASs), brominated flame retardants (BFRs), and other perfluorinated compounds (PFCs).

3. Classification and types of POPs

There are two main categories of POPs on the basis of the source from which they originate. One is intentionally produced and the other one is unintentionally produced (Fig. 1). Considering the main group of unique 12 POPs include 10 intentionally generated pollutants i.e. aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, and polychlorinated biphenyls (PCBs) and 2 unintentionally generated contaminants- polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [6].

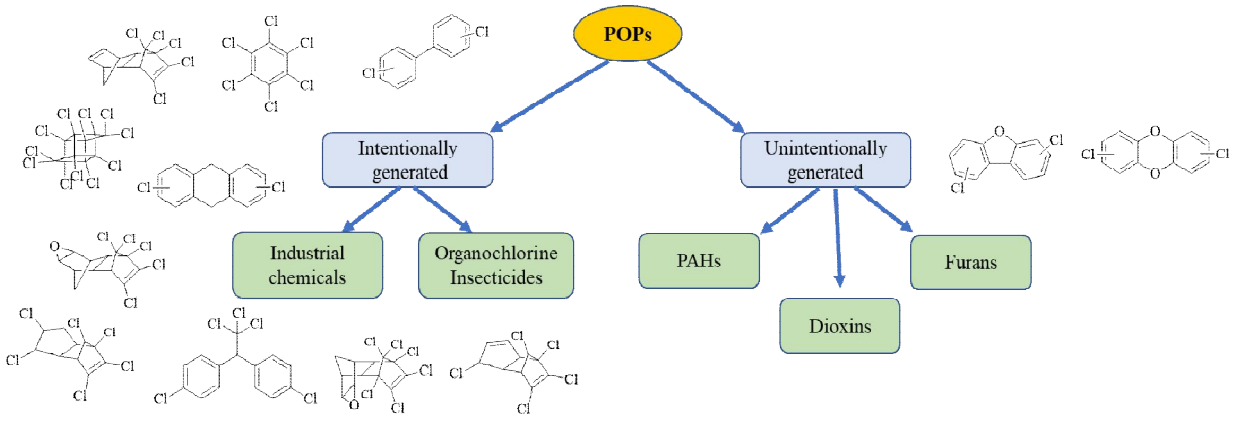


Fig. 1: Types of POPs with examples

3.1. Intentionally generated POPs

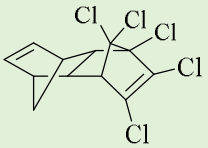
These are mostly chlorinated compounds and have highly lipophilic organic moieties linked with chlorine atoms. These compounds are generally known as organochlorine compounds (OCs) and are produced as a result of different chemical reactions that involve chlorine. For example, dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs). They can be classified into two types that are organochlorine pesticides and industrial chemicals [7].

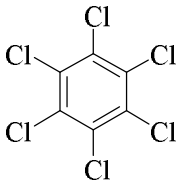
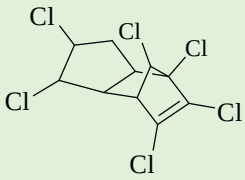
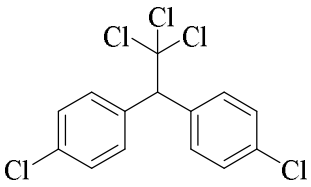
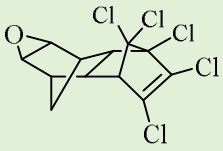
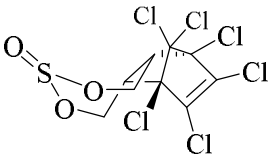
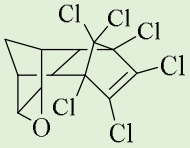
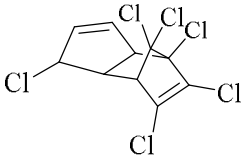
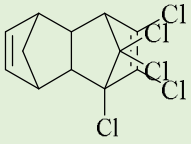
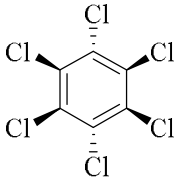
3.1.1. Organochlorine pesticides (OCPs):

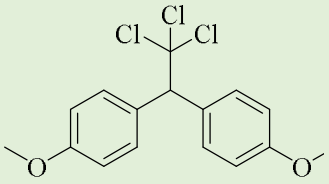
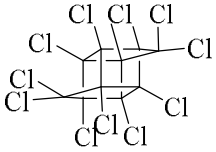
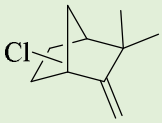
OCPs are a class of substances that are commonly employed as pesticides and due to their prolonged persistence, these are also categorized under POPs. They may be insecticides, fungicides, herbicides, rodenticides, nematicides, and acaricides. For example, aldrin, dieldrin, heptachlor, and endrin. They are mostly man-made synthetic organic compounds but some are natural say for example nicotine. Some OCPs along with their chemical structure, usage, toxicity values and WHO recommendations based on the toxicity values are listed in Table 1. These are considered as the most widely used pesticides in developing countries of Asia [8].

Approximately 80% of pesticides used in agriculture are released into the environment by volatilization, runoff, infiltration, transit down the food chain, and other ways. Therefore, the use of OCPs has been prohibited in many countries for a considerable period, but their residues are still causing a significant impact on the environment and the ecosystems. These may be neurotoxic, genotoxic, and carcinogenic in nature. OCPs when applied in the fields, get strongly adsorbed to the soil particles as these are hydrophobic in nature with very high adsorption coefficients. Their residues can be detected on the surface layers of soil after adsorption without draining into the soil profile, allowing them to survive in the soil for months to years [9].

Table 1: Common OCPs along with their chemical structures, usage, half-life, toxicity values, and recommendations by WHO

Sr No	Chemical Name	Structure	Use	Persistence Half-life	Toxicity in rats (mg/kg)	WHO Recommendation on the basis of LD50
1	Aldrin		Insecticide	High 4–7 years	Oral: 39 to 60 Dermal: 100	Highly hazardous

2	Benzene hexachloride (BHC)		Acaricide Insecticide Rodenticide	High 3 – 6 years	Oral: 10,000	Moderately hazardous
3	Chlordane		Insecticide	Very High 10 years	Oral: 200-700 Dermal: 530–690	Moderately hazardous
4	DDT		Acaricide Insecticide	High 2–15 years	Oral: 113–130 Dermal: 2510	Moderately hazardous
5	Dieldrin		Insecticide	Moderate 9 months	Oral: 46 Dermal: 50–120	Highly hazardous
6	Endosulfan		Insecticide	Moderate 35-150 days	Oral: 18 to 220	Highly hazardous
7	Endrin		Avicide insecticide	Moderate-High 1-12 Years	Oral: 3 Dermal: 15	Highly hazardous
8	Heptachlor		Insecticide	High 2 years	Oral: 40– 220 Dermal: 119–320	Highly – Moderately hazardous
9	Isobenzan		Insecticide	High 2.8 years	Oral: 4.8	Highly hazardous
11	Lindane		Rodenticide Acaricide Insecticide	Moderate 15 months	Oral: 88 – 270	Moderately hazardous

12	Methoxychlor		Insecticide	Moderate < 120 Days	Oral: 5000–6000	Less hazardous
13	Mirex		Insecticide	Very High 10 years	Oral: 600–740	Less hazardous
14	Toxaphene (Camphechlor)		Acaricide Insecticide	Very High 11 Years	Oral: 80–293	Slightly hazardous

Source: Pesticides properties database (PPDB)

3.1.2. Industrial chemicals:

Thousands of chemicals are being produced in the industries and are used worldwide in large quantities for various preparations such as dyes, resins, plasticizers, antioxidants, surfactants, food preservatives, sanitizers, and detergents. As a result, these harmful compounds are releasing in the environment continuously, especially in wastewater discharged from industries or domestic outlets. Till date, these pollutants have been reported in surface water and wastewater. Some of these have been grouped into the priority pollutants as they cause serious health issues to aquatic organisms. Polychlorinated biphenyls (PCBs) and per and poly-fluoroalkyl substances (PFASs) are the most important types of industrial chemicals found extensively in the agro-ecosystem and causing health hazards.

3.1.2.1. Polychlorinated biphenyls (PCBs)

PCBs have been discovered in water, sediments, avian tissue, and fish tissue all across the world. These substances are classified as special wastes because they include 2-10 chlorine atoms linked to the biphenyl molecule. This class also includes monochlorinated biphenyls (biphenyl molecules with one chlorine atom added). The basic chemical skeleton of chlorinated biphenyls and some commonly found PCBs are shown in Table 2. PCBs were having numerous industrial applications and were used extensively around 1960-80 as insulating condensers, heat exchangers, plasticizers, flame retardants, fire-resistant transformers, papers, asbestos, etc. Their remains are still present at industrial sites and have been found in building doors and windows, as well as in paints used in swimming pools and garages [10]. It is believed that over 200 commercial PCB-containing products are now accessible on the market.

Table 2: Some previously reported PCBs along with their chemical structures

PCB 10 [a]	PCB 11 [b]	PCB 24 [a]
PCB 30 [a]	PCB 62 [a]	PCB 65 [a]
PCB 77 [b]	PCB 95 [b]	PCB 116 [a]
PCB 118 [b]	PCB 126 [b]	PCB 153 [b]

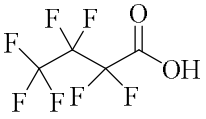
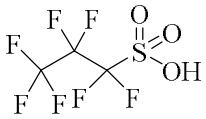
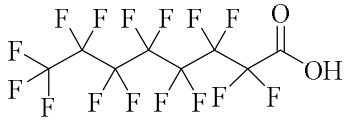
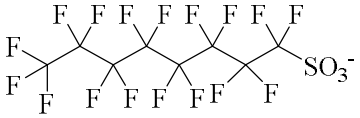
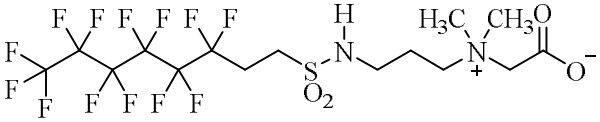
a[11], b[12]

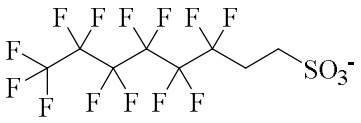
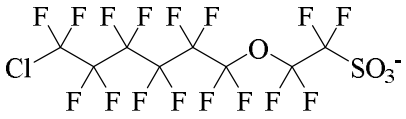
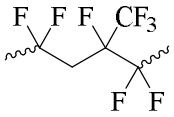
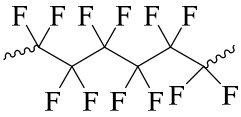
3.1.2.2. Per and poly-fluoroalkyl substances

For more than 50 years, PFASs have been produced and are widely present in the environment. These are non-stick, non-wetting, non-toxic, fire-resistant, and heat resistant. As a result, they have been used in nearly every aspect of labor, from cookware to firefighting foams, paper coatings, and textiles, and so on [13]. These are organofluoride compounds made up of oligomers and polymers in which the hydrogen atoms in the hydrocarbon skeleton have been replaced by fluorine atoms. Per fluorinated sulfonic acids (PFSAs), perfluoro carboxylic acids (PFCAs), high-molecular-weight fluoropolymers, and low-molecular-weight perfluoro alkanolamines are the four categories. Out of these, PFSAs and PFOA, have received the most attention. The most commonly discovered PFASs are mentioned in Table 3. They are both hydrophobic and lipophobic in nature, and they contain a CF bond, which is one of the strongest chemical connections and provides these molecules with extremely high chemical and thermal stability. Due to these reasons, they are resistant to the typical environmental degradation processes like photolysis, hydrolysis, and atmospheric photooxidation, thereby persisting and bioaccumulating in the environment

for years [14]. The National Toxicology Program has also conducted research on PFOA, other PFCAs and PFSAs in order to better understand their toxicity and persistence in human blood [15]. PFOA-contaminated water has been shown to have a negative impact on mammary gland development in mice [16]. Another study found that PFOS exposure can influence the nervous and endocrine system in rats; however, their mechanisms are yet to be established [17].

Table 3: Different types of well-known PFASs, their chemical structures, and sources.

Sr No.	Molecular Structure	Sources	References
1	 Perfluorobutanoic Acid (PFBA)	Stain repellants, food packaging carpets	[18]
2	 Perfluorobutane sulfonic Acid (PFBS)	Fire retardant foams, metal coating, mist suppressant	[19]
3	 Perfluorooctanoic acid (PFOA)	Fire retardant foams, ceramic glaze	[20]
4	 Perfluorooctanesulfonic acid (PFOS)	Water purification, non-stick utensils, textile industry	[21]
5	 6:2 Fluorotelomer sulfonamide alkyl betaine (FTAB)	Cleansing products, metal coating, textile industries	[22]

6	 6:2 Fluorotelomer sulfonate (FTSA)	Chemically resilient components, rug coverings	[23]
7	 Chlorinated polyfluorinated ether sulfonate (F53-B)	General waterproofing lubricants, gaskets power-utility stoppers	[24]
8	 Viton A/B	Fire retardant foams, metal coating, mist suppressant	[25], [26]
9	 Polytetrafluoroethylene (PTFE)	Fire retardant foams, metal coating	[27]

3.2. Unintentionally produced POPs

These are mostly undesired by-products of combustion or other chemical reactions that take place in the presence of chlorine or chlorinated substances. Polycyclic aromatic hydrocarbons (PAHs), dioxins, and furans are the three primary categories.

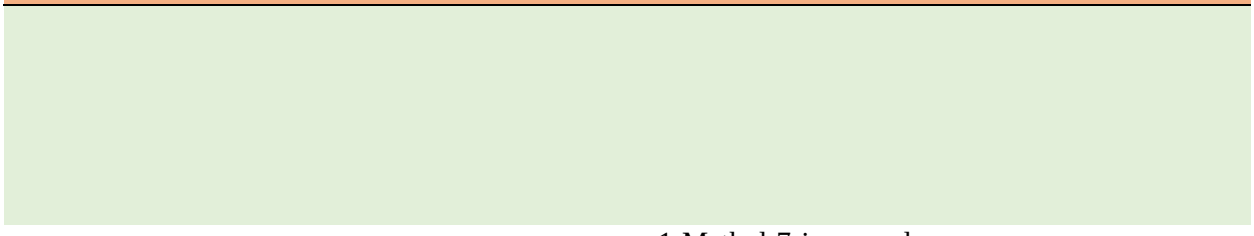
3.2.1. Polycyclic aromatic hydrocarbons (PAHs)

Both natural and anthropogenic sources release PAHs into the environment [28]. The phenomena including incomplete burning of fuels, garbage, some organic substances such as tobacco and plant material, forest fires, and volcanic eruptions lead to the exposure of PAHs to the environment. This is a large class of chemical compounds that include two or more fused aromatic rings, ranging from two-ring naphthalene and its derivatives to complex structures with up to 10 rings. PAHs with up to six rings are known as ‘small’ PAHs, while those having more than six aromatic rings are called ‘large’ PAHs [29]. Some of the PAHs are posing a serious threat to human health as these can be carcinogens, mutagens, and teratogens as well. Because of their physicochemical properties, PAHs are highly mobile in the

146 environment, allowing them to spread through air, soil, and water bodies, where their presence is
147 ubiquitous. Some of the commonly found PAHs and their chemical structures are shown in Table 4.

148 **Table 4: Pyrogenic and petrogenic PAHs reported in the literature**

149

Pyrogenic PAHs			
Naphthalene	Acenaphthylene	Acenaphthene	Fluorene
Anthracene	Phenanthrene	Fluoranthene	Pyrene
Chrysene	Benz[a]anthracene	Benzo[b]fluoranthene	Benzo[k]fluoranthene
Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene	Benzo[g,h,i]perylene	Dibenz[a,h]anthracene
Pyrogenic PAHs			
			
1-Methylphenanthrene	9-Ethylphenanthrene	1-Methyl-7-isopropyl phenanthrene	5-Methylchrysene

150

6-Ethylchrysene	Acenaphthenequinone	1,4-Anthraquinone	9,10-Phenanthrenequinone

The US Environmental Protection Agency (US EPA) has designated 16 PAHs as priority pollutants. Benzo[a]pyrene is a well-known human carcinogen among these key PAHs and is frequently employed as an indication of PAH exposure [30]. Furthermore, these are categorized based on their origins as pyrogenic PAHs, which are produced as a result of fossil fuel combustion, and petrogenic PAHs, which are peculiar to crude oil and polluting water following an oil spill [31]. Petrogenic PAHs differ from pyrogenic PAHs in that they are either heavily alkylated or oxygenated to produce PAH quinones.

3.2.2. Dioxins and dibenzofurans

Chlorinated dibenzofurans (furans) and chlorinated dibenzo-p-dioxins (dioxins) have similar chemical properties and toxic effects, thereby being a major concern for decades. 2,3,7,8-TCDD; 2,3,7,8-TCDF and PCB-126 are examples of these kinds of substances. Nowadays, there has been a new group called dioxin-like PCBs (DLPCBs) which includes a specific subgroup of PCBs. Polychlorinated dioxins (PCDDs) and dibenzofurans (PCDFs) are released from anthropogenic sources and activities rather than natural processes [32]. These have been reported to be carcinogenic, as well as have been found to put adverse impacts on the reproductive system, immune system, and other human health risks. Treatment of PCDDs and PCDFs includes the low-temperature thermal degradation facility which has resulted in the efficient decomposition of these toxic substances from the municipal solid waste incineration fly ash [33]. Recently, significant reductions have been reported in the atmospheric levels of PCDDs and PCDFs which might be because of some technical improvisations like waste incinerators, smelters, cement kiln plants, modifications of motor vehicles and also substituting coal/diesel in domestic heating with the natural gas controls [34]. Further, some air control pollution devices were helpful in the significant removal of PCDD/Fs from hazardous waste disposals with 93.1% removal efficiency, consequently resulting in high sulfur content in the hazardous waste [35].

Furthermore, their structural analogs in which bromine substitutes all of the chlorine atoms i.e. polybrominated dioxins and dibenzofurans (PBDD/Fs) have similar physicochemical properties but their half-lives are reported to be longer than that of the chlorinated ones [36]. It has been found that the thermal discharge of waste electronic items releases PBDDs and PBDFs up to 50–500 times in comparison to that of PCDD/Fs [39] (Wu et al., 2020). Soils in e-waste burning areas have been found to

be rich in PBDFs (88% of the total contaminants) which showed a major concern for the environment[38,39].

4. Extraction methods of POPs in the environmental samples

Extraction of POPs from solid environmental samples has frequently been done using various organic solvents with or without addition of heat. The basic extraction techniques are liquid/liquid extraction and soxhlet extraction. A number of extraction techniques along with the analytical methods used for various POPs have been summarized in Table 5. Different methods have different recoveries depending on the type of analyte and the sample type. For instance, some reports have suggested that sediments and soils be freeze-dried [40]; while others have reported lower recoveries of PCBs from freeze-dried sediments [41].

4.1. Soxhlet extraction

This method involves extractors in which a high amount of sample is mixed with the organic solvents and extracts the component without filtering. The major limitations of this method were large amounts of solvents (about 500 mL), and high extraction time (up to 2 days). Hence, some amendments have been made to the traditional soxhlet extraction like automated, focused microwave-assisted, and high-pressure soxhlet extraction. For example, the analysis of PCBs in fish and sediment samples achieved the best recoveries [42,43]. From sediment samples of the baltic sea, PCBs were extracted using accelerated solvent extraction (ASE) with solvent and toluene for soxhlet extraction [44]. Furthermore, 58 POPs including PAHs, OCPs, PCBs were detected in different atmospheric samples using Soxhlet extraction with 1:1 acetone: n-hexane for isolation purposes and solid phase extraction (SPE) cartridges. The average recoveries obtained were 67-114% for three different kinds of POPs [45]. Similarly, a modified soxhlet extraction was adopted for the detection of 8 different classes of POPs including PCDD/Fs, PBDEs, PBDD/Fs, PCBs, OCPs, polychlorinated naphthalenes (PCNs), short-chain chlorinated paraffins (SCCPs) and Dechlorane Plus (DP) in sediment and fish samples with 45 to 120% average recoveries.

4.2. Liquid-liquid extraction

Liquid-liquid extraction (LLE) was found to be very tedious and labor intensive, hence solid-phase extraction (SPE) was its possible replacement. It offers less solvent exposure, quick processing, and easy handling as compared to the LLE [46,47]. Solid-phase extraction was used for the extraction of POPs from water and wastewater samples, even with high loadings of analytes which resulted in the reduction of the solvent usage and the analysis time [48]. OCPs and PCBs were successfully extracted from human serum samples with this method by using n-hexane-DCM mixture with recoveries of 99 to 120% for PCBs and 88 to 115% for OCPs [49]. Recently, 18 different POPs (mostly OCPs and PCBs) were extracted from the marine trout samples using LLE with average recoveries ranging between 73-112%

[50]. Meanwhile, several POPs were extracted from the soil leachate samples using LLE method [51] Some unique samples require solid phase microextraction (SPME) techniques and headspace sampling.

4.3. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is another efficient method for removing PCBs from the soil, sediments, and other solid samples. The primary determinants of recovery rates in this approach are optimizing temperature, pressure, and flow rate. For example, PCBs were removed from sediment samples using this process at 200°C and 150-650 atm pressure with a 95% recovery rate [52]. PCBs were extracted from fatty acid samples using this approach with a basic alumina combination as an alternative to silica/silver nitrate (1:10, w/w) [53]. But poor repeatability is the major drawback of this method which has not been improved yet.

4.4 Passive sampling

This is also an effective method for assessing water samples utilizing semi-permeable membrane devices (SPMDs). SPMD sampling is a type of passive sampling for water, air, or sediments. Some other passive sampling techniques have been recently reviewed in the literature which is mainly based on the free flow of analytes from the sampling medium to the collecting medium [54]. Furthermore, some samples necessitate cleanup processes, which include the removal of co-extracted lipids from such samples prior to analysis. This will be determined primarily by the type of analyte. Because PCBs are highly stable in acidic conditions, it will be an effective strategy to conduct out PCB cleanup processes employing sulfuric acid or acid-impregnated silica columns for the elimination of lipids. Following that, sulfur must be removed from the samples in order to reduce co-extractive interferences and lengthen the detector's lifetime. Sulfur can thus be eliminated by introducing copper granules during the extraction process [55].

4.5. Solid-phase extraction and microextraction

The solid-phase microextraction method is an effective sample preparation technique for integrating several operations such as sample collection, extraction, analyte enrichment, and isolation from sample matrices, and has been used to extract analytes from gaseous, liquid, and solid samples [56]. A novel SPME was developed for estimations of various POPs (BTEX, PAHs, and PCBs) in which SPME fibers were used that were almost 180 times more sensitive than commercial fibers [57]. SPME was employed for the determination of PCBs from water samples with detection limits of 0.08-0.89 ng/L in treated sewage samples [58]. Dispersive micro-solid phase extraction (D-μ-SPE), in which the solid extracting phase is suspended in the liquid sample has been found to be more advantageous over the conventional SPE in terms of operational simplicity, speed, recovery, and handling of large sample volumes [59, 60].

5. Analytical techniques for POPs

Different types of chromatographic techniques have been employed for POPs analysis, such as gas chromatography (GC), ultra-high-performance liquid chromatography/or ultraperformance liquid chromatography (UHPLC/UPLC), high-performance liquid chromatography (HPLC), liquid chromatography (LC), and capillary liquid chromatography (CLC). A number of analytical methods used for the detection and quantification of various POPs have been summarized in this study.

The traditional HPLC is regularly used for the analysis of ionic PFAS, specially PFCA and PFSA, whereas GC is used for the analysis of volatile and semi-volatile PFAS. Particles collected on C18 extraction disks can be extracted quantitatively without Soxhlet or PLE extraction. PFAS have been extracted from sediments collected from different lakes by sonicating them in methanol (recoveries: 88-102%) and analyzed by UPLC/ESI-MS/MS and obtained the total concentrations ranging from 0.61 ppb to 26 ppb [61]. LC-MS/MS method was also developed for the analysis of hydroxylated PCBs with a LOD value of 0.1 ng/mL after applying suitable cleanup to them [62, 63,64]. In addition to this, liquid chromatography (LC) with tandem mass spectrometry (MS/MS) or high-resolution mass analyzer (HRMS) like time of flight (TOF) or Orbitrap have been used mostly for the analysis of POPs in food samples [65].

One of the most important analytical methods for the analysis of POPs is gas chromatography (GC). Pressure or temperature-programmed injection techniques, combined with increased injection volume, have been proven to be quite effective without having any detrimental effects [66]. The boiling temperatures of the compounds and their interactions with the stationary phase of the column determine the efficiency of GC-based separation. Most POPs are semi-volatile, with polarities ranging from mild to non-polar, hence well adapted to GC-MS measurement because of their physicochemical features, with the exception of PFAS-related compounds, which are always tested using the LC-MS/MS technique [67]. In the case of OCPs, it has been reported that both GC-MS and LC-MS based methods gave significantly similar results except for dichlorodiphenyltrichloroethane (DDT) and its metabolites, where GC-MS/MS was found to give better results than LC-MS/MS [68]. Detection of PCBs and PBDEs in serum samples of livestock in the US, the higher concentration of PCBs and PBDEs were detected in the livestock's serum, but their origin is still unclear [69]. GC-MS-based methods have been used to confirm the presence of PCBs in the transformer oils and detected in air samples too [70]. Several GC-ECD methods have also been reported for the analysis of PCBs from sediments, serum, fish tissue, and indoor air samples in addition to the GC-MS methods [71]. In addition to this, recently atmospheric pressure chemical ionization associated with GC-MS as an ionization source has detected a large number of molecular ions which provided a wide scope of screening. GC-APCI-MS methods are found to be highly sensitive and selective for the analysis of various POPs in environmental as well as biological samples at trace levels with LOD values around 10 to 100 times lower than other traditional GC-MS methods [72].

Recently, PBDEs, PCBs, PCDD/Fs, PBDD/Fs, furans, and other THs (total L-thyroxine (TT4), total 3,3′,5-triiodo-L-thyronine (TT3), and total 3,3′,5′-triiodo-L-thyronine (TrT3) has been detected and determined in human breast milk using GC-high resolution mass spectrometer (GC-HRMS) with three different columns [73].

Recently, a new rapid on-site detection approach has been developed which was highly sensitive with LOD values in parts-per-trillion levels i.e. less than 5.25 ng/L in aquatic samples with approximately 30 minutes of total analysis time without the use of vials. This approach was developed by coupling a portable GC-MS with an on-site pre-equilibrium solid phase microextraction (SPME) sampling method and has been recently used for the detection of three kinds of POPs i.e. PCBs, OCPs, and PAHs) [74]

Table 5: Determination of POPs in different sample matrices using various extraction methods and analytical techniques

Sr No.	Analytes	Matrix	Extraction Method	Analytical Techniques	LOD values	References
1	PCBs	Urine	SPE	LC/MS/MS	0.01 ng/mL	[75]
2	PCBs	Plasma	SPE	LC/MS/MS	0.01 ng/mL	[76]
3	EPPs, PCBs	Sediment	LLE	LC/MS/MS	0.01-0.4 ng/g	[77]
4	PCBs	Water	LLE	RP-HPLC	0.25 mg/mL	[78]
5	PCBs	Mammals	LLE	RP-HPLC	2.5 mg/kg	[79]
6	PCBs, PCDFs	Fish	LLE	RP-HPLC	2-100 ng/g	[80]
7	PCBs	Herring oil	LLE	RP-HPLC	9-50 ng/g	[81]
9	PFBS, PFOS	Ground, river, and tap water	SPE	LC/(-)ESI-MS/MS	25,000 ng/L (LOQ)	[82]
10	PFOA, PFOS	Surface water	SPE	LC/(-)ESI-MS	0.2–13 ng/L	[83]

					(LOQ)	
11	PFOS, PFOA, PFNA, PFDA,	Rain water	SPE	LC/(-)ESI-MS	0.04–7.2 ng/L	[84]
12	HCB, HCH, PCBs, OCPs	Fish	SE, LLE	GC/ECD, HRGC/ECD	-	[85]
13	PBDEs, PCBs, OCPs	Dolphin	GPC	GC/MS	-	[86]
14	OCPs, PCBs, toxaphene	Bird	LLE, SE	GC/ECD, GC-ECNI-MS	-	[87],[88]
15	PCDD/F, HCB	Air	Swipe/biofilms, passive sample	HRGC/HRMS	-	[89]
16	PCBs, HCH, OCPs, HCB, DDT	Human	LLE, SPE, SE, LSE, hot SE	SPE-HPLC	-	[90]

6. Toxicity behavior of POPs

The ecotoxicological effects of POPs on the environment, biota, and human health have raised a big concern in the past few years which has led to their minimal usage or complete ban in many countries. These are resistant to almost all biodegradation processes, hence are highly persistent and toxic. It has been recently addressed that in children, POPs can cause cancer and tumors in many places, immune system illnesses, reproductive issues, decreased ability to fight disease, slowed growth, and irreversible cognitive function damage. As a result, POPs are a suspected carcinogen [91].

Considering the contamination of the aquatic environment, PCBs and OCPs have emerged as the most toxic among the wide range of POPs. Moderate to high exposure to PCBs (0.25-2 mg/L) has induced abnormalities in developing zebrafish retinas, resulting in visual impairment [92]. PCB 126 exposure has also resulted in heart malformations in the embryos of *Danio rerio* [93]. Many species of *Daphnia* are used as models or indicator organisms for the toxicity determination of PCBs mainly in freshwater [70]. PFASs have also been found to be toxic to the soil, wastewater, animals, and humans [94,95,96,97] .

Certain PAHs, when exposed to animals through food for a prolonged time were found to cause stomach cancer from ingestion, lung cancer from inhalation, and skin cancer from skin contact. For instance, benzo[a]pyrene, benzo[a]anthracene, and chrysene were responsible for significant chromosome aberrations in rodents [86]. Among PAHs, the most common PAH to cause cancer in animals and was the first chemical carcinogen to be discovered is Benzo(a)pyrene [98].

7. Conclusions and way forward

The present compilation of various POPs and their toxicities concludes that new candidate POPs are adding to the list day by day. The 'dirty dozens' are no more dozen in number. Thus, novel research must be focused in developing new analytical approaches for trace estimation of POPs. Moreover, their highly toxic nature clearly indicates that they should be excluded from the environment as soon as possible. Various removal strategies have been proposed for this purpose such as photocatalysis, bio nanocomposites, MOF-based adsorbents or other porous absorbents etc. More work should be done for the development of environmentally benign moieties for the adsorptive removal of these POPs for the well-being of the ecosystem. Future research must also focus on estimation of toxicity/health hazards of POPs to various non-target organisms and associated environment or agro-ecosystem.

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