Review

Polychlorinated biphenyls (PCBs) in the environment: Recent updates on sampling, pretreatment, cleanup technologies and their analysis

A. Vijaya Bhaskar Reddy[a], M. Moniruzzaman[a,b], Tejraj M. Aminabhavi[c,*]

[a] Centre of Research in Ionic Liquids, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
[b] Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
[c] Soniya College of Pharmacy, Dharwad 580 002, Karnataka, India

HIGHLIGHTS

- Extensively discussed the fate and transport of PCBs in the environment.
- Reported on cutting edge analytical techniques for the sampling and analysis of PCBs.
- The analytical challenges and future recommendations proposed for PCBs assessment.
- Could be a complete guide for the analysis of PCBs from any contaminated source.

GRAPHICAL ABSTRACT
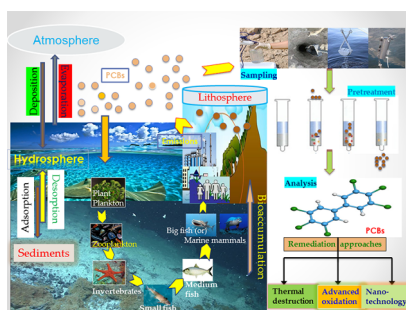
ARTICLE INFO

ABSTRACT

Polychlorinated biphenyls (PCBs) are a class of synthetic organic compounds containing carbon, hydrogen and chlorine atoms. They have been used in various industrial and commercial applications owing to their high boiling points, non-flammability, chemical stability and insulating properties. Also, PCBs are exceptionally stable and prevail in the environment for a very long time. Consequently, they may not just affect the individual organisms, but ultimately the entire ecosystems. The present review describes the sources, fate and transport of PCBs in the environment followed by their accumulation in humans, animals, plants and biota. We provide the description of current knowledge on sampling, pretreatment and cleanup procedures for the best extraction of PCBs from various contaminated sites. Further, the futuristic analytical strategies established for the determination of PCBs and adequate remedial methods are discussed in detail. Also, the analytical challenges and recommendations for future research regarding the PCBs assessment in the environment are summarized. Overall, this review presents comprehensive knowledge on cutting edge technologies available in the field of PCBs analysis.

1. Background and scope of the review

Polychlorinated biphenyls (PCBs) are the synthetic organic compounds produced from biphenyls by the replacement of hydrogens with chlorine atoms. Each PCB homologue contains exact number of isomers viz., monochloro (3), dichloro (12), trichloro (24), tetrachloro (42), pentachloro (46), hexachloro (42), heptachloro (24), octachloro (12), nonachloro (3) and decachlorobiphenyl (1). The number and position of chlorine atoms on phenyl rings differentiate the PCB congeners, and there are total 209 PCB congeners. Among all, 12 PCB congeners

consisting four or above four chlorine atoms with one or no substitution at the *ortho* position are thought to exhibit dioxin-like (DL) toxicity and they are termed as "DL PCBs" [1,2]. Owing to their chemical stability, insulating properties and non-flammability, PCBs have been utilized in various commercial and chemical industries for the wide range of applications such as in heat transfer, rubber and plastic products, hydraulic machines, dyes, pigments and carbonless copy paper [3,4]. The estimated overall global production of PCBs is 1.5 million metric tons, and approximately 10% of which are remaining in the environment as of today [5]. The authorities have raised the detrimental effects of PCBs on the environment including their toxicity, persistency and bioaccumulation. As a result, their production was aborted all over the world from late 1970s to early 1980s.

In the past, a wide number of commercial PCB products have been produced under the commercial names viz., aroclor (USA), chlophen (Germany), kanechlor (Japan) and fenclor (Italy) [6]. Especially in the past few decades, a great attention has been focused to examine the toxicity of PCBs that have shown similar toxicity as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs). Also, some PCBs including PCB-77, PCB-126 and PCB-169 exhibit remarkably high DL toxicity due to the absence of chlorine substituents at the *ortho* position [7]. The toxicity of DL PCB congeners is nearly comparable to the most toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Therefore, the toxic equivalency factor (TEF) of 2,3,7,8-TCDD is described as 1.0, and TEF values of other dioxins and PCB congeners can be calculated with reference to the 2378-TCDD value. These TEF values shall be updated regularly considering the most recent data available from toxicological studies [8]. The TEF values of several PCB analogues recently issued by World Health Organization are presented in Table 1.

Due to their excessive chemical stability and wide range of applications, PCBs are persistent both in biotic and abiotic environments [9]. The distinct physico-chemical properties of PCBs have certified them as indispensable compounds in broad area of industrial applications. But, some specific properties of PCBs have demonstrated them as environmentally perilous compounds. The outstanding dielectric property is one among the most significant properties of PCBs [10]. Also, their poor electrical conductivity and high heat capacity have proved them to be ideal as coolants in electrical equipment. A brief list of significant commercial and industrial applications of PCBs is delineated in Fig. 1. The ease of transportation of PCBs over the long distances in the atmosphere would result in their rampant distribution across continents including the regions where they have never been used before. Therefore, PCBs are observed nearly in all compartments of the global ecosystem at least in trace quantities.

Majority of PCBs in the environment are believed to be the result of leaks from PCB containing electrical capacitors and transformers, but

waste incineration is also a potential source for PCBs. From the available literature, it is evident that PCBs may enter practically into all ecosystems and sustain for years without undergoing biodegradation, oxidation or reduction to any considerable extent [11]. Further, PCBs withstand to breakdown by acids, bases and heat to a large extent due to their hydrophobic property. Also, the high solubility of PCBs in lipids allows them to bind with lipid segments in animal tissues and concentrate in livestock through the food chain. Hence, the major route of human exposure to PCBs is through diet, especially from meat, fish and dairy products. Besides their toxic effects, several breakdown products of PCBs exhibit even more toxicity. For instance, the breakdown products alter the cellular operations in lungs, exhibit negative influence on thyroid hormones, hinder the activity of enzymes in adrenal glands, interfere with estrogen receptors and influence the reproductive system [12].

Considering their adverse effects on the entire ecosystem, PCBs have been categorized into a group of persistent organic pollutants (POPs). In view of their acute toxicity and environmental persistency, several analytical strategies have been developed for sampling, pretreatment and analysis of PCBs in air, water, soil, sediments and other biological contaminated sources at trace concentrations. Even though several review articles have briefly discussed the toxicology, pharmacokinetics and analytical procedures for the characterization of PCBs from different sources in the environment, but no review has described systematically about the sampling, extraction and methods of analysis [13–19]. Therefore, the present review focuses on the fate and transport of PCBs in the environment, latest sampling techniques used or developed for air, water, soil, sediments, plants and biological tissues. Further, this review emphasizes sample extraction methods and their analysis by the state-of-the-art analytical techniques considering the latest research articles as case studies. Finally, the possible remediation approaches followed by the future recommendations are discussed. Overall, this review could be a complete guide for the analysis of PCBs collected from any kind of contaminated source(s).

2. Fate and transport of PCBs in the environment

2.1. Sources, distribution and transport of PCBs in the environment

The widespread use of PCBs in different commercial and industrial applications along with their inappropriate disposal has created severe environmental contamination. The electrical components including capacitors and transformers, as well as other PCB waste from landfills discharge them into air since landfills may not be designed specifically to handle hazardous PCB waste. Approximately, one third of the total PCBs produced in the United States (US) have already entered into the environment [20] and their contamination is continue to rise by

Table 1
A brief overview of TEF values for various PCB congeners issued by World Health Organization.

CAS Number	Chemical name of PCBs	Name of PCB congeners	Log K_{ow}	TEF (Unitless)	
				1998	2005
32598-13-3	3,4,3′,4′-Tetrachlorobiphenyl	PCB No.77	6.36	0.0001	0.0001
70362-50-4	3,4,5,4′-Tetrachlorobiphenyl	PCB No. 81	6.36	0.0001	0.0003
32598-14-4	2,3,4,3′,4′-Pentachlorobiphenyl	PCB No. 105	6.65	0.00003	0.00003
74472-37-0	2,3,4,4′,5-Pentachlorobiphenyl	PCB No. 114	6.6	0.0005	0.00003
31508-00-6	2,4,3′,4′,5-Pentachlorobiphenyl	PCB No. 118	6.74	0.00003	0.00003
65510-44-3	2′,4′,2,3,5-Pentachlorobiphenyl	PCB No. 123	6.74	0.0001	0.00003
57465-28-8	3,4,5,3′,4′-Pentachlorobiphenyl	PCB No. 126	6.89	0.1	0.1
38380-08-4	2,3,4,5,3′,4′-Hexachlorobiphenyl	PCB No. 156	7.18	0.00003	0.00003
69782-90-7	2,3,4,3′,4′,5′-Hexachlorobiphenyl	PCB No. 157	7.18	0.0005	0.00003
52663-72-6	2,4,5,3′,4′,5′-Hexachlorobiphenyl	PCB No. 167	7.27	0.00001	0.00003
32774-16-6	3,4,5,3′,4′,5′-Hexachlorobiphenyl	PCB No. 169	7.42	0.01	0.03
39635-31-9	2,3,4,5,3′,4′,5′-Heptachlorobiphenyl	PCB No. 189	7.71	0.0001	0.00003

*PCB 37 will take into consideration for TEF assignment after certain toxicological studies [8].
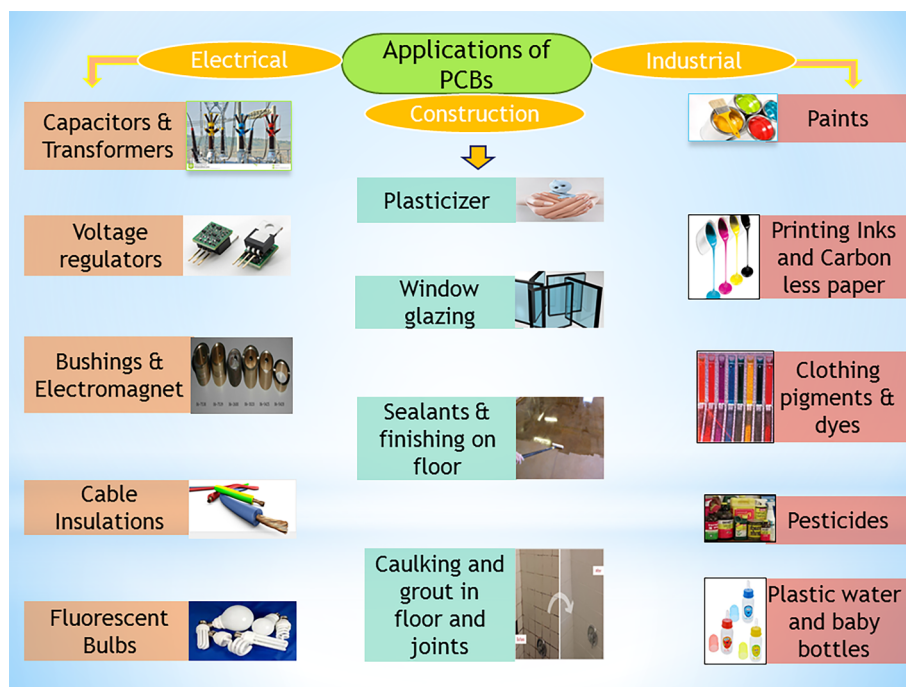
Fig. 1. Illustration of various commercial and industrial applications of PCBs.

dumping the aged electrical appliances. The municipal waste incineration could further increase their contamination by producing harmful byproducts including PCDD/Fs and hydrogen chloride (HCl). However, PCBs may also enter the environment by evaporation of paints, coatings and plastics, downright leakages into sewers and streams, dumping in non-secure landfills followed by other disposal techniques like ocean dumping. Despite the regulations, a few PCBs are being dumped illegally by means of ignorance or negligence. Apart from the above, accidental spills and leakages are the secondary sources that contribute lesser extent to the global PCBs contamination. At first, PCBs were recognized in 1966 during the quantification of DDT and its substances in the environmental samples [21]. Thereafter, PCBs have been evolved as common pollutants in global ecosystem and often identified in air, soil, sediments, water, milk, fish, wildlife, plants, human adipose tissues and blood samples. Surprisingly, PCB residues have been noticed in the regions of no industrial activity including snow deposits in Antarctic [22].

PCBs have been noticed throughout the world at significant concentrations in all environmental matrices and their concentrations in urban air greatly varied with the rural areas. For instance, the average concentration of PCBs reported in North-American cities is $0.5 \, ng/m^3$, which is almost 20-times greater than the reported concentration of $0.02 \, ng/m^3$ in rural locations. Notably, PCBs were found at $0.2 \, ng/m^3$ concentration in Arctic and Antarctic regions, where they have never been used [23]. In the early 80 s, the indoor air concentrations of PCBs were found to be relatively 10-times greater than the outdoor air. Next, the concentration of PCBs in rainwater has been dropped from $0.02 \, ng/m^3$ to $0.005 \, ng/m^3$ in rural locations and from $0.05 \, ng/m^3$ to $0.01 \, ng/m^3$ in urban stations in the early nineties, which are one-fourth lesser than the reported values in the late seventies. In seawater of high industrial areas, the PCBs concentrations were found up to 100-times higher than the respective offshore, wherein samples were collected from upper few millimeters of the surface. Extremely, higher PCB concentrations of $0.3–3.0 \, ng/L$ were found in North Sea and Galveston Bay, the vastly industrialized areas in Texas, US [24].

The degree of chlorination also influences the adsorption of PCBs proportionally on any particulate matter. In water, PCBs can be adsorbed onto the surface of sediments and other organic matter. The two primary routes for PCBs to enter into soil environment are disposal sites and atmospheric transportation. These PCBs are pervasive and remain in the environment for longtime. In sediments of surface water, PCBs accumulate in significant quantities. Indeed, the organic matter, clay surface and micro particles dispersed in water promote the adsorption of PCBs. They remain concealed in the sediments for longer time and gradually released into water, which would then evaporate into the atmosphere/air. Discharge of PCBs from water to air occurs particularly in dry seasons when sediments contain higher PCB concentrations [25]. The PCBs present in air can concentrate on soil through wet deposition during rains and snow falls, otherwise they adhere to particulate substances like dust/soot that readily settle down on the soil surface. Perhaps, PCBs can also be transferred by insects when they come into contact with them. A detailed representation for the transportation of PCBs in the environment is displayed in Fig. 2.

2.2. Adverse effects of PCBs on human and biota

It is very familiar that PCBs induce a wide variety of toxic responses in human, wildlife, plants and laboratory animals. They can penetrate the human body through skin contact, by inhalation of PCBs contaminated vapors and by consuming food contaminated with PCB residues [26]. Consumption of foods contaminated by PCBs especially fish, meat and other poultry products appear to be the main source of exposure even though concentration of PCBs in foods has been decreased since the late seventies [27]. The National Toxicology Program (NTP) and International Agency for Research on Cancer (IARC) have concluded that PCBs are carcinogenic to human. Toxicological studies of PCBs in human were found to increase the rate of melanoma, gall bladder cancer, brain cancer, liver cancer, biliary tract cancer, gastrointestinal tract cancer and possibly connected to breast cancer. The people exposed to high levels of PCBs through skin contact or by consumption experience skin irritations like severe acne and rashes, nose and lungs infections and eye issues [28]. Further, lesser chlorinated PCBs can mimic with the body's natural hormones especially with estrogen. The women exposed to PCBs during their pregnancy may result in serious motor control and neurological issues, and in children they cause short-term memory loss and lowered IQ. In addition, a study
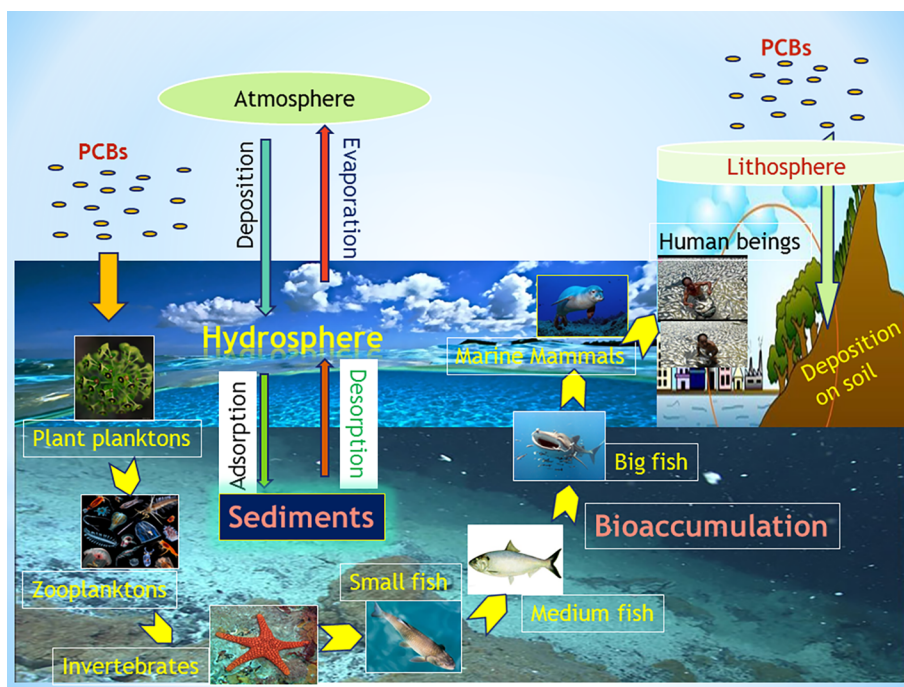
Fig. 2. Representation of possible routes of transportation of PCBs into environment.
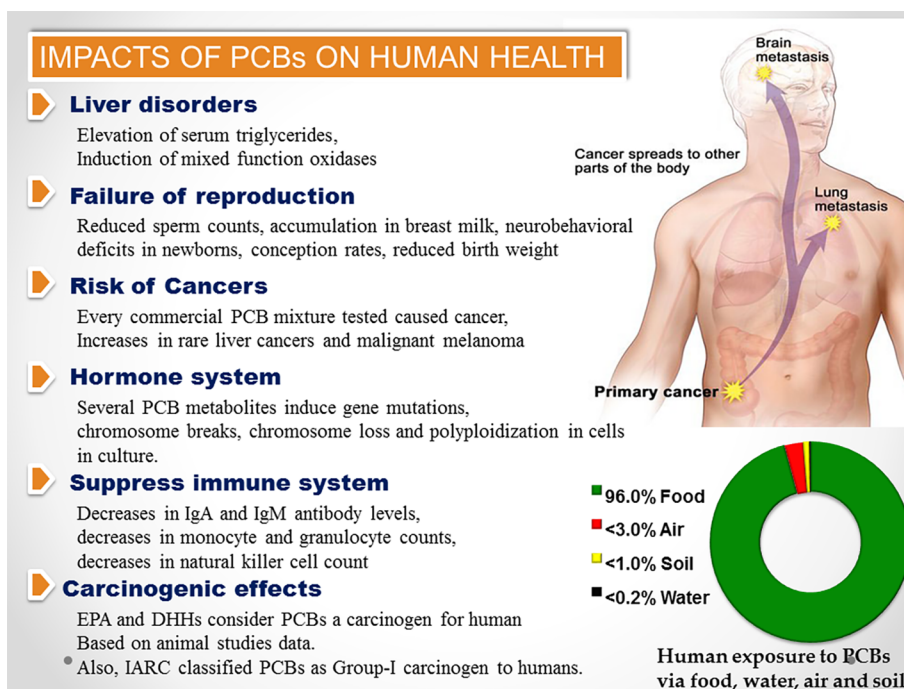

Fig. 3. A list of severe adverse effects of PCBs on human health.

found shortened menstrual cycles in women who consumed fish from Lake Ontario that are highly contaminated with PCBs [29]. Apart from the above, PCBs are thought to influence the sperm counts, alter the sex organs, early puberty and change sex ratios of children. Highly chlorinated PCBs exhibit DL toxicity and alter the metabolism of sex steroids in the body, change the normal estrogen and testosterone levels. A list of adverse health effects of PCBs in human body are presented in Fig. 3.

Investigations on laboratory animals provided the information that PCBs can be absorbed quickly from digestive tract and to a minor extent through skin. In animals, PCBs were observed to impair the stomach,

lungs and pancreas. Based on a short-term exposure study for 7 days, the lowest concentration that was found to harm the tested rats was 2.5 mg/kg body weight per day, which caused a significant decrease in thyroid hormone level in the blood and relative increase of liver weight. Similarly, in a longtime exposure of 2 years, the tumors were developed in nine out of twelve studies and the liver size was significantly increased on the ingestion of PCBs mixture. The lowest PCB concentrations associated to develop these tumors ranged between 1.4 and 5.4 mg/kg body weight/day based on specific PCB mixture tested. Furthermore, PCBs containing more chlorine atoms support the formation of lung tumors in mice, and liver tumors in both rats and mice

[30].

The uptake of PCBs and their negative effects on plants has also been examined. For instance, PCBs firmly bind to the soil organic matter and provides low bioavailability for plants and microorganisms. But accumulation of PCBs in soil is perilous to all kinds of organisms including plants. The higher PCB concentrations affect the biosynthesis, ultrastructure of plant cell, membrane stability and plant DNA. Also, the plants that are highly exposed to PCBs result in reduction of photosynthesis, water/nutrients uptake and show visible symptoms of growth inhibition, browning of root tips and even death [31]. In a recent study [32], the inhibited growth rate was reported in tobacco plants when they cultivated in PCB contaminated soil. Increased DNA damage and reduced growth have significantly affected the tobacco plants. The toxicity induced by PCBs had a strong inhibition on leaf growth and could have restrained the induced mutated cells division, so that mutated parts could not be detected.

2.3. Bioaccumulation and biotransformation of PCBs in human, plants and living organisms

It has been revealed that atmospheric PCBs concentrations correlate with the population size, meaning that urban locations contain significantly higher PCB concentrations than the rural locations. Bioaccumulation of PCBs in human is recognized to take place through their deposition onto terrestrial plants from air and water and then to aquatic autotrophs and invertebrates of the lowest trophic levels, followed by their transfer through food webs. Recently, it was assessed that inhalation makes significant contribution to the total PCBs concentrations present in human body, which likely in populations where PCBs concentrations in air is high and fish consumption is low [33]. In the United States, intake of PCBs in adults by diet has continuously decreased since the late seventies, which attained the lowest by late eighties. During 1991–97, considerably higher dietary exposure was detected around 3.0–5.0 ng/kg body weight/day in adults and 2.0–12 ng/kg body weight/day in kids. Next, a study conducted in Japan during the late nineties estimated the intake of PCBs over 120 food items, and the findings revealed that maximum concentrations (8.39–25.7 ng/kg) of PCBs were found in fish and shellfish. The total uptake of PCBs in adults (assuming an adult weight of 50 kg) was found to be 0.00145 ng/kg body weight/day, which depicts a high degree of PCBs contamination in Japan.

The concentration of PCBs reported in human milk fat in Japan was highest in 1974, but it was decreased to 13% by 1998 (0.2 mg/kg milk fat) [34]. In contrast to above studies, PCBs have been identified only in 1 out of 280 drinking water samples tested in Canada at a concentration of 6.0 ng/L. The PCBs found in breast milk increased from 1970 to 1982 in Canada, then declined to its 1970 value by 1986 [35]. Another study reported the concentration of PCBs in fat of breast milk in Swedish women, in which they have noticed a constant reduction from 0.910 mg/kg to 0.324 mg/kg of milk fat during 1967–1997. Thereafter in the late 80 s, the quantity of PCBs detected in fat of human milk was ranged from 0.2 to 4.0 mg/kg [36]. During 2005–2007, a study conducted in California and Ohio showed the highest level of PCB-153 i.e., 7.4 ng/g lipid in 6–9 years old girls, 5.4 ng/g lipid in 12 to 19 years male and females and 24.2 ng/g lipid in adults aged above 20 years [37]. As of now, the critical concentrations described in international literature for children below three years of age, breastfeeding women and women of childbearing age varied between 700 and 1000 ng of total PCB per gram of maternal plasma lipids.

The major routes of elimination of PCBs from the human system are via feces, urine and breast milk. PCBs can also enter placenta and then pass to umbilical cord blood, later they reach to breast milk in mothers. In any living system, PCBs undergo a variety of transformations followed by their excretion or accumulation in certain tissues. Also, PCBs have high tendency to transform into persistent metabolites, which are capable to accumulate in specific tissues and body fluids rather than

excretion. Further, PCBs can enter into tissues through blood and then rapidly transform into water soluble substances. They can associate with glucuronic acid and glutathione that are the two natural substances available in the body to increase water solubility of xenobiotics and promote their excretion through urine and feces [38]. The speed of the overall process varies with the number of chlorine atoms and their position in the PCBs. For example, the above process becomes slow if the chlorine atoms are present on both the phenyl rings, and the process becomes faster if the phenyl rings contain no chlorine atoms.

Plants uptake PCBs from both soil and air and root is the first tissue to encounter PCBs via absorption process. The content of root extractable lipids strongly influences the uptake of PCBs. Despite many studies on the uptake mechanisms and transformation of PCBs by plants, majority of them have focused on plant root uptake of PCBs [39,40]. Initially, PCBs enrich at the root surface and later transfer to the roots together with water. They then percolate across the cuticle-free unsuberized cell walls of young root hairs that are situated nearly behind the root tip (5 ± 50 mm). Afterwards, they travel towards the xylem transport tissue in the roots along the free intercellular spaces. The cell wall between the cells in root cortex is porous by which PCBs can travel readily from solution to interior before they reach the endodermis [41].

The higher solubility of PCBs in animal fats demonstrates their accumulation in animal fats across the food chain. Generally, PCBs have a tendency to accumulate in living organisms when they are absorbed from the environment by means of bioaccumulation and from food chain via biomagnification. Further, PCBs influence the mixed function oxidase (MFO) enzymes and obstruct the ATPases in marine biota [42]. However, PCB congeners could be transformed by various animal species and vertebrates. The speed and physiological mechanism of PCBs metabolism depends on specific PCB congener and animal species; the rate of bioaccumulation in aquatic organisms relies on the species, its habitat and PCB congener [43]. The concentration of PCBs in sediments is much higher than water and therefore, the concentrations are often high in bottom-feeding species. In aquatic environment, the concentration of PCBs is more in shellfish than the plankton on which they feed; the concentrations are even higher in animals such as large predatory fish or mammals (dolphins, seals and whales) that are placed at the top of the food chain [44]. On the earth, biomagnification progresses by the accumulation of PCBs in worms and insects from soil/plants to finally reach mammals and birds. Also, PCBs accumulate in human through food chain. The concentration of PCBs in fatty tissues of human are at least 100-times higher than in food they eat.

2.4. Persistence and degradation of PCBs in the environment

Persistence of PCBs in the environment depends on the number of chlorine atoms and their positions on biphenyls rings. The two phenyl rings of PCB may lie in the same plane (co-planar PCBs) or in different perpendicular planes (non-planar PCBs). The breakdown of PCBs occurs mainly from sunlight followed by microorganisms and sunlight plays an essential role in the destruction of PCBs present in water, air and soil surface. Generally, the persistence of PCBs in the environment increases with increasing number of chlorine atoms [45]. Light induced degradation is much slower in planar PCBs compared to perpendicular PCBs. In the atmosphere, PCBs prefer to react with water and ozone in the presence of sunlight. The half-life of PCBs containing 1–5 chlorine atoms varies between 3.5 and 83 days. The PCBs present in water breakdown necessarily under the effect of sunlight (photolysis). In shallow water, the half-life time varies from 17 to 210 days for PCBs containing 1 to 4 chlorine atoms during dry seasons [46]. However, winter is not effective and degradation of PCBs by sunlight would be relatively slow. High chlorinated PCB congeners absorb relatively greater amounts of sunlight and cause rapid breakdown. In soil and sediments, most of the degradation of PCBs takes place in microorganisms. But, the rate of degradation depends upon different factors

Table 2
A list of several DL PCB congeners and their degradation half-life times.

Name of PCB congeners	Chemical names of PCBs	Half-life (years)			
		Air	Water	Soil	Sediments
PCB No.28	2,4,4-Trichlorobiphenyl	0.008	0.165	2.966	2.976
PCB No.52	2,5,2′,5′-Tetrachlorobiphenyl	0.171	3.422	9.99	9.993
PCB No.77	3,4,3′,4′-Tetrachlorobiphenyl	0.171	3.422	9.993	9.993
PCB No.81	3,4,5,4′-Tetrachlorobiphenyl	0.171	3.422	9.993	9.993
PCB No.101	2,2,4,5,5′-Pentachlorobiphenyl	0.342	6.845	9.993	9.993
PCB No.105	2,3,4,3′,4′-Pentachlorobiphenyl	0.342	6.845	9.993	9.993
PCB No.114	2,3,3,4,5,4′-Pentachlorobiphenyl	0.342	6.845	9.993	9.993
PCB No.118	2,4,5,3′,4′-Pentachlorobiphenyl	0.342	6.845	6.845	6.845
PCB No.123	2′,4′,3,4,5-Pentachlorobiphenyl	0.342	6.845	9.993	9.993
PCB No.126	3,4,5,3′,4′-Pentachlorobiphenyl	0.342	6.845	9.993	9.993
PCB No.153	2,4,5,2′,4′,5′-Hexachlorobiphenyl	0.684	13.689	18.823	18.823
PCB No.169	3,4,5,3′,4′,5′-Hexachlorobiphenyl	0.684	13.689	18.823	18.823
PCB No.180	2,3,4,5,3′,4′,5′-Heptachlorobiphenyl	1.369	27.379	37.645	37.988

including position and total number of chlorine atoms, concentration of PCBs, nature of microorganisms, available nutrients and temperature. The breakdown process for PCBs using microorganisms might be very slow or may not even happen if the soil and sediments contain oxygen. A list of most common PCB congeners and their degradation half-life data are presented in Table 2.

3. Sampling of PCBs from different sources

PCBs have been identified in discrete sample matrices such as in air, water, soil, sediments, plants, aquatic mammals, fish, benthic organisms, human adipose tissue and many more. Therefore, it is fundamental to acquire the most representative samples for any environmental measurement procedure that should not be overlooked. Contamination may occur at field collection, especially from PCBs present in electrical equipments and building products. Therefore, specific approaches are necessary to collect the samples from different sources. The examination of PCBs in water is quite difficult owing to their high tendency to travel to the fatty environment and their lower water solubility [47]. Therefore, the concentrations of PCBs detected in water samples are quite lower and the analysis could be obstructed by background contamination, which needs extreme care during sample extraction to enhance their concentration. Further, PCBs concentration in air can be evaluated after collecting the samples using filters or passive sampling systems. Next, sediments and biota are the most preferably considered matrices for the analysis of PCBs in the environmental samples. In this section, we have described the specific sampling techniques for the collection of PCBs and their scientific merits over the conventional sampling methods.

3.1. Water sampling for PCBs

Water sampling is particularly sensitive to PCBs contamination on older ships and buildings. The most trivial procedure to collect the surface water samples for PCBs is to grab sampling or spot sampling. This process involves the collection of a single sample or numerous individual discrete samples representing the width and depth integrated profile. The simplest procedure for the collection of samples for PCBs in small and wadeable streams is by hand into the shipping sample containers [48]. In deep water sites including lakes and reservoirs, the samples can be collected with the help of bailers or thief samplers. The commonly available samplers for the collection of PCBs and other chlorinated compounds are Kemmerer, Van Dorn and double check valve bailer devices [49]. These samplers are beneficial to collect discrete samples from the specific depth. Next, the groundwater samples can be collected from the monitoring wells or existing supply wells. The selection of sampling methods varies with the depth of water and size of

the well. Portable peristaltic pumps are convenient to collect the groundwater samples for PCBs from monitoring wells [50]. Similarly, pore water can be collected *in-situ* with the aid of passive sampling devices. The pore water samples of laboratory sediment samples can be obtained from centrifugation, squeezing followed by vacuum filtration.

Recently, a modified water sampling method [51] was established for the PCBs and PCDD/Fs using dual filters of pore sizes 3.0 μm and 0.5 μm and compared the efficiency with conventional sampling method that contains a single filter of 0.5 μm pore size. In the conventional approach, highly concentrated suspended solids were accumulated and formed a dust layer on the filter surface that has created the necessity to abort the sampling process and replacement of filters more often during the sampling process. But, the modified method with dual filters was effective compared to traditional method containing single filter of 0.5 μm pore size. Further, the operation of modified sampling process was impressive, which avoids filter replacement [51].

3.2. Soil and sediment sampling for PCBs

Marine sediments particularly with high organic carbon may accumulate PCBs and other hydrophobic compounds significantly at higher concentrations than the surrounded water. The sampling procedure essentially varies with the intention of observation and natural state of the area to be examined. Typical sampling approaches for the PCBs are stratified fixed sampling, fixed station sampling and stratified random sampling. Mud or swampy sediments that contain high percentage of refined materials are superior to monitor organic contaminants. A variety of grab samplers can be used to collect the surface sediments [52]. Usually, PCBs concentration in sediments exhibit the uneven distribution and thus the total number of grabs collected at a single location could be mixed into poled sediment sample. Stainless-steel buckets must be used in the grab samplers to avoid the possible contamination from plastic materials that contain plasticizers such as phthalates. The grab samplers normally collect the samples from upper layers of the sediments, but may dissipate the unconcentrated flocs at sediment-water interface when moving down. The multiple damped array shallow coring devices are necessary to collect the flocs. Passive sediment devices are useful to collect the samples from sediments formed by the water columns or re-suspended from the seabed [53]. In stagnant fields, the change in flux of PCBs to the seabed as a function of time can be recreated by the examination of dated sediment cores. Therefore, the cores with greater than one meter of length are necessary for this purpose.

Recently, a novel nonequilibrium passive sampling method was reported [54] by applying different polyethylene thicknesses to predict the freely dissolved aqueous PCBs concentration in sediment pore water. This method provides reasonable estimates for freely dissolved

aqueous PCBs concentration proving its potential as another option for nonequilibrium passive sampling for PCBs and other hydrophobic pollutants in sediment pore water. Also, CERP has issued guidelines for the soil and sediment sampling in 2009, in which, it has stated that samplers used for soil sampling may vary from the samplers used for sediment sampling, and sampling a few times where sediments present below the water bodies must be performed carefully, resulting minimum or no harm to the site and preventing the sample loss [55].

3.3. Air sampling for PCBs

There are several advanced techniques available for ambient air sampling of PCBs. Hence, the critical objective of any air sampling task is to acquire an absolute and representative sample. There are gaseous and particulate pollutants in air whose concentration can be reported in milligram/cubic meter of air. Particulate sampling can be accomplished using the high-volume air samplers and dust samplers. Using these samplers, the size of the particles < 10 μm can be captured employing the filter paper [56]. The ratio between weights of filter papers to that of quantity of air elapsed provides the volume of particulate matter present in air. Next in grab sampling, air samples can be taken by filling the clear flasks, but this is very old and conventional ambient air sampling method [57]. Absorption of gaseous pollutants into the liquid medium is another important method for the collection of air samples. Impinger and midget type devices can be used to emphasize the high degree (pollutant) gas-liquid contact. Most of the environmental consultancy firms prefer to use this absorption technique for the ambient air sampling, because the loss of degree of quality is insignificant [58].

Several publications reported the air sampling and analysis of PCBs in recent years. Besides, several guidelines have been established to demonstrate the air sampling procedures and strategies for the analysis of PCBs. Air sampling for PCBs is typically carried out by using XAD resin or polyurethane foam (PUF). Recently, PUF and PUF combined with granular adsorbents were successfully utilized to carry out the air sampling for PCBs [59,60]. Different granular adsorbents (Porapak®R, Chromosorb®102, Amberlite XAD-2, Florisil®PR and Tenax®GC) were combined with PUF to enhance the sampling capacity and the competence of granular adsorbents found to be higher than PUF, but granular adsorbents are expensive and possess higher airflow resistance than PUF [61]. In a further study, silicone was employed for PCBs sampling in indoor air based on its partition properties. Higher sampling rates, greater sensitivity and good precision along with several other practical advantages viz., low cost material, effortless shipment, simple handling proved silicone as efficient and potential material for passive sampling applications [62].

3.4. Biota sampling for PCBs

The concentration of PCBs in biota can be varied significantly at the upper levels of food chain. Therefore, it is important to acquire an illustrative sample from certain populations. PCBs are expected to associate with benthic and suspended solids, phytoplanktons, zooplanktons and natural surface oil films due to their lipophilic property. Absorption of PCBs into aquatic food chains commence with these sediments, planktons or films casually swallowed by fish and invertebrates [63]. Different processes can be used to collect the biota samples, like benthic organisms can be collected from seashore rocks by the aid of grab dredge or trawl in deep waters [64]. Fish samples can be grabbed by means of rod and line or using various trawls and nets based on territory and nature of species under observation. Further, electric fishery methods are exceptionally beneficial to collect the samples [65].

Oslo and Paris Commissions have established the guidelines regarding biota collection for the contaminant analysis. Animals can be preserved in freezers at −25 °C, and the tissues required for the analysis shall be collected under suitable laboratory conditions maintaining a hygienic atmosphere in the laboratory. However, it is crucial to manage

the glass jars in a similar way that has been adopted for the sediment samples. Usually, wet sample extraction is recommended after drying the samples with sodium sulfate (Na_2SO_4) or calcium sulfate ($CaSO_4$) [66]. But, freeze-drying is not suggested considering the loss of lesser chlorinated PCBs before the analysis and due to the risk of cross-contamination.

In a recent study [67], silicone coated glass jars were used to collect seven 'indicator' PCBs along the River Elbe intending to assess C_{free} of PCBs and their $C_{lip \rightleftharpoons sed}$ in sediment samples. In all cases, the $C_{bio,lip}$ quantities were found to be less than $C_{lip \rightleftharpoons sed}$. The results confirmed the close relationship between bioaccumulation of PCBs and thermodynamic potential of sediment-associated HOCs for partitioning into lipids. This procedure gave clear and consistent results compared to other conventional methods that depend on the total concentrations in sediment and biota-sediment accumulation factors [67]. Some recent studies have reported plankton sampling following COSTAS protocols (pollutants in trophic system: phytoplanktons, zooplanktons, anchovy, sardine) [68,69] to conclude that 60–200 μm size is characteristic for phytoplanktons and 200–1000 μm for zooplanktons.

4. Sample extraction methods

Sample preparation for PCBs is remarkably a judgmental process on which the accuracy of measurements depends. Most importantly, freeze-drying of PCB samples reduce the recoveries owing to the firm binding and residues obstruction in dried materials [70]. Although, some authors have recommended the freeze-drying for sediments and soils [71], lower recoveries were reported for the PCBs from freeze-dried sediments [72]. Another study reported that loss of water during the processing of fish products result in higher PCBs concentration [73]. Thus, conservation of environmental sediment samples and tissues in their original wet state is regarded as the predominant approach while preparing the samples for PCBs analysis. Moreover, the contamination from lab air can be minimized by preventing drying step; it has a great advantage particularly in old buildings where PCBs are rampant contaminants. Alternatively, homogenized samples shall be mixed with desiccants (free from PCBs) such as sodium sulfate, celite or hydromatrix to bind water [74].

This section describes the several sample extraction methods including solid phase extraction (SPE), supercritical fluid extraction (SFE), soxhlet extraction, solvent extraction and other latest microextraction methods. A summary of the advantages and disadvantages of popular sample extraction methods are presented in Table S1. Furthermore, a complete list of sample extraction techniques available for the extraction of PCBs from different categories of sample matrices is presented in Fig. 4.

4.1. Soxhlet extraction

Soxhlet extraction is a popular and conventional technique for PCBs extraction from different environmental samples including soils, sediments, animals and plant tissues. It allows vast amount of sample i.e., 10–30 g without the need for filtration after the extraction. The method is independent of sample matrix and multiple numbers of soxhlet extractors can be fixed to perform the unabandoned operation. A large variety of organic solvents including dichloromethane (DCM), mixture of DCM-acetone, DCM-hexane, and acetone-hexane have been used for extraction [75]. However, it is not advisable to use non-polar solvents alone. The major disadvantages of the method are their prolonged extraction times varying from 24 to 48 h, consumption of high organic solvent up to 500 mL per sample and the necessity of evaporation after sample extraction. To overcome these drawbacks, some improvements have been made to the conventional soxhlet extraction including automated Soxhlet extraction, high pressure Soxhlet extraction and focused microwave assisted Soxhlet extraction [76].

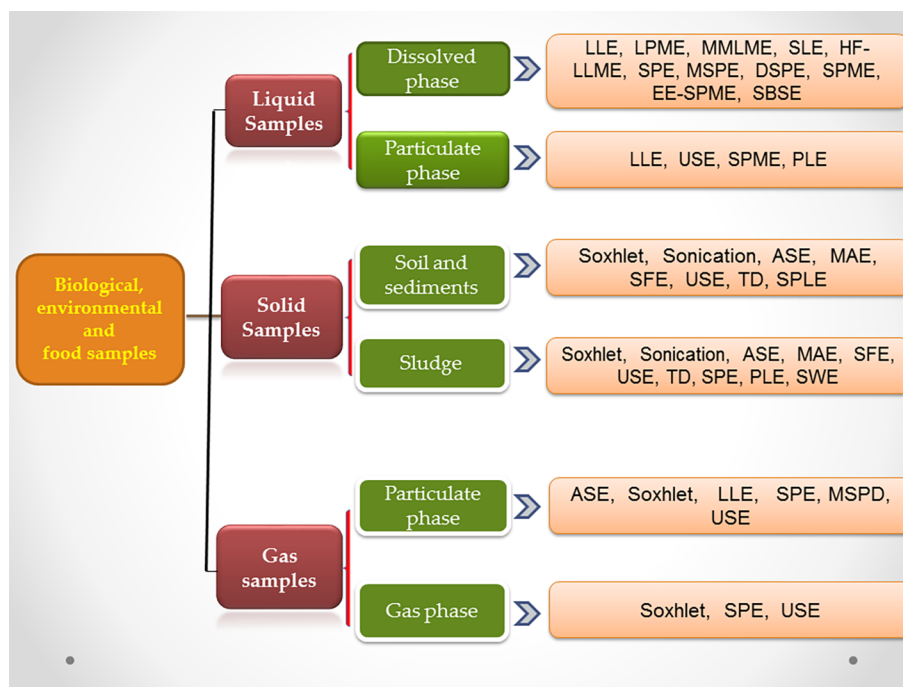A few Soxhlet extraction methods have been demonstrated for the

Fig. 4. Various sample pretreatment options available for the extraction of PCBs.

analysis of PCBs in fish and sediment samples that achieved the best recoveries [77,78]. The accelerated solvent extraction (ASE) was used to extract PCBs from the sediment samples collected in Baltic Sea using n-hexane/acetone (1:1, v/v) for ASE and toluene for Soxhlet extraction. The results showed that sediments containing small quantity of organic carbon were extracted in 5.0 min by ASE using n-hexane/acetone (mentioned in EPA method 3545). Nonetheless, Soxhlet extraction increased the extraction efficiency using toluene solvent for sediments with higher amounts of carbon [79]. The three commonly used extraction techniques viz., soxhlet extraction, ASE and microwave-assisted extraction (MAE) are compared for the extraction of PBDEs and PCBs in soil and fish samples. The extraction recoveries of ASE and MAE were comparable with Soxhlet extraction for PCBs and PBDEs, and even better for several PCB congeners containing large octanol-water partitioning coefficients (K(o/w)). Therefore, consistent extraction recoveries of ASE and MAE procedures have described that elevated pressure and temperature are appropriate to extract PCB congeners from solid matrices efficiently [80].

4.2. Solid phase extraction

SPE is applicable for the pre-concentration of air and water samples containing PCBs. SPE was developed as a possible replacement for the labor-intensive LLE procedure that is difficult to automate and demands high amount of high-purity solvents. In contrast to LLE, SPE offers lesser solvent consumption, rapid processing and the choice of automation [81]. Further, the necessity of transportation and storage of large volume samples in the laboratory can be avoided due to its direct sampling option in the fields [82]. Field-portable SPE prevents the analytes from degradation during sample holding times after sample collection.

In the past, a method described for the pre-concentration of PCBs from seawater using XAD-2 column in SPE. After passing the PCBs onto XAD-2 sorbent (sometimes PUF was used alternatively), the samples were constrained to solvent extraction. Although, this technique is very useful, the cleaning procedure is very cumbersome to confirm a low blank from the resin matrix [83]. Another column extraction technique was reported for fish samples, in which 5.0 g of sample was grounded

with anhydrous sodium sulphate (Na_2SO_4) enveloped with the chromatography column and eluted with DCM. Then gel permeation chromatography (GPC) was applied to eliminate bulk lipids in the next step after concentration [84]. Subsequently, in the next method researchers incorporated sea sand along with Na_2SO_4 to enhance the grinding capacity of the material [85].

A simple SPE method was also reported for the extraction of OCPs and PCBs from the human serum. The method involved the denaturation of serum proteins with water + 1-propanol mixture, followed by sample application over SPE column and subsequent elution with n-hexane-DCM mixture. This method was also applied to real serum samples with recoveries of 99 to 120% for PCBs and 88 to 115% for OCPs from spiked porcine serum samples [86]. Another simple and reliable pretreatment approach was established for the simultaneous cleanup of seawater and the analysis of PCBs using headspace sampling and solid phase microextraction (SPME). The researchers observed that humic acids present in seawater has created unusual negative effects and PCBs recoveries were improved only after the pre-treatment of seawater with $KMnO_4$ at pH 6.0 [87].

4.3. Supercritical fluid extraction

SFE is an effective technique for the extraction of PCBs from soil, sediments and other solid materials. In SFE, the best recoveries for PCBs can be achieved by optimizing pressure, temperature and flow rate. The application of SFE is due to unique property of supercritical fluid. The supercritical fluids contain low viscosity, low toxicity, low flammability and high diffusion coefficients that are more superior to organic solvents practiced in SPE techniques. Carbon dioxide is the typical fluid used in SFE, because it is non-toxic and easy to obtain its critical parameters ($T_c = 31\,°C$ and $P_c = 74\,bar$) [88]. Next, ammonia ($T_c = 132\,°C$ and $P_c = 115\,bar$), nitrogen protoxide ($T_c = 36\,°C$ and $P_c = 71\,bar$) and water ($T_c = 374\,°C$ and $P_c = 217\,bar$) are other popular supercritical fluids that are widely used in SFE. The supercritical fluids can be eliminated at low temperatures without leaving toxic residues, but the required high pressures are dangerous in industrial applications. The contemporary extraction procedures including SFE, MAE and ASE are very impressive due to their speed, consumption of

small volume of solvents and environmental friendly procedures [89].

In a method, PCBs have been extracted from the sediment samples at 20 °C and 150–650 atm pressure. The selected PCBs were spiked onto sand and then extracted in a similar way to that of sediment samples. The recoveries for all individual PCBs in spiked samples were quantitative (> 95%) [90]. In another approach, separation of PCBs from PCDDs and other chlorinated aromatics was attempted due to their similar solubility [91]. A study described the extraction of PCBs from fish and fish-oil employing SFE [92], where samples combined with silica and 10% silver nitrate at different weight ratios were placed in 7.0 mL extraction cells. Samples spiked with different PCBs were supplemented at the top of extraction cell to check the retention behavior of fat-adsorbent compositions. The elution was carried out with 1.5–1.8 mL of hexane to collect the analytes. In continuation, authors have used basic alumina mixture as an alternative to silica/silver nitrate (1:10, w/w) for extracting PCBs from fatty acid samples [93]. Despite its advantages, SFE needs additional improvements to obtain better results. A common limitation of SFE is its poor repeatability, meaning that any developed method is valid for that specific sample matrix and needs further optimization if intended to use for other biota samples containing different fat or lipid content.

4.4. Other extraction methods

Other procedures that are commonly used for the extraction of PCBs are microextraction techniques. The prime choice of techniques under this category include equilibrium liquid-liquid-liquid microextraction (LLLME) followed by exhaustive LLE for the extraction of PCBs from small volumes (μL) of water. Unlike SPME, the extraction phase does not contact the sample solution in LLLME. Alternatively, in LLLME a replaceable polypropylene hollow fiber can be used to bring the analytes into organic phase and eventually into another phase prior to analysis [94]. The possibility of cross contamination and carry over can be greatly minimized by using the disposable sampling apparatus. The subsequent technique is SPME, in which hollow fibers can be utilized to extract the analytes from the aqueous phase by adsorption in solid coatings and absorption in liquid coatings like LLLME. SPME is an alternative and contemporary technique for sample preparation, and it overcome most of the limitations existed in the preparation of aqueous samples [95].

Several other extraction methods have been reported in the literature including blending, microwave, ultrasonic and solvent extraction. A study [96] reported the extraction of PCBs from seals, in which 10 g of sample homogeneously blended with DCM-methanol (2:1, v/v) in Ultra-Turrax blender was employed. The extracts were agitated adding acidified water in a separating funnel and then the organic phase was filtered through anhydrous sodium sulfate followed by solvent evaporation. The residues were dissolved in hexane and treated with sulphuric acid absorbed onto silica gel. Finally, the extract was cleaned by chromatography on basic aluminum oxide and deactivated with 1.0% (w/w) of water [96]. In other study [97], researchers employed an ultrasonic bath for the extraction of PCBs. About 15–20 g of tissue was homogenised in 30 mL of acetone, to which was added 30 mL of n-hexane. The mixture was held for 10 min in ultrasonic bath and washed with 60 mL of 2.0% NaC1. The hexane phase containing fat and lipophilic pollutants was divided and evaporated to dryness. The ASE is also widely applied for the extraction of PCBs in recent years [98].

In a study, ASE was performed by adding 10 mL of toluene to the cell containing 4.0 g of sample, pre-heated the cell for 5.0 min to 150 °C and washed with 5.0 mL of solvent. The extracts were dried under evaporation and reconstituted with 4.0 mL of toluene [99]. Another technique was developed [100] where MAE was used that was approved by the US EPA as Method 3545 [100]. It is a fast and accurate "green" preparation method that necessitated very less amount of solvent. Additionally, the utilization of molecularly imprinted polymers (MIPs) for the extraction of specific analytes is an advanced extraction

technique was beneficial for single analyte or a class of analytes [101].

5. Cleanup procedures for PCBs

During the analysis of PCBs in biological samples including milk, fats and tissues, the recoveries might be hindered by the chromatographic interference of co-extracted fatty materials. Therefore, it is necessary to perform cleanup procedures to remove co-extracted lipids from such samples prior to analysis. If not, the lipophilic substances present in the extract devastate surface of stationary phase and dissipates the resolving power of column [102]. Different techniques are available and they can be used either individually or in combination based on the selectivity and sensitivity of final quantification technique.

All PCBs are stable in acidic environments, and therefore, it is effective to carry out cleanup processes using sulphuric acid or acid impregnated silica columns for the elimination of lipids. Also, it is necessary to remove sulphur from the sediment samples to minimize interferences and to extend the detector lifetime. Hence, sulfur removal can be accomplished by adding copper granules during the extraction. Cleanup procedures can be performed using both non-destructive and destructive methods. Therefore, the present section has summarized both the cleanup technologies considering the reported studies. In addition, the major scientific advantages and disadvantages of each cleanup procedure is presented in Table S2.

5.1. Non-destructive lipid removal

5.1.1. Gel permeation chromatography

GPC is a size exclusion technique that is mainly useful for the sediment and fatty samples. In GPC, smaller molecules such as PCBs retain on the column and larger molecules such as fats will be eluted first. Therefore, PCBs in the sample can be isolated and other interferences can be avoided easily. In a recent study [103], GPC was employed to cleanup the PCBs from milk samples. Initially, fat was separated from the milk by centrifugation and the extractant was mixed with Na_2SO_4. Then, the mixture was treated with petroleum ether and solvent was evaporated. The fat residue was then filtered with GPC followed by silica gel adsorption chromatography [103]. The most extensively used gel in GPC is Bio-Beads S-X3, but Sephadex LH-20, PLRP-S, Bio-Beads S-X2, Bio-Beads S-X4, PL-gels and other polystyrene-divinylbenzene copolymer columns are also other commonly used gels [104]. The common eluents used in GPC cleanup procedure includes DCM-hexane, DCM-cyclohexane, ethyl acetate-toluene, ethyl acetate-cyclohexane and 2-propanol-heptane mixtures. The major drawback with the GPC technique is its complexity for the removal of total lipids. Therefore, a second cleanup procedure such as subsidiary GPC step or additional silica column is necessary to remove the left-over traces of lipids [105]. Another complication of GPC is its inadequate separation of PCBs from other compounds of similar molecular range like OCPs. As a result, supplementary fractionation methods are often necessary.

5.1.2. Column chromatography

The performance of column cleanup operations can successfully contend two kinds of interferences viz., co-extracted components consist of lipids and co-extracted organochlorine pesticides. Typically, alumina and silica gels are the most frequently used stationary phases in column chromatography. In the past, cellulose powder has been used quite often for this purpose. Alumina columns provide superior cleanup for the PCB congeners from bulk components such as lipids. The fundamental advantages of column chromatography are its reasonably low-cost and disposability of stationary phase after its use. For the elution process, either pure solvent or blend of solvents can be used as mobile phase [106].

In a recent study [107], PCBs and PAHs have been separated from the sediment samples using silica gel fractionation chromatography and low-pressure silica gel chromatographic techniques. A single cleanup

procedure was employed to provide two subsamples for the successive analysis of PAHs by GC-FID/MSD and PCBs by GC-ECD. The utilization of solvent and sorbent was reduced greatly by adopting this cleanup procedure [107]. In another study [108], a sensitive and simple process to separate planar PCBs was reported using carbon column chromatography. This method saved time and materials consumption by avoiding the use of benzene, a highly carcinogenic solvent that needs extreme care to handle.

5.2. Destructive lipid removal

5.2.1. Sulphuric acid treatment

Generally, PCBs and many OCPs have high resistance to sulphuric acid (H_2SO_4). Hence, sulphuric acid treatment is most useful to breakdown other aliphatic and aromatic compounds present in environmental samples. In a study, 20 mL of concentrated H_2SO_4 was mixed with 10 mL of sample extract and the mixture was stirred vigorously for 30 s. Then the solution was kept aside for phase separation and the procedure was repeated twice with 10 mL of H_2SO_4. The collected samples were subsequently evaporated to 1.0 mL for further cleanup [109]. Although, several researchers reported the H_2SO_4 treatment, the major limitation is its influence with the analytes (halogenated pesticides) that are to be analysed together with the PCBs [110]. Further, two sample cleanup procedures viz., multi-layer silica gel column chromatography and sulfuric acid treatment methods were compared for separating PCDFs, PCDDs and DL PCBs from food samples. The two cleanup procedures have provided similar isomeric concentrations with purification efficiencies ranging the recoveries from 40% to 120%. These results provide valuable information on the analysis of dioxins from a variety of food stuffs [111].

5.2.2. Saponification

Saponification is useful for the removal of lipids as well as it supports the elimination of sulphur from the sediment samples. In a saponification process, lipids can be eliminated by heating the extract for about 30 min at 70 °C in the presence of 20% ethanolic potassium hydroxide [112]. But, high operating temperatures and long cleanup times in saponification may decompose higher chlorinated PCBs, particularly in the presence of trace metals [113].

Several studies have utilized saponification methods to determine PCBs in environmental samples. Due to poor recoveries for higher chlorinated biphenyls in laboratory studies of sewage sludge, it was found that during degradation of PCBs, chlorines were replaced by ethoxy groups under hot saponification conditions if aromatic compounds contain four or more number of chlorine atoms on one ring. Therefore, extra care should be exercised while dealing with such PCB congeners for the saponification or else other cleanup procedures must be examined to avoid saponification [114]. Even though, % degradation is very low, this process has significant influence on the analysis of non-ortho chlorinated PCBs. The small % degradation of highly chlorinated PCBs produces high bias in the concentrations of non-ortho chlorinated PCBs, which forms after the degradation of higher chlorinated mono-ortho substituted PCBs [115]. Therefore, a simple, sensitive and rapid saponification-HSSPME procedure was adopted for the extraction of PCBs from milk samples. The method provided lower detection limits of < 1.0 ng/mL with improved extraction efficiency and reduced background [116].

6. Advanced techniques for the characterization of PCBs

In recent years, a battery of analytical procedures was used to enhance sensitivity and selectivity as well as to minimize the analysis time for PCBs, but each reported procedure has its own advantages and limitations. The resources and equipments needed for analysis vary with the methods [117]. To the best of our understanding, environmental levels, fate and transportation of PCBs, it is necessary to develop

analytical methods with possible lower detection limits. Therefore, a detailed description on exposure, accumulation, fate and transport of PCBs is presented in this review. Another key factor that must be considered during the method development for PCBs is their identification in human and environment samples. Hence, it is necessary for the methods of analysis to produce data that could confront the scrutiny in a court of law [118]. Moreover, the quick progress in the preparation of reference materials and updated high-quality standards contributed to the significant developments of more precise and accurate analytical methods. An overview of the cutting edge analytical techniques and their utilization in the risk assessment of PCBs is presented in Fig. 5.

The most common and generally considered techniques for the identification of PCBs are gas chromatography with electron capture detector (GC-ECD) and electron ionization mass spectrometry (GC-MS). In recent years, industries have added the most sensitive instruments for analyzing PCB congeners, among which high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS) is the most important hyphenated technique [119]. A collection of mass spectrometers such as magnetic sector, orbitrap, quadrupole (Q-MS), ion traps (IT-MS), time-of-flight (TOF-MS) and triple quadrupole (QqQ-MS) detectors are currently available and are connected to either GCs or LCs. However, the choice of mass detector depends on the adopted separation technique, required information, specificity governed by regulations and mass accuracy [120]. Currently, MS is the most preferable detection technique that is best suitable for the analysis of PCBs in a variety of environmental and biological matrices. Therefore, this section described the contemporary state-of-the-art analytical procedures for the analysis of different PCB congeners mentioning the recently reported methods as case studies.

6.1. Liquid chromatography

HPLC coupled with UV detector is the most conventional and popular chromatographic technique for the analysis of PCBs, in which high performance columns that are packed with 3–10 μm range particles have been used as stationary phases [121]. Reverse phase HPLC is probably the most versatile and frequently used analytical technique for the analysis of PCBs using C18 columns [122]. Next, the latest and most popular detection in LC is MS, popularly known as LC-MS. It is the most powerful analytical technique that is useful in the analysis of organic compounds combining the resolving capacity of liquid chromatography with detection specificity of mass spectrometer. The LC-MS data furnish information regarding structure, molecular weight, identity and quantity of specific sample components and is being upgraded effectively over the past two decades [123]. These instruments have been revolutionized from complex, expensive, highly advanced research tools to economical, robust, easy-to-use routine detectors.

LC-MS is most appropriate technique to characterize large, polar, ionic, thermally unstable and nonvolatile compounds. Some of these compounds can be made susceptible to GC-MS analysis after derivatization, but LC-MS does not require such time-consuming chemical transformations [124,125]. Also, LC-MS is capable of analyzing samples that do not contain chromophores, but using both UV detector and MS detectors makes the LC more effective than stand alone. For instance, UV spectra of different metabolites or degradants are alike and may have complexity in detecting an impurity alone using UV spectra. Also, it is possible for the impurities to contain similar mass, particularly lower molecular weight compounds. But it is uncommon, for any two components to contain identical UV spectra and mass value [126]. LC-MS is suitable to quantify at low detection limits up to 1000 times higher than UV detection. There are several HPLC and LC-MS/MS methods established for the quantification of PCB congeners from various sample matrices and all of them are discussed here. Further, a list of representative liquid chromatography methods reported for PCBs are presented in Table 3 [127–136].

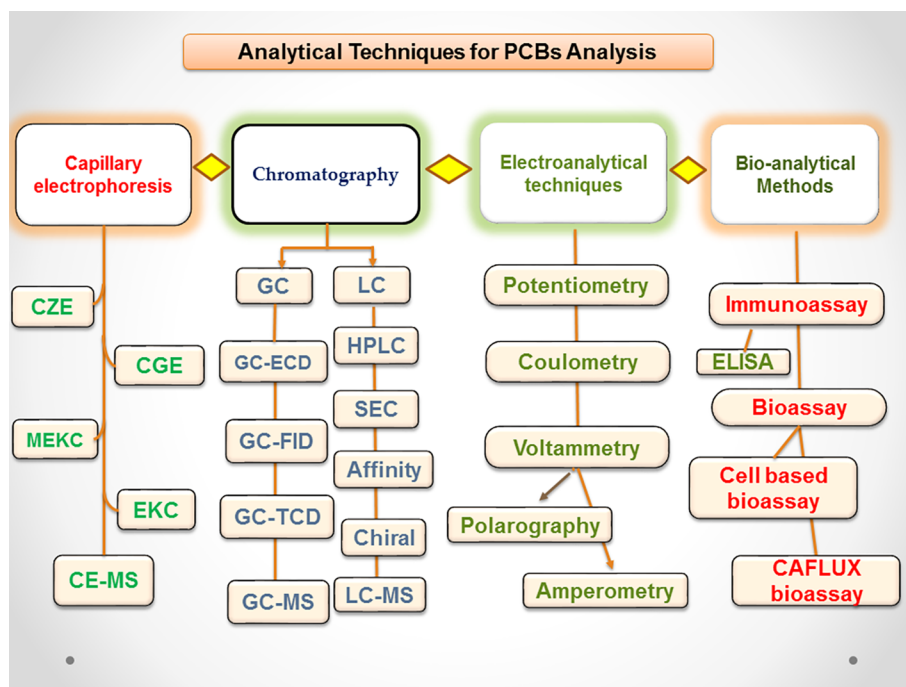Recently, a method was developed for the qualitative and

Fig. 5. A list of advanced analytical techniques available for the analysis of PCBs.

quantitative analysis of multiple EDCs including PCBs from two atmospheric phases using LC-MS/MS and GC-MS/MS following the method validation with spiked sorbents. The authors concluded that the developed method could be useful to monitor seasonal alterations in indoor air pollution possibly at lower LOQ value i.e., < 0.5 ng/m^3 [127]. Next, few methods have been established for the analysis of hydroxylated PCBs from human serum, urine and aqueous samples. A selective and sensitive online SPE procedure was applied for sample cleanup and subsequent analysis of OH-PCBs by LC-MS/MS. The LOD value of 0.1 ng/mL with extraction recoveries between 79% and 125% were observed for all the OH-PCBs. These methods consumed a minimum amount of solvent and samples as well as reduced sample preparation steps and trace concentrations of OH-PCBs in urine, plasma and water without any derivatization [128–130]. Further, a validated multi-residue analytical method was also developed and tested for *Holothuria Tubulosa* specimens and marine sediments to determine 36 organic compounds including PCBs. A Box-Behnken design was utilized to select the significant variables that affected the extraction and cleanup processes. The method was employed for the real sample analysis and found higher bioaccumulation of certain pollutants in *Holothuria* collected at Granada coast (Spain) [131].

In another study [132], biodegradation of PCBs collected from different regions of China was investigated, where seven Pseudomonas strains were identified to compare the potential of bacteria from different regions to degrade biphenyls. The best degradation was obtained using the collected strains, while the left-over concentrations were measured by HPLC [132]. Additionally, several automated HPLC methods were used for the isolation of PCBs, PCDDs and PCDFs from various sample matrices including fish tissues employing a commercial PGC column.

All the reported HPLC methods have provided better results for samples processed from a variety of matrices. These data suggested that sulphur content in sediments often create problems during the analysis of PCBs and PACs by GC-MS. However, the removal of sulphur is no longer difficult by HPLC analysis as it can be eluted along with aliphatic/monoaromatic fraction. The results showed that HPLC methods are beneficial for the identification of PCBs following the number of substituted *ortho* chlorine atoms attached to biphenyl structure

[133–136].

6.2. Gas chromatography

GC is one of the most important analytical tools and two commonly used injection techniques in GC for the separation of PCBs are split/splitless and on-column injection [137,138]. The split/splitless injectors usually vaporize the samples dissolved in suitable organic solvent under increased temperature. Liners packed with light silylated glass wool may promote the performance, but there is a chance for degradation of some chlorinated compounds including PCBs [139]. Recently, temperature-programmed or pressure-programmed injection techniques are found to be more prominent. Although these techniques are advantageous in terms of increased injection volume without associated negative effects, but the recently developed open tubular capillary columns, called high-resolution gas chromatography (HRGC) is quite useful [140].

ECD is the typical detector that is more convenient for the analysis of PCBs, but in recent years, MS techniques have replaced the use of ECD due to many advantages. GC-MS integrates two powerful techniques that help to identify analytes with lower LODs and are effective for quantitative analysis. Low-resolution mass spectrometry (LRMS) delivers sufficient sensitivity for the analysis of biota and sediment samples for PCBs. For the analysis of DL PCBs, HRMS is more beneficial considering their small concentrations. However, LRMS is particularly useful in sample screening [141].

Certain co-planar PCBs with known toxicity can be analysed with HRMS techniques as reported for the analysis of furans and dioxins in environmental samples. HRMS offers lower LODs for PCB analytes, but it needs additional sample cleanup and special instrumentation [142]. The MS in electron-capture negative ionization (ECNI) mode is about 10-fold more sensitive than the ECD for pentachlorinated to decachlorinated PCBs. After the conventional GC-MS, the utility of ion trap with its MS^2 option (GC-ITMS) is also a preferred technique for PCBs identification [143], since it is an economical and alternative technique to HRMS. The recent efforts for the analysis of PCBs using GC methods are listed in Table 4 [144–163].

Most recently, several GC-MS methods have described the analysis

Table 3
Compilation of liquid chromatography methods recently reported for the analysis of PCBs.

Analytes	Extraction method	Analytical technique	Sample type	Analytical column	LOD	Reference
PCBs, PAHs	ASE	LC/MS/MS	Indoor air	Zorbax Eclipse XDB C18 1.8 μm, 4.6 mm × 50 mm	0.5 ng/m^3	[127]
PCBs	SPE	LC/MS/MS	Urine	Kinetex (PFP) 2.6 μm, 4.6 mm × 150 mm	0.01 ng/mL	[128]
PCBs	SPE	LC/MS/MS	Plasma	Kinetex (PFP) 2.6 μm, 4.6 mm × 150 mm	0.01 ng/mL	[129]
PCBs	MISPE	LC/MS/MS	Water	SunFire C18 5.0 μm, 4.6 mm × 250 mm	3.0–28 pg/L	[130]
EPPs, PCBs	LLE	LC/MS/MS	Sediment	HALO C18 I2.7 μm, 4.6 mm × 50 mm	0.01–0.4 ng/g	[131]
PCBs	LLE	RP-HPLC	Water	Kromasil 100–5-C18 5.0 μm, 4.6 mm × 150 mm	0.25 mg/mL	[132]
PCBs, DDE	LLE	RP-HPLC	Mammals	Florisil columns 2.6 μm, 4.6 mm × 150 mm	2.5 μg/g	[133]
PCBs, PCDFs	LLE	RP-HPLC	Fish	Hypercarb (PGC) 5.0 μm, 4.7 mm × 100 mm	9–20 ng/g	[134]
PCBs, PACs	Soxhlet extraction	RP-HPLC	Fish	Millipore 5.0 μm, 10 mm × 250 mm	2–100 ng/g	[135]
PCBs	LLE	RP-HPLC	Herring oil	Amoco PX 21 2–10 μm, 4.5 mm × 250 mm	9–50 ng/g	[136]

of PCB congeners in serum samples. The GC-MS results are comparable to GC-HRMS [144]. In another method used for the identification of PCBs and PBDEs in serum samples of livestock in the US, higher concentration of PCBs in sera of goats and sheep was found than in the cattle. This confirmed the exposure of livestock to PCBs, but it is still uncertain as to where this exposure is originated [145]. Next, two methods have been reported for the evaluation of PCDD/Fs and DL PCBs from air levels and transformer oils using GC-MS. The presence of PCBs in the transformer oils has been confirmed and the authors found the existence of PCBs in air samples [147,148].

Further, few methods have been reported for the analysis of PCBs from different sediments. In all these methods, the sediment cleanup processes were carried out by SPE and SBSE followed by analysis using GC-MS. The authors concluded that different adsorbents used in SPE were effectively useful to recover PCBs from sediments, and GC-MS could successfully characterize the PCBs [149,150]. Different GC-MS procedures have been reported for the analysis of PCBs in different fish samples. The authors further examined PCBs concentration in fish samples collected across the world and estimated non-targeted contaminants in fish samples such as OCPs and PAHs [151–155].

Recently, two analytical methods have been reported to examine PCBs in different food samples including milk, coffee and meat products [156,157]. In one of the methods, ionic liquid-based *in-situ* dispersive liquid-liquid micro-extraction (DLLME) was used for the extraction and subsequent analysis using HS-GC-ECD-MS. This method is rapid and simple compared to conventional SPME-GC-MS methods. In addition to the GC-MS methods, there are several GC-ECD methods reported for the analysis of PCBs from sediments, serum, fish tissue and indoor air samples [158–163]. All the developed methods were successfully validated for their applicability for routine analysis of PCBs. A study utilized narrow-bore gas chromatography column for the separation of PCBs and achieved the sensitivity and recoveries equivalent to conventional GC-ECD. This method minimized the analysis time by 3-folds and could be an effective alternate for rapid analysis of PCBs in sediment samples containing moderate to high concentrations of PCBs [159].

6.3. Capillary electrophoresis

CE enables the separation of charged molecules based on their electrophoretic mobility when subjected to applied voltage. It provides molecular detection after the separation by a light source and detector, and the systems are capable to handle high voltages without overheating the samples [164,165]. CE offers certain advantages over other analytical techniques like HPLC and GC in terms of speed, cost of analysis and ease of method development. However, the separation of neutral compounds was restricted until the evolution of micellar electrokinetic chromatography (MEKC) in 1984. Now, the evolution of increasingly higher number of micelles and other pseudo-stationary phases proved CE as a versatile technique to separate almost all kinds of molecules. MEKC is a typical capillary electrophoresis technique, but its poor selectivity restricts its applicability for the separation of PCBS due to their hydrophobicity [166]. Especially, the problem is critical during the separation of positional isomers of higher chlorinated PCBs. But, the use of cyclodextrins in MEKC provides better separation efficiency for less chlorinated PCBs [167].

There are several CE methods described for the chiral separation of PCBs using surfactants as modifiers. In all the methods, MEKC was employed to enhance the detection sensitivity as presented in Table 5 [168–174]. The cyclodextrin (CD) modified MEKC methods have been reported for the separation of electrically neutral and hydrophobic PCB congeners, in which CD is mixed with micellar solution. In CD-MEKC methods, a water-insoluble hydrophobic solute was diffused between CD and micelles. When the solute is presented in CD cavity, it travels with the electroosmotic velocity; likewise, when it is incorporated into the micelle, it travels with the micellar velocity. Therefore, differential position of the solution between CD and micelles facilitates the separation [168]. A CD-MEKC method was developed for enantiomeric separation of 19 chiral PCBs using 2-morpholinoethanesulfonic acid (MES) as buffer and carboxymethylated γ-cyclodextrin (CM-γ-CD) as pseudostationary phase in the presence of β-cyclodextrin (β-CD) or permethylated β-cyclodextrin (PM-β-CD) [169]. Also, a small amount of urea was incorporated to enhance the solubility of CDs and PCBs in

Table 4
The summary of various gas chromatography based analytical procedures recently developed for the analysis of PCBs.

Analytes selected	Extraction method	Analytical technique	Sample type	Analytical column	LOD	Reference
PCBs	LLE	GC/MS GC/HRMS	Serum	HP-5 ms Ultra Inert 0.25 µm, 30 m × 0.25 mm	1.9–20 pg/g	[144]
PCBs PBDEs	SPE	GC/MS	Serum	BR-5 ms column 0.25 µm, 15 m × 0.25 mm	0.094 ng/mL	[145]
PCBs, Pesticides	SPE	GC/HRMS GC/MS/MS	Serum	BPX5 – SGE column 0.25 µm, 30 m × 0.25 mm	0.11–30 pg/g	[146]
PCBs	Soxhlet extraction	HRGC/HRMS	Air	VF-Xms capillary 0.25 µm, 60 m × 0.25 mm	0.01 ng/sample	[147]
PCBs	SPE	GC/MPI/MS	Oil	BD5 – MS column 0.25 µm, 30 m × 0.25 mm	0.03–4.0 ng/mL	[148]
PCBs	SPE	GC/MS	Complex	DB5 – MS column 0.25 µm, 60 m × 0.25 mm	0.4–8.6 pg/g	[149]
PCBs, PCNs	SBSE	GC/MS	Sediments	HP5 – MS column 0.25 µm, 30 m × 0.25 mm	0.01–0.03 ng/g	[150]
PCBs, PCNs	LLE	GC/MS GC/HRMS	Fish	DB5 – MS column 0.10 µm, 60 m × 0.25 mm	0.03–0.3 pg/µL	[151]
PCBs	Soxhlet extraction	GC/MS	Fish	TR-5MS column 0.10 µm, 30 m × 0.25 mm	0.06–0.15 ng/g	[152]
PCBs	Soxhlet extraction	GC/MS	Dogfish	DB5 – MS column 0.25 µm, 30 m × 0.25 mm	1.0–10 ng/g	[153]
PCBs, POPs	Soxhlet extraction	GC/HRMS	Fish	ZB-5MS column 0.25 µm, 60 m × 0.25 mm	0.01–200 pg/g	[154]
PCBs, PCCDs	MIP	GC/TOF/MS	Tissues	Rtx-5MS fused silica 0.25 µm, 60 m × 0.25 mm	0.02–0.1 pg/g	[155]
PCBs	DLLME	GC/MS/ECD	Tissues	HP-5 ms Ultra Inert 0.25 µm, 20 m × 0.25 mm	2.5–10 ng/L	[156]
PCBs	Ultrasonic extraction	GC/MS	Meat	DB-5MS 0.25 µm, 30 m × 0.25 mm	0.14–0.38 ng/g	[157]
PCBs	Ultrasonic extraction	GC/ECD	Sediments	VF-5MS 0.25 µm, 30 m × 0.25 mm	0.1–0.001 ng/m	[158]
PCBs	SPME	GC/ECD	Sediments	HP-5 narrow-bore 0.1 µm, 10 m × 0.1 mm	0.5–1.3 ng/g	[159]
PCBs	LLE	GC/UV	Water	Rtx-PCB columns 0.25 µm, 30 m × 0.25 mm	100–150 pg/g	[160]
PCBs	ASE	GC/ECD	Food	Rtx-5MS 0.25 µm, 30 m × 0.25 mm	0.18–0.37 ng/mL	[161]
PCBs	SPE	GC/ECD	Air	BP-1 (HP) 0.25 µm, 30 m × 0.25 mm	2.0–40 pg/m^3	[162]
PCBs	SPE	GC/ECD	Serum	DB-5 capillary 0.01–0.3 ng/mL 0.25 µm, 60 m × 0.25 mm	0.01–0.3 ng/mL	[163]

aqueous buffer. The PCBs were separated enantiomerically below 12 min with 50 mM MES buffer containing 10 mM β-CD, 20 mM CM-γ-CD and 2.0 M urea at 45 °C and 20 kV applied voltage [170,171].

In majority of methods, superior selectivity was achieved using β-CD as a buffer additive over the γ-CD. A method reported the suitability of polymeric surfactant polysodium undecyl sulfate (poly-SUS) for separating PCBs through MEKC in the absence of CDs [172]. Next, two MEKC methods have been described for the identification of PCBs using vortex-assisted liquid-liquid-liquid microextraction (VALLLME), a rapid, sensitive and novel micro extraction technique. The main advantage of VALLLME is its aqueous-based extraction, which renders

analysis by direct HPLC or CE techniques. In another method, two separation techniques have been examined for the effective analysis of a wide range of EDCs in the environment. The results proved that CE in MEKC technique using CD modifier has displayed better efficiency for the determination of alkylphenol degradation products [173,174].

6.4. Bioanalytial methods

The difficulty in sample preparation, necessity for higher selectivity and ultra-low detection for the analysis of PCBs is expensive than other analytical methods. Therefore, low-cost and alternative analytical

Table 5
An overview of capillary electrophoresis methods recently established for the analysis of PCBs.

Analytes selected	Sample type	Analytical technique	Analytical column	Surfactant	Reference
PCBs	Spiked	CE-MEKC	Fused Silica Tube L 50/58.5 cm; i.d. 50 μm	Cyclodextrin	[168]
PCBs	Spiked	CE-MEKC	Fused Silica Tube L 50/57 cm; i.d. 50 μm	Cyclodextrin	[169]
PCBs	Spiked	CE-MEKC	Fused Silica Tube L 50/65 cm; i.d. 50 μm	Cyclodextrin	[170]
PCBs	Spiked	CE-MEKC	Fused Silica Tube L 50/58.5 cm; i.d. 50 μm	Cyclodextrin	[171]
PCBs	Spiked	CE-MEKC	Fused Silica-Polyimide Tube L 40/47 cm, i.d. 50 μm	Poly-SUS	[172]
PCBs	Plasma	CE-DAD LC-UV	C18, Hypersil ODS-3 L 250 cm, i.d. 5.0 μm	N/A	[173]
PCBs, EDCs	Bio-solids	CE-MEKC GC-MS	Silica, L 50/57 cm; i.d. 50 μm L 30 m × 2.5 mm; i.d. 0.25 μm	Cyclodextrin	[174]

methods have been developed. Bioassay and immunoassay methods are best suitable to analyze food samples and hazardous waste samples, which can minimize the cost by 50% or more in addition to their rapid sample analysis capacity. But, the major obstacles of these methods are their inadequacy to use labeled internal standards for recovery corrections and the estimation of congener profiles for source distribution. Like standard addition quantitative approach, spiked samples allow the estimation of recoveries to overcome this problem. Immunoassays supplement conventional analysis due to their enhanced sensitivity, competitiveness, ease of performance and discretionary advanced instruments. They depend on precise binding tendency of antibody to PCB analyte, which are particularly helpful when screening large number of samples in parallel to the single analyte in a short time [175].

Enzyme-linked immune-sorbent assay (ELISA) methods have been commercialized for the analysis of PCBs. ELISA has specific binding to antibodies to PCBs, and requires little effort for sample cleanup/extraction and the methods are rapid and economical compared to traditional cleanup methods. This technique is particularly useful for the detection of PCBs from environmental samples containing lower concentrations of 0.5–1.5 ppm [176]. However, this level of sensitivity is inadequate to monitor PCBs in environmental samples, but it can be used in highly contaminated sites to assess the effectiveness of sediment dredging operations. For over the past decade, many immunoassay techniques have been developed for screening PCBs in soils. Several immunoassay methods for PCBs screening are presented in EPA method 4020. These are called as competitive ELISA methods, and the test kits are available for PCBs and other organic compounds. However, these methods have several drawbacks as only total PCBs can be identified, but no individual identification of specific PCB congener is possible [177].

The results of bio/immunoassay methods are comparable with standard GC-HRMS methods in terms of accuracy, sensitivity and selectivity. The results reported for the analysis of PCBs using ELISA methods are documented in Table 6 [178–184]. Also, several analytical methods have been reported to evaluate toxic equivalents (TEQs) of DL PCBs in fish samples. The presence of PCBs was identified and quantified using ELISA, suggesting that ELISA kits are appropriate to evaluate the TEQs of DL PCBs in fish samples. Also, comparative study with conventional GC-ECD and GC-MS analysis pointed-out the suitability of ELISA methods to screen TEQ of DL PCBs in fish samples. The results concluded that concentrations of PCBs derived by ELISA depend on the degree of chlorination, and it is essential to eliminate the extraneous lipids to minimize matrix effects in the immunoassay [178–180].

Several ELISA methods have been directed to characterize PCBs in soil and sediment samples. ELISA methods have been compared with GC-ECD methods and found very good agreement. The PCB-126 concentrations derived by ELISA were greater than the sum of 12 co-planar PCBs produced by GC-MS methods. Therefore, SPLE-ELISA methods are beneficial for qualitative and quantitative analysis of PCBs in soil and sediment samples. Also, these methods have been applied successfully to evaluate PCBs in real soil samples and it was suggested that ELISA methods could be transferred to another laboratory and adapted to other matrices [181–184].

7. Analytical difficulties and improvements

Analytical approaches for the evaluation of PCBs have been under investigation for over the past four decades. Although, the investigation of PCBs in different sample matrices is a developed field of environmental analytical chemistry, the primary methods remain the same for the past two decades except the implementation of MS detectors in place of conventional detectors. However, the contemporary options particularly, the use of high resolution mass spectrometry and isotope labeled standards in the analysis of routine PCBs are overpriced, which has restricted the researchers from developing countries as evidenced by the lesser number of publications on PCBs from Africa, South Asia and South America [185]. Therefore, it is essential to develop economical methods applying new strategies using low solvent use, SPME, and microscale glassware to encourage researchers from the developing countries where they have limited analytical budgets.

The analysis of PCBs in surface waters containing wastewater effluents is an extremely complex task. In such samples, due to the presence of co-eluting compounds, matrix effects like ion-suppression and change in retention times may suppress the detection of PCBs even with the highly advanced MS detectors. As a result, it is often essential to extract PCBs from complex sample matrices. Although, several advanced sample cleanup and extraction procedures have been evolved recently, only a few extraction/cleanup techniques are suitable for isolation of PCBs from the complex matrices [186]. Several standard cleanup methods are not relevant to the analysis of PCBs due to background interferences. Further, co-extracted compounds in environmental samples are structurally identical to the compounds of interest making their removal difficult. Therefore, it necessary to ensure the removal of all interfering compounds using the best available cleanup procedures. Besides the sample complexity and interferences may also arise from the laboratory and field contamination including from

Table 6
A list of ELISA methods recently reported for the analysis of PCBs.

Analytes selected	Sample type	Extraction method	ELISA kit	Analytical technique	LOD	Reference
PCBs	Fish	Soxhlet extraction	EnBioTec	HRGC/HRMS SGE HT-8 column	50 pg/g	[178]
PCBs	Soil,	SPLE	Aroclor ELISA PCB ELISA	GC-MS DB-XLB column	10 ng/g	[179]
PCBs	Soil	Soxhlet extraction	PCB ELISA	GC-ECD Agilent DB5 column	2.5 ng/mL	[180]
PCBs	Mussel tissues	Soxhlet extraction	PCB rapid assay	GC-ECD Agilent HP5-MS column	0.08 ng/mL	[181]
PCBs	Fish extracts	Column chromatography	EnviroGard	GC-ECD Agilent DB5	37–50 ng/g	[182]
PCBs	Soil	SFE	PCB ELISA	GC-ECD Agilent DB-608, DB-1701	1.0 µg/g	[183]
PCBs	Soil	Soxhlet extraction	Sheep polyclonal antibody	GC-ECD Quadrex 007-02 column	0.5–1.29 µg/g	[184]

reagents, solvents, glassware, cleaning solutions, plasticizers and other PCB containing chemicals during the sample processing steps. For instance, the use of plastic apparatus may contribute phthalate esters that can create interferences during sample preparation of PCBs [187]. Further, it is highly recommended to subject the samples to sulfuric acid cleanup that are proposed for PCBs analysis. Because, sulfuric acid cleanup technique removes most other organic compounds including many single component organochlorine or organophosphorus pesticides as well as phthalate contaminants, and this would potentially interfere with the quantitation of PCB congeners [188].

Furthermore, some samples containing PCBs may not appear in the analysis due to weathering or degradation, resulting in unclear matching with the PCB congeners. In such cases, the analytical laboratory needs to provide chromatograms of the affected samples in the laboratory report to further solve the issue. The data user must be aware that additional sampling or other analysis may be more appropriate to accurately quantify PCB congeners [189]. Additionally, quantification of PCBs has been often carried out by aroclor mixture or individual congener standards though a broad range of commercial PCB mixtures are available with varying degrees of mean chlorination. Therefore, shift in congener ratios within a given commercial mixture may cause congener calculation errors because of batch-to-batch production variability. This drawback may create significant bias in the results often over estimating the PCB measurements [190,191].

8. Remediation approaches for PCBs

In the past few years several chemical, physical and biological remediation technologies have been exploited for the PCBs contaminated water, soils and sediments. This section describes the traditional remediation approaches including thermal incineration, phytoremediation, microbial degradation along with the new insights that have appeared from the recent studies on PCBs remediation such as supercritical water oxidation (SCWO), ultrasonic radiation, activated carbon, nanoscale zerovalent iron (nZVI) based reductive dehalogenation and combined nZVI technologies are overviewed. Some of these methods are still in the initial developmental stage, thereby necessitating further research attention [192].

Traditionally, thermal destruction is a widely used approach for the remediation of PCBs, in which PCBs react with oxygen to form CO_2, water and HCl. However, PCBs are the precursors of PCDD/Fs and may produce high amount of more toxic PCDD/Fs on thermal treatment processes such as fire or incineration [193]. Usually, the formation of

PCDD/Fs takes place when cooling the gasses after thermal destruction. It is the formation reaction that depends on gas temperature, existence of chlorine and presence of a catalyst. However, modern incinerators that can withstand high temperatures and provide dioxin removal facility have removed the problem of dangerous emissions. In addition, advanced incineration plants are constructed with the dioxin removal facilities like selective catalytic reduction [194]. Further research has shown that presence of sulphur dioxide minimize the formation of PCDD/Fs during incineration process, because sulphur can scavenge chlorine molecules in the presence of moisture to form SO_3 and HCl. Also, the combination of high temperatures, available oxygen, high heating value fuel and long residence times prevent the formation of PCDD/Fs. For instance, temperatures higher than 700 °C can cause 99% destruction for PCBs without the formation of PCDD/Fs [195].

Photolysis is another possible option for the remediation of PCBs. Recently, several new catalysts have been developed for photodegradation of PCBs. Among all, TiO_2 based catalysts such as carbon-modified titanium dioxide (CM-n-TiO_2) nanoparticles, nafion coated TiO_2 particles (Nf/TiO_2) and platinum loaded TiO_2 (P25) catalysts showed enhanced photocatalytic efficiency [196]. Additionally, graphitic carbon nitride (g-C3N4) is a non-metal π-conjugated polymeric semiconductor that was reported for the photocatalytic degradation of PCBs owing to its distinct properties of thermal stability, low-cost, reusability, non-toxicity, molecular tunability, optoelectric property and visible light responsive nature. Further, TiO_2/g-C_3N_4, graphene/g-C_3N_4, ZnO/g-C_3N_4, MoS_2/g-C_3N_4, Bi_2WO_6/g-C_3N_4 are the supported photocatalysts that have displayed stupendous photocatalytic property compared to metal-free g- C_3N_4 photocatalysts [197].

Next, the destruction of PCBs by Fenton's reaction is an advanced oxidation process (AOP) that conducts degradation in aqueous solutions. In Fenton's reaction, H_2O_2 combines with Fe^{2+} to generate hydroxyl radicals (HO˙) in the presence or absence of light [198]. However, it is widely recognized that ˙OH are effective only under acidic conditions in most cases. Compared to ˙OH radicals, sulfate radicals ($SO4^{˙−}$) are the more powerful oxidants with high redox potential (2.5–3.1 V) and a wide pH range of 2.0–8.0 [199]. Also, high aqueous solubility, stability in subsurface, low-cost and benign end products proved $SO4^{˙−}$ as good choice among AOPs for remediation of PCBs contaminated soil and groundwater. However, the presence of chloride ion ($Cl^−$ is a major reaction product of chlorinated organic contaminants on oxidation with $SO4^{˙−}$) decrease the reactivity of sulfate radical system [200]. Recently, different $SO4^{˙−}$ AOPs were reported for the degradation of PCBs, in which sulfate radicals were generated by

a variety of metals including Fe(II), Fe(III), V(III), V(IV) and V(V) and some nanomaterials. Most of the $SO_4^{\cdot-}$ systems showed efficiency towards the removal of PCBs [201].

Microbial remediation is another potential and green approach in which microorganisms (e.g., bacteria, fungi) are vital to degrade, breakdown, transform and to eliminate the PCB contaminants. The biodegradation of PCBs takes place by two distinct microbial mediated mechanisms i.e., aerobic biodegradation and anaerobic reductive dechlorination. The position of chlorine atoms on biphenyl rings and degree of chlorination may influence the biodegradability of PCB congeners. PCBs with chlorine atoms at *para* positions may undergo biodegradation more preferentially. Aerobic biodegradation involves the oxidative destruction of PCBs by a series of degradation intermediates, whereas anaerobic reductive dechlorination of PCBs involves the expulsion of chlorine atoms in the absence of oxygen. Considering the formation of PCDD/Fs, energy consumption and removal efficiency, reductive dechlorination would be more competent approach for the remediation of PCBs [202]. Different microorganisms that are capable to degrade PCBs were isolated from the soil and freshwater sediments, but hardly few strains are capable to sustain against higher chlorinated PCBs. At first, higher chlorinated PCBs undergo reductive dechlorination under anaerobic conditions and then lower chlorinated compounds proceed to mineralization under aerobic conditions. Although several bacteria are capable to degrade PCBs, their survival and capacity of degradation is quite challenging [203].

Few microorganisms such as *Arthrobacter, Pseudomonas, Rhodococcus* and *Burkholderia* can perform complete mineralization of BP and some PCBs. But, PCBs with higher chlorines exhibit more resistance to degradation and only few strains such as LB400 and *Alcaligenes eutrophus* H850 containing 3,4-dioxygenase are capable to degrade by attacking stable double ring *ortho*-substituted congeners. Even though LB400 is a potential degrader, it has low efficiency compared to *Pandoraea pnomenusa* B356 towards double *para* substituted compounds [204]. Recently, a study demonstrated that *Ensifer adhaerens* bacterium isolated from soil was able to degrade PCBs in contaminated water by combining with biosorption process [205]. In another study, degradation of 9 PCB congeners was reported by combining ozonation and biological method using *Achromobacter xylosoxidans*. Overall, 94% removal for the mixture of 9 PCBs was reported by the combination of biological and chemical methods, i.e., ozonation and *Achromobacter xylosoxidans* [206].

Phytoremediation is another eco-friendly approach that is useful for the removal of PCBs and other chlorinated pollutants in soil, water and sediments with minimum environmental impacts. The process can be outlined in two steps viz., biodegradation of pollutants with microorganisms in soil or groundwater and uptake into plant tissues by their roots followed by their transformation with plant enzymes or direct volatilization into the atmosphere. Various plant species have shown the potential to degrade PCBs including *Medicago sativa* (alfalfa), *Lathyrus sylvestris* (everlasting pea), *Cucurbitaceae* (cucurbits), *Lespedeza cuneate* (Chinese bushclover), *Phalaris arundinacea* (reed canary grass*)*, *Salix alaxensis* (Alaska willow) *Sparganium* (bur-reed), and *Picea glauca* (white spruce) [207]. In a study, *Medicago sativa* has shown 31.4% and 78.4% of decrease in PCB soil concentrations after the first and second years of field scale phytoremediation. *Sparganium* was shown to promote the oxidation of PCBs via rhizodegradation, while *panicum virgatum* (switchgrass) and other popularly used plants have provided degradation of a high and low PCB congener mix [208].

Additionally, SCWO, activated carbon and ultrasonic radiation approaches are relatively modern and practically applied to breakdown PCBs from different contaminated sites. Studies have revealed that activated carbon showed up to 80% degradation efficiency for trichlorobiphenyl and tetrachlorobiphenyl congeners. Importantly, the combination of anaerobic bacteria (biofilm) and activated carbon as a microbial inoculum delivery system has provided outstanding progress in PCBs degradation [209].

Next, SCWO is another clean approach that takes place in water at temperature and atmospheric pressure higher than the critical point of water (647 K and 22.064 MPa). At the supercritical conditions, water lost its hydrogen bonds and starts to shift from polar solvent to non-polar solvent meaning that the solubility of PCBs increases in supercritical water. Thus, PCBs degrade at these supercritical conditions to produce CO_2, water and mineral acids as end products [210]. At the typical operating conditions of 550–650 °C temperature and 250 bar pressures, the SCWO process has achieved over 99% of PCBs degradation. Furthermore, SCWO systems at high temperatures quickly complete the oxidation of PCBs to H_2O and CO_2 without the formation of more toxic PCDD/Fs. Studies have revealed that SCWO system under alkaline conditions in the presence of excess oxygen provide more than 99% of PCBs degradation [211]. However, sticky and non-sticky solids precipitate during SCWO owing to low dielectric constant of supercritical water, which would cause fouling, plugging and erosion that makes the process more expensive.

Ultrasonic radiation is another modern remediation technique for the degradation of PCBs with high efficiency (> 90%). Several studies have examined high PCBs removal efficiency with ultrasonic radiation technology at 40 °C with a hydrazine hydrochloride/palladium catalyst [212]. Further, ultrasound-assisted chemical process (UACP) is a recent variation of ultrasonic radiation that is more efficient for PCB remediation sites. Recently, a study reported more than 97% of Aroclor 1260 degradation using a combination of ultrasonic irradiation and radical generations produced from di-tert-butyl peroxide radical initiator [213].

Additionally, utilization of zerovalent iron nanoparticles (nZVI) is a relatively new approach and is capable to overcome most of the shortcomings in PCBs remediation. Micro-sized zero-valent iron (mZVI) technology was employed for the decontamination of polluted aquifers with permeable reactive barriers (PRB) in the past two decades. In both the cases, Fe^0 acts as reducing agent and transform the contaminants being consumed in the process unlike catalysts. After the evolution of nanotechnology, extremely reactive nZVI particles have been synthesized and evaluated for the detoxification and transformation of various environmental contaminants including PCBs, organochlorine pesticides and chlorinated organic solvents in groundwater [214]. However, the results revealed limited degradation of PCBs in soils so far [215].

Recently, a new two-compartment cell was employed in combination with nZVI particles for the degradation of POPs. The results showed 83% of PCBs removal after 5 days, and the value was much greater than the reported 27% removal in 10 days with EKR/nZVI [216]. Although, reported data showed promising results for the dechlorination of PCBs using nZVI particles, they are unstable and readily lose their reducing power. However, abiotic reductive dechlorination helped to promote the long-term *in-situ* biological dechlorination after nZVI addition. Higher temperatures of around 300 °C were applied to achieve maximum efficiency in the destruction of PCBs up to 95%. It was also found that pH is the key factor in dechlorination of PCBs by nZVI, and it is reported that weakly acidic pH enhanced the rate of dechlorination [217]. A possible dechlorination pattern for PCBs by microbial, photochemical and nZVI technology is presented in Fig. S1.

The use of combined remediation technologies appears to be more effective and economical for contaminated site remediation, which is more popular in recent years. This can be accomplished using the techniques independently or sequentially. Several case studies have been reported in the literature including granular activated carbon and microwave energy [218], thermal desorption and catalytic hydrogenation [219], polymer beads followed by biodegradation of PCBs extracted with solid-liquid two-phase partitioning bioreactor [220], supercritical fluid carbon dioxide extraction with polymer-stabilized palladium nanoparticles, Pd coated iron and an aerobic bacterium, zero-valent metal catalysts [221], electrocatalytic dechlorination with Pd-loaded carbon nanotubes as cathode [222], biosurfactants and bioremediation [223], soil washing and photocatalytic degradation

using TiO_2 [224]. These studies provided encouraging results, but no field application or pilot scale has been established so far.

Recently, a new approach has been developed combining two nanomaterials i.e., activated carbon to adsorb organic pollutants and nZVI to dechlorinate PCBs prepared from pinewood sawdust along with ferric chloride as starting materials in one-step synthesis [225]. This composite has revealed effective dechlorination of PCBs at room temperature and degradation products have been identified completely. However, this porous carbon nZVI material was tested only in aqueous solutions and not studied for real contaminated soils and sediments.

9. Recommendations for future studies

The basic scientific research on PCBs in the past few years has revealed several unexpected discoveries. Mainly, the concentrations of PCBs in the environment are no longer decreasing, but in fact, they are increasing in some geographical regions [226]. PCBs have found to cause serious health effects through some unknown mechanisms rather than the established regulatory patterns. Until now, majority of research efforts concerning adverse health effects associated with PCBs was concentrated on DL PCBs. Exposure to high levels of DL PCBs may damage the liver and can cause chloracne, while chronic exposures to lower levels associate with immune dysfunction and cancer. Further, PCBs not just associate with AhR, but also involved with several nuclear receptors including PXR/CAR, RyRs, estrogen and thyroid hormone receptors [227].

For over decades of research on PCBs toxicity confirms that conventional understanding of environmental health risks associated with PCBs need to be revised. The assumption of diet as the primary route of exposure to PCBs may need to reconfigure considering inhalation as the second essential route of exposure [228]. The recent researches have delivered a convincing data that NDL PCBs are also responsible for significant environmental health risks and developmental neurotoxicity as a significant endpoint of concern. There is thus an urgent need to conduct systematic review on mechanistic literature of human and animals to determine whether current regulatory directions should be re-examined to address the developmental neurotoxicity as an endpoint of concern.

Another pressing research need is to identify specific PCB congeners that can act as developmental neurotoxins and to illustrate the mechanism(s) by which they interfere with neurodevelopment. Response to these queries will instruct the stringent approaches for evaluating risks to the developing brain associated with exposures to PCB mixtures [229]. The consequences of PCBs on adult neurotoxicity, reproductive effects, skin/teeth/bone/nails, endocrine disruption and immune dysfunction should be particularly examined as they are related to cardiovascular diseases, chronic liver and kidney diseases, diabetes, obesity, and cancer.

So far, a variety of remediation technologies have been developed in different ways to optimize the cost, cleanup times, breakdown products and environmental impacts. The efficacy of each technology is site specific as it depends on the contamination aging, soil/sediment type and geomorphologic conditions and other environmental aspects [230]. However, PCBs are intricate contaminants and a thorough knowledge on their physico-chemical characteristics is imperative to best understand their fate and transport from which the best appropriate remediation approaches can be selected. More recently, the utilization of multiple technologies is providing promising results in the remediation of PCBs, but this approach needs more data and pilot scale operations to evaluate their effectiveness. Subsequently, the successful treatment of PCBs not only acknowledged by the selection of effective remediation technology, it also needs to consider the public acceptance justifying environmental and human health impacts of the respective remediation technology, neither of which have been achieved so far [231]. Thus, it is another important issue to discover promising remediation methods for efficient PCBs destruction *in-situ* and *ex-situ* to evaluate their environmental burdens and risks associated with the implementation of the respective technology.

Furthermore, several analytical techniques are currently accessible for the analysis of PCBs present in soil, sediments, fish, food, birds and mammals, human milk and blood samples, and these methods could be performed relatively at lower costs in developing countries. Still, the accessibility to modern capillary GC coupled with ECD or MS detection for the separation and quantification of PCBs is necessary to take part in regional and international resemblance. A few emerging analytical facilities including 2D-GC and "fast GC" using GC-ECD are well suited to perform shortly in developing countries considering their low-cost and competence to support high-resolution separations for PCBs [232].

Overall, novel strategies must be developed to improve the performance of methods to be adopted in developing countries due to the budgetary concerns. However, GC-MS in selective ion mode appears to be a possible alternative to the existing conventional GC-ECD for the quantification of PCBs in complex biological matrices. The GC-MS method avoids false positives of PCB congeners that arise by the co-elution of other PCBs or environmental contaminants such as phthalate esters. In addition, GC-MS allows for accurate and cost-effective analysis for a larger list of PCB congeners. On the contrary, GC-MS is inadequate to separate PCBs having similar/identical fragmentation patterns such as PCB 132 and PCB153. It is likely that legitimate optimization of GC-MS conditions would allow further separation of these compounds. A similar scenario applies to PCBs 138, 160 and 163, which are all hexachlorobiphenyls. Therefore, a proper optimization of GC is crucial for the analysis of PCB congeners irrespective of the selected detectors [233].

10. Concluding remarks

PCBs are the most important environmental hazardous pollutants controlled by Stockholm Convention of POPs and categorized in OSPAR List of Chemicals for Priority Action owing to their toxicity, persistence and bioaccumulation potential. Indeed, PCBs invade into the environment by a variety of human activities, but it is hard to identify their emission sources and media of transportation. The consumption of PCBs contaminated sediments by biota at water-sediment interface introduces PCBs into the food chain. PCB transfer following the "grasshopper effect" evaporates from soil to air at warm conditions and falls on the earth miles away when temperatures cool. Therefore, PCBs have been identified nearly in all environmental matrices such as on surface of groundwater, soil and sediments, indoor and outdoor air, food and living organisms, human milk and blood. This review describes the fate, transport and their exposure on human, environment and biota.

Cleanup of PCBs from a variety of complex sources is a laborious procedure that generates huge amount of waste. Therefore, various sample extraction methods have been highlighted. In addition to simple solvent extraction, there are several advanced extraction methods available including SPE, SOX, SPME, SBSE, USE, SFE, MSPD, ASE, MAE and Soxhlet extraction for the trace pollutants. Destructive methods such as saponification, oxidative dehydration using sulfuric acid and non-destructive methods such as GPC, adsorption columns and dialysis techniques have been discussed to eliminate lipid content. Next, the sample preparation and extract of PCBs, latest sample injection techniques, and suitable analytical columns and standards have been described considering the latest reported methods as case studies.

Although, the analysis of PCBs and other dioxins like pollutants in various environmental samples is difficult to perform by testing laboratories, the latest analytical technologies and guidance bestowed in this review enables the analysis to be easier and encourage the researchers to carry out the analysis using advanced analytical techniques. For the past few years, sensitive analytical methods have been established to determine PCBs from various sample matrices. Advanced techniques including MEKC, ELISA and bioassay have also been evolved for the trace analysis of PCBs in food products. This review discussed

the analytical methods available for monitoring PCBs in a broad array of matrices including water, solids (soils and plant materials), and biota (fish and animal tissue). GC-ECD is more beneficial for the analysis of these compounds. ECD provides higher sensitivity to these electro-negative compounds and results extremely low detection limits. Finally, however, the complete avoidance of PCBs from the atmosphere is a serious and pandemic problem that has plagued researchers for over several decades. More research efforts are still needed to resolve this formidable problem of modern society in order to create a greener and safer environment.

Conflict of interest

All authors declare no conflicts of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2018.09.205.

References

[1] Q. Zhang, Y. Guo, H. Mengyu, L. Hui, G. Cheng, Degradation of selected polychlorinated biphenyls by montmorillonite clay-templated Fe^0/Ni^0 bimetallic system, Chem. Eng. J. 276 (2015) 122–129.
[2] R.F. Seegal, E.F. Fitzgerald, E.A. Hills, M.S. Wolff, R.F. Haase, A.C. Todd, P. Parsons, E.S. Molho, D.S. Higgins, S.A. Factor, K.L. Marek, J.P. Seibyl, D.L. Jennings, R.J. McCaffrey, Estimating the half-lives of PCB congeners in former capacitor workers measured over a 28-year interval, J. Expo. Sci. Environ. Epidemiol. 21 (2011) 234–246.
[3] N.M. Zhu, Y. Li, F.S. Zhang, Catalytic dechlorination of polychlorinated biphenyls in subcritical water by Ni/Fe nanoparticles, Chem. Eng. J. 171 (2011) 919–925.
[4] N.M. Zhu, C.F. Wang, F.S. Zhang, An integrated two-stage process for effective dechlorination of polychlorinated biphenyls in subcritical water in the presence of hydrogen donors, Chem. Eng. J. 197 (2012) 135–142.
[5] L. Wolska, A. Mechlinska, J. Rogowska, J. Namiesnik, Sources and fate of PAHs and PCBs in the marine environment, Crit. Rev. Environ. Sci. Technol. 42 (2012) 1172–1189.
[6] D. Hu, A. Martinez, K.C. Hornbuckle, Sedimentary records of non-aroclor and aroclor PCB mixtures in the Great Lakes, J. Great Lakes Res. 37 (2011) 359–364.
[7] N. Carro, I. Garcia, M. Ignacio, A. Mouteira, Polychlorinated dibenzo-P-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBS) in bivalve mollusk from Galician Rias (N.W., SPAIN), Chemosphere 197 (2018) 782–792.
[8] M.V. Berg, L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyaama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker, R.E. Peterson, The, World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds, Toxicol. Sci. 93 (2006) (2005) 223–241.
[9] S. Zeng, N. Gan, R.W. Mera, Y. Cao, T. Li, W. Sang, Enrichment of polychlorinated biphenyl 28 from aqueous solutions using Fe_3O_4 grafted graphene oxide, Chem. Eng. J. 218 (2013) 108–115.
[10] R. Randoll, W. Wondrak, A. Schletz, Dielectric strength and thermal performance of PCB-embedded power electronics, Microelectron. Reliab. 54 (2014) 1872–1876.
[11] X. Tang, M.Z. Hashmi, B. Zeng, J. Yang, C.F. Shen, Application of iron-activated persulfate oxidation for the degradation of PCBs in soil, Chem. Eng. J. 279 (2015) 673–680.
[12] J. Wu, J.C. Hu, S.J. Wang, J. Xi Jin, R. Wang, Y. Wang, J. Jin, Levels, sources, and, potential human health risks of PCNs, PCDD/Fs, and PCBs in an industrial area of Shandong Province, China, Chemosphere 199 (2018) 382–389.
[13] D. Qizhou, X. Min, M. Weng, A review of polychlorinated biphenyls (PCBs) pollution in indoor air environment, J. Air Waste Manag. Assoc. 66 (2016) 941–950.
[14] C. Zani, E. Ceretti, L. Covolo, F. Donato, Do polychlorinated biphenyls cause cancer? A systematic review and meta-analysis of epidemiological studies on risk of cutaneous melanoma and non-Hodgkin lymphoma, Chemosphere 183 (2017) 97–106.
[15] B.Z. Wu, H.Y. Chen, S.J. Wang, C.M. Wai, W. Liao, K.H. Chiu, Reductive dechlorination for remediation of polychlorinated biphenyls, Chemosphere 88 (2012) 757–768.
[16] R.D. Kimbrough, C.A. Krouskas, Human exposure to polychlorinated biphenyls and health effects: a critical synopsis, Toxicol. Rev. 22 (2003) 217–233.
[17] C. Isabel, M.C. Adams, J.E. Baker, B.V. Kjellerup, Toxicological effects of polychlorinated biphenyls (PCBs) on freshwater turtles in the United States, Chemosphere 154 (2016) 148–154.
[18] Z.J. Jain, P.S. Gide, R.S. Kankate, Biphenyls and their derivatives as synthetically and pharmacologically important aromatic structural moieties, Arab. J. Chem. 10 (2017) 2051–2066.
[19] J. Boix, O. Cauli, Alteration of serotonin system by polychlorinated biphenyls exposure, Neurochem. Int. 60 (2012) 809–816.
[20] R. Lavandier, N. Quinete, R.A. Hauser Davis, P.S. Dias, S. Taniguchi, R. Montone, I. Moreira, Polychlorinated biphenyls (PCBs) and Polybrominated diphenyl ethers (PBDEs) in three fish species from an estuary in the southeastern coast of Brazil, Chemosphere 90 (2013) 2435–2443.
[21] J. Huang, T. Matsumura, G. Yu, S. Deng, M. Yamauchi, N. Yamazaki, R. Weber, Determination of PCBs, PCDDs and PCDFs in insulating oil samples from stored Chinese electrical capacitors by HRGC/HRMS, Chemosphere 85 (2011) 239–246.
[22] S. Eckhardt, K. Breivik, S. Mano, A. Stohl, Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions, Atmos. Chem. Phys. 7 (2007) 4527–4536.
[23] R.F. Herrick, J.H. Stewart, J.G. Allen, Review of PCBs in US Schools: a brief history, estimate of the number of impacted schools, and an approach for evaluating indoor air samples, Environ. Sci. Pollut. Res. Int. 23 (2016) 1975–1985.
[24] G.C. Windham, S.M. Pinney, A. Sjodin, R. Lum, R.S. Jones, L.L. Needham, F.M. Biro, R.A. Hiatt, L.H. Kushi, Body burdens of brominated flame retardants and other persistent organo-halogenated compounds and their descriptors in US girls, Environ. Res. 110 (2010) 251–257.
[25] Q. Zhao, J. Bai, Q. Lu, Z. Gao, J. Jia, B. Cui, X. Liu, Polychlorinated biphenyls (PCBs) in sediments/soils of different wetlands along 100-year coastal reclamation chronosequence in the Pearl River Estuary, China, Environ. Pollut. 213 (2016) 860–869.
[26] D.O. Carpenter, Polychlorinated biphenyls (PCBs): routes of exposure and effects on human health, Rev. Environ. Health 21 (2006) 1–23.
[27] V. Ivanescu, Human health risk assessment posed by PCB exposure in Bucharest Area, Agriculture Agric. Sci. Procedia 6 (2015) 453–458.
[28] B.R. De Castro, S.A. Korrick, J.D. Spengler, A.M. Soto, Estrogenic activity of polychlorinated biphenyls present in human tissue and the environment, Environ. Sci. Technol. 40 (2006) 2819–2825.
[29] M.M. Leijs, L.M.V. Linden, J.G. Koppe, K. Olie, W.M.C. van Aalderen, G.W. ten Tusscher, The influence of perinatal and current dioxin and PCB exposure on reproductive parameters (sex-ratio, menstrual cycle characteristics, endometriosis, semen quality, and prematurity): a review, Biomonitoring 1 (2014) 1–15.
[30] I.K. Korwel, X. Wu, K. Wang, H.J. Lehmler, Identification of lipidomic markers of chronic 3,3′,4,4′,5-pentachlorobiphenyl (PCB 126) exposure in the male rat liver, Toxicology 390 (2017) 124–134.
[31] S.J. Chen, M. Tian, J. Zheng, Z.C. Zhu, Y. Luo, X.J. Luo, B.X. Mai, Elevated levels of polychlorinated biphenyls in plants, air, and soils at an e-waste site in southern china and enantioselective biotransformation of chiral PCBs in plants, Environ. Sci. Technol. 48 (2014) 3847–3855.
[32] B.V. Aken, P.A. Correa, J.L. Schnoor, Phytoremediation of polychlorinated biphenyls: new trends and promises, Environ. Sci. Technol. 44 (2010) 2767–2776.
[33] E. Emily, U.S. Food Still Tainted with Old Chemicals, Environmental Health News on April 22, 2010.
[34] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for polychlorinated biphenyls (PCBs). ATSDR: Atlanta; 2000.
[35] S.A. Korrick, L. Altshul, High breast milk levels of polychlorinated biphenyls (PCBs) among four women living adjacent to a PCB-contaminated waste site, Environ. Health Perspect. 106 (1998) 513–518.
[36] R. Corner, M. Sundahl, L. Rosell, B. Ek-Olausson, M, Tysklind, PCB in indoor air and dust in buildings in Stockholm, Proceedings, Indoor Air (2002) 141–146.
[37] T.P. Whitehead, M.H. Ward, J.S. Colt, M.G. Nishioka, P.A. Buffler, S.M. Rappaport, C. Metayer, Determinants of polychlorinated biphenyls in dust from homes in California, USA, Environ. Sci. Process Impacts 15 (2010) 339–346.
[38] M.A. Alawi, F.T. Al-Tameemi, Levels of polychlorinated biphenyls (PCBs) in human adipose tissue from Baghdad/Iraq, Toxin Rev. 35 (2016) 83–89.
[39] L. Kacalkova, P. Tlustos, The uptake of persistent organic pollutants by plants, Centr. Eur. J. Biol. 6 (2011) 223–235.
[40] J. Liu, J.L. Schnoor, Uptake and translocation of lesser-chlorinated polychlorinated biphenyls (PCBs) in whole hybrid poplar plants after hydroponic exposure, Chemosphere 73 (2008) 1608–1616.
[41] C. Zhang, Y. Feng, Y.W. Liu, H. Chang, Z.J. Li, J.M. Xue, Uptake and translocation of organic pollutants in plants: a review, J. Integr. Agric. 16 (2017) 1659–1668.
[42] H. Javorska, P. Tlustos, R. Kalizzova, Distribution of polychlorinated biphenyl congeners in root vegetables, Pol. J. Environ. Stud. 20 (2011) 93–99.
[43] A.S. Szczybelski, M.J. Heuvel-Greve, T. Kampen, C. Wang, N.W. Brink, A.A. Koelmans, Bioaccumulation of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and hexachlorobenzene by three Arctic benthic species from Kongsfjorden (Svalbard, Norway), Mar. Pollut. Bull. 112 (2016) 65–74.
[44] M.B. Leigh, P. Petra, M. Martina, T. Macek, D.P. Nagle, S.J. Fletcher, Polychlorinated biphenyl (PCB) degrading bacteria associated with trees in a PCB contaminated site, Appl. Environ. Microbiol. 72 (2006) 2331–2342.
[45] W. Qin, G. Fang, Y. Wang, D. Zhou, Mechanistic understanding of polychlorinated biphenyls degradation by peroxymonosulfate activated with $CuFe_2O_4$ nanoparticles: key role of superoxide radicals, Chem. Eng. J. 348 (2018) 526–534.
[46] J.F. Niu, Z.F. Yang, Z.Y. Shen, L.L. Wang, QSPRs for the prediction of photo degradation half-life of PCBs in n-hexane, SAR QSAR Environ. Res. 17 (2006) 173–182.
[47] J.A. Chen, J. Luo, Z. Qiu, C. Xu, Y. Huang, Y.H. Jin, N. Saito, T. Yoshida, K. Ozawa, J. Cao, W. Shu, PCDDs/PCDFs and PCBs in water samples from the three Gorge reservoir, Chemosphere 70 (2008) 1545–1551.
[48] N.T. Thuan, C.L. Tsai, Y.M. Weng, T.Y. Lee, M.B. Chang, Analysis of polychlorinated dibenzo-p-dioxins and furans in various aqueous samples in Taiwan, Chemosphere 83 (2011) 760–766.
[49] M. Kishida, Distribution characteristics and source identification of polychlorinated dibenzo-p-dioxin and dibenzofurans, and dioxin-like polychlorinated

biphenyls in the waters from River Kanzaki, running through Osaka urban area, Japan, J. Environ. Sci. 25 (2013) 441–451.

[50] K.M. Guijarro, A. Ramadan, B. Gevao, Atmospheric concentration of poly-chlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and di-oxin-like polychlorinated biphenyls (dl-PCBs) at Umm-Al-Aish oil field-Kuwait, Chemosphere 168 (2017) 147–154.

[51] D.D. Nguyen, C.L. Tsai, Y.C. Hsu, Y.W. Chen, Y.M. Weng, M.B. Chang, PCDD/Fs and DL-PCBs concentrations in water samples of Taiwan, Chemosphere 173 (2017) 603–611.

[52] T. Li, T. Watanabe, K. Ochi, K. Otsuki, Liquid waste decomposition by long DC arc under atmospheric pressure, Chem. Eng. J. 231 (2013) 155–162.

[53] S. Endo, Y. Yabuki, S. Tanaka, Comparing polyethylene and polyoxymethylene passive samplers for measuring sediment porewater concentrations of poly-chlorinated biphenyls: mutual validation and possible correction by polymer-polymer partition experiment, Chemosphere 184 (2017) 358–365.

[54] Y. Choi, Y. Wub, R.G. Luthy, S. Kanga, Non-equilibrium passive sampling of hy-drophobic organic contaminants in sediment pore-water: PCB exchange kinetics, J. Hazard. Mater. 318 (2016) 579–586.

[55] CERP. Quality assurance system requirements (QASR) manual for the compre-hensive everglades restoration plan (CERP), 2009.

[56] A.E. Sakin, F. Esen, Y. Tasdemir, Effects of sampling interval on the passive air sampling of atmospheric PCBs levels, J. Environ. Sci. Health Part A 52 (2017) 673–679.

[57] K. Vorkamp, P. Mayer, Passive Sampling of Polychlorinated Biphenyls (PCB) in Indoor Air: Towards a Cost-Effective Screening Tool, Aarhus University, 2013.

[58] Z. Shareefdeen, S. Taqvi, A. Elkamel, Air quality management in electronic in-dustries, Compreh. Anal. Chem. 73 (2016) 765–784.

[59] W. Lao, K.A. Maruya, D. Tsukada, An exponential model based new approach for correcting aqueous concentrations of hydrophobic organic chemicals measured by polyethylene passive samplers, Sci. Total Environ. 646 (2019) 11–18.

[60] L. Zhang, L. Dong, W. Yang, L. Zhou, S. Shi, X. Zhang, S. Niu, L. Li, Z. Wu, Y. Huang, Passive air sampling of organochlorine pesticides and polychlorinated biphenyls in the Yangtze River Delta, China: concentrations, distributions, and cancer risk assessment, Environ. Pollut. 181 (2013) 159–166.

[61] R.G. Lewis, M.D. Jackson, Modification and evaluation of a high-volume air sampler for pesticides and semi volatile industrial organic chemicals, Anal. Chem. 54 (1982) 592–594.

[62] K. Vorkamp, L. Odsbjerg, M. Langeland, P. Mayer, Utilizing the partitioning properties of silicone for the passive sampling of polychlorinated biphenyls (PCBs) in indoor air, Chemosphere 160 (2016) 280–286.

[63] Y.X. Sun, Y.X. Hu, Z.W. Zhang, X.R. Xu, B.X. Mai, Halogenated organic pollutants in marine biota from the Xuande Atoll, South China Sea: levels, biomagnification and dietary exposure, Mar. Pollut. Bull. 118 (2017) 413–419.

[64] N. Margarida, P. Marchand, A. Vernisseau, B.L. Bizec, F. Ramos, M.A. Pardal, PCDD/Fs and dioxin-like PCBs in sediment and biota from the Mondego estuary Portugal, Chemosphere 83 (2011) 1345–1352.

[65] E.M. Oziolor, J.N. Apell, Z.C. Winfield, J.A. Back, S. Usenko, C.W. Matson, Polychlorinated biphenyl (PCB) contamination in Galveston Bay, Texas: com-paring concentrations and profiles in sediments, passive samplers, and fish, Environ. Poll. 236 (2018) 609–618.

[66] C.T. Della Valle, D.C. Wheeler, N.C. Deziel, A.J. De Roos, J.R. Cerhan, W. Cozen, R.K. Severson, A.R. Flory, S.J. Locke, J.S. Colt, P. Hartge, M.H. Ward, Environmental determinants of polychlorinated biphenyl concentrations in re-sidential carpet dust, Environ. Sci. Technol. 47 (2013) 10405–10414.

[67] S. Sabine, A. Catherine, M. Christel, C. Evelyn, R. Georg, H. Peter, P. Mayer, Equilibrium sampling of polychlorinated biphenyls in River Elbe sediments – Linking bioaccumulation in fish to sediment contamination, Chemosphere 138 (2015) 856–862.

[68] H. Frouin, N. Dangerfield, R.W. Macdonald, M. Galbraith, P.S. Ross, Partitioning and bioaccumulation of PCBs and PBDEs in marine plankton from the Strait of Georgia, British Columbia, Canada, Prog. Oceanogr. 115 (2013) 65–75.

[69] M. Tiano, J. Tronczynski, M.V. Harmelin, C. Tixier, F. Carlotti, PCB concentrations in plankton size classes, a temporal study in Marseille Bay, Western Mediterranean Sea, Mar. Pollut. Bull. 89 (2014) 331–339.

[70] N. Carro, L. Vilas, I. Garcia, M. Ignacio, A.M. Mouteira, Optimization of a method based on micro-matrix solid-phase dispersion (micro-MSPD) for the determination of PCBs in mussel samples, Anal. Chem. Res. 11 (2017) 1–8.

[71] D.E. Wells, P. Hess, Separation, clean-up and recoveries of persistent trace organic contaminants from soils, sediment and biological matrices, in: E. Barceló (Ed.), Sample Handling and Trace Analysis of Pollutants, Techniques, Applications and Quality Assurance, Elsevier, Amsterdam, 2000, pp. 73–116.

[72] B. Gevao, J.H. Taylor, K.C. Jones, Towards a complete mass balance and model for PCBs and PAHs in a small rural lake, Cumbria U.K, Limnol. Oceanogr. 45 (2000) 881–894.

[73] Z. Liu, H. Zhang, M. Tao, S. Yang, L. Wang, Y. Liu, D. Ma, Z. He, Organochlorine pesticides in consumer fish and mollusks of liaoning province, china: distribution and human exposure implications, Arch. Environ. Contam. Toxicol. 59 (2010) 444–453.

[74] W. Intrchom, S. Mitra, Analytical sample preparation, preconcentration and chromatographic separation on carbon nanotubes, Cur. Opin. Chem. Eng. 16 (2017) 102–114.

[75] C.C. Zhang, N.M. Zhu, F.S. Zhang, Advantage of solvothermal procedure for polychlorinated biphenyls removal from e-waste contaminated site, Chem. Eng. J. 178 (2011) 93–99.

[76] A. Zygler, M. Slominska, J. Namiesnik, Soxhlet extraction and new developments such as soxtec in: Comprehensive sampling and sample preparation// Analytical Techniques for Scientists/ ed. ed. J. Pawliszyn: Elsevier, 2012, s.65-82.

[77] Y. Cui, Z. Wang, J. Cong, L. Wang, Y. Liu, X. Wang, J. Xie, Determination of polychlorinated biphenyls in fish tissues from Shanghai seafood markets using a modified QuEChERS method, Anal. Sci. 33 (2013) 973–977.

[78] J.E. Hess, C.C. Caudill, M.L. Keefer, B.J. Mcllraith, M.L. Moser, S.R. Narum, Genes predict long distance migration and large body size in a migratory fish, Pacific lamprey, Evol. Appl. 7 (2014) 1192–1208.

[79] C. Bandh, Comparison of accelerated solvent extraction and soxhlet extraction for the determination of PCBs in Baltic sea sediments, Environ. Sci. Technol. 34 (2000) 4995–5000.

[80] P. Wang, Q. Zhang, Y. Wang, T. Wang, X. Li, L. Ding, G. Jiang, Evaluation of soxhlet extraction, accelerated solvent extraction and microwave-assisted extrac-tion for the determination of polychlorinated biphenyls and polybrominated di-phenyl ethers in soil and fish samples, Anal. Chim. Acta 663 (2010) 43–48.

[81] Y. Zhao, W. Li, J. Liu, K. Huang, C. Wu, H. Shao, H. Chen, X. Liu, Modification of garlic peel by nitric acid and its application as a novel adsorbent for solid-phase extraction of quinolone antibiotics, Chem. Eng. J. 326 (2017) 745–755.

[82] R. Hartmann, Extraction of PCDD/Fs and PCBs in fish using speed extractor E-914, Procedia Environ. Sci. 18 (2013) 875–881.

[83] A. Birgul, P.B.K. Karakus, H. Alegria, E. Gungormus, H. Celik, T. Cicek, E.C. Guven, Polyurethane foam (PUF) disk passive samplers derived poly-chlorinated biphenyls (PCBs) concentrations in the ambient air of Bursa-Turkey: spatial and temporal variations and health risk assessment, Chemosphere 168 (2017) 1345–1355.

[84] S.Y. Huetstis, M.R. Servos, D.M. Whittle, D.G. Dixon, Temporal and age-related trends in levels of polychlorinated biphenyl congeners and organochlorine con-taminants in Lake Ontario Lake Trout (Salvelinus namaycush), J. Great Lakes Res. 22 (1996) 310–330.

[85] C.P. Madenjian, J.D. Timothy, R.M. Stedman, E.H. Brown, G.W. Eck, L.J. Schmidt, R.J. Hesselberg, S.M. Chernyak, D.R. Passino, Spatial patterns in PCB concentra-tions of lake Michigan lake Trout, J. Great Lakes Res. 25 (1999) 149–159.

[86] K. Conka, B. Drobna, A. Kocan, J. Petrik, Simple solid-phase extraction method for determination of polychlorinated biphenyls and selected organochlorine pesticides in human serum, J. Chromatogr. A 1084 (2005) 33–38.

[87] X. Song, J. Li, L. Chen, Z. Cai, C. Liao, H. Peng, H. Xiong, Determination of polychlorinated biphenyls in seawater using headspace solid-phase microextrac-tion coupled with gas chromatography-mass spectrometry with the aid of ex-perimental design, J. Braz. Chem. Soc. 23 (2012) 132–141.

[88] H. Chikushi, Y. Fujii, K. Toda, Measurement of polychlorinated biphenyls in solid waste such as transformer insulation paper by supercritical fluid extraction and gas chromatography electron capture detection, J. Chromatogr. A 1256 (2012) 267–270.

[89] N. Raza, B. Hashemi, K.K. Hyun, S.H. Lee, A. Deep, Aromatic hydrocarbons in air, water, and soil: sampling and pretreatment techniques, Trends Anal. Chem. 103 (2018) 56–73.

[90] J.J. Langenfeld, M.D. Burford, S.B. Hawthorne, D.J. Miller, Effects of collection solvent parameters and extraction cell geometry on supercritical fluid extraction efficiencies, J. Chromatogr. A 594 (1992) 297–307.

[91] X. Jiang, G. Liu, M. Wang, M. Zheng, Formation of polychlorinated biphenyls on secondary copper production fly ash: mechanistic aspects and correlation to other persistent organic pollutants, Sci. Rep. 5 (2015) 13903.

[92] E.G. Van der Velde, W.D. Haan, A.K. Liem, Supercritical fluid extraction of poly-chlorinated biphenyls and pesticides from soil, Comparison with other extraction methods, J. Chromatogr. A. 626 (1992) 135–143.

[93] E.G. Van der Velde, W.C. Hijman, S.H.M.A. Linders, A.K.D. Liem, SFE as clean-up technique for ppt levels of PCBs in fatty samples, Organohal. Compd. 27 (1996) 247–252.

[94] T.N. Manolis, E.G. Barbounis, M.P. Kavvalakis, E. Vakonaki, E. Renieri, A.I. Vardavas, A.M. Tsatsakis, Rapid method for the simultaneous determination of DDTs and PCBs in hair of children by headspace solid phase microextraction and gas chromatography-mass spectrometry (HSSPME/GC-MS), Drug Test. Anal. 6 (2014) 85–92.

[95] S.K. Kutup, I.G. Vural, V. Hessel, K.D.P. Nigam, N. Kockmann, Liquid-liquid ex-traction system with microstructured coiled flow inverter and other capillary setups for single-stage extraction applications, Chem. Eng. J. 284 (2016) 764–777.

[96] E.S. Hansen, H. Spliid, J.P. Boon, Patterns of chlorinated biphenyl congeners in harbor seals (Phoca vitulina) and in their food: statistical analysis, Arch. Environ. Contam. Toxicol. 28 (1995) 48–54.

[97] G. Bremle, L. Okla, P. Larsson, Uptake of PCBs in fish in a contaminated river system: bioconcentration factors measured in the field, Environ. Sci. Technol. 29 (1995) 2010–2015.

[98] G. Ottonello, A. Ferrari, E. Magi, Determination of polychlorinated biphenyls in fish: optimisation and validation of a method based on accelerated solvent ex-traction and gas chromatography-mass spectrometry, Food Chem. 142 (2014) 327–333.

[99] R.C. Brandli, T.D. Bucheli, T. Kupper, F.X. Stadelmann, T. Joseph, Optimised ac-celerated solvent extraction of PCBs and PAHs from compost, Int. J. Environ. Anal. Chem. 86 (2007) 505–525.

[100] A. Singh, K. Sabally, S. Kubow, D.J. Donnelly, Y. Gariepy, V. Orsat, G.S.V. Raghavan, Microwave-assisted extraction of phenolic antioxidants from potato peels, Molecules 16 (2011) 2218–2232.

[101] L. Wang, W. Fu, Y. Shen, H. Tan, H. Xu, Molecularly imprinted polymers for se-lective extraction of oblongifolin C from Garcinia yunnanensis Hu, Molecules 22 (2017) 508.

[102] O.M.R. Narvaez, J.M.P. Hernandez, A. Goonetilleke, E.R. Bandala, Treatment technologies for emerging contaminants in water: a review, Chem. Eng. J. 323

(2017) 361–380.

[103] A. Glausch, J. Hahn, V. Schurig, Enantioselective determination of chiral 2,2',3,3',4,6'-hexachlorobiphenyl (PCB 132) in human milk samples by multi-dimensional gas chromatography / electron capture detection and by mass spectrometry, Chemosphere 30 (1995) 2079–2085.

[104] K. Holadova, G. Prokupkova, H. Jana, J. Poustka, Headspace solid-phase micro-extraction of phthalic acid esters from vegetable oil employing solvent based matrix modification, Anal. Chim. Acta 582 (2007) 24–33.

[105] K. Silvia, W. Jira, K.H. Schwind, Dioxin and polychlorinated biphenyl analysis: automation and improvement of clean-up established by example of spices, Mol. Nutr. Food Res. 50 (2006) 362–367.

[106] M. Blasco, D. Celia, B. Karim, C. Nerin, Solid-phase extraction clean-up procedure for the analysis of PAHs in lichens, Int. J. Environ. Anal. Chem. 87 (2007) 833–846.

[107] J.K. Jang, A. Li, Separation of PCBs and PAHs in sediment samples using silica gel fractionation chromatography, Chemosphere 44 (2001) 1439–1445.

[108] J.L. Sericano, A.M. El-Husseini, T.L. Wade, Isolation of planar polychlorinated biphenyls by carbon column chromatography, Chemosphere 23 (1991) 915–924.

[109] Y.C. Kuan, I.H. Lee, J.M. Chern, Heavy metal extraction from PCB wastewater treatment sludge by sulfuric acid, J. Hazard. Mater. 177 (2010) 881–886.

[110] L.L. Cao, C.H. Yan, X.D. Yu, Y. Tian, X. Zou, D.S. Lu, X.M. Shen, Determination of polychlorinated biphenyls and organochlorine pesticides in human serum by gas chromatography with micro-electron capture detector, J. Chromatogr. Sci. 50 (2012) 145–150.

[111] Y. Amakura, T. Tsutsumi, K. Sasaki, M. Toyoda, T. Maitani, Comparison of sulfuric acid treatment and multi-layer silica gel column chromatography in cleanup methods for determination of PCDDs, PCDFs and dioxin-like PCBs in foods, Food Hyg. Saf. Sci. 43 (2002) 312–321.

[112] M. Numata, T. Yarita, Y. Aoyagi, M. Yamazaki, A. Takatsu, Investigation of saponification for determination of polychlorinated biphenyls in marine sediments, Chemosphere 58 (2005) 865–875.

[113] A.M. Zimeri, S.W. Robb, S.M. Hassan, R.R. Hire, B.D. Melissa, Assessing heavy metal and PCB exposure from tap water by measuring levels in plasma from sporadic breast cancer patients, a pilot study, Int. J. Environ. Res. Public Health 12 (2015) 15683–15691.

[114] F. Lv, N. Gan, Y. Cao, Y. Zhou, R. Zuo, Y. Dong, A molybdenum disulfide/reduced graphene oxide fiber coating coupled with gas chromatography-mass spectrometry for the saponification-headspace solid-phase microextraction of polychlorinated biphenyls in food, J. Chromatogr. A 1525 (2017) 42–50.

[115] F. Van der Valk, Q.T. Dao, Degradation of PCBs and HCB from sewage sludge during alkaline saponification, Chemosphere 17 (1988) 1735–1739.

[116] M. Llompart, M. Pazos, P. Landin, R. Cela, Determination of polychlorinated biphenyls in milk samples by saponification-solid phase microextraction, Anal. Chem. 73 (2001) 5858–5865.

[117] L.M.R. Mendoza, S. Taniguchi, H.K. Karapanagioti, Advanced analytical techniques for assessing the chemical compounds related to microplastics, Compr. Anal. Chem. 75 (2017) 209–240.

[118] D. Schrenk, C. Martin, Dioxins and polychlorinated biphenyls in foods, Chemical Contaminants and Residues in Food, Second Edition, 2017, 69–89.

[119] Y. Xu, C. Tian, X. Wang, J. Ma, J. Tang, Y. Chen, J. Li, G. Zhang, An improved inventory of polychlorinated biphenyls in China: a case study on PCB-153, Atmos. Environ. 183 (2018) 40–48.

[120] T. Grzeskowiak, B.C. Goslinska, A.Z. Grzeskowiak, Current approaches in sample preparation for trace analysis of selected endocrine-disrupting compounds: focus on polychlorinated biphenyls, alkylphenols, and parabens, Trends Anal. Chem. 75 (2016) 209–226.

[121] D. Li, J. Zhua, M. Wang, W. Bi, X. Huang, D.D. Yong Chen, Extraction of trace polychlorinated biphenyls in environmental waters by well-dispersed velvet-like magnetic carbon nitride nanocomposites, J. Chromatogr. A 1491 (2017) 27–35.

[122] K.J. Adams, N.F. Smith, C.E. Ramirez, F.F. Lima, Discovery and targeted monitoring of polychlorinated biphenyl metabolites in blood plasma using LC-TIMS-TOF MS, Int. J. Mass Spectrom. 427 (2018) 133–140.

[123] L. Fu, X. Lu, J. Tan, L. Wang, J. Chen, Multiresidue determination and potential risks of emerging pesticides in aquatic products from Northeast China by LC-MS/MS, J. Environ. Sci. 63 (2018) 116–125.

[124] A.V.B. Reddy, J. Jaafar, K. Umar, Z.A. Majid, A.B. Aris, J. Talib, G. Madhavi, Identification, control strategies, and analytical approaches for the determination of potential genotoxic impurities in pharmaceuticals: a comprehensive review, J. Sep. Sci. 38 (2015) 764–779.

[125] G. Zhai, X. Wu, H.J. Lehmler, J.L. Schnoor, Atropisomeric determination of chiral hydroxylated metabolites of polychlorinated biphenyls using HPLC-MS, Chem. Cent. J. 7 (2013) 183.

[126] J. Bures, H. Jansova, J. Stariat, T. Filipsky, P. Mladenka, T. Simunek, R. Kucera, J. Klimes, Q. Wang, K.J. Franz, P. Kovarikova, LC-UV/MS methods for the analysis of prochelator-boronyl salicylaldehyde isonicotinoyl hydrazone (BSIH) and its active chelator salicylaldehyde isonicotinoyl hydrazone (SIH), J. Pharm. Biomed. Anal. 105 (2015) 55–63.

[127] S. Laborie, E.M. Guigon, F. Alliot, A. Desportes, L. Oziol, M. Chevreuil, A new analytical protocol for the determination of 62 endocrine-disrupting compounds in indoor air, Talanta 147 (2016) 132–141.

[128] N. Quinete, A. Esser, T. Kraus, T. Schettgen, Determination of hydroxylated polychlorinated biphenyls (OH-PCBs) in human urine in a highly occupationally exposed German cohort: new prospects for urinary biomarkers of PCB exposure, Environ. Int. 97 (2016) 171–179.

[129] N. Quinete, T. Kraus, V.N. Belov, C. Aretz, A. Esser, T. Schettgen, Fast determination of hydroxylated polychlorinated biphenyls in human plasma by online solid

phase extraction coupled to liquid chromatography-tandem mass spectrometry, Anal. Chim. Acta 888 (2015) 94–102.

[130] R. Liang, Y. Zhao, Y. Su, W. Qin, Determination of hydroxylated polychlorinated biphenyls by offline solid-phase extraction-liquid chromatography-tandem mass spectrometry using a molecularly imprinted polymer as a sorbent for sample preconcentration, Talanta 144 (2015) 115–121.

[131] J. Martín, A.Z. Gomez, F. Hidalgo, A.J.I. Yuste, E. Alonso, J.L. Vilchez, Multi-residue analysis of 36 priority and emerging pollutants in marine echinoderms (Holothuria Tubulosa) and marine sediments by solid-liquid extraction followed by dispersive solid phase extraction and liquid chromatography-tandem mass spectrometry analysis, Talanta 166 (2017) 336–348.

[132] J. Shuaia, X. Yua, J. Zhanga, A. Xiongb, F. Xionga, Regional analysis of potential polychlorinated biphenyl degrading bacterial strains from China, Braz. J. Microbiol. 47 (2016) 536–541.

[133] D.L. Hayteas, D.A. Duffield, The determination by HPLC of PCB and p, p'-DDE residues in marine mammals stranded on the Oregon Coast 1991–1995, Mar. Pollut. Bull. 34 (1997) 844–848.

[134] K. Echols, R. Gale, D. Tillitt, T. Schwartz, J.O. Laughlin, An automated HPLC method for the fractionation of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans in fish tissue on a porous graphitic carbon column, Environ. Toxicol. Chem. 16 (1997) 1590–1597.

[135] Y. Zebtihr, C. Ntif, C. Bandh, D. Broman, R. Ishaq, H. Pettersen, An automated HPLC separation method with two coupled columns for the analysis of PCDD/Fs PCBs and PACs, Chemosphere 27 (1993) 1211–1219.

[136] K. Lundgren, B. Bavel, M. Tysklind, Development of a high-performance liquid chromatography carbon column based method for the fractionation of dioxin-like polychlorinated biphenyls, J. Chromatogr. A 962 (2002) 79–93.

[137] Q. Zhou, Y. Sang, L. Wang, S. Ji, Y. Jing, X. Wang, Determination of poly-chlorinated biphenyls by GC/MS with ultrasound-assisted extraction from shell-fish, Front. Agric. China 4 (2010) 489–493.

[138] A.V.B. Reddy, Z. Yusop, J. Jaafar, A.B. Aris, Z.A. Majid, K. Umar, J. Talib, Simultaneous determination of three organophosphorus pesticides in different food commodities by gas chromatography with mass spectrometry, J. Sep. Sci. 39 (2016) 2276–2283.

[139] M. Ros, J. Escobar-Arnanz, M.L. Sanz, L. Ramos, Evaluation of ionic liquid gas chromatography stationary phases for the separation of polychlorinated biphenyls, J. Chromatogr. A 1559 (2018) 156–163.

[140] P.T. Quinto, L. Mondello, Current-day employment of the micro-bore open-tubular capillary column in the gas chromtography field, J. Chromatogr. A 1261 (2012) 23–36.

[141] K. Vorkamp, P. Roose, P. Bersuder, L. Webster, P. Lepom, C. Munschy, R. Bossi, J. Tronczynski, J. de Boer, Determination of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls in biota and sediment, ICES Tech. Mar. Environ. Sci. No. 50 (2012) 22.

[142] I. Dominguez, F.J. Arrebola, R. Gavara, J.L.V. Martinez, A.G. Frenich, Automated and simultaneous determination of priority substances and polychlorinated biphenyls in wastewater using headspace solid phase microextraction and high resolution mass spectrometry, Anal. Chim. Acta 1002 (2018) 39–49.

[143] M. Roszko, K. Szymczyk, R. Jędrzejczak, Separation of polychlorinated dibenzo-p-dioxins/furans, non-ortho/mono/di/tri/tetra-ortho-polychlorinated biphenyls, and polybrominated diphenyl ethers groups of compounds prior to their determination with large volume injection gas chromatography-Quadrupole ion storage tandem mass spectrometry, Anal. Chim. Acta 799 (2013) 88–98.

[144] A. Eguchi, T. Enomoto, N. Suzuki, M. Okuno, C. Mori1, Development of simple analytical methods of polychlorinated biphenyls in human serum by gas chromatography negative ion chemical ionization quadrupole mass spectrometry, Acta Chromatogr. 29 (2016) 1–4.

[145] S. Sethi, X. Chen, P.H. Kass, B. Puschner, Polychlorinated biphenyl and polybrominated diphenyl ether profiles in serum from cattle, sheep, and goats across California, Chemosphere 181 (2017) 63–73.

[146] D. Geng, I.E. Jogsten, J. Dunstan, J. Hagberg, T. Wang, J. Ruzzin, R.R. Lhoret, B.V. Bavel, Gas chromatography/atmospheric pressure chemical ionization/mass spectrometry for the analysis of organochlorine pesticides and polychlorinated biphenyls in human serum, J. Chromatogr. A 1453 (2016) 88–98.

[147] A.P. Francisco, A.C. Nardocci, M.Y. Tominaga, C.S. Rodrigues, J.V. Assuncao, Spatial and seasonal trends of polychlorinated dioxins, furans and dioxin-like polychlorinated biphenyls in air using passive and active samplers and inhalation risk assessment, Atmos. Pollut. Res. 8 (2017) 979–987.

[148] V.T.T. Duong, V. Duong, N.T.H. Lien, T. Imasaka, Y. Tang, S. Shibuta, A. Hamachi, D.Q. Hoa, T. Imasaka, Detection of polychlorinated biphenyls in transformer oils in Vietnam by multiphoton ionization mass spectrometry using a far-ultraviolet femtosecond laser as an ionization source, Talanta 149 (2016) 275–279.

[149] F. Li, J. Jin, D. Tan, J. Xu, Y. Dhanjai, H. Ni, J. Chen Zhang, High performance solid-phase extraction cleanup method coupled with gas chromatography-triple quadrupole mass spectrometry for analysis of polychlorinated naphthalenes and dioxin-like polychlorinated biphenyls in complex samples, J. Chromatogr. A 1448 (2016) 1–8.

[150] D.G. Mateu, A. Pastor, M.D. Guardia, S. Armenta, A.E.T. Francesc, Hard cap espresso extraction-stir bar preconcentration of polychlorinated biphenyls in soil and sediments, Anal. Chim. Acta 952 (2017) 41–49.

[151] D. Xia, L. Gao, M. Zheng, S. Wang, G. Liu, Simultaneous analysis of poly-chlorinated biphenyls and polychlorinated naphthalenes by isotope dilution comprehensive two-dimensional gas chromatography high-resolution time-of-flight mass spectrometry, Anal. Chim. Acta 937 (2016) 160–167.

[152] S. Mona, G. Stanislava, M. Lubomir, Polychlorinated biphenyls in fish from Black Sea Bulgaria, Food Control 72 (2017) 205–210.

[153] A.T.S. Gelaisa, A. Christoph, B.A. Craig, B.A. Costa-Piercea, Non-dioxin like polychlorinated biphenyl indicator congeners in Northwest Atlantic spiny dogfish (Squalus acanthias), Mar. Pollut. Bull. 120 (2017) 414–421.

[154] D. Zacs, J. Rjabova, A. Viksna, V. Bartkevics, Method development for the simultaneous determination of polybrominated, polychlorinated, mixed poly-brominated/chlorinated dibenzo-p-dioxins and dibenzofurans, polychlorinated biphenyls and polybrominated diphenyl ethers in fish, Chemosphere 118 (2015) 72–80.

[155] M. Roszko, K. Szymczyk, J. Renata, Simultaneous separation of chlorinated/brominated dioxins, poly- chlorinated biphenyls, polybrominated diphenyl ethers and their methoxylated derivatives from hydroxylated analogues on molecularly imprinted polymers prior to gas/liquid chromatography and mass spectrometry, Talanta 144 (2015) 171–183.

[156] Z. Cheng, C. Cecilia, P.A. Stephen, A.L. Jared, Rapid and sensitive analysis of polychlorinated biphenyls and acrylamide in food samples using ionic liquid-based in situ dispersive liquid-liquid microextraction coupled to headspace gas chromatography, J. Chromatogr. A 1481 (2017) 1–11.

[157] O. Kuzukiran, A. Filazi, Determination of selected polychlorinated biphenyl residues in meat products by QuEChERS method coupled with gas chromatography-mass spectrometry, Food Anal. Method. 9 (2016) 1867–1875.

[158] S. Afful, J.A.M. Awudza, S.K. Twumasi, S. Osae, Determination of indicator polychlorinated biphenyls (PCBs) by gas chromatography-electron capture detector, Chemosphere 93 (2013) 1556–1560.

[159] R. Montes, M. Ramil, R. Isaac, E. Rubi, R. Cela, Rapid screening of polychlorinated biphenyls in sediments using non-equilibrium solid-phase microextraction and fast gas chromatography with electron-capture detection, J. Chromatogr. A 1124 (2006) 43–50.

[160] C. Qiu, J. Cochran, J. Smuts, W. Phillip, K.A. Schug, Gas chromatography-vacuum ultraviolet detection for classification and speciation of polychlorinated biphenyls in industrial mixtures, J. Chromatogr. A 1490 (2017) 191–200.

[161] Z.H. Li, D. Li, J. Ren, L. Wang, L.J. Yuan, Y.C. Liu, Optimization and application of accelerated solvent extraction for rapid quantification of PCBs in food packaging materials using GC-ECD, Food Control 27 (2012) 300–306.

[162] M.C. Ramil, I.R. Pereiro, R.C. Torrijos, Determination of polychlorinated biphenyl compounds in indoor air samples, J. Chromatogr. A 963 (2002) 65–71.

[163] B. Gomara, L. Ramos, M.J. Gonzalez, Determination of polychlorinated biphenyls in small-size serum samples by solid-phase extraction followed by gas chromatography with micro-electron-capture detection, J. Chromatogr. B 766 (2002) 279–287.

[164] Y. Hu, H. Peng, Y. Yan, S. Guan, S. Wang, P.C.H. Li, Y. Sun, Integration of laminar flow extraction and capillary electrophoretic separation in one microfluidic chip for detection of plant alkaloids in blood samples, Anal. Chim. Acta 985 (2017) 121–128.

[165] A.V.B. Reddy, Z. Yusop, J. Jaafar, N. Hidayati, Z.A. Majid, A.B. Aris, Development and validation of capillary electrophoresis method for simultaneous determination of six pharmaceuticals in different food samples combining on-line and off-line sample enrichment techniques, Food Anal. Method. 11 (2018) 533–545.

[166] G. Hancu, B. Simon, A. Rusu, E. Mircia, A. Gyeresi, Principles of micellar electrokinetic capillary chromatography applied in pharmaceutical analysis, Adv. Pharm. Bull. 3 (2013) 1–8.

[167] Y. Wu, M. Chen, Y. Fang, M. Zhu, Capillary electrophoresis investigation on equilibrium between polymer-related and surfactant-related species in aqueous polymer-surfactant solutions, J. Chromatogr. A 1489 (2017) 134–142.

[168] C.G. Ruiz, Y.B. Martin, A.L. Crego, M.L. Marina, Rapid enantiomeric separation of polychlorinated biphenyls by electrokinetic chromatography using mixtures of neutral and charged cyclodextrin derivatives, J. Chromatogr. A 910 (2001) 157–164.

[169] I. Benito, J.M. Saz, M.L. Marina, J.J. Barbero, M.J. Gonzalez, J.C.D. Masa, Micellar electrokinetic capillary chromatographic separation of polychlorinated biphenyl congeners, J. Chromatogr. A 778 (1997) 77–85.

[170] M.L. Marina, I. Benito, J.C.D. Masa, M.J. Gonzalez, Separation of chiral polychlorinated biphenyls by micellar electrokinetic chromatography using β- and γ-cyclodextrin mixtures in the separation buffer, J. Chromatogr. A 752 (1996) 265–270.

[171] C.G. Ruiz, A.L. Crego, M.L. Marina, Comparison of charged cyclodextrin derivatives for the chiral separation of atropisomeric polychlorinated biphenyls by capillary electrophoresis, Electrophoresis 24 (2003) 2657–2664.

[172] S.H. Edwards, S.A. Shamsi, Micellar electrokinetic chromatography of polychlorinated biphenyl congeners using a polymeric surfactant as the pseudostationary phase, J. Chromatogr. A 903 (2000) 227–236.

[173] M. Ahmad, H.F. Yap, B. Saad, Vortex-assisted liquid-liquid liquid microextraction (VALLLME) technique: a new microextraction approach for direct liquid chromatography and capillary electrophoresis analysis, Talanta 143 (2015) 394–401.

[174] F. Regan, A. Moran, B. Fogarty, E. Dempsey, Development of comparative methods using gas chromatography-mass spectrometry and capillary electrophoresis for determination of endocrine disrupting chemicals in bio-solids, J. Chromatogr. B 770 (2002) 243–253.

[175] G. Ward, A. Simpson, L. Boscato, P.E. Hickman, The investigation of interferences in immunoassay, Clin. Biochem. 50 (2017) 1306–1311.

[176] Y.Y. Lin, G. Liu, C.M. Wai, Y. Lin, Bioelectrochemical immunoassay of polychlorinated biphenyl, Anal. Chim. Acta 612 (2008) 23–28.

[177] T. Xu, J. Wang, S. Liu, C. Lu, W.L. Shelver, Q.X. Li, J. Li, A highly sensitive and selective immunoassay for the detection of tetrabromobisphenol A in soil and sediment, Anal. Chim. Acta 751 (2012) 119–127.

[178] T. Tsutsumi, Y. Amakura, O. Akira, Y. Tanioka, K. Sakata, K. Sasaki, T. Maitani, Application of an ELISA for PCB 118 to the screening of dioxin-like PCBs in retail fish, Chemosphere 65 (2006) 467–473.

[179] J.L. Zajiceka, D.E. Tillitta, T.R. Schwartza, J.S. Christopher, R.O. Harrison, Comparison of an enzyme-linked immunosorbent assay (ELISA) to gas chromatography (GC) – Measurement of polychlorinated biphenyls (PCBs) in selected US fish extracts, Chemosphere 40 (2000) 539–548.

[180] G. Fillmann, T.S. Galloway, R.C. Sanger, M.H. Depledge, J.W. Readman, Relative performance of immunochemical (enzyme-linked immunosorbent assay) and gas chromatography-electron-capture detection techniques to quantify polychlorinated biphenyls in mussel tissues, Anal. Chim. Acta 461 (2002) 75–84.

[181] J.M. Van Emon, J.C. Chuang, B. Alisa, A. Miriam, Determination of polychlorinated biphenyls in soil and sediment by selective pressurized liquid extraction with immunochemical detection, Sci. Tot. Environ. 463–464 (2013) 326–333.

[182] J.C. Chuang, L.S. Miller, D.B. Davis, C.S. Peven, J.C. Johnson, J.M. Van Emon, Analysis of soil and dust samples for polychlorinated biphenyls by enzyme-linked immunosorbent assay (ELISA), Anal. Chim. Acta 376 (1998) 67–75.

[183] J.C. Johnson, J.M.V. Emona, A.N. Clarke, B.N. Wamsley, Quantitative ELISA of polychlorinated biphenyls in an oily soil matrix using supercritical fluid extraction, Anal. Chim. Acta 428 (2001) 191–199.

[184] A.P. Deng, K. Vladimir, U. Robert, M. Franek, Direct competitive ELISA for the determination of polychlorinated biphenyls in soil samples, Anal. Bioanal. Chem. 373 (2002) 685–690.

[185] S. David, W. David, Controlling industrial pollution in the developing world, Environ. Quality Manage. 8 (1998) 69–75.

[186] M. Govindan, S. Moon, Expeditious removal of PCDD/Fs from industrial waste incinerator fly ash using electrogenerated homogeneous Ag(II) ions, Chem. Eng. J. 272 (2015) 145–150.

[187] N. Seltenrich, New link in the food chain? Marine plastic pollution and seafood safety, Environ. Health Perspect. 123 (2015) A34–A41.

[188] D. Muir, E. Sverko, Analytical methods for PCBs and organochlorine pesticides in environmental monitoring and surveillance: a critical appraisal, Anal. Bioanal. Chem. 386 (2006) 769–789.

[189] S. Murinova, K. Dercova, H. Dudasova, Degradation of polychlorinated biphenyls (PCBs) by four bacterial isolates obtained from the PCB-contaminated soil and PCB-contaminated sediment, Int. Biodet. Biodegr. 91 (2014) 52–59.

[190] D.L. Swackhamer, Quality assurance plan: Green bay mass balance study, I. PCBs and Dieldrin. US EPA Great Lakes National Program Office, Chicago, IL 1988.

[191] Y. Uekusa, S. Takatsuki, T. Tsutsumi, H. Akiyama, R. Matsuda, R. Teshima, A. Hachisuka, T. Watanabe, Determination of polychlorinated biphenyls in marine fish obtained from tsunami-stricken areas of Japan, PLoS ONE 12 (2017) e0174961.

[192] A.R. Lisa, S. Du, D.E. Fennell, G.J. Cavallo, Evidence for widespread dechlorination of polychlorinated biphenyls in groundwater, landfills, and wastewater collection systems, Environ. Sci. Technol. 44 (2010) 7534–7540.

[193] E. Weidemann, L. Lundin, Behavior of PCDF, PCDD, PCN and PCB during low temperature thermal treatment of MSW incineration fly ash, Chem. Eng. J. 279 (2015) 180–187.

[194] J.H. Han, F. You, P. Li, Q. Dong, S.H. Qin, D.D. Fan, Properties and reliability evaluation of consecutive pyrolysis and incineration disposal process for FR-4 waste printed circuit boards, Proc. Eng. 211 (2018) 205–214.

[195] K. Yaghmaeian, N. Jaafarzadeh, R. Nabizadeh, G. Dastforoushan, J. Jaafari, CFD modeling of incinerator to increase PCBs removal from outlet gas, J. Environ. Health Sci. Eng. 13 (2015) 1–6.

[196] P. Jyothi, G.G. Achari, C.H. Langford, Reductive dechlorination of PCBs using photocatalyzed UV light, Clean Soil Air Water 40 (2012) 455–460.

[197] K. Prakash, P. Senthil Kumar, P. Latha, K. Saravanakumar, S. Karuthapandian, Design and fabrication of a novel metal-free SiO$_2$/g-C3N4 nanocomposite: a robust photocatalyst for the degradation of organic contaminants, J. Inorg. Organomet. 28 (2018) 268–278.

[198] X.M. Hong, L. Zhao, Y.H. Dong, H. Chen, M. Zhong, Enhanced Fenton degradation of polychlorinated biphenyls in capacitor-oil- contaminated soil by chelating agents, Chem. Eng. J. 333 (2018) 370–379.

[199] G.D. Fang, D.D. Dionysiou, Y. Wang, S.R. Al-Abed, D.M. Zhou, Sulfate radical-based degradation of polychlorinated biphenyls: effects of chloride ion and reaction kinetics, J. Hazard. Mater. 227–228 (2012) 394–401.

[200] G. Fang, W. Wu, Y. Deng, D. Zhou, Homogenous activation of persulfate by different species of vanadium ions for PCBs degradation, Chem. Eng. J. 323 (2017) 84–95.

[201] J. Wang, S. Wang, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, Chem. Eng. J. 334 (2018) 1502–1517.

[202] K. Kim, S.H. Son, K.S. Kim, K. Kim, Y.C. Kim, Environmental effects of supercritical water oxidation (SCWO) process for treating transformer oil contaminated with polychlorinated biphenyls, Chem. Eng. J. 165 (2010) 170–174.

[203] M.L. Cathrine, O. Uhlik, M.B. Leigh, Synergistic processing of biphenyl and benzoate: carbon flow through the bacterial community in polychlorinated-biphenyl- contaminated soil, Sci. Rep. 6 (2016) 22145.

[204] K. Murugan, N. Vasudevan, Intracellular toxicity exerted by PCBs and role of VBNC bacterial strains in biodegradation, Ecotoxicol. Environ. Saf. 157 (2018) 40–60.

[205] L. Xu, X. Chen, H. Li, F. Hu, M. Liang, Characterization of the biosorption and biodegradation properties of Ensifer adhaerens: a potential agent to remove polychlorinated biphenyls from contaminated water, J. Hazard. Mater. 302 (2016) 314–322.

[206] H. Dudasova, J. Derco, L. Sumegova, K. Dercova, K. Laszlova, Removal of polychlorinated biphenyl congeners in mixture Delor 103 from wastewater by

ozonation vs/and biological method, J. Hazard. Mater. 321 (2017) 54–61.

[207] H. Slater, T. Gouin, M.B. Leigh, Assessing the potential for rhizoremediation of PCB contaminated soils in northern regions using native tree species, Chemosphere 84 (2011) 199–206.

[208] A. Wyrwicka, S. Steffani, M. Urbaniak, The effect of PCB-contaminated sewage sludge and sediment on metabolism of cucumber plants (*Cucumis sativus*), Ecohydrol. Hydrobiol. 14 (2014) 75–82.

[209] N. Das, L.V.G. Basak, J.A. Salam, E.A. Abigail, Application of biofilms on remediation of pollutants-an overview, J. Microbiol. Biotechnol. Res. 2 (2017) 783–790.

[210] V. Marulanda, G. Bolanos, Supercritical water oxidation of a heavily PCB-contaminated mineral transformer oil: laboratory-scale data and economic assessment, J. Supercrit. Fluids 54 (2010) 258–265.

[211] Z. Fang, Near-Critical and Supercritical Water and their Applications for Biorefineries, Springer, 2014.

[212] J.Y. Lu, X. Du, G. Lipscomb, 2009. "Cleaning membranes with focused ultrasound beams for drinking water treatment," in Ultrasonics Symposium (IUS), 2009 IEEE International (Rome: IEEE), 1195-1198.

[213] J.R. Chen, D. Kim, J.S. Park, K.I. Gil, T.F. Yen, Reductive dechlorination of polychlorinated biphenyls (PCBs) by ultrasound- assisted chemical process (UACP), Environ. Earth Sci. 69 (2013) 1025–1032.

[214] N.J. Goran, J.E. Atwater, Z.P. Polona, I. Plazl, Dechlorination of polychlorinated phenols on bimetallic Pd/Fe catalyst in a magnetically stabilized fluidized bed, Chem. Eng. J. 274 (2015) 50–60.

[215] H. Zhang, B. Zhang, B. Liu, Integrated nano-zero valent iron and biosurfactants aided remediation of PCB-contaminated soil, Appl. Environ Soil Sci. (2016) 5390808.

[216] H.I. Gomes, C.D. Ferreira, L.M. Ottosen, A.B. Ribeiro, Electroremediation of PCB contaminated soil combined with iron nanoparticles: effect of the soil type, Chemosphere 131 (2015) 157–163.

[217] G. Fan, W. Yu, G. Fang, X. Zhu, D. Zhou, Review of chemical and electrokinetic remediation of PCBs contaminated soils and sediments, Environ. Sci. Proc. Imp. 18 (2016) 1140–1156.

[218] X. Liu, G. Yu, Combined effect of microwave and activated carbon on the remediation of polychlorinated biphenyl-contaminated soil, Chemosphere 63 (2006) 228–235.

[219] M. Aresta, A. Dibenedetto, C. Fragale, P. Giannoccaro, C. Pastore, D. Zammiello, C. Ferragina, Thermal desorption of polychlorobiphenyls from contaminated soils and their hydrodechlorination using Pd- and Rh-supported catalysts, Chemosphere 70 (2008) 1052–1058.

[220] L. Rehmann, A.J. Daugulis, Biodegradation of PCBs in two-phase partitioning bioreactors following solid extraction from soil, Biotechnol. Bioeng. 99 (2008) 1273–1280.

[221] D. Jiang, G. Zeng, D. Huang, M. Chen, C. Zhang, C. Huang, J. Wan, Remediation of contaminated soils by enhanced nanoscale zero valent iron, Environ. Res. 163 (2018) 217–227.

[222] S. Chen, Z.L. Qin, X. Quan, Y.B. Zhang, H.M. Zhao, Electrocatalytic dechlorination of 2,4,5-trichlorobiphenyl using an aligned carbon nanotubes electrode deposited with palladium nanoparticles, Chin. Sci. Bull. 55 (2010) 358–364.

[223] M. Viisimaa, O. Karpenko, V. Novikov, M. Trapido, A. Goi, Influence of bio-surfactant on combined chemical-biological treatment of PCB-contaminated soil, Chem. Eng. J. 220 (2013) 352–359.

[224] X. Zhu, D. Zhou, Y. Wang, L. Cang, G. Fang, J. Fan, Remediation of polychlorinated biphenyl-contaminated soil by soil washing and subsequent TiO_2 photocatalytic degradation, J. Soils Sediments 12 (2012) 1371–1379.

[225] Z. Liu, F.S. Zhang, Nano-zerovalent iron contained porous carbons developed from waste biomass for the adsorption and dechlorination of PCBs, Bioresour. Technol. 101 (2010) 2562–2564.

[226] M.S. McLachlan, E. Undeman, F. Zhao, M. MacLeod, Predicting global scale exposure of humans to PCB 153 from historical emissions, Environ. Sci. Proc. Imp. 20 (2018) 747–756.

[227] M. Bryan, H. Wang, Mechanisms of xenobiotic receptor activation: direct vs. Indirect, Biochim. Biophys. Acta 1859 (2016) 1130–1140.

[228] M.D. Ampleman, A. Martinez, J. DeWall, D.F.K. Rawn, K.C. Hornbuckle, P.S. Thorne, Inhalation and dietary exposure to PCBs in urban and rural cohorts via congener-specific measurements, Environ. Sci. Technol. 49 (2015) 1156–1164.

[229] P. Jennifer, E.A. Houseman, E. Smit, M.L. Kile, A path analysis of multiple neurotoxic chemicals and cognitive functioning in older US adults (NHANES 1999–2002), Environ. Health 16 (2017) 1–11.

[230] A. Halfadji, A. Touabet, Determination of 26 polychlorinated biphenyls congeners in soil samples using microwave-assisted extraction with open vessel and gas chromatography, Green Chem. Lett. Rev. 11 (2018) 209–216.

[231] U. Stoin, A. Mojon, Y. Sasson, Fast and complete *in situ* mineralization of contaminated soils using a novel method for superoxide generation, RSC Adv. 5 (2015) 6571–6577.

[232] A.J. Bergmann, G.L. Points, R.P. Scott, G. Wilson, K.A. Anderson, Development of quantitative screen for 1550 chemicals with GC-MS, Anal. Bioanal. Chem. 410 (2018) 3101–3110.

[233] A. Eguchi, T. Enomoto, N. Suzuki, M. Okuno, C. Mori, Development of simple analytical methods of polychlorinated biphenyls in human serum by gas chromatography negative ion chemical ionization quadrupole mass spectrometry, Acta Chromatogr. 29 (2017) 503–506.