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Recent Status of Global Polychlorinated Biphenyls Contamination

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Authors' contributions

This work was carried out in collaboration among all authors. Author AS designed the initial draft and protocol of the manuscript. Authors MB and SG managed the analysis and drafting of the study. Authors KP and SS performed the literature search. Author KS designed the reference arrangements and figures. All authors read and approved the final manuscript.

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ABSTRACT

Organic pollutants are continuously disrupting the equilibrium of nature. Polychlorinated Biphenyls are a member of the broad family of man-made organic chemicals well-known as chlorinated hydrocarbons. Due to their chemical stability, high boiling point and electrical insulating properties, non-flammability, Polychlorinated Biphenyls are used in various commercial as well as industrial applications. Polychlorinated Biphenyls residues remain in the ecosystem and bioaccumulate in various organisms due to their persistent nature and resistance against natural breakdown agents. This leads to the enlisting of approximately 209 chlorinated congeners in the list of persistent

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organic pollutants (POPs) under the Stockholm Convention. Their residues have been detected in various environmental components even though their production has been banned for more than a decade. High residues of Polychlorinated Biphenyls in water bodies, aquatic faunas, soils and sediments, air, and biota samples have been reported. Therefore, the current review aims at depicting the source and dynamics of Polychlorinated Biphenyls in the environment as well as the exploitation of various detection tools for the analysis of Polychlorinated Biphenyls. Besides, it provides a critical description of worldwide contamination scenarios of Polychlorinated Biphenyls and the need for further advancement in the detection and extensive identification.

Keywords: Polychlorinated biphenyls; contamination; persistency; detection; analysis.

1. INTRODUCTION

Polychlorinated biphenyls are one of the members of the halogenated organic group of concerning environmental contaminants consisting of 209 congeners, out of which only about 130 (di- to deca-PCBs) are found in commercial mixtures. Due to prominence in physicochemical properties like thermochemical stability, dielectric properties, insulating properties, PCBs have been used commercially in various sectors like dielectric fluids in transformers and capacitors, heat exchangers, hydraulic lubricants, caulks along with joints, lubricating oils, and paints, carbon-free copy (“NCR”) paper, attachments and plastics [1]. These stages of applications show various effects on the emission of PCBs in the ecosystem. For instance, the carbonless paper has resulted in environmental discharges after recycling. Applications in caulks tend to stay in place for a long period. Most PCBs were sealed off in electronic appliances, which create a huge environmental impact by accidental exposure of saved, stored, or disposed of PCBs. Moreover, widespread contamination is the result of the partitioning of PCBs between aquatic and solid phase, especially due to their high octanol-water partition coefficients (Kow). Taking their undesirable effects on the entire ecosystem into consideration, PCBs are characterized into a group of persistent organic pollutants (POPs). Furthermore, because of their acute toxicity and environmental persistency, several analytical strategies have been developed by various researchers, and based on them; significant quantities of PCBs have been recognized from different environmental matrices [2]. Therefore, it is of the critical need to focus on the detection tools available for analyzing PCBs and the current scenario of PCB contamination worldwide.

2. SOURCE AND DYNAMICS OF PCB CONTAMINATION

The distribution of PCBs in the ecosystem is the sole source of environmental contamination. The dynamics make it to few steps ahead towards biomagnification and health effects. PCBs tend to partition between air and water due to low vapor pressure and hydrophobicity. This leads to the fact that PCBs can be found in every part and parcel of the environment. Due to imprudent applications and disposal in the United States, almost one-third of PCBs have entered nature already [3] and their emission is still ongoing, mounted through dumping of old electrical equipments. Anthropogenic activities are the main reason behind the spillage of PCBs in the environment. Past disposal, Improper disposal, leakage, Internal release, leaching, ingestion of contaminated fish, etc can induce the PCB contamination. Besides, stringent regulations, a few PCBs are unlawfully disposed of due to negligence or ignorance. As a result of thermo-chemical stability, PCBs become persistent environmentally and are amongst the most prominent environmental pollutants. When these undesirable features are combined with the low water solubility of PCBs, the great concern emerges, because these substances may get accumulated through the food chain and reach aquatic organisms, fish, and humans. The biotransformation of PCBs leads to adverse health effects both for humans and biota. PCBs are considered carcinogenic to humans by the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP). Apart from endocrine-disrupting effects, PCBs tend to hamper reproductive ability and neuron developments in humans. Besides, every component of the ecosystem e.g. birds, aquatic animals, etc have been detected with these toxic PCBs [4-5].

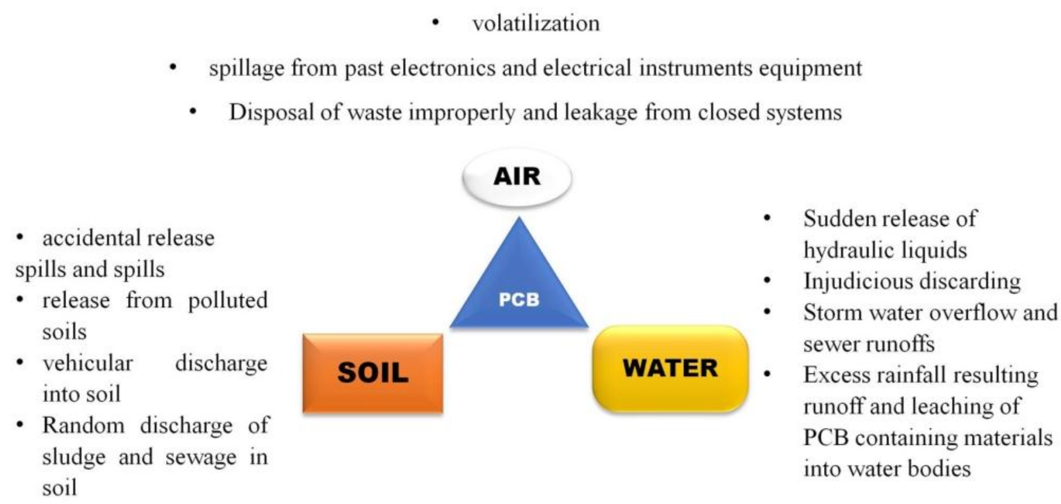

Fig. 1. Source of exposure of polychlorinated biphenyls

3. DETECTION TOOLS FOR PCBs

GC is one of the most significant analytical tools and the two most widely used GC injection procedures for PCB isolation are on column and split/splitless injection [6]. Recently, thermal or pressure injection methods are very popular. Although these methods are advantageous depending on the increased injection volumes that can be applied without any side effects associated with them, the new method incorporating open tubular capillary columns (high-resolution gas chromatography (HRGC) is also proved to be very useful [7].

ECD is the standard detector most suited for PCB analysis, but in the last few years, MS detectors have replaced ECD because of its versatile benefits. GC-MS combines two can help to identify analytes with low LODs and are also useful in quantitative studies. Analysis of PCBs in biota and sediment samples can be done with sufficient sensitivity using low-resolution mass spectrometry (LRMS). But for analyzing DL PCBs, HRMS has a huge advantage when considering their ability to focus on small concentrations. For sample testing, LRMS is very important [8] while for certain planar PCBs, HRMS techniques are considered to be an improved method as suggested by the reports of analysis of furans and dioxins in environmental matrices.

HRMS provides low LODs for PCBs but requires additional sample cleaning and specialized tools [9]. Besides, reports of analysis of PCBs from other sources have also been reported. For each of these methods, waste cleaning procedures were performed using SPE and SBSE which were followed by GC-MS. Researchers concluded that the various SPE adsorbents might help to detect PCBs from the muds, and GC-MS could be able to successfully detect PCBs.

Recently, PCBs have been detected in various food samples including coffee, milk, and meat products using two novel analytical methods [10-11]. In one of these methods, ionic liquid-based in-situ microextraction (DLLME) was used for subsequent extraction and analysis using HS-GC-ECD-MS. The study used a thin-layer metal chromatography column to separate PCBs and found a sensitivity and specificity equal to standard GC / ECD.

Besides, PCBs can be detected using bioanalytical methods including the competitive ELISA assay and CALUX bioassay. Further, liquid chromatography based methods have also been found to be very useful involving HPLC with UV detector or LC-MS/MS, etc. Capillary electrophoresis has also been used for isolating PCBs particularly Micellar Electrokinetic capillary electrophoresis and CE-MS detector based methods are effective in the separation of hydrophobic solutes like PCBs.

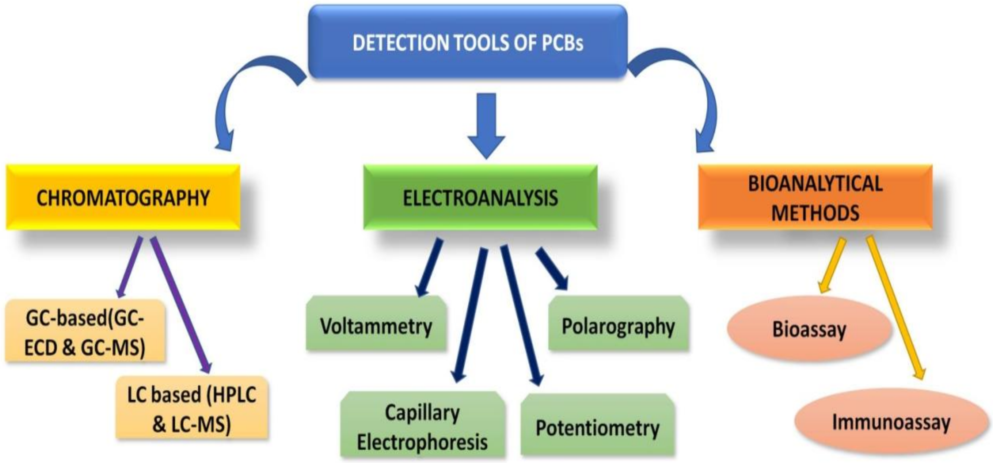

Fig. 2. Bunch of detection tools available for analyzing polychlorinated biphenyls

4. GLOBAL DETECTION OF PCBs

Due to the hydrophobicity and persistent nature of PCBs, they have been detected in soil, sediments, air, milk, wildlife, water, fish, plants, human adipose tissues and blood samples at significant concentrations since the year 1966 [12].

4.1 In Water

Using various analytical methods and instruments, PCBs have been found across the global water bodies starting from the local streams, sewage sites, and major rivers of different countries and even in the oceans. In the marine environment of industrial highs, PCB concentrations were found to be 100 times greater than the relevant sea surface, where samples have been collected from a few millimeters depth on the surface. Specifically, the highest concentrations of PCBs of about 3.0 ng / L were detected in one of the largest industrial areas in Texas i.e. the North Sea and Galveston Bay [13]. In one study, polychlorinated biphenyls' (PCBs) melt-related release in proglacial lakes and glacier streams of the catchment of the Silvretta glacier, located in the Swiss Alps displayed that release of PCBs due to accelerated glacier melt was only detected in the proglacial lake, but not in the other compartments of the Silvretta catchment [14]. Furthermore, greater concentrations of about 18 Penta and Hexa congeners were identified at the Lake Superior, the largest freshwater body in North America [15]. Besides, the simultaneous quantification of PCBs in Mississippi river water by GC-MS [16], Hawaiian water bodies, and fishes contain toxic levels of PCBs [17]. Individual PCBs have been detected in surface water bodies of Johannesburg city using passive samplers [18]. In the Yangtze river basin of China, PCBs have been detected in surface water [19]. Nassar [20] quantified toxic PCB congeners using GC-MS at the three sampling sites across the Nile river and most importantly the concentrations of drinking water PCBs in these areas were significantly higher than USEPA limit. Previously, water bodies along with sediments, aquatic faunas near an e-waste dumping site at Lagon and Oslo in Nigeria were detected with a higher concentration of about 28 Hexa and tetra PCB congeners [21]. Recently, in an urban lake of Shanghai, a total of 18 PCBs were detected along with PAHs and OCPs due to leakage of capacitor equipment, sewer drainage of industries, and exfoliation of ship paints [22]. Nguyen detected serious contamination of PCBs in groundwater samples of Taiwan while in surface water samples, he found a relatively lower concentration of dl-PCBs and PCDD/Fs [23]. Apart from all these scientists are on their road to develop some novel techniques for detection of PCBs from complex matrices e.g. successful detection of PCB 118,153 and 126 in water using benzopyrene fluorescence [24].

In India, Kaur et al. [25] detected PCBs and other POPs in sediments, water, and tissues in River Sutlej, Hooghly estuary sediments [26]. Besides, Ganges river basins [27], Chilka lake, and Yamuna river waters [28] have been reported containing PCBs.

4.2 In Soil and Sediments

PCBs can be exposed to the soil environment via 2 primary pathways including atmospheric transportation and disposal sites. Being pervasive in nature, they can be able to remain in the soil for a long period. In surface water sediments also, PCBs tend to accumulate in significant concentrations and clay, organic matter, and particulates dispersed in water trap PCBs through adsorption. Using various sampling tools and some guidelines provided by CERP [29], PCBs have been quantified in agricultural soils, marine sediments, soils near industries, etc. In 2005, a study on surface soil contaminated PCBs in about 52 sites across China reported that the average concentration of PCBs in all these sites tends to be 515 pg/g dry weight which is 1/10th of the global background soil in 1998. Moreover, the nature of the congeners detected signified a fresh signature of exposure of PCBs in these provinces [30]. Vane et al. [31] detected presence of Penta, Hexa, and Hepta PCB congeners with a significant concentration near the surface soils of east London, UK whereas, in urban soils of USA, Martinez et al. [32] have quantified about 164 PCB congeners with a mean concentration of 56 µg/kg. Similar profiles have also been identified in Glasgow, Scotland in urban soils where a higher proportion of Penta-CB was also observed [33]. Temporal changes in quantities of chlorinated PCB congeners indicate the dominance of highly chlorinated congeners and degradation of tri and tetra congeners via volatilization. Similar is in the case of depletion of lighter PCBs in urban soils as compared to rural sites, in France wherein approximately 22 PCBs have been identified [34]. Besides, in Moscow, 17 toxic congeners were detected in urban and periurban soils [35] while in about 5 European cities, 19 PCBs have been quantified with a range of concentrations 0.79-73 µg/kg [33]. However, a significant contribution of tri-CB reported in the Tianjin region of China was attributed to the recent localized production of this congener group [36]. Recently, elevated levels of about 30 PCBs have been traced in the Nepalese surface soil with a dominance of toxic hexachlorinated congeners [37]. In a study of agricultural soils near an industrial area have been collected in Anseong, Korea, and about 29 PCB congeners were detected above their permissible limit [38]. Apart from the above, a higher concentration of PCBs in Mexican soils has been found to create health hazards [39] while in Scotland, soil to grass transfer of PCBs resulted in food web poisoning. A multi-media fate model determines the high pollution levels of PCBs in soils of Switzerland. Metropolitan areas of Buenos Aires have been detected with high PCB concentration in soils, street, and dusts, etc [40]. Also, a total of 33 PCB congener's high concentrations have been detected in soils of the different metropolitan environments across India [41].

Besides, in sediments also PCBs have been found in trace amount including the surficial sediments of the Persian Gulf contained higher concentrations of PCBs ranging from 2.95-7.95 ng/g dry weight [42], historically contaminated sediments of urban river networks of Shanghai [43] as well as sediments of Yellow river basin of China and Adriatic sea core sediments also were identified with these kinds of toxic chlorinated congeners [44].

4.3 In Air

PCBs are observed worldwide at significant concentrations and in most of the cases, quantities of PCBs in urban air varied widely than that of rural areas. For example, 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 Antarctic and Arctic regions, where they have never been used [45]. In the early 80s, 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 [46]. In a study, ambient air samples were collected using a passive sampling method deploying polyurethane foam disks and it depicted a higher concentration of chlorinated pollutants and especially PCBs in highly urbanized South and East Europe [47]. However, in Korea, mean PCBs concentration detected in both urban and rural areas varied widely as the atmospheric concentration of lower molecular weight congeners in urban areas might be predominantly influenced by local sources as compared to the rural areas [48]. PCBs after remaining concealed in sediments for a long period, gradually release onto the water and therefore volatilized/dispersed into the air. This water-air movement happens, particularly during dry months. This kind of case was observed during sampling of gaseous and freely dissolved PCBs in air and water of Lakes Erie and Ontario during 2011-12. A Sum of 29 PCBs detected in aqueous solutions with the range varying from 1.5-105 pg/L whereas the total atmospheric concentration was 7.7-634 pg/m^3 across both the lakes [49]. In a recent study on indoor air concentration of PCBs, Denmark showed the extraordinarily highest levels in both gas and particle phase [50] whereas lowest levels were detected in Lzmir [51] and Pohang [52]. Moreover, Harrad et al. [53] assessed human exposure to PCBs through inhalation, dust ingestion, and diets in the UK, USA, Canada, and New Zealand. The average levels of indoor air PCBs were nearly equal in the case of the USA and Canada and In the case of the UK and New Zealand. Wang et al. [54] assessed the human daily intake of PCBs from indoor and outdoor air dust in Hong Kong and Guangzhou and he showed that levels of PCBs in Hong Kong are less than the other province indicating an avg concentration of 4-264 ng/g for Hong Kong air. Recently, air samples from thermal power provinces near Kuthaya, Turkey depicted that due to extraordinary volatilization during dry months especially in summer, PCBs have been highly distributed in the air [55]. Besides, the urban air of Southern Italy has also been traced with a higher quantity of PCBs [56].

In India, no production reports of PCBs were reported and imports were banned since 1998 but surprisingly, the global database shows India is producing more PCBs than in other neighboring countries. Airborne samples from urban, rural, and wetlands along the Indian coast [57] evidenced greater concentrations (216-1077 pg / m^3) than were found in other Asian countries (5- 4040 pg / m^3). A similar study in the Punjab province of Pakistan reported that total PCB values ranged from 34 to 389 pg / m^3 in the air, much lower than Indian standards [58]. Furthermore, Goel et al. [59] quantified 32 priority PCBs in the air near the transformer plants at Kanpur, Uttar Pradesh, and also assessed the toxicological risk using the Junge Parkow model.

4.4 In Biota, Foods and Other Stuff

Apart from the soil, water, and air, different aquatic faunas, humans, and several other matrices were reported to contain toxic congeners. Moreover, in foods, PCBs have been detected like in farmed fishes produced in Greece [60], high levels of PCBs, PCDDs, PCDFs have been detected while in Bluefin tuna, toxic levels of PCBs have been identified [61]. Marine fishes of Persian gulfs and various types of seafood in the coastal areas of Bangladesh contains a higher amount of PCBs [62]. Further, fish samples of the black sea, Bulgaria [63], local feral fish in three Gorges River, China [64], and fishes obtained from Korean markets [65] were reported to contain a toxic amount of PCBs. To evaluate contamination by PCBs in a tropical bay exposed to different anthropogenic pressures, samples of bivalves: clams (*Anomalocardia brasiliana*), mangrove mussel (*Mytella guyanensis*), and mangrove oyster (*Crassotrea rhizophorae*), were collected from different parts of Brazil, Bahia, Todos os Santos Bay, and the results showed that highest concentrations of PCBs being detected in mangrove oyster, followed by clams and mangrove mussel [66]. In meat samples obtained in Italy, PCBs were detected with an abundance of lower chlorinated congeners and were predicted to be highly carcinogenic to people residing in that area [67]. Recently, quEChERS extraction method has been tried to detect PCBs in breast milk from pregnant women [68]. Moreover, Swedish environmentalists showed a temporal declining trend of all types of dioxins and also estimated concentrations up to 2040 [69]. During 1991 to 97, dietary exposure was detected in significantly higher concentration around 2.0-12 ng/kg body weight/day in kids and 3.0-5.0 ng/kg body weight/day in adults. Next, a study carried out in Japan during the late 90s estimated PCBs' intake over 120 food items, and the result exposed that utmost concentrations (8.39-25.7 ng/kg) of PCBs were found in shellfish and fish. The total uptake of PCBs in adults was found to be 0.00145 ng/kg body weight/day, which depicts a high degree of PCBs contamination in Japan [70]. 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 [71]. In the late 80s, the quantity of PCBs detected in fat of human milk was ranged from 0.2-4.0 mg/kg [72]. 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 to 1000 ng of total PCB per gram of maternal plasma lipids.

5. CONCLUSION

Based on the review, we can conclude that PCBs, being a hazardous organic pollutant, invades into the environment from various sources, and due to their persistence and low water solubility they tend to retain in the ecosystem for long. The fundamental scientific research on PCBs in the past few years has shown numerous unexpected innovations. Principally, the concentrations of PCBs in the environment are no longer lessening, but in fact, they are increasing in some geographical regions [73]. Depending on several regulatory approaches and scientifically justified procedures, researchers have found out trace quantity of PCBs in several matrices and these findings lead to the enlisting of PCBs under persistent organic pollutants by Stockholm Convention. Some recent advances in analysis techniques like the introduction of Raman Spectroscopy, benzopyrene fluorescence, immunosensors, polarography, and voltammetric techniques have proved to be a boon to quantify PCBs from other complex matrices. But more databases and inventories of industrial chemicals and hazardous substances should be developed in addition to extensive site surveys after source identification. In the future, for the sake of environmental management and implementation of Integrated Pollution Prevention and Control (IPPC), operational monitoring obligations should be shifted towards the industrial companies. The public authorities remain the charge of national surveys, assessment, reporting, and inspections.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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