



A preliminary assessment of polychlorinated biphenyls in surface waters

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ABSTRACT

*A preliminary assessment of levels of polychlorinated biphenyls (PCBs) in surface waters was carried out and discussed in this paper. Total concentrations of Σ PCBs ranged between 1.03-21.79 ng L⁻¹ with the mean and median value of 12.91 ng L⁻¹ and 11.26 ng L⁻¹ (± 1.61 ng L⁻¹), respectively. Average concentration of twelve WHO's dioxin like-PCBs (DL-PCBs) was 7.67 \pm 1.18 ng L⁻¹ and accounted for 67.1% of Σ PCBs. The 2, 3, 7, 8-tetrachloro dibenzo-*p*-dioxin (TCDD) relative toxicity equivalency (TEQ) for DL-PCBs was calculated using WHO toxicity equivalency factors (TEFs), and ranged between 0.001-0.135 ng-TEQ L⁻¹ with an average value of 0.048 \pm 0.011 ng-TEQ L⁻¹. The group homolog of PCBs was dominated by 4-6 chlorinated biphenyls. The observed concentrations were lower than the guideline values for eco-toxicological risk.*

Keywords: Surface water, Polychlorinated Biphenyls (PCBs), Toxicity Equivalency (TEQ)

INTRODUCTION

For last decades of years, several persistent organic compounds have been synthesized and released into the environment for direct or indirect application. Among them; polychlorinated biphenyls (PCBs) are known as environmental and human health concern. Therefore, PCBs were listed in the Stockholm Convention as one of 12 persistent organic pollutants (POPs), due to their resistant to chemical, physical and biological degradation and being ubiquitously found in all environments of the earth [1]. PCBs are odorless, tasteless, colorless or light color synthetic chemical compounds. They have extremely high boiling points and are nonflammable chemicals which were primarily used in transformers and capacitors and also in many other industrial applications such as lubricants, flame retardants, plasticizers and paint additives. PCBs are amongst the industrial chemicals and have no known natural sources in the environment but they entered the environment through many anthropogenic sources including leakages of PCBs containing transformer oils, waste disposals and by the burning of some wastes in municipal and industrial incinerators [2]. PCBs have been found world-wide in the regions far from their original sources [3-4] and known as long range atmospheric transport (LRAT) pollutants.

Some PCB congeners, especially non- and mono ortho PCBs have toxicity similar to 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (TCDD) are hereby referred as dioxin-like (DL). Toxicity equivalency factors for DL-PCBs have been established by WHO [5] to assess the potential relative toxic potencies associated with binding to the Ah receptor, compared to that of TCDD [6]. These dioxin-like PCBs are formed unintentionally in the same way as polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzo-*p*-furans (PCDDs/Fs) [7]. Potential sources of PCBs are chemical and petrochemical plants, ferrous and non-ferrous metal smelting operations, paper and pulp industries, cement production and fuel combustion. Smaller non-point sources include domestic biomass burning, landfill, fires and open burning as well as by natural processes such as vegetation fires [8].

Polychlorinated biphenyls (PCBs) are classified as probable human carcinogens (Group B2) by EPA, and International Agency for Research on Cancer (IARC) has included these chemicals in Group 2A of carcinogens with wide range of health effects including carcinogenicity, neurological and reproductive disorders, and suspected hormonal disorders [2].

As a party to the Stockholm Convention, India is agreed by the objectives of the treaty with the intention of reducing, and ultimately eliminating persistent organic pollutants including polychlorinated biphenyls. National implementation plan has been developed and submitted to Stockholm Convention on Persistent Organic Pollutants. PCBs have never been produced in India but used in industrial applications [8]. Earlier studies in India on PCBs with various matrices revealed PCBs contamination in environmental samples including water [9-10], soils [11-15], sediments [16-19], atmospheric air [20-23] and biota including humans [24-26]. In this study, a preliminary study was carried out to investigate PCBs in surface waters from different ponds in National Capital Region, India.

MATERIALS AND METHODS

Water Sampling

Surface water samples from different locations in National Capital Region, India collected from major ponds during January 2010. Amber glass bottles (1L) used for sampling, which were washed successively with detergent, water, distilled water and solvents before sampling. 1L surface water sample was collected using stainless bucket and transferred to sampling bottle. The glass bottle was filled to the top with the sample water to eliminate air bubbles. After proper labeling, the sample bottles were transported with ice to the laboratory and stored at 4°C followed by an extraction within 7 days.

Solvents, Chemicals and Standards

HPLC grade solvents (acetone, hexane and dichloromethane) used in sample processing were procured from Merck India. Silica gel (100–200 mesh) procured from Sigma-Aldrich (USA), activated at 130 °C for 16 h and used during extract clean-up as absorbent in column chromatography. Anhydrous sodium sulphate (Merck, India) was cleaned with solvents and stored in the sealed desiccator. Reference standard solutions of PCB congeners were purchased from Dr Ehrenstorfer (GmbH, Augsberg, Germany). Working standard solutions with appropriate concentrations were used for instrument calibration and other quality control analysis.

Analytical Methodology

Samples were extracted with dichloromethane and purified using activated silica gel column. Briefly 1L water sample was extracted thrice with dichloromethane. The dichloromethane extract containing organic pollutants was collected through a funnel containing anhydrous sodium sulphate to remove traces of water contents and then evaporated to 1-2 ml under reduced pressure at 40° C in water bath using rotary evaporator (Eyela, Tokyo, Japan). Sample extracts were cleaned using silica gel chromatography. A glass column (10x300 mm) was packed with 2 cm layer of anhydrous sodium sulphate, overlaid with 5 cm layer of activated silica gel (about 10.0 g) and topped with another 2 cm of anhydrous sodium sulphate. After rinsing the column with hexane, concentrated sample extract was loaded with three washings of hexane and then eluted with a mixture of hexane and dichloromethane (DCM) (1:1 v/v). The eluted extract was concentrated to near 2-5 ml using Rotatory vacuum evaporator and TurboVap (Caliper, USA) under a gentle stream of pure nitrogen. An additional 20-25 ml hexane was added to the concentrated extracts and evaporated to remove traces of dichloromethane. Finally, eluted fraction was concentrated to 1.0 ml and transferred to auto sampler vial for analysis. One µl clean extract was injected onto a gas chromatograph equipped with an electron capture detector (GC-ECD) for quantification.

Selected polychlorinated biphenyl congeners (CB -52, -70, -74, -77, -81, -105, -114, -118, -123, -126, -128, -138, 156, -157, -167, -169 -170, -187, and CB-189) were separated and quantified with gas chromatograph (Shimadzu 2010, Tokyo, Japan) attached with autosampler, and equipped with an Electron Capture Detector (ECD ⁶³Ni) on a silica capillary column (HP-5MS Agilent) 60 m x 0.25 mm x 0.25 µm film. The temperature program of the column oven was set to 170 °C for 1 min then increased with 3 °C min⁻¹ to 270 °C kept for 1 min then further ramped with 10 °C min⁻¹ to 290 °C at and kept for 3 min. The injector and detector temperature were maintained at 225 °C and 300 °C, respectively. Purified nitrogen gas was used as carrier at the flow rate of 1.0 ml. min⁻¹.

Analytical Quality Control

Certified reference standards solutions purchased from Dr. Ehrenstorfer (GmbH Germany) used for the instrument calibration and PCB quantification. Individual PCB congeners were identified in the cleaned sample extract by comparing the accurate retention time from the standard mixture and quantified using the response factors from five level calibration curves of the standards. Appropriate quality assurance quality control (QA/QC) analysis was performed including analysis of procedural blanks (analyte concentrations were <MDL 'method detection limit'), random duplicate samples (Standard deviation <5), calibration curves with the r^2 value of 0.999. Each sample was analysed in duplicate and the average was used in calculations. Calculated concentrations were reported as less than the limit of detection if the peak area did not exceed the specified threshold (three times the noise). Concentrations below the limit of detection were assigned zero values for the statistical analysis.

Dioxin-like PCB congeners are assigned with the toxic equivalent factors based on the relative toxicity with 2, 3, 7, 8-tetrachloro dibenzo-*p*-dioxin (TCDD) [5] (Van den Berg *et al.*, 2006). Toxic equivalent quantities (TEQ) were calculated by multiplying the concentration of individual dl-PCB congener with the corresponding WHO toxicity equivalent factors (TEFs). The concentration of PCBs and their toxicity equivalency were reported as ng L⁻¹ and ng-TEQ L⁻¹, respectively.

Table 1: Concentration of PCBs in Pond waters

PCB congeners	Concentration (ng L ⁻¹)						% of Σ PCBs
	Min	Max	Mean	Med	SD	SE†	
PCB -52	1.30	4.20	3.14	3.60	1.13	0.25	6.4
PCB -70	1.70	2.10	1.97	2.10	0.23	0.05	2.4
PCB -74				BDL			
PCB -77*	0.73	5.00	2.32	1.90	1.25	0.28	13.2
PCB -81*	1.41	4.48	2.77	2.80	1.04	0.23	7.9
PCB -105*	0.29	2.74	1.35	1.38	0.90	0.20	3.3
PCB -114*	1.50	5.95	2.98	2.68	1.46	0.33	9.7
PCB -118*	1.57	3.09	2.09	1.98	0.58	0.13	4.3
PCB -123*	1.03	4.20	2.17	1.90	1.06	0.24	9.7
PCB -126*	0.60	1.35	0.99	1.00	0.35	0.08	1.6
PCB -128	1.30	2.80	1.90	1.60	0.79	0.18	2.3
PCB -138	0.41	3.73	2.07	2.28	1.02	0.23	7.6
PCB -156*	0.56	3.46	1.77	1.44	0.96	0.21	6.5
PCB -157*				BDL			
PCB -167*	1.30	4.60	2.39	2.12	1.01	0.22	7.8
PCB -169*	0.35	1.89	1.08	1.12	0.56	0.12	3.1
PCB -170	0.81	4.10	2.36	2.16	1.22	0.27	7.7
PCB -187	0.78	3.82	2.78	3.16	1.02	0.23	9.1
PCB -189*				BDL			
Σ DL-PCBs	1.03	16.12	7.67	9.10	5.32	1.18	67.1
Σ PCBs	1.03	21.79	12.91	11.26	6.25	1.61	100

*DL-PCBs (Dioxin like-PCBs), †SE (standard error)=SD/ \sqrt{N}

RESULTS AND DISCUSSION**Concentration of PCBs**

Concentration range and mean of 19 PCB congeners in pond water samples was presented in Table 1. Concentration of total PCBs varied between 1.03-21.79 ng L⁻¹ with the mean and median values of 12.91 ng L⁻¹ and 11.26 ng L⁻¹, respectively. The distribution pattern of the individual PCB congeners was not consistent, except PCB-77 which was the dominant congener and accounted for 13.2% of total PCBs. Congener number -114, -123 and -187 were the other major contributors with contribution for 9.7%, 9.7% and 9.1% to total PCBs. Concentrations observed in this study were compared with PCBs in surface water from other tropical and European countries. Concentrations of PCBs observed in this study were comparable with those from Yangtze River, China (1.23 to 16.6 ng L⁻¹) [27], Songhua River, China (1.1 to 14 ng L⁻¹) [28]. However, our levels were lower than runoff water at Gdansk airport, Poland (60-440 ng L⁻¹) [29], Baiyangdian Lake (19.46 to 131.62 ng L⁻¹) [30] and Dianchi Lake (13 to 72 ng L⁻¹) [31] in China, Fuglebekken in Svalbard, Norwegian (2-400 ng L⁻¹) [32], Southern Moravia Region, Czech Republic (5.2 to 190.8 ng L⁻¹) [33], Ebro River, Spain (74.58 ng L⁻¹) [34], Shadegan wetland protected area in the northwestern part of Iran (8-375 ng L⁻¹) [35], Hudson River, USA (<9.3-164.3 ng L⁻¹) [36], water bodies and Rivers in Nigeria (6721 ng L⁻¹) [37], but, higher than those from riverine runoff of the Pearl River Delta, China (0.12-1.47 ng L⁻¹) [38].

Group Homolog Profiles of PCBs

PCBs group homolog pattern in pond surface water samples from NCR was depicted in Figure 1. PCBs were primarily produced and used as technical mixtures containing more tri- tetra- and pentachlorinated biphenyls [39]. Tri and tetra-chlorinated biphenyls were primarily used in power capacitors and transformers while higher chlorinated biphenyls were used as an additive [28]. The group homolog of PCBs in this study was dominated with hexa chlorinated biphenyls (35%) followed by tetra and penta chlorinated biphenyls with the contribution of 30% and 29%, respectively to Σ PCBs. Hepta chlorinated biphenyls contributed 17% to total PCBs. The concentration of each homolog was ranged between 0.73-9.90 ng L⁻¹ (mean, 3.45 ng L⁻¹), 1.03-9.35 ng L⁻¹ (mean, 4.59 ng L⁻¹), 0.41-1373 ng L⁻¹ (mean, 4.66 ng L⁻¹) and 0.78-5.03 ng L⁻¹ (3.40 ng L⁻¹), respectively for 4CBs, 5CBs, 6CBs and 7CBs. The PCB patterns show that lighter-weighted molecular PCBs (LWM-PCBs) in the water samples were comparatively higher than those higher-molecular weight PCBs (HMW-PCBs), which suggests that heavier PCBs may have been deposited in bottom sediment, because LMW-PCBs has higher water solubility than HMW-PCBs. In an aquatic system the PCBs comes from wastewater discharges and air deposition which then adsorbed on the suspended particles in water and settle in the bottom sediment.

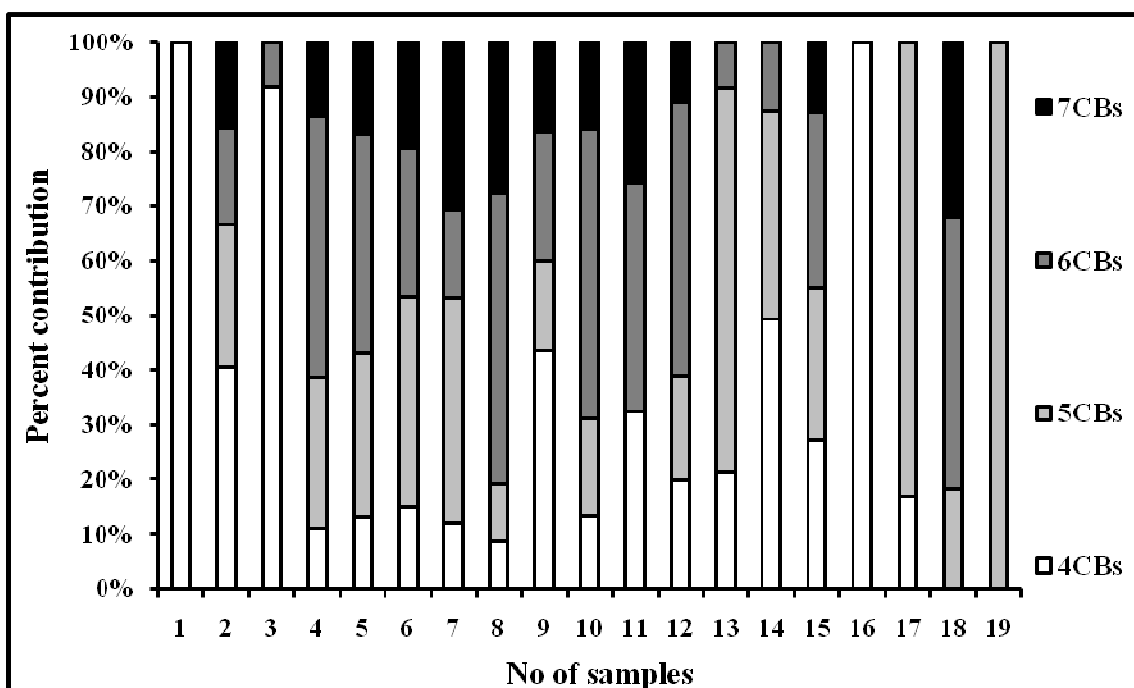


Figure1: Group homolog pattern of PCBs in pond water samples

The possible sources of PCBs may be from biomass burning and depositions of emissions from wood processing, paint and dyeing, chemicals and from electrical and electronic waste recycling units. Emissions from coal and wood combustion and industrial waste incineration sources contributed non ortho PCBs [40]. It has been reported that, activities such as open fires, cooking and heating in residential areas, may have higher emissions of PCBs, especially during the winter season. During such activities, especially burning of mixtures of waste, containing garden wastes, paper, plastics, PVC (polyvinyl chloride) and painted wood may produce relatively large amount of dioxin like-PCBs [41-43]. Polychlorinated biphenyls (PCBs), which have been used in industrial applications, may also be present in the electronic waste stream which can be one possible source for PCBs [23].

Concentration and Toxicity equivalency (TEQ) of DL-PCBs

PCBs are a group of persistent environmental chemicals. Due to their hydrophobic nature and resistance to degradation, PCBs have been found in fatty tissues of both animals and humans. Several PCBs have been shown to cause toxic responses similar to those caused by 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) [6]. In recent years researchers have determined and identified by the World Health Organization that 12 of the 209 PCB congeners are the most toxic to human health and the environment. These twelve polychlorinated biphenyls (PCBs) are considered

to possess dioxin-like toxicity and are known as 'dioxin-like PCBs'. The World Health Organization (WHO) has proposed toxicity equivalency factors (TEFs) for 12 dioxin-like PCBs based on comparison with TCDD, which is considered to be the most potent congener and proven human carcinogen within dioxins and furans group of compounds [44]. Toxicity equivalency (TEQ) concentrations of PCBs with dioxin-like activity, especially the non- and mono-ortho substituted PCBs in pond waters, were calculated by multiplying the concentration of each dioxin-like congener by its WHO's established 2,3,7,8-TCDD TEF [5].

Table 2: Toxicity equivalency of dioxin like-PCBs (DL-PCBs) in Pond waters

DL-PCB congeners	WHO TEF*	Toxicity Equivalency (ng-TEQ L ⁻¹)						% of Σ DL-PCBs
		Min	Max	Mean	Med	SD	SE	
PCB -77	0.0001							
PCB -81	0.0003	0.001	0.001	0.001	0.001	<0.00	<0.001	0.86
PCB -126	0.1	0.060	0.135	0.099	0.100	0.035	0.008	62.95
PCB -169	0.03	0.010	0.057	0.032	0.034	0.017	0.004	36.19
Non ortho	-	0.001	0.135	0.048	0.034	0.049	0.011	100
PCB -105	0.00003							
PCB -114	0.00003							
PCB -123	0.00003							
PCB -126	0.00003							
PCB -156	0.00003							
PCB -157	0.00003							
PCB -167	0.00003							
PCB -189	0.00003							
Mono ortho	-							
ΣDL-PCBs	-	0.001	0.135	0.048	0.034	0.049	0.011	100

*Toxicity Equivalency Factor (Van Den Berg *et al.* 2005)

The concentration of DL-PCBs in pond waters ranged between 1.03-16.12 ng L⁻¹ with an average and median value of 7.67 ng L⁻¹ and 9.10 ng L⁻¹, respectively. The calculated TEQ for 12 DL-PCBs in water samples from NCR ponds is presented in Table 2. Total TEQ was in the ranges of 0.001-0.135 ng-TEQ L⁻¹ with an average and median value of 0.048, ng-TEQ L⁻¹ and 0.034, ng-TEQ L⁻¹, respectively. As shown in Table 2, non-ortho PCBs were sole contributors and accounted for more than 99.99% to total TEQ. Among non ortho PCBs, congener number CB-81, CB-126 and CB-169 were the main contributors and accounted for 0.86%, 62.95% and 36.19%, respectively of Σ TEQ. The toxicity equivalency of major congeners of PCB-126 and PCB-169 ranged between 0.060-0.135 ng-TEQ L⁻¹ and 0.01-0.057 ng-TEQ L⁻¹ with the mean value of 0.099 ng-TEQ L⁻¹ and 0.032 ng-TEQ L⁻¹, respectively. As shown in Table 1, CB-126 and CB-169 congeners were not the major contributors of total PCBs (4.6%), but they represent the higher TEQ values and significantly increasing the TEQ of PCBs with the contribution for >99% to Σ TEQ (Table 2), because both had the high toxicity potency (WHO-TEF=0.1 and 0.03, respectively).

Eco-Toxicological risk assessment

PCBs are a group of synthetic organic compounds that may cause a number of different harmful effects in biota including human. Several government agencies developed regulations and recommendations for PCBs to protect public health. The US FDA has set residue limits for PCBs in various foods to protect from harmful health effects [2]. FDA's recommended limits for PCBs, include 0.2 mg kg⁻¹ in infant and junior foods, 0.3 mg kg⁻¹ in eggs, 1.5 mg kg⁻¹ in milk and other dairy products (fat basis), 2 mg kg⁻¹ in fish and shellfish (edible portions), and 3 mg kg⁻¹ in poultry and red meat (fat basis). The probable eco-toxicological health risk of PCBs in this study was assessed by comparing the observed levels with accepted guideline values. The USEPA has established a maximum contaminant level (MCL) (500 ng L⁻¹) for total PCBs in drinking water [45]. However, the Government of British Columbia recommended the 500 ng L⁻¹ maximum concentrations of total PCBs for irrigation water [46]. The observed concentrations of PCBs in this study were much lower than recommended guidelines for environment and irrigation, indicating no risk to the aquatic environment and human health.

CONCLUSION

The observed concentrations of PCBs including dioxin like PCBs in water samples from National Capital Region, India were below the guideline values, indicating no risk to the aquatic environment and biota. PCB congeners containing 4-6 chlorines accounted the majority of the total PCBs in this study.

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