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Polychlorinated biphenyls in coastal tropical ecosystems: Distribution, fate and risk assessment

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ABSTRACT

Polychlorinated biphenyls (PCBs) though banned still find use in most developing countries including Ghana. PCB congener residues in sediments in the coastal regions of Ghana were determined. Sediment samples ($n=80$) were collected between June 2008 and March 2009, extracted by the continuous soxhlet extraction using (1:1) hexane-acetone mixture for 24 h and analyzed with a CP 3800 gas chromatogram equipped with ^{63}Ni electron capture detector (GC-ECD) and a mixed PCBs standard of the ICES 7 as marker, after clean-up. Validation of the efficiency and precision of the extraction and analytical methods were done by extracting samples spiked with 2 ppm ICES PCB standard and a certified reference material 1941b for marine sediments from NIST, USA, and analyzed alongside the samples. Total PCBs detected in sediments during the dry and wet seasons were, respectively, 127 and 112 $\mu\text{g}/\text{kg}$ dry weight (dw), with a mean concentration of 120 $\mu\text{g}/\text{kg}$ (dw). The composition of PCB homologues in the sediments were dominated by tri-, penta- and tetra-PCBs. There was no correlation between organic carbon (OC) of the sediments and total PCBs content. Risk assessments conducted on the levels indicated that PCB levels in sediments along the coastal region of Ghana poses no significant health risk to humans.

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1. Introduction

Polychlorinated biphenyls (PCBs) are a group of 209 man-made structurally related aromatic chemicals which were manufactured in the United States from 1929 to 1977 primarily for industrial use (Bedard, 2003). Some of the properties of PCBs include their non-flammability, chemical stability, high boiling point and exceptional dielectric strength. As a result, PCBs were used in hundreds of industrial and commercial applications including electrical equipment, heat transfer systems and hydraulic equipment, as plasticizers in paints, plastics and rubber products; in pigments, dyes and carbonless copy paper and many other applications (ATSDR, 2000; Rudel et al., 2008; Weis and Monosoon, 2011). Technical mixtures of PCB congeners were manufactured and sold under several trade names such as Aroclor (USA), Phenoclor (France), Clophen (Germany), Kanechlor (Japan), Fenclor (Italy), and Sovol (USSR) (GreenFacts, 2006). Their production was, however, banned by the United States Congress in 1979 and the Stockholm Convention on Persistent Organic Pollutants in 2001 because of the hazard they pose to the environment and human health (Wiegel and Qingzhong, 2000). Despite the prohibition of its manufacture in the United States and many other countries, PCBs were still authorized by the PCB

regulatory body for use in electrical equipment, essentially as dielectric fluids (or containments in dielectric fluids) (Zhou et al., 2001; Nakata et al., 2002; Otchere, 2005; Carmela, 2010). Admittedly, the major use of PCBs today as a dielectric fluid in electrical equipment servicing industries with large electrical power distribution and consumption continue to pose potential threats to the environment in the event of releases (Bench, 2003).

PCBs are environmentally stable, biologically persistent and lipophilic in nature which enhances their accumulation in the food chain (ATSDR and NCEH, 2008). Once released into the aquatic environment, they can be adsorbed onto suspended particles or taken up and concentrated by aquatic organisms where they could bio-accumulate and biomagnify to about 200–70,000 times along the food chain and pose potential hazards to other organisms and human consumers (Ashley et al., 2000; Fontenot et al., 2000; Pruell et al., 2000; UNEP Chemicals, 2004). PCBs persist in the environment with a half-life of between 3 weeks to 2 years in air. Other sources of PCBs are burning processes (waste incineration and backyard burning), metal industries, contaminated soil and sediments and landfill sites with contaminated sediments (Kivirianta, 2005).

It is now a common knowledge that PCBs pose a major threat to humans and the environment even at very low concentrations (Baars et al., 2004). PCBs enter the body via the lungs, the gastrointestinal tract or the skin, which get circulated throughout the body through the blood and stored in fatty tissues and other several organs such as the liver, kidneys, adrenal glands, brain, heart and skin where they can wreak havoc in diverse ways

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(ATSDR, 2000). PCBs are particularly toxic to fish and invertebrates and are fatal to these animals in even small concentrations (McGraw-Hill Encyclopedia of Science and Technology, 1987; WFPHA, 2000; New Encyclopedia Britannica, 2003).

Effects of PCBs exposure in humans include chloroacne, skin discoloration, liver dysfunction, reproductive effects, dermatitis, dizziness, development toxicity and oncogenicity (ATSDR, 2000; WFPHA, 2000; US EPA, 2003). A positive association has been established between PCB dosing and acute liver damage, with liver disease being the cause of death in a significant number of exposed people. Some PCBs have the ability to alter reproductive processes in mammals (Jacobson and Jacobson, 1996; Winneke et al., 1998). Human foetal exposures of PCBs are associated with neural and developmental changes, lower psychomotor scores, short-term memory and spatial learning effects, and long-term effects on intellectual function. Neurological dysfunction had been associated with prenatal PCB exposure in several Dutch studies (WFPHA, 2000; Faroon et al., 2001; Weis and Monosoon, 2011). Prenatal exposure in animals can result in various degrees of developmental toxic effects (WFPHA, 2000; Faroon et al., 2001). The mechanism of action of PCBs is mediated through binding to aryl hydrocarbon receptor (AhR), causing abnormal activation which may disrupt cell function by altering the transcription of genes. A number of international bodies have labeled PCBs as probable carcinogens (IARC, 1987; ATSDR, 2000).

Most of the PCBs released into the environment are bound to aquatic sediments (Bedard, 2003). PCBs are resistant to biological degradation since they are highly oxidized (Mondello, 2002). Incidentally, a number of studies have shown that accumulation of PCBs in sediments poses potential hazard to sediment-dwelling organisms at concentrations greater than 21.5 µg/kg (dw) of total PCBs (WHO, 1993; Canadian Council of Ministers of the Environment, 1999). The growing awareness of the hazards of PCBs is often not present in developing countries such as Ghana. For this reason; the objectives of this study were to determine the levels and distribution of PCBs in sediments along the entire coastal region of Ghana as well as to determine the toxicity equivalent (TEQ) of PCB 118, and hazard index (HI) in order to estimate their potential biological impact on human and other organism.

2. Material and methods

The sediment samples were collected along the coastal region of Ghana (Fig. 1). Two sets of samples were prepared: one for the wet season (June 2008–November 2008) and the other for the dry season (December 2008–March 2009). Each set of samples consisted of 40 sediment samples taken from ten different locations along the coastal region of Ghana. Four samples were taken from each sampling location. The locations were the Wharf, Half-Assini, Esiana and Shama (all in the Western Region of Ghana); Cape Coast and Narkwa (Central Region), Tema New Town and Ada (Greater Accra) and Akplorwotorkor and Anyanui in the Volta Region (Fig. 1). These locations were randomly selected to determine the distribution pattern of PCB congeners along the entire coastal region of Ghana.

The sediment samples were collected using a grab sampler since it maintains the integrity of the samples and provide an immediate assessment of the present levels of contamination in an area. The samples were then stored in the dark under refrigeration of 4 °C and analyzed within 4 weeks of collection.

US EPA Method EPA 3540C was employed in the extraction of the PCBs from the sediment samples. The sediment samples were freed from pieces of roots, pebbles and debris materials and air-dried to a constant mass at room temperature. The air-dried sediment samples were ground and homogenized in porcelain with mortar, sieved with a 90 µm mesh. Organic carbon (OC) of each sediment sample was determined by heating 10.0 g of the sample in a furnace at 500 °C for 6 h. For the PCBs extraction, 10.0 g of each sediment sample was put into a Soxhlet extraction thimble and placed into a clean Soxhlet funnel. A solvent mixture of 250 mL 1:1 hexane-acetone was placed in a round bottomed flask. The Soxhlet apparatus was assembled and the analyte in the sediment sample were extracted for 24 h (all solvent were analytical with between 95% and 98% purity) at a temperature of 55 °C. The Soxhlet apparatus was cooled to room temperature

before pouring the solvent extract for cleaning. The extracts were concentrated to about 2 mL in a 12 mL vial before clean up.

Clean up procedures also followed a modified version of Method 3630C (USEPA, 1996). About 1 mL of concentrated tetraoxosulphate (VI) acid was added to the crude extract and the mixture vortexed for 30 s to remove any elemental sulphur and also to burn any organic carbon present. The hexane layer was transferred into another clean 12 mL vial after which the extract was washed with approximately 1 mL of saturated sodium tioxocarbonate (IV) in water. Solvent-rinsed chromatographic columns (15 mm × 250 mm), were packed with a plug of glass wool followed by 3 g deactivated silica gel and topped up with sodium tetraoxosulphate (VI). The columns were pre-rinsed with 15 mL hexane after which 2 mL of the analyte was added to the column and eluted with 60 mL hexane. The extracts were then concentrated to approximately 2 mL and kept in sample vial for gas chromatographic analysis. A Gas Chromatograph coupled with Electron Capture Detector (GC/ECD), model CP 3800, was used to analyze the final cleaned extracts (in triplicate).

2.1. Quality control

In order to estimate the efficiency of the extraction and analytical methods, certified reference material 1941b for marine sediments from NIST, USA, was also extracted and analyzed by the GC–ECD. The typical approximate reporting limit for individual PCBs is 1 µg/g (i.e., 1 ppm). A 2.0 ppm PCB mixed standard were analyzed and the percentage recovery calculated based on the standard. Target analytes in samples were tentatively identified and semi-quantifications made. Identifications were made by comparison of retention times, peak shapes and peak patterns of the sample to those of the mixed PCBs standard of the ICES 7. Quantitations were based on sample peak areas or peak heights relative to standard peak areas or peak heights.

2.1.1. Calculation of hazard index

Human health evaluation computerized software-RISC 4.02 (USEPA, 1989) was used in the evaluation of the non-cancer risk assessment. The potential for non-carcinogenic effects was evaluated by comparing an exposure level over the exposure duration (maximum of 7 years) with a reference dose derived for a similar exposure period. This ratio of exposure to toxicity for an individual pathway and chemical is called a hazard quotient. The hazard quotients are usually added across all chemicals and routes to estimate the hazard index. Some, however, will argue that it is more appropriate to only sum the hazard quotients for chemicals that affect the same target organ (e.g., liver or blood). The non-cancer hazard quotient assumes that there is a level of exposure below which it is unlikely that even sensitive populations would experience adverse health effects (USEPA, 1989).

2.1.2. Calculation of toxicity equivalent (TEQ) of PCB 118

The toxicity equivalent (TEQ) of PCB 118 was calculated using World Health Organization TEF values as given in Van den Berg et al. (2005). PCB congener 118 has been assigned a Toxicity Equivalent Factor (TEF) of 0.00001. The TEQ in this study was used to determine whether the PCB levels in the various sediments studied could pose any significant threat to humans or the environment. Only the TEQ of PCB 118 was determined since it is the only dioxin-like PCB among the congeners quantified. TEQs help people to understand the relative toxicity of the chemical release information. ADE refers to average daily exposure to PCBs.

3. Results and discussion

NIST-1941b reference material gave recoveries of between 56.2 and 80.7 as shown in Table 1, with a mean recovery of 70.1% whilst the recovery yield of the 0.2 ppm PCB mix standards from spike triplicate sediment samples ranged from 82% to 90% as shown in Table 2 below which was quite reasonable.

3.1. Organic carbon (OC)

All the sediments analyzed were characterized by low organic carbon contents. The organic carbon (TOC) of the sediments ranged from 0.056 g to 1.033 g/kg, with sediments from the Wharf having the highest TOC while those from Ada had the least. Fig. 3 shows the results for the mean total organic carbon content of each sediment sample. There was no significant correlation between organic carbon (OC) and the concentration of PCB congeners detected in the sediments probably because the

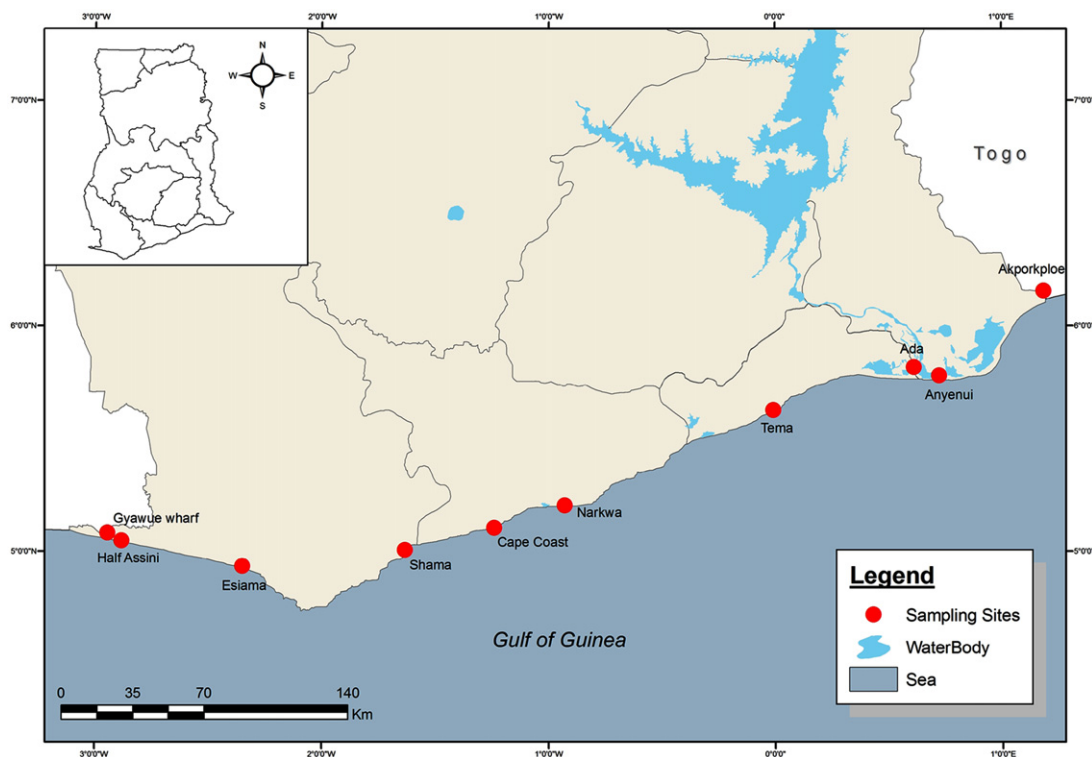


Fig. 1. A site map showing sampling sites.

organic contents of the soils were low and had no significant effect on the sorption and adsorption of the PCBs.

3.2. PCB concentrations and distribution of PCBs

Total PCB concentrations detected in sediments along the coasts of Ghana during the dry and wet seasons were, respectively, 127.6 $\mu\text{g}/\text{kg}$ and 112.6 $\mu\text{g}/\text{kg}$ dw, with mean concentrations of 2.97 $\mu\text{g}/\text{kg}$ and 2.82 $\mu\text{g}/\text{kg}$ dw and standard deviations of 1.99 and 2.06, respectively. The corresponding relative standard deviation (RSD) values computed for the congeners ranged between 0.62 and 1.26 for the dry season and 0.66–1.22 for the wet season. The RSD values implied there were variations within the results for the dry and wet seasons. Table 3 presents the results of the total mean PCB congener concentrations for the dry and wet seasons for all the regions. Concentrations of total PCBs in the regions ranged from 19.60 $\mu\text{g}/\text{kg}$ to 47.89 $\mu\text{g}/\text{kg}$ in the dry season and 15.10 $\mu\text{g}/\text{kg}$ –43.62 $\mu\text{g}/\text{kg}$ in the wet season. The dry season recorded slightly higher concentrations of total PCBs than the wet season, probably due to co-evaporation of PCB congeners with water (Larsson and Soedergren, 1987; GreenFacts, 2006). The general results indicated that the concentrations of PCBs in the sediments studied were not too high. The levels of PCBs compared favourably with the recommended Sediment Quality Guidelines of 21.5 mg/kg by the Canadian Council of Ministers of the Environment (Canadian Council of Ministers of the Environment, 1999); 21.6 $\mu\text{g}/\text{kg}$ by Florida Department of Environmental Protection (MacDonald et al., 1996); 22.7 $\mu\text{g}/\text{kg}$ by the National Oceanographic Atmospheric Association (NOAA, 1996) and 70 $\mu\text{g}/\text{kg}$ by the Ontario Ministry of the Environment (Persaud et al., 1993). Total PCB levels in all the sediments studied were, however, far higher than the Sediment Quality Guideline of 0.02 $\mu\text{g}/\text{kg}$ set by the Netherlands Ministry of Health, Spatial Planning and the Environment (MHSPE, 1999).

The total concentrations of PCB congeners in the coastal regions ranged from 1.6 $\mu\text{g}/\text{kg}$ to 48.78 $\mu\text{g}/\text{kg}$ in the dry season

Table 1
Percentage recoveries of PCB congeners of NIST (1941b).

PCB congener	Actual amount	Observed amount	Percentage recovery
28	4.52	3.65	80.7
52	5.24	4.05	77.3
101	5.11	3.92	76.7
118	4.23	3.02	70.9
138	3.60	2.32	64.4
153	5.47	3.54	64.7
180	3.24	1.82	56.2

Table 2
Recovery of 0.2 ppm PCBs mixed standards from spiked triplicate sediment samples.

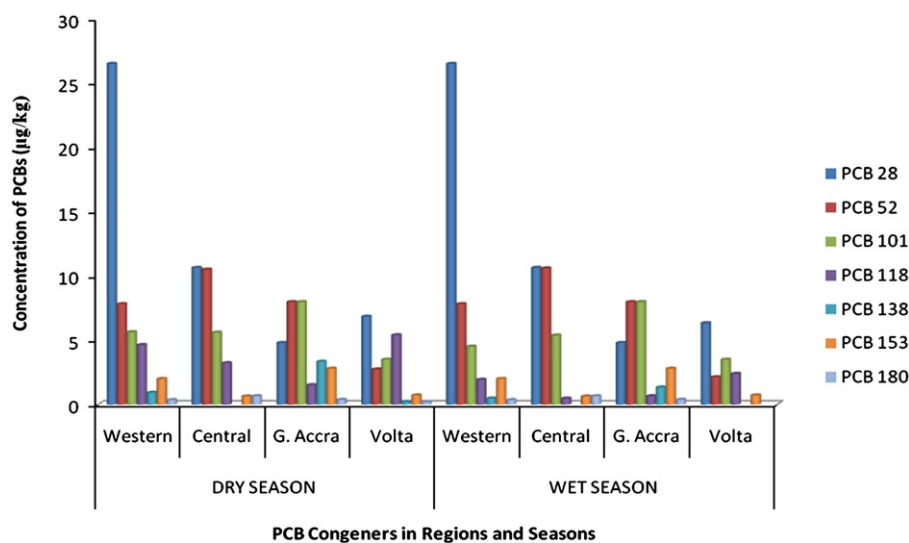
PCB congener	Area count		$R=C_s - C_n$	$R\% = 100R/C_n$
	C_s	C_n		
28	114278	60146.3	54131.7	90
52	111527	59322.87	52204.14	88
101	148329	79746.77	68582.23	86
118	199394	107201.1	92192.92	86
138	190069	103298.4	86770.63	84
153	203236	109857.3	93378.71	85
180	231833	127380.8	104452.2	82

as against 1.4–48.28 $\mu\text{g}/\text{kg}$ in the wet season, with PCB 28 and PCB 180 recording the highest and the least concentrations, respectively. With exception of PCB 153, all the PCB congeners showed a slight decrease in their concentrations during the wet season. Variations in the concentrations of total PCB congeners during the dry and wet seasons were marginal, except PCB 118 and 138 which recorded significant changes in their concentrations during the wet season (i.e., 14.79 $\mu\text{g}/\text{kg}$ and 4.47 $\mu\text{g}/\text{kg}$ in

Table 3

Mean total distribution of PCB congeners in the coastal region of Ghana during the dry and wet seasons.

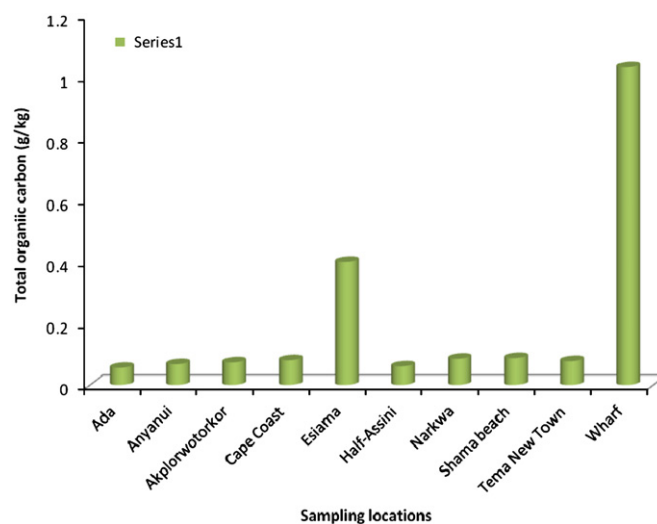
Regions	Dry season				Wet season			
	Western	Central	G. Accra	Volta	Western	Central	G. Accra	Volta
PCB 28	26.5	10.64	4.8	6.84	26.5	10.64	4.8	6.34
PCB 52	7.82	10.5	7.98	2.74	7.82	10.6	7.98	2.14
PCB 101	5.64	5.6	7.98	3.5	4.52	5.38	7.98	3.5
PCB 118	4.64	3.23	1.52	5.4	1.94	0.48	0.66	2.4
PCB 138	0.93	ND	3.34	0.2	0.48	ND	1.34	ND
PCB 153	2	0.64	2.8	0.72	2	0.64	2.8	0.72
PCB 180	0.36	0.66	0.38	0.2	0.36	0.66	0.38	ND
ΣPCBs	47.89	31.27	28.8	19.6	43.62	28.4	25.94	15.1
Mean	6.841	5.212	4.114	2.8	6.231	4.733	3.705	3.02
Stdev	9.074	4.542	2.982	2.627	9.311	4.923	3.278	2.104

**Fig. 2.** Mean total distributions of PCB congeners in sediments along the coastal region of Ghana during the dry and wet seasons.

the dry season as against 5.48 µg/kg and 1.82 µg/kg, respectively in the wet season).

The results indicated a significant negative correlation ($p = -1.00$) between PCB 28 and PCB 180. This pattern of distribution of the PCB congeners may be explained by the fact that higher congeners are sometimes degraded to the lower and less chlorinated species by photolytic processes (Otchere, 2005) or by micro-organisms (Higson, 1992; Robinson and Lenn, 1994). Biodegradation occurs under both aerobic and anaerobic conditions and is the major degradation process for PCBs in soil and sediment (Abraham et al., 2002). No abiotic process is known to significantly degrade PCBs in sediment and soil; however, photolysis of PCBs on surface soil may occur (ATSDR, 2000). It is therefore, stands to reason why the less chlorinated species like PCB 28 appears to be more prevalent in the sediments than the more chlorinated ones like PCB 180. Moreover, research has shown that the congener distribution of PCBs in sediments have a greater proportion of less chlorinated species (Wiegel and Qingzhong, 2000).

On regional basis, (according to Table 3, Fig. 2), Western region recorded the highest total PCB—congener concentration (47.89 µg/kg; 43.62 µg/kg), followed by Central region (31.27 µg/kg; 27.96 µg/kg), then Greater Accra region (28.8 µg/kg; 25.94 µg/kg), with Volta region recording the least concentrations of 19.60 µg/kg and 15.10 µg/kg for the dry and wet seasons, respectively. There seems a general drift of PCBs from the eastern coastline to the western side which indeed needs further studies.

**Fig. 3.** Total organic carbon in the sediments.

The general results showed that the compositions of the PCB homologues were dominated by tri-PCBs > penta-PCBs > tetra-PCBs > hexa-PCBs > hepta-PCBs, respectively. Moreover, more PCB congeners were detected in the sediments studied in the Western and Greater Accra regions than the other regions.

Although environmental distribution of PCBs in general, is global in scale, yet there may be certain specific situations prevailing in an environment that may cause its distribution to be higher or otherwise. Some of the factors include the location of a PCB-containing facility such transformers or capacitors, a PCB waste site or used articles such as electrical equipment like radios, refrigerators, generators, old fluorescent bulbs (WFPHA, 2000; GreenFacts, 2006). It might be due to the large number of transformers and other equipment containing PCB oils in these regions whose contents may leak into the environment and finally find their way into the sea (ATSDR, 2000; UNEP Chemicals, 2004). More PCB congeners were detected in sediments from towns in the Western and Greater Accra regions than the other regions with all the PCB congeners being present. This might be due to the widespread use of PCB oils in transformers, capacitors and other PCB-containing equipment in these areas (Wong et al., 1995; Rudel et al., 2008). The large number of transformers in Accra and Western regions containing PCB oils might be responsible for the differences in the distribution pattern. Furthermore, sediments from the western coasts indicated the highest distribution of PCBs due to the fact that they receive most of the drain water from many parts of the country. The mean regional PCB concentration during the period under consideration was in the decreasing order: Western region ($45.76 \pm 3.01935 \mu\text{g/kg}$) > Central region ($29.62 \pm 2.34052 \mu\text{g/kg}$) > Greater Accra region ($27.37 \pm 2.02233 \mu\text{g/kg}$) > Volta region ($17.35 \pm 3.18198 \mu\text{g/kg}$), respectively (Table 3 below). No significant differences existed between the concentrations of PCB congeners in the dry season and wet seasons, indicating that the contaminants were coming from almost the same source(s).

The composition of PCB homologues in the sediments were dominated by tri-PCBs (i.e., PCB 28, 40.41%) > penta-PCBs (i.e., PCB 101 and PCB 118; 26.8%) > tetra-PCBs (PCB 52, 23.79%) > hexa-PCBs (i.e., PCB 138 and PCB 153; 7.75%) > hepta-PCBs (i.e., PCB 180, 1.25%)(Table 4).

3.3. Distribution of PCB congeners in sediments along the coasts of the western region

Total PCBs detected in the Wharf, Half-Assini, Esiama and Shama during the dry season were, respectively, $10.74 \mu\text{g/kg}$ and $14.14 \mu\text{g/kg}$ as against $8.98 \mu\text{g/kg}$ and $12.04 \mu\text{g/kg}$ for the wet season (Table 3).

The total PCBs analyzed in sediments from the western region during the dry and wet seasons were $47.89 \mu\text{g/kg}$ and $43.62 \mu\text{g/kg}$, respectively, with an average of $45.76 \mu\text{g/kg}$. Levels of total PCBs detected in the region were not too high but were within the Sediment Quality Guidelines (SQGs) of Burton (2002), Canada (Canadian Council of Ministers of the Environment, 1999), Ontario Ministry of the Environment (Persaud et al., 1993). The levels were also far less than the 73 mg/kg measured in the impaired segment of Cedar Creek (BBL, 2005) and the elevated concentrations of $200\text{--}700 \mu\text{g/kg}$ dw measured in the urban areas of Eastern Wisconsin (Wong et al., 1992–1995).

Table 4
Mean PCB congener profiles in sediments.

PCBs	28	52	101	118	138	153	180
Dry season	48.78	29.04	22.72	14.79	4.47	6.16	1.6
Wet season	48.28	28.1	21.38	5.48	1.82	6.16	1.4
Total	97.06	57.14	44.1	20.27	6.29	12.32	3
Mean	48.53	28.57	22.05	10.135	3.145	6.16	1.5
% Distribution	40.41	23.79	18.36	8.44	2.62	5.13	1.25

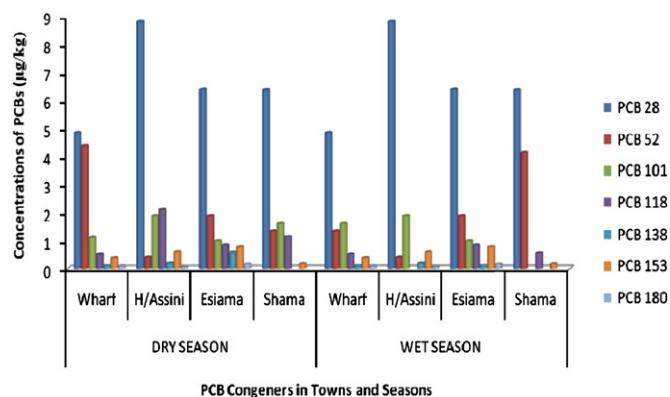


Fig. 4. Mean distribution of PCB congeners in the western region during the dry and wet seasons.

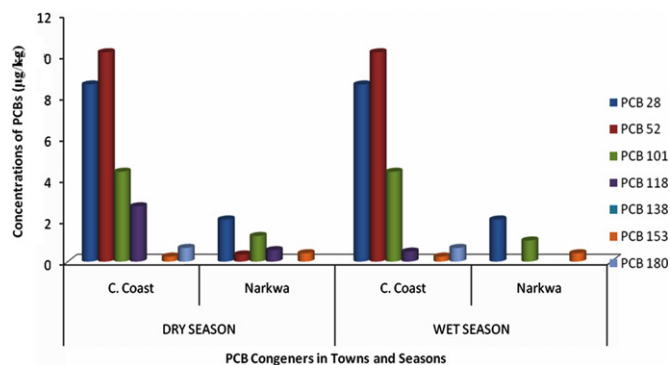


Fig. 5. Mean distribution of PCB congeners in the Central Region (Cape Coast and Narkwa beach) during the dry and wet seasons.

Higher concentrations of PCB 28 were detected in all the study sites in the western region during both seasons, with Half-Assini recording the highest concentrations as shown in Fig. 4, above. Wharf recorded the highest concentrations of PCB 52 and fair amounts of the other congeners during the dry season whereas Shama recorded the highest of PCB 52 and none of PCB 101, 138 and 180 during the wet season. The prevalence of PCB 28 in sediments from all the study sites might be due to the degradation pattern of the highly chlorinated ones to less chlorinated species as reported by Higson (1992), Robinson and Lenn (1994), Wiegel and Qingzhong (2000), Otchere (2005). The compositions of the PCB homologues at the study sites during both seasons were dominated by tri-PCBs, tetra-PCB, penta-PCBs, hexa-PCBs and hepta-PCBs, respectively. Zhang et al. (2007) found tetra-, penta-, and hexa-chlorinated biphenyls as the dominant species in some agricultural soils from Southern Jiangsu, China.

3.4. Distribution of PCB congeners in sediments in the central region

Total PCBs detected in sediments from Cape Coast (Castle area) and Narkwa beach during the dry and wet seasons were $31.27 \mu\text{g/kg}$ and $27.96 \mu\text{g/kg}$, respectively. Table 3 and Fig. 5 illustrate the mean distribution of PCB congeners in the Central Region during this period. It is significant to know that the greater concentrations of total PCBs (about 87% or more) came from Cape Coast beach. This observation is in line with the one made by Wong et al., 1995 that PCBs are industrial-based chemicals and are therefore more prevalent in urban centres and cities than in rural communities. No residues of PCB 52, 118, 138 and 180 were detected in Narkwa in the Central Region during the wet season

while none of PCB 138 was detected in Cape Coast during the same period. Table 3 below illustrates the results.

There was no significance difference between the dry season and wet season distribution of PCBs in the region except that PCB 118 recorded a slightly higher concentration in Cape Coast during the dry season. Moreover, no PCB 138 was detected in Cape Coast and Narkwa during both seasons while none of PCB 52, 101, 118, 138 and 153 was detected in Narkwa during the wet season. The composition of PCB homologues in the region during both seasons was also dominated by tri-PCBs, tetra-PCBs, penta-PCBs, hexa-PCBs and hepta-PCBs. The levels of total PCB congeners in the Central region ranged between 4.57 $\mu\text{g}/\text{kg}$ and 26.7 $\mu\text{g}/\text{kg}$ in the dry season and 3.46–24.5 $\mu\text{g}/\text{kg}$ in the wet season.

The levels of total PCBs detected in Cape Coast and Narkwa were not too high but were also within the Sediment Quality Guidelines of the international community such as FEDP (1996), The Ontario Ministry of the Environment (Persaud et al., 1996) and NOAA (1999).

3.5. Distribution of PCB congeners in sediments in the greater accra region (Tema New Town and Ada)

Table 3 and Fig. 6 illustrate the pattern of distribution of PCB congeners in Greater Accra region (Tema New Town and Ada) during the dry and wet seasons. Total PCB—congener residues detected in sediments along the coast of Tema New Town and Ada during the dry season was 28.8 $\mu\text{g}/\text{kg}$, with a mean of 14.40 $\mu\text{g}/\text{kg}$ and a standard deviation of 1.4425 as against a total of 25.94 $\mu\text{g}/\text{kg}$ with mean distribution of 12.97 $\mu\text{g}/\text{kg}$ and a standard deviation of 0.6364 in the wet season. The concentration of PCB congeners in the area ranged between 0.38 $\mu\text{g}/\text{kg}$ and 7.98 $\mu\text{g}/\text{kg}$ during both seasons. The results indicated that PCB 52 and PCB 101 had the highest and equal concentrations during the wet season while PCB 180 had the least. Apart from PCB 118 and PCB 138 which recorded changes in their concentrations during the wet season (i.e., 0.66 $\mu\text{g}/\text{kg}$ and 1.34 $\mu\text{g}/\text{kg}$ instead of 1.52 $\mu\text{g}/\text{kg}$ and 3.34 $\mu\text{g}/\text{kg}$, respectively in the dry season), all the other congeners recorded the same concentrations for both seasons.

Moreover, the results indicated that PCB congeners were more prevalent in sediments from the towns studied in the Greater Accra region. Again, PCB homologues profile in sediments at Tema New Town and Ada beach were dominated by penta-PCBs (32.99%), tetra-PCBs (27.71%), hexa-PCBs (21.32%), tri-PCBs (16.66%) and hepta-PCBs (1.32%), respectively during the dry season as against penta-PCBs (33.31%) > tetra-PCBs (30.76%) > tri-PCBs (18.50) > hexa-PCBs (15.96%) > hepta-PCBs (1.47%), respectively during the wet season.

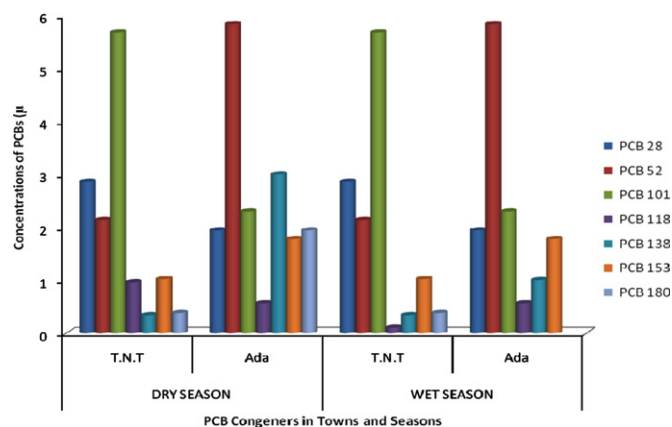


Fig. 6. Mean distribution of PCB Congeners at Tema New Town and Ada beach in the Greater Accra Region during the dry and wet seasons.

Greater Accra, like Western region, showed the presence of all the PCB congeners. This pattern of distribution showed that Greater Accra might be probably highly contaminated with PCBs. This might be due to the presence of more PCB—containing equipment or receptacles like transformers, capacitors, etc., prevalent in Greater Accra than the other regions. This is probable because, Tema New Town, being an industrial city and Ada, an urban town, are likely to have a large number of transformers (Wong et al., 1995). The use of different Aroclors in these transformers as well as for other industrial activities (GNA, 2009; WFPHA, 2000) might be responsible for the wide distribution of PCB congeners in that region.

Notwithstanding these findings, total PCB levels in the sediments studied were not too high but fell within the Sediment Quality Criteria set out by international bodies (NOAA, 1996), (FDEP, 1996), (Canadian Council of Ministers of the Environment, 1999). The levels were also far less than those measured in the impaired segment of Cedar Creek (BBL, 2005) and Wisconsin (NAWQA, 1992–1995).

3.6. Distribution of PCB congeners in sediments at Akplorwotorkor and Anyanui in the volta region

The concentrations of PCB congeners in sediments analyzed during the dry and wet seasons in the Volta region are shown in Table 3, Fig. 7. Total PCB residues detected in these towns during the dry and wet seasons were 19.60 $\mu\text{g}/\text{kg}$ and 15.10 $\mu\text{g}/\text{kg}$, respectively, with means of 9.8 $\mu\text{g}/\text{kg}$ and 7.55 $\mu\text{g}/\text{kg}$ and standard deviations of 4.27 and 5.19, respectively. Concentrations of PCBs congeners detected in this region were the least among the areas studied, with total congener concentrations ranging from 0.2–6.34 $\mu\text{g}/\text{kg}$ in the dry season and 0.72–6.34 $\mu\text{g}/\text{kg}$ in the wet season.

Total PCB levels detected in sediments from the towns in the Volta region were not too high and compared favourably with the Sediment Quality Guidelines set out by NOAA (1996), FDEP (1996), Canadian Council of Ministers of the Environment (1999) and Ontario Ministry of the Environment (Persaud et al., 1990). Levels of PCBs detected were far less than measured in the Cedar Creek (BBL, 2005) and Wisconsin (NAWQA, 1992–1995) but far higher than the Sediment Quality Criteria of 0.02 $\mu\text{g}/\text{kg}$ of total PCBs in sediments in the Netherlands (MHSPE, 1999). Results from the Volta Region also indicated that PCB 28 had the highest concentration during both seasons while PCB 180 had the least or none at all as observed in the other regions.

Again, the composition of PCB homologues in the region was dominated by penta-PCBs, tri-PCBs, tetra-PCBs, hexa-PCBs and hepta-PCBs, respectively. PCB 52, 138 and 153 were not detected at Akplorwotorkor during both seasons. At Anyanui, only PCB 180

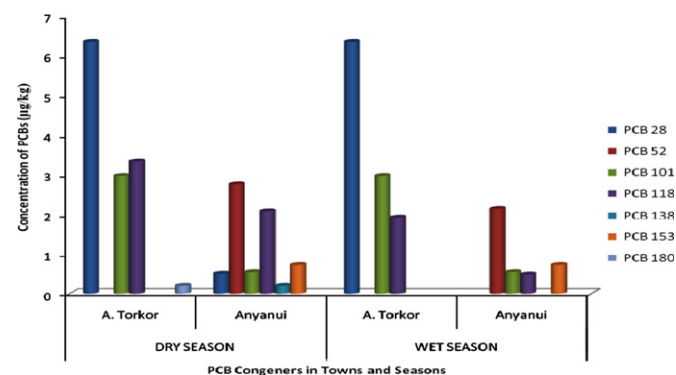


Fig. 7. Mean concentrations of PCB congeners in sediments at Akplorwotorkor and Anyanui during the dry and wet seasons.

was not detected in the dry season but during the wet season, PCB 28, 138 and 180 were not detected as shown in Table 3 above.

3.7. Statistical treatment of PCB congener results in sediments

Data analysis showed some correlation between the dry season and wet season results at $r=0.957$ ($p=0.01$). Correlation analysis of the results also revealed the following significant correlation among the PCB congeners from all the sediments samples analyzed. PCB 28 and PCB 101 showed a strong positive correlation $r=0.518$ ($p=0.01$) and also PCB 28 and PCB 118 correlated positively, $r=0.634$ ($p=0.05$). Furthermore, PCB 101 and PCB 180 also correlated strongly and positively, $r=0.946$ ($p=0.05$). This meant that PCB 28, PCB 101 and PCB 118 came from the same source (probably from aroclors contained in oils used in transformers, capacitors, electrical appliances, etc) (US EPA, 2007). Likewise PCB 101 and 180. Moreover, a very strong negative correlation, $r=-1.00$ ($p=0.01$) was observed between PCB 138 (2,2',3,4,4,5-hexachlorobiphenyl) and PCB 180 (2,2',3,4,4',5,5'-heptachlorobiphenyl) which suggests that PCB 180 often degrades in the sediments to form PCB 138 (Quensen et al., 1998; Wiegel and Qingzhong, 2000).

3.8. Correlation analysis

Furthermore, two-tailed t -test analysis on both the dry and wet seasons' results were in favour of the fact that there was no significant difference between the levels of PCBs.

Analysis of variance (ANOVA) results also indicated that there was no significant difference between the distribution pattern of PCB congeners in the dry and wet seasons.

This implied that the distribution pattern of PCB congeners in sediments along the coastlines studied were basically the same for both the dry and wet seasons and that the PCBs were coming from the same source, mainly transformers, capacitors and other out-dated electrical equipment containing PCB oils (Rudel et al., 2008).

3.9. Comparison of results with standard sediment guidelines, other studies and ecological implications

According to the Sediment Chemical Criteria of the Washington State Department of Ecology, the Sediment Quality Standard for total PCBs is 12.0 mg/kg (dry weight). A number of studies have shown that accumulation of PCBs in sediments poses potential hazard to sediment-dwelling organisms at concentrations greater than 21.5 $\mu\text{g}/\text{kg}$ (dry weight) of total PCBs (WHO, 1993; Canadian Council of Ministers of the Environment, 1999). Sediment quality objectives in the Netherlands by the Ministry of Housing, Spatial Planning and the Environment (MHSPE) for total PCBs are 0.02 $\mu\text{g}/\text{kg}$ dw (MHSPE, 1999). Other Sediment Quality Guidelines for total PCBs include those of National Oceanographic Atmospheric Administration (NOAA, 1996), 22.7 $\mu\text{g}/\text{kg}$ dw; Florida Department of Environmental Protection (FDEP, 1996), 21.6 $\mu\text{g}/\text{kg}$ dw and Ontario Ministry of Environment (Persaud et al. 1990), 70 $\mu\text{g}/\text{kg}$ dw. All these guidelines represent threshold effect levels (TEL). The threshold effects level defines the upper limit of sediment contaminant concentrations of no-effects data (i.e., > 75%, no-effects data). A safety factor of 2 is applied to the TEL values to define a no-observed-effects level (NOEL) for total PCBs in sediments.

Total PCBs detected in sediments studied along the coasts of Ghana ranged from 15.10 $\mu\text{g}/\text{kg}$ to 43.62 $\mu\text{g}/\text{kg}$ dw. The levels of PCBs in the sediments studied were not too high; those in the Volta region were much lower than the recommended levels of 21.5 $\mu\text{g}/\text{kg}$ dw set out by Canadian Council of Ministers of the Environment (1999), 21.6 $\mu\text{g}/\text{kg}$ dw by Florida Department of Environmental Protection,

FDEP (MacDonald et al., 1992, 1996) and 22.7 $\mu\text{g}/\text{kg}$ dw by NOAA (1996), respectively, but those in the Western, Central and Greater Accra regions exceeded these sediment quality guidelines. Although, total PCBs in coastal sediments studied in all the regions were much higher than the sediment quality guidelines of 0.02 $\mu\text{g}/\text{kg}$ dw in the Netherlands (MHSPE, 1999) but they were much less than the 70 $\mu\text{g}/\text{kg}$ dw guidelines by the Ontario Ministry of Environment (Persaud et al. 1992). Moreover, the sediment concentrations of PCBs measured in 2003 in the impaired segment of Cedar Creek ranged from non-detected to 73 mg/kg (BBL, 2005). This level is much higher than those detected in sediments from the coastal region of Ghana. Furthermore, elevated PCB concentrations of 200–700 $\mu\text{g}/\text{kg}$ dw have been measured in the urban areas of eastern Wisconsin (Green Bay, Sheboygan and Milwaukee) by the National Water Quality Assessment Programme (NAWQA) between 1992 and 1995. All these PCB levels are far higher than those detected in Ghana. It is important to know that concentrations of PCBs are generally high in urban settings because they are primarily industrial-based chemicals. Because of differences in sediment characteristics, extraction procedures and different methods of quantification in different studies, total PCB concentrations between two or more studies and their distributions are not easily comparable and should be approached with utmost caution (Wong et al., 1995).

Notwithstanding these limitations, the mere presence of PCBs in the sediments poses some amount of danger to humans, organisms and the environment, more especially, when there is limited data on levels of contamination. Moreover, since the concentrations reported were for only for the seven marker PCBs analyzed, no definite conclusion can be drawn about hazard implication.

3.10. Calculation of toxicity equivalent (TEQ) concentrations and hazard index (HI)

The results of the WHO-TEQ-PCB 118 values (Table 5) ranged from 0.000048 $\mu\text{g}/\text{kg}$ to 0.00094 $\mu\text{g}/\text{kg}$. (Van den Berg et al., 2005). The TEQ in this study was used to determine whether the PCB levels in the various sediments studied could pose any significant threat to humans or the environment. These levels may not pose any significant risk to humans and sediment dwelling organisms.

From Table 6 above, the HI of all the sediments from Western, Central, Greater Accra and Volta regions were all far below unity (i.e., one). Hence, based upon this calculation, it may be concluded that the PCB levels in the sediments studied were not too high and therefore, may not pose any significant risk to humans and sediment dwelling organisms.

4. Conclusion

The levels of total PCBs of between 15.10 $\mu\text{g}/\text{kg}$ and 43.62 $\mu\text{g}/\text{kg}$ dw determined in sediments along the coastal regions of Ghana were not too high but were consistent with the Sediment

Table 5
Mean PCB 118 TEQ values in sediments.

Sum of PCB 118 (TEQ) ($\mu\text{g}/\text{kg}$ or ng/g)			
Sampling sites (regions)	Dry season	Wet season	Average
Western region	0.000464	0.000936	0.000702
Central region	0.000313	0.000048	0.000181
Greater accra region	0.000152	0.000066	0.000076
Volta region	0.000542	0.000242	0.00035

Table 6
Hazard index (HI) of PCBs in sediments in some coastal regions of Ghana.

Region/town	Sample	TEQ (pg/g)	ADE	Hazard index (HI)	
				Commercial	Mean
Western	Wharf	W1	0.0897	0.049963	0.038433
		W2	0.0279	0.01554	0.011954
		W3	0.1458	0.081211	0.06247
		W4	0.0576	0.032083	0.024679
	Half-Assini	HA1	0.0882	0.049127	0.03779
		HA2	0.1548	0.086224	0.066326
		HA3	0.0546	0.030412	0.023394
		HA4	0.0951	0.052971	0.040747
	Esiama	E1	0.1236	0.068845	0.052958
		E2	0.3117	0.173617	0.133552
		E3	0.1254	0.069848	0.053729
		E4	0.0456	0.025399	0.019538
		SB1	0.1134	0.063164	0.048588
		SB2	0.1218	0.067843	0.052187
		SB3	0.0258	0.014371	0.011055
		SB4	0.0522	0.029075	0.022365
Central reg	Cape coast	C1	0.3198	0.178129	0.137022
		C2	0.0576	0.032083	0.024679
		C3	0.1326	0.073858	0.056814
		C4	0.258	0.143706	0.110543
	Narkwa	N1	0.0102	0.005681	0.00437
		N2	0.0168	0.009358	0.007198
		N3	0.0386	0.0215	0.016538
		N4	0.684	0.380988	0.293068
	G. accra	TN1	0.0369	0.020553	0.01581
		TN2	0.036	0.020052	0.015425
	Tema new town	TN3	0.0498	0.027739	0.021338
		TN4	0.0666	0.037096	0.028535
		TN5	0.0402	0.022391	0.017224
		TN6	0.105	0.058485	0.044988
		TN7	0.054	0.030078	0.023137
	Ada	Ad1	0.1506	0.083884	0.064526
	Ad2	0.114	0.063498	0.048845	
	Ad3	0.0852	0.047456	0.036505	
	Ad4	0.0828	0.04612	0.035477	
Volta reg.OLTA REG.	AL1	0.0555	0.030914	0.023378	
		AL2	0.0552	0.030746	0.023443
	Anyanui	AL3	0.0162	0.009023	0.006941
		AL4	0.066	0.036762	0.028278
		AT1	0.0534	0.029744	0.02288
	A. Torkor	AT2	0.0831	0.046287	0.035605
		AT3	0.1146	0.063832	0.049102
		AT4	0.1026	0.057148	0.04396

Quality Guidelines of total PCBs by the international community such Canada (Canadian Council of Ministers of the Environment, 1999), the United States of America (NOAA, 1996; FDEP, 1996) and the Netherlands (MHSPE, 1999). Moreover, Risk assessments conducted on the sediments results using HI risk management strategy indicated that PCB levels in the sediments from all the regions studied might not pose any significant risks to human health since they were far below unity.

However, the mean TEQ values of between 0.001735 µg/kg and 0.0045755 µg/kg dw (i.e., 1.735–4.5755 pg) were beyond the recommended TDI (tolerable daily intake) of WHO-TEQ of the UK Committee on Toxicity of Chemicals in Food, Consumer Products and Environment (COT) of 2 pg WHO-TEQ/kg bw (COT, 2001), hence might be injurious to human health. The levels of total PCBs determined in the study and the corresponding high TEQ values indicated that Ghana still has highly unacceptable levels of PCBs in her environment and it is therefore, in doubt, whether Ghana will be able to totally eliminate PCBs in its environment by 2028 in accordance with the Stockholm Convention. Further study is required to identify specific congeners that are major components of Aroclors used in these electrical equipment. And other sources

This study is very important to Ghana because it gives first-hand information about the levels and distribution of PCBs along the coastal region which serve as centres for a wide range of commercial activities, both locally and internationally. It will also contribute to the global inventory and pave the way for adequate risk assessment where necessary. This will go a long way to augment the efforts of Ghana's EPA towards elimination of PCBs in line with the Stockholm Convention.

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