Levels of Polychlorinated Biphenyls in Plastic Resin Pellets from Six Beaches on the Accra-Tema Coastline, Ghana

Irene A. Agbo,1,2 and Daniel Abaye2

1 Graduate School of Nuclear and Allied Sciences, University of Ghana, Legon, Accra, Ghana
2 School of Basic and Biomedical Sciences, University of Health and Allied Sciences, PMB 31 Ho, Volta Region, Ghana

Corresponding Author:
Daniel Abaye
School of Basic and Biomedical Sciences
University of Health and Allied Sciences
PMB 31
Ho, Volta Region, Ghana
dabaye@uhas.edu.gh
Tel. +233 (0)507 066237

Introduction
Polychlorinated biphenyls (PCBs) are a chlorinated group of organic compounds which are manufactured by the direct chlorination of a biphenyl ring system. They are aromatic molecules that can have different numbers of chlorine substitutions on a biphenyl molecule resulting in the formation of congeners (Figure 1a, 1b, and 1c). A congener of PCBs is, therefore, a biphenyl molecule that has two or more chlorine atoms substituted on it. Examples are trichlorobiphenyl and pentachlorobiphenyl, which have three and five chlorine substitutions, respectively. PCBs have a particular combination of physical and chemical properties which have made them useful in the past. Some of these properties include having a high dielectric constant and resistance to acids and bases as well as to heat, making PCBs useful as insulating materials in electric equipment, transformers and capacitors, heat transfer fluids and as lubricants. PCBs have low solubility in water and their insolubility in aqueous medium makes them lipophilic; thus, they are soluble in fatty substances of living organisms as well as in non-polar substances. PCBs also enter the environment due to their use as oil plasticizers in plastic products such as polyvinyl chloride pipes, neoprene, and as fire retardants. Decommissioning of old transformers and poor handling of PCB-containing equipment are also known to be sources of PCBs in the environment. Oceans act as reservoirs for many

Background. Polychlorinated biphenyls (PCBs) are organic compounds, known to be carcinogenic and banned by the Stockholm Convention. PCBs are hydrophobic substances able to accumulate in organic materials, including plastic pellets. Plastic resin pellets are industrial raw materials that are remolded finished products for industrial and domestic use, commonly used for packaging. Plastic resin pellets were chosen as the medium for monitoring hydrophobic contaminants because they are able to adsorb PCB contaminants. Pellets can be unintentionally washed into the ocean where hydrophobic contaminants such as PCBs are also deposited.

Objectives. We aimed to identify PCB congeners and quantify PCB pollution levels in the marine environment using resin plastic pellets collected from six beaches along the Accra-Tema coastline in Ghana.

Methods. Plastic resin pellets (5 g) were extracted with 200 mL of n-hexane for 16 hours by Soxhlet extraction. Concentrations of PCBs from the extracts were determined using gas chromatography with an electron capture detector.

Results. The individual PCB congeners detected were PCB 28, 52, 101, 105, 138, 153, 156 and 180. PCB 28 was detected at all six beaches, with a total concentration of 43.5 ng/g pellet (mean/beach 7.25 +/- 2.47 ng/g pellet; CV = 34%), while PCB 138 was only detected on one beach (Castle Beach) at a total concentration of 0.8 ng/g pellet. The concentration of PCBs ranged from 7.4 ng/g (Sunset Beach) to 47.5 ng/g (Castle Beach) (mean 16.4±15.4 ng/g per beach; CV=94%).

Discussion. PCB concentrations at Castle Beach have been studied previously, showing an increase from 39 ng/g to 47.5 ng/g, whereas levels decreased significantly from 28 ng/g to 14.2 ng/g in Sakumono Beach over the span of three years.

Conclusions. The concentrations of four detected PCB congeners (28, 52, 101 and 156) were significantly higher than the World Health Organization (WHO) allowable daily intake of 6 ng/g food per day for PCBs. A more efficient industrial and domestic waste disposal system is advocated for Ghana.

Competing Interests. The authors declare no competing financial interests.

Keywords. Polychlorinated biphenyls (PCBs), plastic resin pellets, marine pollution, beach pollution, Accra-Tema, beaches, Ghana

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pollutants, including PCBs. A field adsorption experiment demonstrated that PCBs adsorb to plastic resin pellets from seawater.\(^7\) Plastic resin pellets can be unintentionally released into the environment, both during manufacture and transport of plastic resin pellets as well from rubber factories, and are subsequently washed into the ocean where hydrophobic contaminants such as PCBs are also deposited.\(^8\) Because of their hydrophobic nature, PCBs accumulate in organic materials such as plastic resin pellets.

There is no formal production of PCBs in Ghana, however, PCBs are released into the environment through their applications in transformers and capacitors as dielectric fluid and heat transfer medium, respectively.\(^9\) Even though importation of PCBs and PCB-containing equipment was banned in 1972, most components containing PCBs are old imported stock or unmonitored imported stock since the ban came into force (Figure 2), although unintentional production of PCBs cannot be ruled out.\(^10\) The coastal beaches in Ghana, especially along sections of the study sites, reflect the unregulated waste disposal habits of the populace. Domestic and industrial wastes including PCBs are discarded into coastal rivers, lagoons and the ocean, including the sea, where plastic resin pellets are also carried by surface run-off directly onto beaches. The marine environment serves as one of the final sinks of both PCBs and plastic resin pellets. Because PCBs and plastic resin pellets are hydrophobic substances, PCBs are adsorbed onto the plastic resin pellets which are mistaken as food by marine organisms.\(^7\) Humans and other marine organisms then consume the smaller marine organisms and PCBs join the food chain.

PCBs are among the global environmental contaminants of concern. They are among the twelve hazardous chemicals called the 'dirty dozen', known to be cancerous and which have been banned by the Stockholm Convention.\(^10\) The US Food and Drug Administration (FDA) mandates tolerances of 0.2-3.0 µg/g PCBs for all foods, with a tolerance level in fish of 2 µg/g. The FDA also limits PCBs in paper food packaging materials to 10 µg/g.\(^11\) The Food and Agriculture Organization (FAO) and the World Health Organization (WHO) allowable daily PCB intake is 6 ng/g (food) per day.\(^12\)
Research

The principal objective of this study is to investigate PCB pollution in coastal areas of Ghana, between Accra and Tema, using beached plastic resin pellets as the passive carriers of PCBs. Our specific objectives were four-fold. First, to identify any PCB congeners present in the pellets from the selected beaches. Second, to determine the concentrations of these PCB congeners in the marine environment. Third, to generate baseline data as a basis for future studies that will serve as Ghana’s contribution towards the global mapping of persistent organic pollutants (POPs). Finally, a subsidiary aim was to raise awareness and to buttress the point that poor industrial and domestic waste disposal practices, where waste including electrical and electronic materials, components of capacitors, plastics etc. are discarded into coastal rivers, lagoons or directly into the sea have a direct effect on the health of local people.

Methods

Study Site
Six beaches close to locations of industrial or residential activity along the coastal line between Accra and Tema in the Greater Accra Region, Ghana were chosen. The beaches from west to east are Sunset Beach, Bola Beach, Castle Beach, La Beach in Accra, Sakumono Beach and Mighty Beach in Tema. The beaches are located between longitude N 05° 31’ 44.64” and latitude W 00° 13’ 31.20”, covering an approximate distance of 24 km (Figure 3). These are all sandy beaches used by beachgoers. The study area is much larger than the study conducted by the International Pellet Watch, 2009 where contamination of PCBs was investigated on two beaches, Sakumono Beach and Castle Beach.

Sample Collection and Preparation
Plastic resin pellet samples were collected from the selected beaches on the high tide line of the sea when the tide was out (Figure 4a). The beach pellets were preserved in aluminum foil, sealed in zip-lock bags and stored.
or virgin pellets are either fresh and unused or more recently deposited on the beach. Samples were not classified according to their polymer types (e.g., polypropylene, polyethylene, polystyrene) because no near-infrared spectroscopy instrument was available to determine functional groups. Virgin (white) plastic resin pellets used as controls were obtained from a plastic company (Ecoplast Plastic Co. Ltd. Accra, Ghana).

Ten (10) μL of isodrin (as internal standard, concentration 10 ng/mL; 0.1 ng added) was added to a 5 g sample of each classified pellet type, mixed thoroughly and extracted with 200 mL of n-hexane for 16 hours by Soxhlet extraction. The solvent was removed in a rotary evaporator under vacuum in a water bath at 40º C. Each extract was re-dissolved in 5 mL n-hexane. The resultant solution was cleaned using a 5 cm deactivated silica gel chromatography column and topped with a 1 g layer of anhydrous sodium sulfate (Na₂SO₄) (the bottom of the column was plugged with ashed glass wool) to absorb any moisture present in the extract. To set up the column, the silica was first deactivated at 120°C for 3 hours.

The prepared column was first conditioned with 10 mL of n-hexane. The PCB-extract was then taken up in hexane (30 mL) and shaken gently until all the extracts were dissolved. The sample was then transferred onto the silica gel column installed on a vacuum manifold. The eluate was collected in a round bottom flask and dried on a rotary evaporator at a temperature of 40°C. The dried extract was re-dissolved in 0.5 mL hexane, recovered, and transferred into 2 mL injection glass vials using a Pasteur pipette and readied for gas chromatography analysis.

Gas Chromatography with Electron Capture Detector Analysis

The extracts were analyzed for PCB content using gas chromatography with electron capture detector, a Varian CP 3800k gas chromatography with a Nickel-63 detector cell, operated with Star Chromatography Workstation software (Varian Inc, Walnut Creek, CA, USA). Samples (10 μL) were automatically injected into the injection port of the instrument. Nitrogen was used as carrier and make-up gas at a flow rate of 1.0 and 29 mL/min, respectively. Chromatographic separation was performed on a non-polar capillary column (60 m length, 0.25 mm internal diameter, 0.25 μm film thicknesses; SGE BPX-5; SGE Analytical Science, Milton Keynes, UK). The temperature of injector operation in split-less mode was held at 225°C. The oven temperature was programmed as follows: initial temperature was set at 90°C for 3 min and ramped at 30°C/min to 200°C held for 15 min, and raised to 265°C at a rate of 5°C/min, giving a total run time of 35 min. The PCB residues were identified by comparing their retention times with the retention times of a standard mixture of eight PCBs (United Nations Environment Programme (UNEP) PCB Standard Mix 364, UNEP Chemicals, Geneva, Switzerland; The PCB Standard Mix is a Certified Reference Material; PCB 28, 35, 52, 101, 118, 138, 153, 180) and that of a six-component analytical standard mixture (PCB Standard Solution 6, i.e. PCB 28, 52, 101, 138, 153, 180; Sigma-Aldrich, Gillingham, Kent, UK). Quantification of PCBs was based on comparison of PCB peak area with a ten-point linear calibration curve determined using five replicate 10 μL injections with isodrin (Figure 5) concentrations ranging from 0 to 150 ng/mL in hexane. This concentration range was chosen to match the data reported from the
Sakumono Beach and Castle Beach in the International Pellet Watch study.\textsuperscript{17}

The quality of sample analysis was checked using solvent and matrix (virgin white pellets) blanks in replicates of five. All reagents used were exposed to the same extraction procedures and subsequently run to check for interfering substances. Actual samples were analyzed in triplicates and blank-corrected, and then the mean and standard deviation calculated. Blank sample runs were also included in between samples from different beaches. The collection, categorization, processing and analysis of PCBs from the pellets are summarized in Figure 6.

As the electron capture detector response is directly proportional to analyte concentration, PCB congener concentration was determined by interpolation from the calibration curve (Figure 5).

Extraction efficiency was determined by comparing the peak areas of the internal standard (ISTD) in actual samples with peak (P) areas of the internal standard in blanks. The percent extraction efficiency was then calculated as:

$$\text{Efficiency \%} = \left( \frac{P_{\text{ISTD Sample}}}{P_{\text{ISTD Solvent}}} \right) \times 100\%$$

where $P_{\text{ISTD Sample}}$ and $P_{\text{ISTD Solvent}}$ are the peak areas of isodrin internal standard present in a sample and isodrin standard in hexane (solvent, blank only), respectively.

The results obtained from the study were analyzed using Microsoft Excel 2007 (Microsoft, Redmond, WA, USA). Variation in mean concentration among the studied beach locations was assessed using one-way analysis of variance with the level of significance set at $p<0.05$. Results (PCB concentration) are expressed in ng/g per pellet and

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**Figure 5 — A ten-point calibration curve of isodrin (1 to 150 ng/mL) external standard vs peak area**

**Figure 6 — Flow chart showing the procedure for PCB extraction and analysis. Abbreviations: GC-ECD, gas chromatography—electron capture detector**

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were compared with the WHO daily allowable PCB intake of 6 ng/g (food) per day and with data from the 2009 International Pellet Watch study.\textsuperscript{12,17}

### Results

The ten-point linear calibration curve of isodrin (0-150 ng/mL) in the hexane vs peak area resulted in a coefficient of determination, $r^2$, of 0.9928; p<0.05 (Figure 5) n= 5, error bars are ± standard deviations (SD). The efficiency of PCB extraction ranged from 86.4 to 102.7%.

Eight individual PCB congeners were detected: PCB 28, 52, 101, 105, 138, 153, 156 and 180 (Table 1). PCB congeners were detected in all six beaches, i.e. there were no pristine beaches. PCB 28 (Figure 1c) was the most ubiquitous, present in all six beaches, with a total concentration (colored and white pellets) ranging from 3.6 ng/g-pellet (n=3; 1.2±0.44 ng/g; mean±SD) for Tema Sakumono Beach to 10.2 ng/g-pellet (n=3; 5.10±0.34 ng/g; mean±SD) for Tema Mighty Beach (Table 2). The total PCB 28 concentration for all six beaches was 43.5 ng/g (mean/beach 7.25±2.47 ng/g; coefficient of variation (CV) 34%, Figure 7). In contrast, PCB 138 was found only at Castle Beach at a total concentration of 0.8 ng/g-pellet (Figure 7). Total PCB concentration (for all congeners) was, in increasing order; Sunset Beach 7.4, La Beach 8.9, Bola Beach 9.4, Tema Mighty Beach 11.1, Sunset Beach 14.2 and Castle Beach 47.5 ng/g (Figure 8). The total PCB concentration (for all six beaches) was 98.3 ng/g (mean/beach 16.4±15.4; CV 94%).

Castle Beach was found to be the most polluted, with a total (i.e. white and colored pellets) in increasing order; PCB 28: 9.7 (4.85±0.62), PCB 52: 16.7 (8.35±1.25), PCB 101: 8.2 (4.10±1.22), PCB 105: 0.25 (0.18±0.09), PCB 138: 0.8 (0.7±0.21) (only colored pellets were found), PCB 153: 2.8 (1.40±0.42) and PCB 156: 9.0 (4.51 ± 0.44) ng/g-pellet. PCB 180 was, however, not detected at Castle Beach. The results of the analysis are summarized in Table 2.

### Discussion

The colored pellets accumulated higher concentrations of PCBs than the white pellets (Figure 8). This is in line with previous studies.\textsuperscript{13,18} A larger number of PCB congeners from colored pellets were detected in the majority of beaches except for at La Beach and Tema Mighty Beach, where the number of PCB congeners from

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**Table 1 — PCB Congeners (Types) Detected and Their Chemical Names**

| Congener | Chemical Name                          |
|----------|---------------------------------------|
| PCB 28   | 2, 4, 4’ Trichlorobiphenyl            |
| PCB 52   | 2, 2’, 5’ Tetrachlorobiphenyl         |
| PCB 101  | 2, 2’, 4, 5, 5’ Pentachlorobiphenyl   |
| PCB 105  | 2, 3, 3’, 4, 4’ Pentachlorobiphenyl   |
| PCB 138  | 2, 2’, 3, 4, 5’ Hexachlorobiphenyl    |
| PCB 153  | 2, 2’, 3, 4, 4’ Hexachlorobiphenyl    |
| PCB 156  | 2, 3, 3’, 4, 5’ Hexachlorobiphenyl    |
| PCB 180  | 2, 2’, 3, 4, 5’, 5’ Heptachlorobiphenyl |

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**Figure 7 — Total PCB congener (sum of white and colored/fouled) concentrations from plastic pellet samples collected from the six beaches**
white pellets was the same as from colored pellets. No white pellets were detected at Sunset Beach, suggesting, perhaps, that deposition of pellets on the beach is not recent or current.

High variability in the concentrations of specific PCBs was observed with the low chlorinated congeners, particularly PCB 28, 52, and 101 occurring in higher concentrations (Figure 7). The three low chlorinated congeners constituted 82.3% of the total PCB concentration detected. Anaerobic reductive de-chlorination transforms more highly chlorinated congeners to less chlorinated ones through the replacement of chlorine with a hydrogen atom on the biphenyl molecule. This could account for the high levels of low chlorinated PCBs (28, 52, and 101) compared to the high chlorinated ones (PCB 105, 138, 153, 156 and 180). PCB 28 is a less chlorinated congener of PCBs with three chlorine atoms, making the congener less toxic in nature. Since PCB 28 is an indicator PCB, its predominance and occurrences at all study sites is not surprising. Indicator PCBs are congeners whose presence indicates probable PCB pollution.

Even though the high chlorinated congeners were measured in relatively low concentrations, their presence should be of concern as they are highly chlorinated and can decompose under high temperatures into dioxins, known to be carcinogens. Furthermore, some PCB congener concentrations (PCB 28, 52, 101 and 156) were greater than the allowable daily intake of 6 ng/g (food) per day. Plastic resin pellets concentrate (partition) PCB congeners from seawater and because no metabolic process occurs in the pellets, lower chlorinated congeners that could be subject to biological degradation are not depleted. Hence, they remain concentrated in the plastic pellets. Admittedly, humans do not deliberately eat plastic resin pellets. However, the WHO allowable daily intake value is a useful guide in assessing the extent of PCB contamination in the marine environment and fish food sources, and hence risk to humans.

Compared with the 2009 International Pellet Watch study, this study revealed that at Castle Beach, PCB congener levels have risen from a total of 39 to 47.5 ng/g, an increase of 20.5%, while there was an approximately 50% decrease (from a total of 28 to 14.2 ng/g at Tema Sakumono Beach from 2009 to 2012, when the present study was carried out. As the PCB concentrations are within the same order of magnitude, it is an indication that the PCB contamination is consistent and has not decreased overall at the two beaches. The International Pellet Watch study and our results indicate that all six beaches are contaminated with PCBs, with concentrations well in excess of the WHO daily allowable PCB intake of 6 ng/g (food) per day. PCB contamination is most likely due to the decommissioning of old transformers and capacitors containing PCB oils and poor waste disposal practices in the cities of Ghana. We stress the need for better waste disposal mechanisms, monitoring and enforcement of local by-laws regarding the decommissioning of electrical and electronic devices that contain PCB components.

| PCB | BB (Mean ±Standard Deviation) | CB (Mean ±Standard Deviation) | LB (Mean ±Standard Deviation) | TMB (Mean ±Standard Deviation) | TSB (Mean ±Standard Deviation) | SB (Mean ±Standard Deviation) | TOTAL (Mean ±Standard Deviation) |
|-----|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 28  | 6.40 (3.20±0.22)              | 9.70 (4.85±0.62)              | 7.60 (3.80±0.4)               | 10.2 (5.10±0.34)              | 3.6 (1.2±0.44)               | 6.0 (3±0.26)                 | 43.5 (7.25±2.47)              |
| 52  | 0.00 (0.00±0.00)              | 16.7 (8.35±1.25)              | 0.00 (0.00±0.00)              | 10.3 (8.5±1.35)              | 0.00 (0.00±0.00)             | 27.0 (13.50±4.53)            | 10.4 (2.60±3.77)              |
| 101 | 1.20 (0.60±0.09)              | 8.20 (4.10±1.22)              | 0.00 (0.00±0.00)              | 0.7 (0.7±0.37)               | 1.0 (0.17±0.14)              | 0.5 (0.17±0.14)              | 5.14 (0.86±0.99)              |
| 105 | 0.25 (0.13±0.07)              | 0.25 (0.18±0.09)              | 0.00 (0.00±0.00)              | 0.00 (0.00±0.00)             | 0.00 (0.00±0.00)             | 0.00 (0.00±0.00)             | 0.5 (0.17±0.14)              |
| 138 | 0.00 (0.00±0.00)              | 0.8 (0.7±0.21)                | 0.00 (0.00±0.00)              | 0.00 (0.00±0.00)             | 0.00 (0.00±0.00)             | 0.00 (0.00±0.00)             | 0.8 (-)                      |
| 153 | 0.85 (0.43±0.19)              | 2.80 (1.40±0.42)              | 0.65 (0.33±0.10)              | 0.44 (0.23±0.04)             | 0.4 (0.28±0.19)              | 0.4 (0.28±0.19)              | 5.14 (0.86±0.99)              |
| 156 | 0.00 (0.00±0.00)              | 9.00 (4.50±0.44)              | 0.00 (0.00±0.00)              | 0.3 (0.27±0.02)              | 0.4 (0.28±0.19)              | 0.4 (0.28±0.19)              | 9.3 (4.6±0.615)              |
| 180 | 0.65 (0.33±0.08)              | 0.60 (0.30±0.07)              | 0.42 (0.21±0.04)              | 0.00 (0.00±0.00)             | 0.00 (0.00±0.00)             | 0.00 (0.00±0.00)             | 1.67 (0.42±0.30)              |

Table 2 — Totals and (Mean ±standard deviation) concentrations of PCB congeners (white and colored/fouled; ng/g pellet) determined in the six beaches

Abbreviations: BB, Bola Beach; CB, Castle Beach; LB, La Beach; TMB, Tema Mighty Beach; TSB, Tema Sakumono Beach; SB, Sunset Beach

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Conclusion

The marine environment, as characterized by plastic pellets collected from the beaches along the Accra-Tema coastline, was found to be polluted with PCBs. PCB congeners detected in the Ghanaian marine environment were PCB 28, 52, 101, 105, 153, 156, 138 and 180. There were no PCB-free beaches. The distribution of PCBs revealed varying levels of concentrations in the plastic resin pellets studied. The mean PCB concentration for all six beaches was 16.39±15.40 ng/g-pellet. The most polluted beach was Castle Beach where the total PCB (white and colored/fouled) concentration was 47.45 ng/g-pellet, while Sunset Beach was the least polluted beach (7.4 ng/g-pellet). This distribution is largely a reflection of human habitation and activity; Sunset Beach is located to the west of Accra where there is less industrial activity, whereas between Accra and Tema there are more industrial activity centers. The most ubiquitous congener was PCB 28, with a total concentration of 43.5 ng/g (mean/beach 7.25±2.47 ng/g detected in all six beaches. The low chlorinated PCBs 28, 52 and 101 constituted 82.3% of total PCB concentration. PCB 138 was only detected at Castle Beach (0.8 ng/g). However, the concentrations of PCBs 105, 138, 153 and 180 were below the WHO daily allowable intake of 6 ng/g (food) per day.

Unenforced local by-laws or lack of regulation by the local government and the Environmental Protection Agency is leading to pollution of the environment, especially in water bodies, rivers and beaches. Furthermore, since clean beaches attract tourists, including foreigners, the Ministry of Tourism, with the help of the Environmental Protection Agency—Ghana, should work to ensure that the beaches are safe for users. Therefore, the present study is also intended to drive environmental health policy through the Environmental Protection Agency—Ghana. We call for more concerted efforts from the ports and local authorities to improve and increase their supervisory and regulatory activities in the importation, use, decommissioning and disposal of electrical and electronic wastes from Ghanaian cities.

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