

## LEVELS OF POLYCHLORINATED BIHPENYLS IN PLASTIC RESIN PELLETS COLLECTED FROM SELECTED BEACHES IN GHANA

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### Introduction

Polychlorinated biphenyls (PCBs) are among environmental contaminants of concern world-wide. PCBs are released into the environment mainly through their applications in transformers and capacitors as dielectric fluid and heat transfer medium. PCBs are hydrophobic substances and are able to accumulate in organic substances such as plastic pellets. According to Mato *et al.* (2001), beached plastic resin pellets adsorb high levels of PCBs from the marine environment. These plastic pellets are ingested unintentionally by aquatic organism, which are eaten by human beings thereby introducing the PCBs into the food chain (Endo *et al.*, 2005). In Ghana, there is no production of PCBs (Ghana NIP, 2007) The marine environment is a major source of protein for most Ghanaians. In Ghana, studies have been conducted to determine PCB levels in different media including air, sediment, and aquatic organisms such as fish (Adu-Kumi, 2010; Kuranchie-Mensah, 2011). However, the use of plastic fragments and plastic resin pellets as media for monitoring PCBs has received little attention, save the work of the 'International Pellets Watch' in September 2009 where PCBs were detected in significant levels (28 µg/kg) in beached plastic resin pellets collected from the Sakumono Beach in Tema. The principal objective the current study is to investigate PCBs pollution in coastal areas of Ghana (Accra and Tema as case studies) using beached plastic resin pellets. The specific objectives are: (1) identify PCB congeners present in the pellets from the selected beaches; (2) determine the levels of PCBs congeners in the marine environment; and (3) generate baseline data for further studies and data that will serve as Ghana's contribution towards the global mapping of POPs pollution.

### Materials and methods

The study area included; Accra beach between the Art Centre and Osu Castle, Sunset Beach and Nordsee-Beach in Korle Gonno, Labadi Beach, Sakumono Beach and Mighty Beach in Tema, all in the Greater Accra Region of Ghana. These are all sandy beaches accessed by humans. Plastic resin pellet samples were collected from the selected locations on the high tide line of the sea using stainless tweezers. The plastic resin pellets were then kept in aluminum foil, sealed in zip-lock bags and stored in a refrigerator under a temperature of -18 °C until analysis was performed. Virgin plastic resin pellets were obtained from a plastic company in Accra to serve as control in experiment. Sorting was done according to colours, using the sense of sight. Hence, three colours were obtained and these included white, coloured, and slightly discoloured or fouled. Samples could not be classified according to their polymer types (e.g., polypropylene, polyethylene, polystyrene) due to the non-availability of the near-infrared spectroscopy for plastics in the laboratory.

Five (5) grams of the samples were weighed, wrapped in filter paper and placed in cellulose extraction thimbles, labeled according to the colour groups or sample ID and spiked with 5 µL of isodrin. The thimbles were then placed in the Soxhlet extraction funnel that had been pre-cleaned with *n*-hexane and oven dried and also labeled with sample ID. The pellet samples were then extracted with 200 ml of *n*-hexane for 16 hours by Soxhlet extraction. After extraction, the extracts were concentrated to dryness on a rotary evaporator with water bath at 40 °C, fitted to a vacuum pump. The residues were re-dissolved in 10 mL *n*-hexane. A virgin cellulose extraction thimble together with a filter paper was extracted in the same manner as the samples to obtain the blank. One sample in each batch was spiked with 1 mL of 0.01 mg/kg mixed standard of PCBs for the recovery analysis. The extracts obtained were rotary evaporated to dryness. Each extract was dissolved in 10 mL *n*-hexane prior to clean-up. The same extraction procedure was followed for the other samples in sequence. Spiked samples were treated in a similar manner. Clean up of the sample was done to remove residual co-extractives by transferring the extracts into a chromatographic column packed with glass wool containing 1.8 g of 5% H<sub>2</sub>O, deactivated silica gel topped with 1 g layer of anhydrous sodium sulfate to absorb any moisture present in the

extract. Preparation of silica (SiO<sub>2</sub>) involved activation of SiO<sub>2</sub> at 120°C for 3 hrs. High Performance Liquid Chromatography (HPLC) grade water (1.5 g) was added to 98.5 g in a 250 mL Erlenmeyer flask and shaken well until the entire lumps breakdown was even. The column was prepared by stuffing it with a thin layer of glass wool and then adding 2g of silica to it. Sodium sulphate (1 g) was then added to absorb any moisture from the extracts. The prepared column was first conditioned with 10ml of n- hexane, and then 30 ml n- hexane was added to the extract and swelled gently until all the extract dissolved in the solvent. The sample was transferred onto the silica gel column. The eluate was then collected in a round bottom flask and labeled. It was then concentrated to dryness on a rotary evaporator at a temperature of 40 °C. The eluate was redissolved in 1.5 mL iso-octane, recovered and transferred quantitatively into 2 mL injection glass vials using a pasteur pipette. Recovery of the column was determined using 0.01 mg/L mixed standard solution of PCBs. The eluate was analyzed for PCBs using gas chromatograph equipped with electron capture detector (GC ED). The 0.5g of the extract was then taken for elemental analysis using instrumental neutron activation analysis (INAA) technique to determine the amount of substituted chlorine in the extracts.

Analysis of sample extract was performed using Shimadzu 2010 coupled with electron capture detector and Ni-63, which is a radioactive beta emitter. Carrier and make up gas was nitrogen at a flow rate of 1.0 and 29 mL/min and 1µL volume of the extracts was injected. The temperature of injector operating in split-less mode was held at 225 °C at a pressure of 1.441 bar, oven temperature was 225 °C and electron capture detector was set at 300 °C. Pulsed pressure was 4.5 bar, pulsed time was 1.5 min and, purged flow was 55.4 mL/min with a purge time of 1.4 min. 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 for 15 min, raised to 265 °C at a rate of 5°C/min for 5 min then to 275 °C at the rate of 3 °C/min and allowed to stay for 15 min, giving a total run time of 58 min.. The chromatographic separation was done on a SGE BPX-5 of 60 m capillary column with 0.25 mm internal diameter and 0.25 µm film thicknesses and equipped with 1 m retention gap (0.53 mm, deactivated). The PCB residues were identified by comparing their retention time with those of a standard mixture of PCBs. Quantification was based on comparison with calibration curves in concentration range from 6 to 200 nag/mL and the peak area.

Total chlorine and EOC1 were also determined using the instrumental neutron activation analysis (INAA). About 0.2 g of the plastic resin pellets was weighed into a small vial or capsule and encapsulated. The samples were packed into an irradiation capsule, heat-sealed and then irradiated. The counting was done for about two minutes. Samples were sent to the irradiation sites by means of a pneumatic transfer system. The samples and comparator standards were all irradiated using thermal irradiation. The samples were irradiated with a thermal flux of  $5 \times 10^{11} \text{ ncm}^{-2}\text{s}^{-1}$  with the reactor operating at 15 KW. Total Chlorine and EOC1 were determined in the samples after two (2) minutes irradiation. The irradiated samples were counted using a computer based gamma-ray spectroscopy system, consisting of an N-type high purity Germanium (HPGe) detector model GR2518 mounted on liquid nitrogen as a coolant, high voltage power supply model 3103, Spectroscopy amplifier model 2020, ACCUSPEC multi-channel analyzer emulation software card (all manufactured by Canberra industries inc.), and a micro-computer for data acquisition, evaluation and analysis. The qualitative and quantitative analyses of the nuclides were achieved using the ORTEC MAESTRO 32 software. The quantitative analysis was done by converting the counts as area under the photo peak of the radionuclide by the comparator method. Table 3.2 shows the nuclear data for the irradiations of chlorine.

The quality of sample analysis was assured through the analysis of solvent blanks and matrix blanks samples. All reagents used during the analysis were exposed to same extraction procedures and subsequently run to check for interfering substances. In the blank for each extraction procedure no PCB was detected. For Instrumental Neutron Activation Analysis, the samples were validated using the prepared standard of known concentration to quantify the measured values. To ensure that quality results were obtained in the experimental operation, a PCB recovery study was undertaken. This involved spiking of the plastic resin pellets with PCB standard (100 µg/mL) solution. The recoveries for PCBs ranged from 75.5% to 92%. The results obtained from the study were analysed using SPSS version 16.0 (SPSS Inc., Chicago, and II, USA). The mean and corresponding standard deviations were computed while the ranges were compiled from the minimum and maximum concentrations in the study. Variation in mean concentration among the studied locations was assessed using one-way analysis of variance (ANOVA). The levels of significance was set at  $p < 0.05$ .

## Results and discussion

The study revealed the presence of PCB in plastic resin pellets sampled from six locations along the coastal stretch in Accra and Tema. The individual PCB congeners investigated were PCB-28 (2, 4, 4' Trichlorobiphenyls); PCB-52 (2, 2', 5, 5' Tetrachlorobiphenyls); PCB-101 (2, 2', 4,5,5' Pentachlorobiphenyls); PCB-105 (2,3,3',4,4' Pentachlorobiphenyls); PCB-118 (2,3',4,4',5 Pentachlorobiphenyls); PCB-138 (2,2,3,4,4',5 Hexachlorobiphenyls); PCB-153 (2, 2', 3, 3', 4, 4 Hexachlorobiphenyls); PCB-156 (2,3,3',4,4',5 Hexachlorobiphenyls); and PCB-180 (2,2',3,4,4',5,5' Heptachlorobiphenyls). PCB numbers; 18 and 118 were not detected in any of the samples. PCB-28 was detected in all the samples from the six locations with an incidence percentage of 83.3 %. The presence of PCB - 28 in all sample locations is an indication that other PCBs may be present in the sample matrix. The most abundant PCB congeners in the samples studied were identified to be PCB numbers; 28, 52, 101, 153, and 180. Each one of these was detected in samples from at least three sample locations.

The percentage distribution of each PCB-congener detected in the plastic resin pellet samples collected from the six sites is summarized in Figure 1. The total concentrations (sum of eight congeners) are 40.5 µg/kg, 27 µg/kg, 10.4 µg/kg, 0.4 µg/kg, 5 µg/kg, 9.3 µg/kg, 0.8 µg/kg, and 1.6 µg/kg for PCB 28, 52, 101, 105, 153, 156, 138, and 180 respectively. The percentage distribution of the individual congeners (Figure 1) are in the decreasing order of PCB-28 (43%) > PCB-52 (28%) > PCB-101 (11%), > PCB-156 (10%) > PCB-153 (5%) > PCB-180 (2%) > PCB-138 (1%) > PCB-105 (0%).

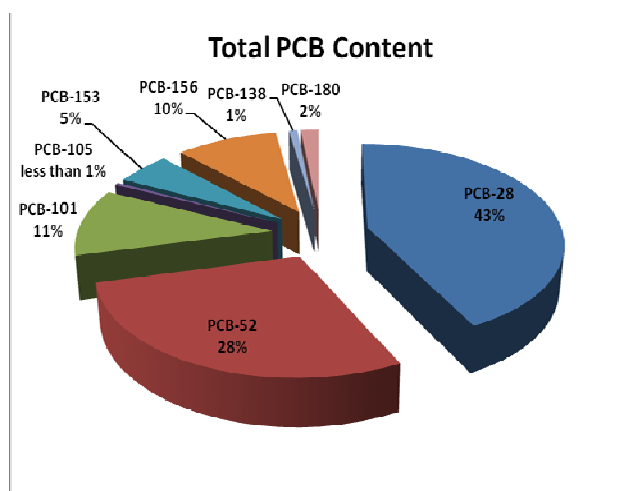


Figure 1: Percentage Distribution of Selected Polychlorinated Biphenyls in Plastic Resin Pellets from the Selected Beaches in Ghana.

PCB 156 occurred in samples from two locations at Accra Independence Square Beach (AISB) and Tema Sakumono Beach (TSB) while 138 occurred only at AISB. The highest concentration of PCB 28 was in detected in samples from Tema Mighty Beach (TMB) (3.4 µg/kg) while the lowest was detected in samples from TSB (0.4 µg/kg) although the difference in the mean concentrations were not significant ( $p > 0.05$ ). The mean concentrations of detectable PCB-101 varied significantly ( $p < 0.05$ ) among the sampled location and are in the range of 0.33 µg/kg at Korle Gonno Beach (KGB) to 2.7 µg/kg at AISB. The detectable concentration of PCB 153 and 180 are in the range of (0.13 - 0.93) µg/kg and (0.13- 0.2) µg/kg respectively.

The high variability in the concentrations of specific PCBs was observed with the low chlorinated congeners particularly PCB numbers; 28, 52, and 101 occurring with high concentrations. According to Ye *et al.*, (1992), 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) than the high chlorinated ones. PCB-28 is a less chlorinated congener of PCBs with three chlorine atoms, one attached to the ortho position of one ring and one

para position on the same ring while the third chlorine on the para position of the second ring. This makes the congener less toxic in nature. Since PCB-28 is an indicator PCB, its predominance and occurrences in all study sites is not surprising. Out of these PCBs, PCB numbered; 105 and 156 are dioxin like PCBs (coplanar PCBs) which are more toxic than the other congeners. These compounds are very stable and resistant to biodegradation and metabolism hence very toxic in nature. Even though these congeners were measured in low concentrations, their presence in the environments should be of concern. According to Teuten *et al.*, (2009), plastic resin pellets concentrate (partition) PCB congeners from seawater and because no metabolic process occurs in the pellets, lower chlorinated congeners that could even be subject to biological degradation are not depleted. Hence they remain concentrated in the plastic pellets. For the global environment, time series of the fraction of secondary emissions increase in the long-term for all congeners.

PCBs are chlorinated hydrocarbons and by knowing the percentage chlorine contained in these PCB formulations, a “total chlorine” reading can give an accurate analysis of the concentration of PCB in the sample. Extractable, organically bound chlorine (EOCl) is used as a measure of pollution caused by chlorinated organic compounds such as PCBs. The extractable organochlorine content in PCBs is an important parameter for the quantification of total chlorine content in the plastic resin pellets.

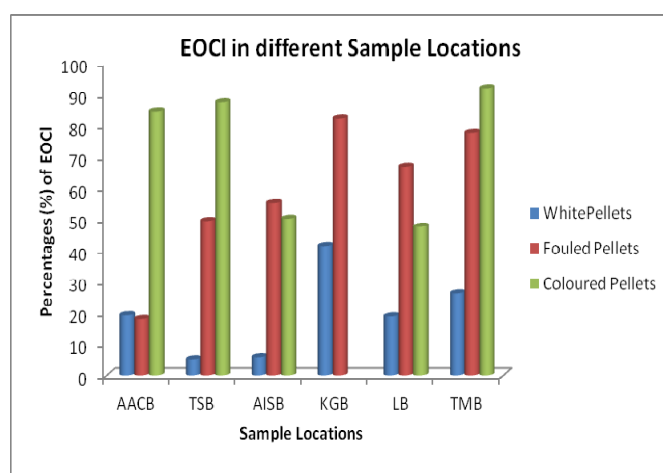


Figure 2: Comparison of Extractable Organochlorine in the Pellets from the Various Locations. AACB= Accra Art Centre Beach; AISB= Accra Independence Square Beach; KGB=Korle Gonno Beach; LB =Labadi Beach; TMB=Tema Mighty Beach; TSB =Tema Sakumono Beach KGB=Korle Gonno Beach

The range of the EOCl is between 111.1 mg/kg and 195.71 mg/kg. The total number of chlorine attached to the PCB congeners identified using INAA ranges from 4.49 mg/kg to 17.24 mg/kg. Though the highest EOCl was in the pellets from the Korle Gonno Beach, the total chlorine content of PCBs from this same beach is the lowest (4.49 mg/kg). The highest chlorine content (17.24 mg/kg) was detected in the Accra Independent Square Beach. This could be that the various congeners of PCBs identified in the extract are very low. This shows that other PCB congeners and several unidentified chlorinated organics such as polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated naphthalenes (PCNs) that the GC-ECD could not detect might be present in the extract at very low levels. The high concentration of EOCl is an indication that it is not only the PCBs that are adsorbed to the plastic pellets but other chlorinated contaminants might be adsorbed as well.

## References

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