

Levels and Risk Assessment of Polychlorinated Biphenyls (PCBS) in Soils from Informal E-Waste Recycling Sites in Cameroun

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ABSTRACT

This study assessed the levels and human health risk of polychlorinated biphenyls (PCBs) in soils of e-waste recycling sites in Douala, Cameroun. Surface soil samples from these sites were collected and analyzed by Gas Chromatography- Electron Capture Detector to quantify the levels of 30 PCBs (including 10 dioxin-like PCBs). The investigated 30 PCBs were detected in all the soil samples. The mean and standard deviation of the total PCBs in Makea, Ngodi and New Bell recycling sites were 32.1 ± 4.48 , 31.9 ± 0.10 and 72.8 ± 13.5 ng/g, respectively. Between 26-46% of the $\Sigma 30$ PCB concentrations were comprised of the dioxin-like PCB congeners. The toxic equivalent (TEQ) values of 10 dioxin-like PCBs were lower than the Canadian soil quality guidelines of dioxin (4 pg TEQ g^{-1}). Human health risk through ingestion, dermal contact, and inhalation was lower than the values of cancer risk (10^{-6}) indicating low adverse effects of PCBs in the recycling sites.

Keywords: polychlorinated biphenyls, health risk, e-waste, Douala

INTRODUCTION

Electronic and electrical waste (e-waste) recycling which hitherto is considered a lucrative business has negative impacts on the environment and health of the public, especially in developing nations, such as Cameroun, Ghana, India, and Brazil where environmental regulations are absent or weakly implemented (Garlapati, 2016). E-waste includes end-of-life electronic products such as television sets, computers, printers, toys, mobile phones and photocopy machines etc. E-waste has contributed enormously to the growing problem in the field of waste management in the world (Halluite et al., 2005). Based on the report of the United Nations Environment Programme, UNEP (2005), 20 to 50 million tonnes of e-waste are generated worldwide annually, and the amount is expected to increase by 3 to 5% per annum (Commission of the European Communities, 2000). Technological advancement has resulted in high demand for latest and highly efficient materials as opposed to old and obsolete ones. In the United States, it was estimated that over 500 million computer became out-dated between 1997 and 2007 (NSC, 1999). It was also reported that 50% to 80% of the e-waste collected for recycling in industrialized countries, such as the U.S. was illegally transported to Asian countries, such as China, India, and Pakistan, for recycling and disposal (BAN and SVTC, 2002). However, the recycling industries in these countries are often crude

and do not have the appropriate facilities to safeguard environmental and human health. In China alone, about 4 million personal computers are discarded per year (UNEP, 2005).

Crude methods such as mechanical shredding of electronic equipment, open burning of plastics and wires, and acid leaching of printed circuit boards have been used for e-waste recycling. These have led to pollution by the release of hazardous chemicals including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyls ethers (PBDEs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and heavy metals such as Cr, Cd, Cu and Pb into the air, dust, soil, river water and sediment (Leung et al., 2007; Li et al., 2007; Wong et al., 2007).

Polychlorinated biphenyls (PCBs) are a group of POPs produced as by-products of industrial or thermal processes by the direct chlorination of biphenyls. There are 209 individual congeners of PCBs (Mills et al., 2007; Haddaoui et al., 2016). PCBs have been used in many nations because of their high thermal stability and this has led to environmental pollution (Hornbuckle et al., 2006). As a result of their toxic characteristics, PCBs have either been restricted or banned, but they are still found in the environment, even far from their emission sources (Gandhi et al., 2015). Electronic waste recycling centres have become hot spots for Persistent Organic Pollutants (POPs) and heavy metals (Leung et al., 2007). Increased levels of blood lead in children and PCBs in the serum of e-waste workers, and dioxins in the human milk of mothers indicated serious threat to the health of local people due to uncontrolled e-waste recycling activities (Bi et al., 2007; Chan et al., 2007; Huo et al., 2007).

Majority of the domestic and/or imported e-waste in Cameroon through the scrap dealers reach the informal recyclers which consists of unregulated and unregistered, low-technology units where both adults and children process e-waste through dangerous procedures without safety measures. In this study, The PCBs in surface soil samples from three informal e-waste recycling sites in Douala, Cameroun were investigated with a view to ascertain their levels and health risks.

MATERIALS AND METHODS

Sampling Sites

Surface soil samples (0–20 cm depth) were collected between February and June 2017 from three informal e-waste recycling sites that are Ngodi, Makea and New Bell in Douala, Cameroun. At each sampling site, composite samples consisting of 10 sub-samples were collected into pre-cleaned glass bottles. Samples were stored in ice chest and transported into the laboratory for analysis.

Soil Sample Extraction and Clean-up

5 g of soil sample was placed into a beaker and extracted with 20 mL of acetone/n-hexane (1:1 v/v). The beaker was sonicated for 10 min in an ultrasonic bath and the extract was transferred to another beaker. The extraction was repeated with 10 mL of the solvent mixture. The extracts were combined and concentrated to about 1 mL. Thereafter, samples were cleaned-up and fractionated on a multilayered silica gel column containing from bottom: 3 g of silica gel and 3 g of anhydrous sodium sulphate. The sample extracts were loaded in the above-mentioned multilayer column and subsequently eluted with 20 mL of n hexane. The purified extract was concentrated and then re-constituted in 2 mL hexane.

Instrumental Analysis

Soil samples were analyzed for PCBs with a gas chromatograph (GC) (Agilent 7890) equipped with a 5977A mass spectrometer (MS) detector. HP-5MS fused capillary column (30 m, 0.25 mm, 0.25 μ m) was used. Helium was the carrier gas at 1.0 mL/min under constant-flow mode. The oven temperature started at 100 °C for 1 min and increased to 140 °C (0 min hold time) at a rate of 4 °C/min, then ramped to 180 °C (0 min hold time) at a rate of 20 °C/min then to 210 °C (0 min hold time) at a rate of 3 °C/min and finally to 290 °C (10 min hold time) at a rate of 8 °C/min. Splitless injection of 1 μ L sample was performed with a 3 min solvent delay time. Injector temperature was 250 °C. Thirty PCB congeners viz., PCB-8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 77, 81, 82, 87, 99, 101, 105, 114, 118, 123, 128, 138, 153, 156, 157, 167, 170, 179, 180 and 189 were analyzed in Single Ion Monitoring (SIM) mode. Compounds were identified based on their retention time, target and qualifier ions, and were quantified using the external standard calibration procedure.

Quality Assurance/Quality Control (QA/QC)

QA/QC was performed using procedural blanks and multi-level calibration curves (r^2) ranged from 0.997-0.999. The limit of detection was between 0.001 and 0.0014 ng/g for PCBs. The concentrations of the targeted compounds in the procedural blanks were below the quantification limit of the instrument. In this study, all the data were expressed on a dry-weight basis (ng/g dry weight).

Statistical Analysis

Statistical analyses were performed using statistical software package SPSS version 16.0. Test of significance for variability in the distribution of PCB congeners among different sites were carried out using one way Analysis of Variance (ANOVA).

Toxic Equivalency (TEQ) and Health Risk Assessment

The Toxic Equivalency (TEQ) values of PCBs were calculated by multiplying the detected concentration with the corresponding Toxic Equivalent Factors (TEFs) provided by the World Health Organization (WHO) (Van den Berg et al., 2006).

$$TEQ = (C_i \times TEF_i)$$

where C_i is the individual dioxin-like PCBs concentration in the soil sample, and

TEF_i is the TEQ factor assigned to individual dioxin-like PCBs.

In this study, the following equations were applied to assess health risks of PCBs (USEPA, 1997; 2009):

$$CR_{ingest} = (C \times IngR \times EF \times ED \times CF \times SF_{oral}) / (BW \times AT)$$

$$CR_{dermal} = (C \times SA \times AF \times ABS \times EF \times ED \times CF \times SF_{oral} \times GIABS) / (BW \times AT)$$

$$CR_{inhal} = (C \times InhR \times AF_{inh} \times EF \times ED \times IUR) / (PEF \times BW \times AT)$$

where CR_{ingest} : the cancer risk via accidental soil ingestion, CR_{dermal} : the cancer risk (soil dermal contact); CR_{inhal} : the cancer risk (soil inhalation), C : concentration of soil PCBs ($mg\ kg^{-1}$), $IngR$: the rate of ingestion ($100\ mg\ soil/day$), CF : conversion factor ($10^{-6}\ kg/mg$), EF : exposure frequency ($350\ days/year$) ED : exposure duration ($70\ years$), BW : body weight ($70\ kg$), AT : averaging time (days); calculated as $70 \times 365 = 25,550$, SA : skin surface area available for contact ($3300\ m^2$) AF : adherence factor from soil to skin ($0.2\ mg/cm^2$), SF_{oral} = the factor of oral slope ($2\ mg\ kg^{-1}\ d^{-1}$) $^{-1}$), PEF : emission factor of particle ($1.36 \times 10^9\ m^3\ kg^{-1}$), $InhR$: inhalation rate ($15.8\ m^3/day$), AF_{inh} : the lungs absorption factor (1.0), ABS : absorption factor (0.10), IUR : the risk unit for inhalation ($5.7E-01\ (mg\ m^3)^{-1}$), $GIABS$: the fraction of pollutant taken by gastrointestinal tract (1.0).

RESULTS AND DISCUSSION

PCBs Concentrations in Soil Samples

The mean concentrations of the total PCBs in surface soils are shown in [Table 1](#). The mean and standard deviation of $\Sigma 30$ PCB in Makea, Ngodi and New Bell recycling sites were 32.1 ± 4.5 , 31.9 ± 0.1 and 72.8 ± 14 respectively. The corresponding values for $\Sigma 10$ dl-PCB were 14.7 ± 2.1 , 13.9 ± 0.9 and 19.0 ± 8.2 ng/g respectively. Dioxin like PCBs accounted for 26–46% of the total PCB concentration in the soil samples. New Bell recycling site had the highest concentration of the total PCBs and dioxin-like PCBs which indicated higher contamination when compared with other recycling sites in Douala. The total PCB levels in the E-waste recycling sites in Douala were however below the Dutch action value, the Australian and New Zealand ecological investigation level of $1000\ \mu g/kg$, as well as the Canadian soil guideline for residential areas of $1300\ \mu g/kg$ (Canadian Environmental Quality Guidelines, 2003). This study showed lower PCB contamination levels than previously reported for contaminated soils in China (Zhao et al., 2008; Shen et al., 2009) and slightly higher than the reported concentration from South Africa (Nieuwoudt et al., 2009). The $\Sigma 10$ dl-PCBs in the present study were lower than what was observed in the e-waste metal recovery site in India (Chakraborty et al., 2016).

Table 1. The mean and standard deviation of PCBs (ng/g) in soils from recycling sites in Douala, Cameroun

Pollutants	Makea	Ngodi	New Bell
PCB 8	ND	ND	0.08±0.1
Total Di-PCBs	ND	ND	0.08±0.1
PCB 28	0.4±0.0	0.44±0.1	1.06±0.8
PCB 37	0.17±0.1	0.25±0.2	2.59±2.0
Total tri-PCBs	0.57±0.1	0.69±0.2	3.65±2.8
PCB 44	ND	0.01±0.01	2.13±2.7
PCB 49	0.18±0.1	0.27±0.2	13.95±11
PCB 52	0.45±0.3	0.43±0.04	7.44±5.2
PCB 60	0.67±0.02	0.76±0.1	4.44±4.2
PCB 66	0.59±0.03	0.63±0.1	1.55±0.3
PCB 70	1.58±0.3	0.78±0.1	5.64±6.2
PCB 74	0.83±0.01	0.56±0.5	2.21±1.5
PCB 77	1.45±0.3	0.93±0.1	3.48±2.6
PCB 81	1.87±0.3	1.93±0.1	1.82±0.2
Total tetra-PCBs	7.59±1.4	6.29±1.3	42.6±34
PCB 82	0.25±0.03	0.64±0.3	0.47±0.3
PCB 87	0.72±0.01	0.86±0.2	0.71±0.01
PCB 99	0.85±0.04	0.93±0.1	0.89±0.1
PCB 101	1.27±0.3	1.21±0.03	1.09±0.2
PCB 105	1.14±0.02	1.15±0.01	1.33±0.1
PCB 114	ND	ND	ND
PCB 118	2.18±0.5	1.53±0.5	4.60±4.9
PCB 123	1.26±0.1	1.29±0.1	1.22±0.04
Total penta-PCBs	7.66±1.0	7.58±1.1	10.3±5.6
PCB 128	3.57±0.6	3.83±0.3	3.28±0.4
PCB 138	1.66±0.3	1.70±0.04	1.53±0.2
PCB 153	ND	0.57±0.8	0.71±1.0
PCB 156	1.26±0.2	1.33±0.2	1.16±0.1
PCB 157	1.45±0.1	1.47±0.01	1.43±0.01
PCB 167	2.24±0.5	2.38±0.3	2.06±0.3
Total hexa-PCBs	10.2±1.7	11.3±1.6	10.2±2.0
PCB 170	0.98±0.04	0.95±0.01	0.96±0.1
PCB 179	1.43±0.2	1.46±0.01	1.36±0.1
PCB 180	1.83±0.2	1.85±0.1	1.76±0.2
PCB 189	1.92±0.1	1.88±0.01	1.91±0.1
Total hepta-PCBs	6.16±0.5	6.13±0.1	5.98±0.4
Σ30 PCBs	32.1±4.5	31.9±0.1	72.8±14
Σ10 DL-PCBs	14.7±2.1	13.9±0.9	19.0±8.2
TEQ (pg TEQ g⁻¹)	1.05±0.2	1.00±0.1	1.30±0.5

As described in **Figure 1a-c**, the lower chlorinated congeners such as tri-, tetra-, and penta-PCB were the abundant pollutants in all the sites, accounting for almost 50 % of the total PCBs. The tetra-PCB was the most prevalent homolog in New Bell and hexa-PCB in Makea and Ngodi, while dl-PCB was the least prevalent in all the sites. The concentrations in **Table 1** showed that the mean values of di-, tri-, tetra-, penta-, hexa- and hepta-PCB in Makea, Ngodi, and New Bell were ND, 0.57±0.1, 7.59±1.4, 7.66±1.0, 10.2±1.7 and 6.16±0.5; ND, 0.69±0.2, 6.29±1.3, 7.58±1.1, 11.3±1.6 and 6.13±0.1; and 0.08±0.1, 3.65±2.8, 42.6±34, 10.3±5.6, 10.2±2.0 and 5.98±0.4 ng/g, respectively.

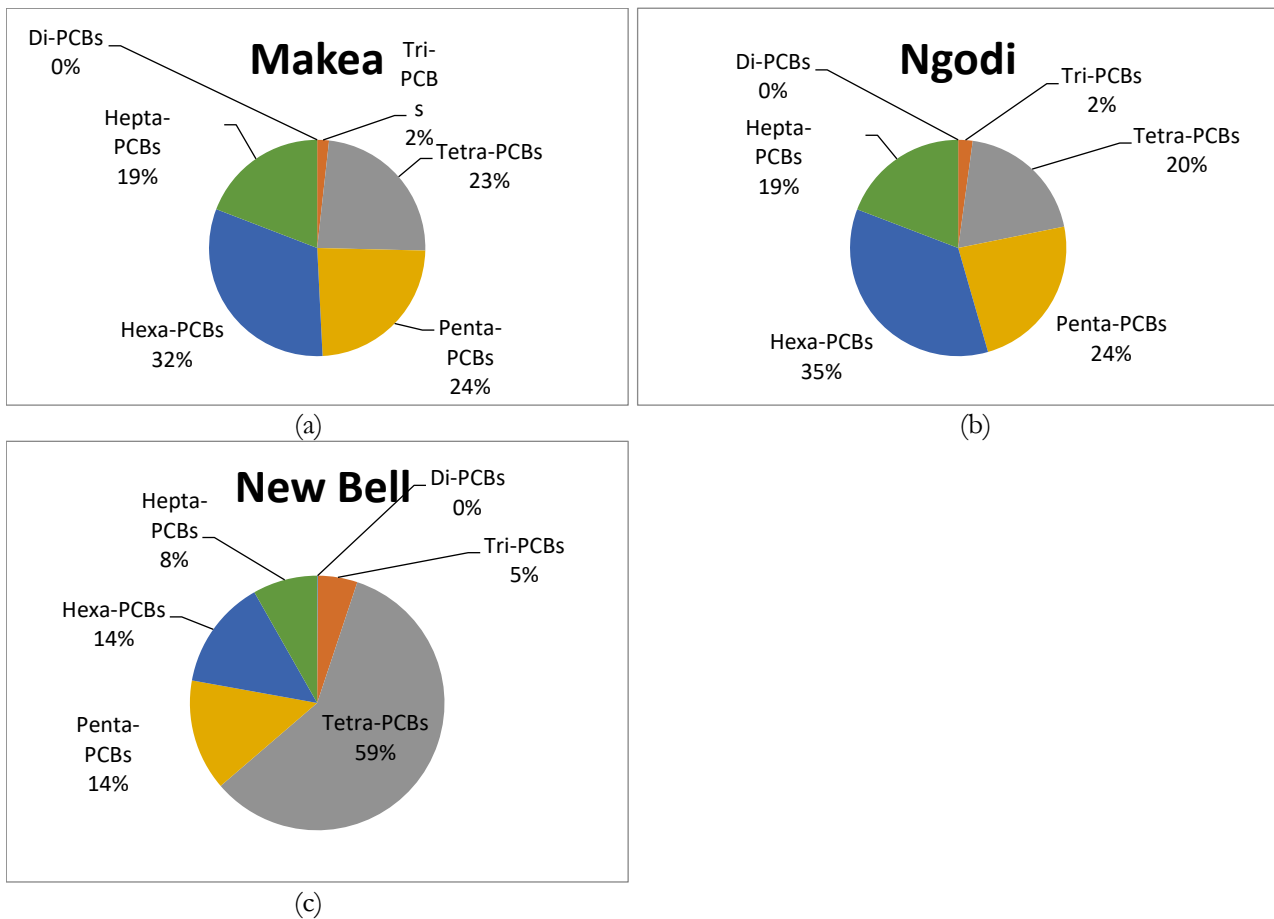


Figure 1. The percentage distribution of the PCB congeners in soil samples collected from e-waste recycling sites in Douala, Cameroun

In Cameroun, open burning of cable wires, circuit boards and atmospheric transport could be the sources for PCB pollution in the area, and no quality standard has been set for PCBs in soils. The composition of PCBs in this study was compared with the study conducted by Tang et al., 2010 who reported that low-chlorinated PCB homologs accounted for 69 - 87% of the total PCBs in soil samples collected from an e-waste recycling site in Wenlin, China (Tang et al., 2010a). Di-, tri-, tetra-, and penta-PCBs were the prevalent congeners in soil sample around the recycling area of Taizhou, China (Tang et al., 2010b). Bi et al. (2002) reported that tetra- and penta-PCBs were predominant in Taizhou in 1993, 1997 and 1999. Similar results were reported by Shen et al. (2009). The high concentration of low-chlorinated PCBs implies that the sites had been used for the disposal of dielectric medium in transformers and capacitors containing Arochlor 1242 and 1254 (Tang et al., 2010b). Several researchers have reported abundance of highly chlorinated PCBs such as hexa-PCBs and hepta-PCBs in urban and industrial soils (Meijer et al., 2002; Nakata et al., 2005; Syed et al., 2013). Higher chlorinated PCBs are less volatile, strongly retained to fine soil particles and not easily biodegraded (Ge et al., 2013). High affinity to soil organic matter and hydrophobicity contribute to high abundance of PCBs (Qiang et al., 2012).

Risk Assessment

Risk associated with PCB concentrations in the recycling sites was done using TEQs. New Bell recycling site showed the highest range of TEQs (1.30 ± 0.49 pg TEQ g^{-1}) followed by Makea (1.05 ± 0.15 pg TEQ g^{-1}) and Ngodi (1.00 ± 0.05 pg TEQ g^{-1}). The risk of PCBs reported in this study was lower than what was reported in India (Chakraborty et al., 2016). The obtained TEQ values of dioxin-like PCBs in the present study did not exceed the Canadian soil quality guidelines of dioxin (4 pg TEQ g^{-1}). TEQ values of soil in the study area were lower than what was reported in Punjab Province, Pakistan (Syed et al., 2013) and higher than those obtained in the study conducted by Ma et al. (2009) in top soils of Harbin, China.

The risk for human by soil particles in the present study was assessed through calculation of cancer risk caused by ingestion, dermal contact, or inhalation. The results clearly showed that the health risk effects of PCBs on human are low, as indicated by the values of cancer risk ranging from 2.9×10^{-12} to 1.99×10^7 for all sites investigated (Table 2).

Table 2. Cancer risks for human by ingestion, dermal contact, and inhalation

Cancer Risk	Makea	Ngodi	New Bell
Ingestion	8.7945E-08	8.4932E-08	1.9945E-07
Dermal	5.8044E-08	5.6055E-08	1.3164E-07
Inhalation	2.9119E-12	2.8121E-12	6.6039E-12

CONCLUSION

The soils from the abandoned e-waste recycling sites in Douala, Cameroun were contaminated with PCBs at low levels and derived human health risk of PCBs was lower than those reported in other industrial sites worldwide. The TEQ values of dioxin-like PCBs in the present study were lower than the Canadian soil quality guidelines of dioxin (4 pg TEQ g⁻¹). The use of primitive and unsafe methods to recycle e-waste can lead to exposure to a variety of toxic substances to human health. These findings recommended that polices to control activities in e-waste recycling areas must be developed and enforced.

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