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Baseline

Monitoring of organic micropollutants in Ghana by combination of pellet watch with sediment analysis: E-waste as a source of PCBs

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Plastic resin pellets collected at 11 beaches covering the whole Ghanaian coastline were analyzed for polychlorinated biphenyls (PCBs). PCB concentrations ($\sum$13 congeners) were higher in Accra, capital city, and Tema (39–69 ng/g-pellets) than those in rural coastal towns (1–15 ng/g-pellets) which are close to global background, indicating local inputs of PCBs. River sediments were also analyzed for PCBs together with molecular markers. Sedimentary PCBs concentrations were highest at a site (AR02) downstream of an electronic waste (e-waste) scrapyard. At the site (AR02), concentration of linear alkylbenzenes (LABs), a marker of municipal wastewater, was lower than another site (AR03) which is located at the downstream of downtown Accra. This result suggests that PCBs are introduced more to the river from the e-waste site than from activities in downtown Accra. PAHs concentrations were relatively higher in urban areas with strong petrogenic signature. Abundance of triphenylbenzenes suggested plastic combustion near e-waste scrapyard.

Polychlorinated biphenyls (PCBs) were massively produced in the 1950s to the 1970s in industrialized countries (e.g., US, France, Russia, Japan). Cumulative world production was up to 1.3 million tons. Due to their toxicity, persistence, bioaccumulation and biomagnification, their production ceased in 1993 (Breivik et al., 2002) and their usage has been regulated by the Stockholm Convention and associated legislation. Due to the long-range transport and transboundary movement of electronic equipment containing PCBs, these compounds are widely distributed and found even in areas where they were not produced (e.g., Pozo et al., 2006). To protect the ecosystems, it is important to monitor PCBs in order to identify their sources. The present study focused on Ghana where PCB pollution by electrical and electronic waste (e-waste) has been of concern as mentioned below.

The emissions of PCBs have been decreasing in former use regions. On the other hand, high levels of PCBs have been recently recorded far from source regions (Jaward et al., 2004; Gioia et al., 2008, 2011). Potential source of the high PCB levels in the African region might be due to illegal dumping of waste containing PCB, which is released through volatilization and uncontrolled burning, and the storage and breakup of old ships (Gioia et al., 2011). In addition, it is a concern that hazardous substances including PCBs might be emitted to the environment as a result of uncontrolled disposal or inappropriate waste management/recycling (UNEP, 2009). In 2006, the world's production of electrical and electronic waste (e-waste) was estimated at 20–50 million tons per year (UNEP, 2005). Large quantities of second-hand or used electrical and electronic equipment (EEE) generated in developed countries were imported by developing countries (Robinson, 2009). However, developing countries, lack the infrastructure and resources for environmentally sound management of e-waste arising from such imports when they reach their life span (SBC, 2011a). Informal recycling of e-waste in West Africa is an emerging problem due to the rapidly growing use of EEE in Africa, and particularly due to imports from industrialized countries. West Africa serves as the major trading route for used EEE into the African continent, with Ghana and Nigeria as the main import hubs (SBC, 2011a). In Ghana, it is estimated that 215,000 tons of EEE were imported and 179,000 tons of e-waste were generated in 2009 (SBC, 2011a). Some of the electronic equipment introduced to Ghana was found to contain PCBs (Ghana EPA, 2007).

There are e-waste sites (e-waste scrapyards and dumping sites) in Accra, the capital city of Ghana and some studies on e-waste

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have been conducted (Asante et al., 2011, 2012; Feldt et al., 2014). From the studies, elevated levels of PCBs and brominated flame retardants (BFRs) in breast milk (Asante et al., 2011), heavy metals in urine (Asante et al., 2012), and OH-metabolites of aromatic hydrocarbons in urine (Feldt et al., 2014) were observed in the residents around the e-waste sites. However, levels of PCB pollution in environmental compartments including sediments, soils and waters, near e-waste sites have not been investigated. Thus, we undertook monitoring of PCBs in coastal waters along the Ghanaian coast and river sediments from Accra, by focusing on the impacts of e-waste sites have on the surrounding environments.

For the monitoring of PCBs in coastal waters, we applied pellet watch. Plastic resin pellets are small granules, generally in the shape of a cylinder or disk with diameters less than 5 mm. These plastic particles are the industrial feed stock for production of plastic products. A small portion of these are unintentionally released into the environment during land handling and transport. Because polyethylene (PE) pellets, a major type of plastics, are lighter than water, such pellets are carried by surface run-off, streams and river waters and finally reach the ocean, and distributed on beaches all over the world. The pellets sorb and concentrate hydrophobic organic pollutants including PCBs from surrounding sea water (Mato et al., 2001). Since 2005, we have been conducting pellet watch globally, which has revealed spatial patterns of distribution of POPs and demonstrated the relevance of Pellet Watch with conventional POPs monitoring, i.e., mussel watch (Ogata et al., 2009). Several country scale monitoring demonstrated that pellet watch approach is effective in identifying pollution sources in target countries (Karapanagioti et al., 2011; Mizukawa et al., 2013). Thus, we applied the pellet watch approach to the Ghanaian coast. Through the analysis of pellets from remote islands, we set global background level of POPs (e.g., 10 ng/g-pellet for PCBs), above which local inputs of POPs are suspected. The present study relied on the background level to judge the local inputs of PCBs to the Ghanaian coast.

For the sediment samples, two types of hydrophobic molecular markers, i.e., linear alkylbenzenes (LABs) and polycyclic aromatic hydrocarbons (PAHs), were analyzed together with PCBs. Molecular markers are useful when estimating the contribution of specific sources (e.g., urban wastewater, incineration of waste) to the pollutant loads. LABs are feed stock of linear alkylbenzenesulfonates (LAS) which are widely used as synthetic detergents and small but significant amounts of LABs are contained in LAS-type synthetic detergents. LABs are less biodegradable and hydrophobic and, therefore, LABs are used as markers of hydrophobic pollutants such as PCBs in municipal wastewater. In the case of Accra, PCBs might be derived from industrial activities in downtown Accra and wastewater from downtown Accra may contribute to PCBs in the river in addition to emission from e-waste site.

PAHs are a group of hydrocarbons consisting of two or more fused benzene rings. They are contained in crude oil and petroleum products and also are generated through the combustion of organic matter. The present study utilized triphenylbenzene (TPB) among PAHs. TPB has been proposed as a marker of plastic combustion because it might be generated specifically from the combustion of polyoxyethylene moieties of some antioxidants (Simoneit et al., 2005). Plastic combustion may occur following e-waste dismantling processes. Therefore, occurrence of TPB might be associated with combustion activity in e-waste scrapyards. The present study also aimed to elucidate the status of PAH pollution, not only TPB but also a whole range of PAHs, in Ghanaian sedimentary environment. This was because some of PAHs are carcinogenic and understanding the pollution levels of PAHs and their source identification is important. However, no information is available on PAHs in Ghanaian aquatic environments. To fill the knowledge gap, the present study measured PAHs in 9 sediment samples collected from rivers and lagoons in Ghana.

The purpose of the present study was to monitor pollution status of organic micropollutants in coastal waters along the southern coast line of Ghana, with special emphasis on PCBs and e-waste site.

Plastic resin pellets were collected from eleven Ghanaian beaches in 2009 and 2013 (Fig. 1). Among the eleven locations, Accra and Tema are large cities. Accra is the capital city and Tema is the biggest port in Ghana. Detailed information, including the coordinates of the sampling locations, is listed in Table S1, where the eleven locations are listed in longitudinal order from east to west (illustrated in Fig. 1). Pellet samples were collected from the high-tide line of the sandy beaches by using soap-rinsed fingers or with the aid of stainless-steel tweezers. About 100 pellets were collected from each beach. The pellets were wrapped in aluminum foil and carried to our laboratory in Tokyo. In some cases, samples were put into paper envelops and sent to Tokyo via air mail. Pellets were sorted and PCBs are analyzed as described in Ogata et al. (2009), as follows. Pellets were sorted with a near-infrared spectrometer (Plascan-WTM OPT Research Inc., Tokyo, Japan) into polyethylene (PE), polypropylene (PP), and other polymers. Yellowing PE pellets (with a yellowness of >40) were selected for chemical analysis. Median PCB values were obtained by analyzing 5 pools of pellets (each pool consisting of five randomly selected pellets) from each location.

PCBs were extracted from pellets by soaking in hexane. The extracts were separated through fully activated silica gel columns into three fractions: Fraction I (n-alkanes and hopanes), Fraction II (PCBs and LABs), and Fraction III (PAHs). In Fraction II, 38 PCB congeners ranging from dichlorobiphenyl (CB8) to decachlorobiphenyl (CB209) were determined by gas chromatography/ion-trap mass spectrometry. The sum of 13 congeners (i.e., CB66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206) is expressed as $\sum$13 PCBs which are used for Fig. 2. The instrumental conditions for PCBs are described in Hirai et al. (2011). Recovery correction was not applied because good recoveries had been confirmed prior to the sample analysis. The reproducibility of this analytical procedure (i.e., column chromatography and instrumental determination) was confirmed by analysis of four aliquots from a single extract of pellets from Tokyo Bay, Japan. The relative standard deviations (RSDs) of the concentrations of individual congeners were less than 14% except for CB18, which had RSD of 17%. Recovery was tested by spiking the aliquots of the extracts with authentic standards; recoveries were 71–121% for all the PCB congeners contained significantly in standards mixtures except for CB189, which showed recoveries of 83–146%. A procedural blank using only solvent was run with every set analyzed (5 pools). Analytical values less than 3 times the corresponding blanks were considered below the limit of quantification (LOQ). The LOQs were normally 0.07 ng/g-pellet for $\sum$13 PCBs

To determine the sources of PCBs, surface sediments were collected at five locations from rivers in Accra and at two control sites, one from a lagoon in western Ghana and another from the Volta Lake (Table S2). Each sample comprised the top 2 cm from sediment cakes collected with an Ekman dredge. The samples were stored at −30 °C and freeze-dried before analysis. The sediment samples were analyzed for PCBs together with LABs and PAHs. PCBs, LABs, and PAHs in sediments were extracted and purified according to Rinawati et al. (2012). Briefly, 1–7 g of freeze-dried sediment was extracted by pressurized fluid extraction in a Dionex ASE 200 accelerated solvent extractor with a 3:1 mixture of dichloromethane:acetone (v/v). The extract solutions were spiked with PAH and alkylbenzene (AB) surrogates. The PAH surrogate consists of anthracene-d_{10}, p-terphenyl-d_{14}, and benz[a]anthracene-d_{12}. The AB surrogate consists of 1-C_n LAB (n = 8–14). Structures of LABs are expressed as “m-C_n”, where “m” means the phenyl substitution position on the alkyl chain and “n” means the number of alkyl