Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Distribution of PBDEs, HBCDs and PCBs in the Brisbane River estuary sediment

Alfred K. Anim[a], Daniel S. Drage[b,c], Ashantha Goonetilleke[a], Jochen F. Mueller[b], Godwin A. Ayoko[a,*]

[a] Queensland University of Technology (QUT), Science and Engineering Faculty, 2 George St., GPO Box 2434, Brisbane, QLD, 4001, Australia
[b] Queensland Alliance for Environmental Health Sciences, The University of Queensland, 39 Kessels Road, Coopers Plains, QLD 4108, Australia
[c] School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Keywords:
Sediment
Brisbane River
Persistent
PBDEs
PCBs
HBCDs

ABSTRACT

To date, very little or no data exist in literature for some brominated flame retardants (BFRs) and polychlorinated biphenyls in Queensland sediments. These pollutants were measured in the sediments along the Brisbane River estuary. The target compounds were regularly detected in measurable concentrations: PBDEs = 33.3–97.8% (n = 45), PCBs = 94.1–100% (n = 51) and HBCDs = 79–98% (n = 48). Consistently, > 90% of the observed Σ_8PBDE concentration was attributed to BDE-209. Mean PBDE levels (ng/g dry wt.) were: 4.4 ± 3.2 (Σ_8PBDE) and 4.4 ± 3.0 (BDE-209) across 22 sampling sites. The mean Σ_7PCB and ΣHBCD were 5.4 ± 4.5 and 1.0 ± 1.5 ng/g dry wt. respectively. The 25% (α-HBCD), 8% (β-HBCD) and 67% (γ-HBCD) diastereoisomer contributions observed were consistent with values reported in the literature. Contaminant levels are fairly distributed along the River and were generally low compared to similar studies around the world.

Polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecanes (HBCD) are incorporated as additive brominated flame retardant (BFR) compounds in domestic and industrial products (Abdallah et al., 2013) to either retard or prevent burning processes. Consumer products such as plastics, foam and textiles, computer and television casings, carpets and furniture contain PBDEs. HBCD have also gained wide applications in polystyrene foam for thermal insulation in buildings and upholstered furniture (automobile interior textiles) and, electric and electronic equipment (Covaci et al., 2006; NICNAS, 2015) whilst polychlorinated biphenyls (PCBs) have been applied historically as heat transfer fluids in transformer and capacitor oils as well as other industrial uses (ink and paints, carbonless copy paper, and wood floor finishers).

Due to the physico-chemical properties, including persistence and potential for bioaccumulation as well as toxicity of these compounds to humans and the ecosystem, National and Global legislations to restrict/ban their production and use have been formulated. PBDEs have been reported to disrupt oestrogen and thyroid hormones (Costa & Giordano, 2011; Zhang et al., 2008; Xu et al., 2015) as well as lead to reduced male fertility and ovarian development (Ni et al., 2013). PCBs were classified as human carcinogens in 2013 by the International Agency for Research on Cancer (Lauby-Secretan et al., 2013). Toxic effects on immune system disorders, behavioural alterations and reproduction defects have also been attributed to PCBs (Grossman, 2013; ATSDR, 2000). Even though studies on human toxicity due to HBCD contamination are currently inconclusive, developmental neurotoxicity and endocrine disruption have been identified as potential toxicological effects in humans (NICNAS, 2015; Deng et al., 2009; Focant et al., 2004).Accordingly, PCBs, the penta- and octa-BDE commercial formulations and HBCD have been listed as persistent organic pollutants (POPs) in 2001, 2009 and 2013, respectively under the Stockholm Convention, meaning that these chemicals are subject to legislative bans and restrictions (Stockholm Convention, 2015; Su et al., 2015). The application of commercial HBCD for cavity wall insulation in the building industry is; however, exempt from this ban until 2024 (Koch et al., 2015). In Australia, the importation and use of commercial penta-BDE and octa-BDE were banned in 2005 (NICNAS, 2007; Toms et al., 2015). Although deca-BDE is currently not listed under the Stockholm Convention, both national and international considerations are still ongoing for its inclusion on the restricted/banned list (Gevao et al., 2014).

BFRs and PCBs are ubiquitous and can undergo long-range atmospheric transport (LRAT) and deposit in regions far distant from their emission sources (Olukunle et al., 2015; Li et al., 2015; Zhao et al., 2008; D. Chen et al., 2015; Y. Chen et al., 2015). As a result, their

* Corresponding author.
E-mail address: g.ayoko@qut.edu.au (G.A. Ayoko).

http://dx.doi.org/10.1016/j.marpolbul.2017.05.002
Received 27 January 2017; Received in revised form 26 April 2017; Accepted 1 May 2017

environmental contamination has been recognised worldwide (Kim et al., 2014; Law et al., 2014; Law et al., 2003; de Wit, 2002), including regions where they have never been manufactured such as Ghana in West Africa (Asante et al., 2011) and the Arctic (de Wit et al., 2010). In Australia, indoor dust has been found to contain high levels of PBDEs (Toms et al., 2015). House or airborne dust contaminated with organic pollutants such as BFRs and PCBs can settle on hard surfaces such as roofs and roads, and subsequently be washed-off into rivers thereby providing a pathway for the deposition of these pollutants in sediment via stormwater runoff (Chen et al., 2006).

Sediment serves as a sink for these pollutants (Abdallah et al., 2013; Suehring et al., 2016; Morris et al., 2004). These compounds have low water solubility and can be taken up from sediment by aquatic organisms and subsequently humans through the food chain. However, studies on BFR and PCB contamination in the sediment of Australian rivers are generally very limited, and this is particularly the case for the Brisbane River estuarine area, which is located through major urban and industrial hubs in the Queensland state with increased susceptibility to contaminated stormwater.

Unlike reports on sediments from the Sydney estuary in Australia, which showed HBCD contamination of 1.8–5.3 ng/g dry weight (Drage et al., 2015) and similar reports from other parts of the world (Morris et al., 2004; Drage et al., 2015; Feng et al., 2012), no data has currently been cited in literature on HBCD contamination in Queensland sediment. Data on PCB contamination of the Brisbane River estuary sediment is also very limited and does not represent the contamination status for at least the last decade (Müller et al., 1999; Shaw & Connell, 1980). A report by Muller et al. in 2004 suggests sources of PCBs and distribution of dioxin-like compounds (Müller et al., 2004) along the Brisbane River estuary. However, a more recent study across freshwater, estuarine and marine sediments in Australia only analysed PBDE congeners, reporting a mean concentration of 4.7 ng/g dry weight for Σ_7BDE (BDE-47,99,100,153,154,183,209) (Toms et al., 2008). That study analysed only a few (n = 9) sediment samples from Queensland and this may not reflect the current level of contamination in the study area (Brisbane River) due to the subsequent spread of urbanization and industrialization in recent years. Furthermore, two major flood events occurred in the Brisbane area in 2011 and 2013. These events submerged large numbers of buildings for days and washed-off household materials and automobiles into the Brisbane River (BoM, 2015). Given the ubiquitous and persistent properties of BFRs and PCBs, it is important to investigate the current burden of PBDEs, PCBs and HBCD contaminants in sediment along a wider stretch of the Brisbane River. Accordingly, this research study focused on the distribution of PBDEs, HBCD and PCBs contamination in bed sediment along the Brisbane River estuarine area.

The Brisbane River has a catchment area of about 13,560 km^2. The River flows from Mount Stanley through the Brisbane City and discharges into Moreton Bay. The study area spanned the Brisbane River, measuring about 70.5 km long between Karana Downs (designated upstream) and the Port of Brisbane (designated downstream), which encompasses varying land use that would contribute to contamination of the River estuarine sediment. These land uses include farmlands and rural residential areas (upstream section), parklands, commercial activities and urban-residential areas (midstream section), and industrial areas (downstream section). Thus, waste inputs from these areas could be incorporated into the estuarine sediment. Fig. 1 shows the study area with the designated sections and the sampling sites. Tributaries and stormwater drainage are the major inflows into the Brisbane River. Economically, the Brisbane River supports agricultural activities as well as transportation.

Grab surface sediment samples at a depth of 0-3 cm were collected for this study between 2014 and 2015 as described elsewhere (Duodu et al., 2016). Sample collection and handling were in accordance to Australian-New Zealand standards (Standards Australia & Standards New Zealand, 1999). Sediment samples in direct contact with the sides of the grab sampler were excluded. Each sample was transferred into a pre-cleaned tightly capped and labelled glass bottle. The samples were transported to the laboratory on dry ice in a thermos insulator box and stored at -20 °C prior to preparation and analysis.

The reagents/chemicals used throughout the sample preparation and analysis were of high purity. Sulphuric acid (98% purity) and HPLC grade organic solvents; n-hexane and dichloromethane were supplied by Merck (Darmstadt, Germany). Copper powder (< 425 μm, 99.5%), Florisil (60–100 mesh) and silica gel (pore size 60A, 40-63 μm, high purity) were obtained from Sigma-Aldrich. $^{13}C_{12}$-labelled PCBs (marker-7 PCB mix), $^{13}C_{12}$-labelled PCB-141 (recovery standard) and $^{13}C_{12}$-labelled PBDEs (method 1614 labelled stock solution) were supplied by Cambridge Isotope Laboratories. Native PCB (PCB-28, 52, 101, 118, 138, 153 and 180) were obtained from AccuStandard (Dutch seven PCBs standard). Individual native and $^{13}C_{12}$-labelled α-, β-, and γ-HBCD, $^{13}C_{12}$-BDE-77 and $^{13}C_{12}$-TBBPA were supplied by Wellington laboratories (Guelph, Ontario, Canada).

The samples were first frozen at -20 °C followed by freeze drying for 48 h using an Alpha 1–4 LDplus freeze dryer (John Morris Scientific, Australia). The dried samples were ground using a mortar and pestle to loosen any lumps and then sieved through a 250 μm sieve. Total organic carbon (TOC) content were determined as described by Schumacher (2002, and references therein). The powdered samples were kept in a cold room prior to extraction and analysis. Essentially, 99 mL ASE dionium cells were packed (from bottom upwards) in the following order: 2 × microfiber filter, florisil, hydromatrix, microfiber filter, 44% acid silica, microfiber filter, Cu powder and hydromatrix. The packed cells were pre-cleaned on the ASE 350 using the extraction protocol for one static cycle. For analysis, 8–10 g of each dry sediment sample were added to the pre-extracted packed cell and spiked with 5 ng of $^{13}C_{12}$-labelled BDEs − 28, − 47, − 99, − 100, − 154, − 153, − 183, α- β- and γ- HBCD, PCBs − 28, − 52, − 101, − 118, − 138, − 153 and − 180 and 50 ng of BDE-209. The cells were then loaded onto the ASE 350. Cells were extracted with n-hexane: dichloromethane (3:2, v/v ratio) at 90 °C with a heating time of 2 min and a static time of 5 min (Abdallah et al., 2013; Drage et al., 2015). Each cell underwent three static cycles with a rinse volume of 50% (cell volume) using extraction solvent and purged for 120 s at the end of each static cycle. The extracts were concentrated to approximately 1 mL on a rotary evaporator (Buchi Rotavapor R-114, Switzerland) at 40 °C. Extracts were then transferred to 5 mL glass tubes and concentrated to near-dryness on a 40 °C hot plate and under a gentle stream of nitrogen. Samples were reconstituted in 150 μL hexane and 50 μL of 20 ppb $^{13}C_{12}$-labelled BDE-77, PCB-141 and TBBPA (used as recovery determination standards (RDSs)) in hexane. Extracts were transferred into glass-inserted amber autosampler vials for GC–MS/MS analysis for PBDEs and PCBs, followed by GC-NCI/MS analysis for BDE-209. After GC-based analyses extracts were solvent exchanged into methanol and analysed for HBCD via HPLC-MS/MS.

Analysis of PBDEs (except for BDE-209) and PCBs was carried out with a single injection on a Thermo Fisher Trace GC Ultra coupled to a Thermo Fisher TSQ Quantum XLS triple quadrupole mass spectrometer. One microliter of final extract was injected at 80 °C in a splitless mode for analysis on a DB-5MS column (30 m × 0.25 mm × 0.25 μm thickness). The transfer line temperature was maintained at 280 °C using He as a carrier gas at a flow rate of 1 mL/min. The temperature programme, which started at 80 °C was held for 2 min then ramped at 20 °C/min to 180 °C and held for 0.5 min before final ramping at 10 °C/min to 300 °C where it was held for 10.5 min to complete one run. The MS was operated in selective reaction monitoring mode (SRM). Full MS/MS parameters are provided in the Supporting Information (Table SI-1).

BDE-209 was measured on a Shimadzu GCMS-QP2010 Plus. An Agilent DB-5MS column (15 m × 0.25 mm × 0.1 μm thickness) was used. The injector was operated in splitless mode with an injection volume of 1 μL. The injection port and transfer line temperature were