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Polybrominated diphenyl ethers (PBDEs) and hexabromobiphenyl in sediments of the Diep and Kuils Rivers in South Africa

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ABSTRACT

This study reports the concentrations of polybrominated diphenyl ethers and hexabromobiphenyl in bottom sediment of two rivers within the city of Cape Town. Following the isolation of the target compounds by mechanical shaking technique, the routine analyses and structural elucidation of the target analytes were performed with high capillary gas chromatography with electron capture detection (GC-μECD) and gas chromatography-time-of-flight-mass spectrometry (GC-TOF-MS) techniques, respectively. The mean concentrations of the total PBDE varied in the range of 0.06 – 2.47 ng/g in the Diep River. These values were relatively higher in the Kuils River. The mean concentrations of BB 153 ranged from not detected (ND) –0.39 ng/g. Similarly, the mean concentrations of BB 153 in the Kuils River were in the range of ND –1.21 ng/g. The statistical analyses performed on these data showed that majority of the PBDE congeners, except BDE 209 had strong positive correlation with the total organic carbon (TOC). Although effluent discharges from nearby wastewater treatment plants were identified as important source of PBDEs, other notable sources, including grey water intrusion could contribute to the contamination of the upstream of both rivers.

1. Introduction

Current knowledge about the widespread distribution and possible deleterious health effects of certain organic pollutants, especially some brominated flame retardants (BFRs) in the environment are quite revealing (Daso et al., 2010; Kefeni et al., 2011). There are increasing concerns over the release of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) from various consumer products, including furniture, carpets, plastics, computers and electronics, amongst others. Both PBDEs and PBBs are additive BFRs and may be easily released from the treated products during their usage. (de Wit, 2002). Elevated levels of these contaminants have been detected in dust and related matrices, especially in indoor environment (Kefeni & Okonkwo, 2012).

The various mechanisms through which these contaminants are released have not been fully understood. Although, studies have shown that indoor environments, especially offices and homes as well as car interiors could contain higher concentrations of these contaminants than the outdoor environments (Harrad et al., 2006; 2008; Fromme et al., 2009), thus having grievous implications for human exposure.

Several sanitary activities, including washing, vacuuming of floors and other surfaces may result in the significant transfer of these contaminants into the wastewater streams. Amongst the likely sources of these pollutants into freshwater bodies, especially rivers, lakes and streams, WWTP discharges have been identified as important point sources of these contaminants (Song et al., 2006, Daso et al., 2012; Olujimi et al., 2012). The tracking of most organic pollutants entering freshwater bodies could be quite tasking if their source pathways are highly varied. Hence, the choice of an appropriate environmental indicator for the assessment of these pollutants is essential.

Sediment is a complex heterogeneous matrix containing considerable amount of organic carbon fractions together with

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inorganic constituents. The synergistic association between the organic carbon constituents and most organic pollutants has been widely explored to assess the extent of pollution in aquatic environment. Consequently, the analysis of PBDEs concentrations in sediment samples collected from freshwater as well as

marine water systems has extensively been carried out globally (Yun et al., 2008; Ramu et al., 2010; Vane et al., 2010; Pan et al., 2011; Zhao et al., 2011). Presently, there is limited information in Africa on PBDE levels in different environmental matrices, including bottom sediment. To date, only few studies have reported PBDEs in bottom sediment in South Africa. Olukunle et al., (2012) reported on the levels of PBDEs in bottom sediment collected from the Juskei River in Gauteng Province where elevated PBDE levels at certain sampling points were attributed to pollution resulting from waste dumping and uncontrolled influx of sewage.

Recently, the assessment of inland and coastal sediments within eThekwini Metropolitan Municipality in KwaZulu Natal Province was conducted for different BFRs (La Guardia et al., 2013). In their study, the sum of PBDEs up to 25,400 ng/g was found rivalling those previously reported in heavily impacted regions of the world. Surprisingly, the important sources of these BFRs into the South African environment are still not clearly defined. However, these chemicals may likely enter into the environment during the manufacturing and use of BFR-containing products, disposal and from variable non-point sources such as atmospheric deposition, agricultural and urban run-offs.

PBDEs and PBBs are hydrophobic contaminants, hence their removal in aqueous matrices may be facilitated through adsorption onto finely suspended solids. The gravity induced settling of these solids results in the accumulation of these contaminants in the bottom sediment of the impacted water bodies. Notable point sources of these contaminants, especially WWTP discharges may result in the transfer of these contaminants into the food chain through bioaccumulation and subsequent biomagnification processes (Shaw et al., 2009; Kuo et al., 2010). Besides the physical processes involved in their redistribution in the aquatic environment, majority of these contaminants may also undergo biotransformation processes resulting in the newer compounds with different physicochemical properties, toxicity and bioaccumulation potentials.

The Diep and Kuils Rivers investigated in this study are known for the conveyance of treated WWTP effluent as well as urban runoff within the city of Cape Town. These rivers flow through a significant proportion of the residential as well as industrial areas of the city. More so, these rivers transverse several commercial farmlands before emptying their contents into the adjacent oceans. The beneficial usage of compost derived from WWTP sludge in some of these commercial farms is growing rapidly in the city. This practice, though is beneficial could result in possible migration of these contaminants through agricultural runoff into these rivers. More so, with the increasing number of informal settlements within the city, the intrusion of grey water from these settlements most of which are not connected to the urban sewer system could highly impact the rivers, especially during high precipitation periods.

Globally, studies have been conducted to evaluate the occurrence and levels of PBDEs and PBBs in aquatic environment. Unfortunately, there is still paucity of data regarding the occurrence of these contaminants in most parts of Africa, including South Africa. This study was aimed to obtain baseline information with respect to the concentrations of selected PBDE congeners as well as hexabromobiphenyl (BB 153) in bottom sediment of two major rivers in the city of Cape Town. It was also part of our objective to identify the potential sources of these contaminants into the investigated rivers.

2. Materials and methods

2.1. Chemicals and materials

All organic solvents (n-hexane, dichloromethane, acetone and isooctane) purchased from Merck (Modderfontein, South Africa) were doubly-distilled prior to use. Anhydrous sodium sulphate was purchased from Radchem (Pty) Ltd. (Roodepoort West, South Africa). BDE 77, silica gel (60–200 mm) and copper powder were supplied by Sigma-Aldrich (Aston Manor, South Africa). High purity gases (Helium – 99.999%; nitrogen 99.999%) were purchased from by Afrox (Pty) Ltd. (Cape Town, South Africa). Unlabelled individual reference PBDEs and Pentachloronitrobenzene (PCNB) were produced by Cambridge Isotope Laboratories (CIL) (Andover, MA, USA). BB 153 was produced by Chiron AS (Trondheim, Norway). These standards were locally supplied by Industrial Analytical (Pty) (Midrand, South Africa).

2.2. Description of the study area

Two rivers were investigated in this study, namely: the Diep and Kuils Rivers. The Diep River has its source from the Perdeberg and Riebeeck-Kasteel Mountains around Malmesbury which is outside the borders of Cape Town. The river flows south-easterly direction for approximately 65 km before forming an extensive vlei popularly known as the Rietvlei which is renowned for its recreational potentials. Several tributaries join the Diep River on its way to the sea and these include the Klein River, the Groen River and the Mosselbank River which drains the Durbanville and Kraaifontein areas. The major activities along the catchment of the Diep River include large-scale crop and pastoral farming where WWTP derived compost materials are used as soil conditioners. This river is also bound to the Vissershok landfill site as well as an informal settlement just before it drains through the Potsdam WWTP area.

The Kuils River, on the other hand, was historically seasonal, draining a vast area of sand dunes, and recharging the Cape Flats Aquifer before ever reaching the sea. The river drains through a large expanse of land and never reached the sea, but emptied into a system of pools, or “*kuils*”, which are now occupied by the Khayelitsha Township (Brown & Magoba, 2009). The river which has its source from the low hills near the present town of Durbanville has witnessed a tremendous change along its catchment over the years. Treated effluent from the Bellville WWTPs is discharged into the Kuils River via an underground pipeline which is connected to the river some few distances away from the plant. As a result, more convenient sampling points were carefully selected around the Zandvliet WWTP point of discharge into the river. The map of the study area showing the sampling points in both rivers is presented in Fig. 1.

2.3. Sample collection, preparation and instrumental analyses

Bottom sediment samples ($N=36$) from a depth of 0–5 cm were collected bi-monthly from the Diep and Kuils Rivers between April 2010 and March 2011 spanning through the different seasons of the year. For this purpose, the entire study period was sectionalised into different seasons as follows: March–May (autumn), June–August (winter), September–November (spring) and December–February (summer). These samples correspond to the upstream, point of discharge and downstream sampling points of the two rivers. At each sampling point, several grab samples were collected and pooled together to form a composite sample. Upon collection, samples were iced *en-route* the laboratory. On arrival in the laboratory, the large debris in these samples was removed and the rest of the samples were dried in vacuum oven set at 50 °C.