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Concentrations of Polybrominated Diphenyl Ethers in Sediments from Jukskei River, Gauteng, South Africa

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Abstract This study determined concentration levels of polybrominated diphenyl ethers (PBDEs) in sediment samples collected from Jukskei River in South Africa. Final extracts, after concentration and dilution to 200 μL were analyzed by injecting 1 μL in the GC–ECD and GC–MS. Results obtained showed good recoveries (73%–114%, with RSD < 17%). The concentrations of ∑PBDEs in sediment for the seven sampling sites ranged from 0.92 to 6.76 ng g^{-1} dry weight and total PBDEs with a total BDE sum of 23.85 ng g^{-1} dry weights. Concentrations of PBDEs obtained in the present study are significantly lower than the values reported from developed countries.

Keywords Concentrations · PBDEs · Sediment · Jukskei

Polybrominated diphenyl ethers (PBDEs) are chemicals used as additives in a wide range of industrial and consumer products such as paints, plastics, textiles, furniture, electronics, polyurethane foams and construction materials to retard the ability to catch fire (de Wit 2002). They belong to the group of organohalogenated flame retardants which include chlorinated and brominated flame retardants. Brominated flame retardants (BFRs) have been shown to be the most effective in the inhibition of fires and are materials of choice because of their low cost and lower loading of substrate (Bientinesi and Petarca 2009).

Of all the BFRs, PBDEs are the most commonly used compared to polybrominated biphenyls (PBBs), hexabromocyclodecane (HBCD) and tetrabromo bisphenol A (TBBPA) (de Wit 2002). Three major commercial formulations of PBDEs were produced globally in the last decade; penta-BDE, octa-BDE and deca-BDE. The penta and octa-BDE derivatives were banned by the European Union (EU) in August 2004 (BSEF 2006), since they have been recognised as persistent organic pollutants (POPs) and included on the list of POPs under the Stockholm Convention (UNEP 2009). However, deca-PBDE is still being used without any restrictions. Recent trend shows that the production of deca-BDE among brominated flame retardants is second after TBBPA. There is increasing concern of these substances in the environment because they have been reported to be persistent, bio-accumulate and toxic (de Wit et al. 2006). Since PBDEs are used as additives in products, they have the potential to be released into the environment thereby settling in dust, water, sediment and biota (de Wit 2002). Consequently, PBDEs can bio-accumulate in fatty tissues thereby biomagnifying up in the food chain. Several studies have confirmed the presence of PBDEs in fish, birds, adipose tissue, breast milk and serum of humans (Covaci et al. 2003; Sudaryanto et al. 2008). The presence of PBDEs in river sediments has been reported by many researchers (Qiu et al. 2010).

So far, little is known about the production, use and distribution of PBDEs in and around African countries including South Africa. Studies conducted to date in some South African waters have shown the presence of

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organochlorinated compounds (Sibali et al. 2008). With the exception of recent studies by Polder et al. (2008) and Odusanya et al. (2009) who reported on the presence of HBCD and PBDEs in bird eggs and landfill leachates respectively in South Africa, the authors are not aware of any report on the concentration of PBDEs from any South African water system and probably in Africa. Therefore, the main objective of the present study is to report for the first time concentrations of PBDEs in sediment from Jukskei River, South Africa.

Materials and Methods

Pure standards (1.2 mL of 50 mg L^{-1}) of each certified standard solutions of sixteen PBDEs congeners (BDE-3, 15, 17, 28, 47, 66, 77, 85, 99, 100, 126, 138, 153, 154, 183, and 209) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Copper powder (purity 99.98%, Saarchem (Pty) Ltd., Muldersdrift, South Africa), silica gel (100–200 mesh), sodium sulphate (purity 99.9%), glass wool and HPLC grade solvents: acetone, hexane, dichloromethane, methanol, nonane (99.8% purity) and toluene (Sigma Aldrich Germany), were purchased from Industrial Analytical Pty. Ltd., South Africa. Microsoft Office Excel 2007 was used for statistical analysis.

The Jukskei River is one of the largest Rivers in Johannesburg with the catchment covering an area of 800 km^2 including many of the highly industrialised and urbanised parts of Johannesburg. This River which is one of the main tributaries of the Crocodile River flows northward through to Hartebeespoort dam and ultimately drains into the Indian Ocean. It is characterised by high level of pollution mainly from contaminated storm water run-off, effluent discharges from industries and wastewater treatment works, sewage systems, leachates from old landfill sites and overcrowding along the river bank in Alexandra area (Campbel 1996). The map of Gauteng showing the position of Jukskei Catchment and the sampling points are shown in Fig. 1.

Sediment samples were collected at a depth of 0–5 cm below the surface with stainless grab sampler into previously cleaned wide mouth 500 mL bottles wrapped with aluminium foil. The samples were collected from seven points along the stretch of Jukskei River in January 2010 (1 ms^{-1}; rainy weather flow rate) from the most accessible

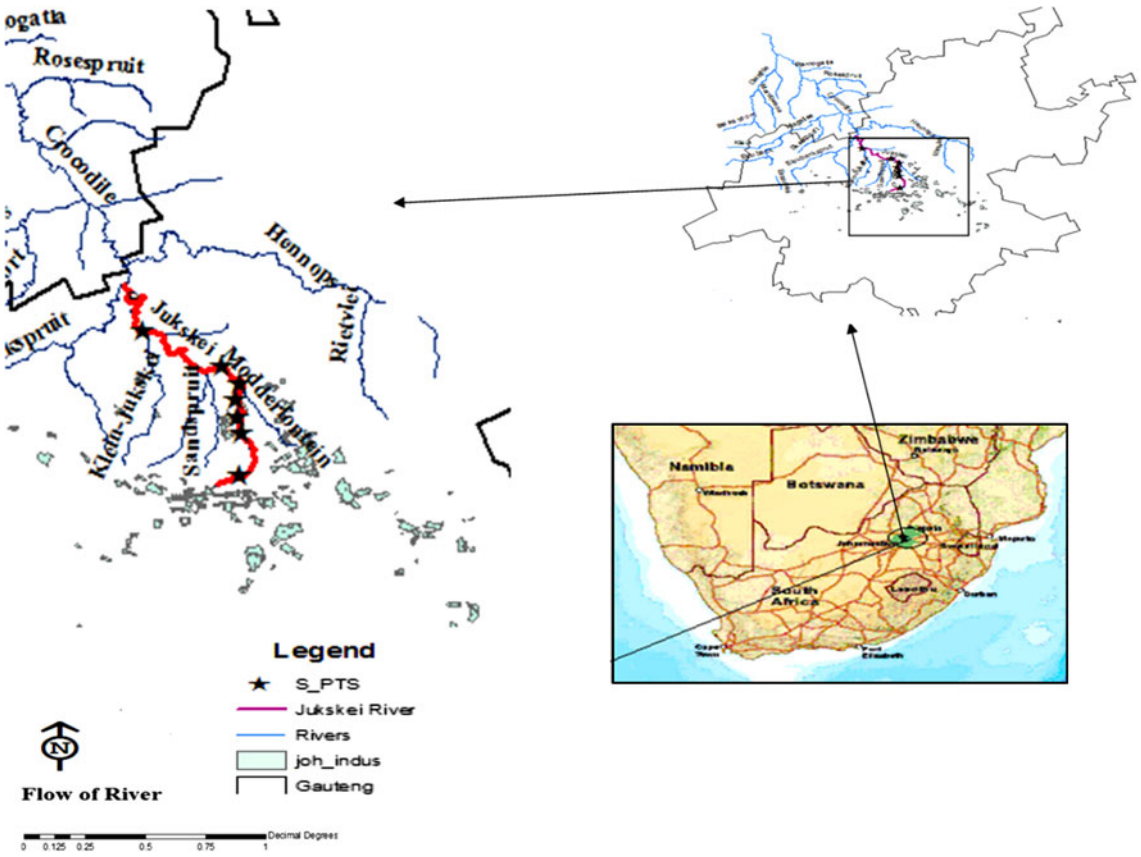

Fig. 1 Map of South Africa (*bottom right*) and Gauteng (*top right*) showing position of Jukskei River, Johannesburg industries and sampling points

Table 1 Geographical coordinates of sampling sites along the stretch of Jukskei River

Points	Latitude	Longitude	Name
A	− 25.9482	27.9575	Knoppieslaagte
B	− 26.0847	28.10878	Eastgate
C	−26.0321	28.11142	Waterval
D	−26.0056	28.07836	Kyalami
E	−26.0570	28.1040	Buccleuch
F	−26.1090	28.1140	Eastbank
G	−26.178	28.107	Bruma Lake

points using geographical information system GIS. At each point, three samples of sediment were collected; two from the banks and one from the middle of the River. After collection, samples were transported to the laboratory in cooler boxes and were kept frozen at −20°C until extraction and analysis. Sampling points and coordinates are given in Table 1.

Pre-extracted and spiked sediment samples from Jukskei River were used for developing the Soxhlet method. About 10 g of dried and sieved (150μ) sediment samples were weighed into glass fibre thimble pre extracted in a Soxhlet apparatus and extracted with 170 mL (hexane : acetone, 2:1, v/v) for 10 h. Extracts were reduced to 1 mL by rotary evaporation, before subjecting to column cleaning.

All extracts were treated with 2 g copper powder to remove elemental sulphur before clean-up. Pasteur pipette column (5 mm i.d × 230 mm) was plugged with glass wool at the bottom and packed with activated neutral silica gel, basic silica gel, acidic silica gel and sodium sulphate from bottom to top in the following order: neutral silica gel (0.2 g), basic silica gel (0.2 g), neutral silica gel (0.2 g), acidic silica gel (0.4 g), neutral silica gel (0.2 g) and sodium sulphate (0.2 g) at the top. Glass wool was used for partitioning between each level of packed materials. Each of the packed Pasteur pipette columns was first eluted with 20 mL of *n*-hexane after which the extract was transferred onto it. Subsequently, it was eluted with 2 × 10 mL of *n*-hexane: dichloromethane mixture (3:1, v/v). The extract was further concentrated under a gentle flow of nitrogen to about 100 µL. Finally, the concentrated extract was changed over to toluene by addition of 250 µL to the mixture and concentrated to a final volume of 200 µL and ready for analysis.

Extracts were analysed using Agilent 7890A GC system (serial number: US 92023178, made in USA). 1 µL solutions of the extracted sample was injected by Agilent Technologies 7693 auto sampler into split/splitless injection port on DB-5 column (30 m, 0.25 mm ID, 0.10 µm d_f). The following chromatographic conditions were used: helium as the carrier gas at a flow rate of 1.5 mL min^{-1}, splitless time of 1 min, injection temperature of 290°C and oven programme of 90°C for 1 min, ramped by 30°C min^{-1} to 300°C for 5 min and 10°C min^{-1} to 310°C for 1 min. The GC was coupled to an Agilent 5975C inert MSD with triple axis detector, operated in EI mode. Operating conditions were set as follows: ion source; 250°C, and transfer line at 300°C. Identifications were carried out using full scan, by monitoring the presence of the mass spectra of molecular ion and two qualifier ions of each congener at the elution retention time. Each congener was quantified against five level external standard calibration curves. BDE209 was analysed separately on gas chromatograph-electron capture detector (GC–ECD) equipped with digital pressure and gas flow control using ZB-5 capillary column of (15 m, 0.25 mm i.d., 0.25 µm d_f) with temperature programming, except the final hold time which was changed to 3 min. Nitrogen was used as a carrier and make up gas with a flow rate of 2.5–30 mL min^{-1}, respectively.

Several quality control measures were taken to ensure the correctness and integrity of the results. These include the use of pre-extracted river sediments fortified with low concentrations (0.5–1.5 ng μL^{-1}) of pure PBDE standards, to assess recovery. Three sediment samples collected at each site were homogenised and pre-treated for extraction, followed by triplicate analysis. Same procedure was used for blank and real sample analysis. Chromatographic conditions were monitored to check for variation in retention times, while test standards were run after every five samples and a blank was run after each sample.

Results and Discussion

The chromatogram of mixture of 16 PBDEs standards is shown in Fig. 2. The PBDEs were well resolved with only a single co-elution (BDE85 and BDE126) using GC–ECD and GC–MS. Limit of detection (LOD) ranged from 0.03 to 0.32 ng g^{-1} for lower congeners except for BDE 209 which was 4.66 ng g^{-1}.

The results of Soxhlet extraction of pre-extracted sediment can be seen in Fig. 3. The recoveries obtained are as follows: BDE3(55.91%), BDE15(100%), BDE17(41.7%), BDE28(130%), BDE47(99%); BDE77(120%), BDE85 (120%), BDE 99(66.1%), BDE126(95%), BDE154(66%), and BDE209 (57%).

Representative chromatogram of GC–MS for PBDEs in sediment samples is shown in Fig. 4, while the concentrations of PBDEs in sediment samples collected at seven different sites on Jukskei River namely; Knoppieslaagte (A) Eastgate (B), Waterval(C), Kyalami (D), Buccleuch (E), Eastbank (F) and Bruma Lake (G) in January 2011(one season) are shown in Fig. 5.

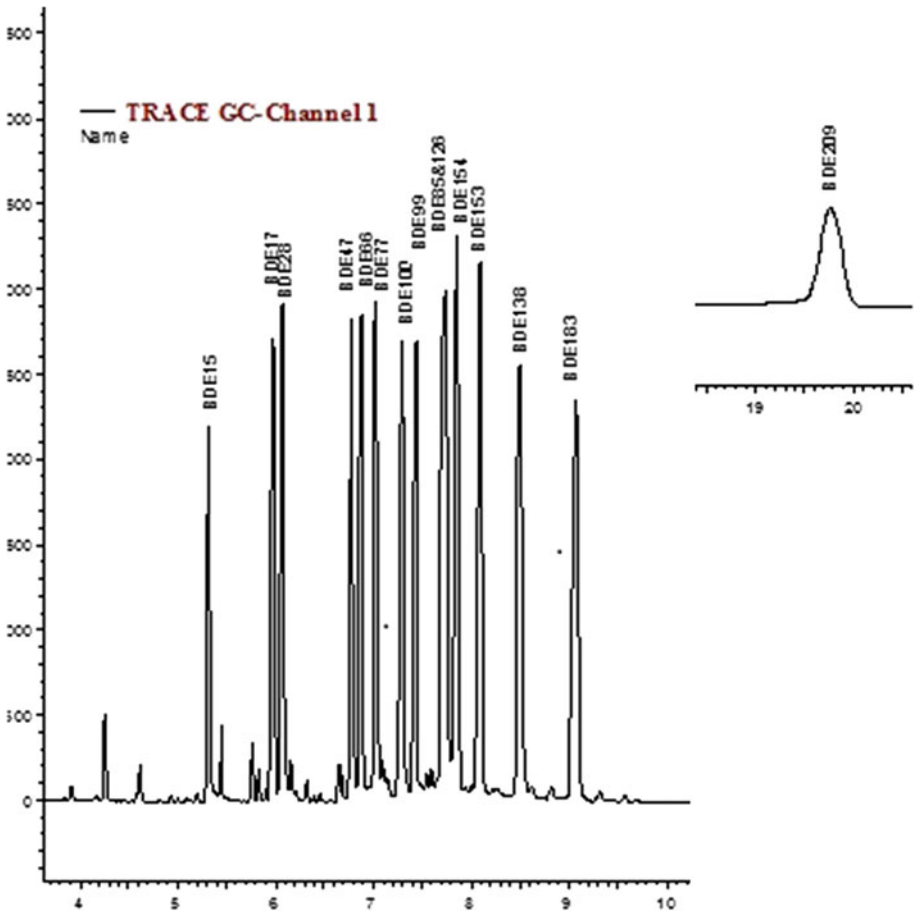

Fig. 2 GC–ECD chromatogram of 16 mixture of PBDEs (0.5 ng μL^{-1})

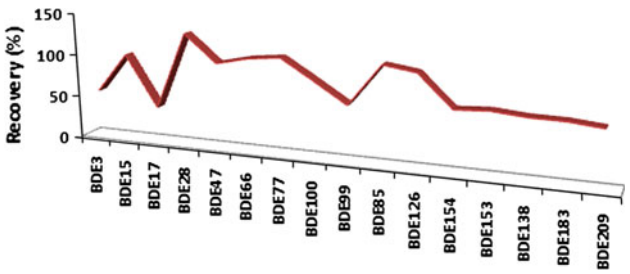

Fig. 3 Evaluation of Soxhlet method recovery efficiency of PBDEs from spiked pre-extracted river sediment

From Fig. 5, a total of 11 PBDEs (BDE17, 28, 47, 66, 77, 99, 85, 153, 138,183 and 209) congeners were detected in sediment samples from the seven sampling sites on Jukskei River. BDE209 was found in all the sediments samples from the seven sampling points suggesting its dominance among PBDEs congeners in river sediment. Similar observation has been reported (Hu et al. 2010). BDE209 contribution to total PBDEs for S1, S4 and S6 amounted to 78%, 74% and 70% respectively and lower percentage values of 30%, 45%, 20% and 42% recorded for S2, S3, S5 and S7 respectively. BDE99 was also detected at all the sites with S7 showing the highest concentration [6.76 ng g^{-1}dry weight (d.w)]. The observed value is not surprising since in terms of land use, the sampling point is surrounded by illegal dumping of waste and sewage works. BDE47 was detected at sites S2, S5, S6 and S7. BDE17, 28, 66, 153 and 183 were detected at sites S5, S6, S7 and S2 at levels below 1.0 ng g^{-1} d.w. PBDEs concentrations in river sediments have been reported in several regions and congener pattern was in the order BDE47 > 66 > 100 > 154 > 183 > 153. In the present study the pattern is as follows: BDE209 > 99 > 47 > 77 > 85 > 138 > 66 > 17 > 153 > 183.

As can be seen from Fig. 6, the $\sum_{11}$PBDEs from the seven sites ranged from 0.92 to 6.76 ng g^{-1} d.w with S7 showing the highest value. The influence of land use may have contributed to the observed values. It is well known that sampling point S7 is surrounded by various human activities such as waste dumping site and sewage treatment plants. This was followed by S6 > S1 > S2 > S4 > S5 > S3. A total sum of 23.85 ng g^{-1} d.w was obtained in the present study. In a study conducted in Spain, the $\sum_{12}$PBDE reported ranged from 2.7 to 135.94 ng g^{-1} d.w

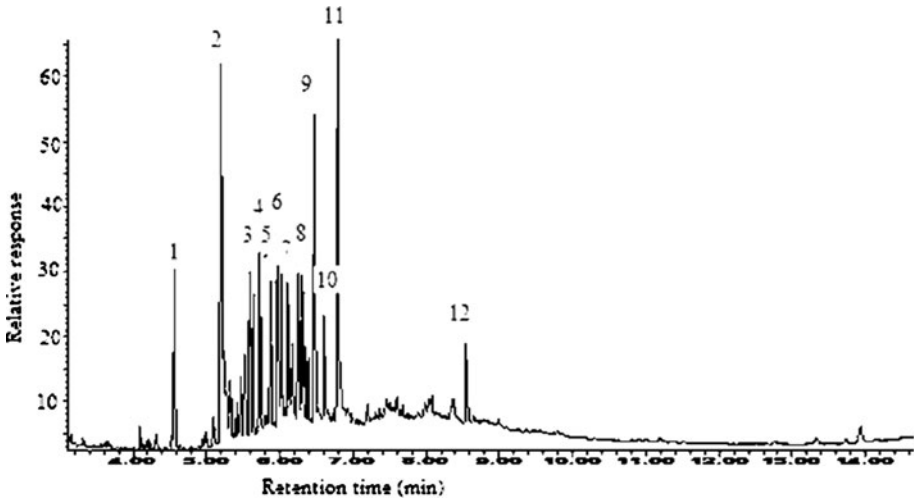

Fig. 4 GC–MS chromatogram of a sediment sample from Jukskei River (1 = BDE17, 2 = BDE28, 5 = BB49, 6 = BDE47, 7 = BDE66, 8 = BDE77, 9 = BDE99, 10 = BDE85, 11 = BDE138)

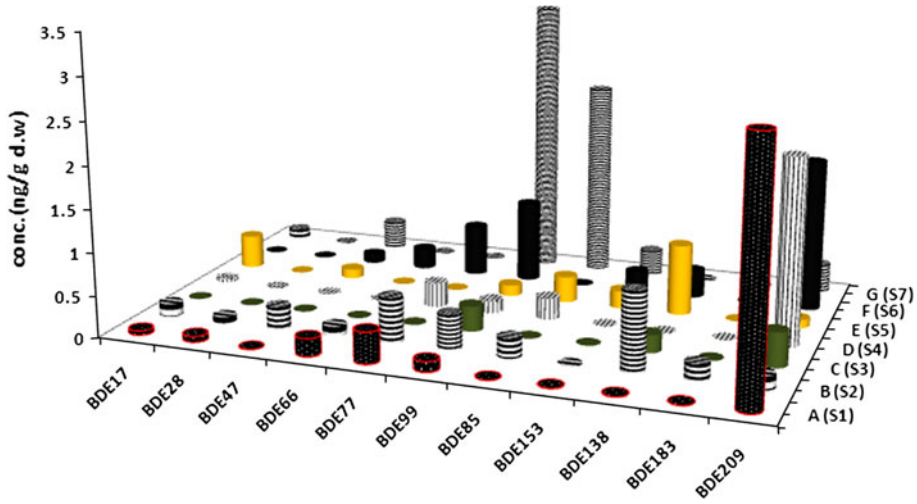

Fig. 5 Concentration levels of detected PBDEs in Jukskei sediment samples

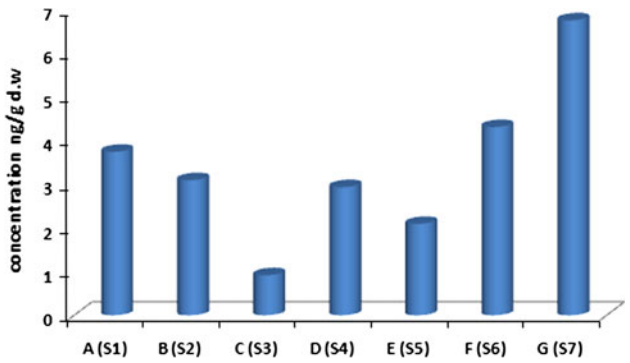

Fig. 6 The sum of PBDE congeners detected at individual sampling sites

(Eljarrat et al. 2005), in Hong Kong $\sum_{15}$PBDEs of 1.7–53.6 ng g^{-1} d.w was reported (Liu et al. 2005) and in Fuhe River and Baiyangdian Lake in China, $\sum$PBDEs of 300.7 and 23.7 ng g^{-1} d.w were reported (Hu et al. 2010). The reported sums of BDE are significantly higher than the sum obtained in the present study with the exception of the value from Baiyangdian Lake.

The present study has shown the presence and levels of PBDEs in sediment samples collected from Jukskei River in Gauteng, South Africa. Relatively, the highest concentration was detected at Bruma Lake. The observed high concentration from this sampling point may be attributed to the pollution from waste dumping and sewage inflow at this point. However, BDE209 was the predominant congener among the BFRs and this is in agreement with findings by other researchers. The low concentration of the ΣPBDEs of 23.85 ng g^{-1} d.w obtained in the present study may have been influenced by the heavy rain that was experienced a month before the samples were collected. Further studies need to be conducted in order to assess the influence of seasonal variation on BDE concentration for comprehensive characterisation of the BFR profiles within the catchment.

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