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RESEARCH ARTICLE

Alkylphenol ethoxylates and brominated flame retardants in water, fish (carp) and sediment samples from the Vaal River, South Africa

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Abstract Alkylphenol ethoxylates (APEs) and brominated flame retardants (BFRs) are known to be bio-accumulative, persistent, and endocrine disruptors and can cause adverse health effects in animals and humans. In this study, environmental samples were collected from sites along the Vaal River, South Africa in order to determine the concentrations of APEs and BFRs in water, sediment, and fish samples. The highest concentrations of these pollutants were observed from discharge of the Rietspruit WWTW. Measurable levels of both APEs and BFRs were observed with APEs exhibiting higher concentrations than BFRs in all the matrices. The concentrations observed for APEs and BFRs were as follows: 1.00–3.85 μg/L APEs, 0.09–0.26 μg/L PBDEs, ND- 0.14 PBBs and 0.51–1.77 μg/L HBCD for water samples; 47–63 ng/g lipid APEs, 3.24–12.4 ng/g lipid PBB, 4.63–33 ng/g lipid PBDEs and 10–13 ng/g lipid HBCD for fish; and 40–184 ng/g (wet weight (ww)) APEs, 2.93–5.9 ng/g (ww) PBB, 10–24 ng/g (ww) PBDEs, and 15–52 ng/g (ww) HBCD for sediment samples. The concentrations of APEs and BFRs in water samples were found to be in the range with the results reported in the literature while the concentration in fish and sediment were lower than the concentrations reported in other studies.

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Keywords Alkylphenol ethoxylates · Brominated flame retardants · Water, fish, and sediment samples · Vaal River · Waste water treatment works

Introduction

Alkylphenol ethoxylates (APEs), a class of nonionic surfactants, have been widely utilized as industrial, agricultural, and household chemicals. They are commonly used as detergents, dispersive agents in paper and leather manufacturing, emulsifiers for pesticides formulations, wetting agents, and industrial products (Datta et al. 2002). Due to their endocrine disrupting properties, nonylphenol (NP) and octylphenol (OP) were designated as priority hazardous substances in the Water Framework Directive (Directive 2000/60/EC 2000), and most of their uses are currently regulated (Directive 2003/53/EC 2003). A major route for the treatment and disposal of many chemicals such as APEs used in industrial and domestic applications is via sewage treatment works (Soares et al. 2008). Reported removals of APEs in sewage treatment works are highly variable (9–94 %) depending on the region and type of unit treatment process used. These results are of concern since they indicate that sewage treatment works are only partially efficient in removing such compounds (Farre et al. 2002; Fujita et al. 2000). Pathways to the terrestrial environment include spraying of pesticides that contain APEs as formulates, landfilling of sludges, or application of sewage or paper and pulp mill sludge to agricultural soils. Runoff from these terrestrial sources is another pathway to aquatic systems. Although the use of nonylphenolic compounds as non-ionic surfactants has been substantially reduced in some countries due to voluntary agreements, they are still found in effluents of waste treatment plants although at decreasing concentrations

(Rice et al. 2003; Jensen and Jepsen 2005; Johnson et al. 2005; Gatidou et al. 2007)

Brominated flame retardants (BFRs) are a group of chemical substances of anthropogenic origin that contain bromine. These compounds are found in a wide variety of materials including paints, plastics, textiles, furniture, and electronics and may be either covalently bonded to the polymer or additively mixed into the final product (Covaci et al. 2003). Furthermore, BFRs are routinely included in the manufacture of household goods, and an increasing consumer demand for such products has been reflected in the global BFR production patterns over the past several years (Ward et al. 2008). Despite the ban on usage of polybrominated biphenyls (PBBs) (Hites 2006) and some polybrominated diphenyl ethers (PBDEs) (penta-BDE and octa-BDE) in the European Union since August 2004 (BSEF 2006), the production of some of these compounds continues to be generally high, and it is estimated that more than 200,000 tons of BFRs including hexabromocyclododecane (HBCD) are produced globally each year (Birnbaum and Staskal 2004). Like most of the halogenated organic compounds, BFRs generally have limited biodegradability, are persistent, and tend to accumulate in the environment (Segev et al. 2009). A growing concern for BFRs has risen because of their occurrence and persistence in the environment similar to other halogenated pollutants such as polychlorinated biphenyls (PCBs) (Dirtu 2009). Thus, once the flame retardant enters into the environment, it can be attached to a particle for transport in water or delivery to the sediment or end up on an airborne dust particle and travel distances far from production and/or emission site. Hence, traces of BFRs are found in terrestrial, freshwater, and marine ecosystems at various locations far from where they are produced or used (Birnbaum and Staskal 2004; de Wit et al. 2006; Polder et al. 2008).

One of the greatest challenges confronting global water resources is water pollution caused by numerous human activities. Freshwater systems, particularly the rivers which are receptacles for most urban sewage, industrial, and agricultural discharges as well as highly contaminated wastes from informal settlements are most affected (Azevedo et al. 2001; Esperanza et al. 2004; Gatidou et al. 2007; Daso et al. 2011). Of serious concern is exposure of APEs and BFRs to aquatic organisms (Datta et al. 2002; Lacorte et al. 2010). Additionally, aquatic organisms bio-accumulate APEs and BFRs as well as their metabolites or degradation product (de Wit 2002; de Wit et al. 2006; Núñez et al. 2007; Sibali et al. 2010); thus, interest has grown in determining these pollutants in various environmental matrices (Cathum and Sabik 2001; Rice et al. 2003; desJardins Anderson and MacRae 2006; Fiedler et al. 2007; Hiebl and Vetter 2007; Núñez et al. 2007; Peng et al. 2007; Losada et al. 2009; Lacorte et al. 2010). Recently, studies have confirmed the presence of APEs and BFRs in water and sediments in South Africa (Sibali et al. 2010; Daso et al. 2011; Olukunle et al. 2012). However, reports on levels of these pollutants in any fish species from South Africa are still scarce. Also, detailed source inventories about the production, use and distribution of APEs and BFRs are not known in and around African countries including South Africa. Therefore, an important goal of the study was to report on the simultaneous quantification of seven APEs isomers (NP, nonylphenol monoethoxylate (mono-NPE), nonylphenol di-ethoxylates isomers (di-NPE1 and di-NPE2), octylphenol penta ethoxylates (OPPE), nonylphenol penta ethoxylates isomers (NPPE1 and NPPE2); six PBDEs congeners (BDE47, BDE100, BDE99, BDE154, BDE153, BDE183) together with pentabromobiphenyl (PBB101) and HBCD in water, fish, and sediment samples from sites selected on the Vaal River catchment which is one of the largest river catchments in South Africa. It is hoped that the results obtained in the present study will serve as valuable references for future risk assessment and environmental management measures in the Vaal River Catchment.

Materials and method

Sample collection, preparation, and chemicals

Sampling was conducted between September and December 2013. Fish, water, and sediment samples were collected from selected sites in Vereeniging, Gauteng as shown in Fig. 1 and Table 1. This study was conducted to determine the temporal trend and distribution of APEs and BFRs in fish, water, and sediment within the Vaal River, Gauteng region. These sampling sites were affected by waste water treatment works (WWTW), industrial effluents as well as overall increase in human population around the catchments. Site A was affected by final effluent from Leeuwkuil and Sebokeng waste water treatment works which treat mainly domestic wastewater from the surrounding townships; site B samples were affected by effluent from Meyerton WWTW as well as agricultural activities while site C samples were affected by effluent from the Rietspruit WWTW and industrial effluent from surrounding industries.

Water sampling procedure involved dipping each bottle (250-mL brown bottle) below the surface water and allowing it to fill. Altogether, a total of twelve (12) water samples were collected. Sediment samples were collected at a depth of 0-5 cm below the surface with stainless steel grab sampler into previously thoroughly cleaned wide mouth 250-mL brown bottles. A total of twelve (12), altogether, sediment samples were also collected.

Twelve (12) predatory fish altogether, Carp, were collected from the mentioned sites in the Vaal River. The selected fishes were caught using a fishing rod. Fish selected for analysis

Table 1 Description of sampling point with GIS

Point ID	Site Name	GIS
Site A	C-V17 Vaal River @ Barrage Outlet	Lat: 26° 7′ 64″ S Long: 27° 6′ 84″ E
Site B	Kookfontein 454 IQ Meyerton WWTW final effluent discharging into Fouriespruit	Lat: 26° 34′ 47″ S Long: 27° 59′ 21″ E
Site C	CRV2 - Rietspruit Weir @ Loch Vaal	Lat:26° 7′ 29″ S Long: 27° 7′ 18″ E

were killed by a blow to the head. The fish were individually wrapped in aluminum foil and placed in plastic bags packed with ice for transport to the laboratory where the samples were frozen pending preparation of the tissue samples. Fish tissue samples were prepared following the guidance in EPA (2000a). Techniques to minimize potential for sample contamination were used. During sample preparation, non-talc nitrile gloves were worn and heavy-duty aluminum foil cutting board was used. The gloves and foil were changed between samples and the cutting board cleaned between samples. The fish were thawed enough to remove the foil wrapper and rinsed with tap water, then deionized water to remove any

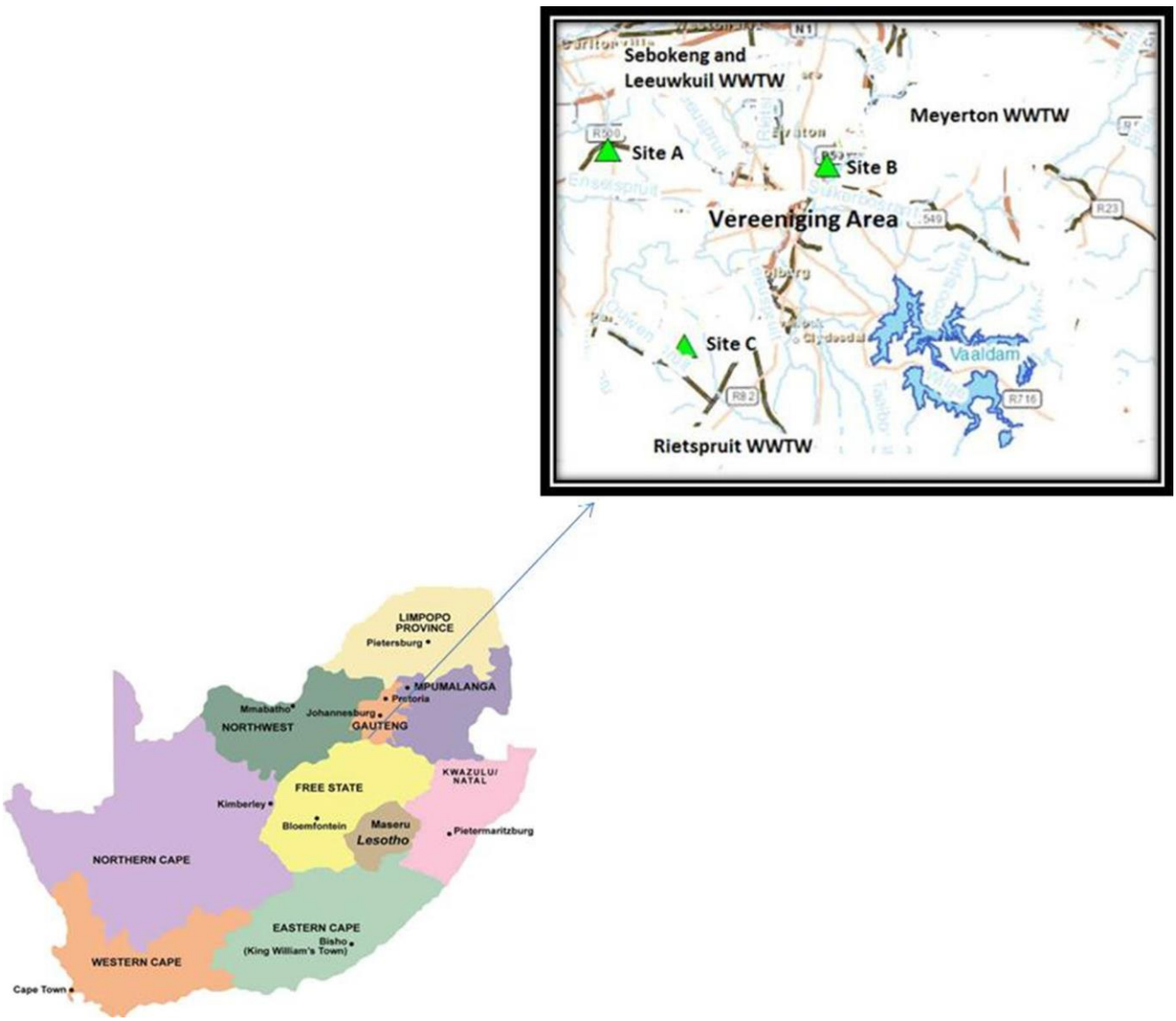

Fig. 1 Map of South Africa (bottom) showing three selected sampling points around Vereeniging area (top)

adhering debris. Before use, the skins were removed and the sample, muscle tissues, collected.

Standards and reagents

Derivatizing agents (heptafluorobutyric anhydride (HFBA) was of analytical grade purchased from Sigma-Aldrich, South Africa. The solvents acetone, methanol, dichloromethane, and hexane used in the study were of GC grade and were used without further purification. NP (purity 99.9 %) and PBB101 (purity 99.9 %) of analytical grade were purchased from Laboratories Dr Ehrenstorfer-Schäfers, Augsburg, Germany together with NPE (purity 96 %), NPPE (purity 97 %), and OPPE (purity 98 %) of technical grade. Each certified standard solutions (1.2 mL of 20 mg/L) of six PBDEs congeners (BDE47, BDE100, BDE99, BDE154, BDE153 and BDE183) were purchased from AccuStandard (USA) together with HBCD (purity 98 %) of technical grade. Anhydrous sodium sulfate (purity 99.9 %), granular powder was purchased from Merck, sodium sulfate cartridges were purchased from Chemetrix, South Africa while Helium as He 5.5 pure was purchased from Air Product South Africa, Vereeniging.

Sample treatment, recovery test, and analysis

The procedure for isolation of APEs and BFRs from water samples was achieved by solid phase extraction (SPE). Briefly, about 250 mL of sample preserved with acetic acid and methanol (MeOH) was extracted using Strata-X Polymeric Reverse Phase SPE cartridge (500 mg/6 mL from Separations, South Africa). Before use, the SPE cartridge was conditioned with 6 mL of 30 % MeOH in DCM followed by the addition of 6 mL of MeOH at a flow rate of approximately 10 mL/min and the compounds eluted with 3×2 mL of mixture of DCM-hexane (4:1). Thereafter, elutes were collected and reduced to dryness under gentle stream of nitrogen and derivatized with heptafluorobutyric anhydride as described in our previous report (Chokwe et al. 2014). Prior to analysis by GC/MS, 20 μL of internal standards (both Chrysene and PBB80) were added to each of the samples. The recovery from tripled analyzed water samples were as follows: NP (66 %), OPPE (109 %), di-NPE1 (84 %), di-NPE2 (79 %), mono-NPE (76 %), NPPE1 (83 %), NPPE2 (110 %), BDE47 (83 %), BDE100 (90 %), BDE99 (96 %), BDE154 (82 %), BDE153 (70 %), BDE183 (90 %), PBB101 (76 %), and HBCD (76 %).

The sediment extraction procedure for this study was aided by sonication coupled with SPE clean-up of the extracts. Briefly, 5 g wet sediment was mixed with 20 g anhydrous sodium sulfate and grinded with pestle and mortar until free flowing. The mixture was extracted with hexane/acetone (4:1) at 55 °C for 45 min in two cycles using ultrasonic bath (Ultrasonic Cleaner, UC-20 (20 L) 230 VAC; Anatech Instruments, South Africa). The extracts were combined, 2 g Cu added to remove elemental sulfur and evaporated to dryness using TurboVap II apparatus. Residue was re-constituted in 2.5 mL MeOH, diluted to 250 mL, and acidified with acetic acid for SPE clean-up as well as derivatized using the method described in the preparation of water samples. The percentage recovery of the analytes from tripled analyzed sediment samples were as follows: NP (66), OPPE (67), di-NPE1 (65), di-NPE2 (64), mono-NPE (62), NPPE1 (69), NPPE2 (64), BDE47 (77), BDE100 (82), BDE99 (83), BDE154 (99), BDE153 (78), BDE183 (89), PBB101 (92) and HBCD (65).

Similarly for fish, 5 g of the tissue was weighed and mixed with 20 g anhydrous sodium sulfate. The contents were extracted with 20 mL of hexane/acetone mixture (4:1) at 55 °C for 45 min in two cycles. After the ultrasonic extraction, the extracts were combined and placed in separating funnel. Roughly, 10 mL of concentrated sulfuric acid was added, the mixture shaken for 5 min and phase separated. The acid layer was washed once with 25 ml of hexane. The hexane extracts were combined and washed with 40 % (v/v) sulfuric acid for further removal of residual lipids. The phases were separated and the organic phase evaporated to dryness using TurboVap II instrument. The residue was re-constituted with 2.5 mL of MeOH, diluted to 250 mL with MilliQ water and acidified to pH 3 with acetic acid. The mixture was then passed through a pre-conditioned SPE cartridge as described above for further clean-up as well as the same derivatization prior to analysis. Tripled percentage recovery analysis from tissue samples were as follows: NP (61), OPPE (69), di-NPE1 (76), di-NPE2 (79), mono-NPE (75), NPPE1 (57), NPPE2 (50), BDE47 (91), BDE100 (63), BDE99 (65), BDE154 (73), BDE153 (60), BDE183 (67), PBB101 (89), and HBCD (64).

The heptafluorobutyric derivatives of alkylphenol ethoxylates and tetrabromobisphenol A, PBBs, PBDEs, and HBCD were determined by Agilent 6890 GC equipped with 5975 mass selective detector (MSD) fitted with Agilent autosampler A673. The GC separation was performed on a capillary column (Restek RTx-1614, film thickness 0.10 μm, 15 m×0.25 mm I.D., (Chromspec cc South Africa)). The GC/MS conditions used for analysis were as follows: carrier gas He; linear velocity, 40 cm/s; injector temperature, 280 °C; transfer line temperature, 300 °C; ion source 150 °C. The GC temperature program conditions were as follows: initial temperature 50 °C, heated to 120 °C by a temperature ramp of 7.5 °C/min then 275 °C by a temperature ramp of 15 °C/min then finally heated to 300 °C (held for 2 min) by a temperature ramp of 25 °C/min.

Quality assurance

Due to lack of certified reference materials, spiking method were used to determine the recoveries of the determinants

Table 2 Individual concentration of APEs and BFRs in water samples

Compounds	Site A	Site B	Site C
	μg/L	μg/L	μg/L
NP	0.08	0.08	0.08
OPPE	ND	0.55	1.93
di-NPE1	0.14	0.13	0.94
di-NPE2	0.34	0.23	0.35
mono-NPE	0.44	0.73	0.55
NPPE1	ND	ND	ND
NPPE2	ND	ND	ND
PBB101	0.09	0.14	ND
BDE100	0.09	ND	0.08
BDE99	ND	0.12	0.12
BDE154	ND	ND	0.06
BDE153	ND	0.13	ND
BDE183	ND	ND	ND
HBCD	0.51	1.77	0.93

ND not detected

from fish, water, and sediment matrices. For water samples, the average triplicates recoveries of the targeted analytes were above 65 % with relative standard deviation of less than 20 % for all compounds except for NPPE2 which was 35. The reason for this high RSD is not known. The average triplicates recoveries from fish sample were above 50.02 % with RSD of less than 15. For sediment samples, the average triplicates recoveries were above 60 % with relative standard deviation of less than 15. Several other quality assurance measures were also routinely observed in this study and included running blanks in between samples, analyzing samples as triplicates as well as analyzing test standard after every five samples. The quantification was accomplished using internal standard mode, relating alkylphenol and alkylphenol ethoxylates to chrysene while the BFRs were related to PBB80. The limit of detection (LOD) was defined as a signal/noise ratio of 3. For all the analytes, good linear regression of 0.997 was obtained. LOD ranged from 0.01–0.20 μg/L and 0.12–0.48 ng/g in water and solid samples, respectively. The concentrations were expressed as microgram per liter in water samples, nanogram per gram of wet weight (ww) in sediment samples and nanogram per gram lipids in fish samples.

Results and discussions

A total of seven APEs isomers; six PBDEs congeners together with pentabromobiphenyl (PBB101), and hexabromocyclododecane (HBCD) were determined and quantified in water, fish, and sediment samples in the Vaal River, Gauteng. Consequently, ∑APEs, ∑PBDEs, ∑PBB, and ∑HBCD in the discussion that follows refer to the sum concentration of all the aforementioned compounds in water, fish, and sediment samples.

Concentration of APEs and BFRs in water

The concentrations of APEs and BFRs are presented in Fig. 2 and Table 2.

The concentration of APEs from the selected sites ranged between 1.00–3.85 μg/L as shown in Fig. 2. The highest concentrations of APEs were detected from site C which receives effluent from Rietspruit WWTW and industrial effluent from the surrounding areas. Among the BFRs, HBCD was the highest detected followed by the PBDEs with PBBs being the least detected. The concentration of PBB was almost similar from all the sampling points.

Comparing the concentrations of APEs and BFRs (Table 2) obtained to those reported in the literature, our results from water samples were similar to those reported. For example, Gatidou et al (2007) reported an average mono-NPE concentration (μg/L) at 0.56 from effluent from Mytilene WWTW in Greece. Azevedo et al. (2001) reported nonylphenol at concentration ranges of 0.03 to 30 μg/L in surface water from Portugal. Hoai et al. (2003) reported an average di-NPE concentration (μg/L) of 0.560 in water from Neya River, Japan. The nonylphenol and nonylphenol ethoxylates concentration from this study was also comparable with concentration reported by Rice et al. (2003) from Cuyahoga River, Ohio. A concentration ranges 0.04 to 0.50 μg/L of NP was reported

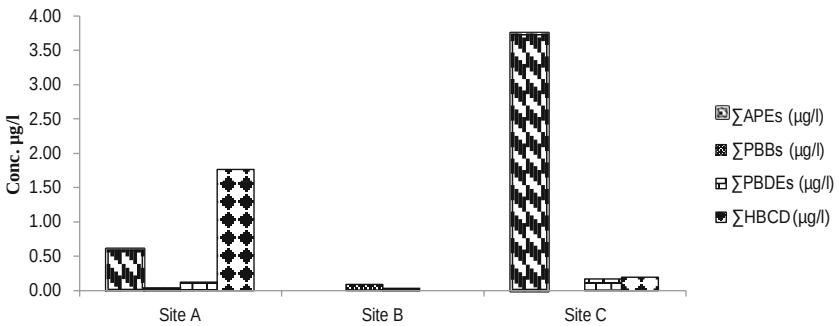

Fig. 2 Concentrations of APEs and BFRs in water samples

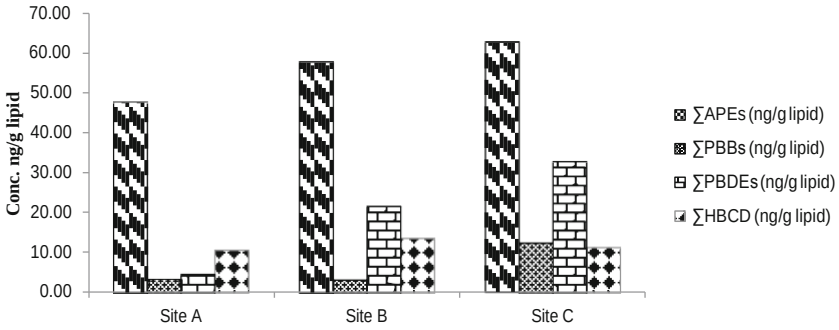

Fig. 3 Levels of APEs and BFRs in fishes around the Vaal River

in surface water from Ogun and Ibeche rivers in Nigeria (Oketola and Fagbemigun 2013). DesJardins Anderson and MacRae (2006) reported PBDEs concentration (μg/L) ranges of 0.31 to 0.90, from Penobscot River, Central Maine.

Concentration of APEs and BFRs in fish samples

All target compounds were quantified except for BDE154/153 in samples from site A and BDE183 in samples site B which were below the limit of detection. Concentration ranged from 47–63 ng/g lipid for ∑APEs, 3–12.4 ng/g lipid for ∑PBBs, 4.63–33 ng/g lipid for ∑PBDEs, and 10.6–14 ng/g lipid for ∑HBCD. The results also showed the prevalence APEs in fish compared to the BFRs (Fig. 3). Among the APEs, the lower ethoxy, i.e., di-NPE and mono-NPE were found to be the most abundant than NPPE, while within the PBDEs, congener BDE99 was more abundant. This predominance of the penta congeners is consistent with previous studies, which indicated that BDE47 and BDE99, in particular, bio-accumulate and bio- magnify up the food chain (McDonald 2002; desJardins Anderson and MacRae 2006; Peng et al. 2007; Lacorte et al. 2010). Another factor that might be important is debromination of the higher substituted congeners resulting in increasing concentration of lower substituted BDEs over time (Stapleton et al. 2004).

Findings from this study were compared to those previously reported. With the APEs, it was observed that the concentration obtained in this study were lower than concentration from other countries. For example, Schmitz-Afonso et al. (2003), Rice et al. (2003) and Datta et al. (2002) reported APEs concentrations of 4900 ng/g lipid, 32–920 ng/g lipid and 18 2075 ng/g lipid, respectively. For the BFRs, Peng et al. (2007) reported PBDEs concentration range of 25.1–152 ng/g lipids from fish in rivers from Taiwan. desJardins Anderson and MacRae (2006) reported PBDEs concentration range of 800–29000 ng/g lipid in fish from Penobscot River in Central Maine. Hiebl and Vetter (2007) reported HBCD concentration range of 40–60 ng/g lipid in fish from Germany.

Concentrations of APEs and BFRs in sediment samples

The concentrations of APEs and BFRs in sediment samples from the sampled sites in the Vaal River followed the same pattern as the fish samples (Fig. 4). NP was not detected in any of the sediment samples. The abundance of both HBCD and PBB101 were almost similar from all the sampling sites. The concentration of PBDEs ranged from 10.5–24.5 μg/g (ww) with site C having the highest concentration.

When compared to results from other studies, the results for sediments samples from this study showed that the level of alkylphenol ethoxylates concentration obtained in this study was lower than the concentration obtained by Rice et al. (2003) from the Cuyahoga River, Ohio. The concentration (ng/g) of APEs from Cuyahoga River was detected at a maximum of 1020 ng/g. Oketola and Fagbemigun (2013) reported

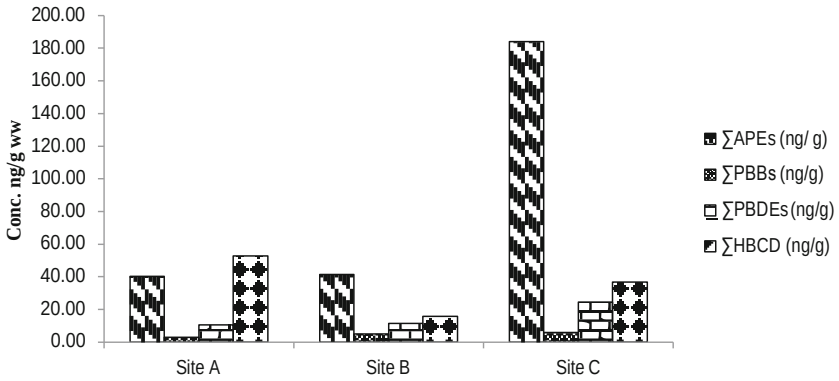

Fig. 4 Levels of APEs and BFRs in sediment samples around the Vaal River

NP concentration of up to 79.4 ng/g from major Rivers in Nigeria. The concentration of PBDEs from this study was higher than the concentration reported by Lacorte et al. (2010) and lower than the concentration reported by other researchers (Eljarrat et al. 2005; Liu et al. 2005; Hu et al. 2010).

Conclusion

All seven APEs isomers and six PBDEs congeners together with PBB101 and HBCD were detected in most of the water, fish (Carp) and sediment samples collected from the Vaal River. Relatively, the concentrations of these pollutants were higher in samples receiving effluents from Rietspruit WWTW. This may be attributed to the fact that this WWTW treat both domestic and industrial waste water from the surrounding areas. Among the APEs compounds, lower ethoxymers (i.e., mono-NPE and di-NPE) were the predominant compounds and this is in agreement with findings from other researchers. HBCD was the most abundant BFRs in both water and sediment samples. Among the PBDEs, penta-BDEs were more abundant, and this is in agreement with other studies which indicated that BDE47 and BDE99 bio-magnify up the food chain. The concentration of the pollutants in this study provides an important reference for future risk assessment and environmental measure in the Vaal River Catchment.

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Compliance with ethical standards The selected fishes from Barrage, Kliprivier, and Rietspruit were caught using fishing rod. Fish selected for analysis were killed by a blow to the head. The fish were individually wrapped in aluminum foil, placed in plastic bags packed with ice for transport to the laboratory where the samples were frozen pending preparation of the tissue samples. This procedure does not have a negative environmental impact and was approved by the Tshwane University of Technology ethics committee. There is no potential conflict of interest in this study.

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