

Occurrence and Risk Assessment of Polybrominated Diphenyl Ethers in Surface Water and Sediment of Nahoon River Estuary, South Africa

Chinemerem Ohoro (✉ greatnemerem@yahoo.co.uk)

University of Fort Hare Faculty of Science and Agriculture <https://orcid.org/0000-0002-8167-6314>

Abiodun Adeniji

National University of Lesotho

Lucy Semerjian

University of Sharjah College of Health Sciences

Anthony Okoh

University of Fort Hare Faculty of Science and Agriculture

Omobola Okoh

University of Fort Hare Faculty of Science and Agriculture

Research Article

Keywords: Polybrominated diphenyl ethers, risk, physicochemical properties, contamination source, Estuary

Posted Date: October 25th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-913715/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

The concentrations, potential sources, and compositional profile of PBDEs in the surface water and sediment of Nahoon Estuary, East London, South Africa, were investigated with solid-phase extraction and ultra-sonication, respectively, followed by gas-chromatography-electron capture detection. The seasonal range of the contaminants' concentrations in water and sediment samples in spring season were Σ PBDE 329 ± 48.3 ng/L (25.32–785 ng/L) and Σ PBDE 4.19 ± 0.35 ng/g dw (1.91–6.57 ng/g), but Σ PBDE 62.1 ± 1.50 ng/L (30.1–110 ng/L) and Σ PBDE 65.4 ± 15.9 ng/g dw (1.98–235 ng/g) in summer, respectively. NH1 (first sampling point) was the most contaminated site with PBDE in the Estuary. The potential source of pollution is attributed to the stormwater runoff from a creek emptying directly into the Estuary. This study's dominant PBDE congener is BDE- 17, ranging from below detection limit to 247 ng/L and 0.14–32.1 ng/g in water and sediment samples, respectively. Most commonly detected at all the sites were BDE- 17, 47, 66, and 100. Most BDE- 153 and 183 are found in sediment in agreement with the fact that higher brominated congeners of PBDE adsorb to solid materials. There was no correlation between the congeners and organic carbon and organic matter. However, the human health risk assessment conducted revealed that the PBDE concentration detected in the estuary pose low ecotoxicological risk. Nevertheless, constant monitoring should be ensured to see that the river remains safe for all the users, as it serves as a form of recreation to the public and a catchment to some neighbourhoods around the river.

1.0 Introduction

Polybrominated diphenyl ethers (PBDEs) are utilized broadly as brominated flame retardants (BFRs) in various materials (such as plastics, electronics and building materials). They have been listed as Persistent Organic Pollutants (POPs) in the Stockholm Convention in 2009 and 2017 (Wu et al., 2020), and are resistant to environmental degradation. Lower brominated congeners like tetra-, penta- and hexa- exhibit a high affinity for lipids and are accumulated in the bodies of animals and humans (Siddiqi and Clinic, 2003). They are ubiquitous and toxic in the environment and have constituted a pronounced hazard to human health and ecosystems (Wu et al., 2020). Evidence shows that tetra- and penta-BDEs are more toxic and bioaccumulative than octa and deca-congeners (He et al., 2006; Lee and He, 2010; Robrock et al., 2008; Siddiqi and Clinic, 2003); and consequently, PBDEs have been linked with thyroid hormone imbalance, tumors, and neurodevelopmental toxicity in children and young adults (Siddiqi et al., 2003). There has been global contamination of PBDEs due to the slow removal of PBDEs as they show environmental persistence (Siddiqi and Clinic, 2003). Human beings may be exposed to PBDEs by oral intake of contaminated dust, or food, dermal contact with soil or dust, and inhalation of contaminated air (Johnson-Restrepo and Kannan, 2009; Li et al., 2015; Trudel et al., 2011).

Contamination of the environment with PBDEs has been reported in several studies in South Africa (Chokwe et al., 2019a; Daso et al., 2013b; Odusanya et al., 2009a; Olisah et al., 2020a; Olukunle et al., 2012). South Africa is faced with water scarcity, and there is growing demands on this resource with population increase and economy expansion. The country must take urgent steps to protect the water

quality while providing the wide-ranging necessities for water (Momba et al., 2006; Ohoro et al., 2019). Materials comprising PBDEs are not given appropriate treatment (incinerated) before discarding into the landfill sites in South Africa, unlike other developed countries like Japan, resulting in high concentration in South Africa, thereby exposing humans to EDCs (Odusanya et al., 2009b). There is no documented information concerning production volume, distribution, and use of PBDEs in and around Africa, including South Africa (Odusanya et al., 2009b; Olukunle et al., 2012), nor its consumption (Daso et al., 2017). There is an assumption that products containing these chemicals are probably imported into South Africa from time to time (Odusanya et al., 2009b). Therefore, the trend observed with this chemical could be due to their consumption form or products that contain them (Daso et al., 2012). Sources of brominated fire retardants (BFRs) into the South African environment are still vague. However, they may enter the environment during the manufacturing and use of BFR-containing products, disposal, and from varying non-point sources such as atmospheric deposition, urban and agricultural runoffs (Daso et al., 2016), and the plastic industry which is the largest consumer of BFR (Chokwe et al., 2019a). The large metallurgical and chemical industries, smelting and mining companies, and a fast-growing petrochemical-based synthetic sector may also boost the use of BFRs in South Africa (Polder et al., 2008).

Hence, there are no existing national laws in South Africa to regulate the production and use of these chemicals. Consequently, the potentially harmful impact would occur if not properly managed (Daso et al., 2016).

There is scarcity of reports on PBDEs in the rivers of South Africa, as many reports were on leachates (Odusanya et al., 2009b; Olukunle et al., 2015), sediments (Chokwe et al., 2019b; Daso et al., 2016) and fish (Olisah et al., 2020a). Overflow valves release materials into the river during high rainfall periods (Bornman et al., 2018; Newman and Watling, 2007; Talbot et al., 1985). Several estuaries in the Eastern Cape Province, South Africa, such as Sundays and Swartkops, are contaminated with PBDEs, as reported (Olisah et al., 2020b, 2020a). Some other pollution activities have been documented in Nahoon Estuary (Osode, 2007). Limited irrigation takes place in the horseshoe valley from Nahoon (Edge and Framework, 2007), and nitrogen and phosphorus in the system is attributed to pollution source within Nahoon Estuary (Cotiyane et al., 2017). Nahoon Estuary is generally prone to regular flood and drought. The tidal creek at Nahoon Estuary is narrow and small compared to other creeks in South Africa (Geldenhuys et al., 2016). Many unnamed tributaries enter the Nahoon Dam; for instance, Nqgkana and Kwetyana tributaries enter the Nahoon Dam from the north, and the Rwantsa tributary joins from the west. Furthermore, many small farm dams exist as tributaries of Nahoon River (Bickerton, 1981).

Final effluents discharged at Bats Cave into the Indian Ocean, in the middle of Eastern beach and Nahoon, and by the East Bank Reclamation Works, East London, South Africa, can cause the effluents to disperse onto both shores by wave action (Cotiyane et al., 2017; Ebomah et al., 2019; Momba et al., 2006). A report also showed that the effluent was discharged in Nahoon River due to an electrical fault (Osode, 2007). This study aims to (1) evaluate the occurrence of PBDEs in the surface water and

sediments of the Nahoon River estuary and (2) to evaluate the risk associated with PBDEs to human health.

2.0 Materials And Method

2.1 Study area

The Nahoon Estuary (32°59' S, 27°57' E), widely used for weighty recreational boating (Adams et al., 2016), is located in the warm temperate biogeographic area of South Africa between the Beacon Bay and the East London environs of Nahoon in the Eastern Cape. This perpetually open Estuary is moderately short, and measures 5 km from the mouth through the Abbotsford Bridge, restraining the tidal effect. The Nahoon Estuary was classified as fair in health rank, with adequate loss of habitat and high pollution density, and was apportioned the Ecological Category C (Cotiyane et al., 2017). The map of the study site and the sampling coordinates are shown respectively in Table 1 and Fig. 1.

Table.1: Sampling sites coordinates and descriptions

Site code	Latitude	Longitude	Description
NH1	32°58'36.7"S	27°55'49.1E	Creek
NH2	32°58'34.7"S	27°55'43.8"E	Open place
NH3	32°58'32.4"S	27°55'38.6"E	Outdoor recreation
NH4	32°58'28.5"S	27°55'35.1"E	Open air for recreation
NH5	32°58'24.9"S	27°55'34.3"E	Under the bridge

2.2 Sampling and sample pretreatment

All glassware and sampling equipment were soaked over-night with acid, washed with detergent and rinsed successively with deionized water and acetone (analytical grade); glassware were thereafter heated at 105°C for 4 h before use. Five samples per season each of water samples were collected in triplicates (altogether 30 water samples), respectively in October and December 2020. No sampling was done in both autumn (March to May) and winter (June to August) seasons due to the global COVID-19 pandemic and logistic reasons during this study. Surface water samples (within 15 cm depth) from the Nahoon River Estuary were collected using a metal bucket sampler into 1 L amber glass bottles, which were twice washed with the sample water before sample collection to avoid cross contamination. After being transported to the laboratory in iceboxes, the samples were filtered through Whatman No. 1 filter paper (140 µm) within 12 h and extracted immediately. Physicochemical parameters of water were measured *on-site* using Hanna multi parameters (HI929829) for pH, temperature, total dissolved solids, electrical conductivity, salinity, Resistivity, oxidation-reduction potential, and turbidity, HACH (DR900) for total suspended solids, and HACH portable meter (HQ400) for Dissolved oxygen.

Surface sediment samples (0–40 cm depth) were collected with a Van Veen grab sampler at Nahoon River Estuary in triplicate. No sediment sample was collected at point NH5 in the spring season (September to November) because of the sampling point's inaccessibility on that day. The collected samples were separately enfolded in pre cleaned aluminum foil, conveyed to the laboratory in a cooler box containing ice packs at 4 °C. Pieces of debris and large stones were removed in the laboratory; sediment samples were air-dried in a dark room, blended and homogenized thoroughly with mortar and pestle, and sieved independently with 250 µm mesh sieves and extracted afterwards (an aliquot of the wet sample was reserved for moisture content and an aliquot each was also used for the measurement of organic carbon and organic matter). Organic matter (OM) and organic carbon (OC) of the sediment was determined using loss on ignition method (Sikora and Moore-Kucera, 2014; Wang et al., 2011).

2.3 Extraction and purification

Water extraction

Extraction was modified and carried out according to the work previously reported (Kowalski and Mazur, 2014). Strata™ C18 – E (55 µm, 70A, 500mg, 6 mL) solid phase extraction cartridge from Phenomenex (Torrance, CA, USA) were conditioned with ethyl acetate (6 mL) and distilled water (6 mL) at 1 mL min⁻¹ flow rate. Thereafter, 500 mL of the filtered water sample was spiked with surrogate standard (PCB 209, procured from Wellington Laboratories, Ontario, Canada) and extracted through the conditioned cartridge at a flow rate of 10 mL min⁻¹, after which the column was dried for 3 hrs, and then the analyte was eluted with 2 × 2.5 mL of ethyl acetate. The extract was evaporated to dryness under a gentle stream of nitrogen and reconstituted with acetonitrile (1 mL) before gas chromatography – micro electron capture detection (GC-µECD) analysis.

Sediment extraction: Sediment extraction was done based on a modified ultrasonically assisted extraction method reported in literature (Olukunle et al., 2015), and analytes were measured with gas chromatography-electron capture detector (GC-µECD). Approximately 10 g of sample was weighed into a clean amber bottle for ultrasonication (100 mL). Afterward, each of the samples was spiked with surrogate standard (PCB-209) and allowed to soak and equilibrate for 1 h. The samples were allowed to soak overnight afterwards with 20 mL acetone: n- hexane (1:2, v/v) in an airtight amber bottle (100 mL), followed by extraction at 45°C for 30 min in an ultrasonicator (LASEC South Africa Pty Ltd, single frequency 40Hz, 6 L). After sonication, the sediment sample with extract was left to cool and settle for 60 min at 0 °C before the extract was drawn out of the vial using a Pasteur pipette into another bottle. The extracts were centrifuged at 5000 rpm for 5 min. Extraction was done recurrently for two extra times on every single sample with fresh solvents, and the extracts (about 60 mL) were collected. The crude extracts volume containing PBDEs was reduced by rotary evaporator to 1 mL with a Büchi Rotavapor R-210 (vapor: 40°C, bath temperature: 40°C, and cooling water temperature: 20°C). The glass chromatographic column (10 mm x 30 cm) used for cleanup was packed with glass wool, silica gel (1 g; 100–200 mesh), copper powder (2 g; < 63 µm) in layers from the bottom with and topped up with 0.5 g Na₂SO₄ (anhydrous), separating each layer with glass wool to enhance cleaning. The packed column

was pre-saturated with DCM (8 mL), and then n-hexane (8 mL). Approximately 1 mL of the sample extract was put into the column and allowed to run. The adsorbed analyte was then eluted with n-hexane (6 mL) at 5 mL min⁻¹ flow rate, and transferred carefully into pre-cleaned amber glass tubes. Nitrogen gas (N₂) was fizzed through the eluate and then concentrated to dryness. Sample was then reconstituted to 1 mL with n-hexane before injection onto the GC- μ ECD under optimized instrumental conditions.

2.4 Instrumental analysis

PBDEs were analyzed with a 7820A GC coupled to a G239AE μ ECD (Agilent Technologies, Santo Clara, CA, USA). An HP-5 (Agilent Technologies, Santo Clara, CA, USA - 19091J-413:1) capillary column (30 m x 320 μ m x 0.25 μ m i.d. film thickness) was used for congeners separations. The oven temperature program follows thus: 100°C with 1 min holding time, raised to 190°C with no holding, a second ramp to 255°C at 5°C/min with 0.5 min holding time, and a final ramp to 310°C at 2°C/min with 10 min holding time, giving a run time of 61.25 min. The injection and detection temperatures were set to 230°C and 325°C, respectively, with carrier gas pressure of 108.43 kPa with an average velocity of 48.868 cms⁻¹. The carrier gas used was helium at a flow rate of 1.0 mL/min. All samples were injected in splitless mode with a volume of 1 μ L. The external calibration method was used for quantification, and a standard mixture with seven levels of concentration formed the calibration curves at 5-120 μ g/L for all congeners of PBDEs (BDE-17, 47, 66, 100, 153, 183) diluted with isooctane.

2.5 Quality assurance and quality control (QA/QC)

Silica gel, copper powder and anhydrous Na₂SO₄ were heated at 350°C before use to eliminate impurities. Silica gel and Na₂SO₄ were kept in a glass jar pre-cleaned, rinsed with a solvent (acetone/*n*-hexane), and sealed to prevent contamination and absorption of moisture. All organic solvents used in the course of the experimental and instrumental methods were of HPLC grade or equivalent. Procedural and solvent blanks were analyzed for every set of 5 samples to check for interferences and cross-contamination. Surrogate standard PCB-209 (200 μ l of 18 μ g/L) was spiked into each sample (double distilled water and pure sand purchased from Sigma-Aldrich), and analyzed in triplicate for quality control and assurance (quantification achieved using Agilent Chemstation software) and the mean concentrations were reported. The GC syringe was automated to wash twice, each with n-hexane and acetone, before and after sample injection to prevent cross-contamination. The recoveries (Table S1) for the analytes for water and sediment were within the standard range of recovery (APHA, 2005), except for BDE 66 that was > 140% in the water, which indicated this method could simultaneously quantify most PBDEs in water. Hence, BDE-66 was not quantified in the water samples because it did not give a satisfactory recovery for water. LOD and LOQ (Table S1) were calculated using 3.3 (Sy/S) and 10 (Sy/S), respectively (Ibrahim et al., 2018; Olisah et al., 2019). The instrument's precision, estimated as the relative standard deviation (RSD) was estimated from 8 replicate injections of a middle level calibration standard (30 μ g/L) in accordance with standard methods, (Caruso and Santoro, 2014).

2.6 Statistical/data analysis

The following statistics: regression analysis, descriptive analysis, distribution percentage, composition pattern of PBDEs in surface water were calculated with Microsoft Excel 2016. Pearson correlation coefficients between individual compounds and the physicochemical parameters and dendrograms were analyzed using SPSS software package. The percentage distribution of PBDEs was calculated across all seasons. Samples below LOD were treated as zero all through the statistical analysis. Concentrations were shown as ng/g dry weight (dw) for sediment samples, and ng/L for water samples.

2.7 Risk assessment

Risk assessment was conducted for water and sediment samples using a model as shown in the equations (1) and (2) (Olisah et al., 2020a; Yin et al., 2019).

1.2.8.1 Estimated daily intake (EDI)

$$EDI = C \times IV / BW \quad (1)$$

Where EDI is the estimated daily intake for target PBDEs (ng/kg/day), C is the mean seasonal concentration of PBDE in water (ng/L), BW is the body weight of 60 kg (World Health Organization, 2010), and IV is the ingestion volume of 2 L (Yahaya et al., 2017).

1.2.8.2 Non-carcinogenic risk

Non-carcinogenic risks for water samples were calculated using Eq. (2) below:

$$HQ = EDI / RFD \quad (2)$$

Where HQ is the hazard quotients, and RfD values (100 ng/kg bw/day for BDE-47, and 200 ng/kg bw/day for BDE-100 and 153) are the USEPA values as reported by USEPA 2019 (Jiang et al., 2005; Wang et al., 2019).

Eco-toxicological risks posed by PBDE in sediment samples were evaluated by employing the assessment as given in Eq. (3) (Canada Environment Protection, 2006; Ge et al., 2018; Yin et al., 2020).

$$HQ = C / PNEC \quad (3)$$

Where C is the concentration of PBDEs in sediment, PNEC is the predicted no-effect concentration below which no adverse effect is envisaged. The concentrations of 31, and 9100 ng/g dw were used for penta and octa-BDE, respectively (Chen et al., 2010; M. H. Wu et al., 2017). Tri-penta-BDE (17, 47, 66, 100) and hexa-octa-BDE (153, 183) were assumed to be penta and octa-BDEs, respectively, as classified by USEPA (Wu et al., 2013).

FEQG values and the homologues grouped into tetraBDE (BDE-47), pentaBDE (BDE-100), and hexaBDE (BDE-153) were extracted from Federal Environment Quality Guideline (FEQG) for PBDEs (Environment Canada, 2013).

HQ < 0.1 specifies no ecotoxicological, HQ between 0.1-1 shows a low ecotoxicological risk, HQ between 1–10 indicates a moderate ecotoxicological risks, and HQ > 10 indicates high ecotoxicological risk (Ge et al., 2018; Yin et al., 2020)

3.0 Result And Discussion

3.1 Spatial distribution, seasonal variation, and potential sources of pollution

The concentrations range for Σ_5 PBDEs were 25.3–785 ng/L (Σ_5 PBDEs 329 ± 48.3 ng/L) in spring water samples and 30.1–110 ng/L (Σ_5 PBDEs 62.1 ± 1.50 ng /L) in summer water samples across the sites (Table 2). The PBDEs concentrations across the points of collection from the two matrices were significantly different ($p < 0.05$). This can be attributed to non-uniformity of the activities at the sampling sites. Points NH1 and NH2 are closer to the creek, which is a point of discharge to the Estuary, NH3 is characterized by its leisure activities, and road activities at point NH5 under the bridge. This variation probably contributed to differences in the concentrations of PBDE. The PBDEs concentrations in the spring water samples were higher than the summer samples. This could be attributed to atmospheric wet deposition and also the heavy runoff of foul-smelling stormwater on the sampling day (Luo et al., 2014; Zhan et al., 2019). With spring being a raining (wet) season in South Africa and windy, both wet and dry depositions are possible, especially in the coastal environment. Higher rainfall always support more of wet deposition than dry ones (Castro-Jiménez et al., 2011; Cetin et al., 2016; Mai et al., 2005). The highest contamination was observed in the spring water sample at NH1 with BDE- 17, 47, and 100 detected at 247, 190, and 178 ng/L, respectively (Table S4); suggesting ubiquitous usage of the commercial penta-BDE at the area (La Guardia et al., 2006). This dominance was also reported elsewhere with BDE-17, 47 and 100 at concentrations 2.0, 5.8, and 0.4 ng/L (Olisah et al., 2020a). This heavy pollution is attributed to a heavy fresh discharge observed at the creek (NH1) on sampling day. The water sample concentration of BDE- 17 was below the detection limit in NH4 in spring, NH3, NH4, and NH5 in summer season but relatively higher in NH5 in spring (137 ng /L) (Table S4). This variance could be as a result absence of microbial degradation as BDE-17 is a one of the major products of microbial degradation of high molecular weight PBDEs in the environment (Trinh et al., 2019). Point NH5 is a rocky steep under the bridge and occupied by some homeless individuals and characterized by vehicular emission and careless garbage dump by the road users (Anh et al., 2018; Ohoro et al., 2021). The anthropogenic waste could be why there was a higher concentration at this spot (Zhou et al., 2021) than at NH3 and NH4, which are closer to the potential most polluted area of this sampling site.

The Σ_6 PBDEs in spring sediment samples was 1.91–6.57 ng/g (Σ_6 PBDEs 4.19 ± 0.35 ng/g dw), and 1.98–235 ng/g (Σ_6 PBDEs 65.4 ± 15.9 ng/g dw) in summer sediment samples (Table 2). The sediment concentration of PBDEs was relatively higher in summer than in spring, higher temperature in spring notwithstanding; contrary to previous studies, which reported no detection of PBDE concentrations of sediments (Nouira et al., 2013), and higher concentration in summer season than spring (Hansson et al.,

2006; Khairy and Lohmann, 2017). Similar report was documented on high summer concentration (Hansson et al., 2006). This could be attributed to atmospheric wet deposition (Tlili et al., 2012) and high turbidity observed in summer, preventing photodegradation (Fang et al., 2008; Pan et al., 2016). Estuarine sediment acts as a vital sink of PBDEs originated by several anthropogenic activities (Díaz-Jaramillo et al., 2016), though lesser concentrations in sediments compared to water was observed. Lower concentration of sediment than water is likely as a result of dilution of overlying water as also reported elsewhere (Chen et al., 2009). BDE- 17 and 66 showed the relatively highest concentrations in all sampling points, suggesting PBDE contaminants from an industry (Deng et al., 2007; Wu et al., 2015), except in NH1 which receives discharges from runoff. Nahoon Estuary is in East London, which is economically developed, densely populated, and characterized by its seaport. Consequently, Nahoon Eastuary could be receiving discharges from industrial waste which might have high PBDE concentration. Pollution of Nahoon Estuary with PBDE could also be attributed to improper plastic waste disposal from tourists, as plastics are major contributor of PBDE to the environment. No sediment sample was collected at NH5 in spring because of the lack of accessibility of the sampling point on the day of sampling. The point with the highest sediment concentration is NH3. This is where recreational activities and swimming take place. The high concentration of PBDEs could be attributed to anthropogenic pollution as this place is sometimes littered with wastes from leisure activities. There is possibility of NH3 receiving other forms of waste other than from recreational activities and runoff from the creek.

3.2 The contamination level of PBDEs in this current study compared with other countries

The concentration of PBDEs in the water and sediment samples is summarized in (Table S4, supporting information). The concentration ranges from BDL-247 ng/L in the spring season and BDL-70.2 ng/L in summer for water. PBDEs in sediment ranges from 0.16–3.42 ng/g dw in spring and 0.25–112 ng/g dw in summer. It is worthy of note that this high concentration which seems unusual for a River was observed at the point of discharge of runoff freshly discharged from a creek on sampling day. PBDES in the Estuary could probably come from flame retardants that contains plastic products and polyurethane foams (Oros et al., 2005). Comparing the concentration of water samples in this finding with previous studies in South Africa, the concentrations from this study were higher than reports from Jukskei River, Cape town (below detection limit) (Olukunle et al., 2012), Sundays River Estuary (2.5–39.1 ng/L) and Swartkops River (2.5–169 ng/L) in Port Elizabeth (Olisah et al., 2020a). The high concentration from Swartkops was not out of place as runoffs from Motherwell and Markman canal were noticeably discharging into Swartkops river Estuary (Olisah et al., 2020a). Higher concentrations from South Africa was also reported from Diep River (320–485 ng/L) in Cape town, which also received effluent discharges from wastewater treatment plant (Daso et al., 2013a). Although, BDE-209 was investigated in Diep River but were below detection limit in most cases (Daso et al., 2013a). Furthermore, the values from this study were higher than 18 ng/L (mean) in the Netherlands (De Boer et al., 2003), and 7.87 ng/L in South China (Yang et al., 2015). It was observed that the sediment concentrations in this study were lower than bdl-212 ng/g in the U.S.A, which possibly could be from leaching and emission from a nearby refuse dump (Oros et al., 2005), but higher than 0.5-3 ng/g in the U.S.A (Song et al., 2004). BDE-47 and 100 which are

the most bioaccumulative congeners from the commercial pentaBDE mixture among others (Oros et al., 2005), were the dominant congeners in all the above mentioned sites. Compared to Federal Environmental Quality Guideline (FEQG), water and sediment values were below the standards except the pentaBDE which has higher values than the FEQG standards both in spring and summer seasons for water (4.25–178 and 7.36–11.5 ng/L) and sediment samples (0.21–0.41 and 0.26–25.7 ng/g dw) respectively.

Table 2
Mean concentrations of PBDEs in surface water and sediments of Nahoon River estuary in ng/L and ng/g dw, respectively

		Spring				Summer			
Surface water									
Congener	Mean (n = 5)	Max	Min	DF (100%)	Mean (n = 5)	Max	Min	DF (100%)	
BDE 17	140 ± 91.2	247	BDL	80	23.5 ± 31.5	70.2	BDL	40	
BDE 47	68.9 ± 76.7	190	4.27	100	7.92 ± 2.80	12.4	5.43	100	
BDE 100	44.0 ± 64.4	178	4.25	100	8.95 ± 2.96	11.5	7.36	100	
BDE 153	5.88 ± 75.7	6.39	4.97	100	6.59 ± 1.77	8.00	5.82	100	
BDE 183	5.79 ± 0.98	5.56	5.41	100	7.02 ± 1.01	8.80	5.13	100	
∑PBDE	329 ± 48.3				62.1 ± 1.50				
Sediment									
BDE 17	1.42 ± 1.14	2.77	0.44	100	17.4 ± 12.2	32.0	0.14	100	
BDE 47	0.27 ± 0.03	0.29	0.24	100	3.14 ± 3.25	8.75	0.28	100	
BDE 66	1.47 ± 1.36	3.42	0.27	100	8.88 ± 17.8	31.4	0.29	100	
BDE 100	0.20 ± 0.08	0.41	0.21	100	7.25 ± 10.4	25.69	0.26	100	
BDE 153	0.19 ± 0.08	0.27	0.08	100	6.00 ± 10.7	25.1	0.63	100	
BDE 183	0.56 ± 0.07	0.64	0.47	100	22.7 ± 49.9	112	0.25	100	
∑PBDE	4.19 ± 0.35				65.4 ± 15.9				
BDL: below detection limit; D- frequency of detection; N = number of samples									

3.3 Impact of physicochemical parameters on concentrations of PBDEs in Nahoon Estuary

The temperature range across the five sampling points in the spring and summer season was 20.7–21.3 °C and 24.5–26.6 °C, respectively. There was no significant difference for the physicochemical properties of samples collected (Table 3) from the different sampling points ($p > 0.05$). Higher concentrations were observed in water in the spring season than in summer. High temperatures and strong sunshine in summer help the transfer of PBDEs via wet/dry deposition, and consequently, promoting the degradation of higher brominated diphenyl ethers to lower brominated diphenyl ethers (Shao et al., 2018). Although, there is paucity of experimental data accessible on properties and temperature dependence of PBDEs. PBDEs are endothermal, so the solubility increased with increased temperature (Kuramochi et al., 2007). Although, sediment also recorded higher levels of pollutants in summer, this could be due to other factors like higher turbidity observed in summer season. The pH affects the chemical processes of the water body and can help measure the degree of the effluent trail in the water body (Chapman, 1996). However, PBDEs' chemical features are not affected by pH (Fontana et al., 2009). The pH range across the five sampling points in the spring and summer season was 8.27–8.65 and 8.3–8.94, respectively. The range of pH for both are same, implying that the influence pH on the concentrations of PBDE detected in this site is negligible. The salinity values were 28.8–34.4 PSU and 33.5–33.8 PSU for spring and summer seasons, respectively. Salinity showed no effect on the sorption of BDE-47 on plastics as reported (Xu et al., 2019), but can influence PBDEs' distribution (Anim et al., 2017). Increase in salinity decreases solubility of many chemicals, and causes adsorption of organic contaminant to the suspended particles and then deposited on to the sediment (Y. Wu et al., 2017). It was observed that increase in salinity decreased the concentration of PBDE in surface water of the study site and vice versa. Conductivity is the extent of water's capability to conduct an electric current. Rough estimate of conductivity specifies the water's mineral content and could be significantly higher in polluted water or any that receives a large quantity of urban runoff (Chapman, 1996). It is an indicator for salinity of water (Rusydi, 2018). The electrical conductivity was about 44.4–46.5 mS/cm and 51.0–55.5 mS/cm for both spring and summer. Higher conductivity brings about warmer water (Olisah et al., 2019), and consequently lower concentration due to degradation. From this study, the concentration of PBDEs in water was higher in spring than in summer because spring season had lower conductivity value than summer. The oxidation-reduction property (ORP) of water is a characteristic of state of natural water. Increase in DO increases ORP (Chapman, 1996). Value of ORP for this present study ranges from 23.3–70.8 MvORP and 22.7–55.1 MvORP in summer and spring correspondingly. Increase in temperature and salinity brings about decrease in DO (Chapman, 1996). The DO of this study ranges from 5–5.59 mg/L and 5.88–8.55 mg/L in summer and spring in that order. Areas of high concentration level causes decrease in dissolved DO (Liu et al., 2015). Higher concentration of PBDEs in water samples with lower DO and vice versa was observed for spring and summer seasons, respectively. Turbidity slows the degradation of PBDEs such as BDE-209 (Viganò et al., 2011). In this study, it ranged from 3.97–73 and 10.6–26.4 NTU in summer and spring, respectively. Higher molecular congeners of POPs are known to adsorb to particulate matters and subsequently settle down in the sediment (Moon et al., 2012; Wang et al., 2016; Zhou et al., 2019), and turbidity could have prevented debromination of PBDEs by obstructing the penetration of light (Rügner et al., 2013; Viganò et al., 2011) Moreover, natural organic matter is known to inhibit degradation of dibromophenyl ether (Zhu et al., 2018). Organic matter speeds up the gas/particle partitioning. The

organic matter in this study ranged from 0.30–0.60% and 0.21–0.27% in summer and spring. This could also explain the reason for higher concentration in spring, as organic matter was lower. High concentration of suspended solids suggests potential elevation of hydrophobic endocrine disruptors concentration, which is as a result of compounds having high log K_{ow} values linked with the non-settleable solids (Langford et al., 2007). However, lower concentration was observed in summer in this study, probably because of high temperature. The range of TSS was 4.0–15.0 mg/L. TSS is inversely related to particulate organic carbon content (Chapman, 1996). Resistivity assesses the lateral spread of salinity (Chapman, 1996), and was measured to be 21.0–22.7 and 19.0–20.0 ohm-cm for spring and summer seasons, respectively. The summary of the physicochemical properties of the water collected from the study area is presented in Table 3.

Table 3
Physicochemical properties of surface water and sediment samples

Parameters	Spring		Summer	
	Mean ± STD	Range	Mean ± STD	Range
Temp.[°C]	21.0 ± 0.28	20.7–21.3	25.9 ± 0.79	24.5–26.6
pH	8.48 ± 0.17	8.27–8.66	8.65 ± 0.22	8.33–8.94
EC [mS/cm]	45.7 ± 1.02	44.4–46.5	51.5 ± 61.0	51.0–51.5
TDS [g/L]	22.9 ± 0.51	22.2–23.3	25.6 ± 80.1	25.5–25.7
Sal.[psu]	29.7 ± 0.74	28.8–34.4	33.6 ± 0.12	33.5–33.8
Turb.FNU	17.8 ± 5.97	10.6–26.4	31.4 ± 28.8	3.97–73.0
mVorp	32.2 ± 13.1	22.7–55.1	55.4 ± 19.3	23.2–70.8
RES(Ohm-cm)	21.9 ± 0.60	21.0–22.7	19.6 ± 0.43	19.0–20.0
DO (mg/L)	6.84 ± 1.11	5.88–8.55	5.31 ± 0.26	5.00–5.59
TSS (mg/L)	8.33 ± 3.25	4.00–12.7	9.13 ± 4.21	4.00–15.0
% MC	63.3 ± 1.05	62.5–64.8	30.0 ± 3.69	25.0–35.0
% OC	0.25 ± 0.02	0.21–0.27	0.29 ± 0.07	0.17–0.35
%OM	0.42 ± 0.04	0.37–0.47	0.50 ± 0.12	0.30–0.60
Temp- temperature; TDS- total dissolved solid; EC- electrical conductivity; Sal- salinity; mVorp- oxidation-reduction potential; Turb- turbidity; DO- dissolved oxygen; TSS, total suspended solid; MC- moisture content; OC- organic content; OM- organic matter				

3.4 Correlation of PBDEs in water and sediment with physicochemical properties

The Pearson correlation analysis between PBDEs concentration in water and sediment with the physicochemical parameters was performed (Tables S2 and S3). Correlation values for BDE-17 versus 47 ($r = 0.91$, $p < 0.01$), BDE- 100 ($r = 0.79$, $p < 0.01$), BDE- 183 ($r = 0.78$, $p < 0.01$), were observed in water samples. All the congeners correlated strongly among themselves except for BDE-153, which showed no correlation with BDE- 17, 47, and 183. The positive correlation effect suggested that the congeners all came from the same source, except BDE- 17. The temperature and pH did not show any correlation with the congeners. Correlation values for EC versus BDE-17 ($r = -0.87$, $p < 0.01$), BDE- 47 (-0.77 , $p < 0.01$), BDE- 100 (-0.77 , $p < 0.01$), and BDE-183 (-0.86 , $p < 0.01$) were observed. This implies that the congeners decrease with an increase in EC. There was no correlation between EC, TSS, and DO with BDE- 153. The correlation of EC with all the physicochemical parameters was observed, only pH correlated with EC and resistivity. Negative correlation was observed between salinity and all congeners except BDE-153 with a very poor correlation ($r = 0.128$), suggesting “salting out” effect (Y. Wu et al., 2017). In sediment samples, BDE- 47, 100, 153, and 183 showed a very strong correlation with all except BDE- 17. There was no correlation between the congeners with the OM and OC, all the congeners and physicochemical parameters correlated with moisture content. The observed positive correlation may propose a potential impact of physicochemical parameters on the PBDEs concentrations.

3.5 Contamination pattern and source apportionment of pollution in Nahoon Estuary using a dendrogram

Dendrogram demonstrating the ranked cluster analysis (Hellar-Kihampa et al., 2013) of PBDEs of water and sediment samples from 5 sampling points at the Nahoon River Estuary is illustrated (Fig. 3). Locations in the same clusters show similar contamination. The study site of PBDEs concentrations was classified with hierarchical cluster analysis by employing the rescaled distance cluster combined with the average linkage method as reported elsewhere (Olisah et al., 2021). The mean water samples (NHW1, NHW2, NHW3, NHW4, NHW5) and sediment samples (NHS1, NHS2, NHS3, NHS4, NHS5) across the sites were represented. The cluster analysis showed that the area of study is clustered into four major groups based on their mean concentrations in both water and sediment. The first group is NHS3. This is the site with the highest concentration of PBDEs. BDE-183 has the highest concentration of all the congeners in this site. This is possibly an indication of the presence of commercial octa-BDE from local anthropogenic source (La Guardia et al., 2006). The second cluster comprises NHS5 with the second-highest concentration of PBDEs, having BDE-17 as the highest concentration from this point. The third cluster consists of NHS2, NHS1, and NHS4. These are the sites with the third-highest concentrations of PBDEs. The fourth cluster consists of NHW1, NHW4, NHW2, NHW5, and NHW3, which are class of cluster with low concentrations.

3.6 Compositional patterns of PBDEs in the surface water and sediments

The summary of the percentage distribution of the Σ_6 PBDE is given in Fig. 2. In water samples, the dominant congener is BDE- 17 (43%), which came majorly from NH1 > NH2 > NH3 > NH4, followed by BDE-

47 (27%), and BDE- 100 (26%) correspondingly, all suggesting that NH1 and NH2 are the most polluted points which are the closest point to the creek where the runoff from unknown source is being discharged to the Estuary. The dominant congener in the sediment is BDE- 183 (33%), majorly at point NH3, followed by BDE- 17 (27%), emanating from NH5 and NH3, BDE- 66 (15%), coming from NH3 and NH1, and BDE- 100 (11%), coming from NH3, NH5, NH1. All the congeners are detected at NH4 in low concentration. The highest concentrations of the congeners in sediments were from point NH3, with BDE-183 having the highest concentration (112 ng/g). BDE-183 is an indicator of octa-BDE; therefore, the relatively high concentration is an indication of possible extra contribution from octa-BDE products as similarly reported (Chen et al., 2009). Furthermore, lower brominated congeners could be because of debromination or higher congeners or extensive use of products of penta-BDE mixtures as stated earlier.

3.7 Ecotoxicological risk assessment

The result from the ecotoxicological risk is given (Table 4), which indicates that HQ for water samples shows no risk in the concentrations of PBDEs, while pentaBDE in sediment samples suggests possible low non- cancer risk (0.2) To further evaluate the probable eco-toxicological risk of PBDEs in water and sediment samples in Nahoon River Estuary, the Federal Environment Quality Guidelines (FEQG) standards for PBDEs of Canada (Environment Canada, 2013) was adopted as was also reported elsewhere (Ge et al., 2014). The mean concentrations from the two seasons each (Table 5) were compared with BDE-17, 66, and 183 were not included in the homologues in the evaluation of the ecotoxicological risk as they were not given in this guideline. It was observed that hexaBDEs and tetraBDE in both water and sediments pose no risk. However, pentaBDE in both water and sediment samples for the two seasons were above the standard values for FEQG. Although, the concentrations of pentaBDE from this study is higher than the standard values for FEQG; it does not pose threat to water, though low potential non-cancer risk for sediment is envisaged. Therefore, this calls for special concern so as to ensure safety of aquatic lives, tourists, and athletes

Table 4
Hazard quotient (HQ) for ecotoxicological risk

Water			
Congener	Mean (ng/L)	EDI (ng/L)	HQ
BDE 47	38.4	1.28	0.0
BDE 66	36.6	1.22	0.0
BDE 100	26.5	0.88	0.0
BDE 153	6.23	0.21	0.0
Sediment			
Homologue	Mean (ng/g dw)	PNEC (ng/g)*	HQ
PentaBDE	5.48	31	0.2
OctaBDE	14.7	9100	0.0
*PNEC values for water (ng/L) and sediment (ng/g) extracted from literature (Canada Environment Protection, 2006); EDI = Estimated daily intake; HQ = Hazard quotient			

Table 5
Comparison of the PBDEs concentration of the present study with FEQG for both water (ng/L) and sediment (ng/g dw)

		This study		
Homologue	Congener	FEQG**	Spring	Summer
Water				
TetraBDE	BDE-47	24	4.27–190	5.43–12.4
PentaBDE	BDE-100	0.2	4.25–178	7.36–11.5
HexaBDE	BDE-153	120	4.97–6.39	5.82–8.00
HeptaBDE	BDE-183	17	5.41–3.56	5.13–8.80
Sediment				
TetraBDE	BDE-47	39	0.24–0.29	0.28–8.75
PentaBDE	BDE-100	0.4	0.21–0.41	0.26–25.7
HexaBDE	BDE-153	440	0.08–0.27	0.63–25.1
**FEQG values extracted from the literature (Environment Canada, 2013)				

4.0 Conclusion

This present study investigated PBDE (BDE-17, 47, 66, 100, 153, and 183) in water and sediment samples from Nahoon River Estuary using SPE and USE, respectively. Quantification was done with GC- μ ECD. BDE-17 was the highest detected congener. NH1 appeared to be the highest contaminated location for water samples, while NH3 has the highest concentration in sediment. Spring season gave higher concentration (329 ng/L) than summer in water samples, while sediment samples gave higher concentration in summer season (65.4 ng/g). OM and OC did not correlate with the congeners. The pentaBDE detected in both matrices were higher than the FEQG. However, this concentration is not high enough to cause ecotoxicological risk in water samples, but low eco-toxicological risk is envisaged in sediment samples. This research is therefore essential to Nahoon River Estuary because of its significance in use for recreation. It has shown that even with the efficiency of restraint and prohibition on Nahoon River pollution, PBDE is being detected in the Estuary. Albeit, the Estuary's proper monitoring should be adopted to ensure that the runoff entering does not raise the hazard quotient of the contaminants in the Estuary.

Declarations

Author Contributions: Conceptualization, data collection and analyses and preparation of the manuscript (C.R.O); data analyses, review and updating of the manuscript (A.O.A., O.O.O., L.S and A.I.O); Supervision and funding of the research (O.O.O. and A.I.O).

Funding: The research was funded by the South African Medical Research Council (grant number UFH/SAMRC/P790).

Acknowledgments: The authors are grateful to the South African Medical Research Council (SAMRC) for funding support.

Conflicts of Interest: The authors declare no conflict of interest.

Ethical Approval: Not applicable in this section

Consent to participate: Not applicable in this section

Consent to publish: Not applicable in this section

Availability of data and materials: All the data generated and analysed during the current study in this article are included in this published article

References

1. Adams JB, Cowie M, van Niekerk L (2016) Assessment of completed ecological water requirement studies for South African estuaries and responses to changes in freshwater inflow. Water Research Commission
2. Anh HQ, Tomioka K, Tue NM, Tri TM, Minh TB, Takahashi S (2018) PBDEs and novel brominated flame retardants in road dust from northern Vietnam: Levels, congener profiles, emission sources and

- implications for human exposure. *Chemosphere* 197:389–398.
<https://doi.org/https://doi.org/10.1016/j.chemosphere.2018.01.066>
3. Anim AK, Drage DS, Goonetilleke A, Mueller JF, Ayoko GA (2017) Distribution of PBDEs, HBCDs and PCBs in the Brisbane River estuary sediment. *Mar Pollut Bull* 120:165–173.
<https://doi.org/10.1016/j.marpolbul.2017.05.002>
 4. APHA (2005) Standard methods for the examination of water and wastewater. Am. Public Heal. Assoc. Washington, DC, USA
 5. Bickerton IB (1981) Estuaries of the Cape: Synopses of available information on individual systems, Part II
 6. Bornman E, Strydom N, Clemmesen C (2018) Appraisal of Warm-Temperate South African Mangrove Estuaries as Habitats to Enhance Larval Nutritional Condition and Growth of *Gilchristella aestuaria* (Family Clupeidae) Using RNA:DNA Ratios. *Estuaries Coasts*. <https://doi.org/10.1007/s12237-018-0375-x>
 7. Canada Environment, Protection (2006) Canadian Environmental Protection Act, 1999. Ecological Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). Canadian Environmental
 8. Caruso A, Santoro M (2014) Detection of Organochlorine Pesticides by GC-ECD Following U.S. EPA Method 8081. *Detect. Organochlor. Pestic. by GC-ECD Follow. US EPA Method 8081:4*
 9. Castro-Jiménez J, Mariani G, Vives I, Skejo H, Umlauf G, Zaldívar JM, Dueri S, Messiaen G, Laugier T (2011) Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France). *Environ Pollut* 159:1948–1956.
<https://doi.org/https://doi.org/10.1016/j.envpol.2011.03.012>
 10. Cetin B, Odabasi M, Bayram A (2016) Wet deposition of persistent organic pollutants (POPs) in Izmir, Turkey. *Environ Sci Pollut Res*. <https://doi.org/10.1007/s11356-016-6183-6>
 11. Chapman D (1996) *Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring - Second Edition* Edited by
 12. Chen D, Hale RC, Watts BD, La Guardia MJ, Harvey E, Mojica EK (2010) Species-specific accumulation of polybrominated diphenyl ether flame retardants in birds of prey from the Chesapeake Bay region, USA. *Environ Pollut*. <https://doi.org/10.1016/j.envpol.2009.10.042>
 13. Chen L, Huang Y, Peng X, Xu Z, Zhang S, Ren M, Ye Z, Wang X (2009) PBDEs in sediments of the Beijiang River, China: Levels, distribution, and influence of total organic carbon. *Chemosphere*. <https://doi.org/10.1016/j.chemosphere.2009.03.033>
 14. Chokwe TB, Magubane MN, Afafe OA, Okonkwo JO, Sibiyi IV (2019a) Levels, distributions, and ecological risk assessments of polybrominated diphenyl ethers and alternative flame retardants in river sediments from Vaal River, South Africa. *Environ Sci Pollut Res* 26:7156–7163.
<https://doi.org/10.1007/s11356-018-04063-4>
 15. Chokwe TB, Magubane MN, Afafe OA, Okonkwo JO, Sibiyi IV (2019b) Levels, distributions, and ecological risk assessments of polybrominated diphenyl ethers and alternative flame retardants in

- river sediments from Vaal River, South Africa. *Environ Sci Pollut Res*.
<https://doi.org/10.1007/s11356-018-04063-4>
16. Cotiyane P, Adams J, Rajkaran A (2017) Key factors that drive phytoplankton biomass and community composition in the urbanised Nahoon Estuary, South Africa. *African J Aquat Sci* 42:245–257. <https://doi.org/10.2989/16085914.2017.1373058>
 17. Daso AP, Fatoki OS, Odendaal JP (2016) Polybrominated diphenyl ethers (PBDEs) and hexabromobiphenyl in sediments of the Diep and Kuils Rivers in South Africa. *Int J Sediment Res*. <https://doi.org/10.1016/j.ijsrc.2013.10.001>
 18. Daso AP, Fatoki OS, Odendaal JP (2013a) Occurrence of polybrominated diphenyl ethers (PBDEs) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) in water samples from the Diep River, Cape Town, South Africa. *Environ Sci Pollut Res*. <https://doi.org/10.1007/s11356-013-1503-6>
 19. Daso AP, Fatoki OS, Odendaal JP, Olujimi OO (2013b) Polybrominated diphenyl ethers (PBDEs) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa. *Environ Monit Assess* 185:431–439. <https://doi.org/10.1007/s10661-012-2565-5>
 20. Daso AP, Fatoki OS, Odendaal JP, Olujimi OO (2012) Occurrence of selected polybrominated diphenyl ethers and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) in sewage sludge and effluent samples of a wastewater-treatment plant in Cape Town, South Africa. *Arch Environ Contam Toxicol* 62:391–402. <https://doi.org/10.1007/s00244-011-9720-9>
 21. Daso AP, Rohwer ER, Koot DJ, Okonkwo JO (2017) Preliminary screening of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) flame retardants in landfill leachate. *Environ Monit Assess*. <https://doi.org/10.1007/s10661-017-6131-z>
 22. De Boer J, Wester PG, Van Der Horst A, Leonards PEG (2003) Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from the Netherlands. *Environ Pollut* 122:63–74. [https://doi.org/10.1016/S0269-7491\(02\)00280-4](https://doi.org/10.1016/S0269-7491(02)00280-4)
 23. Deng WJ, Zheng JS, Bi XH, Fu JM, Wong MH (2007) Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. *Environ Int* 33:1063–1069. <https://doi.org/10.1016/j.envint.2007.06.007>
 24. Díaz-Jaramillo M, Miglioranza KSB, Gonzalez M, Barón E, Monserrat JM, Eljarrat E, Barceló D (2016) Uptake, metabolism and sub-lethal effects of BDE-47 in two estuarine invertebrates with different trophic positions. *Environ Pollut* 213:608–617. <https://doi.org/10.1016/j.envpol.2016.03.009>
 25. Ebomah K, Sibanda T, Adefisoye M, Nontongana N, Nwodo U, Okoh A (2019) Evaluating nahoon beach and canal waters in Eastern Cape, South Africa: A public health concern. *Polish J Environ Stud* 28:1115–1125. <https://doi.org/10.15244/pjoes/85266>
 26. Edge U, Framework P (2007) BUFFALO CITY MUNICIPALITY (North Eastern Urban Edge Case Study)
 27. Environment Canada (2013) Federal Environmental Quality Guidelines Cobalt
 28. Fang L, Huang J, Yu G, Wang L (2008) Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane. *Chemosphere* 71:258–267. <https://doi.org/10.1016/j.chemosphere.2007.09.041>

29. Fontana AR, Silva MF, Martínez LD, Wuilloud RG, Altamirano JC (2009) Determination of polybrominated diphenyl ethers in water and soil samples by cloud point extraction-ultrasound-assisted back-extraction-gas chromatography-mass spectrometry. *J Chromatogr A* 1216:4339–4346. <https://doi.org/10.1016/j.chroma.2009.03.029>
30. Ge J, Liu M, Yun X, Yang Y, Zhang M, Li QX, Wang J (2014) Occurrence, distribution and seasonal variations of polychlorinated biphenyls and polybrominated diphenyl ethers in surface waters of the East Lake, China. *Chemosphere* 103:256–262. <https://doi.org/10.1016/j.chemosphere.2013.12.014>
31. Ge W, Mou Y, Chai C, Zhang Y, Wang J, Ju T, Jiang T, Xia B (2018) Polybrominated diphenyl ethers in the dissolved and suspended phases of seawater from Sanggou Bay, east China. *Chemosphere* 203:253–262. <https://doi.org/10.1016/j.chemosphere.2018.03.184>
32. Geldenhuys C, Cotiyane P, Rajkaran A (2016) Understanding the creek dynamics and environmental characteristics that determine the distribution of mangrove and salt marsh communities at Nahoon Estuary. *South African J Bot* 107:137–147. <https://doi.org/10.1016/j.sajb.2016.04.013>
33. Hansson K, Cousins AP, Brorström E (2006) Atmospheric concentrations in air and deposition fluxes of POPs at Råö and Pallas, trends and seasonal and spatial variations
34. He J, Robrock KR, Alvarez-Cohen L (2006) Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). *Environ Sci Technol*. <https://doi.org/10.1021/es052508d>
35. Hellar-Kihampa H, De Wael K, Lugwisha E, Malarvannan G, Covaci A, Van Grieken R (2013) Spatial monitoring of organohalogen compounds in surface water and sediments of a rural-urban river basin in Tanzania. *Sci Total Environ* 447:186–197. <https://doi.org/10.1016/j.scitotenv.2012.12.083>
36. Ibrahim RS, Khairy A, Zaatout HH, Hammoda HM, Metwally AM (2018) Digitally-optimized HPTLC coupled with image analysis for pursuing polyphenolic and antioxidant profile during alfalfa sprouting. *J Chromatogr B Anal Technol Biomed Life Sci* 1099:92–96. <https://doi.org/10.1016/j.jchromb.2018.09.021>
37. Jiang QT, Lee TKM, Chen K, Wong HL, Zheng JS, Giesy JP, Lo KKW, Yamashita N, Lam PKS (2005) Human health risk assessment of organochlorines associated with fish consumption in a coastal city in China. *Environ Pollut*. <https://doi.org/10.1016/j.envpol.2004.09.028>
38. Johnson-Restrepo B, Kannan K (2009) An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. *Chemosphere* 76:542–548. <https://doi.org/10.1016/j.chemosphere.2009.02.068>
39. Khairy MA, Lohmann R (2017) Using Polyethylene Passive Samplers to Study the Partitioning and Fluxes of Polybrominated Diphenyl Ethers in an Urban River. *Environ Sci Technol*. <https://doi.org/10.1021/acs.est.7b02418>
40. Kowalski B, Mazur M (2014) The simultaneous determination of six flame retardants in water samples using SPE pre-concentration and UHPLC-UV method. *Water Air Soil Pollut* 225. <https://doi.org/10.1007/s11270-014-1866-4>
41. Kuramochi H, Maeda K, Kawamoto K (2007) Physicochemical properties of selected polybrominated diphenyl ethers and extension of the UNIFAC model to brominated aromatic compounds.

- Chemosphere 67:1858–1865. <https://doi.org/10.1016/j.chemosphere.2006.05.076>
42. La Guardia MJ, Hale RC, Harvey E (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ Sci Technol* 40:6247–6254. <https://doi.org/10.1021/es060630m>
 43. Langford K, Scrimshaw M, Lester J (2007) The impact of process variables on the removal of PBDEs and NPEOs during simulated activated sludge treatment. *Arch Environ Contam Toxicol*. <https://doi.org/10.1007/s00244-006-0052-0>
 44. Lee LK, He J (2010) Reductive debromination of polybrominated diphenyl ethers by anaerobic bacteria from soils and sediments. *Appl Environ Microbiol*. <https://doi.org/10.1128/AEM.01872-09>
 45. Li C, Zhao Z, Lei B, An J, Zhang X, Yu Y (2015) Polybrominated diphenyl ethers in the air and comparison of the daily intake and uptake through inhalation by Shanghai residents with those through other matrices and routes. *Environ Sci Pollut Res* 22:1750–1759. <https://doi.org/10.1007/s11356-014-3264-2>
 46. Liu WX, He W, Qin N, Kong XZ, He QS, Yang B, Yang C, Jorgensen SE, Xu FL (2015) Temporal-spatial distributions and ecological risks of perfluoroalkyl acids (PFAAs) in the surface water from the fifth-largest freshwater lake in China (Lake Chaohu). *Environ Pollut*. <https://doi.org/10.1016/j.envpol.2015.01.028>
 47. Luo P, Ni HG, Bao LJ, Li SM, Zeng EY (2014) Size distribution of airborne particle-bound polybrominated diphenyl ethers and its implications for dry and wet deposition. *Environ Sci Technol* 48:13793–13799. <https://doi.org/10.1021/es5042018>
 48. Mai ChenChen, Luo ChenChen, Yang, Sheng, Peng, Fu, Zeng EY (2005) Distribution of Polybrominated Diphenyl Ethers in Sediments of the Pearl River Delta and Adjacent South China Sea. *Environ Sci Technol* 39:3521–3527. <https://doi.org/10.1021/es048083x>
 49. Momba MNB, Osode AN, Sibewu M (2006) The impact of inadequate wastewater treatment on the receiving water bodies - Case study: Buffalo City and Nkokonbe Municipalities of the Eastern Cape Province. *Water SA* 32:687–692. <https://doi.org/10.4314/wsa.v32i5.47854>
 50. Moon HB, Choi M, Yu J, Jung RH, Choi HG (2012) Contamination and potential sources of polybrominated diphenyl ethers (PBDEs) in water and sediment from the artificial Lake Shihwa. *Korea Chemosphere* 88:837–843. <https://doi.org/10.1016/j.chemosphere.2012.03.091>
 51. Newman BK, Watling RJ (2007) Definition of baseline metal concentrations for assessing metal enrichment of sediment from the south-eastern Cape coastline of South Africa. *Water SA*. <https://doi.org/10.4314/wsa.v33i5.184089>
 52. Nouira T, Risso C, Chouba L, Budzinski H, Boussetta H (2013) Polychlorinated biphenyls (PCBs) and Polybrominated Diphenyl Ethers (PBDEs) in surface sediments from Monastir Bay (Tunisia, Central Mediterranean): Occurrence, distribution and seasonal variations. *Chemosphere*. <https://doi.org/10.1016/j.chemosphere.2013.06.017>
 53. Odusanya DO, Okonkwo JO, Botha B (2009a) Polybrominated diphenyl ethers (PBDEs) in leachates from selected landfill sites in South Africa. *Waste Manag* 29:96–102.

<https://doi.org/10.1016/j.wasman.2008.02.011>

54. Odusanya DO, Okonkwo JO, Botha B (2009b) Polybrominated diphenyl ethers (PBDEs) in leachates from selected landfill sites in South Africa. *Waste Manag* 29:96–102.
<https://doi.org/10.1016/j.wasman.2008.02.011>
55. Ohoro CR, Adeniji AO, Okoh AI, Okoh OO (2021) Polybrominated diphenyl ethers in the environmental systems: a review. *J Environ Heal Sci Eng*. <https://doi.org/10.1007/s40201-021-00656-3>
56. Ohoro CR, Adeniji AO, Okoh AI, Okoh OO (2019) Distribution and chemical analysis of pharmaceuticals and personal care products (PPCPs) in the environmental systems: A review. *Int J Environ Res Public Health* 16. <https://doi.org/10.3390/ijerph16173026>
57. Olisah C, Adeniji AO, Okoh OO, Okoh AI (2019) Occurrence and risk evaluation of organochlorine contaminants in surface water along the course of Swartkops and Sundays River Estuaries, Eastern Cape Province, South Africa. *Environ Geochem Health* 41:2777–2801.
<https://doi.org/10.1007/s10653-019-00336-0>
58. Olisah C, Okoh OO, Okoh AI (2020a) Polybrominated diphenyl ethers (PBDEs) in surface water and fish tissues from Sundays and Swartkops Estuaries, Eastern Cape Province, South Africa: Levels, spatial distribution, seasonal variation and health implications. *Reg Stud Mar Sci* 36.
<https://doi.org/10.1016/j.rsma.2020.101319>
59. Olisah C, Okoh OO, Okoh AI (2020b) Spatial, seasonal and ecological risk assessment of organohalogenated contaminants in sediments of Swartkops and Sundays Estuaries, Eastern Cape province, South Africa. *J Soils Sediments* 20:1046–1059. <https://doi.org/10.1007/s11368-019-02487-0>
60. Olisah C, Rubidge G, Human LRD, Adams JB (2021) A translocation analysis of organophosphate pesticides between surface water, sediments and tissues of common reed *Phragmites australis*. *Chemosphere*. <https://doi.org/10.1016/j.chemosphere.2021.131380>
61. Olukunle O, Okonkwo J, Kefeni K, Lupankwa M (2012) Concentrations of polybrominated diphenyl ethers in sediments from Jukskei River, Gauteng, South Africa. *Bull Environ Contam Toxicol* 88:461–466. <https://doi.org/10.1007/s00128-011-0481-y>
62. Olukunle OI, Okonkwo OJ, Wase AG, Sha'ato R (2015) Polybrominated diphenyl ethers in car dust in Nigeria: Concentrations and implications for non-dietary human exposure. *Microchem J*.
<https://doi.org/10.1016/j.microc.2015.05.023>
63. Oros DR, Hoover D, Rodigari F, Crane D, Sericano J (2005) Levels and distribution of polybrominated diphenyl ethers in water, surface sediments, and bivalves from the San Francisco. *Environ Sci Technol* 39:33–41. <https://doi.org/10.1021/es048905q>
64. Osode AN (2007) the Impact of Wastewater Quality on Receiving Water 2007
65. Pan Y, Tsang DCW, Wang Y, Li Y, Yang X (2016) The photodegradation of polybrominated diphenyl ethers (PBDEs) in various environmental matrices: Kinetics and mechanisms. *Chem Eng J* 297:74–96. <https://doi.org/10.1016/j.cej.2016.03.122>

66. Polder A, Venter B, Skaare JU, Bouwman H (2008) Polybrominated diphenyl ethers and HBCD in bird eggs of South Africa. *Chemosphere* 73:148–154.
<https://doi.org/10.1016/j.chemosphere.2008.03.021>
67. Robrock KR, Korytár P, Alvarez-Cohen L (2008) Pathways for the anaerobic microbial denomination of polybrominated diphenyl ethers. *Environ Sci Technol* 42:2845–2852.
<https://doi.org/10.1021/es0720917>
68. Rügner H, Schwientek M, Beckingham B, Kuch B, Grathwohl P (2013) Turbidity as a proxy for total suspended solids (TSS) and particle facilitated pollutant transport in catchments. *Environ Earth Sci* 69:373–380. <https://doi.org/10.1007/s12665-013-2307-1>
69. Rusydi AF (2018) Correlation between conductivity and total dissolved solid in various type of water: A review. *IOP Conf Ser Earth Environ Sci* 118. <https://doi.org/10.1088/1755-1315/118/1/012019>
70. Shao Y, Han S, Ma L, Luo M, Yang G, Liu W, Xu D (2018) Polybrominated diphenyl ethers in surface waters around Beijing: Occurrence, distribution and sources. *Appl Geochemistry* 98:58–64.
<https://doi.org/10.1016/j.apgeochem.2018.09.011>
71. Siddiqi MA, Clinic M (2003) New Pollutants – Old Diseases. *Clin Med (Northfield Il)* 1:281–290
72. Siddiqi MA, Laessig RH, Reed KD (2003) Polybrominated diphenyl ethers (PBDEs): new pollutants-old diseases. *Clin Med Res*. <https://doi.org/10.3121/cmr.1.4.281>
73. Sikora LJ, Moore-Kucera J (2014) Soil Test Methods From the Southeastern United States. Southern Cooperative Series Bulletin
74. Song W, Ford JC, Li A, Mills WJ, Buckley DR, Rockne KJ (2004) Polybrominated diphenyl ethers in the sediments of the great lakes. 1. Lake superior. *Environ Sci Technol* 38:3286–3293.
<https://doi.org/10.1021/es035297q>
75. Talbot MMJF, Branch EB, Marsland SA, Watling RJ (1985) Metal surveys in South African estuaries. X. Blind, Ihlanza, Nahoon and Quinera rivers. *Water SA*
76. Tlili K, Labadie P, Alliot F, Bourges C, Desportes A, Chevreuil M (2012) Polybrominated diphenyl ether dynamics in ambient air and atmospheric bulk/wet deposition in downtown Paris (France). *Water Air Soil Pollut* 223:1543–1553. <https://doi.org/10.1007/s11270-011-0963-x>
77. Trinh MM, Tsai CL, Chang MB (2019) Characterization of polybrominated diphenyl ethers (PBDEs) in various aqueous samples in Taiwan. *Sci Total Environ*.
<https://doi.org/10.1016/j.scitotenv.2018.08.204>
78. Trudel D, Scheringer M, Von Goetz N, Hungerbühler K (2011) Total consumer exposure to polybrominated diphenyl ethers in north america and europe. *Environ Sci Technol* 45:2391–2397.
<https://doi.org/10.1021/es1035046>
79. Viganò L, Roscioli C, Guzzella L (2011) Decabromodiphenyl ether (BDE-209) enters the food web of the River Po and is metabolically debrominated in resident cyprinid fishes. *Sci Total Environ* 409:4966–4972. <https://doi.org/10.1016/j.scitotenv.2011.07.062>
80. Wang G, Peng J, Xu X, Zhang D, Li X (2016) Polybrominated diphenyl ethers in sediments from the Southern Yellow Sea: Concentration, composition profile, source identification and mass inventory.

- Chemosphere 144:2097–2105. <https://doi.org/10.1016/j.chemosphere.2015.10.088>
81. Wang Q, Li X, Liu S, Zhang D, Duan X (2019) The effect of hydrodynamic forcing on the transport and deposition of polybrominated diphenyl ethers (PBDEs) in Hangzhou Bay. *Ecotoxicol Environ Saf* 179:111–118. <https://doi.org/10.1016/j.ecoenv.2019.04.026>
 82. Wang Q, Li Y, Wang Y (2011) Optimizing the weight loss-on-ignition methodology to quantify organic and carbonate carbon of sediments from diverse sources, in: *Environmental Monitoring and Assessment*. <https://doi.org/10.1007/s10661-010-1454-z>
 83. World Health Organization (2010) WHO human health risk assessment toolkit: chemical hazards. IPCS Harmon. Proj. Doc
 84. Wu MH, Pei JC, Zheng M, Tang L, Bao YY, Xu BT, Sun R, Sun YF, Xu G, Lei JQ (2015) Polybrominated diphenyl ethers (PBDEs) in soil and outdoor dust from a multi-functional area of Shanghai: Levels, compositional profiles and interrelationships. *Chemosphere* 118:87–95. <https://doi.org/10.1016/j.chemosphere.2014.06.022>
 85. Wu MH, Tang L, Xu G, Ma J, Liu N, Wang L, Lei JQ (2013) Polybrominated diphenyl ethers in surface sediments from principal watersheds of Shanghai, China: Levels, distribution, influencing factors, and risk assessment. *Environ Sci Pollut Res* 20:2651–2660. <https://doi.org/10.1007/s11356-012-1163-y>
 86. Wu MH, Xu BT, Xu G, Wang MN, Ma J, Pan CY, Sun R, Han T, Tang L (2017) Occurrence and profiles of polybrominated diphenyl ethers (PBDEs) in riverine sediments of Shanghai: a combinative study with human serum from the locals. *Environ Geochem Health*. <https://doi.org/10.1007/s10653-016-9843-z>
 87. Wu Y, Wang X, Li Y, Ya M, Luo H, Hong H (2017) Polybrominated diphenyl ethers, organochlorine pesticides, and polycyclic aromatic hydrocarbons in water from the Jiulong River Estuary, China: levels, distributions, influencing factors, and risk assessment. *Environ Sci Pollut Res* 24:8933–8945. <https://doi.org/10.1007/s11356-015-4782-2>
 88. Wu Z, He C, Han W, Song J, Li H, Zhang Y, Jing X, Wu W (2020) Exposure pathways, levels and toxicity of polybrominated diphenyl ethers in humans: A review. *Environ Res* 187:109531. <https://doi.org/10.1016/j.envres.2020.109531>
 89. Xu P, Ge W, Chai C, Zhang Y, Jiang T, Xia B (2019) Sorption of polybrominated diphenyl ethers by microplastics. *Mar Pollut Bull* 145:260–269. <https://doi.org/10.1016/j.marpolbul.2019.05.050>
 90. Yahaya A, Okoh OO, Okoh AI, Adeniji AO (2017) Occurrences of organochlorine pesticides along the course of the Buffalo river in the eastern cape of South Africa and its health implications. *Int J Environ Res Public Health* 14. <https://doi.org/10.3390/ijerph14111372>
 91. Yang Y, Xie Q, Liu X, Wang J (2015) Occurrence, distribution and risk assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in nine water sources. *Ecotoxicol Environ Saf* 115:55–61. <https://doi.org/10.1016/j.ecoenv.2015.02.006>
 92. Yin H, Tang Z, Meng T, Zhang M (2020) Concentration profile, spatial distributions and temporal trends of polybrominated diphenyl ethers in sediments across China: Implications for risk

- assessment. *Ecotoxicol Environ Saf*. <https://doi.org/10.1016/j.ecoenv.2020.111205>
93. Yin S, Guo F, Aamir M, Liu Y, Tang M, Liu W (2019) Multicenter biomonitoring of polybrominated diphenyl ethers (PBDEs) in colostrum from China: Body burden profile and risk assessment. *Environ Res* 179:108828. <https://doi.org/https://doi.org/10.1016/j.envres.2019.108828>
94. Zhan L, Lin T, Cheng H, Wang Z, Cheng Z, Zhou D, Qin Z, Zhang G (2019) Atmospheric deposition and air–soil exchange of polybrominated diphenyl ethers (PBDEs) in a background site in Central China. *Environ Sci Pollut Res* 26:31934–31944. <https://doi.org/10.1007/s11356-019-06312-6>
95. Zhou H, Tam NFY, Cheung SG, Wei P, Li S, Wu Q (2019) Contamination of polybrominated diphenyl ethers (PBDEs) in watershed sediments and plants adjacent to e-waste sites. *J Hazard Mater*. <https://doi.org/10.1016/j.jhazmat.2019.120788>
96. Zhou Y, Sun J, Wang L, Zhu G, Li M, Liu J, Li Z, Gong H, Wu C, Yin G (2021) Multiple classes of chemical contaminants in soil from an e-waste disposal site in China: Occurrence and spatial distribution. *Sci Total Environ* 752. <https://doi.org/10.1016/j.scitotenv.2020.141924>
97. Zhu X, Beiyuan J, Lau AYT, Chen SS, Tsang DCW, Graham NJD, Lin D, Sun J, Pan Y, Yang X, Li XD (2018) Sorption, mobility, and bioavailability of PBDEs in the agricultural soils: Roles of co-existing metals, dissolved organic matter, and fertilizers. *Sci Total Environ* 619–620, 1153–1162. <https://doi.org/10.1016/j.scitotenv.2017.11.159>

Figures

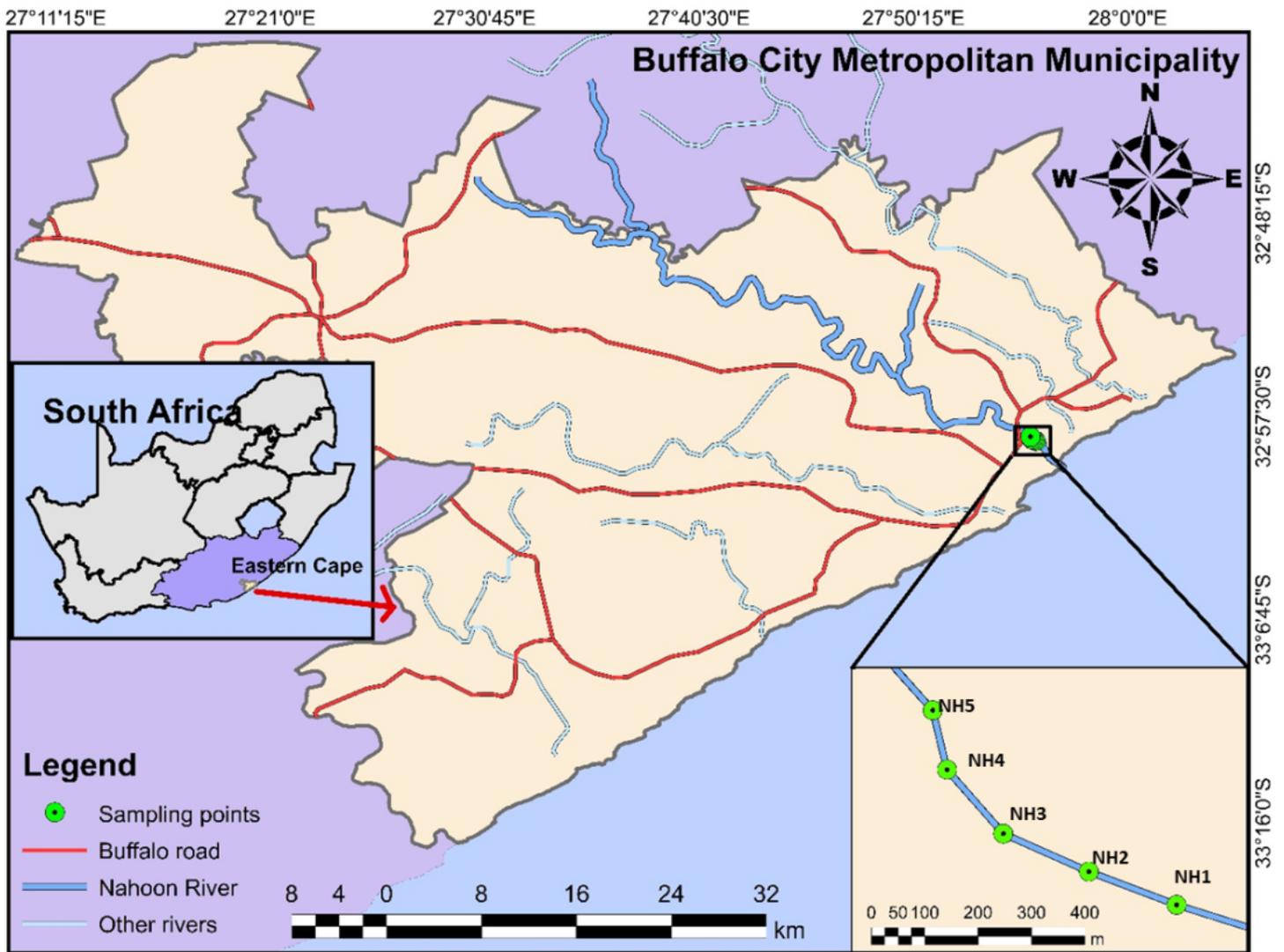


Figure 1

Location map of the study location within South Africa and the five sampling points (NH1, NH2, NH3, NH4, NH5) within the Nahoon River estuary

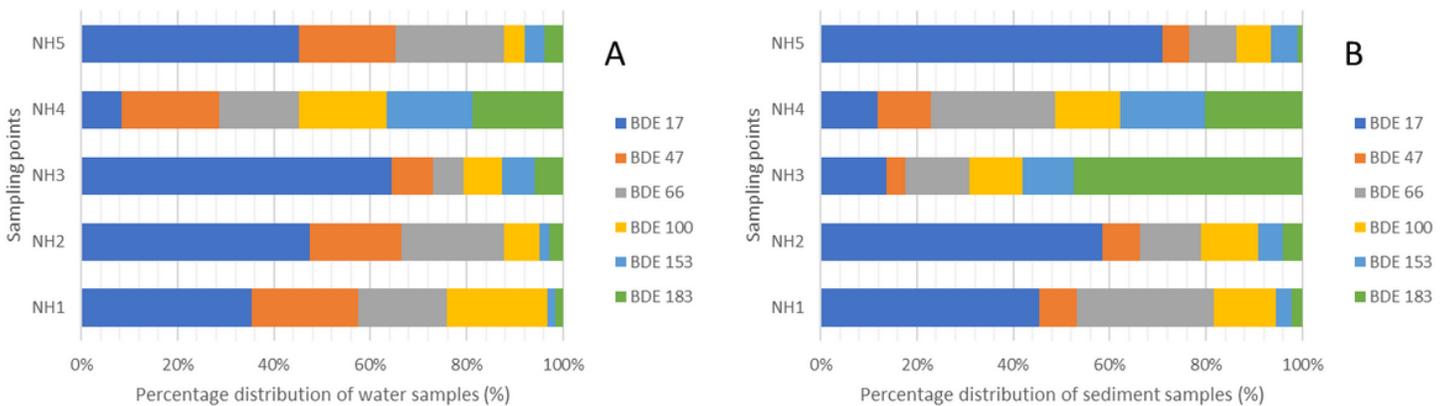


Figure 2

