Research article

Occurrence and probabilistic risk assessment of PAHs in water and sediment samples of the Diep River, South Africa

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A B S T R A C T

This study investigated the levels of polycyclic aromatic hydrocarbons (PAHs) in water and sediment samples of the Diep River freshwater system of Western Cape Province, South Africa. A solid-phase extraction - gas chromatography - flame ionisation detection (SPE-GC-FID) method was utilised to simultaneously determine the 16 United States Environmental Protection Agency (US EPA) listed priority PAHs in water and sediment samples. The seasonal averages of individual PAH detected at the studied sites, ranged between not detected (Nd) and 72.38 ± 9.58 μg/L in water samples and between Nd and 16.65 ± 2.63 μg/g in the corresponding sediment samples. The levels of PAHs measured in water and sediment samples were subjected to probabilistic risk assessment to predict the possibility of regulatory values being exceeded. The average percentage exceedence of 63.26 was obtained for PAHs in water samples of the Diep River, while the corresponding average percentage exceedence obtained for sediment sample was 63.71. Sufficient exposure of humans and aquatic organisms to the exceedance levels obtained, would cause adverse health effect.

1. Introduction

Water is essential to the existence of humans and wildlife as well as the sustenance of aquatic ecosystem. The release of organic pollutants such PAHs into the aquatic environment may negatively affect this essential resource. PAHs are introduced into the aquatic environment from natural and anthropogenic sources. Natural sources of PAHs include forest fires, volcanic emissions, natural oil seeps, coal deposits, plant debris and certain biological (biogenic) processes (Grueiro-Noche et al., 2010; Orecchio, 2010). Anthropogenic sources of PAHs in aquatic environments can be grouped into pyrogenic and petrogenic. Pyrogenic sources include the combustion of fossil fuel such as which occurs in automobiles, power plants, industries that burn coal and petroleum, and waste incinerators, amongst others (Dong and Lee, 2009). Petrogenic sources include crude oil and petroleum products such as kerosene, petrol, diesel, lubricating oil, and asphalt (Boonyatumanond et al., 2007). PAHs derived from anthropogenic sources have been shown to enter

aquatic systems through direct discharges, run-off and atmospheric deposition (dry/wet deposition, air-water gaseous exchanges) (Boulou-bassi et al., 2006).

The levels of contaminants in an aquatic environment may vary with seasons (temporal distribution), spatially and also within various components of the aquatic environment such as vegetation, fish, sediment, water and other aquatic resources (Wang et al., 2012; Li et al., 2017). For instance, Liu et al. (2016) reported significant temporal variation in levels of PAHs in water sampled from the urban river networks of Shanghai (China). An average detection level of dissolved Σ_{16}PAHs in water samples during winter and summer were 183.54 ng/L (71.92–460.53 ng/L) and 106.67 ng/L (46.53–221.54 ng/L), respectively, while sediment samples Σ_{16}PAHs averages were 4944.97 ng/g (352.37–36198.23 ng/g) and 2336.63 ng/g (456.11–14948.40 ng/g) during winter and summer, respectively. The variations were attributed as the consequence of mobility and dilution effect. The study stations were noted to have shallow-water level and slow flowing water velocity

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during winter and high volume and even flooding during summer. This resulted in poor scour and dilution ability of the rivers, hence the higher PAHs levels in winter and dilution effect on PAHs in summer. Thus, the significant seasonal variation in water and sediment samples were attributed to possible high-volume flooding PAHs dilution in summer, coupled with accelerated microbial degradation of PAHs resulting due to elevated temperatures. Sediments generally concentrates more PAHs, compared to the corresponding water columns, due to the sorption tendency of hydrophobic pollutants for sediments. In a study reported by Chen et al. (2007), the 2- and 3-rings PAH components were reported to be the dominant PAHs in water samples, while the 3- and 4-rings compounds dominate the sediment system.

Polycyclic aromatic hydrocarbons are persistent organic chemical compounds, and are prioritised ubiquitous environmental contaminants (Sun et al., 2009). Their environmental stability and high hydrophobic (lipophilic) nature, results in their bioaccumulation in biota especially in aquatic organisms. This may result in chronic or acute toxicity and sub-lethal effects (Olivella et al., 2006; Cardellicchio et al., 2007; Boitsov et al., 2009). Furthermore, PAHs have been reported to be of concern to human health, as they have been shown to be probably carcinogenic, mutagenic and teratogenic (Yamada et al., 2003). Data on pollution trends are of great importance to increase understanding in cause-effect relationships, agent identification, source identification as well as developing appropriate strategies for adequate and effective control of contaminants, all essential for environmental management and protection (Gómez-Gutiérrez et al., 2007; Campillo et al., 2017).

Studies, globally and in South Africa in particular, have presented data on PAHs levels in various compartments of the aquatic environments. There is a general acknowledgement and suggestion for the need of more data, on these prioritised emerging micro-pollutants (Shi et al., 2005; Degger et al., 2011; Zeng et al., 2013; Karaca and Tasdemir, 2014), coupled with the need to present the risk associated with the levels at which they were detected in the environments. In this study, the occurrence levels, spatial and seasonal variations of the 16 US EPA priority PAHs was monitored and measured in some surface water and sediment samples, and the data utilised in Weibull probabilistic approach and percentile ranking for evaluating the PAHs risk assessment.

2. Material and methods

2.1. Standards and reagents

The 16 PAHs were purchased from Supelco, Bellefonte, PA, USA. Solvents including n-hexane, dichloromethane, acetonitrile, acetone, Supelclean (ENVI -18 SPE tubes 6mL) C18 solid phase extraction tubes, and all other chemicals were obtained from Sigma-Aldrich (South Africa).

2.2. Study area; The Diep River sites

The Diep River catchment has industrial areas, agricultural areas, formal and informal settlements and wastewater treatment works with a total area of 1495 km^2. The catchment is low and flat (making it ideal for crop cultivation) but has isolated mountains (the Perdeberg, Kasteelberg and Paarlberg mountains) on its eastern boundary. The Diep River catchment is bound by the following towns: Riebeek-West (to the north), Paarl (to the east), Atlantis (to the west) and Milnerton (to the south) (Mafejane et al., 2002).

The Diep River, an important freshwater ecosystem (utilised for irrigation and recreation) in the Western Cape province of South Africa, had been reported to be negatively impacted as a result of anthropogenic activities (Jackson et al., 2009; Shuping et al., 2011; Daso et al., 2016). To investigate the source inputs of the 16 US EPA priority PAHs and present the associated probable risk, with the levels at which they were detected in the freshwater system of the Diep River, three sites were

selected. Description of the three sampling sites (DA, DB and DC) in the Diep River is presented in Figure 1.

2.3. Sampling and sample pre-treatment

Surface water and sediment samples were collected from selected sites (DA, B and DC) for this study. The choice of sampling bottles, sample preservation method, holding time and analytical method were carried out based on established procedures.

2.3.1. Sampling and pre-treatment of water

Water was sampled in triplicates and collected consistently monthly at interval of 30 days once a month during year a one-year period. The full details of which has been reported previously (Awe et al., 2020).

2.3.2. Sampling and pre-treatment of sediment

Surface sediment samples were concurrently collected with water samples during same sampling campaign at the sites. Sediments were generally sampled after water sampling to avoid perturbation and resuspension of the sediment system into the water phase. Sediment samples (top 1–2 cm bottom surface layer) were carefully collected using a stainless-steel grab sampler. Five representatives of the 1–2 cm top bottom sediment layer samples were collected at each point to obtain a composite sediment sample. The samples were wrapped in aluminium foil pre-treated with DCM and transferred to the laboratory in an ice chest at 4 °C (Guo et al., 2007). Samples were air dried prior to further analysis.

3. Analysis of sample

The method of analysis utilised in this study has been reported in one of our previous studie. The summary and additional information are however provided.

3.1. Method validation

The method of validation utilised, had been reported previously (Awe et al., 2020). In brief, linearity range, detection limit, quantification limit, precision, accuracy and recovery, which are established parameters by the International Conference on Harmonisation (ICH, 2005) were utilised.

3.2. PAHs analysis

A solid-phase extraction - gas chromatography - flame ionisation detection (SPE-GC-FID) method developed, was utilised for the simultaneous recovery and determination of the 16 PAHs. An Agilent 7890A GC-FID system equipped with an auto-sampler and a DB-EUPAH column (20 m × 0.18mm I.D) were employed for PAHs chromatographic analysis and separations respectively.

3.2.1. Extraction and Spe clean-up of PAHs from samples

The clean-up of PAHs in water and sediment samples were carried out with C18 solid phase extraction tubes (Supelclean ENVI -18 SPE tubes 6mL), purchased from Supelco, Bellefonte, USA.

3.2.1.1. PAHs extraction and SPE clean-up from water samples. The extraction of PAHs from water samples was carried out with n-hexane in five extraction sequences (25, 20, 15, 10 and 10 mL) and utilised 250 mL of Milli-Q water as matrix for the recovery procedure. The details of which have been reported previously (Awe et al., 2020).

3.2.1.2. PAHs extraction and SPE clean-up from sediment samples. Coarse/detritus materials and sewage were carefully sorted and removed from air-dried sediment samples. After which, the sediment samples were crushed and sieved through a 250 μm aperture. This was
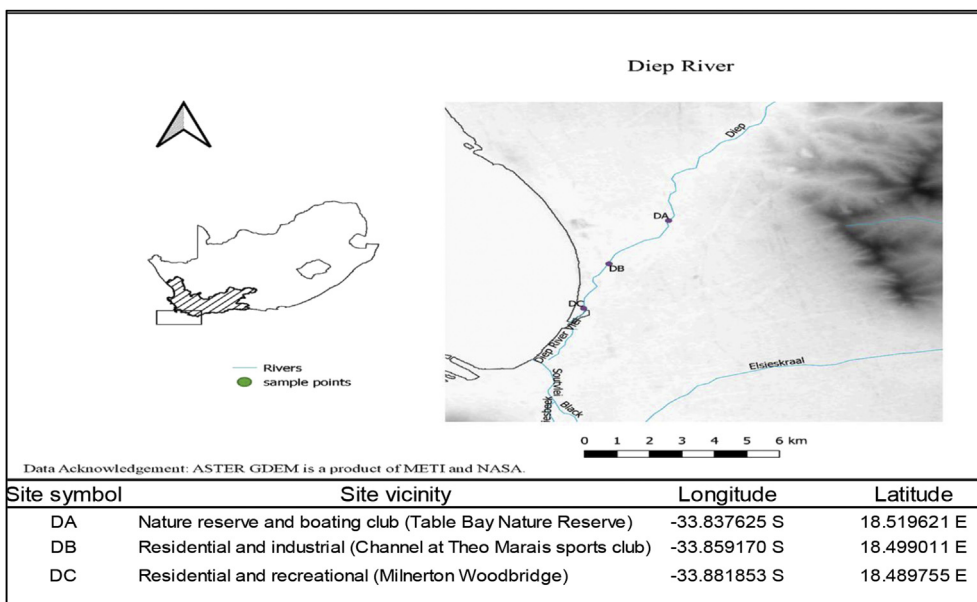
Figure 1. Sampling sites at the Diep River.

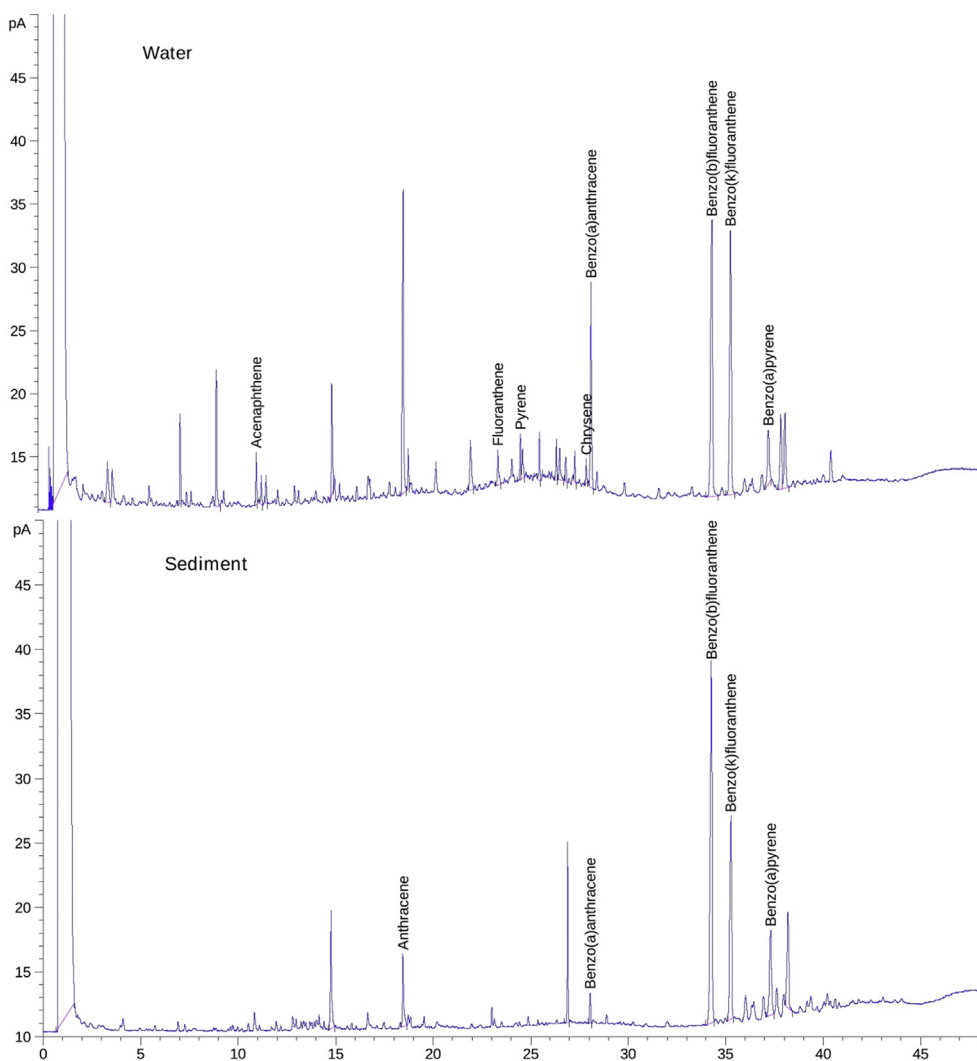| Site symbol	Site vicinity	Longitude	Latitude
DA	Nature reserve and boating club (Table Bay Nature Reserve)	-33.837625 S	18.519621 E
DB	Residential and industrial (Channel at Theo Marais sports club)	-33.859170 S	18.499011 E
DC	Residential and recreational (Milnerton Woodbridge)	-33.881853 S	18.489755 E

Figure 2. Chromatograms for water and sediment sample.

Table 1. Seasonal occurrence (average ± SD) of PAHs in the Diep River sediment samples (sites DA, DB and DC).

PAHs (µg/g)	Site DA				Site DB				Site DC			
	Summer (Dec to Feb)	Autumn (Mar to May)	Winter (June to Aug)	Spring (Sept to Nov)	Summer (Dec to Feb)	Autumn (Mar to May)	Winter (June to Aug)	Spring (Sept to Nov)	Summer (Dec to Feb)	Autumn (Mar to May)	Winter (June to Aug)	Spring (Sept to Nov)
Nap	1.81 ± 0.17	0.63 ± 0.37	0.03 ± 0.03	0.96 ± 0.82	2.15 ± 0.15	Nd	Nd	1.80 ± 1.06	1.63 ± 0.55	0.28 ± 0.83	0.67 ± 0.63	0.85 ± 0.46
Acy	0.05 ± 0.02	Nd	0.04 ± 0.03	0.28 ± 0.33	0.34 ± 0.27	0.36 ± 0.20	Nd	0.44 ± 0.55	0.10 ± 0.17	0.23 ± 0.13	0.12 ± 0.10	Nd
Can	0.06 ± 0.03	0.08 ± 0.08	0.08 ± 0.01	0.19 ± 0.03	0.04 ± 0.04	1.92 ± 1.24	0.48 ± 0.42	0.64 ± 0.37	0.34 ± 0.52	0.24 ± 0.31	0.05 ± 0.08	0.16 ± 0.08
Flu	Nd	0.24 ± 0.14	0.03 ± 0.02	0.06 ± 0.07	0.01 ± 0.02	0.63 ± 0.26	1.84 ± 1.37	0.22 ± 0.16	0.13 ± 0.12	0.02 ± 0.07	0.05 ± 0.09	0.12 ± 0.07
Phe	0.03 ± 0.01	Nd	0.06 ± 0.01	1.10 ± 1.41	0.04 ± 0.03	15.01 ± 3.22	13.03 ± 2.75	0.20 ± 0.25	1.29 ± 1.13	0.08 ± 0.74	0.12 ± 0.11	0.06 ± 0.02
Ant	0.08 ± 0.02	Nd	0.12 ± 0.06	0.20 ± 0.09	0.08 ± 0.07	3.01 ± 1.04	0.05 ± 0.05	0.20 ± 0.05	0.09 ± 0.08	0.12 ± 0.05	0.06 ± 0.03	0.14 ± 0.03
Flt	0.06 ± 0.02	0.67 ± 0.63	0.53 ± 0.23	0.62 ± 0.38	6.45 ± 10.66	3.83 ± 2.02	0.22 ± 0.21	2.95 ± 2.09	0.20 ± 0.20	1.17 ± 0.99	0.55 ± 0.49	1.59 ± 1.96
Pyr	0.01 ± 0.01	0.20 ± 0.11	0.04 ± 0.02	0.16 ± 0.10	0.56 ± 0.91	1.36 ± 0.34	2.36 ± 1.64	0.29 ± 0.13	0.00	0.09 ± 0.07	0.06 ± 0.06	0.05 ± 0.06
BaA	0.27 ± 0.03	0.69 ± 0.29	0.31 ± 0.17	0.29 ± 0.23	0.88 ± 1.05	2.56 ± 1.92	2.30 ± 2.30	0.79 ± 0.26	0.51 ± 0.61	0.54 ± 0.52	0.31 ± 0.07	0.63 ± 0.60
Chy	0.08 ± 0.07	1.53 ± 1.52	0.24 ± 0.17	0.71 ± 1.02	1.92 ± 1.05	2.10 ± 0.78	2.94 ± 0.54	1.21 ± 1.04	0.21 ± 0.22	0.48 ± 0.31	0.22 ± 0.13	0.78 ± 1.15
BbF	Nd	1.19 ± 0.19	0.18 ± 0.14	0.15 ± 0.09	2.90 ± 4.40	16.65 ± 2.63	5.07 ± 2.57	0.81 ± 0.68	1.56 ± 1.70	1.02 ± 0.25	0.65 ± 0.30	0.30 ± 0.16
BkF	0.14 ± 0.07	2.26 ± 1.39	0.33 ± 0.12	0.50 ± 0.66	3.46 ± 5.07	12.28 ± 6.29	5.09 ± 4.05	1.24 ± 1.03	1.44 ± 1.18	1.63 ± 0.54	0.86 ± 1.02	0.71 ± 0.30
BaP	0.12 ± 0.02	1.30 ± 0.45	0.24 ± 0.03	0.30 ± 0.26	0.13 ± 0.23	5.79 ± 2.24	6.54 ± 2.88	0.52 ± 0.54	1.99 ± 1.10	1.60 ± 0.20	1.22 ± 0.48	0.62 ± 0.11
IcP	0.07 ± 0.07	0.90 ± 0.36	0.21 ± 0.03	0.67 ± 0.99	2.33 ± 2.30	2.39 ± 1.86	1.65 ± 1.35	0.30 ± 0.20	0.08 ± 0.14	0.50 ± 0.53	0.24 ± 0.21	0.10 ± 0.18
DBA	0.07 ± 0.07	0.96 ± 0.60	0.18 ± 0.05	0.37 ± 0.40	1.90 ± 1.39	1.22 ± 0.60	3.32 ± 2.72	0.35 ± 0.30	0.06 ± 0.10	0.79 ± 0.56	0.22 ± 0.22	0.15 ± 0.07
BgP	0.14 ± 0.15	0.75 ± 0.54	0.26 ± 0.04	0.41 ± 0.33	Nd	1.60 ± 1.43	2.02 ± 0.99	0.21 ± 0.09	0.19 ± 0.33	0.79 ± 0.63	0.144 ± 0.10	0.16 ± 0.11
$\sum_{16}$ PAHs	2.98 ± 0.44	11.38 ± 0.64	2.87 ± 0.14	6.97 ± 0.30	23.18 ± 1.77	70.71 ± 5.32	46.91 ± 3.34	12.05 ± 0.75	9.81 ± 0.70	9.58 ± 0.53	5.54 ± 0.35	6.40 ± 0.43
% C PAHs	25.16	77.44	58.62	42.84	58.35	60.79	57.37	43.20	59.59	68.52	67.13	51.31

Site DA: Nature reserve (upstream). Site DB: Theo Marais Sports Club – industrial and residential area. Site DC: Woodbridge (downstream). Nd: not detected. C PAHs: Carcinogenic PAHs.

followed by the extraction of the PAHs analytes from 2 g of sieved sediment samples with n-hexane and DCM in three extraction sequences of 20 mL n-hexane for 10 min, 10 mL DCM/n-hexane (1:3) for 10 min and 10 mL n-hexane for 10 min, using ultrasonic agitation at 30 °C in a total time of 30 min.

Briefly, 2 g dry weight (dw) of the prepared sediment sample was weighed into 50-mL amber coloured bottle. Thereafter, 10 mL of the extracting solvent was added, and the bottle covered with aluminium foil line cap, and carefully swirled vigorously before placing, in the sonicator, pre-set at a temperature (30 °C). The sample was sonicated for 10 min each for extraction sequence of n-hexane, DCM/n-hexane (1:3) and 10 mL n-hexane, respectively. The extracts from the three extraction sequences were carefully decanted into a clean amber bottle, combined and cleaned up.

The PAHs extract was cleaned-up using solid phase extraction (SPE) tubes, fitted onto a vacuum manifold with the vacuum regulated to give a flow rate of 4–5 mL/min. About 1 g Na_2SO_4 was spread over each SPE column to remove water residue in extracts. Extracts were then loaded on the n-hexane and DCM preconditioned SPE tubes and eluted. This was followed by column wash to release trapped analytes residue, by rinsing the solid phase column in 3 cycles with 3 mL DCM. The resulting eluents were concentrated to less than 1 mL in a rotary evaporator at 100 rpm and water bath temperature of 30 °C. Each sample concentrate extract was reconstituted to 1 mL in DCM, and transferred into 1 mL amber coloured vial for GC-FID analysis separation and quantitation.

3.3. Analysis of data

The Microsoft EXCEL software was used for descriptive statistics. The Weibull probabilistic and percentile ranking methodologies were utilised to determine the exceedence of detected levels of PAHs in water and sediment samples relative to quality guidelines.

4. Results and discussion

The chromatograms for the PAHs separation and quantification, in the selected water and sediment samples are presented in Figure 2.

4.1. Levels of PAHs in surface water samples of the Diep River

The seasonal averages of individual PAH detected ranged between Nd and 72.38 µg/l. Chrysene levels were dominant at all the sites with concentration levels that ranged from 11.16 ± 1.73–25.54 ± 17.92 µg/l, 3.55 ± 1.75–72.38 ± 9.58 µg/l, and 5.36 ± 3.12–41.96 ± 39.96 µg/l at DA, DB and DC sites, respectively. Site DB (near a refinery) was the most contaminated sites of these sites, with the prevalence of 3-ringed PAHs. Phe and Ant were the two 3-ringed PAHs detected at high concentrations at DB at a maximum of 37.93 µg/l and 23.00 µg/l respectively.

The water samples of the Diep River were considered to be highly contaminated with PAHs, as some of the detected PAH fractions, exceeded 0.015–5.800 µg/l water quality guideline threshold, recommended by CCME for the protection of aquatic life (Canadian Council of Ministers of the Environment (CCME), 1999).

4.2. Levels of PAHs in sediment samples of the Diep River

Sediment concentration levels of the 16 PAH fractions measured in the Diep River varied between sampling sites and seasons and are presented in Table 1.

The levels of the $\sum_{16}$PAHs in sediments of site DB were the highest and ranged between 12.05 ± 0.75 and 70.71 ± 5.32 µg/g followed by site DA, which ranged between 2.87 ± 0.14 and 11.38 ± 0.64 µg/g, and DC, 5.54 ± 0.35 and 9.81 ± 0.70 µg/g. The observed levels of Phe, (0.04 ± 0.03–15.01 ± 3.22 µg/g); Flt, (0.22 ± 0.21–6.45 ± 10.66 µg/g); Pyr, (0.29 ± 0.13–2.36 ± 1.64 µg/g); BaA, (0.79 ± 0.26–2.56 ± 1.92 µg/g); Chy, (1.92 ± 1.05–2.94 ± 0.54 µg/g); BbF, (0.81 ± 0.68–16.65 ± 2.63 µg/g); BkF, (1.24 ± 1.03–12.28 ± 6.29 µg/g); BaP, (0.13 ± 0.23–6.54 ± 2.88 µg/g); IcP, (0.30 ± 0.20–2.39 ± 1.86 µg/g), DBA (0.35 ± 0.30–3.32 ± 2.72 µg/g) and BgP, (Nd - 2.21 ± 0.09 µg/g) at site DB were significantly higher than observed in sites DC (downstream) and DA (upstream). BbF, BkF, and BaP were most concentrated in site DC sediments with concentration range, 0.30 ± 0.16–1.56 ± 1.70 µg/g; 0.71 ± 0.30–1.63 ± 0.54 µg/g and 0.62 ± 0.11–1.99 ± 1.10 µg/g respectively, while site DA had comparatively lower PAHs levels. The detected concentrations may not be unconnected with water low course traversing
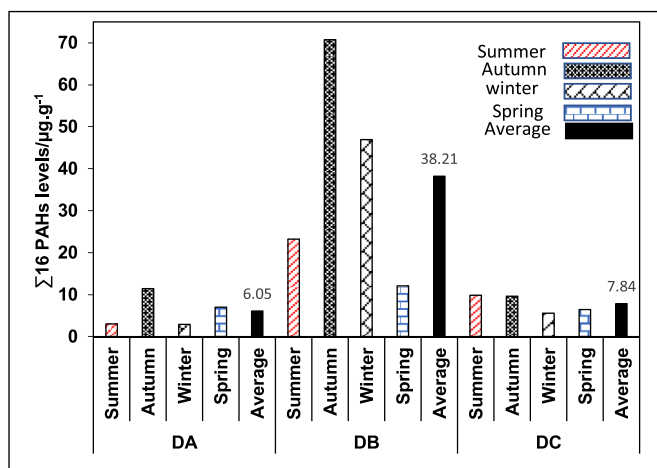
Figure 3. Seasonal variations and annual average levels of 16 US EPA PAHs in sediment samples of the Diep River.

through an industrial part and then opening up its content to the Sea. However, Nap concentration across all sampling site were comparable; DA, $(0.03 \pm 0.03$–1.81 ± 0.17 μg/g), DB, (Nd – 2.15 ± 0.15 μg/g); and DC, $(0.28 \pm 0.83$–1.63 ± 0.55 μg/g), although it was not at detectable levels during autumn and winter at site DB.

The seasonal proportion of carcinogenic PAHs observed (ranging from 2.87 μg/g to 70.71 μg/g $\sum_{16}$PAHs) in the sediment samples across all study sites was between 25.16% and 77.44%, while levels of each of the fractions in the sediment samples ranged between Nd and 16.652 μg/g. Result from this study indicated fairly higher levels of the $\sum$PAHs than those observed for lower $\sum$PAHs fractions in some African waters, but consistent with other studies elsewhere in the world. In a study reported by Nekhavhambe et al. (2014), a total PAHs concentrations of up to 14.755 μg/g in sediments (of Nzhelele River) and 61.764 μg/g in runoff sediment (from Univen parking) was previously reported for selected $\sum_6$PAHs. The relatively high $\sum_6$PAH levels measured, was attributed to automobile exhausts emission, atmospheric disposition, release from domestic heating and refuse burning, as well as discharge of lubricating oil. The level of the $\sum_{10}$PAHs reported in sediments of Vhembe District Rivers (South Africa) range 27.10–55.93 μg/g (Edokpayi et al. 2016), with the combustion of biomass identified as possibly the major source of the PAHs. da Silva et al. (2007) reported a range of 77–7751 μg/kg $\sum$PAHs in Guanabara Bay sediment in Brazil; Wang et al. (2001), 7.3–358 μg/g $\sum$PAHs in Boston Harbor, USA; Qiao et al. (2008), 2091.8–4094.4 ng/g $\sum$PAHs in Taihu lake, China; Kafilzadeh et al. (2011), $\sum$PAHs 167.4–530.3 ng/g in Kor River, Iran; Oyo-Ita et al. (2013), and Offiong et al. (2012), $\sum$PAHs ranged from 1670 to 20100

ng/g in Calabar River, Nigeria and 15.5–9770 μg/kg in Cross River, Nigeria.

The levels of PAHs detected varied with seasons, with the detected levels in autumn generally higher (Figure 3). As observed with water samples, site DB appeared to be the most contaminated site with an annual average of 38.21 μg/g for the priority Σ_{16}PAHs; attributed to being associated with industrial activity (petrochemical refinery) while site DA upstream traversing nature reserve being the least contaminated [annual average of 6.05 μg/g, priority Σ_{16}PAHs] (Figure 3).

5. Polycyclic aromatic hydrocarbon partitioning and distribution by ring size

The distribution of PAHs in water samples from the studied sites have been reported previously (Awe et al., 2020). In summary, the 4-ringed PAHs were the most abundant, followed by the 3-ringed congeners at all study sites, except for site DC where more of the 5-ringed congeners occurred more relative to the 3-ringed congeners (Table 2). The least abundant was the 2-ringed PAH. The prevalence of the 4-ringed PAHs at all the sites was attributed to pyrogenic sources while the prevalence of the of the 3-ringed PAHs at site DB relative to sites DA and DC, was attributed to petrogenic sources.

The PAH distribution obtained in sediment samples from studied sites showed that the 5-ringed PAHs were the most abundant, followed by the 4-ringed PAHs (except at DB with higher 3-ringed PAHs) as shown in Table 2. This PAHs compositional pattern in sediment samples, differed from that observed in corresponding water samples. The HMW PAHs (5- and 6- ring) had the highest proportion in contrast to the 4-ringed PAHs in water samples. The prevalence of HMW PAHs in sediment samples had been previously reported (Guo et al., 2007; Chen and Chen, 2011). This was attributed to pollution sources and the more recalcitrant nature of the HMW compounds unlike the LMW PAHs. The HMW PAHs are less susceptible to biodegradation and photo-oxidation in water (Abdel-Shafy and Mansour, 2016).

The site DB is associated with oil refining and the higher 3-ringed PAHs observed could be attributed to petroleum contamination from industrial effluent (Santos et al., 2018). The predominance of HMW PAHs relative to LMW PAHs in sediment samples had been attributed to pyrogenic PAHs from combustion of fossil fuels and vehicle exhausts (Nekhavhambe et al., 2014).

The PAH levels in sediment samples were higher than those measured in corresponding water samples. Higher levels of PAHs in sediment samples had been previously reported (Qiao et al., 2008; Ma et al., 2013; Hong et al., 2016). Sediment serves as sink for PAHs and therefore accumulates PAHs. Benzo[b]fluoranthene followed by Phe and then BkF were the PAHs with the highest concentrations measured in sediment samples. The maximum concentrations of 16.65 μg/g, 15.01 μg/g and

Table 2. Fractions of PAHs congeners in water and sediment samples of the Diep River.

PAHs		Site		
		DA	DB	DC
Water samples	% 2-ringed	4.46	3.13	4.65
	% 3-ringed	17.70	28.32	14.63
	% 4-ringed	50.14	42.06	49.23
	% 5-ringed	13.24	11.74	15.85
	% 6-ringed	14.46	14.75	15.65
Sediment samples	% 2-ringed	14.19	2.58	10.97
	% 3-ringed	11.16	25.14	11.16
	% 4-ringed	26.41	21.40	23.57
	% 5-ringed	35.31	43.93	46.36
	% 6-ringed	12.93	6.95	7.95

Site DA: Nature reserve (upstream). Site DB: Theo Marais Sports Club – industrial and residential area. Site DC: Woodbridge (downstream).

Table 3. Quality threshold limits of PAHs in water and sediment for the protection of aquatic life.

PAHs	Carcinogenicity	Water µg/L	Sediment µg/g		
		WQG	ISQG	PEL	FSSB
Naphthalene	NC	1.10000	0.03460	0.39100	0.1760
Acenaphthylene	NC	-	0.00587	0.12800	0.0059
Acenaphthene	NC	5.80000	0.00671	0.08890	0.0067
Fluorene	NC	3.00000	0.02120	0.14400	0.0774
Phenanthrene	NC	0.40000	0.04190	0.51500	0.2040
Anthracene	NC	0.01200	0.04690	0.24500	0.0572
Fluoranthene	WC	0.04000	0.11100	2.35500	0.4230
Pyrene	NC	0.02500	0.05300	0.87500	0.1950
Benzo [a] anthracene	C	0.01800	0.03170	0.38500	0.1080
Chrysene	C	-	0.05710	0.86200	0.1660
Benzo [b] fluoranthene	C	-	-	-	0.0272
Benzo [k] fluoranthene	C	-	-	-	0.2400
Benzo [a] pyrene	SC	0.01500	0.03190	0.78200	0.1500
Benzo [ghi] perylene	NC	-	-	-	0.1700
Indeno [123-cd] pyrene	C	-	-	-	0.0170
Dibenzo [ah] anthracene	C	-	0.00622	0.13500	0.0330

NC: Non-Carcinogenic. C: Carcinogenic. WC: Weakly Carcinogenic. SC: Strongly Carcinogenic. ISQG: Interim Sediment Quality Guideline. PEL: Probable Effect Level. FSSB: Freshwater Sediment Screening Benchmarks. WQG: Water Quality Guideline.
Adapted from CCME 1999; US EPA 2006.

Table 4. Summary of statistics of the tests of the Weibull distribution of the annual concentrations (µg/L) of PAHs in water samples of the Diep River.

PAHs	Weibull plots				Centile values (%)				Exceedence values		
	n	R^2	a	B	20	40	60	80	US EPA (WQG)	CCME (WQG)	Average
Nap	36	0.5733	0.8002	-1.2880	0.000	1.020	2.500	10.660	19/36 (52.70%)	19/36 (52.70%)	63.26 %
Acy	36	0.7627	0.9277	-1.3980	0.590	2.030	3.650	5.960	-	-	
Can	36	0.5019	0.8888	-0.9050	0.480	0.790	1.156	2.765	5/36 (13.88%)	5/36 (13.88)	
Flu	36	0.6367	1.0350	-1.3780	0.000	1.099	2.823	5.131	13/36 (36.10%)	13/36 (36.10%)	
Phe	36	0.8396	0.8711	-1.8620	1.018	2.710	6.405	14.130	35/36 (97.22%)	35/36 (97.22%)	
Ant	36	0.8729	1.0211	-1.6890	1.287	1.966	3.145	6.718	36/36 (100.00%)	36/36 (100.00%)	
Flt	36	0.8829	1.2000	-2.3520	1.707	4.215	6.422	9.143	30/36 (83.33%)	30/36 (83.33%)	
Pyr	36	0.2148	0.3979	-0.6674	0.000	0.079	0.610	5.768	15/36 (41.66%)	15/36 (41.66%)	
BaA	36	0.9465	1.2338	-3.6958	7.260	8.507	16.494	32.468	36/36 (100.00%)	36/36 (100.00%)	
Chy	36	0.9562	1.1890	-3.7719	7.270	14.218	18.237	32.959	-	-	
BbF	36	0.2088	0.7777	-0.7492	0.000	0.000	0.000	0.888	-	-	
BkF	36	0.5912	1.4420	-1.3014	0.000	0.000	1.432	3.852	-	-	
BaP	36	0.3987	1.1690	-1.0205	0.000	0.000	0.473	0.845	16/36 (44.44%)	16/36 (44.44%)	
IcP	36	0.9260	1.2000	-2.7790	2.904	4.237	8.156	14.462	-	-	
DBA	36	0.9540	1.3250	-3.1802	3.789	5.907	9.256	14.434	-	-	
BgP	36	0.7910	1.0755	-1.9592	1.431	2.312	3.602	9.482	-	-	

n: no of compounds. a: slope. b: intercept. US EPA: United States Environmental Protection Agency. CCEM: Canadian Council of Ministers of the Environment. WQG: Water Quality Guideline.

12.28 µg/g were recorded for BbF, Phe and BkF respectively in autumn at site DB.

5.1. Probabilistic risk assessment of PAHs in water and sediment samples

The levels of PAHs in water and sediment samples at the studied sites were evaluated through probabilistic methodologies to predict the exceedence of detected levels to available quality guidelines (Table 3). The mean levels of PAHs detected over a one-year period were ranked, utilising Weibull probabilistic approach and percentile ranking (Berninger and Brooks, 2010; Corrales et al., 2015).

5.1.1. Water sample probabilistic risk assessment

The environmental percentile distribution and percentage exceedence of the priority 16 PAHs in water samples from the Diep River is presented in Table 4. The distribution of PAHs in surface water at 80th centiles for the Diep River was estimated to range between 0.845 and 32.959 µg/L. Over 40% exceedence was estimated for strongly carcinogenic BaP, 100% exceedence for carcinogenic BaA and over 95% exceedence for Ant, based on US EPA water quality guidelines (WQG) for PAHs. The average percentage exceedent for PAHs with available US EPA (WQG) was 63.26%.

The difference in dominance of the individual PAHs may be linked to contaminant sources, with pyrogenic sources favouring the formation of ≥ 4-ringed PAHs, while petrogenic sources favours the formation of ≤ 3-ringed PAHs. Pyrogenic sources include the combustion of fossil fuel such as which occurs in automobiles, power plants, industries that burn coal and petroleum, and waste incinerators, amongst others (Dong and Lee, 2009). Petrogenic sources include crude oil and petroleum products such as kerosene, petrol, diesel, lubricating oil, and asphalt (Boonyatumanond

Table 5. Summary of statistics of the tests of the Weibull distribution of the annual concentrations (μg/g) of PAHs in sediment samples of the Diep River.

PAHs	Weibull plots				Centile values (%)				Exceedence values		
	n	R^2	a	b	20	40	60	80	US EPA (FSSB)	CCME (ISQG)	FSSB Average
Nap	36	0.8457	0.5560	-2.4532	0.0000	0.3672	1.0817	1.7719	8/36 (22.22%)	28/36 (77.77%)	63.71%
Acy	36	0.7502	0.6745	-1.7304	0.0000	0.0019	0.1006	0.2727	18/36 (50.00%)	18/36 (50.00%)	
Can	36	0.8949	0.7655	-2.4646	0.0353	0.0085	0.1511	0.6045	31/36 (86.11%)	31/36 (86.11%)	
Flu	36	0.7553	0.6151	-1.7357	0.0000	0.0289	0.1345	0.3347	20/36 (55.55%)	23/36 (63.88%)	
Phe	36	0.7559	0.4427	-1.8346	0.0251	0.0529	0.2004	2.5123	14/36 (38.88%)	25/36 (69.44%)	
Ant	36	0.7936	0.7293	-2.1123	0.0000	0.0766	0.1182	0.1613	24/36 (66.67%)	27/36 (75%)	
Flt	36	0.9625	0.7359	-3.4089	0.1348	0.4069	0.7300	2.0210	21/36 (58.33%)	30/36 (83.33%)	
Pyr	36	0.8290	0.6333	-2.0129	0.0146	0.0484	0.1361	0.4075	12/36 (33.33%)	21/36 (58.33%)	
BaA	36	0.9091	1.1550	-5.0445	0.2124	0.3398	0.5592	1.1697	34/36 (94.44%)	36/36 (100.00%)	
Chy	36	0.9492	0.7209	-3.1997	0.1010	0.2498	0.8118	2.1866	10/36 (27.77%)	32/36 (88.88%)	
BbF	36	0.9449	0.6310	-3.1278	0.1395	0.4322	0.9956	2.3319	33/36 (91.66%)	-	
BkF	36	0.8899	0.8221	-4.3132	0.2341	0.7637	1.5682	2.5498	28/36 (77.77%)	-	
BaP	36	0.9646	0.7058	-3.4844	0.1815	0.5997	1.0718	2.0597	29/36 (80.55%)	33/36 (91.66%)	
IcP	36	0.9189	0.6631	-2.7083	0.0858	0.1972	0.4835	1.1012	30/36 (83.33%)	-	
DBA	36	0.9447	0.7414	-3.0826	0.1253	0.2118	0.4825	1.1632	32/36 (88.88%)	32/36 (88.88%)	
BgP	36	0.9154	0.7103	-2.7016	0.0817	0.2367	0.2982	0.8435	23/36 (63.88%)	-	

n: number of compounds. a: slope. b: intercept. US EPA: United States Environmental Protection Agency. FSSB: Freshwater Sediment Screening Benchmarks. CCEM: Canadian Council of Ministers of the Environment. ISQG: Interim Sediment Quality Guideline.

et al., 2007). PAHs derived from anthropogenic sources may enter aquatic systems through direct discharges, run-off and atmospheric deposition (Bouloubassi et al., 2006).

5.1.2. Sediment sample probabilistic risk assessment

The environmental percentile distribution and percentage exceedence of the priority 16 PAHs in sediment samples of the Diep River is presented in Table 5.

The distribution of PAHs in sediments at 80th centiles for the Diep River was estimated to range between 0.1613 and 2.5498 μg/g. These values were higher than those estimated for the corresponding water samples. The percentage exceedence recorded for the strongly carcinogenic BaP in sediment was 80.55%, based on US EPA freshwater sediment screening benchmarks (FSSB) for PAHs. This percentage exceedence was almost two-fold greater for BaP in the corresponding surface water (44.44%).

This reaffirms the need for a holistic environmental assessment to estimate the health of the environment. A singular environmental medium assessment will not be sufficient in estimating the risk contaminants pose to humans. The estimated average US EPA FSSB exceedent percentages for the 16 priority PAHs in sediment samples was 63.71%. This study showed that sediment samples had higher US EPA (FSSB) exceedent percentage for strongly carcinogenic BaP compared to surface water and that the sediment compartment was more contaminated than the surface water.

Of note in sediments, is the high level of the Phe (3-ringed PAH), which is a major constituent of crude oil and coal tar. In a report by Santos et al. (2018), elevated levels of phenanthrene in aqueous sediment was linked to atmospheric deposition and petroleum contamination. The potential of Phe causing neurotoxicity, endocrine- and reproductive disruption, cytotoxicity, genotoxicity, oxidative damage and growth impairment in fish has been reported by Machado et al. (2014). This potential toxicity of phenanthrene, earned it a classification of priority pollutant as well as one of the most aggressive contaminants in numerous countries (Machado et al., 2014).

6. Conclusions

The 16 PAHs were detected in water and sediment samples collected from the Diep River.

The spatial and temporal levels of PAHs in water and sediment samples from the Diep River showed seasonal variations. The prevalence of Chrysene (Chy) and Benzo[a]anthracene (BaA) were noticed in water samples. In sediment samples however, Benzo[b]fluoranthene (BbF) was the compound with highest levels relative to other PAHs. The surface water and sediment samples of the Diep River were heavily impacted by carcinogenic PAHs. The probabilistic risk assessment revealed that potential risks are associated with the compounds at the levels they occurred.

Declarations

Author contribution statement

Adetunji Ajibola Awe: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Beatrice Olutoyin Opeolu: Conceived and designed the experiments.

Olatunde Stephen Olatunji: Analyzed and interpreted the data; Wrote the paper.

Olalekan Siyanbola Fatoki, Vanessa Angela Jackson, Reinette Snyman: Contributed reagents, materials, analysis tools or data.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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