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

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ABSTRACT
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 samples 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 (Booyatumanond 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) (Boulo Sour 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 Σ16PAHs 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 Σ16PAHs 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 concentrations 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...
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. Poly cyclic 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., 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. 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).

The Diep River, an important freshwater ecosystem (utilised for irrigation and recreation) in the Western Cape province of South Africa, has been reported to be negatively impacted as a result of anthropogenic activities (Jackson et al., 2009; Shuping et al., 2011; Dado 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 re-suspension 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 study. 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 ID) 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 ENV1 -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 | Site DA (μg/g) | Site DB (μg/g) | Site DC (μg/g) |
|------|---------------|---------------|---------------|
|      | (Dec to Feb)   | (Mar to May)   | (Jun to Aug)   | (Sep to Nov)   |
| Nap  | 1.81 ± 0.17   | 0.63 ± 0.37   | 0.03 ± 0.03   | 0.96 ± 0.82   |
|      | 2.15 ± 0.15   | 1.80 ± 1.06   | 0.55 ± 0.28   | 0.83 ± 0.07   |
| Acy  | 0.05 ± 0.02   | 0.04 ± 0.03   | 0.28 ± 0.33   | 0.34 ± 0.27   |
|      | 0.36 ± 0.20   | 0.44 ± 0.55   | 0.10 ± 0.17   | 0.23 ± 0.13   |
| Can  | 0.06 ± 0.03   | 0.08 ± 0.08   | 0.01 ± 0.03   | 0.04 ± 0.04   |
|      | 1.92 ± 1.24   | 0.48 ± 0.42   | 0.64 ± 0.37   | 0.34 ± 0.52   |
| Flu  | 0.12 ± 0.06   | 0.06 ± 0.07   | 0.01 ± 0.02   | 0.06 ± 0.07   |
|      | 1.84 ± 1.37   | 0.22 ± 0.16   | 0.13 ± 0.12   | 0.02 ± 0.07   |
| Phe  | 0.03 ± 0.01   | 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   |
| Ant  | 0.08 ± 0.02   | 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   |
| 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   |
| BaA  | 0.32 ± 0.27   | 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   |
| 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   |
| BbF  | Nd            | 0.19 ± 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   |
| BaP  | 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   | 4.23 ± 1.03   |
| IcP  | 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   |
| DBA  | 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 ± 1.25   | 0.30 ± 0.20   |
| BGP  | 0.14 ± 0.15   | 0.75 ± 0.54   | 0.26 ± 0.04   | 0.41 ± 0.33   |
|      | 1.60 ± 1.43   | 2.02 ± 0.99   | 0.21 ± 0.09   | 0.19 ± 0.33   |
|      | 9.79 ± 0.63   | 0.144 ± 0.10  | 0.16 ± 0.11   |
| SUM  | 2.98 ± 0.44   | 11.38 ± 0.64  | 2.87 ± 0.14   | 6.97 ± 0.30   |
| PAHs | 23.18 ± 1.77  | 70.71 ± 5.32  | 46.91 ± 3.34  | 12.05 ± 0.75 |
| % C  | 25.16         | 77.44         | 58.62         | 42.84         |
| PAHs | 58.35         | 60.79         | 57.37         | 43.20         |
|      | 59.59         | 68.52         | 67.13         | 51.31         |

4.1. Levels of PAHs in surface water 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 to 25.54 ± 17.92 μg/l, 3.55 ± 1.75 to 72.38 ± 9.58 μg/l, and 5.36 ± 3.12 to 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 SUMPAHs 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 ± 0.26–1.92 μg/g); Chy, (1.92 ± 1.05–9.58 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 ± 0.23–1.64 μg/g); DBA, (0.35 ± 0.30–3.32 ± 2.72 μg/g) and BGP, (Nd ± 22.09 μg/g) at site DB were significantly higher than observed in sites DC (downstream) and DA (upstream). BbF, BkF, and BaP were the 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 ± 0.11–1.90 ± 1.10 μg/g respectively, while site DA had comparatively lower PAH levels. The detected concentrations may not be unconnected with water low course traversing.
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 ± 0.03–1.81 ± 0.17 μg/g), DB, (Nd – 2.15 ± 0.15 μg/g); and DC, (0.28 ± 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 \(\sum_{2}\)PAHs than those observed for lower \(\sum_{15}\)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 14,775 μg/g in sediments (of Nzhelele River) and 61,764 μg/g in runoff sediment (from Univen parking) was previously reported for selected \(\sum_{3}\)PAHs. The relatively high \(\sum_{2}\)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 \(\sum_{16}\)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 77–7775 μg/kg \(\sum_{16}\)PAHs in Guanabara Bay sediment in Brazil; Wang et al. (2001), 7.3–358 μg/g \(\sum_{16}\)PAHs in Boston Harbor, USA; Qiao et al. (2008), 2091.8–4094.4 ng/g \(\sum_{16}\)PAHs in Taihu lake, China; Kalfizadeh et al. (2011), \(\sum_{16}\)PAHs 167.4–530.3 ng/g in Kor River, Iran; Oyo-Ita et al. (2013), and Offong et al. (2012), \(\sum_{16}\)PAHs ranged from 1670 to 2010 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 DA appeared to be the most contaminated site with an annual average of 38.21 μg/g for the priority \(\Sigma_{16}\)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 \(\Sigma_{16}\)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

| 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      | 21.14       | 11.16       |
|              | % 4-ringed  | 26.41      | 21.40       | 23.37       |
|              | % 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).
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 carcinogetic 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 /C21 4-ringed PAHs, while petrogenic sources favours the formation of /C20 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 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| C | -        | -             | -       | 0.1700 |
| Indeno[123-cd]pyrene| C | -        | -             | -       | 0.0170 |
| Dibenzo[ab]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  R²  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 | 13/36 (36.8%) | 13/36 (36.8%) |
| Can        | 36  0.5019 0.8888 | -0.9050 0.480 0.790 1.156 2.765 | 5/36 (13.8%) | 5/36 (13.8%) |
| Flu        | 36  0.6367 1.0350 | -1.3780 0.000 1.099 2.823 5.131 | 35/36 (97.2%) | 35/36 (97.2%) |
| Phe        | 36  0.8396 0.8711 | -1.8620 1.018 2.710 6.405 14.130 | 36/36 (100%) | 36/36 (100%) |
| Ant        | 36  0.8729 1.0211 | -1.6890 1.287 1.966 3.145 6.718 | 36/36 (100%) | 36/36 (100%) |
| Flt        | 36  0.8829 1.2000 | -2.3520 1.707 4.215 6.422 9.143 | 30/36 (81.3%) | 30/36 (81.3%) |
| Pyr        | 36  0.2148 0.3979 | -0.6674 0.000 0.079 0.610 5.768 | 15/36 (41.7%) | 15/36 (41.6%) |
| IsA        | 36  0.9465 1.2338 | -3.6958 7.260 8.507 16.494 32.468 | 36/36 (100%) | 36/36 (100%) |
| Chy        | 36  0.9562 1.1890 | -3.7719 7.270 14.218 18.237 32.959 | - | - |
| BKF        | 36  0.2088 0.7777 | -0.7492 0.000 0.000 0.000 0.888 | - | - |
| BKF        | 36  0.5912 1.4420 | -1.3041 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 (44.4%) | 16/36 (44.4%) |
| 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.
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 Olutunde: Analyzed and interpreted the data; Wrote the paper.

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

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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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 |       |       |       |       |
|------|---------------|-------|-------|-------|-------|
|      | n  | R²  | a    | b     | 20   | 40   | 60   | 80   |
| Nap  | 36 | 0.8457 | 0.5560 | -2.4532 | 0.0000 | 0.3672 | 1.0817 | 1.7719 |
| Acy  | 36 | 0.7502 | 0.6745 | -1.7304 | 0.0000 | 0.0019 | 0.1006 | 0.2272 |
| Can  | 36 | 0.8949 | 0.7655 | -2.4646 | 0.0353 | 0.0085 | 0.1511 | 0.6045 |
| Flu  | 36 | 0.7533 | 0.6151 | -1.7357 | 0.0000 | 0.0289 | 0.1345 | 0.3347 |
| Phe  | 36 | 0.7559 | 0.4427 | -1.8346 | 0.0251 | 0.0529 | 0.2004 | 2.5123 |
| Ant  | 36 | 0.7936 | 0.7293 | -2.1123 | 0.0000 | 0.0766 | 0.1182 | 0.1613 |
| Flt  | 36 | 0.9625 | 0.7359 | -3.4089 | 0.1348 | 0.4069 | 0.7300 | 2.0210 |
| Pyr  | 36 | 0.8290 | 0.6333 | -2.0129 | 0.0146 | 0.0484 | 0.1631 | 0.4075 |
| BaA  | 36 | 0.9091 | 1.1550 | -5.0445 | 0.2124 | 0.3398 | 0.5592 | 1.1697 |
| Chl  | 36 | 0.9492 | 0.7209 | -3.1997 | 0.1010 | 0.2498 | 0.8118 | 2.1866 |
| BBF  | 36 | 0.9449 | 0.6310 | -3.1278 | 0.1395 | 0.4322 | 0.9956 | 2.3319 |
| BKF  | 36 | 0.8899 | 0.8221 | -4.3132 | 0.2341 | 0.7637 | 1.5682 | 2.5498 |
| BaP  | 36 | 0.9646 | 0.7058 | -3.4844 | 0.1815 | 0.5997 | 1.0718 | 2.0597 |
| IcP  | 36 | 0.9189 | 0.6631 | -2.7083 | 0.0858 | 0.1972 | 0.4835 | 1.1012 |
| DBA  | 36 | 0.9447 | 0.7414 | -3.0826 | 0.1253 | 0.2118 | 0.4825 | 1.1632 |
| BgP  | 36 | 0.9154 | 0.7103 | -2.7016 | 0.0817 | 0.2367 | 0.2062 | 0.8435 |

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 exceedance 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 contaminant in numerous countries (Machado et al., 2014).

6. Conclusions

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