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Persistent and carcinogenic polycyclic aromatic hydrocarbons in the north-western coastal marine environment of India

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Abstract: The carcinogenic and endocrine-disrupting PAHs were investigated in surface water of the north-western creeks of India. The concentrations of ΣPAHs were found to vary in the range of 114.32–347.04 μg L^{-1}, (mean 224.78 ± 8.85 μg L^{-1}), out of which 49.12% contribution is due to ΣC-PAHs. The assessment of toxicity and biological risk arising due to individual C-PAHs was made by calculating their toxic equivalent quantity. The level of individual C-PAHs was reported exceeding the final chronic values, Canadian water quality guideline values and Netherlands maximum permissible concentration values set for the protection of aquatic life. The mean BaP concentration (10.32 ± 2.75 μg L^{-1}) was above the European Directive 2008/105/EC Environmental Quality Standards (EQS) value; while the sum of BkF + BbF (26.76 μg L^{-1}) and BghiP + InP (19.59 μg L^{-1}) were significantly higher than that set by the EQS. The results of the present study will help in understanding the global distribution and fate of PAHs which is required for implementing the necessary steps towards mitigation of the ecotoxicological risk arising due to the existence of such contaminants in the aquatic environment across the world.

Keywords: *PAHs*; eco-toxicological threat; marine pollution; creek surface water; risk assessment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) representing an important group of persistent organic pollutants (POPs) have raised concerns at a global level owing to their toxic behavior and prolonged persistence in the environment [1]. They represent a group of aromatic hydrocarbons having two or more than two fused benzene rings which are hydrophobic and are considered as ubiquitous contaminants in the marine environment. They are usually found scattered into the particulate matter, sediments and water bodies via natural and anthropogenic combustion [2,3]. PAHs having 2 or 3 rings are known as LMW (Low molecular weight) PAHs which are more prone to biodegradation as well as to photo-degradation, while PAHs with 4 to 6 rings also known as HMW (High molecular weight) PAHs have greater resistance to degradation [4]. Atmospheric deposition, oil leakages, combustion activities are the major sources for distribution and accumulation of PAHs in water, sediments and marine organisms [5–7]. Depending on their source of emission in the environment, PAHs are categorized mainly into two types: petrogenic and pyrogenic PAHs. Petrogenic PAHs arise due to spillage of crude and refined oil, while pyrogenic PAHs arise due to the combustion of fossil fuel, incineration of domestic and industrial waste, burning of biomass and production of asphalt. Previous studies have reported that PAHs of petrogenic origin are of 2 or 3 aromatic rings, while PAHs of pyrogenic origin are very often characterized by 4–6 rings [8]. The compounds are widely distributed in the aquatic environment throughout the world [9]; creating an adverse impact on aquatic life and through the food chain they pose a threat to human health [10]. They are considered harmful to the human being and marine organisms owing to their carcinogenic, mutagenic and teratogenic effects [11]. Owing to their low volatility and long-time persistence they are reported to have an adverse impact on benthic organisms [12]. In view of the environmental concerns arising due to PAHs as reported worldwide in different studies [5,6,13–17], the United States Environmental Protection Agency (USEPA) has classified 16 PAHs as priority pollutants [18].

Considering the tremendous human health hazards arising due to PAHs, scientists across the world have shown deep concerns in understanding the distribution, fate and deposition of these persistent POPs in the industrialized belts, as well as in pristine environments far away from the emission source. To have proper understanding regarding the origin of PAHs, their fate and distribution in the environment at a global level, it is necessary to have experimental based data from different parts of the world. It is expected that the key processes responsible for the global distribution of PAHs can only be identified based on such experimental data. Despite the increasing environmental pollution-related issues along the Versova and Malad creeks of Mumbai as evident from the previously published work [19,20], no scientific study was carried out to understand the distribution of PAHs residues in the aquatic ecosystem of the creek. The Malad creek also known as Marve Creek extending up to the distance of about 8km is having Versova creek to the east and Madh Island to the west having dense mangrove forest (Figure 1). The Versova creek which is having the Arabian Sea to the south is in proximity to the fisherman village where the fishing population is dependent mainly on the fishing activity as a source of income. The extensive pollution at the intersection of the Versova creek and the Arabian Sea which is the fish breeding area has raised the fish mortality. These have created a deep impact on the livelihood of the fishing population and also have raised the sustainability concern of the creek ecosystem. Because the pollution issues in Mumbai due to POPs in general and PAHs particular have not been given much attention, in the present paper attempts were made to overcome this deficit by performing the in-

depth and systematic scientific study of PAHs concentrations in the aquatic environment of the Malad and Versova Creeks situated in the north-western part of Mumbai. The present study was therefore carried out with objectives to (i) investigate the PAH distribution, composition profiles and seasonal variations in surface water of the creeks (ii) predict the different sources of PAHs and (iii) evaluate the ecological risk assessment due to individual PAH and total PAHs through a toxic equivalent quantity (TEQ) that is based on toxic equivalence factors (TEF). To predict the ecological integrity of the creeks and probable risk to the aquatic life of the creek and adjoining Arabian Sea of Mumbai, the results of the present study were compared with Environmental Quality Standards (EQS) European Directive 2008/105/EC values, Maximum Permissible Concentration (MPC) values (Netherlands), water quality guidelines values (Canada) and Final chronic values (FCV) set for aquatic life protection. The findings of the present study were also compared with that reported in water bodies across the world, to understand the probable ecotoxicological threat to the creek. The results of the present study will provide baseline information regarding the global distribution of PAHs contaminants which will further help in making policy decisions on conservation and sustainable development of marine environment across the world.

2. Experimental

2.1. Sampling procedure and preservation of samples

The thirty surface water samples were collected every time (six samples each from five different sampling locations) from the north-western Malad and Versova Creeks of Mumbai at an interval of every fifteen days for the period of two years from January 2017 to December 2018. For sampling, five different sampling locations were selected namely Mogra sewer drainage to Malad creek at N 19.166125, E 72.819649 (L1), Daravli Village at N19.160372, E 72.803370 (L2), Versova jetty at N19.143442, E72.803775 (L3), Madh Jetty at N19.144485, E72.802237 (L4) and Madh fort at N19.131927, E72.794789 (L5) along the creek as shown in Figure 1. The grab surface water sampling was done using a submersible pump from the level of 20 cm below the surface and the samples were stored in amber colored glass bottles of capacity 2.5L. To avoid the growth of micro-organisms, the collected surface water samples were maintained at pH of 2 using 4M hydrochloric acid, further, the bottles were sealed with paraffin wax and stored at −4 ^{o}C. The suspended particulate matters present in the water samples were removed by filtration through 142 cm glass fiber Whatman filters having an effective pore size of 0.7 μm. The dissolved organic compounds were retained on the mixed resins packed in a glass column of 400 mm length and 25 mm internal diameter. The mixed resin column was prepared by mixing XAD-2 and XAD-4 resins in the proportion 1:1.
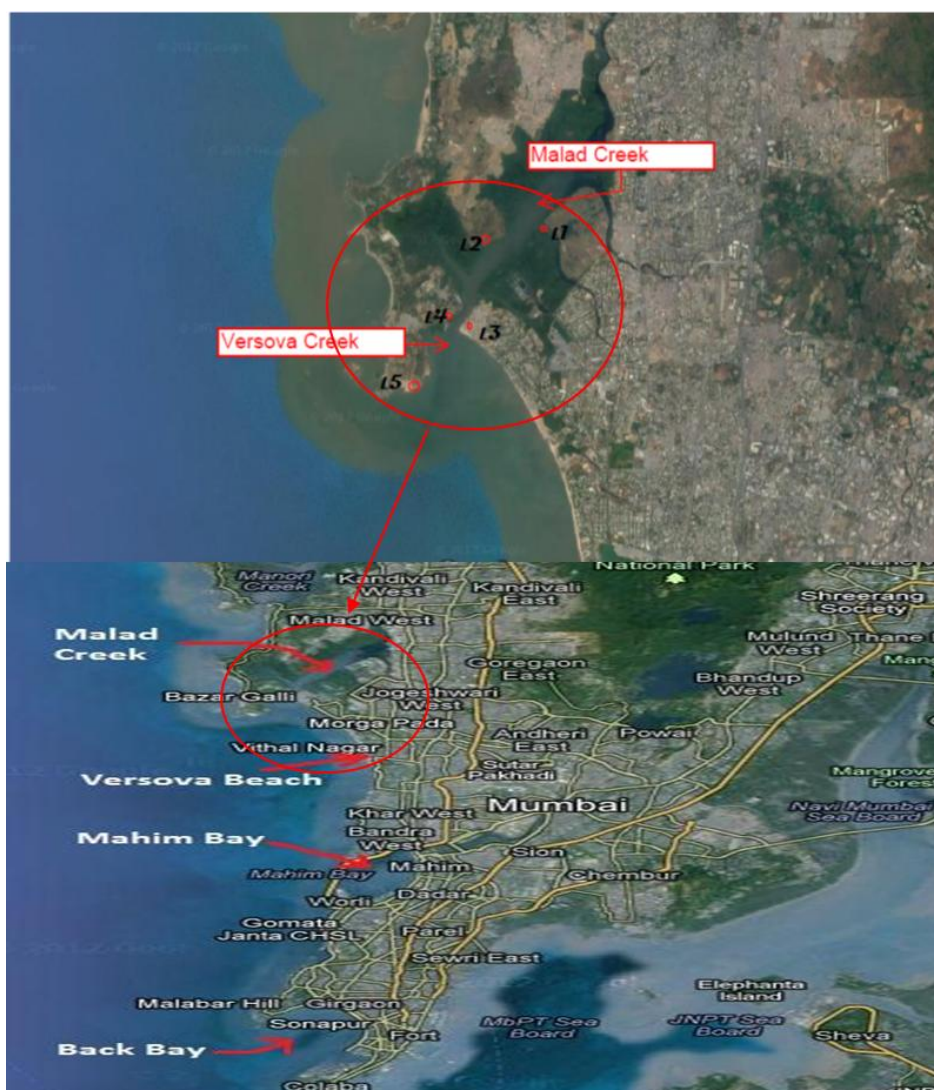
Figure 1. Geographical map indicating the different sampling stations of Malad and Versova Creek near Mumbai, India.

2.2. Reagents and chemicals

EPA Method 610 specified mixture of 16 PAHs compounds, a mixture of perdeuterated PAHs surrogates namely naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; perylene-d_{12} were supplied by Ultra Scientific Inc. (North Kingston of RI in the USA). Solid hexamethyl benzene manufactured by Aldrich Chemicals, Gillingham, Dorset, USA of 99% purity was used as an internal standard. The SRM 1491 which was used as a PAH standard reference material was supplied by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). The organic solvents used for analysis were re-distilled and used. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were extracted for 72 h in a Soxhlet extractor using dichloromethane and methanol mixture in a proportion of 1:1. The extracted silica gel and alumina were dried at room temperatures and then heated for 12 h at a temperature of 180 and 250 °C respectively. Sodium sulfate was precombusted at 450 °C and stored in an airtight container. XAD resins, supplied by Supelco, were treated with methanol using a Soxhlet extractor to remove the polymeric impurities and further

soaked in methanol before analysis. During the actual analysis, the methanol from the resin column was removed by elution using distilled water. The target analytes of the present study 17 EPA priority PAH compounds namely Acenaphthene (Ace), Acenaphthylene (Acy), Anthracene (Ant), Benzo (a) anthracene (BaA), Benzo(a)pyrene (BaP), Benzo(e)pyrene (BeP), Benzo(b)fluoranthene (BbF), Benzo(g,h,i)perylene (BghiP), Benzo(j)fluoranthene (BjF), Benzo(k)fluoranthene (BkF), Chrysene (Chr), Dibenzo(a,h)anthracene (DahA), Fluoranthene (Fla), Fluorene (Flu), Indeno (1,2,3,-c,d) pyrene (InP), Phenanthrene (Phe) and Pyrene (Pyr).

2.3. Analytical methodology

Since detailed discussion regarding the procedures adopted for elution of dissolved organics from XAD resins and processing glass fiber filters is made by [21], only a short explanation is mentioned here. The spiked surrogate standards on the XAD resin column were first eluted with methanol (50 mL) and then with dichloromethane (50 mL) by adjusting the solvent flow rate of 5 mL min^{-1}. Further, the column resins were taken in the flask and equilibrated with 2:1 mixture of dichloromethane and methanol using an ultrasonic bath. Both the extracts were combined and back-extracted three times using equivalent amount (as the volume of MeOH) of a saturated solution of sodium chloride and dichloromethane (50mL). The residual methanol from the dichloromethane fraction was removed by extraction using distilled water, while the residual water from the dichloromethane fraction was removed by passing through a glass column packed with 15 g of precombusted anhydrous sodium sulfate.

The sample extract was reduced to nearly 1 mL under a gentle flow of nitrogen. Concentrated extracts were fractionated on 1:2 alumina: silica gel glass column by successively eluting with solvents like n-hexane (15mL), 70 mL of dichloromethane and n-hexane mixture prepared in the ratio 3:7 and methanol (30mL). By blowing nitrogen gas, the second fraction containing PAHs was ultimately reduced to nearly 0.2 mL to which a known amount of internal standard was added before the actual instrumental analysis. The above experimental scheme is graphical represented in Figure 2.

2.4. Instrumental analysis

The quantitative analysis of PAHs was performed using gas chromatograph (GC) (model HP-5890A) coupled with mass spectrometer (MS) (model HP-5973MSD) working in selective ion monitoring and 70 eV electron impact modes. For analysis, a capillary column HP-5MS (50 m × 0.32 mm × 0.17 μm film thickness) was used. The carrier gas used was helium (99.999%) at the constant flow rate of 1.5 mL min^{-1}. The 1 μL of concentrated sample was injected in a splitless mode. During the GC analysis, the temperature of the injector and detector were maintained respectively at 270 ºC and 280 ºC. The temperature of the oven was maintained initially constant at 60 ºC for the period of 5min, and then raised to 290 ºC at the rate of 3 ºC per minute which was kept constant for further 40 min. The identification of sample chromatographic peak was made based on their mass spectra and retention time. The quantification of the individual PAH component was made by using the internal calibration method by plotting a five-point calibration curve.
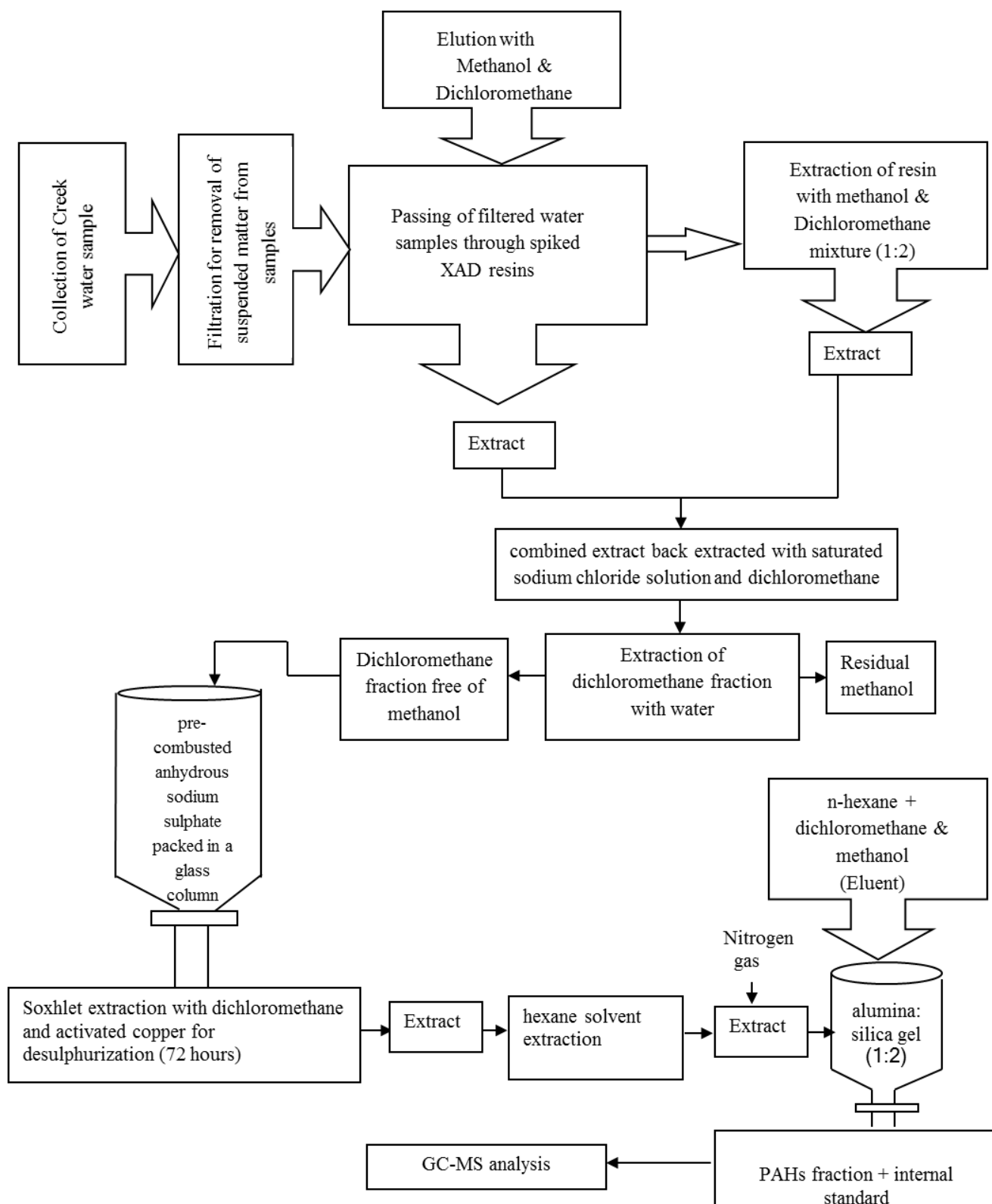
Figure 2. Graphical representation showing the experimental scheme followed during the analysis of PAHs in creek water samples.

2.5. QA and QC analytical procedures

As a part of quality assurance and control procedures, weekly calibration of analytical instruments was made using reference materials. In the present study all the experimental data were subjected to a strict quality control procedure by performing the routine field samples analysis in duplicate, analysis of procedural blanks (solvents) and spiked blanks (solvents spiked with 16 PAHs standards). The sample analysis in duplicate was made to eliminate the error arising during the extraction of the sample, the results of which showed satisfactory precision. During every sampling period, distilled water carried in glass bottles was subjected to the actual field environment which was treated as a field blank. The field blanks thus obtained were given similar treatment to that given for the field samples. The analysis of field blank and procedural blank samples does not indicate any detectable level of target analytes. The average recoveries of perdeuterated PAHs surrogates namely naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} in creek water samples was found to vary in the range of $90.5 \pm 8.7\%$ to $102 \pm 5.3\%$. The correction of reported PAHs concentrations was made based on the recoveries of surrogates. The PAHs recoveries in the NIST SRM 1491 were in the range of 89% to 105% of the certified values. The limit of detection for different PAHs was in the range of 0.009 to 1.9 ng L^{-1} and it was found to be three times of S/N level in blank samples. During duplicate analysis of PAHs in the water sample, the relative standard deviation (RSD) was in the order of 4% to 10%.

2.6. Statistical analysis

The results of the present study were subjected to statistical analysis by application of one-way ANOVA method based on the significance criteria of P<0.05 and P<0.01. For performing various statistical calculations, the IBM SPSS version 20 statistical software was utilized.

3. Results and discussion

3.1. PAHs distribution in Malad and Versova Creek water

The mean concentration of individual PAHs based on their ring sizes, carcinogenic PAHs detected at different sampling stations, as well as the overall mean concentration is presented in Table 1. The overall mean concentrations (μg L^{-1}) of individual PAHs increased in the order of: Acy $(1.97 \pm 0.82) <$ Ace $(2.07 \pm 0.77) <$ BjF $(7.77 \pm 3.01) =$ InP $(7.77 \pm 3.52) <$ Ant $(8.59 \pm 2.93) <$ BkF $(9.11 \pm 2.79) <$ BaP $(10.32 \pm 2.75) <$ BghiP $(11.82 \pm 3.15) <$ Flu $(11.88 \pm 3.27) <$ BeP (12.47 ± 4.97) $<$ BaA $(15.35 \pm 7.02) <$ DahA $(15.36 \pm 5.26) <$ BbF $(17.65 \pm 8.42) <$ Phe $(19.34 \pm 8.31) <$ Pyr $(20.49 \pm 7.00) <$ Fla $(25.74 \pm 6.79) <$ Chr (27.08 ± 11.33). Based on the overall mean concentration, Chr (12.05%), Fla (11.45%) and Pyr (9.12%) were the three most abundant PAHs (Table 1). Apart from the heavily polluted creeks, the acceptable levels of individual PAH in surface and coastal waters are 0.05 μg L^{-1} while levels above 10000 μg L^{-1} suggest heavy PAHs pollution [22]. Higher PAH concentration gives an indication from the industrial point sources and shipyards, atmospheric deposition and urban runoff. In the present study, the overall mean PAHs concentrations found in the creek water at five different sampling stations (224.78 ± 8.85 μg L^{-1}) are several orders of magnitude higher than those reported in seawater of Hainan Island, China [23] and superficial water from the Japaratuba River, Brazil [24]. The level of PAHs as reported in the present study was comparable

with the PAHs level in some creeks of Niger Delta, Nigeria [25]; in Quanzhou Bay, China [26] and in Bufalo River estuary in the Eastern Cape Province, South Africa [27]. However, the PAHs level reported in the creek water of the present study was much lower than that reported in the Mvudi and Nzhelele Rivers, South Africa [28] and in rivers, surface runoff at Thohoyandou, Limpopo Province, South Africa [29]. The total PAH concentrations found in creek water of the present study are compared with those reported earlier by other researchers in water bodies from different part of the world (Table 2).

Concerning the ring size, the overall average percentage contribution of 2-, 3-, 4-, 5- and 6-ring PAHs to the ΣPAHs was 1.80, 17.71, 39.44, 32.33 and 8.72% respectively (Table 1). Based on the percentage contribution of 17 PAHs based on ring size detected in the present study indicate the dominance of 4-rings PAHs followed by 5 and 3- ring PAHs. Similar dominance of 3, 4 and 5 ring PAHs was also observed along the Japaratuba River, Brazil [24]. Such PAHs assemblages are generally released due to pyrolysis/combustion of fossil materials, which finally enters the marine environment via coastal and river runoff [30,31]. The overall mean concentrations of 2 and 3-rings LMW PAHs in the water samples was in the range of 23.10–77.17 $\mu g\ L^{-1}$ with a mean value of 43.85 ± 7.77 $\mu g\ L^{-1}$, while the concentrations of 4, 5 and 6-rings HMW PAHs was found to vary in the range of 89.50–279.06 $\mu g\ L^{-1}$ with a mean of 180.93 ± 8.74 $\mu g\ L^{-1}$. Thus overall results indicate that the major contribution of 80.50% was due to the HMW PAHs as compared to the 19.50% contribution of LMW PAHs to the ∑PAH (Table 1). Previous studies have reported that the less volatility of HMW PAHs [32] and their wide range of emission sources like domestic heating, industrial emissions, and agriculture-related activities [33] are responsible for their exceeding concentration over LMW PAHs. The total of 8 PAHs namely BaA + BaP + BbF + BjF + BkF + Chr + DahA + InP are reported to be carcinogenic PAHs (ΣC-PAHs) [34]. The overall result of the present study indicated that ΣC-PAHs was found to vary in the concentration range of 54.09–186.59 $\mu g\ L^{-1}$ with a mean concentration of 110.41 ± 8.76 $\mu g\ L^{-1}$ which contribute to 49.12% to the ∑PAHs (Table 1). The overall maximum contribution to the ΣC-PAHs was due to Chr (24.52%) which decreases in the order of BbF (15.98%) > BaA (13.91%) > DahA (13.91%) > BaP (9.35%) > BkF (8.25%) > BjF (7.04%) = InP (7.04%) (Table 1).

Table 1. Mean total concentration of PAHs in the surface water samples from Versova and Malad Creek near Mumbai, India. (Values in $\mu g.L^{-1}$).

PAHs	Aroma tic rings	L1	L2	L3	L4	L5	Overall Mean sd($\pm$)	Range	% contribution to $\sum$PAHs (overall)	% contribution to $\sum$C-PAHs (overall)
Ace	2	1.75	2.05	2.11	2.99	1.43	2.07 $\pm$0.77	0.98–4.36	0.92	
Acy	2	1.88	1.83	2.30	2.56	1.29	1.97 $\pm$0.82	0.85–5.14	0.88	
Ant	3	8.58	7.71	7.30	12.52	6.83	8.59 $\pm$2.93	3.73–16.02	3.81	
Flu	3	11.16	10.52	10.47	15.92	11.34	11.88 $\pm$3.27	5.54–19.48	5.28	
Phe	3	29.41	16.58	13.04	21.88	15.80	19.34 $\pm$8.31	6.35–52.50	8.61	
Fla	4	26.06	23.38	20.00	31.81	27.42	25.74 $\pm$6.79	9.53–44.55	11.45	
Pyr	4	21.24	18.02	15.30	28.38	19.52	20.49 $\pm$7.00	7.75–45.61	9.12	
BeP	5	11.90	8.06	12.42	20.48	9.48	12.47 $\pm$4.97	5.49–27.95	5.55	
BghiP	6	13.77	11.31	8.96	13.31	11.75	11.82 $\pm$3.15	5.78–19.88	5.26	
BaA	4	13.15	21.30	10.60	19.09	12.63	15.35 $\pm$7.02	6.33–47.45	6.83	13.91
Chr	4	41.49	21.90	19.60	28.54	23.85	27.08 $\pm$11.33	14.07–71.08	12.05	24.52
BaP	5	12.14	10.09	8.48	11.33	9.54	10.32 $\pm$2.75	5.94–20.26	4.59	9.35
BbF	5	28.62	14.80	8.54	15.87	20.42	17.65 $\pm$8.42	4.59–47.53	7.85	15.98
BjF	5	10.43	5.70	4.71	10.34	7.66	7.77 $\pm$3.01	3.23–16.79	3.46	7.04
BkF	5	10.17	8.81	6.19	11.86	8.52	9.11 $\pm$2.79	3.22–16.98	4.05	8.25
DahA	5	13.12	14.06	14.15	22.85	12.63	15.36 $\pm$5.26	6.79–31.41	6.83	13.91
InP	6	8.58	4.67	5.91	13.35	6.35	7.77 $\pm$3.52	2.49–18.22	3.46	7.04
$\sum$C-PAHs*		137.69	101.33	78.19	133.22	101.62	110.41 $\pm$8.76	54.09–186.59	49.12	100.00
$\sum$2-rings PAHs		3.63	3.88	4.42	5.55	2.71	4.04 $\pm$0.79	1.83–8.92	1.80	
$\sum$3-rings PAHs		49.14	34.81	30.81	50.32	33.98	39.81 $\pm$7.04	19.29–73.30	17.71	
$\sum$4-rings PAHs		101.93	84.60	65.51	107.82	83.42	88.66 $\pm$9.45	41.25–141.22	39.44	
$\sum$5-rings PAHs		86.37	61.52	54.49	92.73	68.27	72.68 $\pm$6.04	35.91–112.02	32.33	
$\sum$6-rings PAHs		22.36	15.98	14.87	26.66	18.10	19.59 $\pm$3.90	9.57–33.71	8.72	
$\sum$LMW PAHs (2+3 rings)		52.77	38.69	35.23	55.87	36.69	43.85 $\pm$7.77	23.10–77.17	19.50	
$\sum$HMW PAHs (4+5+6 rings)		210.66	162.10	134.87	227.21	169.79	180.93 $\pm$8.74	89.50–279.06	80.50	
$\sum$PAHs (2+3+4+5+6 rings)		263.44	200.79	170.10	283.08	206.48	224.78 $\pm$8.85	114.32–347.04	100.00	

*Note: C-PAHs = BaA + BaP + BbF + BjF + BkF + Chr + DahA + InP

Table 2. Distribution of PAH in the aquatic environment from various regions around the world (Values in $\mu g.L^{-1}$).

Location	Year of Sampling	N^a	PAHs Range	References
Thohoyandou, Limpopo Province, South Africa	2005–2006	6	29.2 to 3064.8	[29]
South East Rivers State, Niger Delta	-	16	8 – 249	[25]
Cauca River , Colombia	2010–11	12	0.052–12.888	[15]
Mithi River, Mumbai	2009–11	17	70.19–257.33	[16]
Mvudi and Nzhelele Rivers, South Africa	-	16	13174–26382	[28]
Alexandria coastal Sea water, Egypt	-	16	8.971–1254.756	[61]
Bufalo River Estuary in the Eastern Cape Province, South Africa	2015–16	16	14.91–206	[27]
Malad and Versova creek, Mumbai	2017–18	17	114.32–347.04	Present Study

Table 3. Diagnostic PAH ratios used to infer sources.

PAHs ratios	L-1	L-2	L-3	L-4	L-5	Mean	Vehicles [62,63]	Gasoline exhaust [64,65]	Firewood fire [65]	Coal [62, 65-67]	Diesel [64]	Coke oven [63]
BaP/BghiP	0.88	0.89	0.95	0.85	0.81	0.88	0.3–0.78	0.3–0.4	-	0.9–6.6	0.46–0.81	5.1
Phe/Ant	3.43	2.15	1.79	1.75	2.31	2.29	2.7	3.4–8	3	3	7.6–8.8	0.79
BaA/Chr	0.32	0.97	0.54	0.67	0.53	0.61	0.63	0.28–1.2	0.93	1.11	0.17–0.36	0.70
BeP/BaP	0.98	0.80	1.46	1.81	0.99	1.21	-	1.1–13	0.44	0.84–1.6	2–2.5	2.6
Ant / Ant + Phe	0.23	0.32	0.36	0.36	0.30	0.31	-	-	-	-	-	-
BaA/ BaA + Chr	0.24	0.49	0.35	0.40	0.35	0.37	-	-	-	-	-	-
Fla/ Fla + Pyr	0.55	0.56	0.57	0.53	0.58	0.56	-	-	-	-	-	-
LMW/HMW PAHs	0.25	0.24	0.26	0.25	0.22	0.24	-	-	-	-	-	-

3.2. PAHs source analysis

The identification and assessment of PAHs emission source based on their diagnostic ratio is the common practice adopted by the present-day researchers. Based on the diagnostic ratios the researchers have identified the PAH pollutants as being originated from petroleum combustion or due to the coal and biomass burning. Such diagnostic ratios also help to differentiate the origin of PAHs due to diesel emission or due to the combustion of gasoline [35]. Because the compounds involved in each of the PAH diagnostic ratios have nearly the same molecular weight, the researchers have assumed their identical physicochemical properties [36].

In the present study, the same technique has been employed to identify the probable PAHs sources. The PAHs compositional pattern gives interesting information on their probable sources of emission in the environment [37]. The major pyrogenic sources of PAHs include incomplete combustion of wood and fossil fuels while oil and petroleum leakage constitute petrogenic sources [38]. It was reported previously that the high-temperature combustion process like vehicular exhaust, anthropogenic combustion or pyrogenic sources are the major sources leading to the liberation of 4 to 6 rings HMW PAHs in the environment [39]. Previous researchers suggested that combustion processes taking place at low to moderate temperatures burning of coal will be responsible for contributing 2 to 3- rings LMW PAHs in the environment [40]. Pyrogenic sources will increase the concentration of HMW PAHs over LMW PAHs thereby reducing LMW/HMW ratios below 1. On the other hand, petrogenic sources will increase the concentration of LMW PAHs over HMW PAHS resulting in increasing the value of LMW/HMW ratio above 1 [41,42]. In the present study, the calculated ratio values of LMW/HMW PAHs in the creek water samples were 0.25 (L1), 0.24 (L2), 0.26 (L3), 0.25 (L4) and 0.22 (L5) with an overall value of 0.24 (Table 3). Similar results were also observed in the surface water of Bufalo River Estuary, South Africa and Tiber River estuary, Italy in which the concentration of HMW PAHs was greater than LMW PAHs making the value < 1 [27,43]. The LMW/HMW PAHs ratio value below 1 suggests the major influence of pyrogenic emission sources [44]. The persistence of HMW PAHs in the sediments which get released back in the aquatic environment is responsible for their dominance making the LMW/HMW PAHs ratio value below 1 [45]. Some researchers have also used the Fla/ (Fla + Pyr) ratio to identify the source of PAH pollution in the environment [46]. The ratio values below 0.4 indicate petroleum contamination; values in the range of 0.4–0.5 indicate the origin of PAHs due to petroleum combustion; ratio values greater than 0.5 suggests biomass combustion as a source of PAHs [47]. In the present investigation, the calculated Fla/ (Fla + Pyr) ratio values were 0.55 (L1), 0.56 (L2), 0.57 (L3), 0.53 (L4) and 0.58 (L5) with an overall mean value of 0.56 which indicate the pyrogenic source of PAHs emission in the study area due to the combustion of biomass like grass, wood, and coal (Table 3) [47]. Similar results were also observed in the surface water of Tiber River estuary, Italy in which the Fla/ (Fla + Pyr) ratio values were found to exceed 0.5 indicating a variable impact from urban traffic emissions and biomass burning [43]. The high thermodynamic stability of Phe over Ant is also used to differentiate the pyrogenic and petrogenic sources of PAHs in the environment. According to some researchers, the ratio value of An / (An+Phe) less than 0.1 indicate the petrogenic source (petroleum contamination), while the ratio value greater than 0.1 suggest pyrogenic (combustion) sources of PAHs in the environment [46]. The results of our study indicate that the calculated Ant/ (Phe + Ant) ratio values were 0.23 (L1), 0.32 (L2), 0.36 (L3), 0.36 (L4) and

0.30 (L5) with an overall the mean value of 0.31, indicating the pyrogenic source of PAHs emission in the present study area (Table 3). Similar results were also observed in the surface water of Tiber River estuary, Italy in which the Ant/ (Ant+Phe) ratio values were found to exceed 0.1 which attributed the origin of PAHs to pyrogenic sources [43]. Some researchers have calculated the BaA / (Chr+BaA) ratio to differentiate between the petroleum, coal combustion and vehicular emission sources of PAHs in the environment [48]. The ratio value less than 0.20 suggests the petroleum source; values ranging from 0.20 to 0.35 suggest the coal combustion source while values exceeding 0.35 indicate vehicular emission source of PAHs in the environment [48]. In the present study, the calculated values of BaA/ (Chr+BaA) ratio were 0.24 (L1), 0.49 (L2), 0.35 (L3), 0.40 (L4) and 0.35 (L5) with an overall average value of 0.37 indicating that the PAHs in the study area might have arisen due to the vehicular emissions (Table 3). Similar results were also observed in the surface water of Tiber River estuary, Italy in which the BaA/ (Chr+BaA) ratio values were found to exceed 0.35 suggesting vehicular emissions [43]. The overall results suggest that pyrogenic sources like the combustion of fossil fuels and vehicular emissions are responsible for PAHs emission in the study area which was also supported by the results of previous the investigation performed along the Harbour Line, Mumbai, India [49]. The ratio of BaP/BghiP gives valuable information to differentiate between traffic and non-traffic emissions of PAHs in the environment. The ratio values < 0.6 indicate non-traffic emission, while the values > 0.6 indicate traffic emission [50]. In the present study, the calculated values of ratio were 0.88 (L1), 0.89 (L2), 0.95 (L3), 0.85 (L4) and 0.81 (L5) with an overall average value of 0.88 suggesting coal as an emission source of PAHs in the environment (Table 3). Other PAHs ratios like Phe/Ant, BaA/Chr and BeP/BaP with PAHs isomers of identical molecular weight have also been used to identify the sources of PAH emission (Table 3). The PAHs diagnostic ratios values calculated at different sampling stations of the present study area, suggests coal, vehicle and gasoline combustion as the major sources responsible for emission of PAHs.

3.3. Toxicity risk assessment of PAH isomers

Bioaccumulation of PAHs in food chains will create extreme toxicological and biological impacts on biota and even human beings [51]. Therefore, in the present section we have given more stress on potential toxicological impacts of PAHs on the biological life present in the aquatic marine environment. It is reported that LMW PAHs possess high lethal toxicity in comparison to HMW PAHs [52]. Previous studies have reported LC_{50} below 10 µg L^{-1} for various marine organisms like mysid [53]. In the present investigation, the maximum mean total PAHs concentration in the water samples were found at L4 (283.08 µg L^{-1}) while the minimum concentration was found at L3 (170.10 µg L^{-1}), with an overall mean PAHs concentration of 224.78 ± 8.85 µg L^{-1}. The PAH level in the creek water samples of the present study clearly shows the concentrations exceeding 10 µg L^{-1} which might create the acute toxicity threat to the biological life of the creek [52]. The PAHs level of our study were found to exceed the previously reported values of 0.012–0.4996 µg L^{-1} in the water samples of Suez Canal, Egypt [54]; 0.103–2.667 µg L^{-1} in the water samples of Blachownia reservoir, South Poland [55]. Among PAHs, carcinogenic PAHs possess extreme threat owing to their potentially carcinogenic toxicities. In the present study the ΣC-PAHs levels in the sampling locations L1 (137.69 µg L^{-1}), L2 (101.33 µg L^{-1}), L3 (78.19 µg L^{-1}), L4 (133.22 µg L^{-1}) and L5 (101.62 µg L^{-1}) of the Malad and Versova creek which accounts for 52.27, 50.47, 45.96, 47.06 and

49.22% of the ΣPAHs. The overall ΣC-PAHs concentration level in the marine aquatic environment of the Malad and Versova creeks was 110.41 ± 8.76 μg L^{-1} which corresponds to 49.12% of the ΣPAHs.

The toxicity assessment of carcinogenic PAHs in the present study was made based on toxic equivalency factors (TEFs) of BaP. To estimate the carcinogenic toxicity of C-PAHs, toxic equivalent quantity (TEQ) was calculated as a product of the concentration of individual C-PAH and the corresponding TEF value of BaA (0.1), Chr (0.01), BbF (1), BkF (0.1), BaP (0.1), InP (0.1), and DahA (1) [56] using the following equation:

$$TEQ_{PAHs} = TEF_i \text{ x } C_{PAHi}$$
(1)

Where, C_{PAHi} is the concentration of individual carcinogenic PAH in μg L^{-1}; TEF_i is the toxic equivalence factor of corresponding C-PAHs relative to BaP. In the present investigation, the total TEQ_{PAHs} calculated for the creek water samples were L1 (46.56 μg L^{-1}), L2 (33.57 μg L^{-1}), L3 (26.00 μg L^{-1}), L4 (44.57 μg L^{-1}) and L5 (36.99 μg L^{-1}) with an overall mean value of 37.54 μg L^{-1}. The TEQ values for different carcinogenic PAHs detected in the aquatic marine environment of Malad and Versova creeks of Mumbai are presented in Table 4.

The experimental findings of our study indicated that the overall mean BaP concentration in the creek water samples (10.32 ± 2.75 μg L^{-1}) was found to exceed the value of 0.05 μg L^{-1} suggested by European Directive 2008/105/EC EQS; while BkF + BbF value (26.76 μg L^{-1}) and BghiP + InP value (19.59 μg L^{-1}) were extremely high than the values of 0.03 and 0.002 μg L^{-1} respectively as suggested by the Environmental Quality Standards (EQS) indicating the probable ecological risk to the creek ecosystem. Similar findings were reported previously at Tiber River of Italy where the researchers have observed the BaP level of 0.0122 μg L^{-1}, while BkF + BbF and BghiP + InP values were calculated as 0.0248 and 0.0348 μg L^{-1} respectively [43]. The observed overall mean concentration level of BaA (15.35 ± 7.02 μg L^{-1}), BaP (10.32 ± 2.75 μg L^{-1}), Chr (27.08 ± 11.33 μg L^{-1}), Fla (25.74 ± 6.79 μg L^{-1}), BbF (17.65 ± 8.42 μg L^{-1}) and DahA (15.36 ± 5.26 μg L^{-1}) were above the Final chronic (FCV) values of 3.8, 1.6, 3.5, 12, 1.1 and 0.6 μg L^{-1} respectively suggested for protection of aquatic life [57]. The overall mean concentration levels of Ant (8.59 ± 2.93 μg L^{-1}), BaA (15.35 ± 7.02 μg L^{-1}), BaP (10.32 ± 2.75 μg L^{-1}), Chr (27.08 ± 11.33 μg L^{-1}), Phe (19.34 ± 8.31 μg L^{-1}), Fla (25.74 ± 6.79 μg L^{-1}), BghiP (11.82 ± 3.15 μg L^{-1}), BkF (9.11 ± 2.79 μg L^{-1}) in the present study were higher than the Netherlands maximum permissible concentration (MPCs) values of 0.07, 0.01, 0.05, 0.34, 0.3, 0.3, 0.033 and 0.04 μg L^{-1} [58]. The overall mean concentration values of Ant (8.59 ± 2.93 μg L^{-1}), BaA (15.35 ± 7.02 μg L^{-1}), BaP (10.32 ± 2.75 μg L^{-1}), Phe (19.34 ± 8.31 μg L^{-1}), Pyr (20.49 ± 7.00 μg L^{-1}), Flu (11.88 ± 3.27 μg L^{-1}) and Fla (25.74 ± 6.79 μg L^{-1}) were reported higher than the maximum limit of 0.012, 0.018, 0.015, 0.4, 0.025, 3.0 and 0.04 μg L^{-1} respectively suggested by the Canadian water quality guidelines essential for the protection of aquatic life [59]. Based on the overall toxicity assessment indicate the probable ecological threat to the marine biological life of the Malad and Versova creek.

Table 4. Toxic equivalent quantity (TEQ) for various C-PAHs detected in the surface water of Versova and Malad Creek near Mumbai, India.

Sampling Stations		L-1		L-2		L-3		L-4		L-5	
C-PAHs	Toxic Equivalency Factors (TEFs)	Observed concentration (μg L^{-1})	TEQ (μg TEQ L^{-1})	Observed concentration (μg L^{-1})	TEQ (μg TEQ L^{-1})	Observed concentration (μg L^{-1})	TEQ (μg TEQ L^{-1})	Observed concentration (μg L^{-1})	TEQ (μg TEQ L^{-1})	Observed concentration (μg L^{-1})	TEQ (μg TEQ L^{-1})
BaA	0.1	13.15	1.32	21.3	2.13	10.6	1.06	19.09	1.91	12.63	1.26
BaP	0.1	12.14	1.21	10.09	1.01	8.48	0.85	11.33	1.13	9.54	0.95
BbF	1	28.62	28.62	14.8	14.80	8.54	8.54	15.87	15.87	20.42	20.42
BkF	0.1	10.17	1.02	8.81	0.88	6.19	0.62	11.86	1.19	8.52	0.85
Chr	0.01	41.49	0.41	21.9	0.22	19.6	0.20	28.54	0.29	23.85	0.24
DahA	1	13.12	13.12	14.06	14.06	14.15	14.15	22.85	22.85	12.63	12.63
InP	0.1	8.58	0.86	4.67	0.47	5.91	0.59	13.35	1.34	6.35	0.64
			Total TEQ$_{PAHs}$ 46.56		Total TEQ$_{PAHs}$ 33.57		Total TEQ$_{PAHs}$ 26.00		Total TEQ$_{PAHs}$ 44.57		Total TEQ$_{PAHs}$ 36.99	

Mean of Total TEQ$_{PAHs}$ = 37.54

Table 5. Correlation coefficient matrix for individual PAH isomers in the surface water samples collected along Versova and Malad Creek near Mumbai, India.

PAHs isomers	Ace	Acy	Ant	BaA	BaP	BeP	BbF	BghiP	BjF	BkF	Chr	DahA	Fla	Flu	InP	Phe	Pyr
Ace	1.000																
Acy	0.847	1.000															
Ant	0.860	0.733	1.000														
BaA	0.720	0.645	0.661	1.000													
BaP	0.597	0.628	0.714	0.712	1.000												
BeP	0.769	0.638	0.805	0.350	0.471	1.000											
BbF	−0.047	−0.017	0.221	0.101	0.532	0.091	1.000										
BghiP	0.509	0.414	0.619	0.548	0.724	0.458	0.630	1.000									
BjF	0.360	0.274	0.583	0.269	0.634	0.597	0.713	0.709	1.000								
BkF	0.521	0.353	0.674	0.502	0.619	0.559	0.499	0.737	0.689	1.000							
Chr	0.198	0.245	0.413	0.189	0.651	0.331	0.845	0.657	0.752	0.545	1.000						
DahA	0.852	0.664	0.806	0.590	0.486	0.823	0.040	0.574	0.461	0.605	0.236	1.000					
Fla	0.549	0.450	0.684	0.503	0.602	0.613	0.490	0.727	0.709	0.724	0.467	0.673	1.000				
Flu	0.693	0.505	0.753	0.494	0.539	0.764	0.225	0.691	0.594	0.684	0.346	0.831	0.716	1.000			
InP	0.608	0.490	0.743	0.226	0.411	0.834	0.309	0.504	0.681	0.643	0.458	0.696	0.637	0.640	1.000		
Phe	0.318	0.327	0.508	0.296	0.669	0.403	0.832	0.667	0.765	0.581	0.927	0.360	0.535	0.388	0.535	1.000	
Pyr	0.702	0.568	0.783	0.572	0.663	0.735	0.428	0.727	0.706	0.695	0.481	0.744	0.752	0.785	0.731	0.560	1.000

3.4. Statistical correlation

The statistical correlation data in the present work was adopted to understand the origin of PAHs compounds. It provides us the information if the PAHs compounds detected in the creek water sample originated from the same source or from different sources. The correlations between the individual PAHs were studied by the previous researchers with an intention to predict the origin of the PAHs from identical or from different sources [60]. In the present study, based on the correlation coefficients matrix between the individual PAHs, it was observed that a significant positive correlation exists between most of the compounds (Table 5). In-depth analysis of the correlation data indicate that correlation coefficient values were quite significant having values higher than 0.5 in the majority of cases having $P<0.01$ or $P<0.05$ indicating that PAHs in the present study area might have arise from the identical sources (Table 5).

4.. Conclusions

Based on the results of the present study it can be concluded that the overall mean PAHs concentrations (157.96 ± 4.91 μg L^{-1}) found in creek surface water at five different sampling stations of north-western Malad and Versova creeks of Mumbai were significantly higher than that reported in water bodies across the world. The contribution of 4, 5 and 3 ring PAHs to the ∑PAHs were 39.57, 32.26 and 17.67% respectively. The concentrations of HMW PAHs (180.93 ± 8.74 μg L^{-1}) and LMW PAHs (43.85 ± 7.77 μg L^{-1}) which corresponds to 80.50 and 19.50% contribution to the ΣPAH. The overall mean concentration of ΣC-PAHs (110.41 ± 8.76 μg L^{-1}) which correspond to 49.12% contribution to ΣPAHs. The overall mean concentration of carcinogenic PAHs like BaA (15.35 ± 7.02 μg L^{-1}) and BaP (10.32 ± 2.75 μg L^{-1}) were significantly higher than the FCV limits (3.8 and 1.6 μg L^{-1}), Netherlands maximum permissible concentration (MPCs) values (0.01 and 0.05 μg L^{-1}) and Canadian water quality guideline value (0.018 and 0.015 μg L^{-1}) respectively which are essential for the protection of aquatic life. The observed BaP level was also found to exceed the value of 0.05 μg L^{-1} suggested by the European Directive 2008/105/EC EQS. The overall mean concentration of carcinogenic PAHs like Chr (27.08 ± 11.33 μg L^{-1}) and BkF (9.11 ± 2.79 μg L^{-1}) were found to exceed the Netherlands maximum permissible concentration (MPCs) values of 0.34 and 0.04 μg L^{-1} respectively. The overall mean concentration of carcinogenic Chr (27.08 ± 11.33 μg L^{-1}), BbF (9.11 ± 2.79 μg L^{-1}) and DahA (15.36 ± 5.26 μg L^{-1}) were found to be higher than the respective FCV limits of 3.5, 1.1, 0.6 μg L^{-1} respectively. Based on the previous research across the world, it is very clear that the health effect arising due to such POPs in combination with other potentially toxic contaminants in the marine environment requires regular check. The results of our study also suggest the urgent requirement of establishing the systematic monitoring and assessment program to detect the persistent organic pollutants (POPs) in the marine environment to adopt the required remedial steps. It is no doubt that such POPs in general and carcinogenic PAHs pollutants, in particular, will pose a tremendous threat to the marine biological life and also to the human population via the food chain. The results of the present study will help in understanding the global distribution and fate of carcinogenic PAHs which is required for implementing the necessary steps towards mitigation of the ecotoxicological risk arising due to the existence of such contaminants in various environmental medium across the world.

Acknowledgment

Conflict of interest

References

1. Kanzari F, Syakti AD, Asia L, et al. (2014) Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune), France. *Sci Total Environ* 478: 141–151.

2. Abdel-Shafy HI, Mansour MSM (2016) A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egypt J Pet* 25: 107–123.

3. Lin Y, Qiu X, Ma Y, et al. (2015) Concentrations and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in the atmosphere of North China, and the transformation from PAHs to NPAHs. *Environ Pollut* 196: 164–170.

4. Friedman CL, Pierce JR, Selin NE (2014) Assessing the Influence of Secondary Organic versus Primary Carbonaceous Aerosols on Long-Range Atmospheric Polycyclic Aromatic Hydrocarbon Transport. *Environ Sci Technol* 48: 3293–3302.

5. Basavaiah N, Mohite RD, Singare PU, et al. (2017) Vertical distribution, composition profiles, sources and toxicity assessment of PAH residues in the reclaimed mudflat sediments from the adjacent Thane Creek of Mumbai. *Mar Pollut Bull* 118: 112–124.

6. Singare PU (2015) Studies on Polycyclic Aromatic Hydrocarbons in Sediments of Mithi River of Mumbai, India: Assessment of Sources, Toxicity Risk and Biological Impact. *Mar Pollut Bull* 101: 232–242.

7. Tongo I, Ezemonye L, Akpeh K (2017) Levels, distribution and characterization of polycyclic aromatic hydrocarbons (PAHs) in Ovia river, Southern Nigeria. *J Environ Chem Eng* 5: 504–512.

8. Hong WJ, Jia H, Li YF et al. (2016) Polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs in the coastal seawater, surface sediment and oyster from Dalian, Northeast China. *Ecotoxicol Environ Saf* 128: 11–20.

9. Qin XB, Sun HW, Wang CP, et al. (2010) Impacts of crab bioturbation on the fate of polycyclic aromatic hydrocarbons in sediment from the Beitang Estuary of Tianjin, China. *Environ Toxicol Chem* 29: 1248–1255.

10. Gu YG, Lin Q, Lu TT, et al. (2013) Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in surface sediments from Nan'ao Island, a representative mariculture base in South China. *Mar Pollut Bull* 75: 310–316.

11. Hawliczek A, Nota B, Cenijn P, et al. (2012) Developmental toxicity and endocrine disrupting potency of 4-azapyrene, benzo[b]fluorene and retene in the zebrafish Danio rerio. *Reprod Toxicol* 33: 213–223.

12. Liu LY, Wang JZ, Wei GL, et al. (2012) Polycyclic aromatic hydrocarbons (PAHs) in continental shelf sediment of China: implications for anthropogenic influences on coastal marine environment. *Environ Pollut* 167: 155–162.

13. Lewis MA, Russel MJ (2015) Contaminant profiles for surface water, sediment, flora and fauna associated with the mangrove fringe along middle and lower eastern Tampa Bay. *Mar Pollut Bull* 95: 273–282.

14. Santana JL, Massone CG, Valdes M, et al. (2015) Occurrence and source appraisal of polycyclic aromatic hydrocarbons (PAHs) in surface waters of the Almendares River, Cuba. *Arch Environ Contam Toxicol* 69: 143–152.

15. Sarria-Villa R, Ocampo-Duque W, Paez M, et al. (2016) Presence of PAHs in water and sediments of the Colombian Cauca River during heavy rain episodes, and implications for risk assessment. *Sci Total Environ* 540: 455–465.

16. Singare PU (2016) Carcinogenic and endocrine disrupting PAHs in the aquatic ecosystem of India. *Environ Monit Assess* 188: 1–25.

17. Yan J, Liu J, Shi X, et al. (2016) Polycyclic aromatic hydrocarbons (PAHs) in water from three estuaries of China: distribution, seasonal variations and ecological risk assessment. *Mar Pollut Bull* 109: 471–479.

18. Manoli E, Samara C, Konstantinou I, et al. (2000) Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere* 41: 1845–1855.

19. Mane S, Sundaram S (2014) Studies on some aspects on the biology of green mussel Perna viridis (Linnaeus, 1758) from Versova creek, Mumbai, northwest coast of India. *Int Res J Sci Eng* 2: 47–50.

20. Shirke S, Pinto SM, Kushwaha VK, et al. (2016) Object-based image analysis for the impact of sewage pollution in Malad Creek, Mumbai, India. *Environ Monit Assess* 188: 95–99.

21. Zeng EY, Yu CC, Tran K (1999) In situ measurements of chlorinated hydrocarbons in the water column off the Palos Verdes Peninsula, California. *Environ Sci Technol* 33: 392–398.

22. WHO (1998) Polynuclear aromatic hydrocarbons. Guidelines for Drinking-Water Quality, 2nd edition. Addendum to Vol.2 Health Criteria and Other Supporting Information. World Health Organization, Geneva, pp. 123–152.

23. Xiang N, Jiang C, Yang T, et al. (2018) Occurrence and distribution of Polycyclic aromatic hydrocarbons (PAHs) in seawater, sediments and corals from Hainan Island, China. *Ecotoxicol Environ Saf* 152: 8–15.

24. Santos E, Souza MRR, Vilela Junior AR, et al. (2018) Polycyclic aromatic hydrocarbons (PAH) in superficial water from a tropical estuarine system: Distribution, seasonal variations, sources and ecological risk assessment. *Mar Pollut Bull* 127: 352–358.

25. Nwineewii JD, Marcus AC (2015) Polycyclic Aromatic Hydrocarbons (PAHs) In Surface Water and Their Toxicological Effects in Some Creeks of South East Rivers State (Niger Delta) Nigeria. *IOSR J Environ Sci Toxicol Food Technol* 9: 27–30.

26. Yang D, Qi SH, Zhang Y, et al. (2013) Levels, sources and potential risks of polycyclic aromatic hydrocarbons (PAHs) in multimedia environment along the Jinjiang River mainstream to Quanzhou Bay, China. *Mar Pollut Bull* 76: 298–306.

27. Adeniji AO, Okoh OO, Okoh AI (2019) Levels of Polycyclic Aromatic Hydrocarbons in the Water and Sediment of Bufalo River Estuary, South Africa and Their Health Risk Assessment. *Arch Environ Contam Toxicol* 76: 657–669.

28. Edokpayi JN, Odiyo JO, Popoola OE, et al. (2016) Determination and Distribution of Polycyclic Aromatic Hydrocarbons in Rivers, Sediments and Wastewater Effluents in Vhembe District, South Africa. *Int J Environ Res Public Health* 13: 387, 1–12.

29. Nekhavhambe TJ., van Ree T, Fatoki OS (2014) Determination and distribution of polycyclic aromatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa. *Water SA* 40: 415–424.

30. Eganhouse RP, Simoneit BRT, Kaplan IR (1981) Extractable organic matter in urban stormwater runoff. 2. Molecular characterization. *Environ Sci Technol* 15: 315–326.

31. Hoffman EJ, Mills GL, Latimer JS, et al. (1984) Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. *Environ Sci Technol* 18: 580–587.

32. Agarwal T, Khillare P, Shridhar V, et al. (2009) Pattern, sources and toxic potential of PAHs in the agricultural soils of Delhi, India. *J Hazard Mater* 163: 1033–1039.

33. Xing XL, Qi S, Zhang J, et al. (2011) Spatial distribution and source diagnosis of polycyclic aromatic hydrocarbons in soils from Chengdu Economic Region, Sichuan Province, western China. *J Geochem Explor* 110: 146–154.

34. Sprovieri M, Feo ML, Prevedello L, et al. (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbor (southern Italy). *Chemosphere* 67: 998–1009.

35. Ravindra K, Wauters E, Grieken RV (2008) Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses. *Sci Total Environ* 396: 100–110.

36. Tobiszewski M, Namiesnik J (2012) PAH diagnostic ratios for the identification of pollution emission sources. *Environ Pollut* 162: 110–119.

37. Cao ZH, Wang YQ, Ma YM, et al. (2005) Occurrence and distribution of polycyclic aromatic hydrocarbons in reclaimed water and surface water of Tianjin, China. *J Hazard Mater* 122: 51–59.

38. Boonyatumanond R, Wattayakorn G, Togo A, et al. (2006) Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Mar Pollut Bull* 52: 942–956.

39. Mostert MMR., Ayoko GA, Kokot S (2010) Application of chemometrics to analysis of soil pollutants. *Trends Anal Chem* 29: 430–435.

40. Mai BX, Qi SH, Zeng EY, et al. (2003) Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. *Environ Sci Technol* 37: 4855–4863.

41. Rocher V, Azimi S, Moilleron R, et al. (2004) Hydrocarbons and heavy metals in the different sewer deposits in the Le Marais' catchment (Paris, France): stocks, distributions and origins. *Sci Total Environ* 323: 107–122.

42. Wang XC, Sun S, Ma HQ, et al. (2006) Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Mar Pollut Bull* 52: 129–138.

43. Montuori P, Aurino S, Garzonio F, et al. (2016) Distribution, sources and ecological risk assessment of polycyclic aromatic hydrocarbons in water and sediments from Tiber River and estuary, Italy. *Sci Total Environ* 566–567: 1254–1267.

44. Zhang W, Zhang S, Wan C, et al. (2008) Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environ Pollut* 153: 594–601.

45. Chung MK, Hu R, Cheung KC, et al. (2007) Pollutants in Hongkong soils: polycyclicaromatic hydrocarbons. *Chemosphere* 67: 464–473.

46. Li G, Xia X, Yang Z, et al. (2006) Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environ Pollut* 144: 985–993.

47. De La Torre-Roche RJ, Lee WY, Campos-Diaz SI (2009) Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. *J Hazard Mater* 163: 946–958.

48. Akyuz M, Cabuk H (2010) Gaseparticle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. *Sci Total Environ* 408: 5550–5558.

49. Dhananjayan V, Muralidharan S, Peter VR (2012) Occurrence and distribution of polycyclic aromatic hydrocarbons in water and sediment collected along the Harbour Line, Mumbai, India. *Int J Oceanogr* Article ID 403615, 7.

50. Katsoyiannis A, Sweetman AJ, Jones KC (2011) PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two Decades of source Inventory and air concentration data from the UK. *Environ Sci Technol* 45: 8897–8906.

51. Pozo K, Perra G, Menchi V, et al. (2011) Levels and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Lenga Estuary, central Chile. *Mar Pollut Bull* 62: 1572–1576.

52. Law RJ, Dawes VJ, Woodhead RJ, et al. (1997) Polycyclic aromatic hydrocarbons (PAH) in seawater around England and Wales. *Mar Pollut Bull* 34: 306–322.

53. Barron MG, Podrabsky T, Ogle S, et al. (1999) Are aromatic hydrocarbons the primary determinant of petroleum toxicity to aquatic organisms? *Aquat Toxicol* 46: 253–268.

54. Agroudy NA, Soliman YA, Hamed MA, et al. (2017) Distribution of PAHs in Water, Sediments Samples of Suez Canal During 2011. *J Aquat Pol Toxicol* 1: 1–10.

55. Pohl A, Kostecki M, Jureczko I, et al. (2018) Polycyclic aromatic hydrocarbons in water and bottom sediments of a shallow, lowland dammed reservoir (on the example of the reservoir Blachownia, South Poland). *Arch Environ Prot* 44: 10–23.

56. US Environmental Protection Agency (USEPA), (2012) Regional screening levels for chemical contaminants at superfund sites. Regional screening table. User's guide. (Access date: November 2012). <http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/usersguide.htm>.

57. Di Toro DM, McGrath JA, Hansen DJ (2000) Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. *Environ Toxicol Chem* 19: 1951–1970.

58. Kalf DF, Crommentuijn T, van de Plassche EJ (1997) Environmental quality objectives for 10 polycyclic aromatic hydrocarbons (PAHs). *Ecotoxicol Environ Saf* 36: 89–97.

59. Canadian Council of Ministers of the Environment (CCME) (2010) Canadian Soil Quality Guidelines, Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs)-Environmental and Human Health Effects. ISBN 978-1-896997-94-0 PDF.

60. Yang B, Xue N, Zhou L, et al. (2012) Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. *Ecotoxicol Environ Saf* 84: 304–310.

61. Omayma EA, Sawsan AM, El Nady MM (2016) Application of polycyclic aromatic hydrocarbons in identification of organic pollution in seawater around Alexandria coastal area, Egypt. *J Environ Life Sci* 1: 39–55.

62. Daisey JM, Leyko MA, Kneip TJ (1979) Source identification and allocation of polynuclear aromatic hydrocarbon compounds in the New York City aerosol: methods and applications. In: Jones, P.W., Leber, P. (Eds.), Polynuclear Aromatic Hydrocarbons. Ann Arbor Science, Ann Arbor, pp. 201–215.

63. Harrison RM, Smith DJT, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environ Sci Technol* 30: 825–832.

64. Rogge WF, Hildemann LM, Mazurek MA, et al. (1993) Source of fine organic aerosol 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ Sci Technol* 27: 636–651.

65. Gschwend PM, Hites RA (1981) Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. *Geochimica et Cosmochimica Acta* 45: 2359–2367.

66. Mitra S, Bianchi TS, Mckee BA, et al. (2002) Black carbon from the Mississippi River: quantities, sources and potential implications for the global carbon cycle. *Environ Sci Technol* 36: 2296–2302.

67. Masclet P, Bresson MA, Mouvier G (1987) Polycyclic aromatic hydrocarbons emitted by power station, and influence of combustion conditions. *Fuel* 66: 556–562.