

Fishing harbours as a source of PAHs pollution? A case study from Veraval harbour west coast of India

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Abstract

Worldwide, studies on Polycyclic Aromatic Hydrocarbons (PAHs) especially focusing on fishing harbours, have been found in a limited magnitude only. The characteristics of 16PAHs and their associated ecological adversities in different environmental compartments of Veraval fishing harbour have been investigated. The concentrations of total PAHs in dissolved, particulate and sediment phase varied from 358.19-42712 ngL⁻¹, 1450.83-15291.60 ngg⁻¹dw and 1263.53-217560.30 ngg⁻¹dw, respectively. Two approaches adopted for the source apportionment of PAHs: Molecular Diagnostic Ratios Method (MDR) and Principal Component Analysis (PCA), implied the impact of potential anthropogenic PAH sources, including petroleum leakage, pollution from boat repairing, maintenance and burning of coal emissions. The interpretation and integration of indices such as the total toxicity equivalence (TEQ^{carc}), mean risk quotient (M-RQ) and mean effect range-medium quotient (M-ERM-Q) indicated that the harbour areas were under severe threat of ecological risk due to the highest concentration of PAHs, while the offshore region signified a high or moderate level of risk. The present study provides effectual scientific insight into the role of fishing harbours in PAHs pollution.

Keywords: Pollution, POPs, PAH, Ecological Risk, Harbour

1. Introduction

Coastal ecosystems undergo significant level of anthropogenic stress greatly from ports, fishing harbours, industries, release of sewage and effluent, tourism activities, etc. globally that eventually lead to the degradation of coastal biodiversity (Yuan et al., 2016; Hader et al., 2020; Gairin et al 2022). Many places in the west coast of India face the similar situation especially states like Gujarat which, covers a coastline area of 1600 km. Gujarat is one of the major fish landing regions in India (MPEDA, 2022), contributing 18.9 % of the total marine fish landings of the country (CMFRI, 2020) and has 107 fish landing centres (FLC) (DoF, 2020). These FLC are of great importance that they contribute to the economic growth of the country and provide occupations for the local populace. Monitoring the environmental quality of FLC are important as they can impact the quality of the fish handlings and can affect the health of the people working in these environments. According to the fisheries statistics (Commissioner of fisheries, 2022), 28355 mechanised boats are operating in the Gujarat state which includes trawlers, gill setter, modified bagnet setter, doll net setter etc. The trawlers and doll net setters operating in the west coast of India use 88 to 118 HP diesel engine. (Prajith et al., 2014). The high number of mechanised boats operating in the fishing harbours can make these locations as possible sites for organic pollution, especially with petroleum hydrocarbons (Mora et al., 2022). Emissions like smoke, particulate matter, PAHs, sulfur oxide etc., from these Diesel engines cause many environmental problems (Lon et al., 2006; Yang et al., 1999), in these PAHs were tagged as priority pollutants by the United States Environmental Protection Agency (USEPA) and as per International Agency for Research on Cancer (IARC), seven out of which are classified under the potentially carcinogenic pollutants (Zheng et al., 2016).

PAHs are organic compounds having a minimum of 2 benzene rings with carbon and hydrogen in them (Ravindra et al., 2008). They are considered as a widespread class of environmental pollutants, which are basically toxic in nature and can cause genotoxic, teratogenic and carcinogenic effects in organisms. They can cause potential human health risks which gives them global attention (Wang et al., 2017; Liang et al., 2017; Duodu et al., 2017; Xiang et al., 2018). Several striking epidemiological studies have pointed to the link between cancerous growth on human tissues, to that of the PAHs exposure (Ali, 2019; Li et al., 2020). PAHs contamination are found in various aquatic environmental compartments, including water, suspended particulate matter, sediment, and biota. Among these, sediment serves as the primary aquatic repository for PAHs owing to the presence of organic matter. The susceptibility of sediment to re-suspension actions can result in discharge into the water, thereby causing re-pollution. This poses a dual risk, directly impacting benthic organisms and, indirectly, exposing pelagic organisms to the potential adverse effects of PAHs (Liu et al., 2016). Studies on the

origin and cycling of PAHs in fishing harbours are important, for pollution management as well as the health improvement of persons associated with the fishing industry.

According to several studies, Veraval harbour is a highly polluted zone, primarily due to anthropogenic pressure and industrial discharge, particularly with regard to heavy metal accumulation (Sundararajan et al., 2017; Majithiya et al., 2018). According to Central Pollution Control Board report, Veraval harbour receives 20000 m³ and 24000 m³ wastes discharged from the fish processing industry and municipal sewage system, on a daily basis (CPCB, 2009-2010). The water inside the harbour often remains under anoxic conditions due to the continuous accumulation of such organic and industrial effluents, as well as the hindrances in their proper dilution, together with the formation of NH₄⁺-N and H₂S (Majithiya et al., 2018). Despite the abundance of fishing vessels, no research has been done to examine the PAHs contamination in this area. Moreover, the distribution of PAHs in water, sediment and suspended particulate matter (SPM) phases holistically in the coastal waters of Indian has not been investigated comprehensively.

Hence, the current study aims at investigate the PAHs pollution in Veraval harbour and its adverse effects on the coastal waters. The main objectives of the present study are: (1) To find out the spatial distribution and extent of 16 USEPA priority PAHs in water, sediment and SPM from Veraval harbour and coastal waters. (2) To find out the source of PAH pollution by using the molecular diagnostic ratios method (MDR) and principal component analysis (PCA) tools. (3) To estimate the potential biological impacts, using indices such as total toxicity equivalence (TEQ^{carc}), mean risk quotient (M-RQ) and mean effect range-median quotient (M-ERM-Q).

2. Materials and methods

2.1. Study area and sample collections

Veraval Harbour in Gujarat was chosen for the current study due to its significance as one of Asia's major fishing harbours with a large number of active fishing vessels (Hardikar et al., 2019). Veraval is a port town, situated on the coast of the Arabian Sea, and the chief source of economy for the populace is fishing-related activities. The town has a number of large and small industrial units as well as numerous fish-processing factories that export high-quality seafood globally (Borade et al., 2015; Sundararajan et al., 2017).

Water, SPM and sediments were collected from 17 locations within Veraval harbour and adjacent coastal areas on March 2019 (Fig. 1). In order to assess and interpret the pollution status in a better way, the study area had been divided into three, as: Harbour (S1- S4), and the locations

consisting of depth less than 10 meters as near shore (S5- S11), within 20-30 meter depth, as offshore area (S12- S17). Furthermore, S17, which is at a distance of 10 Km from the harbour.

Surface sediment samples (0-5cm) were collected by van Veen grab sampler and stored in glass containers at -20°C . Water samples for studying dissolved and suspended (SPM) forms of PAHs were collected in 1L amber-coloured glass bottles by using a Niskin water sampler from each sampling location. One litre of sea water collected for SPM were filtered through pre-combusted $0.7\mu\text{m}$ glass fiber filter membranes (Whatman GF/F, UK) and filters were kept in aluminium foil. All samples were stored at -20°C until extraction.

2.2. Extraction and analysis

The sediment extraction method was adopted from Singare, (2015) with minor modifications. 10 g of lyophilized (Labconco, USA) sediments were soxhlet-extracted with dichloromethane for 48h. The extract was treated with activated copper granules for removing elemental sulfur and concentrated by rotary evaporator (Buchi-R3, Switzerland), re-dissolved in 2 mL n-hexane. Cleanup processes were done by activated 2:1 silica/alumina column and eluted with 20 mL of n-hexane (aliphatic fraction) and 70 mL of 2:1dichloromethane/n-hexane (aromatic fraction). Aromatic fraction concentrated using rotary evaporator, dried under a stream of nitrogen gas and dissolved in 1 mL n-hexane, kept in -20°C before analysis. For SPM extraction, filter paper was lyophilized, weighed and same procedure performed as sediment. Water samples were extracted by solid phase extraction method by using Strata PAH cartridges (Phenomenex, USA). 100 mL water sample was passed through preconditioned (with 20ml dichloromethane: methanol and Milli-Q water) 1.5g/6 mL SPE cartridge and washed with 5 mL of 1:1 methanol and Milli-Q water. Eluted with 6 mL of dichloromethane and dry under a gentle stream of nitrogen and redissolved in 1 mL of n-hexane and stored at -20°C until analysis.

2.3. GC-MS analysis

The 16 PAHs such as Naphthalene (Nap), acenaphthylene (Acy), acenaphthene(Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a] anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[g, hi]perylene (BghiP), dibenzo[a,h]anthracene (DBA) and indeno [1,2,3-cd]pyrene (IND) were determined by using gas chromatograph coupled with Mass spectrometry (Agilent 7890B-MSD5977B) with HP-5MS Column (30 mm length, 0.25 mm inner diameter, 0.25 μm thickness). Mass-to-charge ratio was identified by selected ion monitoring mode (SIM) with an electron impact ion source (EI) of 70Ev. The oven temperature was started at 100°C ramp at $10^{\circ}\text{C min}^{-1}$ to 200°C (1.5 min), ramp at $25^{\circ}\text{C min}^{-1}$ to 250°C (2min) and then ramp at $5^{\circ}\text{C min}^{-1}$ to a final temperature 300

$^{\circ}\text{C}$ holds at 10min. Helium was used as carrier gas with flow rate is 0.8 mL min^{-1} . The ion source and quadruple temperature were $230 \text{ }^{\circ}\text{C}$ to $150 \text{ }^{\circ}\text{C}$, respectively.

2.4. Quality control and quality assurance

All analyses were conducted according to the standard quality control procedure including method blank, spiked blank and a sample duplicate were extracted and analyzed with every successive batch. The five-point calibration method was used for the standardization of the method. The certified reference material (Sigma-Aldrich, CRM-104) used for finding out the extraction efficiency in sediment samples ranged 78 -85% and for water samples, SPE gives 85-92% of total recovery and suspended sediments showed 73-80% of recovery efficiency for 16 PAHs. The detection limits (LOD) were found a range of 0.01 to 0.3 ng L^{-1} for water and 0.02 to 1.8 ng g^{-1} SPM and sediment. Furthermore, the limits of quantification (LOQ) was established at 0.1 to 0.3 ng L^{-1} for water and 0.2 to 2.1 ng g^{-1} for SPM and sediment. GC residue analysis grade solvents were used for all extractions (Sigma-Aldrich, USA). Glassware was muffle furnaceed at 350° C , washed with GC grade organic solvents before use.

2.5 PAH source apportionment

Molecular diagnostic ratio (MDR) and principal component analysis (PCA) tools are employed for identifying the sources of PAHs. In MDR analysis, the ratios of PAH isomers play a key role. Specifically, values such as $\sum\text{LMW}/\text{HMW} >1$, $\text{Ant}/(\text{Ant}+\text{Phe}) <0.1$, $\text{IND}/(\text{IND}+\text{BghiP}) <0.2$, and $\text{BaA}/(\text{BaA}+\text{Chr}) <0.2$ are indicative of petrogenic sources according to Magi et al. (2002). Conversely, if $\text{Fla}/(\text{Fla}+\text{Pyr})$ and $\text{IND}/(\text{IND}+\text{BghiP})$ exceed 0.5, and $\text{BaA}/(\text{BaA}+\text{Chr})$ surpasses 0.35, combustion of grass, wood, or coal is likely (Li et al., 2006). Ratios falling between 0.4-0.5, 0.2-0.35, and 0.2-0.5 suggest the potential sources as fossil fuel, coal, or petroleum combustion, respectively (Wang et al., 2006). PCA serves as a robust tool for source identification, elucidating the total variability within the original data of PAHs. Represented through minimal factors known as Principal Components, PCA allows for the differentiation of complex characteristics associated with the pollution source (Dudhagara et al., 2016; Zheng et al., 2016). The Kaiser-Meyer-Olkin (KMO) statistic has been employed to affirm the applicability of PCA in the analytical framework (Liu et al., 2009).

2.6 Potential ecological risk assessment

In the present study, use of different indices such as total toxicity equivalence (TEQ^{carc}), mean risk quotient (M-RQ) and mean effect range-medium quotient (M-ERM-Q) for the assessing the ecological risk of 16 PAHs in sediment, SPM and water from the study area. The total toxicity equivalence (TEQ^{carc}) was determined by the total sum of the multiplied values of individual

carcinogenic PAHs (CPAHs) and their corresponding Benzo[a]pyrene based toxic equivalency factors (TEFs). The TEQ^{carc} derivation formula is given in equation (1)

$$TEQ^{carc} = \sum (CPAH_i \times TEF_i) \quad (1)$$

where $CPAH_i$ is the concentration of carcinogenic PAHs such as benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBabA) and indeno[1,2,3-cd]pyrene (IP) and 0.1, 0.001, 0.01, 0.01, 1, 1 and 0.1 are the concerned TEF values of the each CPAHs compounds proposed by USEPA (1993).

The mean risk quotient (M-RQ) is used to find out the ecological risk assessed by following equation (2)

$$M-RQ = \sum (C_i / C_{QV}) / n \quad (2)$$

where, C_i is the measured value of PAHs in sediment, SPM and water in the study area. C_{QV} is the quality values of concerned PAHs compounds and n is the number of compounds which used for deriving RQ. Cao et al. (2010) proposed negligible concentration of (NCs), which is a hundred times lesser than the maximum permissible concentration (MPCs) is considered as the C_{QV} in this study. The range of M-RQ values such as <0.1, 0.1-1.0, 1-10, 10-100 and >100 are explained as the study area under negligible, low, low to moderate, moderate to high and very high risk respectively to the ecological environment (Akhbarizadeh et al., 2016; Wang et al., 2016)

The mean effect range-medium quotient (M-ERM-Q) was estimated by using the equation (3)

$$M-ERM-Q = \sum (C_{sed} / ERM_i) / n \quad (3)$$

Where C_{sed} is the level of PAHs concentration in sediment samples ERM_i is the corresponding effect range medium values and n is the total number of PAHs compounds which is considered for assessing M-ERM-Q. The M-ERM-Q values are classified according to the level of biological effects i.e., ≤ 0.10 is considered as no harmful biological effects, 0.11-0.50 indicate possible adverse effects and 0.51-1.50 implies that moderate adverse effects and >1.50 is highlighting significant adverse biological effects in the sediment compartment (Li et al., 2015).

3. Results and discussion

3.1 PAHs in Water, SPM and Sediment

The total PAH ($\sum 16$ PAHs) concentration in water has been found to be in the range of 358.19-42712.40 ng L⁻¹ (median 4390.08 ng L⁻¹) with the mean concentration of 9712.78±12184.42 ng L⁻¹ (Fig. 2a, b & c, Table 1). Distribution of ring wise compounds, 2-3 rings the level varies from 314.11

to 3394.2 ng L⁻¹, in 4 ring, it is 8.30-12931.03 ng L⁻¹ and in 5-6 ring, it is 3.85-1290.85 ng L⁻¹. 2-3 ring (LMW-PAHs) shows high abundance on a range of 51% to 96%, when it comes to the dissolved phase (Fig. 3). Chen. (2008) classified the water bodies in to 4, based on concentration of PAHs, such as: low polluted, 10–50 ng L⁻¹; slightly polluted, 50–250 ng L⁻¹; moderately polluted, 250–1000 ng L⁻¹; and highly polluted, \geq 1000 ng L⁻¹. Depending on this classification, the harbour area, nearshore area and some station in the offshore regions are identified to be highly polluted regions, while stations S16 and S17 which are away from the harbour are found as moderately polluted locations. The low octanol-water partition coefficient, higher water solubility and vapour pressure (Simpson et al., 2005; Sarria – Villa et al., 2016) have been regarded as the responsible factors for the excessive dissolution of low molecular weight PAHs (LMW-PAHs) compounds in water.

The Σ 16PAHs concentration in the particulate phase (SPM) varies over a range of 1450.83-15291.60 ng g⁻¹dw (median 6293.98 ng g⁻¹dw), with the mean value of 6361.72 \pm 4166.78 ng g⁻¹dw. Distribution of ring wise compounds in SPM showed a variation level of 410.8-2688.92 ng g⁻¹dw in 2-3 ring compounds, 4 ring compounds it is 359.2-4374.86 ng g⁻¹dw, 5-6 rings as 591.52-8419.40 ng g⁻¹dw, and 4-6 ring compounds carry utmost abundance in a range of 56%- 92%. The PAHs concentration recorded in SPM (1450.83- 15291.60 ng g⁻¹) as per the present research is more in abundance, in comparison with the PAHs concentration (909.9-8222.4 ng g⁻¹) found at the fishing harbour of Tunis (Mzoughi & Chouba, 2011). Data on PAHs accumulation in SPM from Pearl estuary and its coastal area (422-1850 ng g⁻¹), Tiber estuary (123.4-1232.5 ng g⁻¹), Xiamen coast (274.5-2038.9 ng g⁻¹) were also found low than Veraval (Luo et al., 2006; Montuori et al., 2016; Tang et al., 2018).

In the sediment phase, the PAHs concentration is identified in a range of 1263.53- 217560.30 ng g⁻¹dw (median 6941.97 ng g⁻¹dw) with the mean of 23660.59 \pm 52338.41 ng g⁻¹dw. As per the sediment PAHs level classification of Baumarad et al. (1999), the values, 0-100 ng g⁻¹ is low, <100-1000 ng g⁻¹dw is high and >5000 ng g⁻¹dw is considered to be very high. According to this classification Veraval harbour and near shore regions (except S7 and S11) indicate a very high-level value, while all the other chosen stations show high level of PAHs contamination. The sediments vary on a range of 2-3 ring compounds varies 390.80-608848 ng g⁻¹dw, 4 ring 344.74-71891.97 ng g⁻¹dw and 5-6 ring compounds 527.99-139579.85 ng g⁻¹dw, while similar to that of the particulate phase, 4-6 ring compounds, show high dominance on a range of 53.9%-97.2%. In comparison with LMW compounds, HMW compounds are accumulated in a greater quantity in sediments, because of the high affinity towards the organic matter, as well as the resistance to microbial degradation, (Gustafsson et al., 1996; Woo et al., 2001; Simpson et al., 2005).

In summery the total spatial distribution of PAHs in water, SPM and sediments subsides from the harbour to offshore regions. The excessive number of fishing boats, the oil contamination due to boat maintenance activities inside the harbour, and the direct discharge of municipal and industrial effluents pollute the harbour region to a greater extent. Moreover, the increased PAHs distribution in harbour is controlled by several factors, especially, as a result of the impediment in proper dilution of pollutants, owing to the specialized construction of harbour breakwater system that blocks the wave, tidal and wind action. Nonetheless, in comparison with the near shore sites, the PAHs level in station 9 and 10, which are situated adjacently to the mouth of the Dewka river is higher. The observable reasons are the release of industrial and sewage waste into the river, the emission of fly ash from the coal based thermal power plant, in addition to high boat traffic in the aforementioned zones.

3.2 Comparison of PAHs pollution in Veraval harbour with other coastal regions in Indian and fishing harbours worldwide

Results of the present study was compared with the PAHs pollution reported in Indian waters and with the PAHs concentration recorded from fishing harbours globally are presented in Table 2. More number of studies were available on the concentration of PAHs in sediments in the coastal region of India when compared sediments. Comparison of \sum PAHs concentrations in the water found high \sum PAHs values at Malad-Versova creek (114320-347040 ng L⁻¹) of Mumbai coastal belt (Singare and Shirodkar, 2021a) and Gomti river (600-84200 ng L⁻¹) in the North coastal region of India (Malik et al., 2011) than Veraval harbour (358.19- 42712.40 ng L⁻¹). Concentration of PAHs in sediments shows locations like Alang-Sosiya, Gulf of Cambay (78000-719000 ng g⁻¹), Bhavnagar Coast (5020-981180 ng g⁻¹) and Gulf of Kutch (118280-1099410 ng g⁻¹) in the West coast of India recorded high PAHs than Veraval harbour (1263.53- 217560.30 ng g⁻¹) (Reddy et al., 2005; Dudhagara et al., 2016; Rajpara et al., 2017).

Internationally studies are scarce on PAHs pollution in fishing harbours. PAHs in water at Western Mediterranean harbour (1-60 ng L⁻¹) (Pane et al., 2005) and West coast of the Gulf of Tunis (139.2-1008.3 ng L⁻¹) (Mzoughi & Chouba, 2011) were low. PAHs pollution in sediments of Hsin-ta harbour (98.1-2048 ng g⁻¹) recorded by Fang et al. (2003), West coast of the Gulf of Tunis (363.3-7026.4 ng g⁻¹) (Mzoughi & Chouba, 2011), Tripoli (243-2965 ng g⁻¹) (Merhaby et al., 2015) and Tema harbour (2750-5130 ng g⁻¹) by Botwe et al. (2016) were relatively low than Veraval harbour. The sediments of Auckland harbour (2000-998000 ng g⁻¹) (Ahrens & Depree, 2004) and small craft harbour in Nova Scotia (37-336770 ng g⁻¹) (Davis et al., 2018) were highly polluted. SPM PAHs values in Veraval were more or less similar to the West coast of the Gulf of Tunis harbour (909.9-8222.4 ng g⁻¹).

3.3. PAH Source apportionment

3.3.1. Using ring number and MDR Tool

Anthropogenically originated PAH sources can be divided into two: incomplete combustion of petroleum products, coal and biomass (pyrogenic), as well as the resultant of the direct release of petroleum products (Boonyatumanond et al., 2006). Primary source identification can be carried out based on the concentration of ring wise distribution of PAHs in environmental samples (Fang et al., 2003; Cao et al., 2005). The composition pattern based on the ring number in the study area is provided in fig. 3.

In sediments and SPM, 5-6 rings (25%- 64% and 25%- 69% respectively) and 4 rings (19%- 54% and 23%- 49% respectively) dominate. And the distribution of 2-3 ring in the offshore region slightly exceeds that of the harbour region. The high molecular PAHs (4-6 rings) are usually produced from the high-temperature combustion of petroleum or fossil fuels. (Stogiannidis & Laane, 2015). In water, the composition of low molecular weight PAHs is found between 51- 95%. As per the study, in the offshore region, high molecular weight PAHs could not be identified, hence, high composition trend of low molecular weight PAHs can be seen, which indicates that the source might be of petrogenic origin. (Fernandes et al., 1997).

PAHs undergo various changes and transformations due to environmental conditioning, such as photolysis, volatilisation, biodegradation etc. But this particular method is not always preferable (Wakeham, 1996), since it might lead to several misinterpretations regarding the source apportionment through ring number composition. Therefore, source identification based on isomers that have the same physico-chemical properties can be a more reliable approach (Yunker et al., 2002).

In fig. 4, the scatter plot represents the distribution of MDR in water, SPM and sediment in the study area. Based on this, $BaA/(BaA+Chr)$ vs $Ant/(Ant+Phe)$, showing coal and petroleum combustion are found to be the source in all three environmental compartments, except in water samples from the sites, S9 and S17. According to $Fla/(Fla+Pyr)$, most of the water and SPM samples from the sites, point to the sources of origin as direct petroleum contamination and combustion. Meanwhile, the sources for sediments indicate coal and petroleum combustion. Based on $IND/(IND+BghiP)$ water, SPM and sediment matrices from the sites, show petroleum and coal combustion as its origin of source, except in some water samples collected from the stations, such as, S5, S8 and S11 that show petrogenic source. The ratio of LMW, HMW shows majority of the sediments and SPM are of pyrogenic origin, while, that of water is petrogenic in Veraval.

In conclusion, the resultant MDR ratios indicate a mixed response regarding the sources. Due to that, region wise specific source analysis and interpretation seems impossible. So, it can be assumed that the PAHs sources in the study area are petroleum combustion, direct petroleum contamination and atmospheric deposition. Meanwhile, PAHs inputs from the continuous pyrogenic and petrogenic sources may hinder the process of source identification to an extent (Wagener et al., 2010; Lubecki & Kowalewska, 2012). Under such circumstances, the visible ground truth information regarding sources based in the study area, can be interpreted in along with the aforementioned findings (Qi et al., 2019). The activities such as, fueling, boat cleaning, washing, boat maintenance and scrapping works, direct disposal of used cooking oil to harbour waters etc., are mostly centred around in harbour area, and they add to the direct release of engine oil, as well as in the combustion of diesel fuel. The fly ash deposition from a coal based terminal plant, 2.6 Km West of Veraval harbour can be considered as a strong pyrogenic source, that usually prevents bio and photo degradation, when mixed with oil, and may result in contradictory source information (Fang et al., 2007), which may be one among the reasons for the contradictory information regarding source identification.

3.3.2. Principal component analysis (PCA)

The PAH loading through varimax rotation factor in water, SPM and sediment are illustrated in Table 3. The kaiser-meyer-olkin (KMO) test had been employed to confirm the adequacy of the test with 'df' values such as 66, 120, and 120 were obtained. When 17 samples and 16 PAHs components in sediments were used for PCA analysis, 2 principal components were extracted with 96.3% total variance, out of which, PC1 showed 93.2% variance, while Nap (2 ring), Fle, Phe and Ant (3 ring) found to be having high loading (values higher than 0.85) and Acy (2 ring), Flu, Pyr, BaA, BbF, BkF, Bap, DBA, BghiP and IND (4-6 ring) were found to be with moderate loading. The 3 ring components such as Fle, Phe and Ant are predominantly produced as a result of coal or biomass combustion (Chen et al., 2005; Zhang et al., 2009; Zheng et al., 2016), and Nap can be considered as a petrogenic origin (Khalili et al., 1995; Dobbins et al., 2006). Meanwhile, the moderate loading of 4-6 rings indicates vehicular emission because of high-temperature combustion of petroleum products as well as coal burning. (Harrison et al., 1996; Larsen & Baker, 2003; Jiang et al., 2009). PC2 represents 3.6% variance with the high loading of Ace, which is produced out of the high input of petrogenic sources, such as, oil spill or engine oil residue (Marr et al., 1999; Dobbins et al., 2006). 17 samples and 16 variables have been used in SPM for PCA analysis, through which two principal components have been extracted with 88.6% total variance, among that, PC1 showed 73.3% variance. Nap, Acy, Ace (2 ring), Fle, Ant, and Chr (3 ring) showed heavy loading and Phe, Fla, Pyr, BaA, BbF, BaP, IND (4-6 rings) showed moderate loading. Two ring compounds have been made as a result of the spill or

volatilization of petroleum or petroleum products (Marr et al., 1999; Larsen & Baker, 2003; Wang et al., 2007) Meanwhile, Fle, Ant and Chr are produced due to the combustion of coal or natural gas (Sofowote et al., 2008; Khuman et al., 2018). Since DBA and BghiP shows high loading with 13.6% variance, it indicates that they are emitted because of the combustion of gasoline or diesel engine (Harrison et al., 1996; Larsen & Baker, 2003; Wang et al., 2007).

Compounds like BkF, DBA, BghiP and IND was not detected in water samples collected from offshore locations. Therefore, these are omitted so as to conduct PCA analysis, making use of 17 samples with 12 PAHs compounds and three principal components which have been extracted with 82.5% total variance. In PC1, 73% variance could be seen, and Acy, Ace (2 rings) and Ant (3 rings) showed high loading and Phe, BaA, Chr, and BaP showed moderate loading Acy and Ace are the products of typical petroleum sources and Phe, BaA, Chr and BaP are produced out of coal combustion sources (Duval and Friedlander, 1981). In PC2, with 11.5% variance, Fle could be detected as high loading and Nap, Bbf as moderate loading, among which, Fle and BbF are prominently produced through the combustion of coal and petroleum products (Sofowote et al., 2008). In PC3, with 8.4% variance, Fla and Pyr are identified with high loading which are considered as the products of coal combustion (Harrison et al., 1996; Stogiannidis & Laane, 2015). Overall, in the study area, petrogenic, combustion of coal and petroleum products have been identified to be the sources of PAHs origin. High boat traffic and maintenance works are regarded as the causes for the direct release of diesel oil. The PAHs produced as part of oil combustion are comparatively moderate, and are generally found in the sediment, SPM and water samples, as per the study. When MDR and PCA models were considered for source identification, unstable results were found from the present study area which leads to the assumption that the continuous input of HMW and LMW PAHs are responsible for such visible results.

Comparison of PAHs sources at Veraval and other coastal regions of India reveals that the major reasons for PAHs pollution identified as atmospheric deposition, vehicular emissions, incomplete combustion of wood, coal-fired thermal power plants, grass and fossil fuels, oil and petroleum leakages etc., and in Veraval the major PAHs sources are petroleum spills and atmospheric deposition.

3.4. Potential ecological risk assessment

The estimated values of total toxicity equivalence (TEQ^{carc}), mean risk quotient (M-RQ) and mean effect range-medium quotient (M-ERM-Q) in the study area are depicted in the table 4. M-ERM-Q value varies between 0.09 (S17) to 9.95 (S1). Sites such as S1, S2, and S3 (harbour area) are under significantly adverse effect on organisms, S4, S9 and S10 showed moderate adverse effect and the rest

of the sites from near to off shore stations are facing possible adverse effects except S17, which has no harmful biological effect ($M-ERM-Q \leq 0.10$). The M-RQ values have been the trend of moderate to high risk with the range of 24.66-262.10 (avg. 313.37) in sediment, 28.51-221.53 (avg. 100.73) in SPM and 22.57-3518.69 (avg. 622.18) in water compartments of the study area. In sediment and SPM indicates high risk ($M-RQ \geq 100$) up to harbour and near shore area except for the locations of S7, S11 from sediment, S6, S8, S11 from SPM and remaining offshore sites are under moderate risk level category ($M-RQ 10-100$). The water shows a high risk for S1 to S14 and remaining three stations are under moderate risk status.

The TEQ^{carc} of seven carcinogenic PAHs in the Sediment, SPM and water ranged 0.17-57.78 ng TEQ/g dw, 0.19-3.93 $\mu\text{g TEQ/g dw}$ and 0.0018-0.57 ng TEQ/L respectively in the study area. Based on Canadian soil quality guidelines the level of TEQ^{carc} is more than 0.6 ng TEQ/g is considered as the threshold level and it may cause a serious impact on the food web as well as on human health. In the present study, sediments from the harbour and near shore locations except S7 and S11 are above the threshold value. The ratio of TEQ^{carc} and NCs value (TEQ_{QV}) which corresponding to Benzo[a]pyrene in sediment and water such as 0.027 for sediment and SPM, 0.0005 for water considered as the convenient indices tool for risk assessment. According to TEQ^{carc}/TEQ_{QV} , values are <0.1 indicate negligible risk; 0.1-1.0 indicate low risk; 1-10 indicate low to moderate risk; 10-100 indicate moderate to high risk and ≥ 100 represent the high risk. Based on this classification harbour areas are under high risk, the near shore is moderate to high and the offshore region showing low to moderate risk in all three environmental compartments.

The integration and interpretation of ecological risk assessment values of different indices from various environmental compartments could be a substantial tool for the comprehensive understanding of the risk status of the study area. Based on the M-ERM-Q, M-RQ and TEQ^{carc} values of different environmental compartments in Veraval, poses a high ecological risk in harbour regions, and high to moderate risk at near shore to off shore areas. Majority of cancerous PAHs are not detected in the dissolved phase of offshore region causes less ecological risk. Migratory birds spotted during the sampling time within the harbour area, consume fish waste generated mainly from boat and auction areas, as part of their dietary needs. Fisherman and local boat workers are exposed to dermal contact, from contaminated water and sediments during their occupational activities, which makes them prone to umpteen health issues. Hence, the ecological risks in harbour regions are at a heightened level and the concentration of cancerous PAHs is in excessive quantity in water, sediments and SPM, which can act as a serious threat to those workers.

4. Conclusion

PAH pollution in fishing harbours has not been yet explored in the Indian sub-continent. The current study is the first holistic study on the concentration of 16 PAHs in the dissolved, particulate, and sediment phases from a major fishing harbour, Veraval. Also, the various sources of PAH contamination was investigated by application of several statistical indices. Results indicated mixed source which was probably due to the continuous loading of petrogenic and pyrogenic pollutants from various routes, such as high boat traffic, combustion of coal and municipal and industrial sewage wastes.

Lighter molecular weight PAHs (2-3 ring) were abundant in water where as 4-6 rings fractions were predominant in the sediment and SPM of the Veraval harbour and nearshore region. The harbour regions were contaminated with PAHs of petroleum origin which could be attributed to direct spill of petroleum products, the high number of fishing craft operations and atmospheric deposition of PAHs from coal and biomass combustion. Suspended sediments also acted as a medium for the disposal of PAHs in the harbour. Source identification of PAHs in sediments at Veraval harbour was difficult because of influencing factors such as currents, tides and breakwater structure.

Potential ecological risk assessment indicated that the harbour area was at high risk from PAH pollution which may have significant adverse effects on organisms. The PAH pollution and associated potential risks on the coastal ecosystem signified that the harbour areas were under high threat due to the high concentration of cancerous PAHs, which can adversely affect the balance of food web, finally adding to umpteen health issues to humans. The study concludes that the Veraval harbour and coastal waters require more temporal studies of POPs and other emerging contaminants in different environmental compartments, and their effects especially on marine biota. That will give basic insight for policymakers to take appropriate actions on pollution remediation and facilitate sustainable management of fishery harbours.

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Statements and Declarations

Authors Contributions:

Midhun M. N.: Investigation, Writing-original draft, Methodology, Visualization, Data curation, Formal analysis.

Rakesh P. S: Project planning and administration, Supervision, Methodology, Visualization, Writing-review and editing.

Pooja Y. K.: Investigation, Methodology, Formal analysis, Writing-review.

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The authors declare no competing interests.

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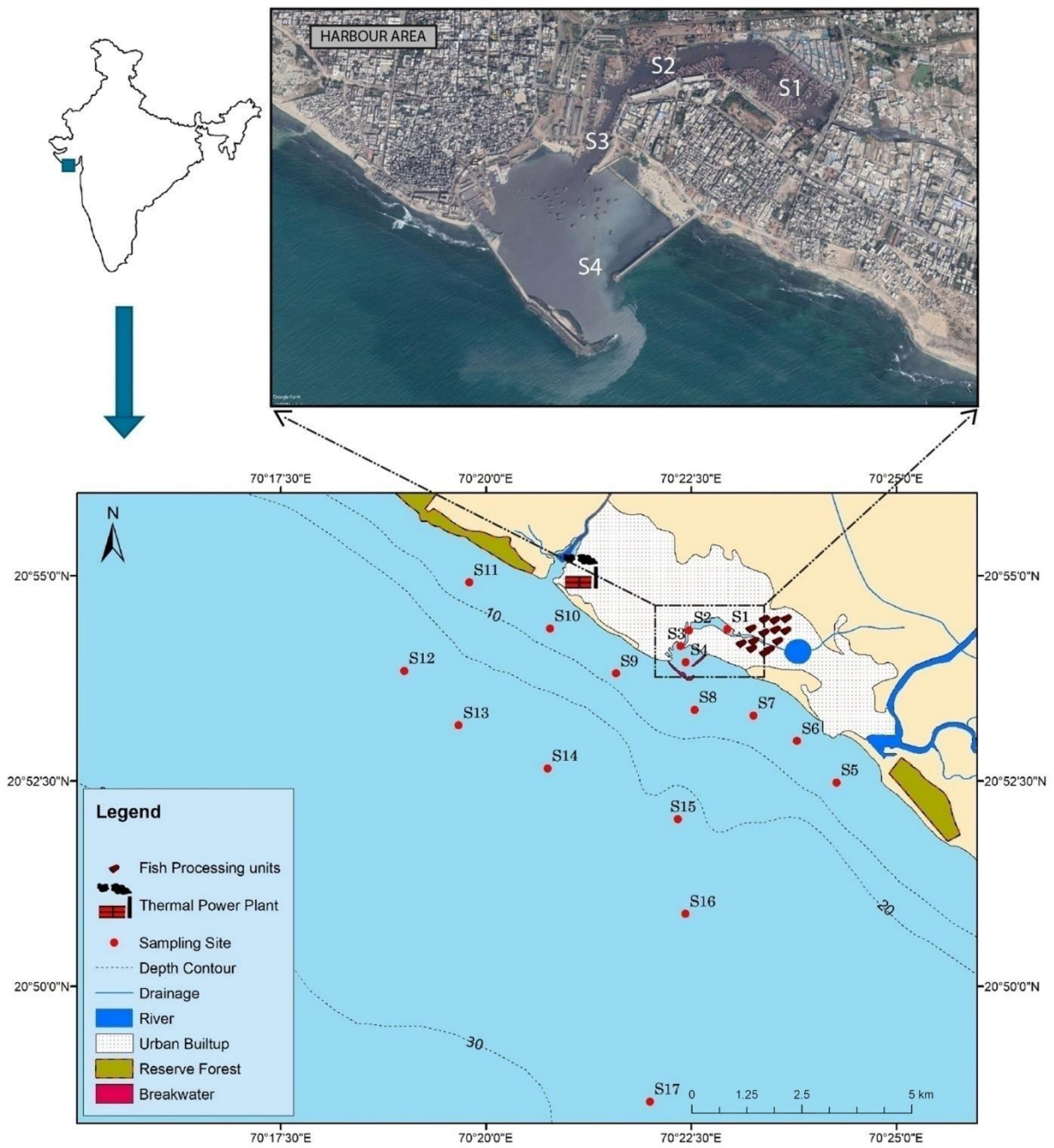


Fig.1. Study area map showing the sampling locations of the Veral coastal area

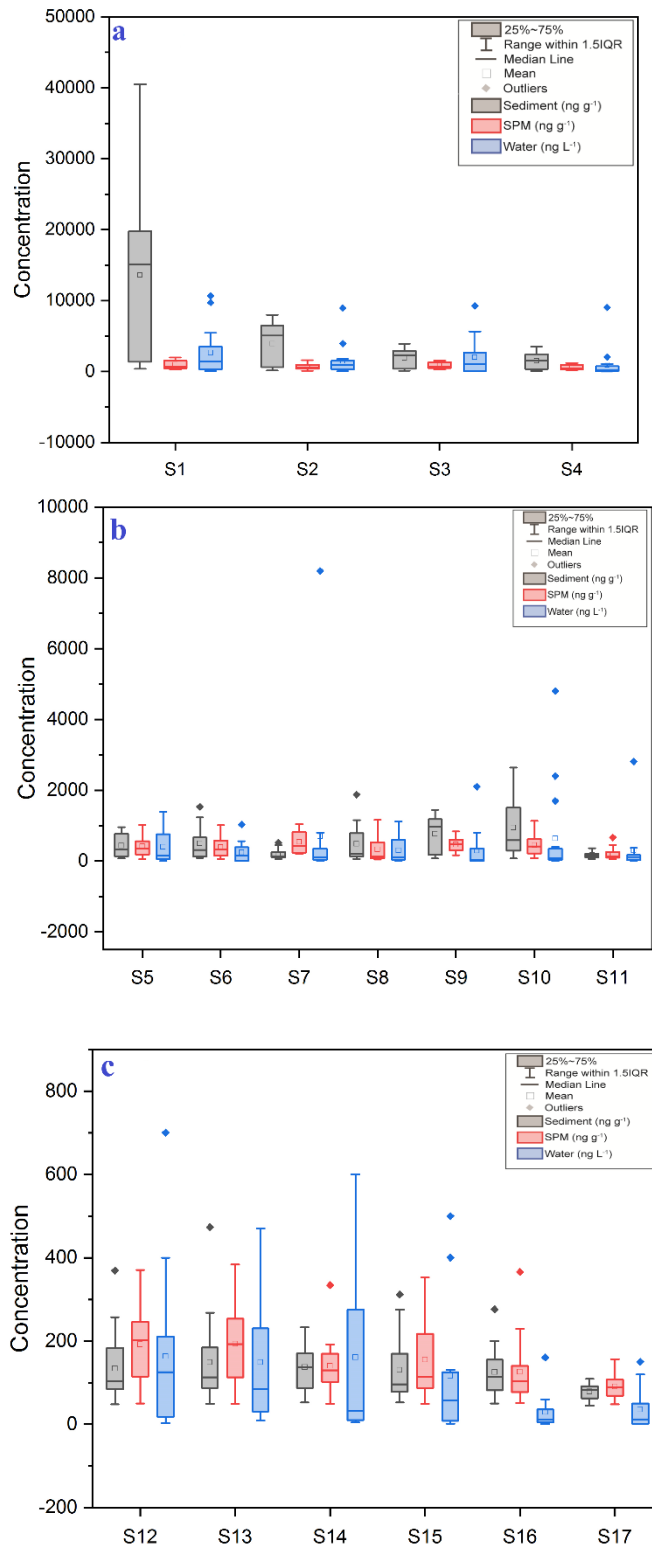


Fig. 2a, b & c. The spatial distribution of total PAHs in sediment, SPM and water from the study area (a- harbour; b- nearshore; c-offshore).

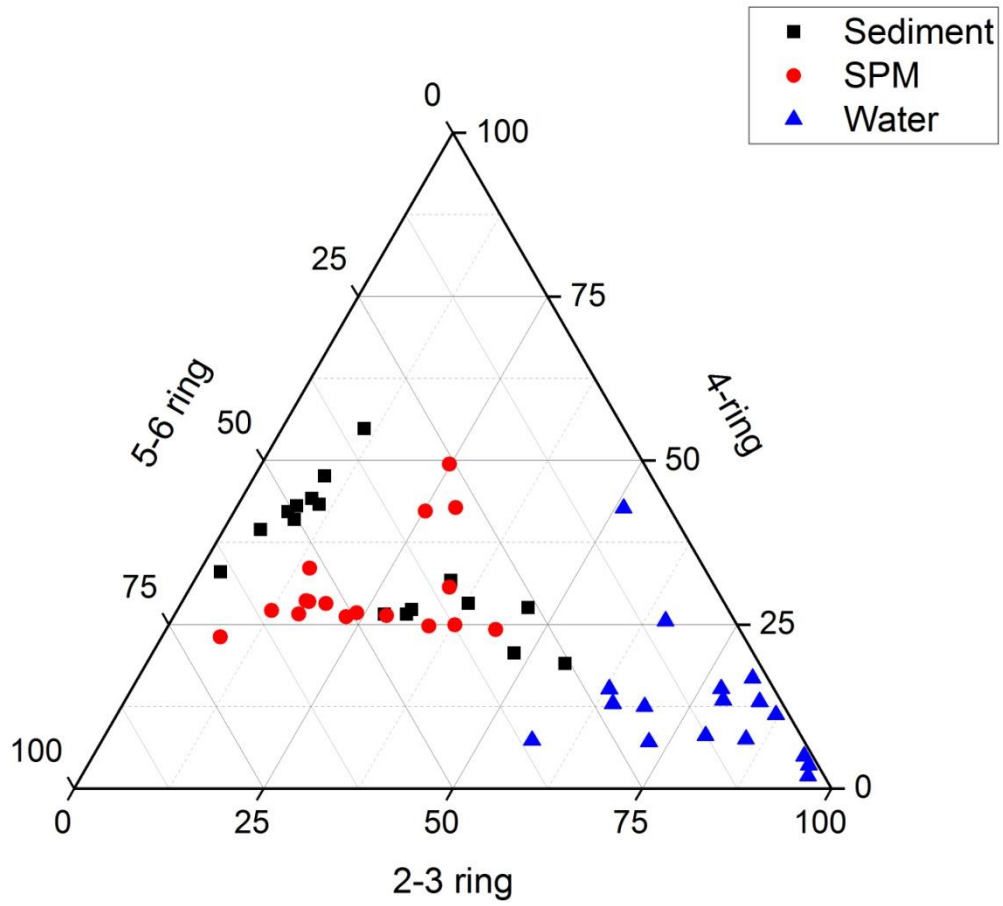


Fig. 3. The ring-wise distribution of PAHs in sediment, SPM and water in the study area

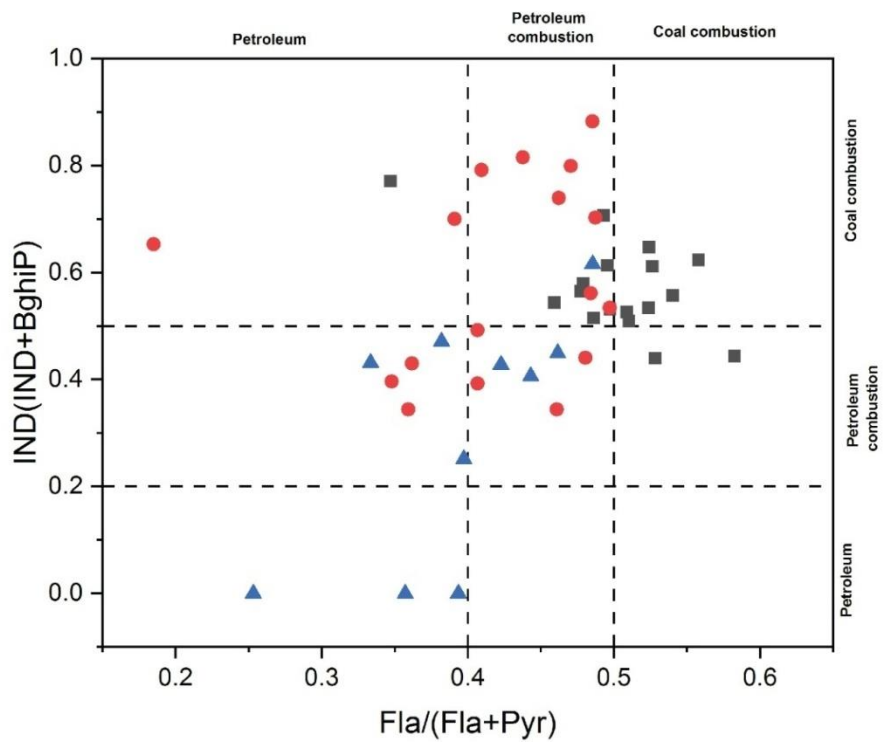
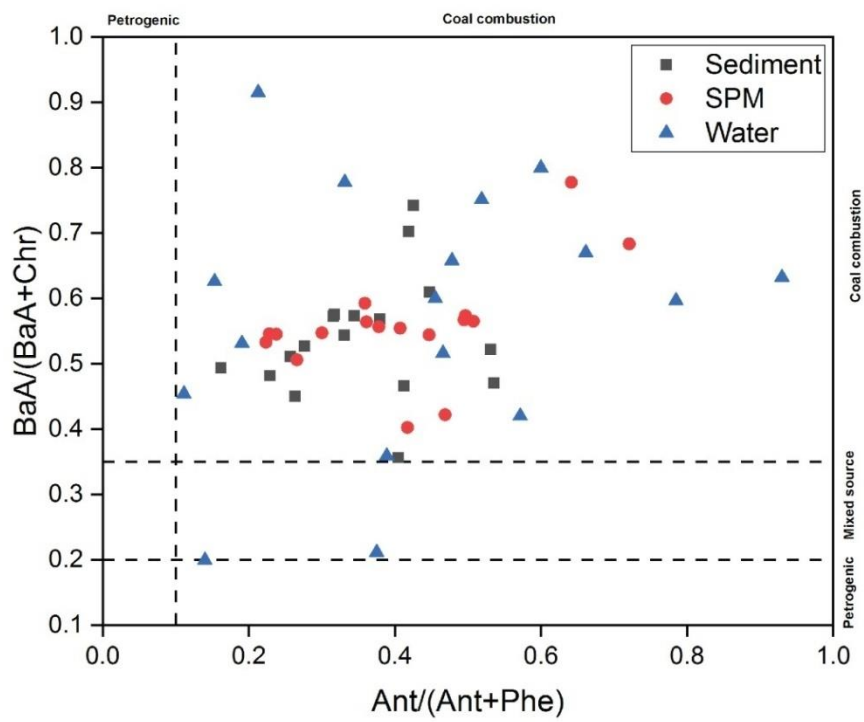


Fig. 4. Scatter plot showing the MDR Pattern in the study area

Table 1. The concentration of individual PAHs in sediment, SPM and water in the study area

PAHs	Sediment (ng g ⁻¹)		SPM (ng g ⁻¹)		Water (ng L ⁻¹)	
	Range	Mean	Range	Mean	Range	Mean
Nap	63.94 - 480.93	154.84 ± 100.73	66.14 - 389.09	161.84 ± 110.21	50.02 - 10660.23	3571.37 ± 3966.05
Acy	53.59 - 383.93	104.09 ± 82.01	49.35 - 352.33	144.75 ± 113.59	10.37 - 4108.00	521.81 ± 993.92
Ace	47.32 - 492.82	123.73 ± 120.30	47.33 - 359.16	135.99 ± 103.18	50.39 - 5450.23	724.81 ± 1312.61
Fle	60.37 - 1114.67	265.47 ± 259.67	61.74 - 428.68	256.58 ± 132.56	20.48 - 3943.08	981.46 ± 1152.19
Phe	91.74 - 1997.79	513.98 ± 494.34	100.38 - 710.53	352.39 ± 182.64	21.79 - 2665.8	736.57 ± 732.95
Ant	64.45 - 1618.34	310.97 ± 381.48	67.19 - 550.06	254.20 ± 163.76	10.8 - 9721.00	1081.75 ± 2316.54
Fla	78.23 - 20594.09	2450.28 ± 4978.27	83.37 - 838.51	316.78 ± 234.73	1.1 - 5320.23	611.87 ± 1319.01
Pyr	79.06 - 21779.53	2571.57 ± 5279.60	84.28 - 889.15	403.57 ± 252.27	2.00 - 5640.20	781.33 ± 1432.75
BaA	81.33 - 17993.26	2143.95 ± 4396.13	104.82 - 1697.22	675.68 ± 463.60	1.1 - 1450.6	260.24 ± 474.88
Chr	74.54 - 11525.09	1500.02 ± 2855.30	86.73 - 1603.56	562.96 ± 462.54	3.00 - 980.4	177.06 ± 318.41
BbF	109.02 - 40493.34	3610.40 ± 9712.76	110.59 - 1633.07	550.66 ± 509.35	1.20 - 416.4	94.87 ± 130.82
BkF	83.07 - 12206.82	1181.52 ± 2918.75	89.23 - 1078.02	353.78 ± 340.96	ND - 445.4	101.18 ± 129.16
BaP	87.71 - 18803.34	2158.02 ± 4557.71	88.59 - 1976.28	699.79 ± 556.73	1.3 - 325.3	53.96 ± 96.36
DBA	45.05 - 31088.85	2499.97 ± 7487.59	56.02 - 1423.28	462.56 ± 460.57	ND - 99.3	25.72 ± 31.73
BghiP	90.96 - 17956.80	1842.83 ± 4366.27	101.84 - 1163.26	400.60 ± 327.90	ND - 175.0	42.22 ± 53.19
IND	101.18 - 19030.70	2228.94 ± 4725.78	98.65 - 1880.94	629.56 ± 506.73	ND - 65.2	28.60 ± 25.01

Table 2. Major sources of PAHs in different environmental matrices from Indian and other fishing harbours globally

Major sources of ΣPAHs in different environmental matrices from East and West coast of India				
Matrix	PAHs number	ΣPAH concentration	Source	Reference
Sediments (ng g⁻¹)				
East coast of India				
Hugli estuary, West Bengal	19	2.5-1081	Sewage/effluents, vehicular emissions	Guzzella et al., 2005
Sundarban Mangrove, West Bengal	16	132 - 2938	Wood and coal combustion, atmospheric deposition, surface runoff	Dominguez et al., 2011
Gomti River, North coast	16	5.24–3,722.87	Atmospheric deposition, combustion source, industrial or natural fires	Malik et al., 2011
Sundarban Mangrove, Bengal	19	9.4 – 4222.8,	Vehicular emissions, biomass burning, coal combustion	Sarkar et al., 2012,
Sundarban Mangrove, Bengal	16	208.3-12933.1	Vehicular emissions, biomass burning, coal combustion	Zuloaga et al.,2013
River Brahmaputra, Guwahati	16	609- 8620	Emissions from diesel, gasoline and wood combustion	Hussain et al., 2015
Ennore estuary, Chennai	20	8.6 -910	Coal-fired thermal power station, motorized fishing boats	Goswami et al., 2016
Hugli estuary, West Bengal	16	3.3-630	Atmospheric deposition, industries, surface runoff, oil spills	Mitra et al., 2019
Hooghly river estuary, West Bengal	17	15.4-1731	Effluents, industries, vehicle emissions, incomplete combustion	Zanardi-Lamardo et al., 2019
Sundarban Mangrove, West Bengal	16	4880-20000	Coal, charcoal, wood combustion rice husking, coal power stations	Balu et al.,2020
Subarnarekha River, West Bengal	16	36.8-670.8	Petroleum combustion, biomass, and coal-burning	Ambade et al.,2021
Vembar group of Islands, Gulf of Mannar	16	0.36 -15.98	Coal incinerating power plants of Tuticorin industrial complex	Pradhap et al., 2021
Subarnarekha River, West Bengal	16	Undetectable-657	Combustion and petrogenic origin	Ambade et al., 2022a
Mahanadi River Estuary, North East coast	16	13.1-685.4	Petroleum, oil, biomass, and coal combustion	Ambade et al., 2022b
West coast of India				
Alang, Gulf of Cambay, Gujarat	16	78000-719000	Ship scrapping	Reddy et., al 2005
Harbour Line, Mumbai	15	2608 - 134134	Urban runoffs, sewage, intense shipping, oil refinery	Dhananjayan et al., 2012
Mithi River, Mumbai	17	1206–4735	Incomplete combustion of fossil fuel/ wood, oil and petroleum leakage	Singare, 2015
Thane Creek, Mumbai	15	902.58- 1643.60	Combustion of organic matter	Sukhdhane et al., 2015
Bhavnagar coast, Gujarat	16	5020-981180	Gas, oil and coal burning, industries	Dudhagara et al., 2016
Cochin estuary, Kerala	18	304-5744	Petroleum spill, vegetation fire, gasoline engine exhaust, vehicular emission	Ramzi et al., 2016
Mudflats of Thane Creek, Mumbai	16	3.14–320.00	Incomplete combustion, garbage dumping ground	Basavaiah et al., 2017
Alang-Sosiya Ship breaking Yard, Gujarat	17	734.83-30396.25	Ship breaking, oil spillage, transportation, industries	Gosai et al., 2017
Navlakhi Port, Gujarat	17	1309.65 - 54240.45	Anthropogenic, heavy transportation, fossil fuel burning, local industries	Gosai et al., 2017
Gulf of Kutch, Gujarat	11	118,280–1,099,410	Petroleum, wood or coal combustion	Rajpara et al., 2017
Thane creek, Mumbai	16	219- 495	Urban runoff, high temperature combustion	Tiwari et al., 2017
Coast of Varkala to Alappad, Kerala	16	13.3822-55831	Atmospheric deposition, urban runoff, domestic and industrial wastewater, spillage of petroleum	Yahiya and Miranda, 2021
Estuaries of Kerala (Kadinamkulam, Anchuthengu, Kappil-Hariharapuram, Kayamkulam)	16	0.47 -126.64	Anthropogenic activities	Radhakrishnan et al., 2021

Malad and Versova creek, Mumbai	17	2915–4204	Incomplete combustion of wood and fossil fuels, oil and petroleum leakage	Singare and Shirodkar, 2021b
Veraval Harbour, Gujarat	16	1263.5-217560.3	Petroleum spill, pyrogenic and atmospheric deposition	Present study
SPM (ng g⁻¹)				
West coast of India				
Veraval Harbour, Gujarat	16	1450.8-15291.6	Petroleum spill, pyrogenic and atmospheric deposition	Present study
Water (ng L⁻¹)				
East coast of India				
Gomti River, North coast	16	600-84200	Atmospheric deposition, combustion source, industrial or natural fires	Malik et al., 2011
Chennai coast, Chennai	1	770 -2230	Sewage, effluents	Sundararajan et al, 2015
Sundarban Mangrove, West Bengal	16	Undetectable- 0.125	Coal, charcoal, wood combustion rice husking, coal power stations	Balu et al.,2020
Subarnarekha River, West Bengal	16	Undetectable-33000	Petrogenic, fuel combustion, coal gas, wood burning	Ambade et al., 2022a
West coast of India				
Thane Creek, Mumbai harbour	7	84.3–377.5	Atmospheric deposition	Pandit et al., 2006
Mahim Creek, Mumbai	17	940-31300	Combustion of grass, wood, coal and fuels	Singare, 2016
Thane creek, Mumbai	16	337 ± 79	Urban runoff, pyrogenic	Tiwari et al., 2017
Coast of Varkala to Alappad, Kerala	16	0.4297-2680.90	Atmospheric deposition, urban runoff, sewage/effluents, spillage of petroleum	Yahiya and Miranda, 2021
Malad and Versova creeks, Mumbai	16	114320-347040	Incomplete combustion of wood and fossil fuels, oil and petroleum leakage	Singare and Shirodkar, 2021a
Veraval Harbour, Gujarat	16	358.2-42712.4	Petroleum spill, pyrogenic and atmospheric deposition	Present study

Major sources of ΣPAHs in different environmental matrices from fishing harbours globally

Sediments (ng g⁻¹)				
Hsin-ta Harbour, Taiwan	30	98.1-2048	Motor oil, power plant	Fang et al., 2003
Auckland Harbour, New Zealand	24	2000-998000	Urban runoff, coal-tar materials, atmospheric fallout	Ahrens and Depree, 2004
West coastal of the Gulf of Tunis (Tunisia)	22	363.3-7026.4	Industrial and vehicle emission, sewage, diesel oil leakage	Mzoughi and Chouba, 2011
Tripoli harbour, Lebanon	16	243-2965	Coal dust deposition, biomass and coal combustion	Merhaby et al., 2015
Tema Harbour, Ghana	16	2750-5130	Organic matter combustion, petroleum spillage	Botwe et al., 2016
Small craft harbour Nova Scotia, Canada	16	37-336770	Anthropogenic contamination	Davis et al., 2018
SPM (ng g⁻¹)				
West coastal of the Gulf of Tunis (Tunisia)	22	909.9-8222.4	Industrial and vehicle emission, sewage, diesel oil leakage	Mzoughi and Chouba, 2011
Water (ng L⁻¹)				
Western Mediterranean harbour	16	1-60	Urban runoff and inputs from the stream	Pane et al., 2005
West coastal of the Gulf of Tunis (Tunisia)	22	139.2-1008.3	Industrial and vehicle emission, sewage, diesel and oil leakage	Mzoughi and Chouba, 2011

Table3. Varimax rotated principal component factors in the study area

PAHs	Sediment		SPM		Water		
	PC 1	PC 2	PC 1	PC 2	PC 1	PC 2	PC 3
Nap	.863	.361	.950	.226	.407	.676	.388
Acy	.731	.642	.937	.275	.911	.260	.234
Ace	.281	.934	.942	.273	.914	.215	.326
Fle	.908	.379	.916	.090	.061	.930	.300
Phe	.912	.327	.887	-.152	.694	.520	.180
Ant	.858	.458	.917	.324	.932	.140	.300
Fla	.766	.640	.878	.296	.210	.272	.935
Pyr	.783	.618	.896	.288	.300	.268	.912
BaA	.783	.619	.767	.595	.614	.486	.608
Chr	.807	.581	.924	.202	.656	.619	.393
BbF	.753	.641	.637	.672	.416	.790	.361
BkF	.759	.638	.669	.613	-	-	-
BaP	.767	.636	.727	.658	.685	.675	-.023
DBA	.730	.659	.242	.901	-	-	-
BghiP	.776	.626	-.322	.795	-	-	-
IND	.811	.578	.701	.686	-	-	-
Variance (%)	93.2	3.6	73.3	13.6	73.0	11.5	8.4

Table 4. The ecological risk quotient values in the study area

	Sediment			SPM			Water			
	M-ERM-Q	TEQ ^{carc} (mg/kg)	TEQ ^{carc} /TEQ _{QV}	M-RQ	TEQ ^{carc} (mg/kg)	TEQ ^{carc} /TEQ _{QV}	M-RQ	TEQ ^{carc} (mg/kg)	TEQ ^{carc} /TEQ _{QV}	M-RQ
S1	9.95	57.78	2139.91	2622.10	3.93	145.63	221.53	0.57	1145.12	3518.69
S2	3.77	13.72	508.32	794.72	1.65	61.22	196.88	0.51	1024.83	1874.16
S3	1.94	5.99	221.81	386.61	3.19	118.25	208.87	0.25	506.30	2457.99
S4	1.37	3.64	134.79	344.19	2.32	86.01	135.94	0.08	156.83	775.45
S5	0.44	1.20	44.49	109.92	1.52	56.21	102.08	0.03	50.87	414.66
S6	0.46	1.15	42.48	131.43	1.53	56.81	83.06	0.01	23.53	183.64
S7	0.19	0.25	9.15	80.26	2.07	76.60	127.23	0.06	119.20	284.19
S8	0.31	2.76	102.28	109.64	1.77	65.59	43.37	0.05	93.64	283.17
S9	0.66	2.44	90.48	166.58	1.41	52.28	119.35	0.03	68.69	157.66
S10	0.93	2.44	90.34	266.74	0.98	36.44	140.64	0.08	162.21	490.18
S11	0.22	0.33	12.16	54.84	0.39	14.33	65.67	0.04	78.95	173.51
S12	0.11	0.21	7.83	43.18	0.61	22.48	50.88	0.02	42.74	184.12
S13	0.17	0.22	8.15	54.03	0.54	20.17	49.40	0.03	66.17	162.77
S14	0.16	0.26	9.56	43.85	0.32	12.00	46.26	0.009	18.22	154.69
S15	0.15	0.17	6.33	58.09	0.34	12.74	46.93	0.003	5.46	87.10
S16	0.14	0.26	9.53	36.48	0.19	6.94	45.83	0.003	6.94	22.57
S17	0.09	0.17	6.23	24.66	0.20	7.59	28.51	0.002	3.68	32.56

Supplementary Data

Table S1a: The concentration of 16EPA PAHs in the sediment samples (ng g⁻¹)

PAHs	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17
Nap	480.93	273.39	159.05	125.19	76.44	122.32	121.51	63.94	94.32	149.67	136.86	114.46	152.06	159.53	241.91	88.15	72.51
Acy	383.93	190.73	99.06	159.04	110.23	86.32	57.24	98.33	81.64	105.12	58.21	56.40	57.90	60.91	55.71	55.25	53.59
Ace	492.82	129.33	133.72	77.76	212.25	315.30	55.86	175.90	73.66	73.20	55.65	48.43	55.16	52.56	54.66	49.84	47.32
Fle	1114.67	639.51	291.45	290.51	100.22	125.37	299.15	60.37	154.43	283.95	260.55	104.50	267.91	154.67	216.11	88.50	61.19
Phe	1997.79	1202.11	999.88	813.94	138.37	126.84	447.97	192.12	437.78	485.48	365.67	257.60	473.68	232.95	275.16	198.60	91.74
Ant	1618.34	632.38	464.80	401.84	102.37	91.37	516.83	130.76	202.04	296.48	126.47	76.43	91.35	83.16	311.75	75.75	64.45
Fla	20594.09	6552.34	3913.28	2699.35	958.90	1536.24	211.42	1155.03	1447.48	1405.66	207.15	169.72	217.15	222.96	123.19	162.50	78.23
Pyr	21779.53	7127.23	3522.56	2957.72	815.33	1100.90	192.30	1031.70	1389.09	2643.82	213.03	199.88	221.16	176.96	118.85	147.50	79.06
BaA	17993.26	6388.36	2994.64	2524.23	915.37	1236.35	115.28	444.84	1249.01	1792.99	166.99	97.01	107.88	133.90	81.33	118.40	87.32
Chr	11525.09	4755.94	2208.60	2123.39	318.24	523.66	129.69	802.54	932.38	1361.39	160.08	104.36	110.49	163.58	74.54	106.30	100.13
BbF	40493.34	7985.15	2855.98	3517.94	716.12	314.26	418.18	492.77	1388.32	1936.09	136.12	369.22	115.11	137.71	115.33	276.12	109.02
BkF	12206.82	2727.92	1005.01	1227.37	321.01	218.37	186.15	211.20	512.02	696.02	86.26	196.70	83.07	91.94	89.32	138.88	87.80
Bap	18803.34	6159.99	2595.02	2303.66	819.24	618.22	120.01	1876.53	1013.39	1498.56	198.68	99.76	132.46	136.52	87.71	131.14	92.14
DBabA	31088.85	5356.51	2411.72	479.58	149.21	314.25	60.83	777.04	1047.28	407.29	69.67	51.84	49.25	73.51	52.54	65.13	45.05
BghiP	17956.80	5355.87	2450.04	1831.86	526.35	712.32	95.22	144.45	1084.41	453.23	118.87	93.09	95.13	119.18	91.15	109.17	90.96
IND	19030.70	7387.92	3848.98	2374.40	662.35	568.26	109.27	113.35	1125.36	1521.61	286.35	110.92	150.96	197.20	101.18	200.19	103.02
ΣPAHs	217560.30	62864.68	29953.79	23907.78	6941.97	8010.32	3136.91	7770.87	12232.61	15110.56	2646.61	2150.32	2380.72	2197.24	2090.44	2011.42	1263.53

Table S1b: The concentration of 16EPA PAHs in the SPM samples (ng g⁻¹)

PAHs	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17
Nap	326.26	389.09	337.99	235.54	72.96	89.37	222.15	66.47	197.91	238.77	97.26	105.4	74.08	94.22	67.54	66.14	70.16
Acy	348.59	352.33	324.66	228.58	49.35	55.96	213.22	53.8	178.6	212.15	70.71	77.39	58.09	65.5	60.14	57.77	53.91
Ace	286.47	359.16	277.64	206.85	123.94	87.65	197.23	47.33	163.83	213.03	49.91	50.39	49.54	49.56	49.63	51.33	48.36
Fle	428.68	434.91	511.52	246.53	254.87	165.39	226.41	61.74	412.18	407.82	134.11	157.021	191.73	185.38	210.45	229.21	103.95
Phe	557.26	612.88	710.53	317.74	122.72	138.98	286.43	100.38	461.88	583.92	291.29	214.24	383.61	334.12	352.46	365.72	156.54
Ant	550.06	540.55	488.1	311.37	316.98	248.67	295.25	81.08	261.27	417.78	163.19	130.26	110.57	121.22	109.85	108.01	67.19
Fla	579.59	838.51	617.85	433.25	438.17	396.15	400.19	90.75	345.67	514.58	89.9	101.82	125.25	107.7	110.6	111.96	83.37
Pyr	836.13	889.15	718.66	455.59	512.2	428.36	450.25	161.76	368.24	660.86	396.15	190.85	182.72	189.94	172.25	163.38	84.28
BaA	1697.22	1171.01	1425.27	921.07	859.39	687.12	906.14	528.57	681.74	761.43	664.01	295.12	271.17	133.32	262.21	116.89	104.82
Chr	1261.92	1603.56	1145.99	703.58	398.12	196.46	697.97	442.58	527.22	1130.89	456.16	235.39	237.58	130.22	218.61	97.37	86.73
BbF	1633.07	540.32	1521.35	1192.26	616.128	439.27	1015.6	149.53	836.71	294.77	120.68	250.15	194.16	129.64	116.24	200.82	110.59
BkF	1009.8	377.14	1078.02	767.65	248.96	212.19	735.32	95.91	546.58	194.44	116.35	124.33	115.13	89.23	107.49	104.8	90.99
Bap	1976.28	1255.96	1548.11	964.04	1022.36	879.36	1041.44	532.2	716.69	736.25	225.73	215.3	211.98	153.53	216.25	88.59	112.42
DBabA	1423.28	117.18	1193.46	1037.93	302.31	459.87	731.03	1108.64	471.2	80.84	60.72	311.43	260.06	128.66	62.62	56.02	58.25
BghiP	496.09	137.26	509.07	425.34	813.58	1012.32	240.39	1163.26	513.39	131.86	108.15	370.47	381.9	192.07	111	101.84	102.28
IND	1880.94	1032.57	1444.84	1005.64	426.78	796.86	955.44	609.73	657.11	580.66	202.97	242.91	246.88	144.68	258.9	98.65	116.99
ΣPAHs	15291.64	10651.58	13853.06	9452.96	6578.818	6293.98	8614.46	5293.73	7340.22	7160.05	3247.29	3072.471	3094.45	2248.99	2486.24	2018.5	1450.83

Table S1c: The concentration of 16EPA PAHs in the water samples (ng L⁻¹)

PAHs	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17
Nap	10660.2	8949.9	9270.1	9030.0	1390.0	1030.5	8200.1	1120.2	2100.4	4800.0	2810.1	400.2	470.2	150.6	120.1	160.6	50.0
Acy	4108.0	1199.1	910.2	950.0	60.1	100.0	330.0	100.4	30.3	80.0	100.1	130.8	200.3	10.4	400.5	10.5	150.1
Ace	5450.2	1505.1	1740.4	320.0	800.9	560.1	160.3	190.2	140.5	300.9	170.5	200.9	400.7	110.1	100.8	50.4	120.1
Fla	1337.0	3943.1	2910.3	2030.0	620.0	230.0	370.0	360.2	500.6	2400.2	370.8	700.4	150.9	550.1	130.8	60.1	20.5
Phe	2665.8	1771.3	1230.0	80.0	910.1	390.1	800.0	600.1	800.1	1700.0	120.7	220.7	260.6	400.5	500.0	21.8	50.0
Ant	9721.0	1543.9	2400.1	1060.0	760.3	420.1	100.1	800.5	130.0	400.8	110.5	140.4	70.5	600.5	90.5	10.8	30.0
Fla	2133.9	904.4	5320.2	340.0	200.0	160.1	300.2	400.2	230.8	80.2	130.3	120.6	40.7	20.4	10.7	8.0	1.1
Pyr	2914.4	1055.0	5640.2	550.0	590.0	230.1	600.0	720.2	350.0	100.8	200.8	210.4	50.9	25.5	23.3	19.1	2.0
BaA	1450.6	912.9	1320.3	190.1	90.2	30.2	50.1	50.8	10.0	126.3	20.1	10.1	100.0	40.1	10.5	10.5	1.1
Chr	980.4	855.5	650.3	110.6	60.1	10.0	60.2	70.1	40.2	111.4	10.5	18.1	9.3	10.1	6.3	3.0	4.1
BbF	308.3	416.4	289.7	228.6	112.4	13.0	34.4	23.2	15.7	60.7	28.7	51.5	17.2	5.8	3.9	1.2	2.4
BkF	445.4	227.6	87.5	47.5	15.0	7.5	97.7	50.2		25.2	40.0	69.4	-	-	-	-	-
Bap	285.4	325.3	50.1	12.1	5.0	7.4	44.1	36.2	26.5	48.4	34.2	12.0	21.4	4.5	1.3	2.3	1.5
DBabA	99.3	46.7	35.2	22.3	-	-	5.1	2.6	5.0	12.6	-	2.5	-	-	-	-	-
BghiP	87.3	54.2	33.2	17.1	5.1	-	12.3	15.2	7.5	15.2	175.0	-	-	-	-	-	-
IND	65.2	44.2	53.2	15.2	-	-	9.4	-	2.5	10.4	-	-	-	-	-	-	-
∑PAHs	42712.40	23754.51	31941.14	15003.56	5619.16	3189.11	11174.14	4540.24	4390.08	10272.90	4322.21	2287.76	1792.52	1928.21	1398.35	358.19	432.84

Table S2a: The molecular diagnostic ratio (MDR) values in the sediment samples

Sample ID	$\Sigma\text{LWW}/\Sigma\text{HMW}$	Fla/(Fla+Pyr)	IND(IND+BghiP)	Ant/(Ant+Phe)	BaA/(BaA+Chr)
S1	0.03	0.49	0.51	0.45	0.61
S2	0.05	0.48	0.58	0.34	0.57
S3	0.08	0.53	0.61	0.32	0.58
S4	0.08	0.48	0.56	0.33	0.54
S5	0.12	0.54	0.56	0.43	0.74
S6	0.12	0.58	0.44	0.42	0.70
S7	0.91	0.52	0.53	0.54	0.47
S8	0.10	0.53	0.44	0.40	0.36
S9	0.09	0.51	0.51	0.32	0.57
S10	0.10	0.35	0.77	0.38	0.57
S11	0.61	0.49	0.71	0.26	0.51
S12	0.44	0.46	0.54	0.23	0.48
S13	0.86	0.50	0.61	0.16	0.49
S14	0.51	0.56	0.62	0.26	0.45
S15	1.24	0.51	0.53	0.53	0.52
S16	0.38	0.52	0.65	0.28	0.53
S17	0.45	0.50	0.53	0.41	0.47

Table S2b: The molecular diagnostic ratio (MDR) values in the SPM samples

Sample ID	$\Sigma\text{LWW}/\Sigma\text{HMW}$	Fla/(Fla+Pyr)	IND(IND+BghiP)	Ant/(Ant+Phe)	BaA/(BaA+Chr)
S1	0.20	0.41	0.79	0.50	0.57
S2	0.34	0.49	0.88	0.47	0.42
S3	0.24	0.46	0.74	0.41	0.55
S4	0.20	0.49	0.70	0.49	0.57
S5	0.17	0.46	0.34	0.72	0.68
S6	0.14	0.48	0.44	0.64	0.78
S7	0.20	0.47	0.80	0.51	0.56
S8	0.08	0.36	0.34	0.45	0.54
S9	0.30	0.48	0.56	0.36	0.56
S10	0.41	0.44	0.81	0.42	0.40
S11	0.33	0.18	0.65	0.36	0.59
S12	0.31	0.35	0.40	0.38	0.56
S13	0.39	0.41	0.39	0.22	0.53
S14	0.61	0.36	0.43	0.27	0.51
S15	0.52	0.39	0.70	0.24	0.55
S16	0.77	0.41	0.49	0.23	0.55
S17	0.53	0.50	0.53	0.30	0.55

Table S2c: The molecular diagnostic ratio (MDR) values in the water samples

Sample ID	$\Sigma\text{LWW}/\Sigma\text{HMW}$	Fla/(Fla+Pyr)	IND(IND+BghiP)	Ant/(Ant+Phe)	BaA/(BaA+Chr)
S1	3.72	0.42	0.43	0.78	0.60
S2	3.69	0.46	0.45	0.47	0.52
S3	1.37	0.49	0.62	0.66	0.67
S4	8.78	0.38	0.47	0.93	0.63
S5	4.21	0.25	0.00	0.46	0.60
S6	5.96	0.41	-	0.52	0.75
S7	8.21	0.33	0.43	0.11	0.45
S8	2.32	0.36	0.00	0.57	0.42
S9	5.38	0.40	0.25	0.14	0.20
S10	16.38	0.44	0.41	0.19	0.53
S11	5.76	0.39	0.00	0.48	0.66
S12	3.41	0.36	-	0.39	0.36
S13	6.49	0.44	-	0.21	0.92
S14	17.15	0.44	-	0.60	0.80
S15	24.05	0.31	-	0.15	0.63
S16	7.13	0.30	-	0.33	0.78
S17	34.62	0.35	-	0.38	0.21