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Sources, Vertical Fluxes and Accumulation of Petroleum Hydrocarbons in Sediments from the Mandovi Estuary, west Coast of India

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ABSTRACT: The Mandovi estuary is highly influenced by mining and tourism related activities in the central west coast of India. Vertical fluxes and accumulation of petroleum hydrocarbons (PHCs) in three sediment cores (D1, C1 and OG) from the Mandovi estuary were assessed using Ultra-Violet Fluorescence (UVF) spectroscopy. The range of PHCs values in estuarine sediments varied from 5.4 to 12.34 µg/g Enrichment of PHCs values in the upper parts of three sediment cores were mostly derived from terrestrial and marine related sources including petrogenic (discharge of land based effluents and petroleum products), pyrogenic (emission of fly ash from industries and vehicles and combustion of petrol from ore-filled barges, boats and ships) and biogenic (mangrove vegetation along the banks of the estuary) sources. The significant positive relationship between mud (silt + clay) and PHCs unveiled that high specific surface of area of mud content raise the level of petroleum hydrocarbons. Cluster analysis was used to discriminate the sediment samples based on their degree of contamination. Values of PHCs in the upper part of sediment cores were distinctly higher than the background but were lower than those found in the Thane creek, west coast India (7.6–42.8 µg/g) and off Chennai, east coast of India (1.8 – 39.72 µg/g). This baseline PHCs data can be used for regular ecological monitoring and effective management for the mining and tourism related activities in the Mandovi estuary.

Key words: Petroleum hydrocarbon, core sediment, pollution, mining, Mandovi estuary

INTRODUCTION

Estuaries are among the most productive marine ecosystems in the world and are critical to the life history and development of many aquatic species. Estuarine regions are vulnerable to contamination by petroleum hydrocarbons (PHCs) originated from domestic and industrial wastewater discharges, boating and shipping activities, and marine operations including tanker traffic and oil production. PHCs are strongly particle associated in aquatic ecosystems due to their hydrophobic properties, and tend to accumulate in sediments (Chapman & Wang, 2001). When hydrocarbons are released directly to water through spills or leaks, certain hydrocarbon fractions will float in water and form thin surface films. Other heavier fractions will accumulate in bottom sediment of estuary because of their high octanol/water partition coefficient (K_{ow}) and low solubility characteristics. Therefore, the study of petroleum hydrocarbon contamination level in estuarine sediment can provide useful information for further understanding of environmental processes and material transport land to sea. Hydrocarbons in petroleum include several types such as normal alkanes (saturated, n-alkanes), unsaturated hydrocarbons, non-symmetric cyclic hydrocarbons (terpanes) and polycyclic aromatic hydrocarbons (PAHs). Predominance of these compounds in the environmental samples may indicate petroleum pollution (Sakari, 2011; Tavakoly Sany *et al.*, 2014). Petroleum contaminants are subject to several changes, such as degradation, photo-oxidation and decay after release. Petroleum hydrocarbons released to the soil may move through the soil to the groundwater. PHCs are carcinogens and affect a variety of biological processes and potent cell mutagens (Veerasingam *et al.*, 2011a, b). Vertical distribution of petroleum hydrocarbons in estuarine sediment cores is commonly used as a historical pollution records (Venkatachalapathy *et al.*, 2010, 2011).

The Mandovi River is located between the Sahyadris hills and the Arabian Sea along the west coast of India (Fig. 1). Mandovi estuary is ~75 km long and

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has a drainage area of about ~ 1895 sq km (Qasim & Sen Gupta, 1981). The mouth of the estuary is 3.2 km in width and its progressively narrows to 0.25 km toward the upstream end. The estuary receives 660 cm/yr of rainfall (Shetye *et al.*, 2007). During monsoon (June to September), the river run-off is higher (~258 m^3/s, measured at the head) than the post- and pre-monsoons (November to May, ~6 m^3/s) (Vijith *et al.*, 2009). Mandovi estuary is meso-tidal, and the tidal ranges are ~2.3 and 1.5 m during the spring and neap tides, respectively. Tidal oscillations are observed and saline waters penetrate nearly 45 km upstream from the river mouth during dry period. The current in this estuary is tide-dominated. (Manoj & Unnikrishnan, 2009). Mangroves are fringe on the banks of the Mandovi estuary consist mainly of species like *Rhizophora mucronata, Pongamia pinnata, Cyperus spp., Bruguiera gymnorrhiza, Avicennia officinalis, Caesalpinia spp., Sonneratia caseolaris* and *Acanthus illicifolius*. These mangroves support the livelihood and have immense ecological and economic value (Fernandes *et al.*, 2012). Mandovi River is used for the transportation of ferromanganese ores from mines located upstream to the Mormugao harbour. About two-thirds of the mining activities for Fe-Mn ores in Goa are located in the Mandovi basin (Pathak *et al.*, 1988). The mining associated activities such as transportation of ores to platforms, ore loading, and effluents from beneficiation plants, barge-building activity and other mining activities do take place within the river basin. A ship-building unit is located on the lower estuary; fishing activity comes to a standstill during monsoon and all the mechanized fishing boats are stationed at the lower estuary (Shynu *et al.*, 2012). Apart from these, the basin has been used for agriculture, farming, tourism and recreational activities. Panaji is the capital of Goa state, located on the shore of the lower estuary. Numerous studies on the physical, chemical, biological and geological characterisation of the sediments and waters of the Mandovi estuary have already been carried out (Alagarsamy, 2006; Shetye *et al.*, 2007; Vijith *et al.*, 2009; Manoj & Unnikrishnan, 2009; Shynu *et al.*, 2012). The impacts of mining activities on the distribution of PHCs and PAHs in waters and surface sediments of the Mandovi estuary have also been documented earlier (Fondekar *et al.*, 1980 and Harji *et al.*, 2008) Regardless of these previous efforts, the long term impact of mining activities and PHCs contamination history in estuarine sediments have not been fully determined. Therefore, the purpose of this study is to evaluate the vertical distribution, sources and relative degree of PHCs contamination in the sediments of Mandovi estuary.

MATERIALS & METHODS

There are three sediment cores (D1, C1 and OG) were collected from the mangrove ecosystem along the Mandovi estuary using a hand-operated corer on 8 January 2013 (Fig. 1). Positions of the sampling locations were identified using a hand-held Garmin Global Positioning System. Soon after collection, the cores were sectioned into 2.5 cm intervals using a plastic knife from the surface. The sub-samples were sealed in clean plastic bags, labelled and stored in an ice box till the completion of laboratory analyses. The texture sizes (sand, silt and clay) of collected sediment samples were estimated using analytical procedure presented by Folk (1968). The collected sediment samples were saponified using KOH methyl alcohol mixture. 10 g of sediment sample was subjected for soxhlet extraction with n-hexane. The concentrated extract, after drying, was separated into alkane and aromatic fractions in an alumina column. Extracts were stored in glass vials and stored in refrigerator until the analysis by Spectrofluorometer. The fluorescence of the samples was measured by Spectrofluorometer (UVF, Shimadzu; make: RF 5301PC Spectrofluorometer).

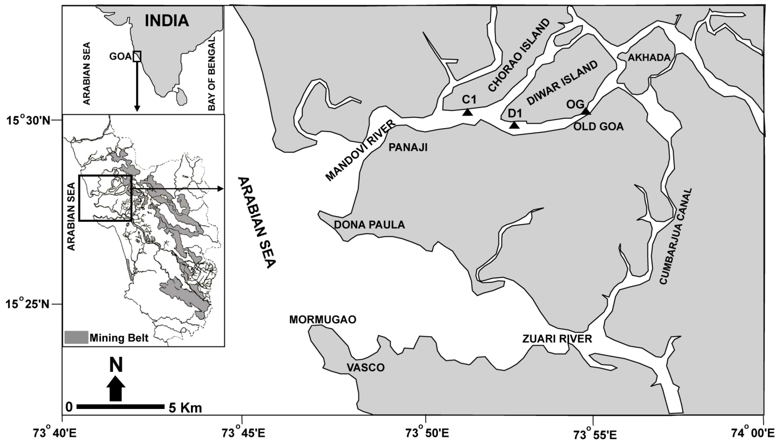

Fig. 1. Location of sampling sites (marked with triangles) in the Mandovi estuarine mangrove ecosystem.

Fluorescence conditions were as follows: excitation at 310 nm and emission at 360 nm (IOC-UNESCO, 1982). A calibration curve was produced with a Bombay High Crude oil standard. Results were provided in µg/g. All blanks, standards and samples were measured in a Teflon capped 1 cm silica fluorescence cell under identical instrumental settings and conditions. Duplicates, spikes and blanks were treated identically using Bombay High crude oil as a standard reference to test the precision, accuracy and solvent purity in the analytical procedure and the data were expressed in terms of Bombay High crude oil equivalents (Veerasingam *et al*., 2010). The cluster analysis (CA) was performed to obtain information about the similarities and dissimilarities present among the sediment samples with respect to depth at three different locations to ascertain the influence of pollution sources in the Mandovi estuary. The computer package XLSTAT was employed to perform the statistical analysis.

RESULTS & DISCUSSION

The vertical distribution of PHCs in three sediment cores from the Mandovi estuary is illustrated in Fig. 2. The ranges of PHCs in sediment cores D1, OG and C1 are 5.4–12.34 µg/g, 8.4–10.4 µg/g and 9.6–11.45 µg/g, respectively. The temporal variations of geochemical properties in sediment cores reflect the complete historical environmental condition of a given region, including any anthropogenic impact (Veerasingam *et al*., 2014). Vertical distribution of PHCs in sediment cores D1, OG and C1 showed low values in the lower parts and intermediate to high values in the upper parts of the cores. With reference to vertical changes of PHCs in D1 core, three distinct horizons - marked as horizon I (0 to 35 cm), horizon II (35 – 75 cm) and horizon III (75 – 100 cm) - can be distinguished. Horizon III is characterised by comparatively low PHCs values and it provides information on 'natural hydrocarbon background signal'. An enhancement of the hydrocarbon concentrations marks the transition horizon II, while a sharp increase of the PHCs separates horizon II and I. In horizon I (above 35 cm), a significant and steady enrichment of PHCs obtained due to increasing anthropogenic influence in the recent past. The other two short cores, OG and C1, showed gradual increase in PHCs from bottom to top (Fig. 2). Singh *et al.* (2014) recently collected a 76cm length of sediment core (near D1 core location in the Mandovi estuary) and found that the sedimentation rate was slower (0.14cm/y) from the bottom to 35cm, which approximately corresponds to the year 1980, and the rate increased thereafter to 1.42cm/y. i.e., the bottom of the core (76 cm from the surface) dates back to 1694. In the present study, the age of bottom sediment layer of D1 core (105 cm), dates back to 1565 (based on the sedimentation rate estimated by Singh *et al.* (2014) using ^{210}Pb dating). Thus, the present results are very useful to reconstruct the past ~450 years of PHCs record as well as to study the impact of past human activities including mining. Based on ^{210}Pb dating results, the values of PHCs have started to increase since 1980s, is also confirmed with another geochemistry (trace metals) data of core sediments by Singh *et al.* (2014) in the Mandovi estuary. Thus, the combination of age dating with PHCs analyses allows us to reliably determine the period of significant changes occurred in the estuarine sediments. Moreover, it is

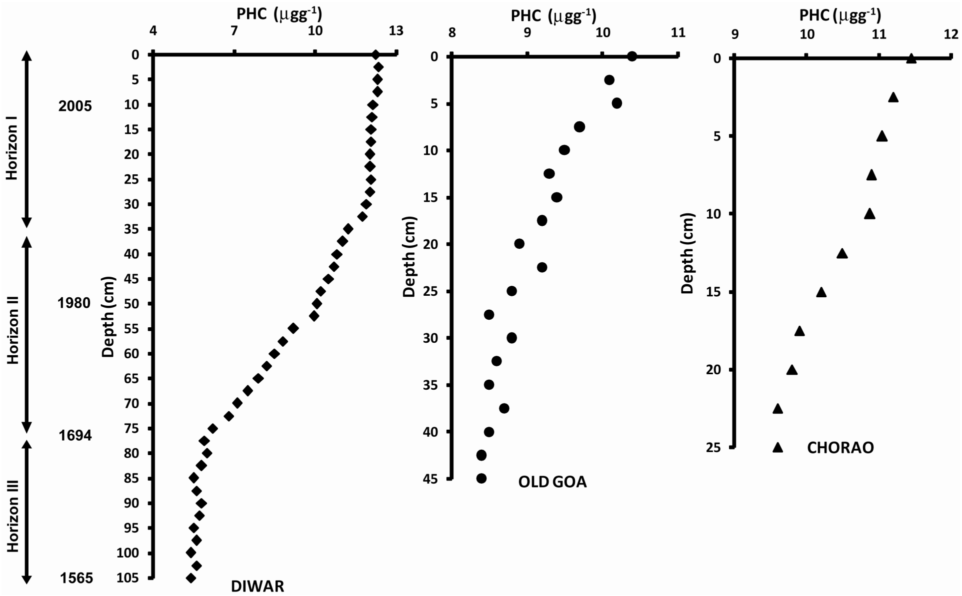

Fig. 2. Vertical distribution of petroleum hydrocarbon concentrations (PHCs) in D1, OG and C1 sediment cores collected from the Mandovi estuarine mangrove ecosystem.

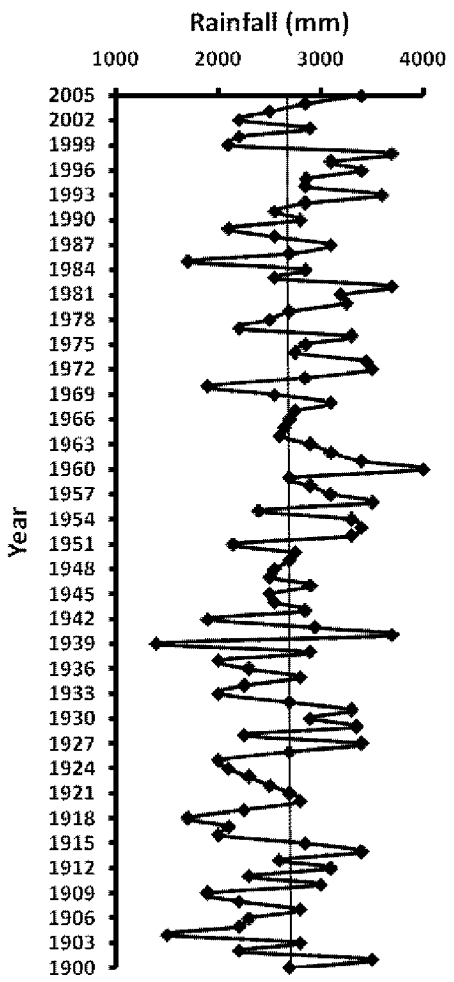

Fig. 3. Rainfall data of last 105 years (1901 – 2005) for a station in Goa

possible to differentiate between the detectable natural and anthropogenically influenced horizons, reflecting "pre-mining sedimentation" in horizon III, a transition stage in horizon II with variable values and increasing trends until 1980. The significant and continuous input of PHCs within the last 30 years into the horizon I can, therefore, be directly linked to onset of intense anthropogenic activities, including shipping, boating, iron ore mining, industry, urban and tourism activities. Though the prospecting of Fe and Mn ore started as early as 1905 in Goa, regular export had commenced only in 1947. During 1971–1980, Goa accounted for 32% of the country's total iron ore production and 55% of its export (Swaminathan, 1982). According to information provided by the Goa Mineral Ore Exporters Association (GMOEA), 54.45 million metric tonnes of mineral ore was exported from Goa in 2010-11, the highest by any state in India. In the last few decades, Goa has largely developed in economy and tourism, and this is seen by the increase of fly ash emission from boats, ships, barges and transportation of vehicles (Singh *et al.*, 2014). The past 105 years (1901–2005) rainfall data of Goa clearly showed the increasing rainfall pattern from 1955 (Fig. 3). Thus, due to the influence of heavy rainfall in this region fine clay particles, atmospheric and vehicle dusts, ores and other pollutants are transported and deposited into the Mandovi estuary. Therefore, high and variable PHCs values in core sediments are attributed by terrestrial pyrogenic and petrogenic sources in this region. Besides terrestrial input, PHCs in the Mandovi estuary could also derived from the Arabian Sea. The major source of oil pollution in the Arabian Sea is the transport of oil in VLCC tankers from the oil terminal to

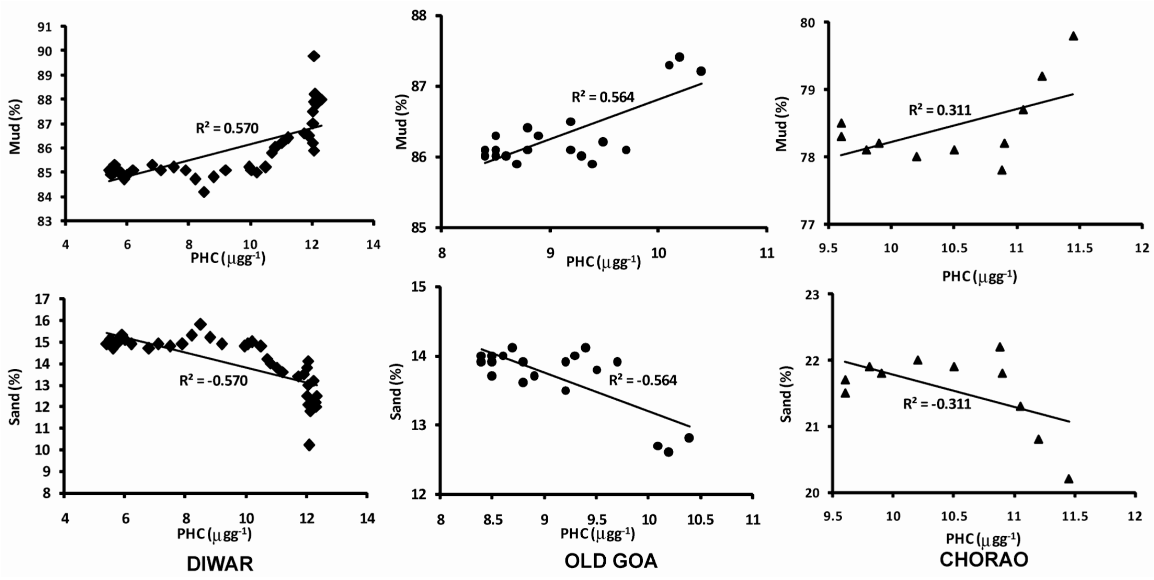

Fig. 4. Scatter plots showing the relationship between sediment texture size and petroleum hydrocarbon in D1, OG and C1 sediment cores collected from the Mandovi estuarine mangrove ecosystem

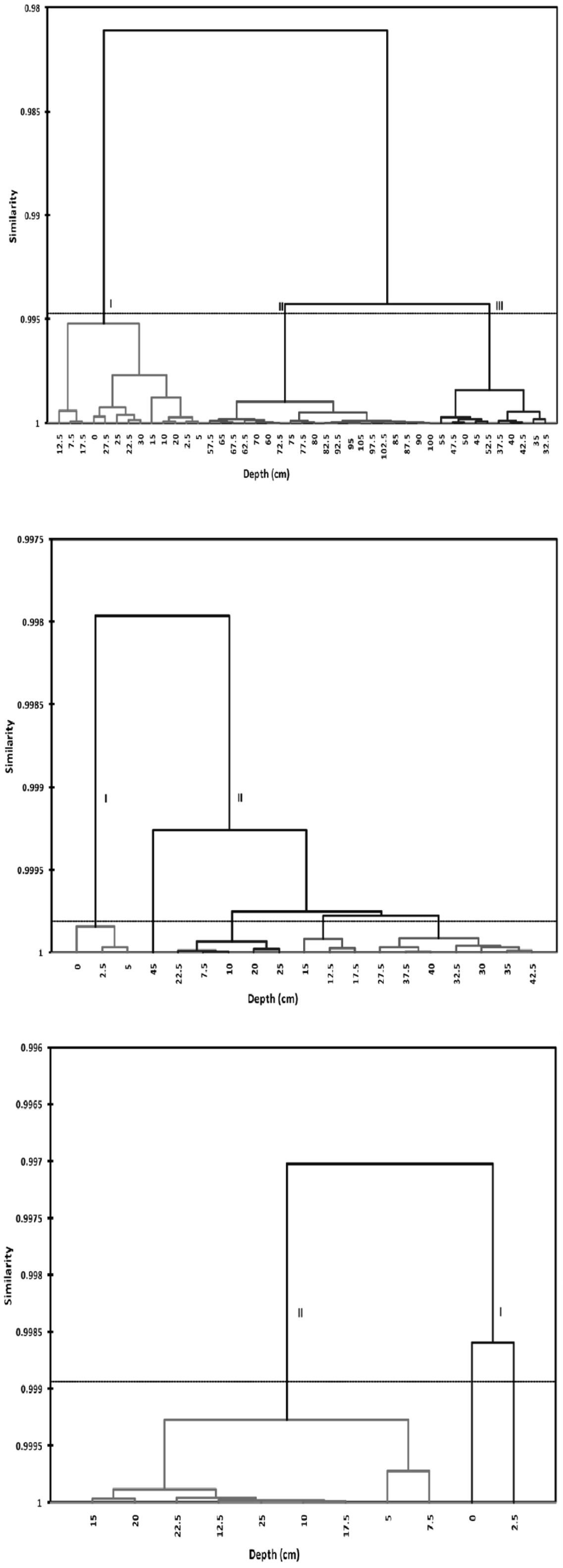

Fig. 5. Cluster analysis to classify the samples based on texture size and petroleum hydrocarbons in core sediments from (a) Diwar, (b) Old Goa, and (c) Chorao

port of Middle East countries along the well known oil tanker routes that passes through the Arabian Sea. For the past few decades, a number of tanker accidents have occurred on these routes, resulting in increased concentration of PHCs (Vethamony *et al.*, 2007). The oil spill is one of the sources for the formation of tarballs, and deposition of tar balls along the Goa coast is a common phenomenon during the southwest monsoon (Suneel *et al.*, 2013a, b). During the pre-monsoon season, saline waters from the Arabian Sea enter into the Mandovi river channel, which facilitates aggregation and settling of marine based pyrogenic and petrogenic hydrocarbons. Recent multi-temporal remote sensing studies in this region revealed that the mangrove coverage in the Mandovi estuary and entire Goa region have been increased from 1973 to 2011 (Misra *et al.*, in press). The gradual increase of mangroves in this region is also a source of biogenic hydrocarbons in core sediments, i.e., the decomposition of mangrove litter and hydrolysis of tannin in mangrove plants releasing various kinds of organic acids (Sarkar *et al.*, 2012).

The scatter plots between texture size and PHCs (Fig. 4) showed that the mud (silt + clay) contents are abundantly associated with petroleum hydrocarbons. Mud contents are able to trap more petroleum hydrocarbons due to their large specific surface area, while sand contents being organically poor and have little ability to retain the hydrocarbons. A similar conclusion based on the presence of heavy metals and magnetic properties in the Mandovi estuary. Further, the hierarchical cluster analysis tree diagram was used to characterise vertical variability of petroleum hydrocarbons associated with different texture sizes in core sediments. The dendogram plot of Diwar sediment core shows three clusters (Fig. 5a). Cluster-I comprised of highly polluted sediment samples (0 to 30 cm) and cluster-II contained moderately polluted sediment samples (32.5 cm to 55 cm), whereas cluster-III consists of less polluted or unpolluted sediments. Old Goa and Chorao sediment cores contained two clusters (Fig. 5b, c). Both the Dendogram plots have clearly discriminated the polluted sediment samples (cluster-I) from moderately polluted sediments (cluster-II). Thus, cluster analysis clearly distinguishes the sites, which are responsible for the enrichment of petroleum hydrocarbons. The concentration of PHCs in the upper parts of sediment cores is significantly higher than the background values (PHCs values at the bottom of sediment D1 core), but are lower than those found in the Thane creek, west coast India (7.6–42.8 µg/g, Chouksey *et al.*, 2004) and off Chennai, east coast of India (1.8 – 39.72 µg/g, Venkatachalapathy *et al.*, 2010). Overall, values of petroleum hydrocarbons in the Mandovi estuary indicate that the qualities of estuarine sediments were in low to moderate state (Table 1).

CONCLUSIONS

Vertical profiles of PHCs in three sediment cores from the Mandovi estuary, west coast of India were studied. The possible sources, vertical fluxes and relative degree of PHCs contamination in estuarine sediments were investigated. PHCs values in sediment cores were ranged from 5.4 to 12.34µg/g. Accumulation of PHCs in the Mandovi estuarine sediments were derived from terrestrial (including industrial, urban, mining and tourism activities) and marine sources (small vessels, tankers, leakages from crude oil transfer, etc). Atmospheric fallout of fly ashes with PHCs was increased due to ore processing, industrial and motor vehicle exhausters. After emitted into atmosphere, these PHCs were brought down by rainfall, and discharged into the estuary with stream flows and surface run-off. The decomposition of mangrove litter and marine related inputs were also enhanced the level of PHCs in the estuarine sediments. The upper parts of all sediment cores highly enriched with PHCs, which were derived from terrestrial and marine related sources including petrogenic, pyrogenic and biogenic sources. Cluster analysis also confirmed that the surface sediment samples are more contaminated than the bottom sediments in all the cores. Significant positive relationship between mud and PHCs showed that the role of mud is incorporating the petroleum hydrocarbons on their surface and increases the level of PHCs. The comparison of other estuarine and coastal regions of the world, the contamination level of PHCs in the Mandovi estuarine sediments were low to moderate state. This study provides baseline data to the decision makers of environmental protection agency with a better scientific understanding for decision making in controlling hydrocarbon pollution in estuarine sediments.

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Table 1. Comparison of petroleum hydrocarbon concentration in the Mandovi estuary with other select estuarine and coastal areas

Location	PHC (µg/g)	References
Narragansett Bay, USA	50–120	Farrington and Quinn, 1973
Scotian shelf, Canada	1.0–94.0	Keizer *et al.*, 1978
Liverpool Bay, UK	29.0	Law 1981
Gulf of Mexico	0.02–190	Kennicutt *et al.*, 1989
Guipuzcoan coast	0.21–0.80	Grimalt *et al.*, 1992
Shetland Island, UK	7–8816	Kingston *et al.*, 1995
Tampa Bay, Florida, USA	200–4300	Sherblom *et al.*, 1995
Straits of Johor, Malaysia	0.7 – 36.7	Abdullah *et al.*, 1996
Arabian Gulf	4 – 56.2	Al-Lihaibi and Al-Omran 1996
Laguna Madre, TX, USA	2.6 – 692	Sharma *et al.*, 1997
Patos Lagoon estuary, Brazil	39 – 11,780	Zanardi *et al.*, 1999
Changjiang estuary, China	2.2 – 11.82	Bouloubassi *et al.*, 2001
Sao Sebastiao, Brazil	20 – 200	Medeiros and Bicego 2004
Todos os Santos Bay, Brazil	8 – 4163	Venturini and Tommasi 2004
Thane Creek, Mumbai coast, India	7.6 – 42.8	Chouksey *et al.*, 2004
Bizerte lagoon, Tunisia	0.05 – 19.5	Mzoughi *et al.*, 2005
Bay of Fort de, France	54 – 1045	Mille *et al.*, 2006
Guanabara Bay, Brazil	77 – 7751	Da Silva *et al.*, 2007
Gulf of Fos, France	7.8 – 180	Mille *et al.*, 2007
Qua Iboe estuary, Nigeria	18.01 – 210.23	Benson *et al.*, 2008
Chennai coast, India	1.88 – 39.7	Venkatachalapathy *et al.*, 2010
Tamil Nadu coast, India	1.48 – 4.23	Veerasingam *et al.*, 2010
Estuaries in Tamil Nadu, India	5.04 – 25.5	Veerasingam *et al.*, 2011a
Pichavaram mangrove ecosystem, India	1.05 – 7.71	Venkatachalapathy *et al.*, 2012
Southeast coast of India	1.58 – 4.07	Lyla *et al.*, 2012
Visakhapatnam coast, India	0.34 – 19.70	Venkatachalapathy *et al.*, 2013
Todos os Santos Bay, Brazil	0.22 – 40101	Silva *et al.*, 2014
Mandovi estuary, India	5.4–12.34	Present study

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