

Petroleum Hydrocarbon Concentrations in the Surface Sediments of Two Major Sea Ports, Bay of Bengal, India

Sundaramanickam Arumugam (✉ fish_lar@yahoo.com)

Annamalai University <https://orcid.org/0000-0002-2682-445X>

Kumar Balachandar

Annamalai University

Kumaresan Saravanan

Annamalai University Faculty of Marine Sciences

Gopalsamy Idayachandiran

Annamalai University

Ajith Nithin

Annamalai University Faculty of Marine Sciences

Research Article

Keywords: Total Petroleum Hydrocarbon, Total Organic Carbon, Ennore, Tuticorin, Creek

Posted Date: February 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-191714/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

This investigation was made to assess the seasonal accumulation pattern of total petroleum hydrocarbon (TPH) in sediments along the two major ports such as Ennore and Tuticorin, located in Southeast coast of India. The level of TPH was found to vary from $2.05\mu\text{g g}^{-1}$ to $17.47\mu\text{g g}^{-1}$. To establish the relationship among the TPH with total organic carbon (TOC) and sediment components, the techniques of correlation analysis and principal component analysis (PCA) were used. The higher accumulation of TPH during monsoon season indicates that all wastes discharged on land was washed and got deposited on the Ennore coast. The significant positive correlation with TOC was noticed and the evidences indicated that the sedimentary organic carbon is acting as a strong binding agent for TPH.

1. Introduction

The comprehensive use of petroleum and its byproducts as a source of energy its widespread distribution in the biosphere has become a matter of serious environmental concern in the entire world (Barakat et al., 2011, Hassan et al., 2018). The Total Petroleum Hydrocarbon (TPH) gets released into the environment through domestic and industrial wastewaters, ship accidents, spills or leaks and other petroleum by-products get emitted from commercial or domestic uses (Mohebbi-Nozar et al., 2015; Yuan et al., 2014).

The marine environment, particularly the coastal and estuarine regions are ecologically sensitive areas with diverse morphology and unique hydrodynamic conditions. These vulnerable and ecologically sensitive areas are often chosen for the establishment of major petroleum based industries for easy transportation and disposal that contributes to significant pollution (NRC, 2003). The near shore areas are subjected to excessive contaminations not only by the anthropogenic inputs but also by the sea based activities (transportation, oil exploration and production etc). Shipping has a significant contribution of TPH by transporting these compounds in the marine environment (Massoud et al., 1996).

Crude oil consists of 17,000 organic compounds approximately and each of these compounds has their own volatility (Marshall and Rodgers, 2004). They are collectively known as Total Petroleum Hydrocarbons (TPH). The petroleum hydrocarbons contamination in marine and coastal sediments is extensive and the environmental consequences on these ecosystems turn out to be very serious. The available TPH in the water and atmosphere tends to accumulate in the sediment by deposition and adsorption which later becomes stable. The tendency of retaining TPH by sediment affects in two ways; on one side it gives stability and on other side it acts as a prime source of environmental contamination (Mirsadeghi et al., 2011). Therefore, marine sediment can be considered as not only a reservoir of wastes and deposits but it also decides about the extent of marine pollutants (Wang et al., 2017).

The coastline of India is 8129 km, out of which 6,000 km is rich in estuaries, creeks, brackish waters, lagoons and lakes etc. The southeast coast of India is considered as an important stretch of coastline with many significant attractive features. Here many major rivers drain into the Bay of Bengal and these coasts are wealthier in marine fauna as compared to other western coasts of India (Ananthan et al.,

2005). The Ennore and Tuticorin are categorized under top 13 major ports in India. In recent years these coastal areas have observed many developments, which have affected both regions drastically.

Significant increase of anthropogenic activities due to urbanization and industrialization disturb and degrade the natural surroundings of the coastal environment. Environmental monitoring program needs to be continued in order to protect the marine environment, especially coastal regions, from continuous pollution of coastal resources. Therefore, monitoring the magnitude of the pollution in these vulnerable areas becomes more significant to establish efficient planning for controlling and combating coastal pollution. Hence, this study is focused to investigate the seasonal variations of Total Petroleum Hydrocarbons in sediments of the selected major harbor regions, Ennore and Tuticorin of Tamil Nadu state situated on the Southeast coast of India.

2. Methodology

2.1 Study area description

Ennore and Tuticorin coasts are heavily industrialized which receive considerable quantity of industrial pollutants and domestic sewage that gets eventually drained into the Bay of Bengal. Both regions are encompassed with similar types of industries such as thermal power plants, oil refineries, petro-chemical industries, etc. The periodic dredging activities in these regions for the natural resources like petrochemicals result in changes in the landscape, sediment transport and add dust to the coastal environment. Different sampling locations were selected in each study area and the details of the sampling stations are

I, Ennore:

Ennore creek - (ENN I and II stations which are located at a distance of 0.5 Km and 2 Km from the shore towards creek). Ennore Shore (ENN III- Ennore creek mouth) and Ennore coast (ENN IV, V and VI stations that are located at 1, 5 and 10 km distance from the shore line to off shore).

II, Tuticorin:

Korampallam channel - (TUT I and TUT II stations are located at 0.5 and 2 km distance from the shore towards channel), Tuticorin shore (TUT III- Channel mouth) and Tuticorin coast (TUT IV, V and VI stations are located at 1, 5 and 10 Km distance from the shore line to off shore) as shown in the Fig. 1.

The sediment samples were collected during the year 2013–2014 covering the four main seasons that is summer, pre-monsoon, monsoon and post-monsoon. The sediment was collected using Peterson grab with an area of 0.1 m². The collected sediment samples were preserved in pre-cleaned polythene bags kept in insulated ice box and brought to the laboratory for further analysis.

About 100 gm. of air dried sediment was sieved by mechanical shaker (Buchanan, 1984) to investigate the composition of sediment. The sand fraction was determined by the amount of sediment retained by sieve of 0.125mm pore size. The remaining portion which passed through the sieve of pore size 0.125 mm but retained by sieve of pore size 0.063mm was taken as silt and the fraction which passed through the sieve of pore size 0.063mm was taken as clay.

The Total Organic Carbon (TOC) was estimated in surface sediment (upper 2cm), collected from the grab by following the method of ammonium ferrous sulfate titration (Walkley–Black method), modified by Schumacher (2002).

The sediment sample was saponified using KOH-methyl alcohol mixture. About 10 gram of sample was subjected for soxhlet extraction with n-hexane. Further, the extract was mixed with a required amount of anhydrous sodium sulphate and shaken well so as to remove moisture. The obtained extract was concentrated by rotary evaporator at 30°C and subsequently by a gentle stream of nitrogen gas to bring to the volume of 1 ml. The TPH was measured using UV-Spectrofluorometer (Cary Eclipse fluorescence spectrophotometer) at 360 nm emission after excitation at 310 nm (IOC-UNESCO, 1984). All the experiments were conducted in triplicate so that the average values are obtained in order to have more accuracy in the results. Further, the data was also subjected to statistical analysis such as correlation coefficient and Principal Component analysis (PCA) using the statistical software SPSS ver. 16.0 and PAST 2.07.

3. Results And Discussion

The results of the percentage compositions of sand, silt and clay of the selected sediment samples from Ennore and Tuticorin coasts are given in Fig. 2. The percentage of sand fraction at Ennore coast was found to have varied from 12.79 to 85.16% with a mean value of $36.28\% \pm 8.68\%$. The maximum percentage of sand (85.16%) was noticed at Ennore creek mouth (ENN-III) during the post monsoon season. The minimum of 12.79% was measured during the pre-monsoon season in the Ennore creek region (ENN-I). The percentage of silt fraction was found to have varied from 10.57 to 59.47% with a mean value of $39.98\% \pm 4.96\%$. The higher percentage of silt (59.47%) was noticed in sample from Ennore creek (ENN-II) during the monsoon season. The lower percentage of silt (10.57%) was observed during the post monsoon season in the sample from Ennore creek mouth (ENN-III) and the percentage of clay fraction was found to have varied from 2.27 to 52.62% with a mean value of $23.74\% \pm 4.42\%$. The maximum percentage of clay fraction (52.62%) was observed during the monsoon season in the Ennore creek sample (ENN-I) and the lower percentage of 2.27% was observed during the summer season in the Ennore creek mouth sample (ENN-III). In Tuticorin samples, the sand fraction was found to have varied from 13.42 to 84.16% with a mean value of $42.20\% \pm 2.65\%$. The maximum percentage of sand (84.16%) was noticed at Tuticorin channel mouth (TUT-III) during the summer season whereas minimum of 13.42% was measured during the post monsoon season in the Korampallam channel (TUT-I). The percentage of silt fraction was found to have varied from 12.07 to 46.14% with a mean value of $32.90\% \pm 1.55\%$. The higher percentage of silt (46.14%) was noticed during the monsoon season in the Korampallam channel

(TUT-I) whereas lower percentage (12.07%) was observed during the post monsoon season in the Tuticorin mouth region (TUT-III). The percentage of clay fraction was found to have varied from 3.57 to 45.63% with a mean value of $24.89\% \pm 1.50\%$. The higher percentage of clay (45.63%) was observed during the monsoon season (TUT-VI) whereas lower percentage (3.57%) was observed during the summer season in the sample from Tuticorin channel mouth (TUT-III).

In general, the average percentage of silt fraction was calculated and found higher when compared with other fractions and it further indicates that the Ennore creek and Tuticorin channel receive higher fractions of silt because of the continuous disposal of sewage into these water ways. When considering the seasonal fluctuation, higher percentage of sand fractions was observed during the monsoon season which led to heavy flooding in the rivers which further erodes the land and makes influx of sand considerably higher, as reported by Veerasingam et al., (2010) and Almeida et al., (2018).

There were reports on sediment compositions available previously in the studied coastal region under present study by Joydas and Damodaran (2009) and Yuan et al., (2017). Particularly, in the continental shelf region of southeast coast of India and west coast of India, respectively. The results of present study have good agreement with before mentioned studies as the sediment composition dominated with higher percentage of sand followed by silt and clay during the monsoon season.

The seasonal and spatial variations in the levels of TOC are presented in Table 1. The total organic carbon was found to have varied from 1.55 to 12.58 mgC g^{-1} with a mean value of $5.38 \pm 0.51 \text{ mgC g}^{-1}$, in the samples from Ennore region. The highest TOC was observed (12.58 mgC g^{-1}) during the post monsoon season in 2014 in sample from station ENN-I of Ennore creek. The lower value of TOC (1.55 mgC g^{-1}) was found during the summer season in 2013 in sample from station ENN-III of Ennore coast. In the samples from Tuticorin region, the TOC was found to have ranged from 1.49 to 7.13 mgC g^{-1} with a mean value of $4.04 \pm 0.27 \text{ mgC g}^{-1}$. The higher value of TOC (7.13 mg g^{-1}) was observed during the post monsoon season in 2014 in sample from station TUT-I whereas, the lower value of TOC (1.49 mg g^{-1}) was found during the summer season in 2013 in sample from station TUT-III. This clearly shows that the TOC level is high in Ennore study area when compared to Tutcorin study area. The increased value of TOC in monsoon season might be due to the higher sedimentation process which is taking place in every monsoon season in addition to the continuous discharge of sewage and industrial wastes into the Ennore creek (ENN-I). Total organic carbon (TOC) and clay shows similar patterns of distribution in both study areas and a positive correlation ($r = 0.894$, $p = 0.01$ and $r = 0.925$, $p = 0.01$) is found which is presented in Table 2.

Table 1
Spatial and seasonal Variation of TOC from Ennore and Tuticorin
harbour sediments.

	SUM '13	PRM'13	MON'13	POM'14
ENN-I	10.24 ± 0.07	10.85 ± 0.06	12.47 ± 0.04	12.58 ± 0.13
ENN-II	5.61 ± 0.05	5.85 ± 0.03	6.42 ± 0.10	6.35 ± 0.06
ENN-III	1.55 ± 0.08	1.66 ± 0.02	2.04 ± 0.03	2.43 ± 0.06
ENN-IV	2.11 ± 0.07	2.39 ± 0.03	2.64 ± 0.05	2.20 ± 0.07
ENN-V	4.14 ± 0.06	4.26 ± 0.07	5.32 ± 0.15	5.05 ± 0.13
ENN-VI	5.25 ± 0.10	5.69 ± 0.03	6.07 ± 0.20	6.36 ± 0.08
TUT-I	6.23 ± 0.09	6.63 ± 0.05	6.99 ± 0.17	7.13 ± 0.04
TUT-II	4.13 ± 0.24	4.73 ± 0.13	5.19 ± 0.19	5.45 ± 0.25
TUT-III	1.49 ± 0.02	1.56 ± 0.05	2.12 ± 0.20	1.72 ± 0.06
TUT-IV	2.16 ± 0.026	2.72 ± 0.04	2.89 ± 0.04	1.70 ± 0.13
TUT-V	3.28 ± 0.07	3.50 ± 0.08	3.98 ± 0.24	4.27 ± 0.23
TUT-VI	5.00 ± 0.45	4.78 ± 0.08	5.60 ± 0.23	5.11 ± 0.04

Table 2
Spatial and seasonal variation of TPH from Ennore and Tuticorin
harbour sediments.

	SUM '13	PRM'13	MON'13	POM'14
ENN-I	14.68 ± 0.35	13.82 ± 0.09	15.70 ± 0.21	17.47 ± 0.06
ENN-II	8.48 ± 0.05	7.30 ± 0.12	9.40 ± 0.06	10.51 ± 0.20
ENN-III	3.45 ± 0.03	3.25 ± 0.07	3.74 ± 0.13	4.18 ± 0.10
ENN-IV	10.49 ± 0.05	9.75 ± 0.09	12.62 ± 0.11	14.28 ± 0.12
ENN-V	9.67 ± 0.08	8.68 ± 0.19	9.45 ± 0.20	10.34 ± 0.14
ENN-VI	8.41 ± 0.12	8.38 ± 0.22	8.69 ± 0.09	9.25 ± 0.11
TUT-I	9.48 ± 0.11	9.68 ± 0.16	9.73 ± 0.19	10.16 ± 0.14
TUT-II	7.20 ± 0.013	6.39 ± 0.20	7.00 ± 0.16	7.34 ± 0.05
TUT-III	2.20 ± 0.13	2.05 ± 0.09	2.18 ± 0.15	2.43 ± 0.23
TUT-IV	4.75 ± 0.21	4.20 ± 0.14	4.89 ± 0.32	5.57 ± 0.27
TUT-V	6.35 ± 0.16	6.75 ± 0.32	6.18 ± 0.10	7.32 ± 0.14
TUT-VI	7.82 ± 0.14	7.65 ± 0.18	8.47 ± 12	8.09 ± 0.03

The results also indicate that the gradual deposition of organic matter observed in present study is may become less significant in course of time, and it might be due to lesser deposition of clay from the river and sewage which in turn does not support to retain TOC. In contrast to the present study, the study made by Hong-Gung Ni et al., (2008) reported high amount of TOC in their study area in spite of having high amount of sand portion. Considering the average values of TOC in the two study areas under our present study, Ennore creek and its coastal areas were found to have higher average values of TOC as compared to Tuticorin study area. This might be due to the higher deposition of the sewage and industrial wastes in the Ennore creek area as compared to Tuticorin. The significant relationship between TOC and clay was reported by Kim et al., (2017) Yan et al., (2019) showed a linear positive relationship between TOC and clay, similar to the results observed in the present study. Recent studies by Hassan et al., (2018) established that this relationship is significant. Generally, fine fractions prevent the diffusion of oxygen into sediments, thus allowing for the conservation of organic matter, which in turn helps the enhancement of total organic carbon (TOC) concentrations in the sediments.

The observed values of TPH in both study areas are presented in Table 2. The total petroleum hydrocarbon at Ennore region was found to have varied from 3.25 to 17.47 $\mu\text{g g}^{-1}$ with a mean level of $9.63 \pm 1.05 \mu\text{g g}^{-1}$. The higher level of TPH was observed ($17.47 \mu\text{g g}^{-1}$) during the post monsoon season, 2014 from samples of station ENN-I of Ennore creek whereas, the lower value of TPH ($13.25 \mu\text{g g}^{-1}$) was observed during the pre-monsoon season, 2013 from samples of station TUT-III of Tuticorin harbour.

g^{-1}) was found during the pre-monsoon season, 2013 from samples of Ennore channel mouth (ENN-III). The total petroleum hydrocarbon (TPH) at Tuticorin was found to have ranged from 2.05 to $10.16 \mu\text{g g}^{-1}$ with a mean value of $6.41 \pm 0.25 \mu\text{g g}^{-1}$. The maximum level of TPH was observed ($10.16 \mu\text{g g}^{-1}$) during the post-monsoon season, 2014 in samples from station TUT-I while the minimum level of TPH ($2.05 \mu\text{g g}^{-1}$) was found during the pre-monsoon season, 2013 in samples from Tuticorin channel mouth (TUT-III).

The higher TPH load recorded in Ennore creek region (ENN-I) might be due to the frequent discharges from nearby petro chemical industries. In the present study, the maximum concentration of TPH was observed during the monsoon season, which clearly indicates that the flood during the northeast monsoonal rainfall transports the higher quantity of TPH to these coastal areas. Similar to the present study Venkatachalapathy et al., (2015), reported higher values of TPH concentration in sediments (1.88–39.76 ppm) from Chennai coast, Southeast coast of India. The TPH concentrations showed extensive fluctuations because of the differential rate of input through river transport in different seasons. Therefore, a distinct seasonal variation could be observed in the levels of TPH in samples from different study areas. The reason for petroleum hydrocarbon values recorded to be lower in ENN-III (Ennore creek mouth) & TUT-III (Tuticorin channel mouth), might be attributed to high proportion of sand which has less efficiency in binding the TPH whereas higher levels of TPH in the Ennore creek and Tuticorin channel (ENN-I & TUT-I) could be noticed due to high proportions of silt and clay.

Similarly, Veerasingam et al., (2010); Muthukumar et al., (2013) reported 4.23 ppm of TPH at Narimanam and 1.48 ppm of TPH at Nagapatinam coasts of Tamil Nadu. Sediments containing fine particles are always found to be good accumulators of organic pollutants presumably because of their greater affinity towards pollutants like TPH (Law and Klungsoyr, 2000). The fine sediment fractions like clay which are dispersed in the water column have high absorbing characters and they effectively scavenge the trace contaminants that enter the aquatic ecosystem (Wang et al., 2014).

Pearson's correlation coefficient was applied for both the study areas to understand the relationships among TPH, TOC and soil characteristic sand the results are presented in Tables 3 and 4. A positive correlation was found between TPH and soil fractions such as clay and silt but the sand showed negative correlation. The significant correlations between TPH with TOC, clay and silt suggest that the TPH is strongly bound with TOC in clay and silt enriched sediments.

Table 3
Correlation matrix in Ennore stations.

	TOC	TPH	Sand	Silt	Clay
TOC	1				
TPH	.723*	1			
Sand	-.931**	-.764	1		
Silt	-.177	-.419	-.017	1	
Clay	.894*	.877*	-.852*	-.509	1
**. Correlation is significant at the 0.01 level (2-tailed).					
*. Correlation is significant at the 0.05 level (2-tailed).					

Table 4
Correlation matrix in Tuticorin stations

	TOC	TPH	Sand	Silt	Clay
TOC	1				
TPH	.965**	1			
Sand	-.918**	-.980**	1		
Silt	.855*	.948**	-.966**	1	
Clay	.925**	.962**	-.983**	.901*	1
**. Correlation is significant at the 0.01 level (2-tailed).					
*. Correlation is significant at the 0.05 level (2-tailed).					

The values of TOC and TPH are depicted in Fig. 5. The variation of TOC, clay and TPH of Ennore station was noticed to have positive correlation between TOC, clay, silt and TPH. In the present study, temporal variations of TOC and TPH values were found with highly positive correlation and are shown in Tables 2 and 3. This indicates that the input of TPH to the study area was related to TOC levels.

As in the case of present study, Zhang et al., (2006), and Adeniji et al., (2017) reported that the TOC has positive relationship with hydrocarbons in the sediments from China, Hong Kong and South Africa respectively. In addition, it was confirmed that the hydrocarbons' levels in the sediments from Ennore and Tuticorin areas were higher and the TOC levels were found to be elevated in the sample sediments ($R^2 = 0.723$, $P < 0.05$ and $R^2 = 0.965$ $P < 0.01$) Tables 3 and 4. Warren et al., (2003) suggested that sorption of hydrocarbons takes place directly on sediment surfaces when the organic matter deposition is

significant. The studies by different researchers (Ruiz-Fernández et al., 2012; Vagge et al., 2018) also support the fact that the silt and clay have significant affinity to TOC and hydrocarbons. The accumulation of hydrocarbons is mainly influenced by the factors such as the type of hydrocarbons and its sources (pyrolytic and / or petrogenic) and most significantly the type of sediment (rated by the presence of organic matter) which receives the TPH (Wang et al., 2014). The high presence of sand fractions in the sediment samples (60–99%) would have no impact on PAHs retention in the sediments. There were conflicting reports (Le Boeuf and Weber, 1997) which proposed that organic particles in sediments containing majority of clay and silt fractions are more likely to be despoiled than those of thicker grained sediments like sand, which is considered to be the most effective factor that influences the sorption characteristics of hydrocarbons.

The level of petroleum hydrocarbon concentrations in the present study are comparable with those reported from coastal and estuarine regions of various countries, Arabian sea along the Indian coast (Sengupta et al., 1993), Shetland Island, UK (Kingston et al., 1995), Straits of Johor (Abdullah et al., 1996), Arabian Gulf reports (Al-Lihaibi and Ghazi 1997), UAE coast research (Shriadah 1998), Bassein-Mumbai coast, India (Chouksey et al., 2004), Jiaozhou Bay, China (Wang et al., 2006), Gulf of Fos, France (Mille et al., 2007) Abu Dhabi, UAE (Abdet al., 2008) and Tamil Nadu coast, India (Veerasingam et al., 2010), Buffalo estuary, South Africa (Adeniji et al., 2017), Delaware River Estuary and Delmarva Peninsula, USA (Kim et al., 2018). The values observed Bouloubassi et al., (2001) at Changjiang estuary, China and Yunker and Macdonald (2003) at Fraser River Basin, Canada were most similar to the values of the present observation made at creek and coastal regions of Indian waters (Table 5).

Table 5
The petroleum hydrocarbon data were reported from selected coastal areas.

Location	PHC (Concentrations)	Reference
Arabian Sea along the Indian coast	0.6–5.8 ppm	Sengupta et al., 1993
Shetland Island, UK	7–8816 ppm	Kingston et al., 1995
Straits of Johor, Malaysia	0.7–36.7 ppm	Abdullah et al., 1996
Arabian Gulf	5.4–92.0 ppm	Al-Lihaibi & Ghazi, 1997
UAE coast	51,000 ppm	Shriadah, 1998
Changjiang estuary, China	2.2–11.82 ppm	Bouloubassi et al., 2001
Fraser River Basin, Canada	1.6–20.6 ppm	Yunker and Macdonald, 2003
Bassein-Mumbai coast, india	7.0–38.2 ppm	Chouksey et al., 2004
Jiaozhou Bay, China	0.54–8.12 ppm	Wang et al., 2006
Gulf of Fos, France	7.8–180 ppm	Miller et al., 2007
Abu Dhabi, UAE	6.14–62.7 ppm	Abd EL Gawad et al., 2008
Tamilnadu coast, India	1.48–4.23 ppm	Veerasingam et al., 2010
Bufalo estuary, eastern Cape Province, South Africa	12.59–1,100 $\mu\text{g g}^{-1}$	Adeniji et al., 2017
Delaware River Estuary, USA	34–159 mg/kg	Kim et al., 2018
Delmarva Peninsula, Virginia USA	38–616 mg/kg	Kim et al., 2018
Saw Mill Creek, Staten Island, NewYork, USA	6524 to9586 mg/kg	Vane et al., 2020
Tamilnadu coast, India	2.05–17.47 $\mu\text{g g}^{-1}$	Present study

The following order of contamination pattern of TPH was found for each location: Ennore creek > Ennore coastal > Tuticorin channel mouth > Tuticorin coastal.

The PCA was employed to concise the data analysis without changing the significance of data. From the analysis, it is evident that TPH, TOC and clay have significant positive loading at Station ENN-I and ENN-II (Fig. 3). The PCA further indicates that Ennore creek was highly contaminated with TPH as compared to other stations. In Tuticorin, the TPH, TOC, silt and clay were found to have positive loading in the stations TUT-I and TUT-II (Fig. 4). The results of the present study show close similarity with the reports made by Lyla et al., (2012).

4. Conclusion

It was noticed in the present study that PAH concentrations were positively correlated with sediment TOC indicating that hydrocarbon adsorption and retention are mainly due to the presence of organic carbon. It was also found that the particle size has influence over the distribution of hydrocarbons in the sediment. It shows that finer the particle size higher is the accumulation level of hydrocarbons. Results of the present study provide a useful benchmark that the gradual declining in the levels of TPH in both study areas show a good authoritative control over the hydrocarbon disposal to these coastal regions. However, Ennore coast is to be paid special attention on TPH pollution as it was recorded with higher levels of TPH pollution when compared to Tuticorin coast. Despite these efforts, erection of new petrochemical industries, vast urban development coupled with intensive shipping activities may lead to elevate the levels of TPH in Ennore coast in near future.

Declarations

Author contributions

A. Sundaramaanickam (A S), K. Balachandar (K B), S. Kumaresan (S K), G. Idayachandiran (G I) and Ajith Nithin (AN).

A S designed the study; K B and G I performed the sample collection and sample Analysis; AS, KB, A N and S K performed the data analysis and data processing; all authors contributed to the manuscript preparation.

Funding Information

This study was supported by a research project "Seawater Quality Monitoring (SWQM)" from Ministry of Earth Sciences (MoES), Government of India (Project File No.MoES / ICMAM-PD/ME/CAS-MB/53/2017).

Conflict of interest:

The authors declare that they have no conflict of interest

Ethics approval:

Not applicable

Consent to participate:

Not applicable

Consent to publish:

Not applicable

Compliance with Ethical Standards

Acknowledgements

We would like to acknowledge authorities of Annamalai University for providing necessary facilities. Authors like to give a special thanks to Prof. T. Balasubramanian, former Director and Dean of CAS in Marine Biology, Annamalai University

References

1. Abd, E.L., Gawad, E.A., Lotfy, M.M., Sadooni, F.N., Katheery, B.E., 2008. Assessment of the Oil Pollution Extent in the Offshore Sediments, Abu Dhabi, UAE. *Aust. J. Ba. Appl. Sci.* 2(3), 617-631.
2. Abdullah A.R., Woon, W.C., Bakar, R.A., 1996. Distribution of Oil and Grease and Petroleum Hydrocarbons in the Straits of Johor, Peninsular Malaysia. *Bull. Environ. Contam. Toxicology*, 57, 155– 162.
3. Adeniji O., Okoh O. O., Okoh A. I. 2017. Petroleum Hydrocarbon Fingerprints of Water and Sediment Samples of Buffalo River Estuary in the Eastern Cape Province, South Africa. *J. Anal. Methods. Chem.* 2629365, 1-13
4. Al-Lihaibi, S.S., Ghazi, S.J., 1997. Hydrocarbon distributions in sediments of the open area of the Arabian Gulf following the 1991 Gulf War oil spill. *Mar. Pollut. Bull.* 34, 941–948.
5. Almeida, M., Danielle Vasconcelos do Nascimento, R.A., Mafalda P. O, Patired V.F., Albergaria-Barbosaa, A.C.R., 2018 Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of a Tropical Bay influenced by anthropogenic activities (Todosos Santos Bay, BA, Brazil) *Mar. Pollut. Bull.* 137, 399–407.
6. Ananthan, G.A., Sampathkumar, P., Soundarapandian, S., Kannan, L., 2005. Observation on environmental characteristics of Ariyankuppam estuary and Veerampattinam coast of Pondicherry, India. *J. Aquatic Biology* 19: 67-72.
7. Barakat, A.O., Mostafa, A., Wade, T.L., Sweet, S.T., Sayed, N.B.E., 2011. Distribution and characteristics of PAHs in sediments from the Mediterranean coastal environment of Egypt. *Mar. Pollut. Bull.* 62, 1969–1978
8. Bouloubassi, I., Fillaux, J., Saliot, A., 2001. Hydrocarbons in surface sediments from the Changiang (Yangtze River) estuary, East China Sea. *Mar. Pollut. Bull.* 42, 1335–1346.
9. Buchanan, J.B., 1984. Sediment analysis. In: Holme N.A, McInyre A.D. (eds), Blackwell scientific publications (Methods for the study of marine benthos), 2: 41-65.

10. Burns, K.A., Villeneuve, J.P., Anderlin, V.C., Fowler, S.W., 1982. Survey of tar, hydrocarbon and metal pollution in the coastal waters of Oman. *Pollut. Bull.*13(7), 240-247.
11. Chouksey, M.K, Kadam, A.N., Zingde, M.D., 2004. Petroleum hydrocarbon residues in the marine environment of Bassein – Mumbai. *Mar. Pollut. Bull.* 49, 637-647.
12. Hassan, H.M., Castillo, A.B., Yigiterhan, O., Elobaid, E.A., Al-Obaidly, A., AlAnsari, E., Obbard, J.P., 2018. Baseline concentrations and distributions of polycyclic aromatic hydrocarbons in surface sediments from the Qatar marine environment. *Mar Pollut Bull* 126:58–62
13. Hong-Gang Ni.,Feng-Hui Lu., Xian-Lin Luo., Hui-Yu Tian., Eddy., 2008. Riverine inputs of total organic carbon and suspended particulate matter from the Pearl River Delta to the coastal ocean off South China. *Mar. Pollut. Bull.* 56: 1150-1157.
14. Hostettler, F.D., Pereira, W.E., Kvenvolden, K.A., van Green, A., Luoma, SN., 1999. A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment core. *Mar. Chem.* 64: 115– 127.
15. IOC-UNESCO, 1984. Manual for monitoring oil and dissolved dispersed petroleum hydrocarbons in marine waters and on beaches. *Manual and Guides 13: UNESCO, Paris.*
16. Joydas, T.V., Damodaran, R., 2009. Infaunal macrobenthos along the shelf waters of the west coast of India, Arabian Sea, *Indian J. Mar. Sci.* 38 (2): 191-204.
17. Kim, B.S.M., Bícigo, M., Figueira, R., Siegle, E., Taniguchi, S., Alcántara-Carrió, J., 2017. Organic and inorganic contamination in sediments from Araçá Bay, São Sebastião, Brazil. *Ocean & Coastal Management* 164:42-51.
18. Kim, A.W., Vane, C.H., Moss-Hayes, V., Engelhart, S.E., Kemp, A.C., 2018. PAH, PCB, TPH and mercury in surface sediments of the Delaware River Estuary and Delmarva Peninsula, USA. *Mar. Pollut. Bull.* 129 (2), 835–845.
19. Kingston, P.F., Dixon, I.M.T., Hamilton, S., Moore, D.C., 1995. The impact of the Braer oil spill on the Macrobenthic infauna of the sediments off the Shetland Islands. *Mar. Pollut. Bull.* 30, 445–459.
20. Law, R. J., 1981. Hydrocarbon concentrations in water and sediments from UK marine waters, determined by fluorescence spectroscopy. *Pollut. Bull.*12(5), 153-157.
21. Law, R.J., Klungsoyr, J., 2000. The analysis of polycyclic aromatic hydrocarbons in marine samples. *Int. J. Environ. Pollut.* 13, 262–283.
22. Lyla, S., Manokaran, S., Khan, A., 2012. Petroleum hydrocarbon distribution in continental shelf region of southeast coast of India. *Intern. J. Sedim. Res.* 27: 73-83.
23. Massoud, M.S., Haggag, S.S., Abd El Hamid, O.H., 1996. *Rev. Roum. Chim.* 41:21.
24. Meniconi, M.F.G., Massone, C.G., Scofield, A.L., Junior, V.J.F., 2005. Oil spill aftermath: temporal evaluation of hydrocarbon sources in Guanabara Bay, Brazil. In: Canada. Environment Canada. Proceedings of the Twenty-eighth Arctic and Marine Oil spill Program (AMOP) Technical Seminar, Calgary (Alberta), Canada, June (7-9): 75-92.

25. Miller, G., Asia, L., Guiliano, M., Malleret L., Doumenq, P., 2007. Hydrocarbons in coastal sediments from the Mediterranean Sea (Gulf of Fos area, France). *Mar Pollut Bull*, 54,566–75.
26. Mirsadeghi, S.A., Zakaria, M.P., Yap, C.K., Shahbazi, A., 2011. Risk assessment for the daily intake of polycyclic aromatic hydrocarbons from the ingestion of cockle (*Anadara granosa*) and exposure to contaminated water and sediments along the west coast of Peninsular, Malaysia. *J. Environ. Sci.* 23(2): 336–345.
27. Mohebbi-Nozar, S.L., PauziZakaria, M.P., Ismail, W.R., Mortazawi, M.S., Salimizadeh, M., Momeni, M., GholamaliAkbarzadeh, G., 2015. Total petroleum hydrocarbons in sediments from the coastline and mangroves of the northern Persian Gulf. *Mar. Pollut. Bull.* 95, 407–411.
28. Muthukumar, A., Idayachandiran, G., Kumaresan, S., Ajith Kumar, T., Balasubramanian, T., 2013. Petroleum Hydrocarbons (TPH) in Sediments of Three Different Ecosystems from Southeast Coast of India, *Intern. J. Pharma. & Bio.* 4(3): 543-549.
29. Mzoughi, N., Dachraoui, M., Villeneuve, J.P., 2005. Evaluation of aromatic hydrocarbons by spectrofluorometry in marine sediments and biological matrix: what reference should be considered? *ComptesRendusChimie*, 8(1), 97-102.
30. NRC, 2003. *Oil in the Sea: Inputs, Fates, and Effects*. National Academy Press, Washington DC. 265.
31. Ruiz-Fernández A. C., Sanchez-Cabeza J. A., Alonso-Hernández C., Martínez-Herrera V., Pérez-Bernal L. H., Preda M., Hillaire-Marcel C., Gastaud J., and Quejido-Cabezas A. J. 2012, Effects of land use change and sediment mobilization on coastal contamination (Coatzacoalcos River, Mexico). *Cont. Shelf. Res.* (37), 57–65.
32. Sahu, K.C., Bhosale, U., 1991. Heavy metal pollution around the island city of Bombay, India. Part I: Quantification of heavy metal pollution of aquatic sediments and recognition of environmental discriminants. *Chem. Geol.* 90, 263–283.
33. Schumacher, B.A., 2002. *Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments*. U.S. Environmental Protection Agency, Washington DC
34. Sengupta, R., Fondekar, S.P., Alagsamy, R., 1993. State of pollution in the northern Arabian Sea after the 1991 Gulf oil spill. *Mar. Pollut. Bull.* 27, 85–91.
35. Shriadah, M.A., 1998. Impacts of an oil spill on the marine environment of the United Arab Emirates along the Gulf of Oman. *Mar. Pollut. Bull.* 36, 876–879.
36. Vagge G., Cutroneo L., Castellano M., Canepa G., Bertolotto R.M., Capello, M. 2018. The effects of dredging and environmental conditions on concentrations of polycyclic aromatic hydrocarbons in the water col*Mar. Poll. Bullet.* 135, 704-713.
37. Vane, C.H., Kim A.W., Hayes, V. M., Turner, G., Mills, K., Chenery, S.R., Barlow, T.S., Kemp, A.C, Engelhart, S.E, Hill, T. D., 2020. Organic pollutants, heavy metals and toxicity in oil spill impacted salt marsh sediment cores, Staten Island, New York City, USA. *Mar. Pollut. Bull.* 151(2020) 110721. <https://doi.org/10.1016/j.marpolbul.2019.110721>.
38. Veerasingam, S., Raja, P., Venkatachalapathy, R., Mohan, R., Sutharsan, P., 2010. Distribution of Petroleum Hydrocarbons in coastal sediments along the Tamilnadu coast, India. *Carp. J. Ear.*

Environ. Sci. 5: 5-8.

39. Venkatachalapathy, R., Veerasingam, S., Rajeshwari, V., 2012. Distribution and Origin of Petroleum Hydrocarbons in Pichavaram mangrove Swamp along Tamilnadu Coast, Bay of Bengal, India. *Geochem. Intern.* 50(5): 476- 480
40. Wang, X.C., Sun, S., Ma, H.Q., Liu, Y., 2006. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Mar. Pollut. Bull.* 52: 129-38.
41. Wang, Z. Liu, Z., Xu, K., Mayer, L. M. Zhang, Z. Kolker, A. S. Wu, W., 2014. Concentrations and sources of polycyclic aromatic hydrocarbons in surface coastal sediments of the northern Gulf of Mexico. *Geochem. Trans.* 15 (1), 2
42. Wang, M., Wang, C., Lib, Y., 2017 Petroleum hydrocarbons in a water-sediment system from Yellow River estuary and adjacent coastal area, China: Distribution pattern, risk assessment and sources. *Mar. Pollut. Bull.* 122, 139–148.
43. Yuan, H., Li, T.G., Ding, X.G., Zhao, G.M., Ye, S.Y., 2014. Distribution, sources and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in surface soils of the Yellow River Delta, China. *Mar. Pollut. Bull.* 83, 258–264
44. Yuan, H.W., Chen, Ye, Y., Lou, Z.H., Jin, A.M., Chen, X.G., Jiang, Z.P., Lin, Y.S., Chen, C.T.A., Loh, P.S., 2017. Sources and distribution of sedimentary organic matter along the Andong salt marsh, Hangzhou Bay. *J. Mar. Syst.* 174, 78–88.
45. Yunker, M.B., Macdonald, M.W., 2003. Petroleum biomarker sources in suspended particulate matter and sediments from the Fraser River Basin and Strait of Georgia, Canada. *Organ. Geochem.* 34: 1525–1541.

Figures

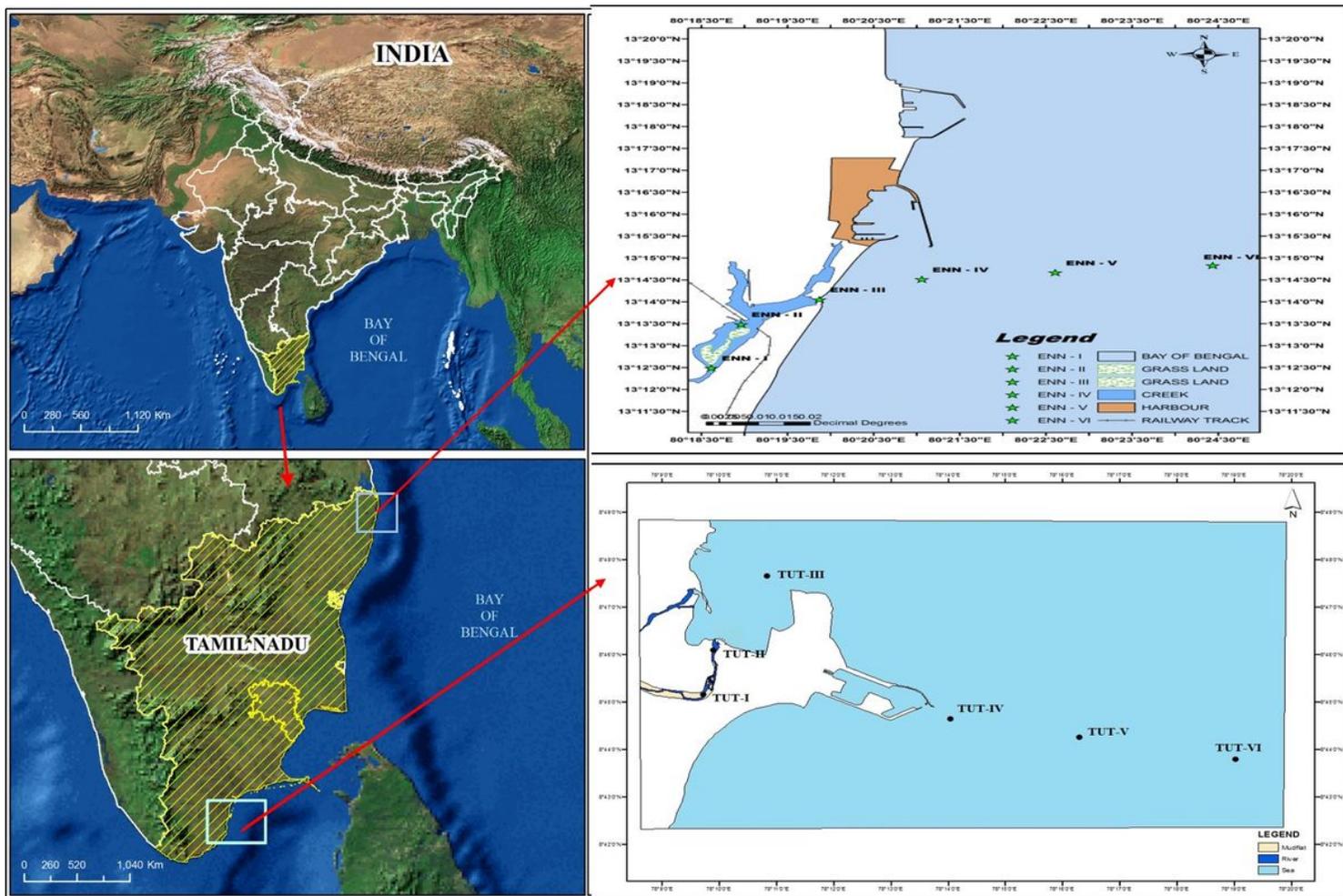


Figure 1

The Ennore and Tuticorin study area with locations of sample stations labeled ENN I, II and III is located Ennore creek ENN IV, V and VI coastal area respectively and TUT I, TUT II, TUT III is located mouth to new harbor TUT IV, TUT V and TUT VI continually to coastal area respectively. In each study area we have selected six different sampling locations details of the sampling are given bellow Ennore: Ennore creek - (ENN I and II stations are located at 0.5 and 2 KM distance from the shore towards creek), Ennore Shore (ENN III- Ennore beach) and Ennore coast (ENN IV, V and VI stations are located at 0.5, 2 and 5 KM distance from the sea shore). Tuticorin: Korampallam channel - (TUT I and TUT II stations are located at 0.5 and 2 KM distance from the shore towards channel), Tuticorin Shore (TUT III- Tuticorin beach) and Tuticorin coast (TUT IV, V and VI stations are located at 0.5, 2 and 5 KM distance from the sea shore). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

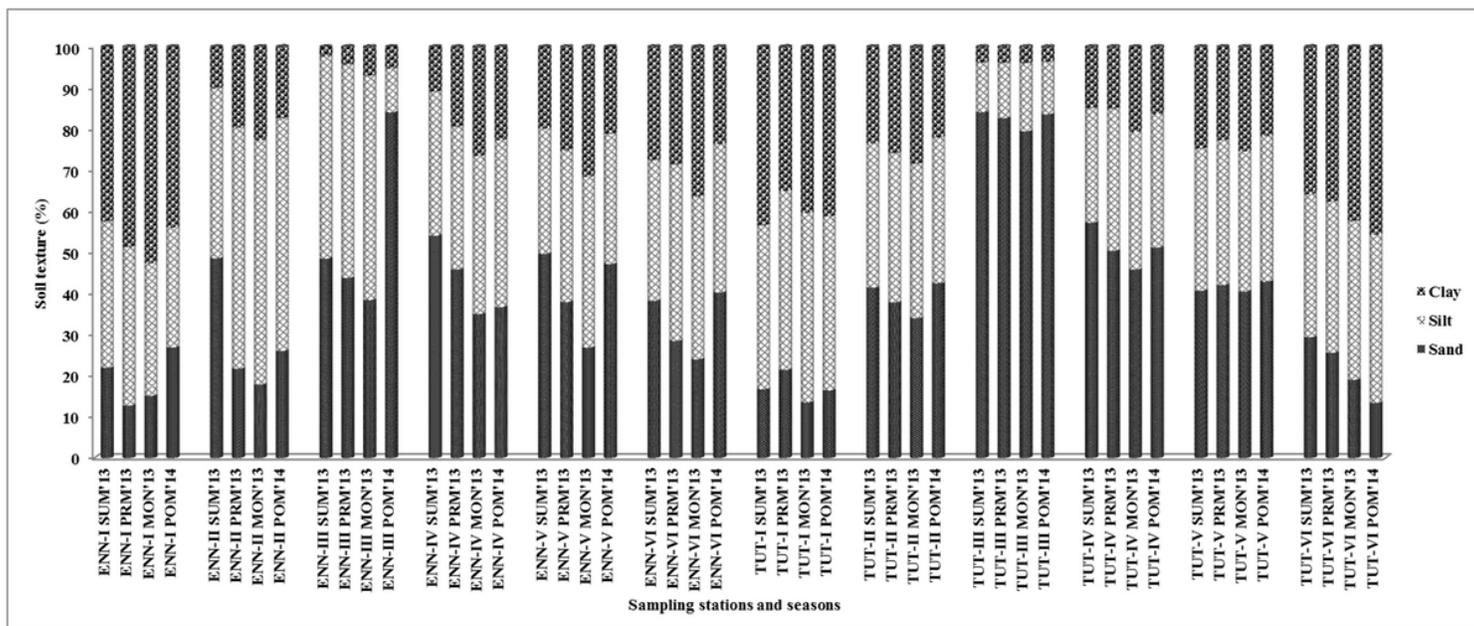


Figure 2

The percentage composition sand, silt and clay in Ennore and Tuticorin harbours sediments.

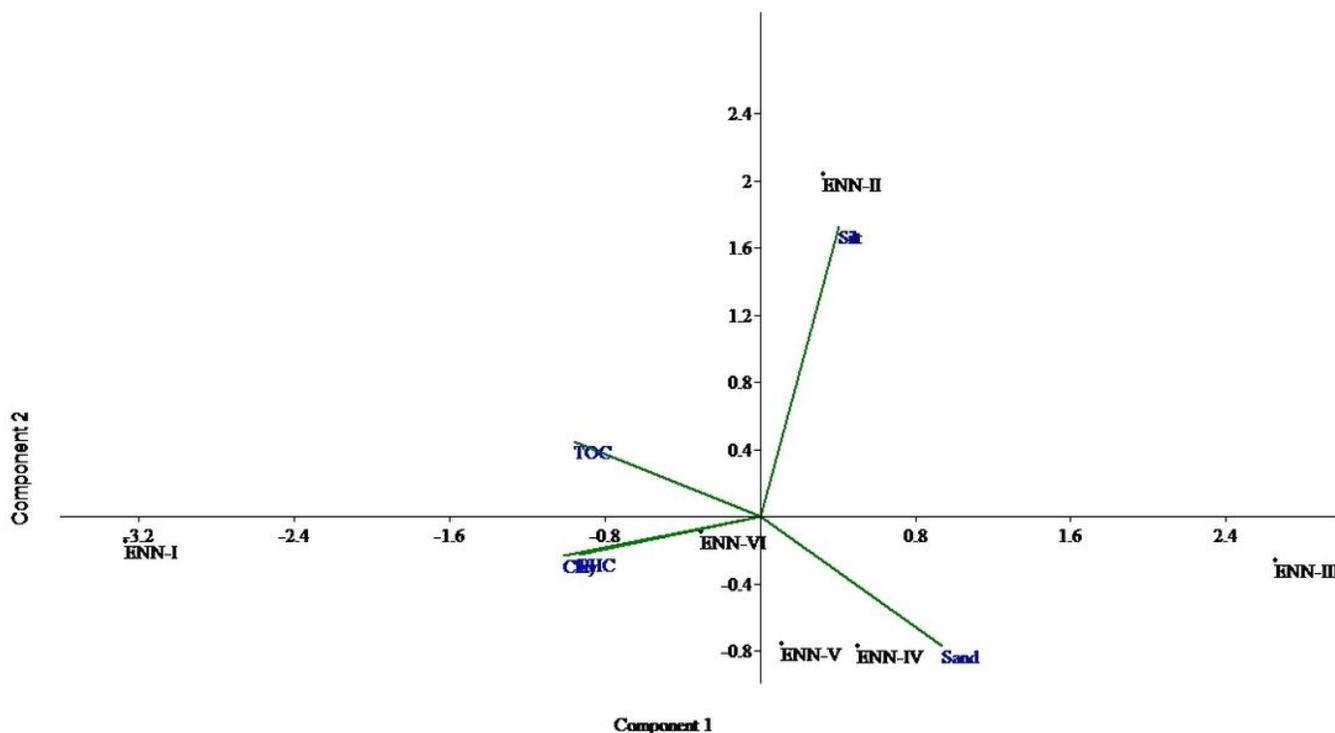


Figure 3

Principal Component analysis (PCA) in sediments of Ennore harbour stations.

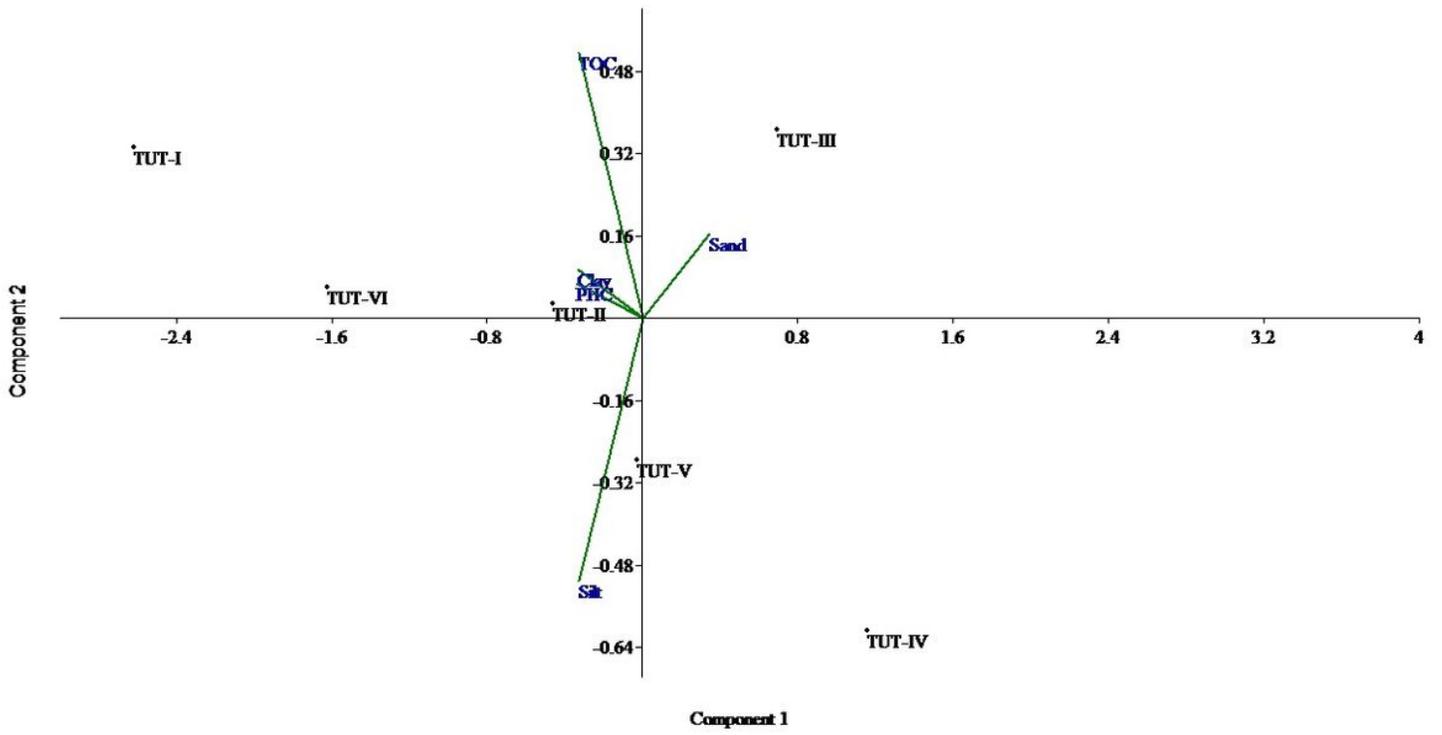


Figure 4

Principal Component analysis (PCA) in sediments of Tuticorin harbour stations.