

Occurrence of total petroleum hydrocarbon and total organic carbon in the sub-tidal and inter-tidal sediments of Vadinar coast, Gulf of Kachchh

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Abstract: The aim of the present study is to assess the petroleum hydrocarbon concentration and total organic carbon content in the sediment samples collected from industrial vicinity at Vadinar coast of Gulf of Kachchh, Gujarat. The study was conducted at six different locations comprising four sub-tidal and two inter-tidal sampling points of Gulf of Kachchh. From the study, it is evident the sediment samples recorded petroleum hydrocarbon concentration ranging from 0.464 - 27.2 µg/Kg and the mean total organic carbon content being 0.602% recorded among all the locations throughout the study period. Among the stations studied, station 6 recorded the highest concentration of PHC which is 27.2 µg/Kg and station 1 recorded the least concentration of 0.464 µg/Kg, whereas the TOC of 1.277% and 0.083% was recorded in the stations S1 and S6 respectively. From the study, it is understood that due to various activities in the industrial vicinity of vadinar coast of Gulf of Kachchh resulted in the presence of petroleum hydrocarbon concentrations to some extent and the recorded concentrations of PHC was well within the prescribed limits of CPCB for PHC in marine waters (100 µg/L).

Keywords: Coastal environment; Total Petroleum Hydrocarbon; Organic matter; Gulf of Kachchh.

1. INTRODUCTION

Crude oil is a mixture of huge number of hydrocarbon (including alkanes, Cycloalkanes, aromatic hydrocarbons) and non-hydrocarbon such as resin and asphalt (Cadwallaer, 1993) produced decay from other organic materials over millions of years (NRC, 2003). Crude oil in general, gains its entry onto the surface of the sea which undergoes physical, chemical and biological changes with time. Further, rapid physico-chemical processes include spreading and movement by wind, currents, injection into the air, evaporation of volatile components, dispersion of small droplets into water, dissolution and chemical oxidation (Nelson-Smith, 1972). Apart from this, crude oil enters into the marine environment by two means majorly, one through a process which involves human or anthropogenic activities such as extraction, transportation, refining, storage, and utilization of petroleum or its products. Apart from this, the prime factor is oil spills which happen in the marine environment which is mostly due to operational failure while transporting such as tankers and pipelines, through which crude oil is transported from one place to the other and the second way of oil pollution in the marine environment is through natural oil seepage (Hunt, 1996). Because of such crude oil pollution in the coastal, marine and estuarine environments in recent years has received major scientific attention with respect to its toxic effects and also based on the level of toxicity which the pollutant has in the ecosystem and individual organism in specific. The major impacts of petroleum hydrocarbon includes impairment of feeding, growth and development of marine organisms which may result in alterations in reproductive and developmental stages and changes in community structure of the organism and its dynamics (Capuzzo, 1985). Textural characteristics of the sediment is also considered to be significant, which influence the type of biological organisms present, especially benthos, in which, meiofaunal species, a major benthic forms in marine environment, renders it highly sensitive to changes in textural characteristics of the sediment (Parsons *et al.*, 1977) and hence studying such environment is of utmost importance to maintain the pristine nature of such ecosystem.

Burone *et al.* (2003) studied on the estimating organic matter, organic carbon, nitrogen, sulfur and granulometric variables in 101 surface sediment samples from Ubatuba Bay to understand on the spatial distribution of organic matter, its origin and relationships among other components. Ouyang *et al.* (2006) studied that the temporal and spatial distributions of TOC in the sediment and its relationships to other contaminants present in the sediments of Cedar and Ortega rivers, USA, using 3-D Kriging analysis which depicted a negative correlation between TOC and PAHs or PCBs. Researches conducted by other researchers confirms that aerobic oxidation of organic matter in the marine sediments is usually conventional (Sørensen *et al.* 1979, Jørgensen and Sørensen 1985; Jørgensen and Revsbech, 1989). In general, PHC concentration is one of the significant and prime organic contaminants found in the organic wastes (RHP, 2004; Commendatore and Esteves, 2004) which has been largely utilized as a tool for detecting the sources of petroleum residues in the marine ecosystem (ATSDR, 1999; Zrafi *et al.*, 2013).

Considering the past studies done on estimating the petroleum hydrocarbon concentration and few studies focused on total organic carbon content of the sediment samples and keeping this scenario in mind, the aim of the present study was to determine the total hydrocarbon concentration (TPH) concentration and total organic carbon (TOC) percentage in the marine sediment along the vadinar coastal stretch of Gulf of Kachchh, Jamnagar.

2. MATERIALS AND METHODS

2.1 Study area

The Gulf of Kachchh (22°15' to 23°40' N; 68°20' to 70°40' E) is located in the northwestern part of India in the state of Gujarat and it is one of the major Gulf systems of India occupying an area of 7350 km². It is 170 km long from Okha in the west to the tail end at Hansthal creek in the east with a maximum width of 75 km and a mean depth of 25 m. The network of creeks and mudflats in the intertidal belt and differential tidal levels at the mouth and tail end lead to several hydrographic peculiarities that are yet to be unraveled fully. The vast coastline of Gulf of Kachchh has attracted by many entrepreneurs for setting up of major and minor industries due to liberalization of industrial policy by the state and central government. Sampling locations for the present investigation was selected based on a preliminary study of the coastline in view of different industrial sources at Vadinar coastal zone and finally six different sites were selected along the Vadinar coast of Gulf of Kachchh as shown in Fig.1

2.2 Sample Collection

The present study was conducted during January to December 2017. A total of six sediment samples were collected using Van-Veen grab sampler, which is made of stainless steel. The samples collected using the grab was used for estimating PHC and TOC estimation without contamination, whereas intertidal sediments were collected using a handheld shovel. After collection, the scooped sediment samples were transferred to polythene bags, labeled and stored under refrigerated conditions for further analysis.

2.3 Petroleum hydrocarbon analysis in soil

Collected sediment samples were thawed, oven dried at 40°C and ground to a fine powder before analysis. Petroleum Hydrocarbons from the sediment samples were extracted by saponifying with methanolic KOH followed by extraction with hexane. Hydrocarbons were then separated using aluminium oxide (alumina) and analyzed keeping the excitation at 310 nm and emission at 360nm as prescribed by IOC-UNESCO, 1982. During the process, the emission scans and synchronous excitation/emission scans have been recorded and evaluated for the petroleum hydrocarbons in the samples. Standard response curves of fluorescence intensity versus concentration are generated for the appropriate oil standard and in this study, arabian crude oil was used for preparation of series of standards. All the measurements were using spectrofluorometer (Shimadzu RF-5301) fitted with a Xenon flash lamp, Hamamatsu monochromators, and 1-cm quartz cell. Spectral data acquisition and processing were carried out by means of the program Fluorescence Data Manager RF-5301PC serially interfaced (RFPC Software) to the Shimadzu Spectrofluorometer.

2.4 Total organic carbon analysis in sediment

Total organic carbon concentration in the sediments was estimated using Walkley and Black (1934) titration method. In this method, carbon is oxidized by the dichromate ion and excess dichromate ion is then back titrated with ferrous ion. This was done by taking sediment sample of 0.5 gm in 500 ml conical flask, to which 10 ml of 1N K₂Cr₂O₇ was added

and shaken to mix thoroughly. Further to this, 20 ml of concentrated H_2SO_4 (containing $AgSO_4$) was added and the mixture was allowed to stand for 30 minutes. To this, 200 ml of distilled water and 10 ml of H_3PO_4 was added further and shaken vigorously and the entire content was then titrated against 0.5 N $FeSO_4$ solution using Diphenyl amine / Ferroin as an indicator.

3. RESULTS AND DISCUSSION

Pollution due to various elements in the aquatic environment has become a serious threat around the world, with ocean and rivers seriously affected. Most of the coastal and marine environment has complex structural and dynamic characteristics that can be easily modified by anthropogenic influence and such environment serves as sinks for various metals transported from the land. The present study was conducted to examine the petroleum hydrocarbon and total organic carbon content at various locations of Jamnagar coast of Gulf of Kachchh.

Petroleum hydrocarbons in general is released into the marine environment through various sources including oil spill accidents, releases from various industrial sources or as by products from various commercial applications and during its entry directly into the water, some fractions of the total petroleum hydrocarbon floats either floats in the water or will accumulate in the sediment at the bottom of the sea depending on the type of fraction present in it. During the present study, the overall minimum, maximum and mean concentration of PHC was in the range of 0.464 $\mu\text{g/g}$ dry.wt (Station 1), 27.2 $\mu\text{g/g}$ dry.wt (Station 6) and 6.350 $\mu\text{g/g}$ dry.wt respectively. Among the six locations studied, the lowest mean concentration of PHC in the entire study period was recorded in S2 with the value being 5.82 $\mu\text{g/g}$ dry.wt. Among the study period, December 2017 recorded the maximum value and the minimum value registered during January 2017. Similar to the present study, the total petroleum hydrocarbons levels were estimated between 1.60 $\mu\text{g/g}$ dry.wt and 10.60 $\mu\text{g/g}$ dry.wt in the study conducted in the sediment samples from the tropical estuary of Todos os Santos Bay, Brazil (Celino et al., 2008). Miguel and Salvador (1998); Akinlua and Ajayi (2008) have also reported on the occurrence of organic pollutants in contaminated soils. Further studies conducted by Li et al (2012) reported the total petroleum hydrocarbon contamination of agricultural soils near a petrochemical complex and the study revealed that high level of TPH was observed in the top soils near to the industrial vicinity. Cortes et al (2012) reported determination of TPH in water and soil /sediment samples in Colombian oil Exploration and Production industry. Further, the present study also revealed that though PHC concentration was recorded during the entire study period in all the sampling stations but there was no much variation in the occurrence except the presence of PHC to a level of 27.2 in sampling station 6 (Fig.2). Further studies by Massoud et al. (1996) on TPH concentration in the sediment as primary cause of oil contamination in the Persian Gulf and suggested that TPH can be used as an indicative parameter in the evaluation of the oil contamination of the environments. Table 1 depicts the petroleum hydrocarbon ($\mu\text{g/g}$) concentrations in marine sediment of present study with selected sites around the world.

Several studies have been conducted earlier examining the effects of petroleum hydrocarbons concentration and the presence of organic carbons in sources such as surface waters, groundwater, soil / sediments matrices. But the occurrence of total organic carbon in any region with no concrete geology source is also considered to be influence by anthropogenic and industrial activities and is considered as abnormal. In the present study, the total organic carbon concentration in the sediment samples revealed a lowest mean concentration of TOC of 0.5255% in station 5 and in case of study period is concerned, the lowest mean concentration of TOC of 0.28% in the month of January 2017. Similar to the present study, Al Darwish (2004) has also examined the distribution of total petroleum hydrocarbon and total organic carbon in oil contaminated sediments from Dubai and recorded positive relationship between these parameters ($r^2=0.98$) and indicated that both these parameters (TOC and TPH) can serve as good indicators for oil contamination. Similar to this study, the Marmara Sea sediment analysis conducted by Kolukırık *et al.* (2011) showed that TPH and TOC concentrations of sediments pore waters has high positive relationship ($r^2=0.99$) and such relationship might be attributed due to decomposition of organic matters in sediments by microorganisms. Further, the present study also recorded the minimum, maximum and mean TOC content of 0.083%, 1.277% and 0.602% respectively (Fig.3). Celino et al. (2008) has indicated that the TOC concentration ranging from 1.04 -3.0% in the sediment samples collected from Todos os Santos Bay, Brazil. Table 2 depicts the total organic carbon content (%) in the marine sediment of present study with selected sites around the world.

From the present study, it is concluded that the petroleum hydrocarbon and total organic carbon concentration recorded in the present study is the need of the hour to understand the environmental health of the coastal environment of vadinar of Gulf of Kachchh. Further, the presence of these two indicative parameters can serve as good indicator for determining the health of the ecosystem.

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APPENDICES – A

List of Figure:

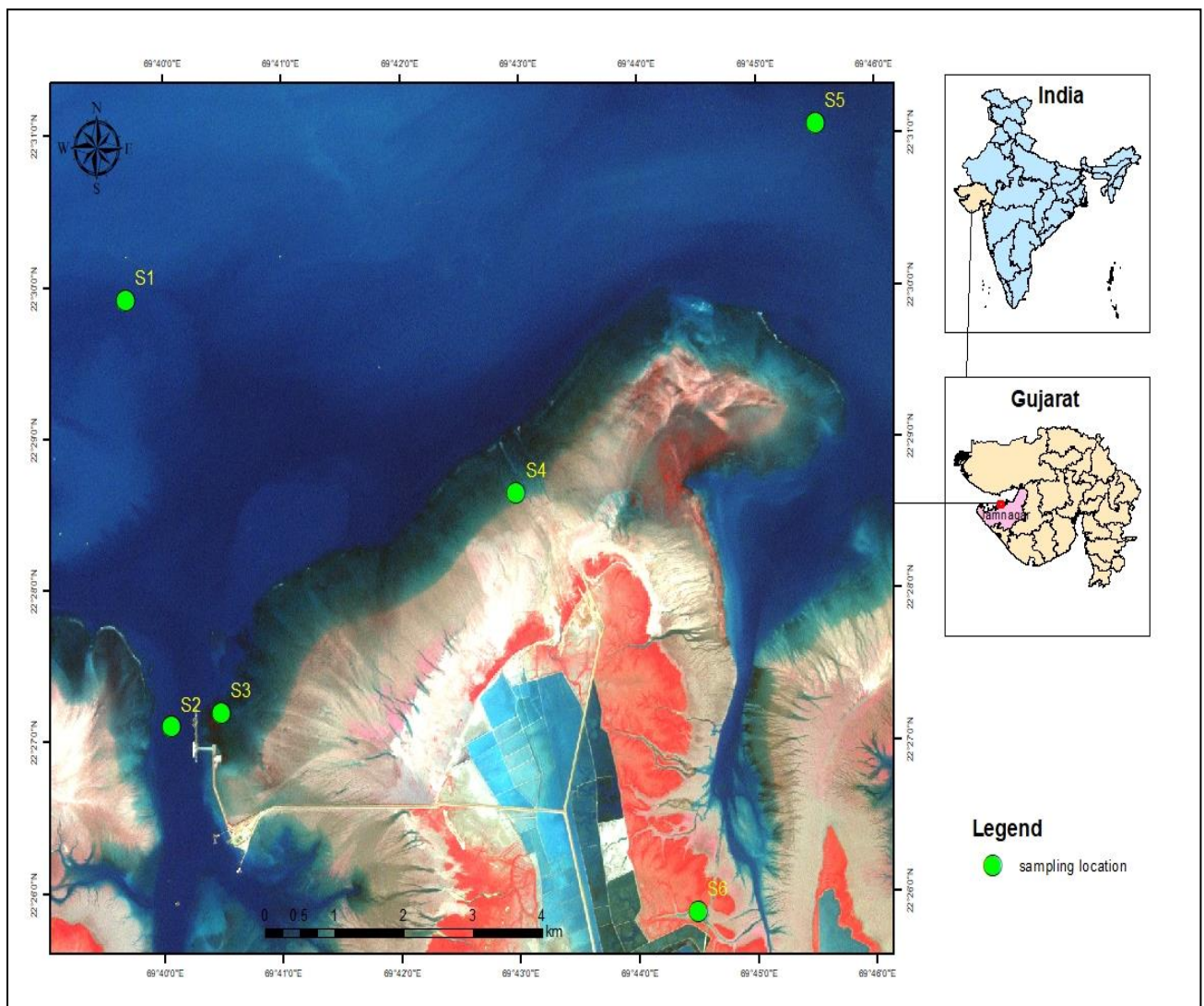


Figure 1: Study area map showing the study locations

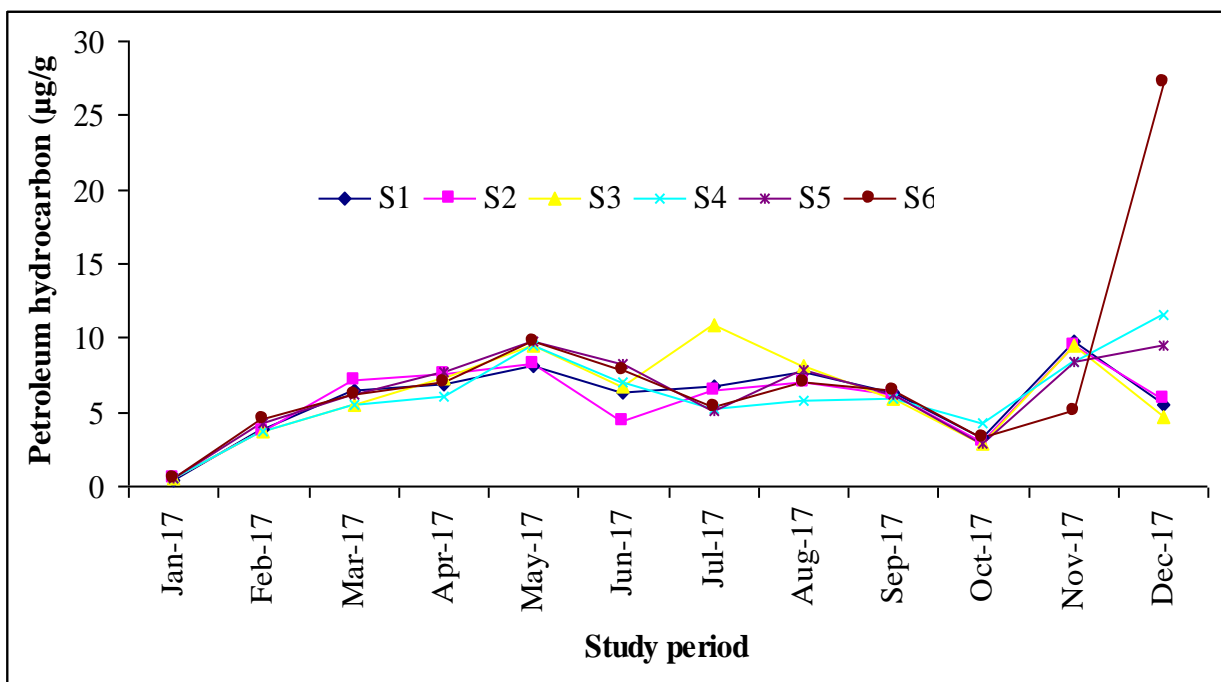


Figure 2: Petroleum hydrocarbon concentration recorded in the sediment samples collected from Gulf of Kachchh

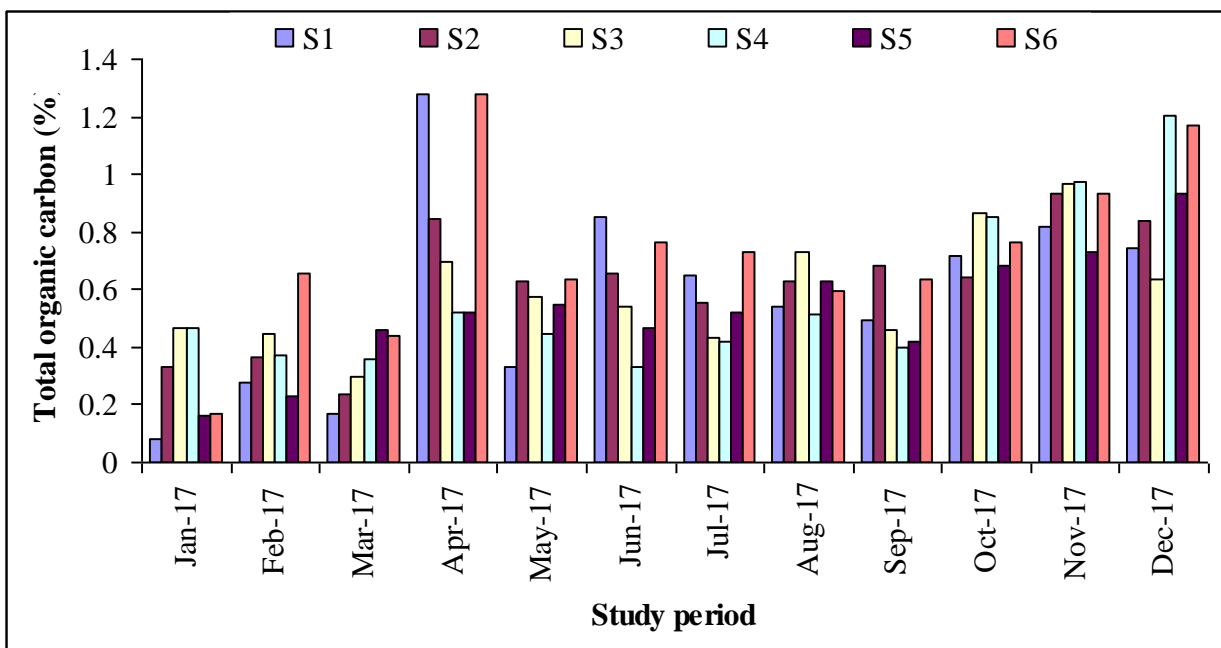


Figure 3: Total Organic carbon content recorded in the sediment samples collected from Gulf of Kachchh

List of table:

Table 1: Comparison of petroleum hydrocarbon (µg/g) in marine sediment of present study with selected sites around the world

Location	Petroleum hydrocarbon (µg/g)	Reference
Bay of Bengal, India	1.88 - 39.76	Venkatachalapathy, et al., 2010
Arabian Sea along the Indian coast	0.6-5.8	Sengupta et al., 1993
Changjiang estuary, China	2.2 – 11.82	Bouloubassiet al., 2001

Straits of Johor, Malaysia	0.7 – 36.7	Abdullah et al., 1996
Abu Dhabi, UAE	6.14 – 62.7	Abd et al., 2008
FraserRiver Basin, Canada	1.6- 20.6	Yunker and Macdonald, 2003
Bizerte lagoon, Tunisia	0.05 - 19.5	Mzoughi et al., 2005
Bassein-Mumbai coast, India	7.0 - 38.2	Chouksey et al., 2004
Gulf of Fos, France	7.8 - 180	Mille et al., 2007
Saudi Arabian	31.0 - 9.6	Fowler et al ., 1993
Bahrain	11.7 - 15.8	Tolosa et al., 2005
Gulf of Kutch, Jamnagar – India	0.464 – 27.2	Present study

Table 2: Comparison of total organic carbon (%) in marine sediment of present study with selected sites around the world

Location	Total organic carbon (%)	Reference
Rosetta Branch - northern part of Egypt	0.92-1.29	Yasser Ahmed El-Amier, et al.,2015.
Tsurumi River, Yokohama- Japan	0.3-6.5	Mohiuddin. K.M, et al., 2010
West coast of Sardinia, western Mediterranean sea- Italian	0.96–4.29	De falco. C, et al ., 2004
South China Sea	0.46- 2.86	Gui-Peng Yang., 2000
Cochin mangroves, south west coast - India.	0.17-4.05	Sunil Kumar, R. (1996).
Gulf of Kutch, Jamnagar – India	0.083 - 1.277	Present study