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Dissemination of Total Petroleum Hydrocarbon (TPHC) in Estuarine Water and Sediment

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ABSTRACT

Total Petroleum Hydrocarbons (TPHC) are complex assemblage of chemicals comprising of a mixture of short and long-chain aliphatic hydrocarbons and aromatic compounds that are commonly present in coastal environments. The study area harbours many major industrial and shipping facilities that may impact the water bodies. TPHC was estimated from water and sediment from three sampling sites of estuary in Hazira industrial area for two consecutive years (2011-2013). Concentration of TPHC in water samples along the estuary ranged between 0.04 to 4.31 µg/L in water and 1.13 to 5.02 µg/g in sediments. The mean concentration of TPHC from all sampling sites was lower than the prescribed standard limit. Non parametric tests were used to analyze the data. No particular trend was observed in the dissemination of TPHC in water and sediment across different sampling sites during different seasons of study ($p>0.05$). The sediments showed the contamination factors below 1 ($Cf< 1$) however it cannot be concluded that the area is not polluted, so continuous monitoring is necessary because the study area is vulnerable and also situated in an industrial location. Very limited studies were conducted on petroleum hydrocarbons in the Indian coastal waters and no report is available yet on the petroleum hydrocarbon profile in both the water and sediment from Tapi estuary. This research effort would be helpful to provide baseline data with reference to TPHC status in Tapi estuary.

Keywords Total petroleum hydrocarbons, Estuary, Water, Sediment, Contamination factor.

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INTRODUCTION

Estuaries are important coastal ecosystems which are formed where there is a convergence of fresh and marine environments and create a salinity gradient from the inner to outer estuary (Prandle 2009). Estuaries have been called the "nurseries of the sea" because the protected environment and abundant food provide an ideal location for organisms to inhabit and reproduce. The increasing contamination level by persistence organic pollutants (POPs) in an aquatic environment is of significant concern as their widespread use have severe impact on aquatic environment(Sany *et al.* 2014).These pollutants have great toxicity potential toaffect humans as they have long half-life and high bioaccumulation characteristics in food web (Ahmadzadeh *et al.* 2011, Haffner and Schecter 2014). Among these contaminants,Total petroleum hydrocarbons are commonly present in coastal environments due to harbor operations, oil spillage andmarine traffic activities (Daskalou *et al.* 2009). Petroleum hydrocarbons consist majorly of three groups of compounds, namely, alkanes, alkenes and aromatics compounds and have a widespread

distribution in the environment. When they enter the water sources,a considerable portion gets distributed in the surface water before getting accumulated in sediment and transferred to biota. All pollutants may get dispersed, diluted or deposited owing to the dynamicity of water and the level of pollution vary from very low to very highly polluted nature. These unwanted substances change the water quality and it becomes unfit for designated uses (Macaulay and Rees 2014).In an aquatic ecosystem water and sediment has close relationship and pollutant get absorbed in sediment. It is therefore the study of sediment is equally important.

Sediment can be defined as particles derived from soil, rock or organic matter transported by water or wind. Sediments in aquatic ecosystem are analogous to soil of terrestrial ecosystem as they are the source of substrate, nutrients and home of living aquatic resources. PHC is hydrophobic, lipophilic and the accumulation in sediments is a potential risk for the organisms in future, so it is also considered as "Chemical Time Bomb" (Muthukumar *et al.* 2013). Petroleum hydrocarbon has received special attention because it is readily adsorbed onto particulate matter and bottom sediments ultimately act as a reservoir for hydrophobic contaminations. Sediment integrates the pollutants over time and it is easy for the sedimentary organisms to concentrate the pollutants in an alarming rate (Mirsadeghi *et al.* 2011).The study of sediment is important for establishing the effects of anthropogenic and natural processes on depositional environment, Venkatachalapathy *et al*. (2011).

Some of the studies conducted on petroleum hydrocarbons in the Indian coastal water and sediments are from Venkatachalapathy *et al*. (2011) (Chennai coastal sediment), Ansari *et al*. (2012) (Orissa coast),Venkatachalapathy *et al.* (2013) (Visakhapatnam coastal sediment), Veerasingam *et al.*(2015) (Mandovi estuary), Rao *et al.* (2016) (Amba estuary) and Rao *et al.* (2019) (Kundalika estuary). Earlier studies in water and sediment of Tapi estuary focused on the physico-chemical characteristics, microbial and heavy metal contamination of the environmental conditions and have reported deteriorated situation of estuary (Kumar *et al.* 2009, Surana *et al.* 2013, Gadhia *et al.* 2014, Surana *et al.* 2015, Gupta *et al.* 2019, Surana *et al.* 2019). However, no report is available yet on the petroleum hydrocarbon profiles in both the water and sediment aspects of the estuary, which is the subject of this present study. Hence, this study would provide useful evidence about anthropogenic impact in water and sediments of Tapi estuary with reference to the level of total petroleum hydrocarbons.

MATERIALS AND METHODS

Study area

Hazira is an industrial area and a transhipment port in the Surat district of the Gujarat state in South western India. It is known as the industrial hub of India and located on the bank of the Tapi estuary, eight kilometers from the Arabian Sea. It is a center for major industrial and shipping facilities like Essar, Kribhco, Shell, Larsen and Toubro, NTPC, ONGC, GAIL, Gujarat State Petroleum Corporation, Ultra Tech Cement and Reliance Industries. Hazira Port is a deep-water liquefied natural gas (LNG) terminal and multi-cargo port in the Tapi estuary.

The Tapi estuary is permanent tropical estuary and one of the major estuaries on the Gulf of Khambhat. The estuary is located at lat 21°40'N and long 72° 40'E. The Tapi River originates in Madhya Pradesh and after its course through Maharashtra, ends in Gulf of Khambhat of the Arabian Sea near Dumas, Surat. Along its course, the river receives industrial effluents released from urban cities like Surat and many chemical and fertilizers industries in and around Hazira industrial area which forms the major source of pollution into the estuary.

Sampling sites

Dumas (Site 1): It is the mouth of the estuary in the southern bank at 21° 06' 21.71" N and 72° 42' 15.33"E. Magdalla (Site 2), situated at 21° 08'47.13" N and 72° 45' 7.81"E. Hazira (Site 3) is located on the bank of Tapi River near the Arabian Sea at 21° 08' 10.53" N and 72°"39' 46.33"E (Fig.1).

Samples collection and analysis

1L water sample was collected from each station

Fig. 1. Sampling sites.

using an amber colored glass bottle (IOC-UNESCO 1984). The bottle was precleaned with n-hexane, rinsed with the ambient water before sampling.Water was extracted twice with 25 ml n-hexane to transfer TPHC in the organic phase and the organic extract was concentrated after drying. Excitation of the extract was measured by using UV spectrophotometer (excitation at 239 nm and emission at 259 nm). All blanks, standards and samples were measured under identical instrumental settings and conditions.

The sediment sample was dried and fine powder was made by grinding. Hundred gm of dried sample was taken in a beaker and 500 ml of distilled water was added and stirred on a magnetic stirrer for an hour. After thorough mixing, the mixture was allowed to settle completely. The clear supernatant was taken without mixing with the sediment. About 300 ml of supernatant was used for estimation of total petroleum hydrocarbon as per the standard method prescribed for water.

The methods for estimation of petroleum hydrocarbons in water and sediment were calibrated using Saudi Arabian crude residue, topped at 1000c (Chouksey *et al*. 2004 and Veerasingam *et al.* 2011). Appropriate blanks were analyzed with each set of samples. The chemicals used for all analyzes were of analytical grade (AR) 99% purity.

Contamination factor (CF)

The contamination factor (Cf = C0-1/ CnC) of PHC was used given by Hakanson method and the level of pollution is arranged as follows: Cf <1 low pollution, 1 ≤ Cf <3 middle pollution, 3 ≤ Cf < 6 notable pollution, Cf >6 high pollution- (C0-1: Present contamination, Cn: Natural background) (Hankson 1980). The report of PHC values from Persian Gulf sediments was categorized into four levels (guideline µg /g) i.e., Unpolluted area /natural background (10-15), slightly polluted / upper permissible limits (15-50), moderately polluted (50-200) and heavily polluted area (>200), Massoud *et al*. (1996).

RESULTS AND DISCUSSION

Distribution of TPHC in water and surface sediments of the study area

Concentration of TPHC in water samples along the

Table 1. Descriptives statistics of total petroleum hydrocarbons (mg/L) in water of Tapi estuary.

Sites	Mean	Std Deviation	Std Error	Minimum	Maximum
Dumas	0.4445	0.82759	0.16893	0.04	4.31
Magdalla	0.3167	0.1874	0.03825	0.15	1.13
Hazira	0.3067	0.12998	0.02653	0.1	0.85

Table 2. Tests of normality.

	Kolmogorov-Smirnova			Shapiro-Wilk		
Parameter	Statistic	Df	Sig	Statistic	Df	Sig
TPHC (Water)	0.409	72	0	0.25	72	0

a. Lilliefors significance correction

estuary ranged between 0.04 to 4.31 µg/L (Table 1, Fig. 2) with the highest concentration (4.31 µg/L) at Dumas (Site1).The distribution of TPHC in different seasons (Pre-monsoon, monsoon and Post monsoon) during two consecutive years is shown in Fig.3.The mean concentration of TPHCfrom all sampling sites was lower than acceptable standard limit for petroleum hydrocarbons given by the European Union Environmental Protection Agency (EUEPA 2009). Comparatively, these values werelower than reported values in India by Rao *et al.* (2016) from Amba estuary (39.7µg/L), Venkatachalapathy *et al.* (2013) from Visakhapatnam coast (0.34 – 19.70 µg/L), Ansari *et al.* (2012) from Orissa coast (2.4-3.8 µg/L), Veerasingam *et al.* (2011) from Tamil Nadu coast (2.28-14.02 µg/L) and Chouksey *et al.* (2004) from Mumbai coast (2.9-39.2 µg/L).

Normality test of the distribution (Table 2)

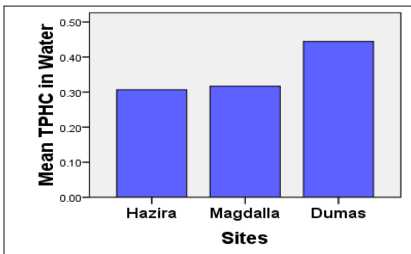

Fig.2

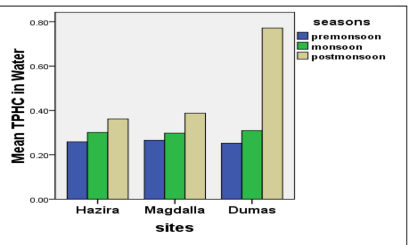

Fig.3

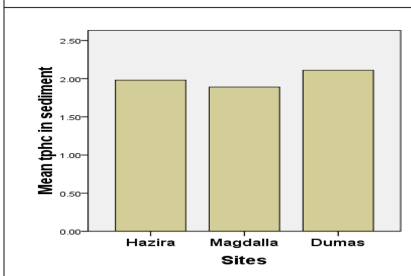

Fig.4

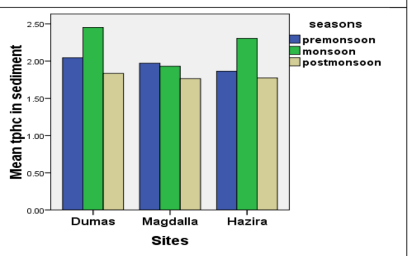

Fig.5

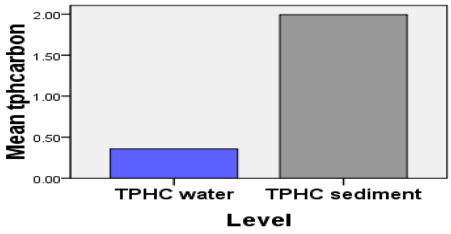

Fig.6

Fig. 2. Mean TPHC in water**. Fig. 3.** Mean TPHC in water and pre-monsoon and post-monsoon. **Fig. 4.** Mean TPHC in sediment. **Fig. 5.** Mean TPHC in sediment and pre-monsoon and post-monsoon. **Fig. 6.** Mean TPHC in carbon.

Table 3. Kruskal-Wallis rank test for analyzes of distribution of TPHC in water(N=24 for each site, total N=72, df,2).

Sites	Mean Rank	Chi-square	Asymp Sig	Seasons	Mean Rank	Chi-Square	Asymp Sig
Dumas	37.58			Pre-monsoon	29.62		
Magdalla	34.08	0.482	0.726	Monsoon	41.44	4.136	0.126
Hazira	37.83			Post-monsoon	38.44		

showed that data are not distributed normally. Non parametric, Kruskal Wallis test indicated that the distribution of TPHC does not differ significantly($p>0.05$) across three sampling sites and does not show significant difference during different seasons during two consecutive years (Table 3). No particular trend was observed in the dissemination of TPHC during different seasons of study and the same trend was also reported by Adeniji *et al.* (2017). This indicates the overall dispersion of TPHC throughout the estuary.

Concentration of TPHC in surface sediments varied in the range from 1.13 to 5.02 µg/g (Table 4, Fig.4) and the highest concentration of 5.02 µg/gwasrecorded from Hazira (Site 3). The distribution of TPHC in sediment during different season (Pre-monsoon, monsoon and Post-monsoon) for two consecutive years is shown in Fig.5. Similarly the sediment of estuaries, harbors, bays and coastal areas are also expected to be with high hydrocarbons because of various factors such as boat traffic, industrial and urban wastages (Kamalakannan 2017). The reported values of TPHC concentration in sediments from different study in India were Rao *et al*. (2019) (Kundalikaestuary, 2.1-16.8 µg/g),Veerasingam *et al.* (2015) (Mandovi estuary, 5.4–12.34 µg/g), Venkatachalapathy *et al.* (2013) (Visakhapatnam coast, 0.34 – 19.70 µg/g) Chouksey *et al.* (2004) (Mumbai coast, 2.0-42.8 µg/g). The reported values were found comparatively higher than the present study.

Normality test for the distribution of TPHC in sediment showed that data are not distributed normally (Table 5). Non parametric, Kruskal Wallis test indicated that the distribution of TPHC in sediment does not differ significantly ($p>0.05$) across three sampling sites and does not show significant difference during different seasons for the two consecutive years (Table 6).The distribution of TPHC in the sediment followed the same pattern as that in water.

The concentration of TPHC in sediment is higher than that in water (Fig.6).This indicates greater accumulation in sediment which can have adverse impact on benthic organisms. Mann-Whitney Test for the distribution of TPHC showed significant difference in value of TPHC in water and sediment ($p<0.05$). Similar findings were concluded by Nour and Sayed (2015), Dumka and Kingdom (2018) Rao *et al.* (2019).

Table 4. Descriptives statistics of total petroleum hydrocarbons (ug/g) in sediment of Tapi estuary.

Sites	Mean	Std Deviation	Std Error	Minimum	Maximum
Dumas	2.1101	0.75168	0.15344	1.13	4.48
Magdalla	1.8893	0.38323	0.07823	1.33	2.99
Hazira	1.9806	0.7276	0.14852	1.3	5.02

Table 5. Tests of normality (sediment).

	Kolmogorov-Smirnova			Shapiro-Wilk		
Parameter	Statistic	Df	Sig	Statistic	Df	Sig
TPHC	.215	72	0.000	0.745	72	0.000

a. Lilliefors significance correction

Table 6. Kruskal-wallis rank test for analyzes of distribution of TPHC in sediment (N=24 for each site, total N=72, df, 2).

Sites	Mean rank	Chi-square	Asymp sig	Seasons	Mean rank	Chi-square	Asymp sig
Dumas	40.29	1.190	0 .552	Pre-monsoon	37.08	2.566	0.277
Magdalla	34.33			Monsoon	41.02		
Hazira	34.88			Post-monsoon	31.40		

Contamination factor of total petroleum hydrocarbons

The level of contamination factor in the sediments covering the study of two years is presented in Table 7. During the present study, in all the stations covering different seasons the concentrations of TPHC were less than the natural background value (10-15 µg/g) as represented by Massoud (1996).The same findings were observed by Muthu kumar *et al.* (2013) in Sediments of three different ecosystems from South east coast of India.

CONCLUSION

The concentration of TPHC in sediments collected from different sampling sites of Tapi estuary is very muchlower when compared to natural background level Table 8. The estuary can be considered as a low polluted region with respect to the distribution of TPHC. The result of TPHC obtained in the present study can beused for the future base-line studies. Even though the sediments showed the contamination factors and risk index below1 (Cf< 1) it cannot be concluded that the area is notpolluted, yet continuous monitoring is necessary because the study area is vulnerable and alsosituated in anindustrial location. Though such kind of study has not been conducted in Tapi estuary in selected sampling locations, this research effort would be helpful to prepare the management policies to conserve the river with respect to TPHC pollution.

Table 7. Season wise mean values of total petroleum hydrocarbon in sediment with contamination factor. * Massoud (1996).

Sites	Seasons	Meanug/g)	Guidelines*	Contamination factor
Dumas	Pre-monsoon	2.0441	10	0.204
	monsoon	2.451	10	0.245
	Post-monsoon	1.8352	10	0.184
Magdalla	Pre -monsoon	1.9719	10	0.197
	monsoon	1.9312	10	0.193
Hazira	Pre-monsoon	1.8634	10	0.186
	monsoon	2.3048	10	0.230
	Post-monsoon	1.7738	10	0.177

Table 8. Mann-whitney test for the distribution of TPHC in Tapi estuary (N=72 for each level, total=144).

Parameter	Level	Mean rank	Sum of ranks	Mann-whitney U	Wilcoxon W	Z	Asymp. sig
TPHC	Water	37.49	2699	71	2699	-10.073	0
	Sediment	107.51	7741				

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