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contaminants of 3 m surface sediments
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PETROLEUM HYDROCARBONS IN SURFACE SEDIMENTS IN KANDLA CREEK (GUJARAT)

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ABSTRACT

Petroleum hydrocarbons in the surface sediments were determined gravimetrically and spectroscopically to evaluate petroleum oil pollution in the Kandla creek. They ranged from 9.6 — 140.5 and 6.5 — 23.3 $\mu\text{g g}^{-1}$ (wet wt.) respectively. Gas chromatographic study indicated the presence of crude oil residues in the sediments.

Key-words : Petroleum hydrocarbons, surface sediments, Kandla creek

Kandla creek (Fig. 1) is one of the major constituents of the creek system in the Gulf of Kachchh along Gujarat coast. It is surrounded by a number of onshore oil installations. Approximately 600 million litres of petroleum products such as motor spirit, Kerosene, light diesel oil, high speed diesel, lubricating oil, furnace oil and naphtha are handled by these installations every month. Transportation and loading — unloading operations are also carried on using mechanical devices which cause occasional spillages at the jetties and installations. Minor leakages also occur in transportation pipelines. Due to this, the creek is vulnerable to oil pollution. Indeed thin oil patches and tar lumps have been observed in the tidal waters. As surface sediments which serve as a long term sink for waterborne oil residues, are indicators of oil pollution (Blummer and Sass, 1972), investigations on surface sediments in Kandla creek were taken up to assess the oil pollution extent.

Surface sediments were collected in March, 1985 using Van-Veen grab. The deep frozen samples were thawed and digested with methanolic potassium hydroxide (0.5N) and benzene (Farrington and Quinn, 1971). The organic phase was separated from the aqueous layer after washing with distilled water. The separated organic layer was dried over anhydrous sodium sulphate and passed through copper powder to remove elemental sulphur (Blumer, 1957). Then it was evaporated to dryness at 30°C at reduced pressure of 50mm to obtain a semisolid residue (A), (Table I). It was chromatographed on alumina: silica gel (1:2, 3 g) column and benzene: hexane (1:4, 30 ml) solvent system to obtain total petroleum hydrocarbons (A-1), (Table I) including aromatics (Farrington and Tripp, 1975). The aqueous phase was acidified to pH 2 and extracted with petroleum ether to get saponifiable residue (B, Table I). A-1 was analysed

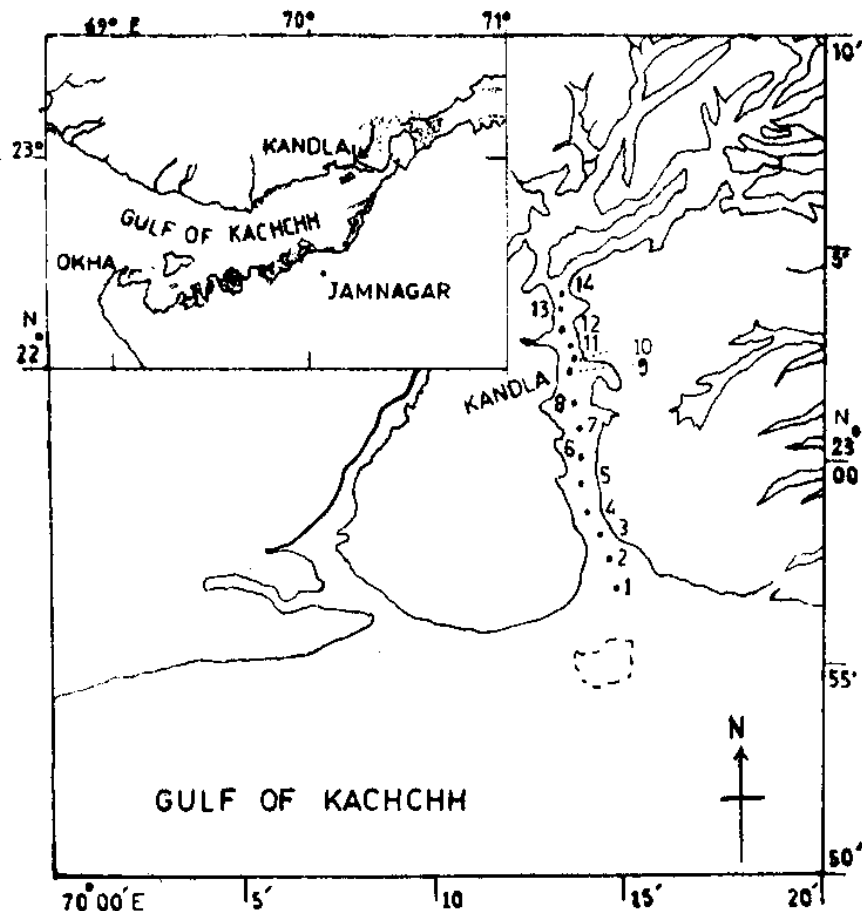


Fig. 1. Map showing Kandla creek and sampling stations.

spectroscopically (A-2) (Table I) at 256 nm on Perkin Elmer, Lambda 5 UV-VIS spectrophotometer (National Academy of Sciences, 1975). Residue of Saudi Arabian Mix Crude having b.p. $\geq 100^\circ\text{C}$ was processed under similar conditions as samples and used as standard for spectroscopic determinations. Gas chromatographic analyses were performed on Perkin Elmer, Sigma 2000 using 40m x 0.25mm ID fused silica glass capillary (FSOT) column with bonded methyl silicone phase (Part No. 0092348, Perkin Elmer, U.S.A.) Flame ionisation detector (FID) and split injector system were maintained at 350°C . The split ratio was 1:100. Nitrogen (100 ml min^{-1}) was used as carrier gas. Column temperature was programmed in $50\text{-}300^\circ\text{C}$ range at the rate of $10^\circ\text{C min}^{-1}$.

Concentration of unsaponifiable organics (A) was found to be in the range of $14.2 - 359.6\ \mu\text{g g}^{-1}$ (wet wt.) while saponifiable material i.e. fatty acid residue was in the range of $3.4 - 92.0\ \mu\text{g g}^{-1}$. Petroleum hydrocarbon concentration (A-1) as determined gravimetrically was found to be in the range of 9.6 to $140.5\ \mu\text{g g}^{-1}$ (wet wt.). But spectroscopic determination (A-2) showed much lower levels (from 6.5 to $23.3\ \mu\text{g g}^{-1}$ wet wt.). The discrepancy may be due to the presence of other compounds with similar characteristics as that of A-1. In the spectroscopic determination (A-2) the residue was estimated as a fraction of

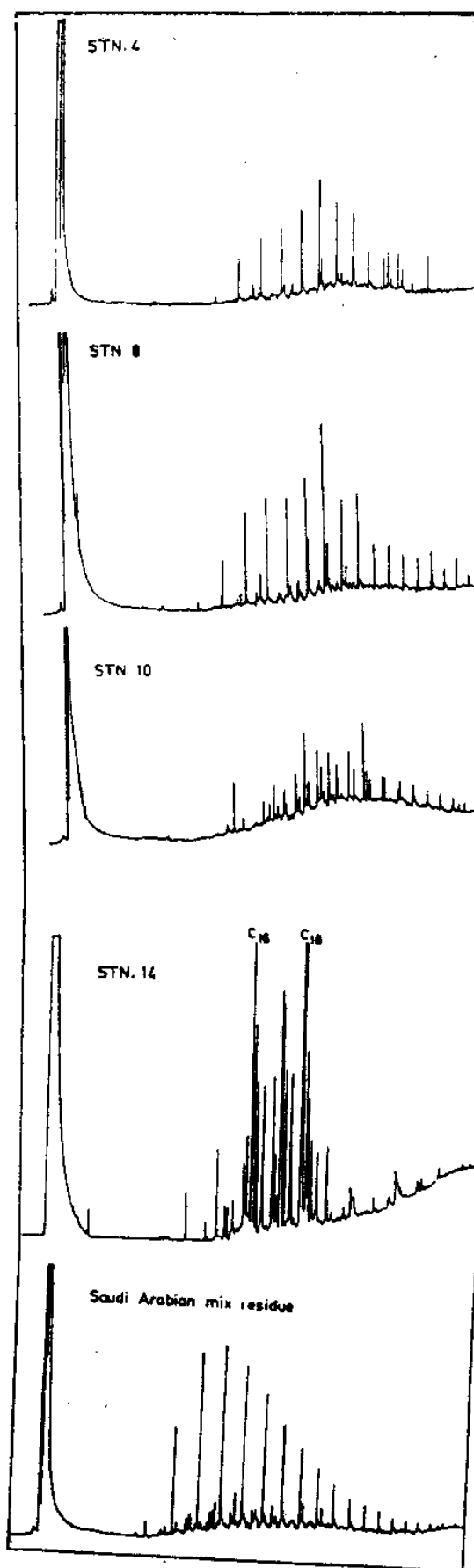


Fig. 2. Gas chromatograms of petroleum hydrocarbons (A-1) obtained for Stn 4, 8, 10, 14 and the Saudi Arabian Mix residue.

the total petroleum residue. Hence, it may be taken that the latter values represent almost near correct levels of contamination in the surface sediments.

Table I — Details of surface sediment workup

Station	Moisture content %	Organic phase $\mu\text{g g}^{-1}$ (wet wt.)			
		Total A	Petroleum hydrocarbons		Aqueous phase $\mu\text{g g}^{-1}$ (wet wt.) B
			gravimetric A-1	spectroscopic A-2	
1	21.4	44.8	32.0	6.5	29.0
2	38.3	77.8	70.3	23.3	92.0
3	8.3	60.0	59.3	20.7	57.0
4	8.1	64.0	64.0	15.4	52.0
5	9.4	14.2	9.6	12.8	35.0
6	7.0	33.2	32.4	14.7	6.2
7	13.1	25.8	12.1	8.7	3.4
8	33.1	78.4	54.0	12.5	22.0
9	13.6	25.4	17.5	13.6	31.0
10	19.6	28.0	26.0	7.7	39.2
11	18.5	21.6	21.1	16.4	39.6
12	44.1	359.6	140.5	18.0	59.8
13	25.7	65.6	44.9	15.5	30.4
14	24.7	86.6	80.4	10.8	35.0

It is often difficult to compare results of such type of investigations due to variation in extraction techniques and analytical methods. Therefore the results were compared only with most generalised values. Previous studies on petroleum hydrocarbon contamination of the sediments of Kandla creek were not reported. Clark and MacLEOD (1977) have reported a range in hydrocarbon content of the sediments in polluted coastal regions from 100 to 12,000 $\mu\text{g g}^{-1}$ and in unpolluted coastal areas or basins, to be usually 70 $\mu\text{g g}^{-1}$. The National Academy of Sciences (1975) concluded that the level of hydrocarbon contamination in polluted coastal regions may be upto 12,400 $\mu\text{g g}^{-1}$ (dry wt.). As per these generalised values Kandla creek does not appear to have shown high contaminants from petroleum hydrocarbons. Probably the strong tidal currents which prevail and these dredging operations in the area may be responsible for the low concentration of petroleum residues in the sediments. Values of petroleum hydrocarbon distribution (4.8 — 9.4 $\mu\text{g g}^{-1}$ wet wt.) in the surface sediments along Goa coast (Fondekar, Topgi and Noronha, 1980) are comparatively lower than those obtained in the present investigation.

Gas chromatographic technique was employed for determining the nature of constituents in the residues as the method affords high discrimination in correlating petroleum to refined petroleum products (Ehrhardt and Blumer, 1972). Representative gas chromatograms of A-1 from Stn 4, 8, 10 and 14 are shown in Fig. 2. Gas chromatographic analyses of A-1 from Stns. 1-5, 7-9, 11 and 12 yielded typical chromatograms having sharp peaks overlying an unresolved complex mixture (UCM) along the baseline. The chromatograms are characteristic finger-

print patterns generally obtainable from whole crude oil residues e.g. Saudi Arabian Mix Residue (Fig. 2) (Wakeham, 1976; Meyers and Takeuchi, 1979). Chromatograms for residues of Stn. 6, 13 and 14 consists of constituents concentrated in C_{16} to C_{18} range. Possibly the contamination might have originated from middle distillate fraction of crude oil (Clark and Brown, 1977). In the chromatogram of A-1 of Stn. 10, the concentration of paraffins is low which indicates a highly weathered residue. The studies could not be extended for source identification purpose due to non-availability of authentic source samples.

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