

Extractable organics in surface sediments from Thana creek and Bombay harbour

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Considerable variations in hydrocarbon and fatty acid levels in surface sediments from Thana creek and Bombay harbour were observed. Sediments from the westernside nearshore locations yielded higher values. The residues were characterised by infrared spectroscopy (IR) and gas chromatography (GLC). The results suggest that the contamination might have originated from crude oil residue.

The study on the extent of pollution in the sea around Bombay has become imperative as huge quantities of wastes from a variety of industries and thickly populated areas are released into it, resulting in substantial deterioration in water quality and aquatic life^{1,2}. The levels of extractable organics in surface sediments from Thana creek and Bombay harbour are reported in this communication.

Materials and Methods

Surface sediments were collected from different locations (Fig. 1) during March 1983 using a van Veen grab and preserved in a deep freeze till the time of digestion which was completed within a month from collection.

Wet sediment (50 g) was digested³ with KOH (0.5 N) in methanol (95%) and benzene mixture (2:1, 350 ml) for 2 h. The residue was separated into water soluble (A) and water insoluble (B) portions³. Column chromatography⁴ of fraction B over alumina-silica gel (1:4, 10 g) with solvent systems: hexane (50 ml), benzene (50 ml) and methanol (50 ml) gave nonpolar (B1), intermediate (B2) and polar (B3) residues respectively. The gravimetric estimations were also made. Total organic carbon (TOC) was determined by dichromate method using ferroin indicator⁵.

The IR spectra of B1, B2 and B3 were scanned as thin films in NaCl cells in the range 4000-600 cm^{-1} on a Perkin-Elmer, 983G infrared spectro-

photometer. Gas chromatographic analysis was performed on a Perkin-Elmer (Sigma 2000) using a glass FSOT column (length 40 m; internal diam. 0.25 mm) with methyl silicon liquid phase (Perkin-Elmer, part No. 0092348) and a flame ionisation detector (FID). Nitrogen (ratio 1:70; 1 ml min^{-1}) was used as the carrier gas. Column temperature was programmed (50°-300°C) at the heating rate of 10°C min^{-1} . FID and the injector were maintained at 350°C.

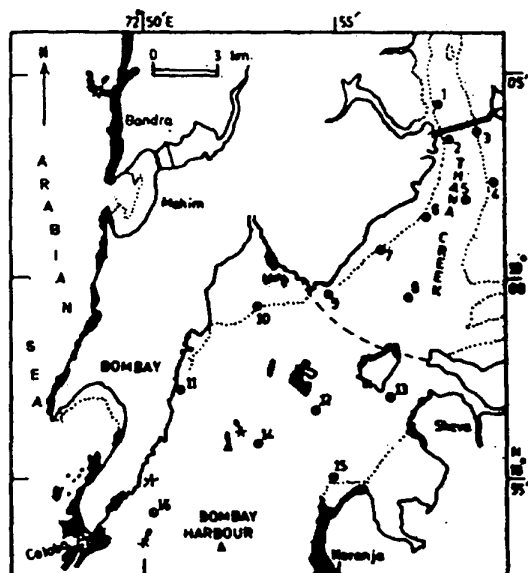


Fig. 1 - Sampling stations

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Results and Discussion

The sediment workup is schematically shown in Fig. 2. Several extraction procedures, viz. alkali digestion^{3,7}, solvent extraction after homogenising^{7,8} and soxhlet extraction^{7,8} are reported. Alkali digestion method has been preferred because the highest recovery for hydrocarbons ($90 \pm 6\%$) and fatty acids ($98 \pm 6\%$) has been reported⁹. The workup procedure has shown very low ($0.6 \mu\text{g g}^{-1}$) contamination with sample blank.

Thana creek—The buildup of organics in the sediments is evident from Table 1. Higher concentrations of organic pollutants were found at sts 2 and 6 to 9. Corresponding total organic carbon

(TOC) values for these stations were 2.2, 2.2, 2.5, 2.4 and 2.3% and unsaponifiable organics (B) were 2752, 3730, 2539, 1039 and 1980 $\mu\text{g g}^{-1}$ respectively (Table 1). All these stations except st 8 are nearshore. Other midstream stations (3 to 5) showed comparatively low values of unsaponifiable residue averaging 812 $\mu\text{g g}^{-1}$. Comparison of TOC with A and B of all stations showed that concentration of extractable organics was very low in the sediments. Aliphatic hydrocarbons (B1, Table 1) constituted about 30-40% of unsaponifiable residue (B) for all nearshore stations but they were about 10-20% for midstream stations except st 8 in which case it was 38%. This exceptionally high value may be due to occasional crude oil spillage by the passing tankers. This indicates that nearshore sediments might have been contaminated by a residue of crude oil origin. Fatty acid residue which was obtained as a polar fraction (A, Table 1) from the aqueous phase was in the range of 39-336 $\mu\text{g g}^{-1}$. St 3 showed the highest value (336 $\mu\text{g g}^{-1}$).

Bombay harbour—TOC values were in the range 0.8-2.4% and unsaponifiable extracts (B) were 461-4456 $\mu\text{g g}^{-1}$ (Table 1) indicating comparatively lesser pollution than in Thana creek. St 10 where refinery outfall exists showed highest value of B (4456 $\mu\text{g g}^{-1}$). Additionally the nearshore sts 11 and 16 at westernside showed high values of B and B1 (Table 1). The saponifiable polar fraction (A, Table 1) had fatty acid residue in the range of 41-301 $\mu\text{g g}^{-1}$.

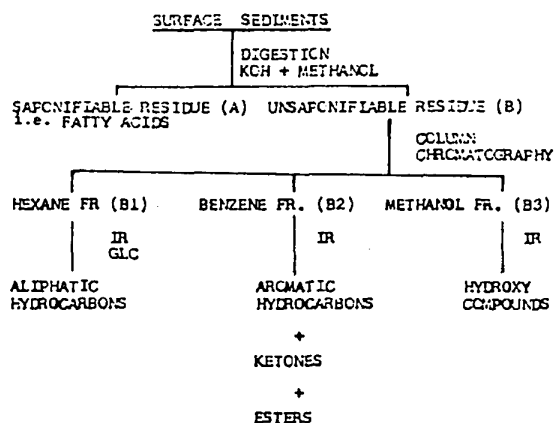


Fig. 2—Flow chart of methodology

Table 1—Gravimetric details of workup of sediment samples

St No.	Depth (m)	Moisture content (%)	Total organic carbon TOC (%)	Saponifiable residue ($\mu\text{g g}^{-1}$ wet wt)	Unsaponifiable residue ($\mu\text{g g}^{-1}$ wet wt)				
					A	B	B1	B2	B3
Thana creek									
1	2.5	59	1.8	39	1267	444	278	408	
2	4.0	60	2.2	224	2752	1054	549	786	
3	4.0	44	1.1	336	980	103	112	191	
4	3.5	51	1.0	117	712	123	127	289	
5	3.5	57	1.2	138	745	141	163	325	
6	4.0	56	2.2	223	3730	1258	683	704	
7	2.5	58	2.5	129	2539	1115	491	590	
8	8.0	58	2.4	99	1039	395	242	419	
9	8.0	48	2.3	76	1980	904	328	560	
Bombay harbour									
10	3.0	55	2.4	301	4456	999	899	837	
11	3.0	58	1.9	136	1644	525	383	398	
12	16.0	56	1.2	101	566	98	77	101	
13	22.0	44	0.8	113	461	106	100	150	
14	12.0	55	1.7	248	532	113	120	176	
15	10.0	53	1.2	41	586	113	126	268	
16	6.5	56	1.5	122	1133	271	191	234	

IR spectra of hexane eluted non-polar fractions (B1) revealed that it might contain alkanes, cycloalkanes and monosubstituted aliphatic hydrocarbons (characteristic peaks at 2923, 2855, 1454 and 1377 cm^{-1} , 1642 cm^{-1} respectively)¹⁰. The intermediate benzene fractions (B2) showed the presence of ketones and polyunsaturated hydrocarbons including aromatics (peaks at 1738 and 1599 cm^{-1} respectively). Spectra of methanol fractions (B3) consisted of broad band around 3372 cm^{-1} due to bonded hydroxy groups and comparatively strong absorptions at 1730, 1659 and 1601 cm^{-1} due to carbonyl groups and unsaturation from alkanols and sterols respectively¹¹.

Gas chromatographic analysis of hexane fractions (B1) yielded a characteristic pattern having several peaks overlying an unresolved envelope of complex mixture of hydrocarbons (UCM). Sharp peaks with UCM were observed for residues from sts 2, 6, 10 and sharp peaks having negligible UCM for residues from sts 4, 5 and 11 suggest that they might have originated from degraded crude oil¹². In the chromatograms of the residues from sts 12, 14, 15 and 16 peaks and UCM were both insignificant. While chromatograms of residues (B1) obtained from sts 1, 7, 8 and 9 mainly consisted of UCM only. The two latter patterns possibly represent highly degraded crude oil residue¹². These general fingerprint patterns consisting of several peaks in all the chromatograms clearly revealed that peaks have originated from crude oil residue^{12,13}.

It is necessary to mention that a comparison among these types of investigations is often difficult due to variation in extraction, cleanup and analytical procedures. Generally hydrocarbon concentration of few $\mu\text{g g}^{-1}$ are found in sediment

from deep sea areas and hydrocarbon content from unpolluted coastal areas or basins is usually $< 70 \mu\text{g g}^{-1}$. Hydrocarbon content of coastal region contaminated with oil¹⁴ may range from 100 to 12,000 $\mu\text{g g}^{-1}$. Comparison of these values indicated that the present study area is polluted.

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