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I have the honour to state that the observations, data and inferences presented in this thesis are the results of original investigations carried out by me and due acknowledgement has been made wherever outside facilities were availed. So far no part of this thesis has been submitted for any degree or award of this or any other university.

References to the related work have been cited in the text and the list of sources of such information is incorporated in this thesis.

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SYNOPSIS

SYNOPSIS

Indiscriminate release of untreated and/or partially treated domestic and industrial wastewaters through ~~point~~ discharges to nearby creeks bays and estuaries around Bombay has imposed considerable strain on these water bodies. Of these, Thana Creek and Bombay Harbour (Hereafter, both together termed as Bay) are the major recipients of the wastewaters and several studies aimed at delineating the impacts of anthropogenic pollutants on the water quality, sediment quality and biological characteristics have been undertaken. Thus, spatial and temporal variations in dissolved oxygen, biochemical oxygen demand, nutrients and dissolved heavy metals have been reported and degree of contamination of bed sediments by trace metals has been established. Biological investigations were generally confined to delineating the impacts of wastewater releases on phytoplankton, zooplankton and macrobenthic populations of the Bay.

Refineries set-up during the nineteen fiftees along the western shores of Thana Creek have been fed by the petroleum crude imported through the Bombay Harbour. The release of wastewater from these refineries which until recently was only partially treated, accidental spillages during loading-unloading operations, bilge discharges in the port and minor but long-term releases of hydrocarbons through domestic and other industrial wastewaters has rendered the bay vulnerable to cotamination by petroleum hydrocarbons (PHC). The levels of dissolved and dispersed PHC however were found to be unexpectedly low and it was presumed that the high suspended load in the Bay effectively scavanged the PHC thus depositing them on the bed sediment though no investigation assessing the degree of sediment contamination has been reported. Hence, the study of levels of PHC in surficial bed sediments and their depthwise variations in selected sediment cores upto a length of 100 cm formed the major part of the investigation discussed in the Thesis. Routine physico-chemical parameters were also determined at a location in Bombay Harbour to delineate changes which might have occurred in the water quality over the years. The existing water quality of the Bombay High was also investigated in the light of the predevelopment baseline. An oil spill on the west coast of Bombay that occurred when the above investigations were in progress was also studied to identify whether it originated from the well-blowout in the Bombay High. The findings of these studies are briefly described below:

(1) The surficial silty-clay sediment with high absorbing capacity sustained abnormally high concentrations of unsaponifiable residue (712-4456 $\mu g\ g^{-1}$, wet wt) and the levels were markedly higher in sediments of the western shores being in the vicinity of the refineries. The highest concentration was associated with the

sediment from Sewree mud-flat in the discharge zone of Mahul Creek known to transport refinery waste to Thana Creek.

(2) Levels around Butcher Island-an area of major unloading operations of crude, were surprisingly relatively low (461-556 $\mu g\ g^{-1}$, wet wt) as compared to the locations on the western shore, perhaps due to the strong tidal currents prevailing in the area which did not favour deposition of PHC.

(3) Aliphatic hydrocarbons constituted 30 to 40 % of the sediment extracts containing nonpolar lipids from nearshore stations and decreased to 10 to 20 % in the sediment at the midstream region. Aliphatic and aromatic hydrocarbons and hydroxy compounds correlated very well with sediment total organic carbon (TOC) with correlation coefficients above 0.8. Such a correlation of fatty acids with TOC was however poor. Infrared spectra of the nonpolar lipids indicated the presence of alkanes, cycloalkanes, monosubstituted aliphatic hydrocarbons, ketones and polyunsaturated hydrocarbons. Several sharp peaks overlying an unresolved envelope of complex mixture of hydrocarbons observed in the gas chromatograms of nonpolar lipids were typical of the weathered petroleum crude.

(4) Geochemical record of oil pollution history of the Bay was evolved by analysing sediment cores a few of which were previously dated. Thus, the sedimentation rate of 0.74 cm yr^{-1} for 100 cm core from Thana Creek would

have the signature of the depositional environment of past 135 years. Hence, the bottom section of this core would represent the sediment deposited in 1848 when there was practically no import of crude oil and there were no industries discharging into the bay. Likewise, the core from the coastal waters of Bombay preserved the pollution history of the depositional environment of about 200 years. Though organic carbon and total phosphorous revealed only marginal enrichment in some instances, the PHC distinctly increased in the surficial sections. Thus, the two cores from the western portion of Thana Creek had PHC concentration of 420-1180 $\mu g\ g^{-1}$ (wet wt) in the top 10 cm of the sediment which sharply decreased to 70-200 $\mu g\ g^{-1}$ (wet wt) at 20 cm depth followed by a gradual decrease to attain levels of 40-60 $\mu g\ g^{-1}$ (wet wt) in the bottom sections. The cores obtained from Dharamtar Creek which opens along the eastern shores of the harbour, though retains a similar profile, the concentrations of PHC are very low with a maximum of 2.7 $\mu g\ g^{-1}$ (wet wt) centered around 7 cm depth. Hence, high anthropogenic input of PHC to the Bay was effectively contained within the system and its influence was only marginal in Dharamtar Creek. The subsurface maxima between 5 and 10 cm in majority of the cores could be due to bioturbation by the rich benthic fauna of the bay.

(5) Comparision of results of water quality of 1982 and 1988 with the baseline of 1976 revealed that the water

quality in Bombay High had not deteriorated due to offshore oil exploitation activities though DO revealed a decreasing trend.

(6) The monthly changes in water quality in Bombay Harbour were highly irregular devoid of definite trends. There was however no evidence of deterioration in water quality from 1976 to 1984.

(7) Infrared, proton magnetic resonance, fluorescence and ultraviolet spectra and chemical characterisation of the oil spill on the west coast of Bombay were analysed to identify its probable source. It was concluded that the origin of the spill was a tanker sludge and that the tanker was carrying Bombay High crude prior to discharge of the sludge. Critical evaluation of spectroscopic methods reported in the literature for the identification of oil spills were found to give ambiguous results and hence unreliable though frequently employed in the past for source identification of oil spills.

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CHAPTER 1

INTRODUCTION

Extensive population growth and industrial development in and around Bombay has created a considerable demand for freshwater which exceeds the supply. While the new sources of freshwater are being developed, the provision for treatment and disposal of wastewater generated, has not kept at par with the increase in water consumption. Hence, the bulk of the wastewater received at the treatment plants is released untreated into the marine environment which has deteriorated the water quality of the nearshore waters to a considerable extent. It has been estimated that the domestic wastewater generated within the Municipal Corporation of Greater Bombay (MCGB) area which exceeded 1.8×10^5 m^3 day^{-1} added 450 t BOD, 60 t N, 11 t P, 0.18 t Cu, 0.36 t Zn and 0.09 t Pb everyday to the marine environment (Zingde, 1988).

In addition, a wide range of industries, majority of which are located in the Thana-Belapur industrial belt, released their wastewater containing a variety of pollutants to the coastal water generally through point discharges. Thus, the Ulhas River and the associated estuary alone received 35 t SS (suspended solids) and 1250, 35, 20, 10, and 3 kg of Zn, Cu, Hg, Pb and Cr respectively through industrial discharges everyday (Patel et al, 1985). The Mahim estuary was considered to be highly polluted and received 0.17 x 10^5 m^3 day^{-1} of partly treated or untreated domestic wastewater which transported 43 t SS, 45 t BOD, 6 t N, 1 t P, 5 kg Co, 14 kg Ni, 19 kg Cu, 44 kg Zn and 2 kg Pb to the receiving water (Sabnis, 1984).

The anthropogenic organic load entering the creeks and bays around Bombay was far in excess of the assimilation capacity of the receiving water. A 6 km stretch of Mahim estuary was totally devoid of dissolved oxygen (DO) and the presence of sulphide was a regular feature. Even in Mahim Bay which is subject to substantial tidal flushing, the DO at low tide is often zero indicating the severity of pollution in the region (Zingde and Desai, 1980). The levels of PO_4^{3-}-P and nitrogen compounds were highly variable and far in excess of that normally observed in the coastal region (Sabnis, 1984). Although in the offshore, where DO levels were appreciably high resulting in high concentrations of NO_3^--N, and NO_2^--N through the oxidation of ammonia transported through domestic waste, these species were generally absent in Mahim estuary revealing effective denitrification

(Sabnis, 1984). The conditions were not so severe in Thana Creek though the region received large quantity of domestic as well as industrial wastewaters, perhaps because of large tidal displacements and good dispersion. However, marked decrease in DO from Bombay Harbour to Thana during May occurred due to the oxygen demand of the organic matter entering the creek (Zingde, 1985). Likewise, marked decrease in DO and enhancement in the levels of nitrogen and phosphorus compounds had also been reported in Versova Creek and Ulhas estuary (Zingde, 1985).

The nearshore waters of Bombay received appreciable loads of trace metals. However their concentrations in water (dissolved) did not reveal conclusive enhancement. It was considered that the metals entering the receiving water in dissolved form were hydrolysed and/or got rapidly fixed to the particulate matter and thus removed from the solution (Zingde et al, 1989). Some trace metals were only marginally enriched in suspended matter in areas receiving wastewater while the concentrations were near to the background at other locations (Patel et al, 1985).

Distribution of trace metals in the surface sediments of the coastal region of Bombay revealed definite increase in concentration in Mahim estuary. The concentration of Cu was as high as

800 ppm (dry wt) and that of Zn exceeded 2500 ppm (dry wt) in the interior of the creek as against 105 and 138 ppm (dry wt) respectively in the coastal sediments of Bombay. Likewise, the organic carbon exceeded 15 % and total phosphorus was over 2000 ppm (dry wt) indicating the severity of sediment contamination in the Mahim estuary. Enrichment of Mn in the surficial layer commonly observed for oxic marine sediments was absent in Mahim estuary with definite trend of concentration increasing with the depth. This was because under extreme reducing conditions prevailing in the estuary, the precipitated Mn oxides were reduced and mobilised. The reduced Mn diffuses through interstitial fluids to the overlying water which contained sulphide. Thus, the mobilised Mn escaped to the water column instead of precipitating at the water sediment interface, increasing the concentration of dissolved Mn in water. It had been estimated that the top 20 cm sediment layer in Mahim estuary contained 1.3 t Ni, 37 t Cu, 106 t Zn and 4.6 t Pb in excess over the expected background (Sabnis, 1984).

The mercury concentration in sediments of Thana Creek varied from 0.17 to 8.21 ppm (dry wt) with marked increase from the harbour to the creek region suggesting substantial inputs of mercury to the interior creek. The mercury enriched layer in the sediment core was about 10-25 cm in the creek region and 0-8 cm in the harbour area where an excess of 14 t of Hg over the natural background had been estimated to be trapped (Zingde, 1981).

Although in recent years the information as regards the common chemical parameters and trace metals in the coastal marine environment of Bombay had been documented in some details, the studies concerning the fate of organic micropollutants entering the region were not reported. The present investigation was therefore aimed at delineating the extent of sediment contamination by petroleum hydrocarbons (PHC) in Thana Creek-Bombay Harbour (Hereafter termed as Bay) region. This area was selected because the port had heavy ship traffic including oil tankers and also because Thana Creek received a large quantity of wastewater from refineries and petrochemical complexes. Routine physico-chemical parameters were also determined at one location in Bombay Harbour for comparison with the historical data which would reveal changes which might have occurred over the years. The water quality of Bombay High was also critically analysed to delineate changes if any since the commencement of offshore operations for the exploitation of petroleum crude.

An oil spill on the south west coast of Bombay which occurred during the course of the present studies was also investigated. Although, minor spillages of oil largely went unnoted, the spill observed on the 19 August 1982 attracted much attention by virtue of its occurrence within a few days from the well-blowout in the Bombay High. As it was widely believed that the oil spill had its origin in the fallout of the well-blowout, it was of interest to identify the source of the spill.

CHAPTER 2

LITERATURE REVIEW

The available literature on marine pollution and its implications to ecology is vast and clearly beyond the scope of this thesis. Hence, important and relevant works pertaining to marine environment of Bombay, PHC in marine environment and identification of oil spills are briefly reviewed.

2.1 Marine environment of Bombay and Bombay High.

(a) Bombay

The coastal marine environment of Bombay had been investigated in sufficient details to delineate the impacts of wastes on the water quality and biological characteristics. The domestic wastewater (1.8×10^5 m^3 day^{-1}) generated in the city was released untreated or partially treated, to nearby creeks, bays or directly to the coastal waters through point discharges. It was estimated that around 450 t of BOD, 63 t of N, 11 t of P, 0.18 t Cu, 0.36 t of Zn and 0.09 t of Pb entered the marine waters every day through domestic wastewater alone ~~(Zingde, 1988).~~ Although the coastal waters also received large quantities of industrial wastewater, reliable information was not available (Zingde, 1985). A rough estimate of the industrial wastewater generated in Bombay and the regions around (New Bombay and Ulhas) was put at 5 x 10^5 m^3 day^{-1}, a major fraction of which being released in the Bay and Ulhas River-Bassein Creek.

The wastewater entering the marine environment had severely deteriorated the water quality in some regions. The salinity of some creeks and bays varied considerably even in dry season under the influence of the wastewater discharges. The incomplete mixing of low saline contaminated inshore water and high saline seawater intruding during flood tide resulted in appreciable vertical salinity gradient. Thus for example, in Mahim Bay this gradient frequently exceeded 7 ppt (parts per thousand), specially during flood tide and although there was no freshwater discharge through Mahim River, the salinities as low as 15 ppt were common during ebb tide in summer (Zingde and Desai, 1980).

Beyond 10 m depth contour (offshore) where the impact of organic waste was low, the DO of 6 mg l^{-1} during August increased to attain maximum (8 to 9 mg l^{-1}) during January-February followed by a decrease till May. Here, the vertical distribution of DO was fairly uniform with only a marginal decrease with depth. Substantial reduction in DO on the contrary, was a common feature in regions receiving organic waste (Zingde, 1985). Thus, in Mahim Bay (Zingde, 1985) and Versova Creek (Zingde et al, 1979) DO levels were tide dependent with values often falling to zero at low tides. The BOD here exceeded 20 mg l^{-1} during low tide while the offshore waters had BOD below 2 mg l^{-1}. A marked decrease in DO along the length of the Bay during postmonsoon occurred as the freshwater entering the head of Thana Creek through the arm of the Ulhas River became negligible after September (Zingde et al, 1979). The less saline surface water in polluted creeks often had low DO as compared to the more saline bottom water and it was not surprising to observe bottom DO as high as 4 mg l^{-1} when the DO at the surface was below 1 mg l^{-1} (Zingde et al, 1979).

From the pattern of DO and BOD distribution it appeared that the organic load (450 t) brought to the coastal water every day was effectively dispersed by the tidal currents and assimilated in the nearshore waters itself and its transport to the offshore was not detectable.

Due to high oxygen demand, the oxidation of organic matter was only partial in the bays and creeks and complete mineralisation occurred only when the waste reached the open coast accounting for high NO_3^--N and PO_4^{3-}-P in the coastal waters

(Zingde, 1985). The polluted creeks on the contrary had high concentrations of NH_4^+-N while NO_3^--N was often low due to the nonavailability of DO for the oxidation of ammonia and the consumption of NO_3^--N and NO_2^--N through denitrification. The conditions often went to reducing and as high as 37-126 μg-at l^{-1} H_2S-S were reported in Mahim estuary (Sabnis, 1984).

The concentrations of dissolved trace metals in the offshore were low and close to the natural background (Zingde et al, 1989; Sahu and Khopkar, 1987). The levels of dissolved Ni, Cu, Zn and Hg were however, somewhat higher in Thana Creek (Zingde et al, 1989; Zingde and Desai, 1981). The water in the Bay has been reported to have about 77 kg of Hg in excess over the expected background (Zingde and Desai, 1981). The other dissolved trace metals in the water column of the Bombay Harbour though varied appreciably, did not reveal major systematic fluctuations and there was no evidence of any increase in the concentrations over the years (Zingde et al, 1989; Patel et al, 1985). In Mahim estuary the concentrations of dissolved trace metals were not only governed by the solubilities of their hydroxides and formation of metal complexes, but also by the solubility of respective metal sulphide under prevailing anoxic conditions. It was therefore, not surprising to observe low levels (2-4 μg l^{-1}) of Cu in Mahim estuary though higher concentrations were observed in nearby coastal water (Sabnis, 1984; Zingde, 1985). Similarly the decrease of Zn was from 103 $\mu g\ l^{-1}$ in Mahim Bay to as low as 6 $\mu g\ l^{-1}$ in the interior of Mahim estuary while levels of Mn increased from 10 $\mu g\ l^{-1}$ in the bay to 150 $\mu g\ l^{-1}$ in the estuary (Sabnis, 1984).

Trace metals in the suspended matter revealed only marginal enrichment of Ni, Cu and Zn in Thana Creek (Zingde et al, 1989) and high enrichment in Mahim Creek (Sabnis, 1984) while the levels in the suspended load of coastal waters were more or less comparable to those observed for other nearshore environments. The variation of metal concentration with salinity revealed considerable scatter and no systematic trend was observed (Zingde et al, 1989).

Trace metals in sediment cores from the coastal waters of Bombay did not reveal any significant enrichment in surface layers (Srinivasan and Mahajan, 1987) while the sediments from Mahim estuary showed considerable enrichment. Thus, the surface concentration of Cu in sediment from Mahim Creek was as high as 800 ppm (dry wt) and that of Zn exceeded 2500 ppm (dry wt) as against 105 and 138 ppm (dry wt) respectively observed in the offshore (Sabnis, 1984). Likewise organic C was as high as 15 % and P exceeded 2000 ppm (dry wt) indicating the severity of sediment contamination in Mahim estuary. It has been estimated that the top 20 cm sediment in Mahim estuary contained 1.3 t of Ni, 37 t of Cu, 106 t of Zn and 4.6 t of Pb in excess over the expected background (Sabnis, 1984). In the Bay the total Hg concentration in the surface sediments varied from 0.17 to 8.21 ppm (dry wt) with definite enrichment in Thana Creek suggesting mercury inputs in the upper reaches. The mercury enriched layer in the sediment cores was about 10-25 cm in the creek and 0-8 cm in the harbour area. An excess of 14 t of Hg over the natural background was estimated to be trapped in these sediments (Zingde and Desai, 1981). Concentrations of Cd in the suspended particles and the sediments were in the range of 0.5 to 6.1 ppm (dry wt) and was largely controlled by the physico-chemical determinants of the environment namely pH, organic matter, cation exchange capacity and industrial inputs (Zingde, 1989). The variation of Zn, Cd and Pb with depth in sediment cores was irregular, perhaps because of the reworking of sediments (Pillai et al, 1987).

The wastewater from Bhabha Atomic Research Centre was the major source of low level radioactive waste to the bay. The main-nuclides present in the waste were 137 Cs, 144 Ce, 106 Ru, 95 Zr/Nb, 90 Sr and its daughter products and traces of 239 Pu. The levels of various radionuclides in water, sediment and benthic organisms were found to be within permissible limits (Patel and Patel, 1982).

Macrobenthic fauna of the Bay indicated three different zones of production. The creek head an area of about 4 km^2 had a rich macrobenthic biomass while a zone of moderate benthic fauna was observed in the Bombay Harbour with the lowest production confined to the middle section of Thana Creek attributed to pollution loads in the vicinity (Govindan et al, 1976). The mangroves of Mahim estuary were totally devoid of marine animals. The bay and the estuary which were a source of rich oyster fishery about 40 years back have been completely devoid of living oysters (Govindan and Desai, 1980-1981). Studies on the distribution of copepods revealed that the polluted regions of Mahim and Thana Creeks had the dominance of **Paracalanus Oithana** and **Acartia** while the generic diversity of copepods was greater in unpolluted areas (Gajbhiye et al, 1981). Likewise, greater diversity of fish larvae off Versova and Bombay Harbour as compared to Mahim and Thana indicated deteriorating environmental conditions around Mahim and Thana

Creek (Gajbhiye et al, 1982). Although chlorophyll a was high in inshore waters, the polluted regions were marked by high phaeophytin suggesting high rate of mortality of phytoplankton. Also, species diversity was high at unpolluted regions compared to cleaner areas (Nair et al, 1981; Gajbhiye et al, 1983).

The levels of trace metals in various species of fishes however were within the permissible limits for human consumption except in isolated cases. Thus, mercury in crab muscle increased from 0.3-1.3 ppm offshore to 7.3 ppm in Thana Creek on wet weight basis (UNEP, 1985).

Studies undertaken in the coastal waters of Thal, a place about 30 km south of Bombay however did not reveal any influence of pollution from Bombay city on the water quality, sediment quality as well as biological characteristics (Zingde et al, 1987; Varshney et al, 1983; Gajbhiye et al, 1983). These studies were undertaken prior to the commissioning of a large fertilizer complex at Thal. Information on present status of the environment is however not available.

(b) Bombay High

Commercial production of crude oil from the offshore wells of Bombay High commenced from 1976. Since then the rate of production has increased from 0.41 to 24.4×10^6 t yr^{-1} (Indian Express, 8

November 1993). Although sporadic reports have been appearing in the local papers in recent years about degradation of the environmental quality due to the oil well operations, no systematic study has been published.

.2 Hydrocarbons in marine environment

Hydrocarbons though minor are ubiquitous compounds in aquatic environments. Their primary natural sources are biosynthesis and organisms. Because of man's increasing dependence on petroleum and its products, the inland waterways, coastal areas and ocean itself are vulnerable to oil pollution. The global marine transport of oil was 1.5×10^{9} t yr^{-1} and the oil spilled at sea has been variously estimated as 3.2×10^{6} t yr^{-1}, which is equivalent to about 0.21 % of the total oil transport of the world across the seas (ITOPF, 1987). This, coupled with the increase in offshore oil exploration and exploitation in several countries of the region made the Northern Indian Ocean susceptible to oil pollution. Although only a few tanker disasters have so far occurred along this route, the effects of oil spills are seen on the beaches of every country of the region in the form of deposits of tar like residues, the frequency and intensity of which depend on the current patterns along the coasts.

This section mainly deals with origin of hydrocarbons in marine environment, the methods of their estimation and the studies undertaken in the seas around India.

2.2.1 Origin of hydrocarbons in marine environment

Hydrocarbons in the marine environment are of biogenic as well as petrogenic origin. They enter marine waters via natural, biological and geochemical processes and through anthropogenic inputs.

(a) Biogenic

Marine organisms biosynthesize hydrocarbons which may be released during metabolism or on death and decomposition of the organism (Farrington and Meyers, 1975). Terrestrial plants also release hydrocarbons to the atmosphere which are ultimately deposited on the land and the sea (Farrington and Meyers, 1975).

(b) Petrogenic

Sometimes natural oil seeps through submarine and coastal sediments releasing petroleum hydrocarbons into the seawater. Transport of hydrocarbons from the sediments during weathering also contributes to the natural inputs although probably small relative to other sources (National Academy of Sciences, 1975). Some hydrocarbons chemically formed during forest fires are eventually delivered to the marine environment (Farrington and Meyers, 1975). There are also chemical reactions occurring during the diagenesis of organic matter in sediment which yield hydrocarbons (Farrington and Meyers, 1975).

(c) Anthropogenic

The anthropogenic inputs of PHC to the marine environment through accidental and intentional discharges is estimated between 1 and 10 million tonnes annually (National Academy of Sciences 1973; 1974). The coastal zone receives much of the oil discharges resulting from tanker accidents, shoreline storage areas, offshore wells, spills associated with tankers, terminal points, ballast water by tankers, industrial and domestic wastewater.

2.2.2 Fate of crude oil in marine environment

A variety of physicochemical processes occur simultaneously immediately after oil is spilled on seawater. Spreading on the surface, followed by evaporation which is highly temperature dependent, appears to be dominant during initial stages. Degree of turbulence also influences the evaporation rate of the spilled oil. The fraction removed by evaporation depends on the composition of crude. As much as 80 % of light oil and as little as 5 % of heavy fuel oil evaporate within few days. Emulsion of water in oil and oil in water may result depending on water turbulence and the type of spilled oil. Dissolution of some components in seawater also occurs continuously.

Photochemical oxidation of thin layers of oil on the ocean surface also occurs, the exact effects and rates of photochemical processes are however not fully understood.

The bacterial degradation of spilled oil may begin shortly after a spill occurs. However, this effect may be significant only after a couple of weeks (Blumer and Sass, 1972; Scarrutt and Zitko, 1972). The extent of bacterial degradation of oil depends on temperature, type of bacteria, levels of nutrients and the composition of oil. Thus, alkane are attacked more readily than aromatic and napthanic compounds (Blumer, 1973; Walker et al, 1973).

Evaporation, dissolution and biological degradation of low boiling components of the spilled oil make residues often denser enough to sink and be deposited on the bed sediment. Sometimes the spilled oil gets adsorbed on the suspended particulate matter and ultimately carried to the sediment. In shallow areas, oil deposited on the bottom is frequently washed ashore to form hard tarry masses. In addition, the oil deposited on the bottom can penetrate deeper into the sediment, be resuspended in the overlying water or be degraded. Penetration into the sediment is believed to be due to various mixing processes including bioturbation. Coarser bottom allows greater penetration than the fine unconsolidated sediments. The highest concentrations of oil are generally associated with silt possibly because of their greater area for adsorption for oil. However, the coarser sediments also have high degradation rates relative to fine sediments, possibly because of greater aeration and nutrient flow into the sediment (Gundlach and Hayes, 1978). The main factor distributing oil in sediment is the rate of biodegradation. Most rapid degradation occurs at the water sediment interface but decreases below the surface and oil trapped a few centimeters below the sediment can remain unchanged for years specially if the sediment is anaerobic (Hughes and MacKenzie, 1975; Gardner et al, 1979).

After oil is deposited in the sediment there is a substantial increase in the hydrocarbon degrading microbial population. Straight chain alkanes are rapidly broken down while the degradation of branched chain alkanes, cycloalkanes and aromatic hydrocarbons is much slower (Blumer, 1973; Walker et al, 1973). High boiling components are very resistant to the microbial degradation (Walker et al, 1976). Different crudes show different rates of degradation because of variations in the relative amounts of different oil components.

2.2.3 Analysis of PHC in marine samples

The analytical procedures for the estimation of PHC in marine samples involve four basic steps:

i) Collection and preservation of samples.
ii) Extraction of organic matter.
iii) Separation of PHC by chromatography.
iv) Quantitative determination of PHC.

The appropriate analytical procedure should however be selected on the basis of the nature and type of the sample, the nature and type of hydrocarbon component to be studied, the equipments available and the type of information required (Farrington and Meyers, 1975; Farrington and Tripp, 1975; Farrington and Quinn, 1971; Farrington et al, 1976).

The sampling programme for the determination of PHC must be designed not only to obtain representative samples but also to avoid contaminants that may be introduced during collection, preservation and storage. However, as some contamination is often possible, the analytical method used must provide for the establishment of background values. These so called blank values represent the PHC levels contributed by the analytical procedure over and above that in the sample.

(a) PHC in Seawater

The seawater sample can be collected with a suitable precleaned glass or a grease free metallic sampler using conventional hydrographic gear strictly without any lubrication. The sample is transferred in a glass bottle and if not extracted immediately is stored into a refrigerator after adding a suitable preservative such as chloroform or carbon tetrachloride (UNESCO, 1984).

Most methods of extraction of water samples are based on liquid-liquid extraction of lipids by suitable organic solvents (Blumer, 1970; Farrington et al, 1976). Various solvents such as methylene chloride, chloroform, carbon tetrachloride, hexane, heptane, petroleum ether and ethyl acetate have been tested for extraction. The best recovery (100 %) with chlorinated solvents has been reported using carbon tetrachloride or methylene chloride (Morito and Albright, 1965; Morinovo and Lebed, 1972).

The total lipid extract is then subjected to PHC separation on absorbent column or thin layer chromatography. Silicagel (partially deactivated with 5 % water) with short alumina (deactivated) bed on top of the silicagel is commonly used for column chromatography. Separate fractions containing saturated, unsaturated and aromatic hydrocarbons and more polar compounds can be obtained by sequential elution with an appropriate solvent (Meyers et al, 1979).

Various analytical techniques have been used for the estimation of PHC. Gravimetric method though simple requiring minimum equipment can only be used for higher concentrations. Ultraviolet absorption technique has been frequently used though the method provides no information on saturated hydrocarbons. Because of low concentration generally encountered in oceanic waters the method is not of much use for determining PHC in water samples. Hence, fluorescence spectrophotometric technique is widely used because of its high sensitivity and specificity. This method is recommended by UNESCO. (UNESCO, 1984). Although infrared spectrometry has also been used, the method is not practical because of its low sensitivity. Gas chromatography has been used for identification and quantification of individual components and was sensitive at ppb levels with flame ionisation detector. The combination of gas chromatography and mass spectrometry represents a powerful analytical technique with advantages of speed and sensitivity, elimination of contamination during isolation and its adaptability to routine analysis (Farrington et al, 1976) . The instrumentation however is very expensive and requires trained technicians.

(b) PHC in sediments

Marine sediments can be obtained using a suitable grab or a corer. It is advisable to use a metal liner instead of an acrylic liner for the corer to avoid contamination. The sediment can be stored in a deep-freeze or under inert atmosphere after freeze drying.

The commonly used methods for the extraction of hydrocarbons from sediment are:

i) extraction by an appropriate solvent in an ultrasonic bath,

ii) soxhlet extraction with hexane or benzene or benzene-methanol mixture over a longer period (24 h),

iii) direct alkaline hydrolysis by refluxing the sediment with a mixture of benzene and methanolic KOH and,

iv) dissolution of rock matrix with concentrated HCl and HF followed by extraction with a suitable solvent.

The recovery studies revealed that the last three methods had comparable efficiencies (Farrington and Tripp, 1975; Rohrback and Reed, 1976).

The extracted total lipids after suitable treatment are subjected to hydrocarbon separation on a chromatographic column similar to the one described above for water samples. The techniques of estimation are also same as mentioned for water samples.

2.2.4 PHC in seas around India

The beaches along the Indian west coast are susceptible to the deposition of tar like residues during monsoon due to the high turbulence and strong onshore components of currents. Intensity of deposition and sizes of tar balls vary a great deal from location to location. About 750 to 1000 t of crude oil residues were reported depositing annually along the west coast of India (Dhargalkar et al, 1977).

PHC in upper 10 m of water column of the coastal Arabian Sea was reported to vary between 0.12 and 2.44 mg l^{-1} with an average of 1.2 mg l^{-1} with higher concentrations in the region of 15^{o} N. Recent studies however revealed concentrations in the range 0.6 to 26.5 μg l^{-1} in the northern Indian Ocean with markedly higher values along the oil tanker route. It was reported that the tanker route in the Bay of Bengal was far less contaminated as compared to many oil tanker routes in similar geographical areas (Sen Gupta et al, 1980). The concentrations of PHC around Andaman and Nicobar Islands were in the range 28 to 83 μg l^{-1} (Topgi et al, 1981). Apart from a report on the distribution of PHC in the coastal waters (22-43 μg l^{-1}) of Goa (Fondekar et al, 1980) and along the West Coast of India (7.5-87.7 μg l^{-1}) (Kadam and Bhangale, 1992) not much information was available on the levels in the nearshore waters of India.

Very little information was available on the levels of PHC in sediments and biota along the Indian coast except for levels in plankton (19.5-83.3 μg g^{-1} dry wt) and sediment (4.8-9.4 μg g^{-1} dry wt) from the coastal waters of Goa (Fondekar et al, 1980). Levels of petroleum hydrocarbon in sediment along the central and northern west coast of India varied in the range of 0.01 to 0.3 μg g^{-1} (wet wt. crysene equivalent) (Anirudh Ram and Kadam, 1991a, 1991b).

CHAPTER 3

MATERIALS AND METHODS

Area of study and sampling locations are given in Figures 3.1 and 3.2. Station positions in the Bay where the prominent land objects were available were fixed with a sextant while Tracer Satellite Navigator and Automatic Omega Navigation System were used for position fixing during R.V. Gaveshani cruise number 115 covering stations G 2569 to 2596, during January 1982.

3.1 Collection and analyses of water

3.1.1 Collection

All plastic Niskin sampler with a closing mechanism at a desired depth was used for collecting subsurface water samples. Sampling at the surface at station 17 (Figure 3.1) was done using a clean polyethylene bucket. Water samples from stations 17 and those of the cruise 115 were analysed for water quality.

3.1.2 Analysis

(a) Salinity and chloride content:

Chlorinity was determined by the argentometric titration method using multi-dosimat E415 (20 ml). Suitable volume of the sample was

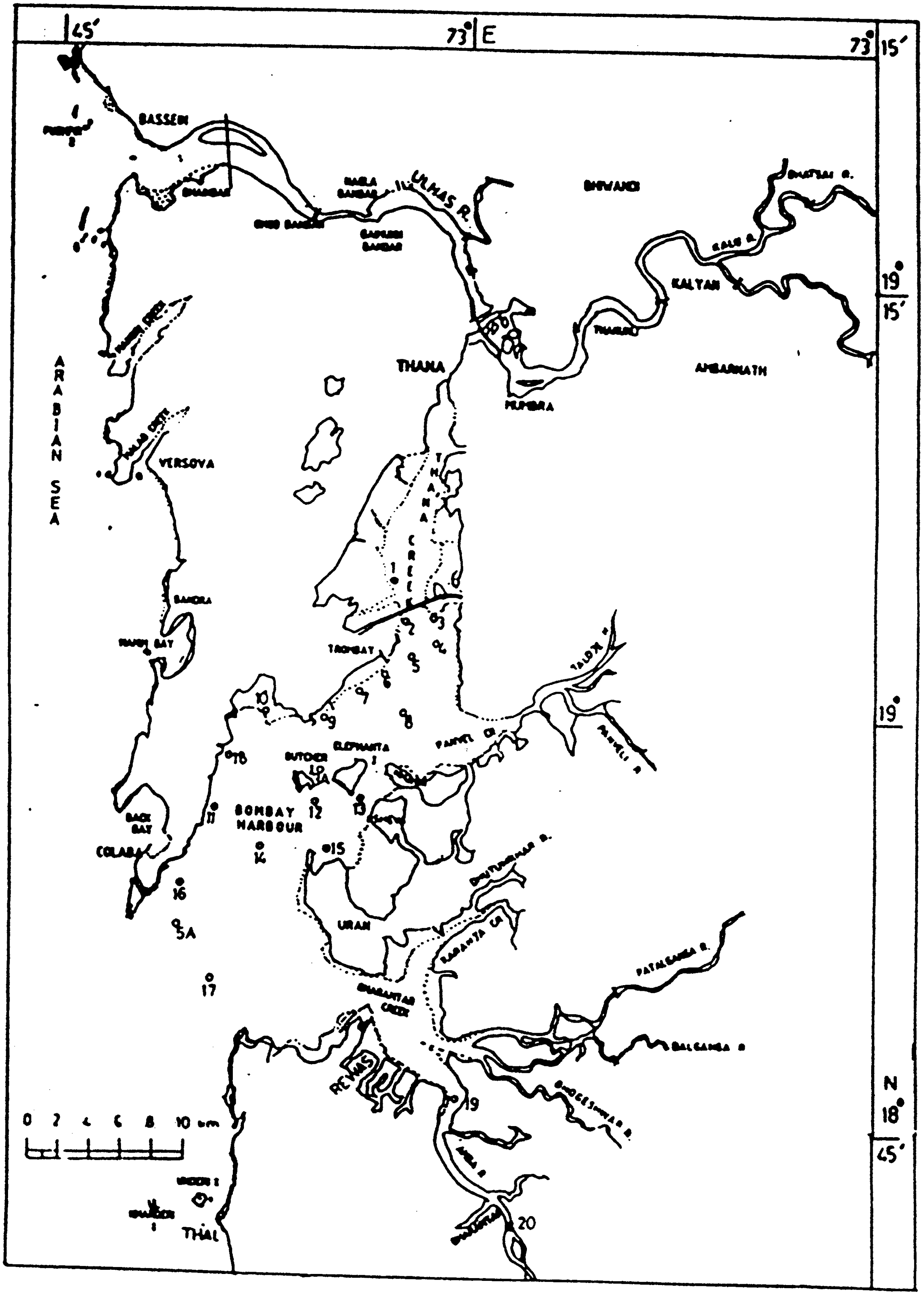

Fig. 3.1 Locations of sampling in Thana creek-Bombay Harbour and Dharmtar creek.

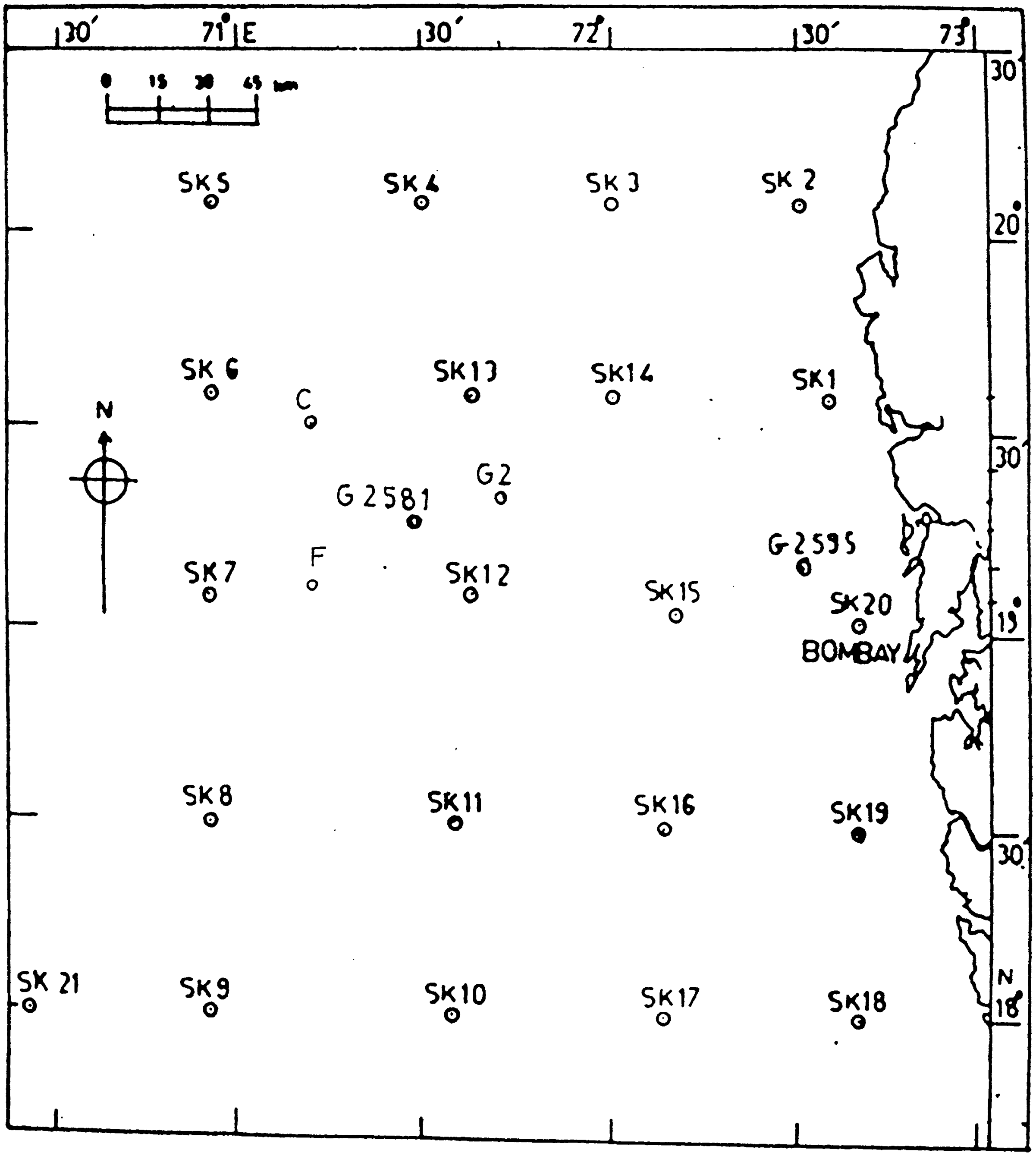

Fig. 3.2 : Location of sampling stations off Bombay.

titrated against silver nitrate (25 g 1-1) with potassium chromate as an indicator. Salinity was calculated from chlorinity from the relation :

S (ppt) = 1.80655 x Cl (ppt) (Grasshoff, 1983 a)

(b) pH:

pH was measured on a battery operated Philips pH meter. The instrument was calibrated with standard buffers just before use.

(c) Dissolved oxygen:

DO was determined by Winkler method. The sample was drawn in a DO bottle by taking care that no turbulence was generated. Reagents A, ($MnCl_2 . 5H_2O$) and B, (NaOH + KI) were quickly added separately. The bottle was immediately stoppered and shaken vigorously. In the laboratory the precipitated hydroxides were dissolved by adding HCl (50%) and the released iodine was titrated against 0.02 N sodium thiosulphate using starch as an indicator (Grasshoff, 1983 b).

(d) Nitrite:

Nitrite in the sample was allowed to react with sulphanilamide in acid solution. The resulting diazo compound was reacted with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo-dye. The light absorption was measured at 543 nm on Spectronic 710 (Bausch and Lomb) spectrophotometer (Grasshoff, 1983 c).

(e) Nitrate:

Nitrate was determined as nitrite as above after its reduction by passing through a column packed with amalgamated cadmium (Grasshoff, 1983 d).

(f) Ammonia:

Ammonium compounds in water give a blue color of indophenol when reacted with phenol in presence of hypochlorite. The absorbance was measured at 630 nm (Koroleff, 1983 a).

(g) Reactive phosphate:

Acidified molybdate reagent was added to the sample to yield a phosphomolybdate complex which was then reduced with ascorbic acid to a highly colored blue compound which strongly absorbs at 882 nm (Koroleff, 1983 b).

3.2 Collection and analysis of sediment

3.2.1 Collection

Surface sediments were collected from stations 1 to 16 (Thana Creek - Bombay Harbour) during March 1983 using a Van-Veen grab of 0.04 m^2 area. The subsample, to a depth of about 0.5 cm was removed from the grab with a solvent rinsed steel spatulla, wrapped carefully in aluminium foil and stored in solvent rinsed glass jars in a deep-freeze (-20^{o}C). Sediment cores upto a depth

100 cm were obtained from stations 1, 8, 18, 19, 20 and G 2595 with a 6 cm diameter piston corer or by hand pressing a core tube into the sediment. Cores were sectioned in the laboratory at every 2 cm interval by vertical extrusion procedure. The sections were individually wrapped in aluminium foil and stored in glass jars in a deep-freeze (-20°C) until analyses. For analysis the required sample was removed from the deep-freeze and thawed at room temperature. A portion of the sediment was dried in an oven at 100 ± 1°C for 24 h for obtaining the moisture content and for further analysis for total organic carbon.

3.2.2 Analysis

(a) Total organic carbon (TOC):

A carefully weighed amount of the powdered sample was placed in a 500 ml conical flask. Exactly 10 ml of 1 N potassium dichromate was added and the contents mixed carefully by swirling followed by addition of conc. H_2SO_4 (20 ml). The mixture was allowed to react for 20 to 30 min and diluted to 200 ml with distilled water followed by addition of conc. H_3PO_4 (10 ml), sodium fluoride (0.2 g) and ferroin indicator (1 ml). The contents in the flask were back titrated with a solution of 0.4 N ferrous ammonium sulphate to a brilliant green color end point (Walkley and Black, 1934).

(b) Lipid extraction:

(i) Alkaline digestion:

The wet sediment (50 g) was saponified by refluxing for 2 h with saponification-extraction reagent in the ratio 1:7. The saponification-extraction reagent was prepared by dissolving KOH (0.45 g) in distilled water (15 ml) and diluting to 350 ml with methanol-benzene mixture in 2:1 ratio (Meyers et al, 1979).

(ii) Separation of hydrocarbons and fatty acids:

After cooling, the contents of the flask were filtered through a Whatman 541 filter paper held in a Buchner funnel and washed three times with benzene-methanol (1:1) mixture. The filtrate and washings were mixed and transferred to a separatory funnel. A volume of distilled water equal to the benzene used in saponification extraction was added to partition the mixture into two phases. The organic phase contained nonpolar lipids and the aqueous methanol phase (pH > 10) contained polar lipids (Meyers et al, 1979).

The aqueous methanol phase was re-extracted twice with petroleum ether (bp 35.8-56.5^{o}C). These extracts (petroleum ether) were combined with the initial organic phase (benzene), dried over anhydrous Na_2SO_4 and evaporated to dryness at 30^{o}C on a rotary evaporator under reduced pressure to obtain a brownish residue hereafter termed as "B".

The aqueous methanol phase having pH > 10 was acidified to pH 2 with conc HCl and extracted 3 times with 50 ml portions of petroleum ether. The combined extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness.

(c) **Quantitative estimation:**

(i) **Gravimetry:**

The organic residue (B) was weighed on a Sartorius (Model 2405) microbalance with an accuracy of ± 1 µg. This gave the total amount of nonvolatile extractable nonpolar material in the sample.

(ii) Spectrofluorometry:

The residue (B) was dissolved in spectroscopic grade hexane and analysed with respect to Bombay High crude as a standard, on a Perkin Elmer (LS-3) Spectrofluorometer using excitation and emission wave lengths of 310, 360 nm respectively.

(d) **Gas chromatography:**

The residue (B) was partitioned into three fractions on column chromatography. The column was prepared by wet packing of 2 g of aluminum oxide (neutral) over 8 g of silica gel in hexane. Both the adsorbants were dried at 120°C for 12 h before use. The residue (B) was dissolved in hexane (2 ml) and loaded on top of the alumina. The column was eluted with 50 ml portions of hexane, benzene and methanol serially. The hexane fraction (B1) contained alkanes, cycloalkanes and monounsaturated alkanes.The benzene fraction (B2) contained polyunsaturated alkanes, aromatic hydrocarbons and ketones and methanol fraction (B3) contained alcohols and possibly sterols (Meyers et al, 1979). These fractions were separately evaporated to dryness at 30°C on a rotary evaporator.

The hexane fraction (B1) dissolved in 1 ml of spectragrade hexane was injected (1-2 µl) in a Perkin Elmer (Sigma-2000) gas chromatograph equipped with a flame ionisation detector (FID). The chromatographic conditions used were as follow

Carrier gas : 1 ml min^{-1}of IOLAR-2 nitrogen
Vent flow : 90 ml min^{-1}
Split ratio : 1:70
Column : 25 m x 0.25 mm inner diameter; liquid phase bonded methyl silicone.
Injector : 350°C temperature

Detector temperature : 350°C
Temperature programming
Initial temperature : 100°C

Initial time : 5 min
Programming rate : $10^{o}C\ min^{-1}$ from
$100^{o}C$ to $325^{o}C$
Final time : 10 min

The carbon numbers were obtained by using n-octadecane ($C_{18}H_{38}$) as an internal standard and also by comparing the gas chromatographic retention times by injecting known standards from C-9 to C-20, C-22 and C-24 under identical conditions as above.

3.3 Oil spill identification

The oil spill observed on 19 August 1982 on the coast of Napean Sea (South Bombay) was sampled and studied as given below inorder to identify the probable source of the spill.

3.3.1 Collection

The oily material deposited on the shore and the intertidal region was obtained by skimming and preserved in precleaned glass bottle in a refrigerator.

Samples of standard crudes were provided by the Bharat Petroleum Corporation Ltd, Bombay.

3.3.2 Cleaning of sample

The sample (10 g) was repeatedly extracted with dichloromethane (200 ml) to dissolve the oil and to facilitate separation from water and debris. The organic layer was dried over anhydrous Na_2SO_4 and filtered through a cotton plug. The filtrate was evaporated at 30°C under reduced pressure to obtain a brown semisolid (bp > 135°C; yield 6.4 g).

3.3.3 Wax content:

Purified sample (1 g) after dissolving in hot methylene chloride (10 ml) was kept in a deep-freeze (-20°C) for 1 h. The precipitated wax was separated by filtration through a cotton filter (Brunnock et al, 1968).

3.3.4 Asphalt content:

Purified sample (1 g) after dissolving in petroleum ether (100 ml) was treated with conc H_2SO_4 (4 ml) and kept aside for 3 h. The residue remaining after separation of the upper ether layer was taken as asphalt content (Brunnock et al, 1968).

3.3.5 Iron content:

Around 15 g of purified sample weighed accurately was ashed in a muffle furnace at 600°C for 6 h and the white residue was dissolved in 100 ml of dilute HCl (0.1 N). The solution was used for the colorimetric determination of iron as follows (Brunnock et al, 1968).

To the solution (1 ml) hydroxylammonium chloride (10 %; 2ml), 2,4,6-tripyridyl S-triazine

(TPTZ) (0.001 M; 2ml), and sodium acetate (3 M, 2 ml) were added sequentially and diluted to 50 ml with distilled water. The absorbance of the resulting blue color was measured at 593 nm on a Spectronic 710 (Bausch and Lomb) Spectrophotometer. The concentration of iron in the sample was determined by plotting appropriate calibration curve.

3.3.6 Spectroscopy

(a) UV Fluorescence:

The sample and standard crudes were dissolved in spectroscopic grade hexane and the fluorescence scanned from 300 to 600 nm by keeping the excitation wave length constant at 280 nm on a Perkin-Elmer (LS-3) spectrofluorometer.

(b) UV absorbance:

Samples prepared as described above for fluorometric analysis, were scanned from 190 to 300 nm on a Perkin-Elmer (Lambda-5) spectrophotometer.

(c) IR absorbance:

IR spectra in the region 600 to 4000 cm^{-1} were recorded as liquid films between NaCl discs on a Perkin-Elmer (983 G) infrared spectrophotometer.

3.3.7 Gas chromatography:

Samples and standards dissolved in 1 ml of spectragrade hexane were injected (1-2 µl) in a Perkin Elmer (Sigma-2000) gas chromatograph equipped with a FID using same conditions described under section 3.2.2 (d).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Bombay Harbour-Thana Creek (Bay):

4.1.1 Study area

Bombay Harbour-Thana Creek is a semi-enclosed basin open to the Arabian Sea at its southwest approach and is also connected at its northern extremity to the Ulhas River through a narrow channel. The tidal inlets of Dharamtar, Nhava-Sheva and Panvel Creeks are tributaries to the Harbour (Figure 3.1) discharging into its eastern shore within the port limits.

Current speeds and directions within the Bay and the associated tributaries are largely due to the tidal movements and show little variation from monsoon to nonmonsoon. The maximum current speed within the harbour often exceeds 100 cm sec^{-1} and the variation from the surface to bottom (1 m above the sediment) is not significant (NIO, 1978). Lateral variations in speed are however present with the currents in the eastern area of the harbour being somewhat stronger. There is overall decrease in the current speed in Thana Creek as compared to the Harbour (MCGB, 1979).

Tidal variations in the Bay are semidiurnal with an appreciable diurnal element. The flood tidal front advances in the Bay in the northeasterly direction and ebbs towards the southwest. At the most northerly location (Thana), the average high tide lag time is 40 min and the low tide average lag time is 1 h 37 min with reference to Apollo Bunder (MCGB, 1979). It has been estimated that on an average about one third of the bay water is renewed per tidal cycle (Patel et al, 1985).

The domestic wastewater estimated around 2.6 x 10^5 m^3 day^{-1} received at treatment plants and pumping stations along the western shore of the Bay was far in excess than the capacity of treatment plants. Wastewater was therefore, often released untreated to the adjacent Bay through point discharges (MCGB, 1979). In addition Thana Creek received industrial wastewater estimated to exceed 1.8 x 10^5 m^3 day^{-1} (MCGB, 1979). The major industries were fertilizer, petrochemical, thermal power, nuclear, pharmaceutical, chemical and textile.

The pollutants released in Ulhas River could also enter the head of Thana Creek through the arm connecting the two water bodies. Such a flow was considered possible because of the difference in time of the occurrences of high and low water in

Thana Creek and Ulhas estuary (Zingde et al, 1979). It was estimated that about 35 t suspended solids and 1250, 35, 20, 10, and 3 kg of Zn, Cu, Hg, Pb and Cr respectively, were released daily into the Ulhas and Kalu-Waldhuni tributaries (Patel et al, 1985).

4.1.2 Physico-chemical parameters:

A few investigations regarding the physico-chemical status of the Bay have been reported (Zingde et al 1979 ; Zingde, ~~et al~~ and Desai, 1981; Zingde et al 1989; NIO, 1978; MCGB, 1979). Hence station 17 was monitored temporally during June, August, September and November 1984 for comparison with the literature reports to delineate changes if any in the water quality over the years. These parameters are discussed below :

(a) Temperature

The changes in water temperature around Bombay were mainly due to the seasonal fluctuations in the solar radiation and the intensity of wind. Evidently the temperature profile followed bimodal structure typical of the West coast of India with one maximum in May and another in November (Sabnis, 1984). Water temperature at station 17 varied temporally more or less in line with the air temperature with a weakly defined maximum in the afternoon. The variation from surface to bottom was often significant during June and September perhaps due to density induced vertical stratification often observed in estuarine environment (Figures 4.1 to 4.4).

(b) **pH**

pH of the surface and bottom layer was similar and varied in the range 7.5 to 8.1 throughout the period of observations. The pH of seawater is mainly controlled by $CO_2/HCO_3^-/CO_3^{-2}$ system. Other weak electrolytes such as borate, phosphate and silicate slightly augment this effect. Since maximum buffering develops at pH values close to 6.0 and 9.0 and since seawater pH is not in the region of maximum buffer capacity, small variations in pH are possible. It was evident from Figures 4.1, 4.2 and 4.4 that the pH was generally below 7.8 as against the pH of seawater (8.0-8.3) ingressing the bay (Martin, 1970). The fall in pH within the bay could be due to oxic diagnosis of organic matter released in the bay leading to decrease in pH (Friedman and Gavish 1970; Riley and Chester 1971). A systematic increase in pH from 7.8 at 0800 h to attain a maximum of 8.1 in the surface water around noon followed by a decrease in the afternoon on 11 September 1984 (Figure 4.3) could be due to high postmoon primary productivity

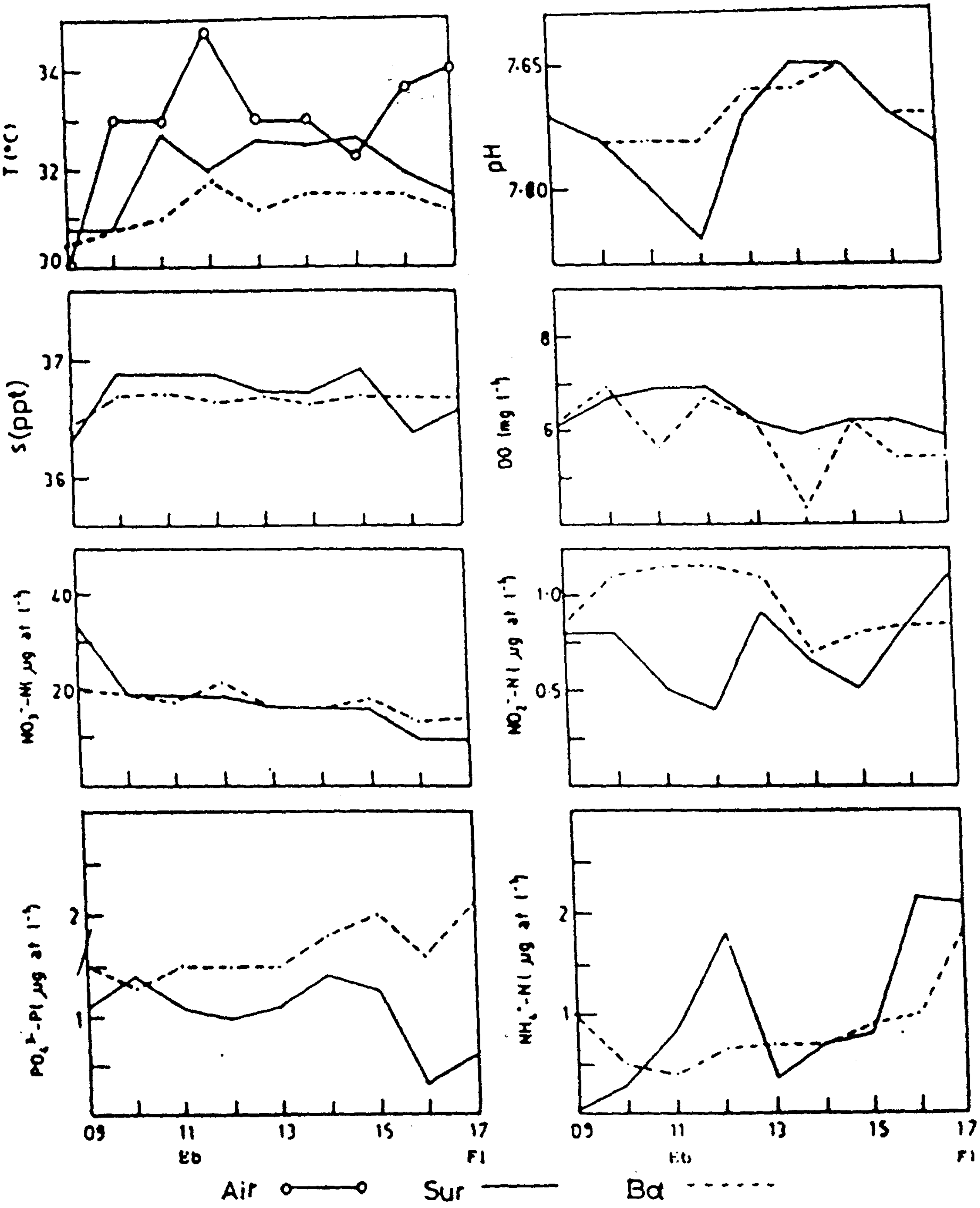

Fig. 4.1 : Variation of some physico-chemical parameters at station 17 on 7 June 1984.

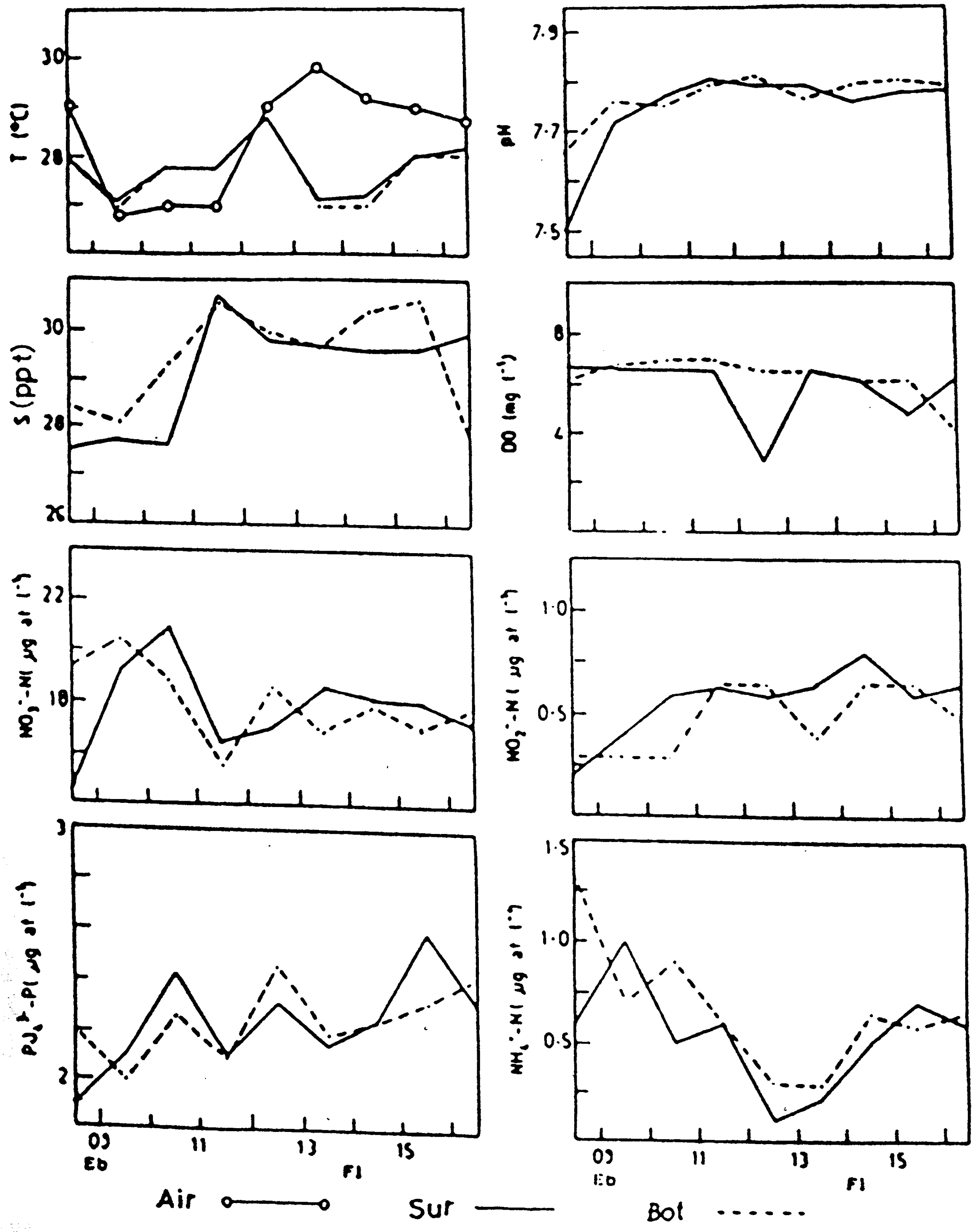

Fig. 4.2 : Variation of some physico-chemical parameters at station 17 on 30 August 1984.

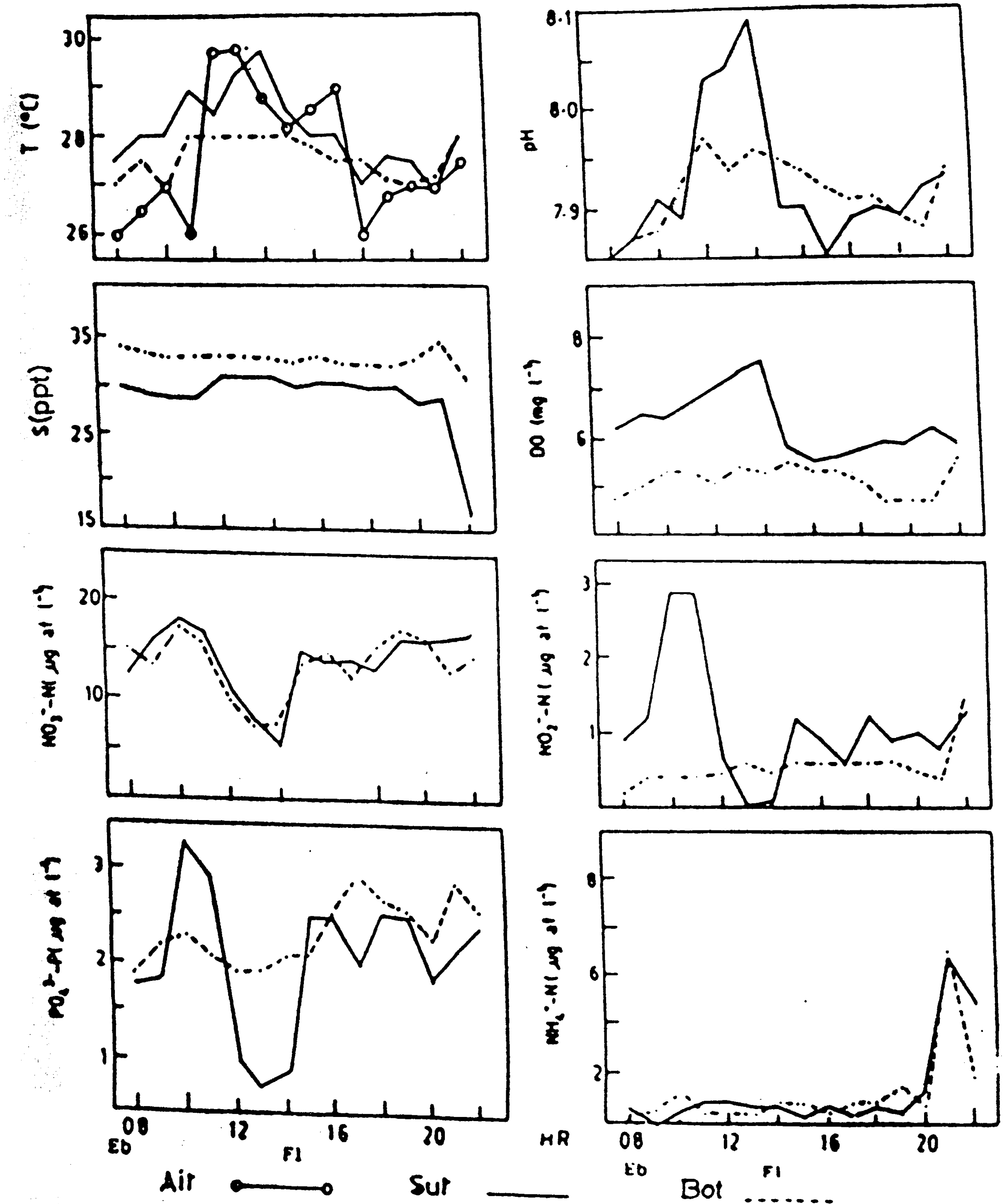

Fig. 4.3 : Variation of some physico-chemical parameters at station 17 on 11 September 1984.

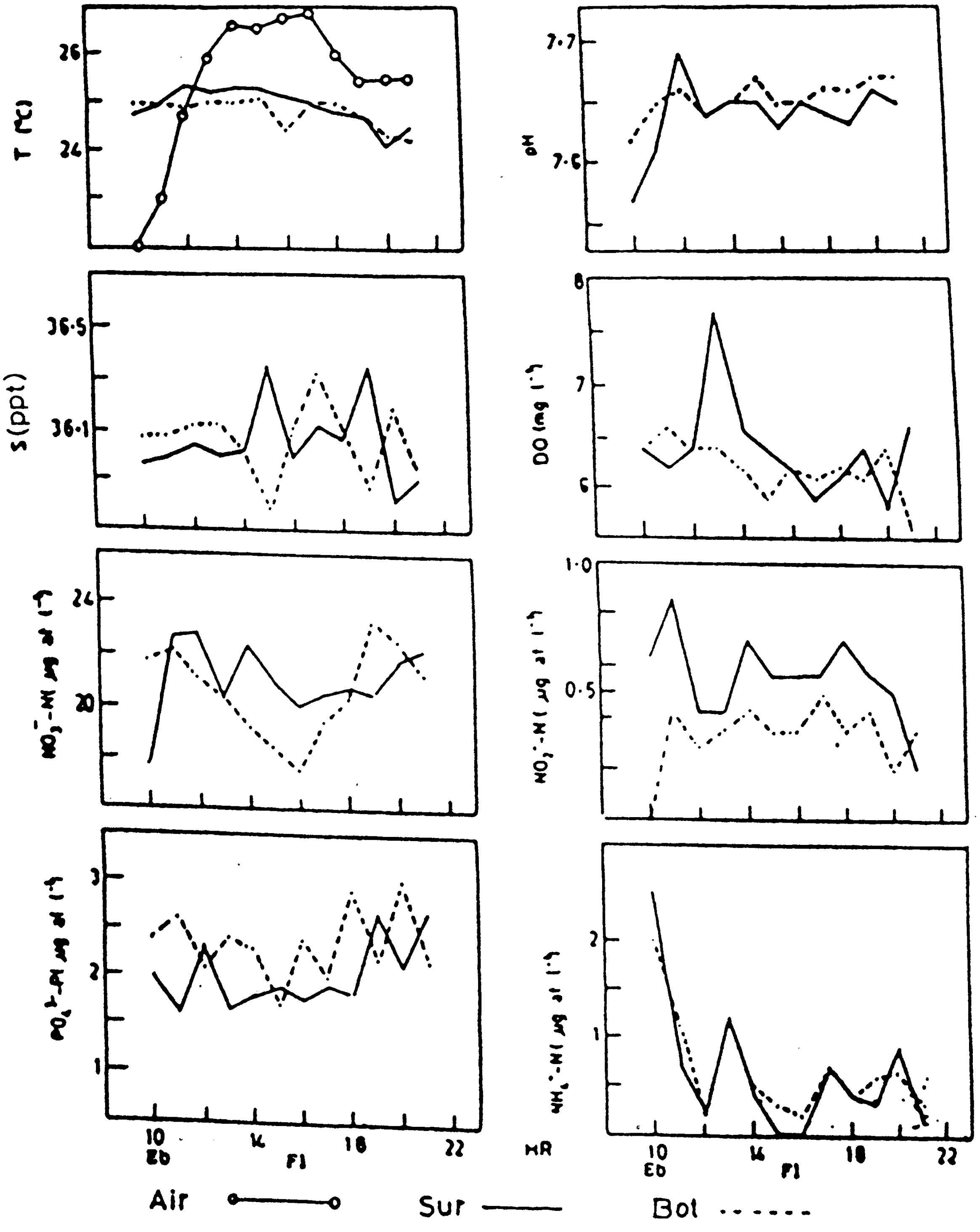

Fig. 4.4 : Variation of some physico-chemical parameters at station 17 on 28 November 1984.

(Narvekar, 1979; Zingde et al, 1981a) as these changes in pH were also followed by similar changes in DO attaining maximum around noon.

(c) **Salinity**

The salinity in the Harbour varied in the range 16.7 ppt to 37.1 ppt and compared well with the earlier results compiled in Figure 4.5. It was also evident from Figure 4.5 that the high salinity during April-May decreased considerably accompanied with the development of a vertical salinity gradient during monsoon perhaps due to the density restricted mixing of less saline surface water with subsurface water of higher salinity. Considerable salinity gradient was also evident at station 17 during August as well as September (Figures 4.2 and 4.3). This gradient decreased as the dry season progressed and the water mass was nearly homogeneous after September (Figures 4.4 and 4.5). The transport of large volume of freshwater through Dharamtar, Nhava-Sheva and Panvel Creeks to the eastern section of the harbour during monsoon resulted in some lateral gradient which was pronounced during July-September specially during low tide (Zingde et al, 1989).

The presence of cold, high saline and low DO subsurface water off Karwar (Gopinath and Joseph, 1980), Mandovi-Zuari estuaries (Sankaranarayanan

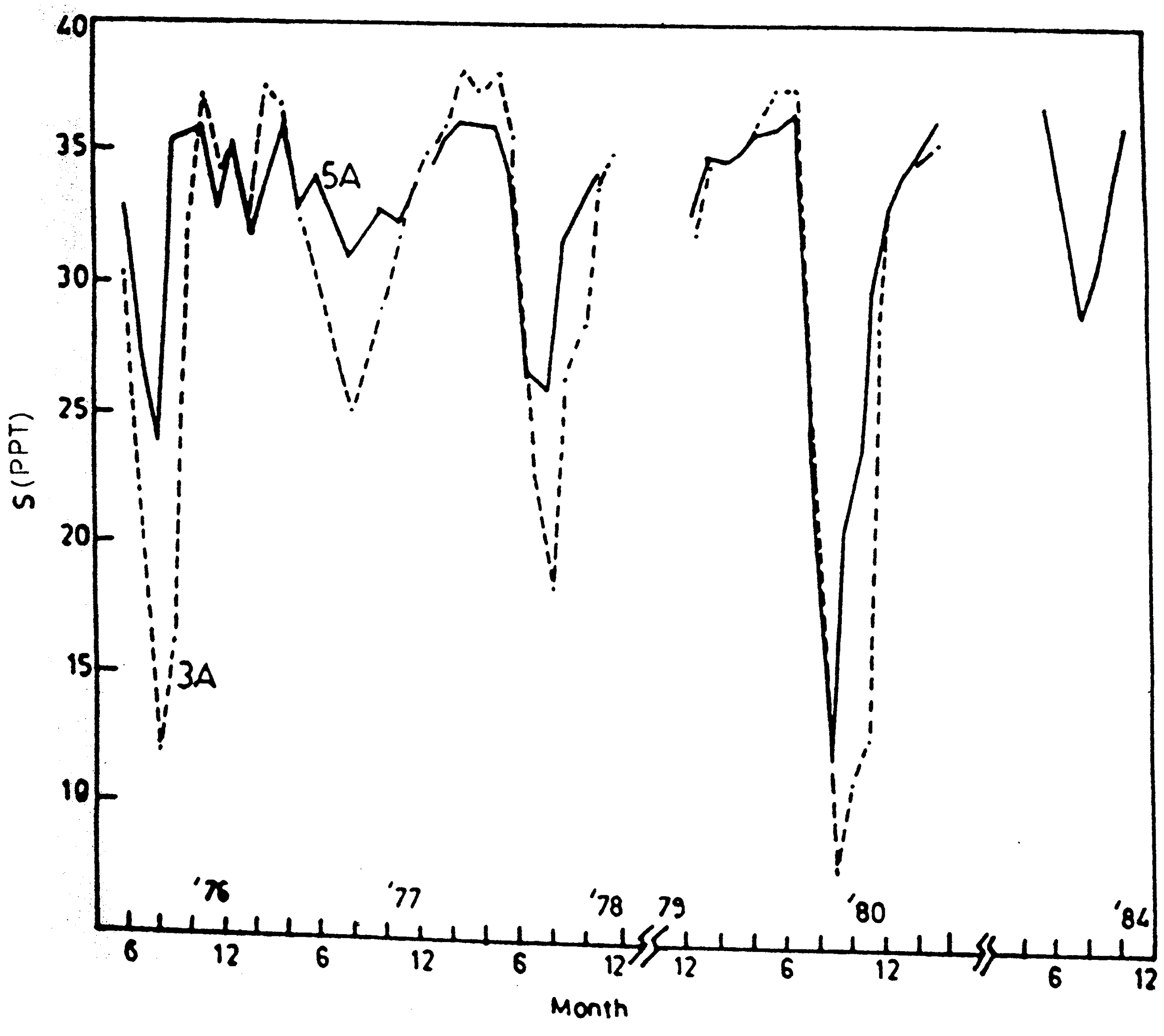

Fig. 4.5 : Variation of salinity in Bombay Harbour during 1976-84.

et al, 1978) and Cochin backwaters (Sankaranarayanan and Qasim, 1972) during monsoon was attributed to the transport of upwelled water on the shelf to the nearshore regions. The vertical salinity gradient observed during monsoon in the Harbour as discussed above did not seem to be due to the intrusion of upwelled water because of the comparable surface and bottom DO in contrast to the characteristic low DO associated with upwelled water mass (Sverdrup et al, 1942 1961). Also, the upwelled water was expected to have high PO_4^{3-}-P and high NO_3^--N (Riley and Skirrow, 1965). However, surface and bottom NO_3^--N values were more or less comparable in the Harbour. Although Figure 4.3 revealed higher PO_4^{3-}-P values in the bottom layer, this could not be attributed to the upwelled water because higher PO_4^{3-}-P in the bottom layer was also observed during June (Figure 4.1) and during November (Figure 4.4) when there was no salinity gradient. This higher PO_4^{3-}-P therefore appeared to be due to the release of PO_4^{3-}-P from the sediment to the overlying water column.

It was evident from Figure 4.5 that high salinities (36.5 ppt - 37.5 ppt) were observed in the Bay just before the commencement of monsoon. These salinities were marginally higher than those encountered in the coastal waters of Bombay (36.0

ppt - 36.5 ppt). It appears that the seawater tends to accumulate in the Bay and enhanced evaporation of this partially stagnated water mass results in higher salinities. In fact salinities as high as 38 ppt were reported in Thana Creek during May (Zingde et al 1979).

(d) Dissolved oxygen

The DO at station 17 varied in 4.3 to 7.3 mg l^{-1} range and no definite differences existed between premonsoon, monsoon and postmonsoon seasons (Figures 4.1 to 4.4) although the values were markedly higher during August perhaps because of high monsoonal turbulence and low salinity. Though temporal variation during June and August was not appreciable, in November (Figure 4.4) the surface DO of 6.4 mg l^{-1} around 0900 h increased to 7.7 mg l^{-1} at 1300 h and sharply decreased to 6.6 mg l^{-1} at 1400 h and remained more or less uniform around 6 mg l^{-1}. Vertical stratification with lower DO in the bottom layer was also observed in this month. Similar trend was also observed during September (Figure 4.3) and could be due to enhanced photosynthetic activity around noon. The water being turbid the rate of photosynthesis leading to the enhancement of DO would be higher at the surface than at the subsurface, resulting in lower DO at the bottom. It was evident from Figure 4.3 that the pH peak was also centered around 1300 h with lower values of PO_4^{3-}-P, NO_3^--N and NO_2^--N supporting this view.

DO distribution in the Bay has been studied in sufficient details earlier (NIO, 1978; MCGB, 1979; Zingde et al, 1979). It was reported that DO of around 6 mg l^{-1} during August decreased to about 4 mg l^{-1} during September and then gradually increased to attain a peak (8.5 mg l^{-1}) during February. This was followed by a gradual decrease till May. This was considered to be due to the combined effect of temperature, photosynthetic activity and biochemical oxidation of the waste entering the water (Zingde et al, 1979). The decrease of DO along the length of the Bay from Harbour mouth to Thana during May was reported (Zingde et al, 1979). The decrease in the Creek region was more pronounced in May indicating the fall of water quality as a result of enhanced stress due to higher temperature and lack of freshwater flow in the area through Ulhas River.

The average DO observed during the present study and reported for earlier years are illustrated in Figure 4.6. It was quite clear that the DO fluctuated widely and definite conclusions were not possible. However from the position of DO values of the present study it appeared that there was no marked decrease in DO

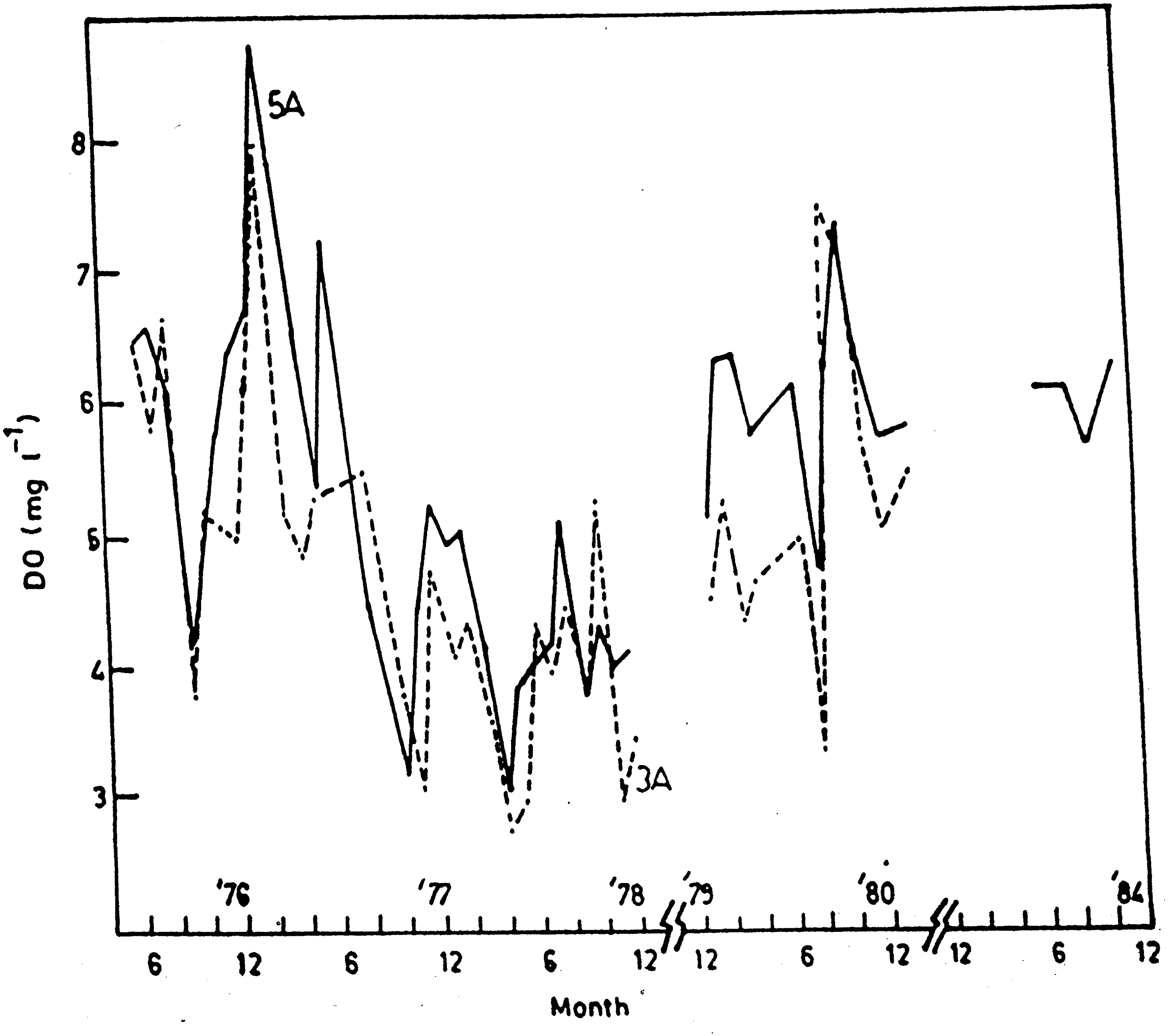

Fig. 4.6 : Variation of DO in Bombay Harbour during 1976-84.

in the Harbour over the years thereby implying that the load of organic matter which was being increasingly released was effectively assimilated.

(e) **Phosphorous and nitrogen compounds**

The important dissolved inorganic forms of nitrogen in seawater are nitrate, nitrite and ammonia. The nitrate is thermodynamically unstable under the prevailing redox conditions and ammonia is biochemically oxidised to nitrate via nitrite under oxic conditions apart from being directly consumed by phytoplankton. Hence nitrate is the predominant species of nitrogen that influences primary productivity (Grosshoff, 1983 d e). The major inorganic form of phosphorous is orthophosphate ion (PO_4^{3-}) though polymeric forms are also known to occur (Koroleff, 1983 b). Hence, concentrations of NO_3^--N were markedly higher at station 17 as compared to those of NO_2^--N and NH_4^+-N (Figures 4.1 to 4.4).

In the absence of external anthropogenic inputs of nutrients the concentrations in the Bay would be similar to those associated with the coastal waters of Bombay during dry season. The concentrations of PO_4^{3-}-P and NO_3^--N in the coastal waters (10 m depth contour) were generally below 1 μg-at l^{-1} and 3 μg-at l^{-1} respectively while those at station 17 varied in 1.5 to 3 μg-at l^{-1} and 18 to 23 μg-at l^{-1} ranges respectively during November (Figure 4.4) when there was no monsoonal freshwater discharge in the bay. Hence, the additional nutrients would be resulting from the wastewater inputs.

Domestic wastewater released in the bay contributed 12 t day^{-1} of nitrogen and 2 t day^{-1} of Phosphorous (Zingde et al, 1989). In sewage which is generally devoid of oxygen, combined nitrogen is present mainly as ammonia and organically bound nitrogen which gets oxidized in the marine environment and ultimately broken down and mineralized into available nitrate (Goldhaber and Kaplan, 1974; Richards, 1965). Although the bay received large volume of domestic waste, the levels of NH_4^+-N at Station 17 (Figures 4.1 to 4.4) suggested that the oxidation of ammonia was almost complete by the time the waste reached this location.

The surface and the bottom layers invariably contained similar levels of NO_3^--N while PO_4^{3-}-P was often higher in the bottom layer (Figures 4.1, 4.2 and 4.4) suggesting that the PO_4^{3-}-P was released from the sediments while such a release was not important in the case of NO_3^--N.

The variations of NO_3^--N and PO_4^{3-}-P in the Bay are illustrated in Figures 4.7 and 4.8. Like DO, these variations were highly irregular and

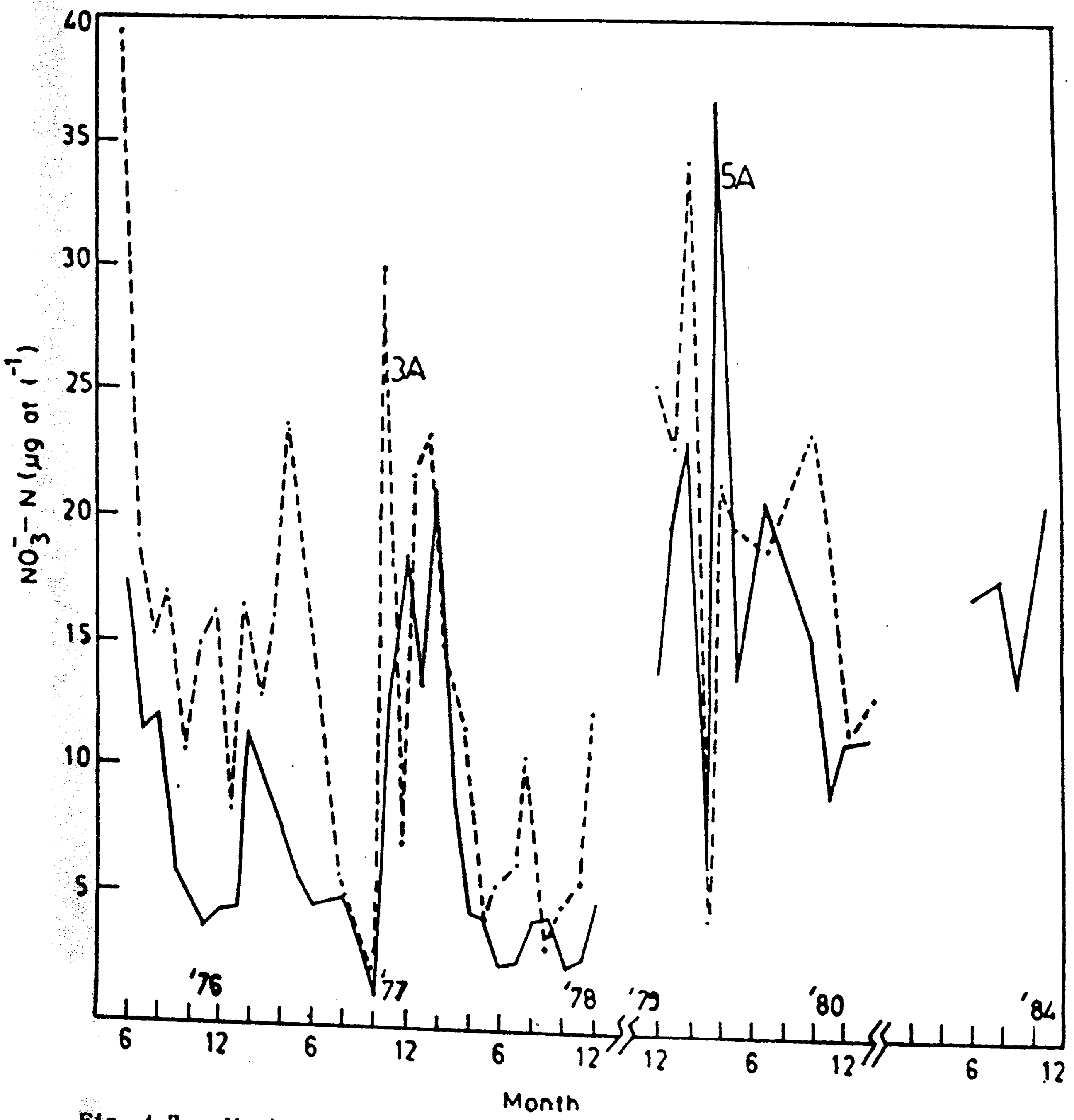

Fig. 4.7: Variation of NO_3^--N in Bombay Harbour during 1976-84

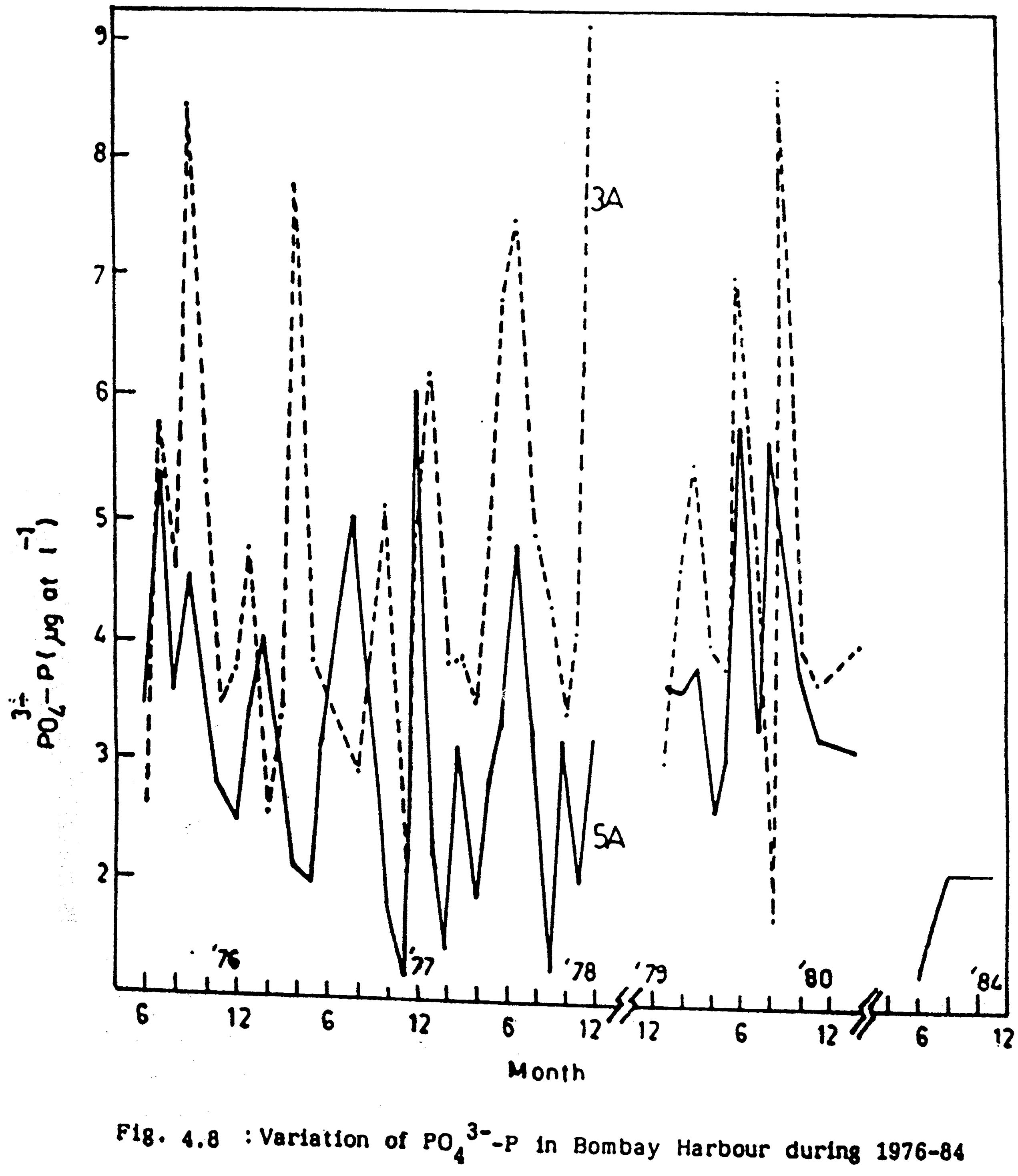

Fig. 4.8 : Variation of PO_4^{3-}-P in Bombay Harbour during 1976-84

definite trends were not evident though the overall concentrations were higher at the inner station.

NO_2^--N levels were low indicating good oxidizing conditions in the area. The diurnal variation of NO_2^--N and NH_4^+-N were also irregular (Figures 4.1 to 4.4).

It was surprising that although an abundant supply of inorganic nitrogen compounds and reactive phosphate phosphorous was available in the bay, the utilization for primary production was not optimum as revealed by consistently high NO_3^--N and PO_4^{3-}-P observed in the Bay. It was possible that some unknown micropollutants hamper the growth of phytoplankton in this region. It could also be possible that the high turbidity in the bay associated with the tidal dispersion of bed material in the water column hindered photosynthesis thus limiting primary production.

4.1.3 Petroleum hydrocarbons

The PHC entered the Bay through a variety of sources such as spillages during loading and unloading operations of crude oil, transportation and discharges from sewage treatment plants, refineries and a variety of other industries. In the marine environment PHC would be partly evaporated, dispersed in the water column, flushed out of the Bay or transported to the bed sediment via adsorption onto the particulate matter which was in abundance in the Bay. Texture analysis of the surface sediments from all the station as given in Table 4.1 indicated that the material mainly consisted of silt and clay generally exceeding 80 % except for station 4 where the silt-clay fraction was around 50 %. Such type of sediment is known to have a high adsorption capacity for oil (Meyers and Quinn, 1973; Hargrave and Philips, 1975). Hence, it was expected that a considerable fraction of the PHC would be adsorbed onto the suspended particulate matter and transferred to the bed sediment. Apart from lateral movements due to tidal currents the settled PHC would penetrate into the deeper sediment, be resuspended into the overlying water or degraded. The bay sediments have been reported to harbour rich macrofauna and meiofauna (Govindan et al, 1976) which would transfer the surficial deposits to deeper layers through bioturbation. The main factor affecting the PHC deposited in the sediment would be the rate of biodegradation converting a hydrocarbon molecule to a fatty acid as the first step (Gibson, 1968; Walker and Cooney, 1973; Kennedy et al, 1975). It is known that degradation is generally active at the sediment water interface and decreases considerably below the surface (Hughes and

Table: 4.1. Sand, silt and clay contents (%) of surface sediments in the Bay.

Station	Sand	Silt	Clay
1	3	80	17
2	5	45	50
3	20	38	42
4	30	30	20
5	5	45	45
6	5	65	30
7	5	70	25
8	2	60	30
9	5	40	55
10	20	75	5
11	5	65	30
12	2	40	55
13	5	60	30
14	0	50	50
15	20	60	20
16	2	40	45

Mackenzie, 1975; Gardner et al, 1979). Hence PHC buried a few centimeters down in the sediment could remain unmodified for years.

To ascertain the extent of PHC contamination in the Bay, surficial sediment samples obtained from locations marked in Figure 3.1 and a few sediment cores upto a depth of 100 cm from station 1, 8, 18, 19, 20 and G 2595 were analysed for extractable organic and PHC. The surficial sediments were not analysed for PHC as fluorometer was not available for these estimations.

Several extraction procedures such as alkali digestion, solvent extraction after homogenisation and soxhlet extraction have been reported in literature (UNESCO, 1982; Farrington and Meyers, 1975; Donald et al, 1978; Meyers et al, 1979). Of these, alkali digetion method (Meyers et al, 1979) was preferred because of its high recovery for hydrocarbons (90 ± 6%) and fatty acids (98 ± 6 %). The flow chart of methodology followed is shown in Figure 4.9. It is evident from Table 4.2 that the surficial sediments contained high levels of unsaponifiable residue varying in 712 to 4456 μg g^{-1} range. The (B1), (B2) and (B3) fractions represented in Table 4.2 were considered to contain aliphatic hydrocarbons, aromatic hydrocarbons and hydroxy compounds respectively (Meyers et al, 1979). Within Thana Creek, the

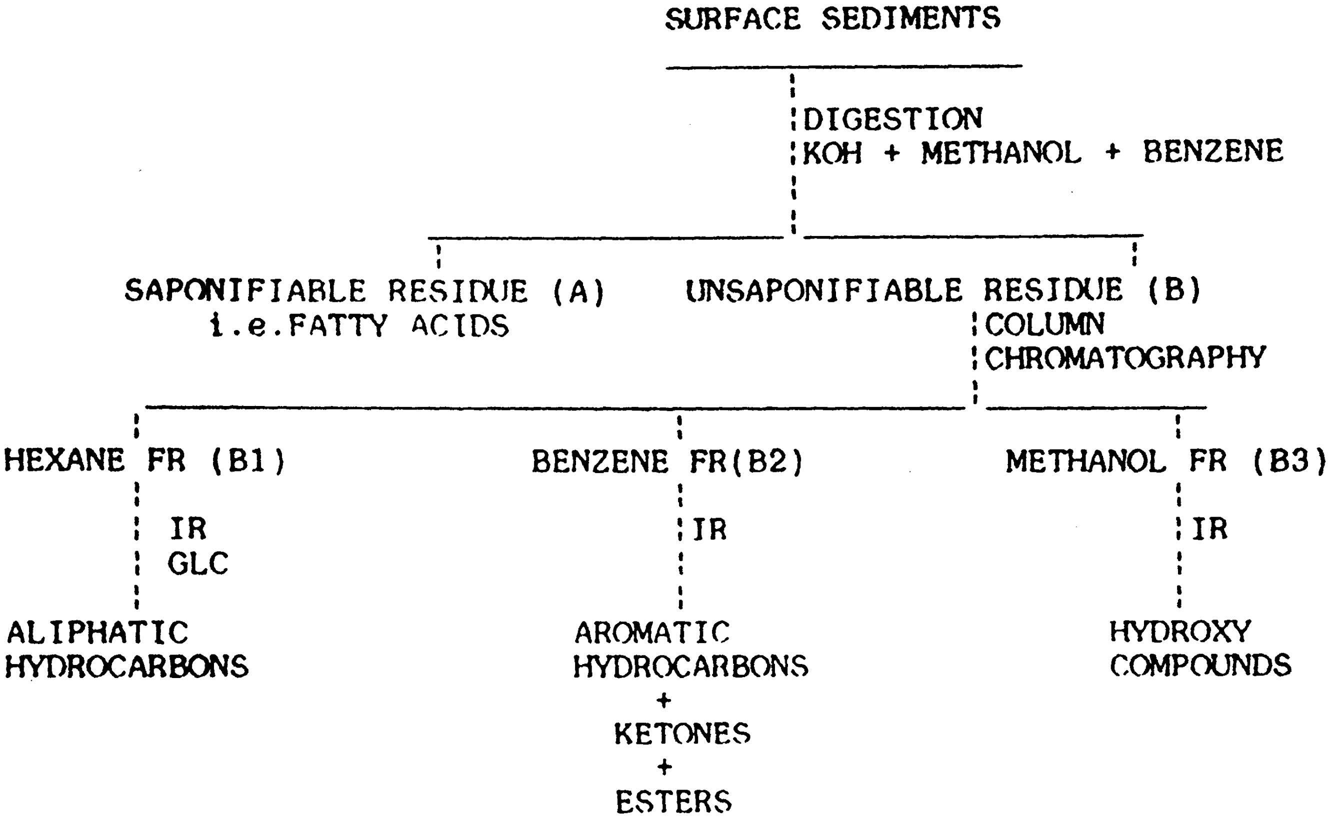

Figure: 4.9 Flow chart of methodology for estimation of PHC residue.

Table:4.2 Gravimetric concentration of non volatile organic extract in surface sediment.

Stn	Date of Collection	Org Carbon %	Water Depth m	Moisture Content %	Fatty Acid µg g^{-1} A	THC µg g^{-1} B	Hexane fraction µg g^{-1} B1	Benzene fraction µg g^{-1} B2	Methanol fraction µg g^{-1} B3
Thana Creek									
1	19.3.83	1.8	2.5	59	39	1267	244	278	408
2	18.3.83	2.2	4.0	60	224	2752	1054	549	786
3	18.3.83	1.2	4.0	44	336	980	103	112	191
4	18.3.83	1.0	3.5	51	117	712	123	127	289
5	18.3.83	1.2	3.5	57	138	745	141	163	325
6	18.3.83	2.2	4.0	56	223	3730	1258	683	704
7	19.3.83	2.5	2.5	58	129	2539	1115	491	590
8	19.3.83	2.4	8.0	58	99	1039	395	542	419
9	19.3.83	2.3	8.0	48	76	1980	904	328	560
Bombay Harbour									
10	17.3.83	2.4	3.0	55	301	4456	999	899	837
11	18.3.83	1.9	3.0	58	136	1644	525	383	398
12	17.3.83	1.6	16.0	56	101	566	94	77	101
13	17.3.83	0.8	22.0	44	113	461	106	100	150
14	18.3.83	1.7	12.0	55	248	532	113	120	176
15	18.3.83	1.3	10.0	53	41	586	113	126	268
16	17.3.83	1.5	6.5	56	121	1133	271	191	234

concentrations of B were markedly high at stations 1, 2, 6, 7 and 9 as compared to stations 3 and 4. It should be noted that the major refineries were located along the western shore of the Bay and discharged their wastewater through point discharges to the Creek. In addition domestic wastewater releases were also channeled through nallas discharging in the western portion of the Creek. The high degree of sediment contamination along the western bank was therefore associated with these inputs. The nearshore accumulation of PHC also suggested that the particulate matter in the water column effectively scavenged the PHC, enriching the sediment. Similar trend was also evident in the Harbour area with markedly higher concentrations confined to stations 10, 11 and 16. The highest concentration of 4456 $\mu g\ g^{-1}$ was obtained at station 10 which was in the vicinity of the Sewree mud flat. Mahul Creek which received wastewater from refineries and other industries discharged in this region. Moreover, the circulation pattern within the bay favoured preferential silt deposition in this region. In the Harbour the major unloading operations of crude oil were undertaken at Butcher Island (Figure 3.1). Hence, stations 12, 13 and 14 were expected to be vulnerable to PHC contamination. Surprisingly concentrations (461-566 $\mu g\ g^{-1}$) in the area were markedly lower as compared to the locations along the western shores. Two plausible explanations could be put forward for this observation. One reason could be that entry of PHC during unloading operations was not high enough to cause serious contamination of the sediment. The other reason could be that due to prevailing strong tidal currents in this area, the PHC were transported away from this area and would have settled in relatively calm regions. Comparison of total organic carbon (TOC) with sum total of residues (A) and (B) indicated that the concentrations of extracted organics were not very high as the percentage of TOC at all the stations. Aliphatic hydrocarbons (Fraction B1) constituted about 30 to 40 % of (B) for nearshore sediment and decreased to 10 to 20 % in the sediment confined to the midstream, except station 8 at which it was 30 %.

Aliphatic (Fraction B1) and aromatic (Fraction B2) hydrocarbons and hydroxy compounds (Fraction B3) correlated very well with sediment TOC with correlation coefficients of 0.85, 0.84 and 0.81 respectively (Figure 4.10). This was not surprising because the capacity of a sediment particle to absorb has been shown to be largely dependent on the coating of organic material (a measure of TOC) on the particle surface (Voudrias and Smith, 1986). The correlation of fatty acids

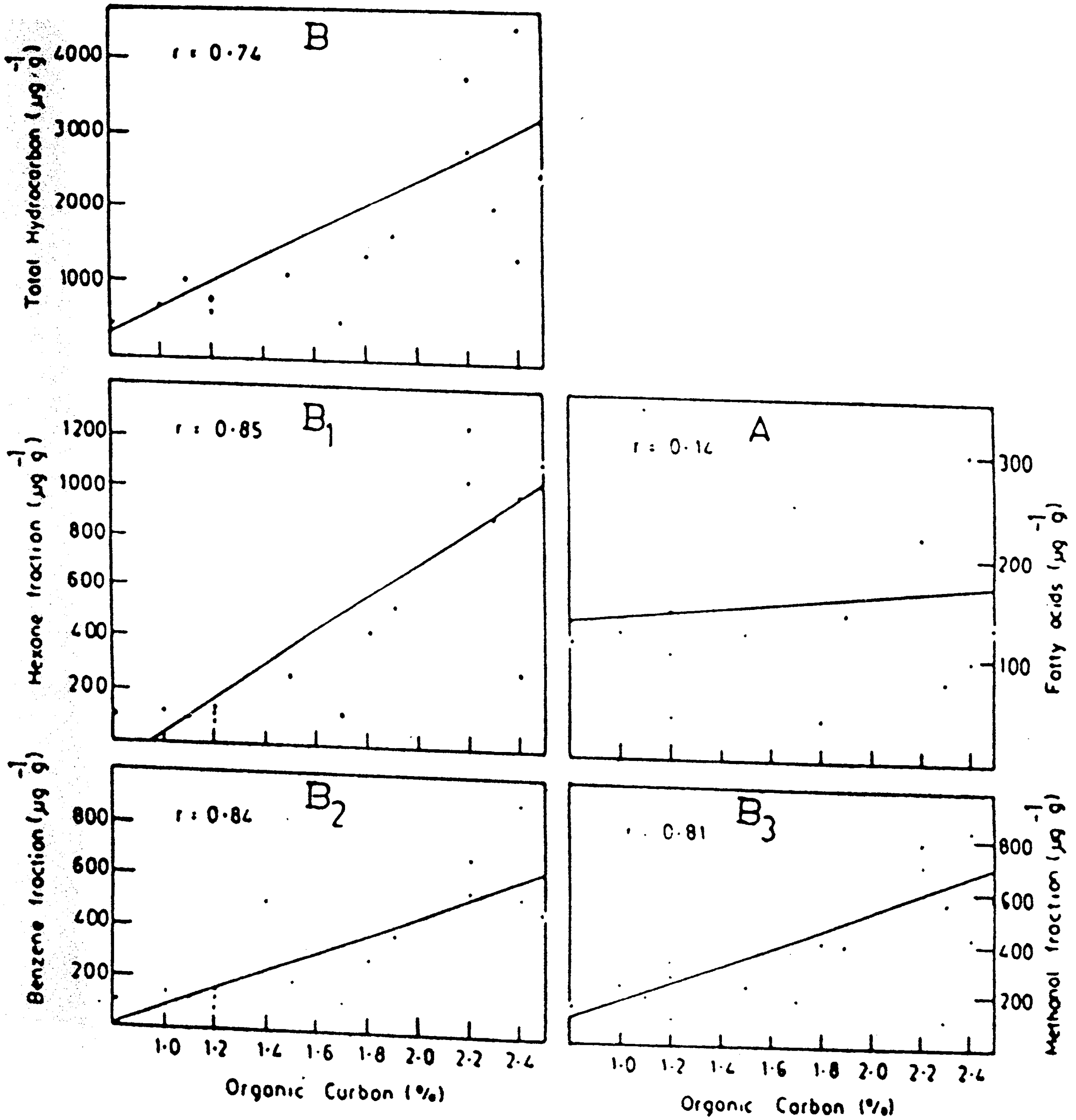

Fig.4.10 : Variation of fractions A, B, B_1, B_2 & B_3 with sediment organic carbon

(Fraction A) with TOC was however poor (Figure 4.10) perhaps because fatty acids were formed through biodegradation of the PHC and not being directly introduced to the marine environment were not incorporated into the sediment through adsorption.

IR spectra (Figure 4.11) of hexane eluted nonpolar fractions (B1) revealed that it might contain alkanes, cycloalkanes and monosubstituted aliphatic hydrocarbons (Characteristic peaks at 2923, 2855, 1454, 1377 and 1642 cm^{-1} respectively). The intermediate benzene fractions (B2) showed the presence of ketones and polyunsaturated hydrocarbons including aromatics (Characteristic peaks at 1738 and 1599 cm^{-1} respectively). IR 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, 1601 cm^{-1} due to carbonyl groups and unsaturation from alkanols and sterols respectively (Figure 4.11).

Gas chromatographs of the hexane fractions (B1) illustrated in Figures 4.12 to 4.19 could be grouped under two distinct classes when assessed with respect to the chromatograph of the standard mixture given in Figure 4.12. The first group consisted chromatographs pertaining to stations 1, 2, 6, 7, 8, 9, 10, and 11 which exhibited a

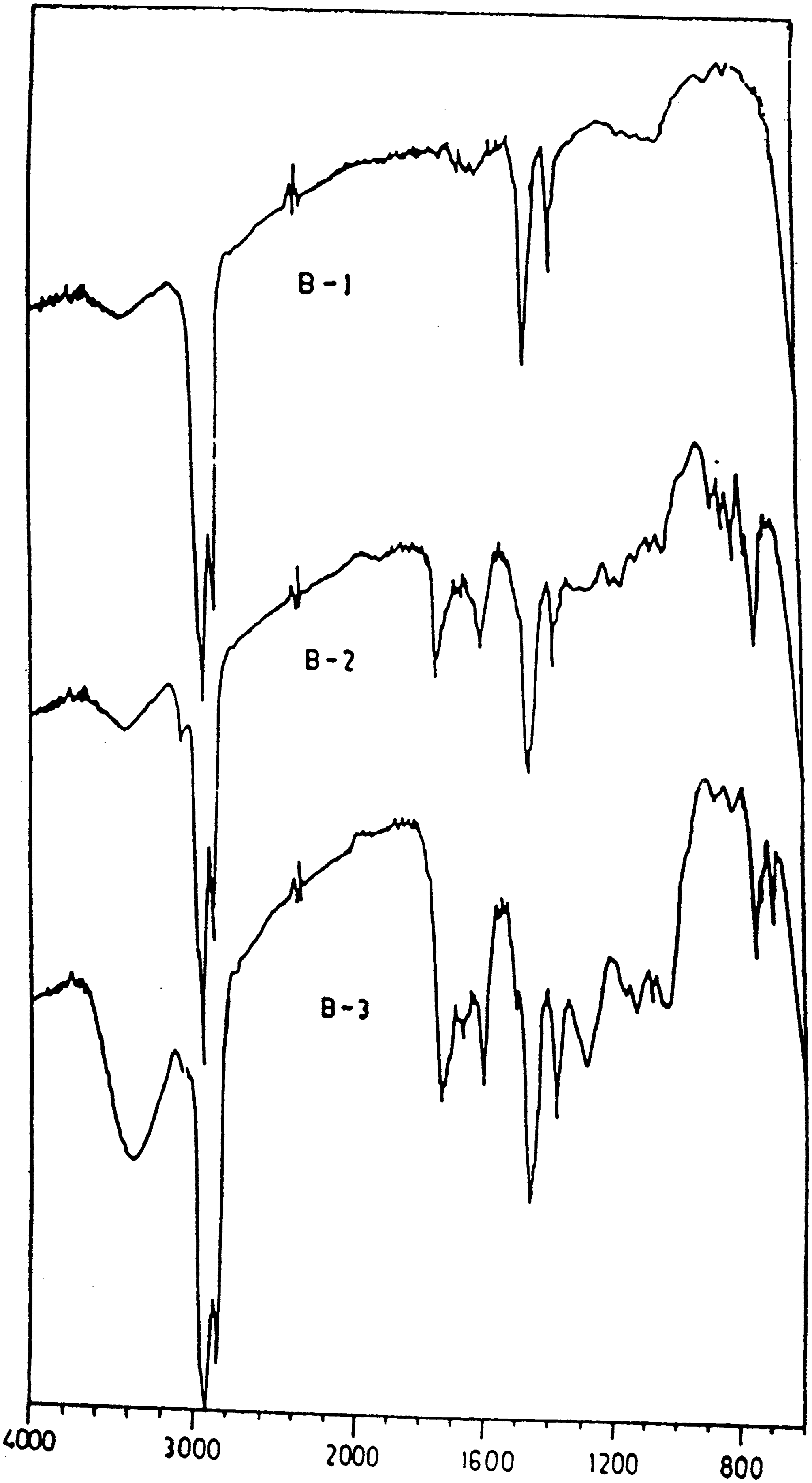

Fig. 4.11 IR spectra of fractions B_1, B_2 and B_3 of sediment extract.

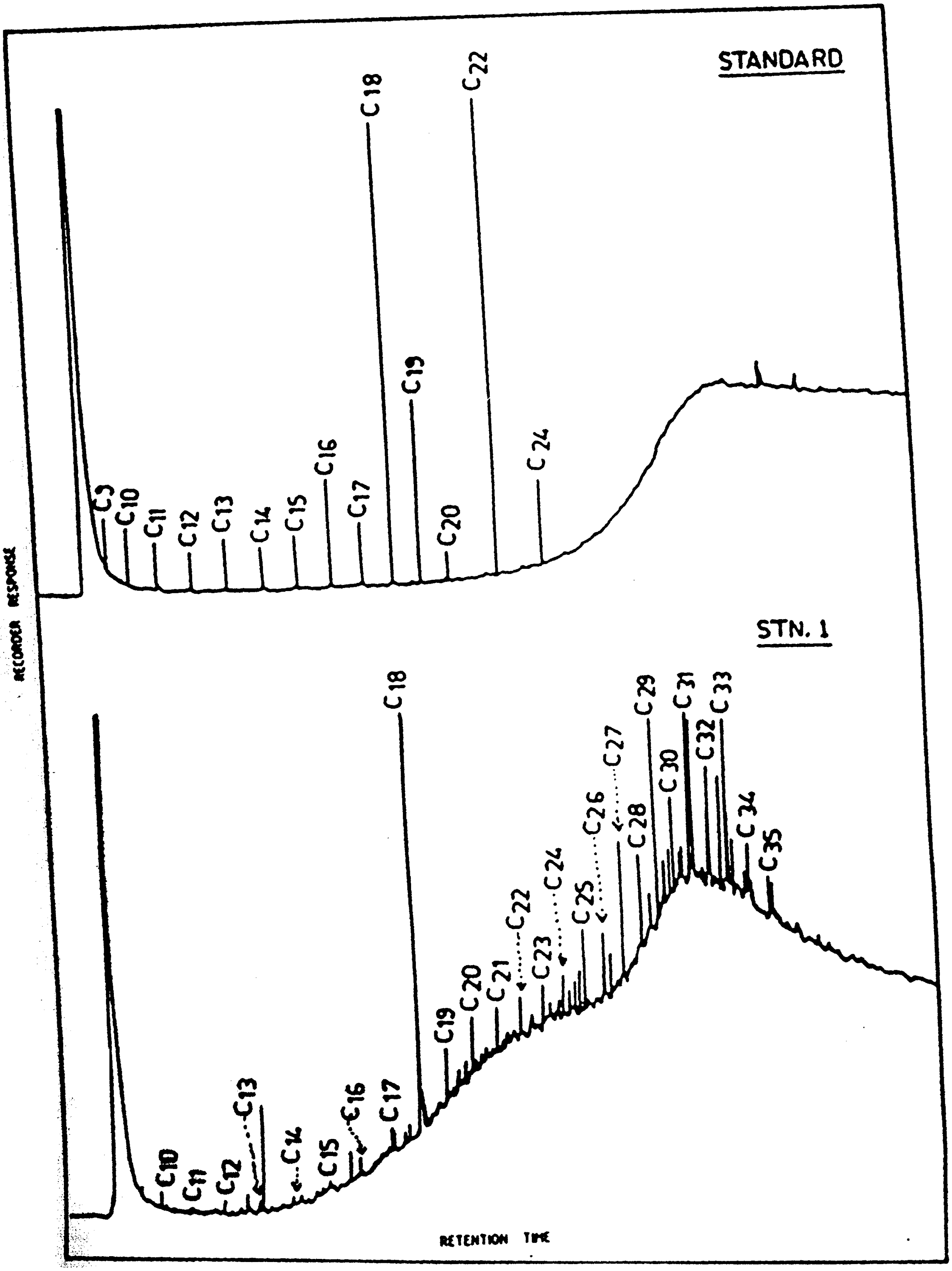

Fig. 4.12 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

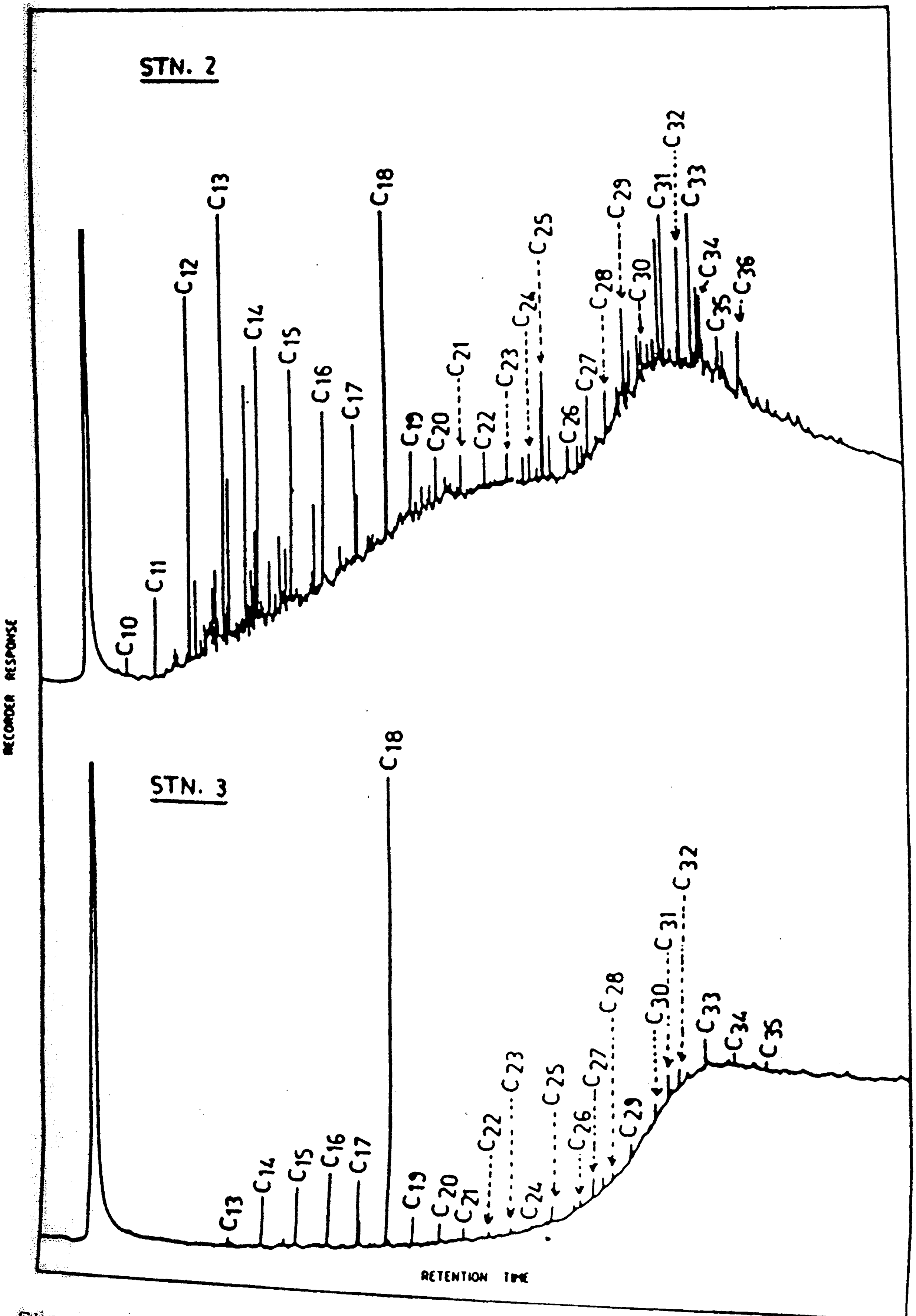

Fig. 4.13 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

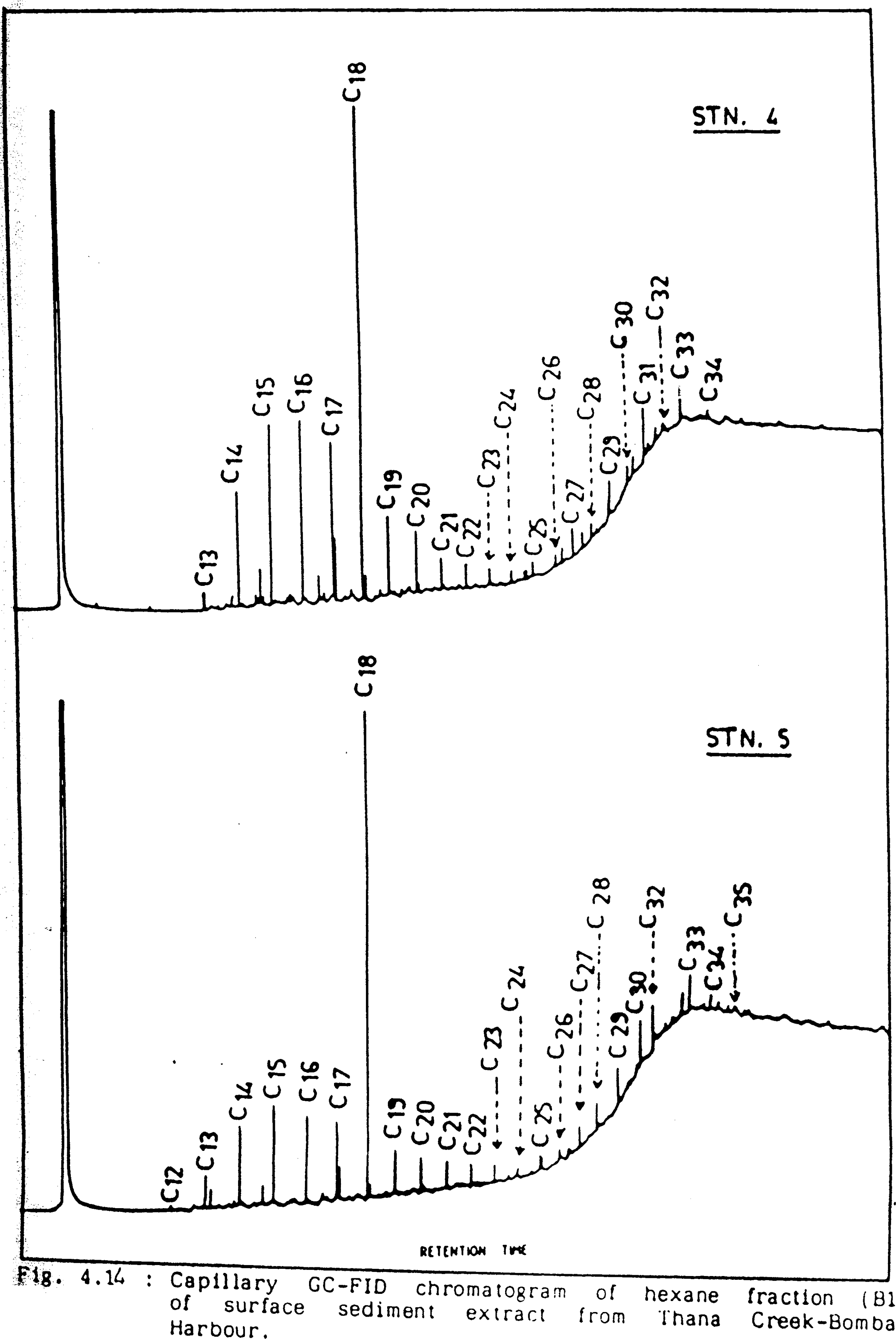

Fig. 4.14 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

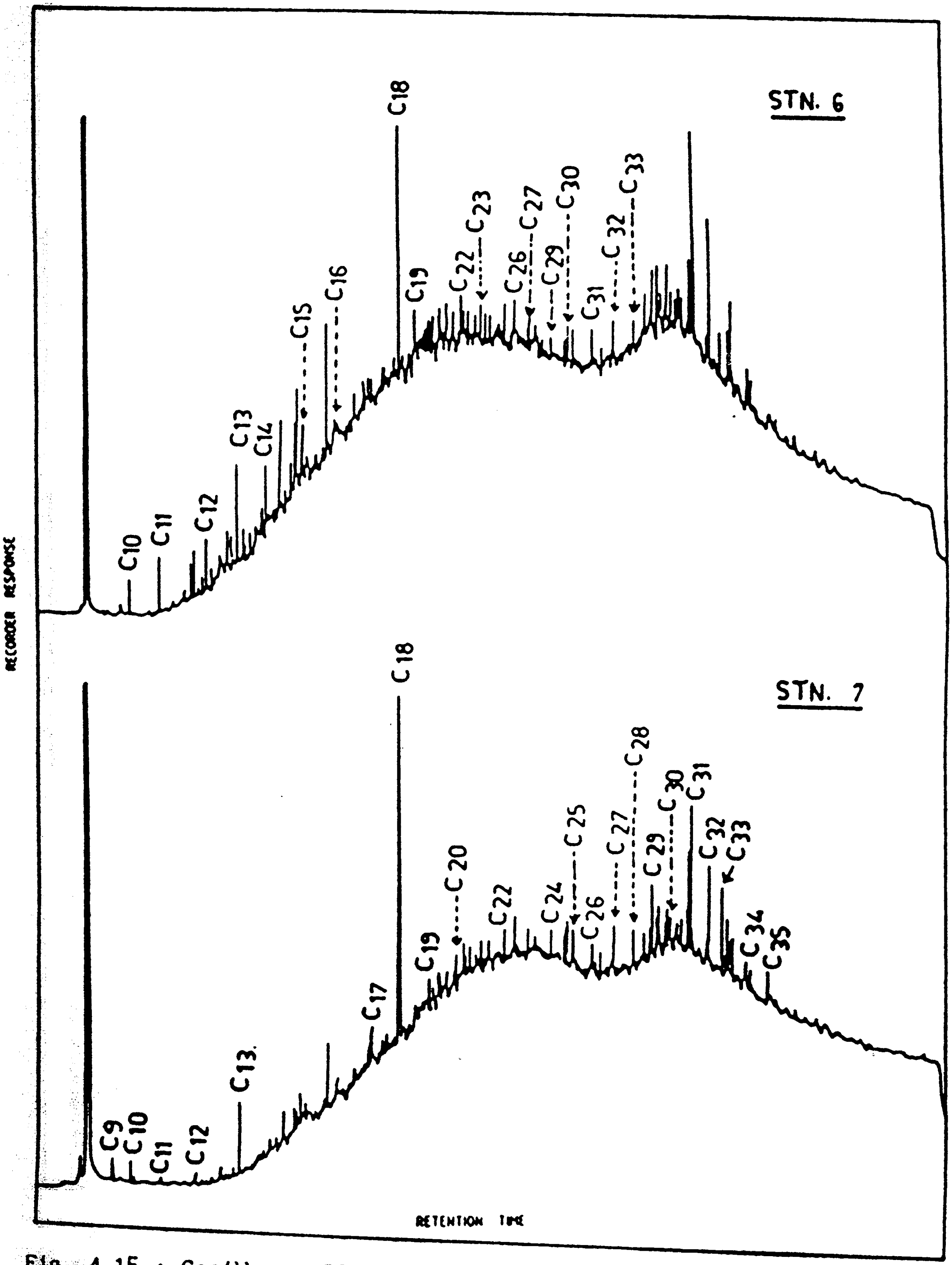

Fig. 4.15 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

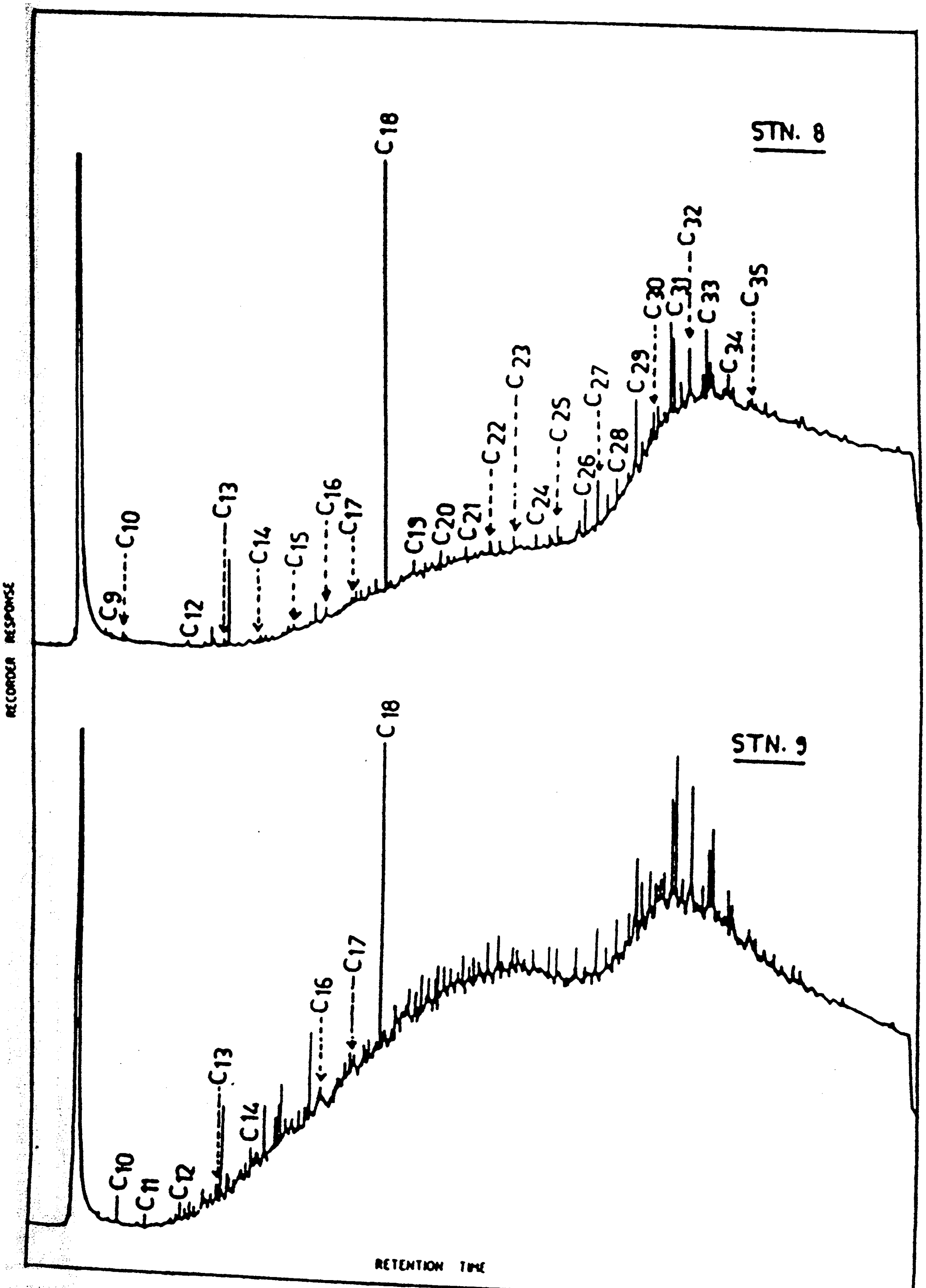

Fig. 4.16 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

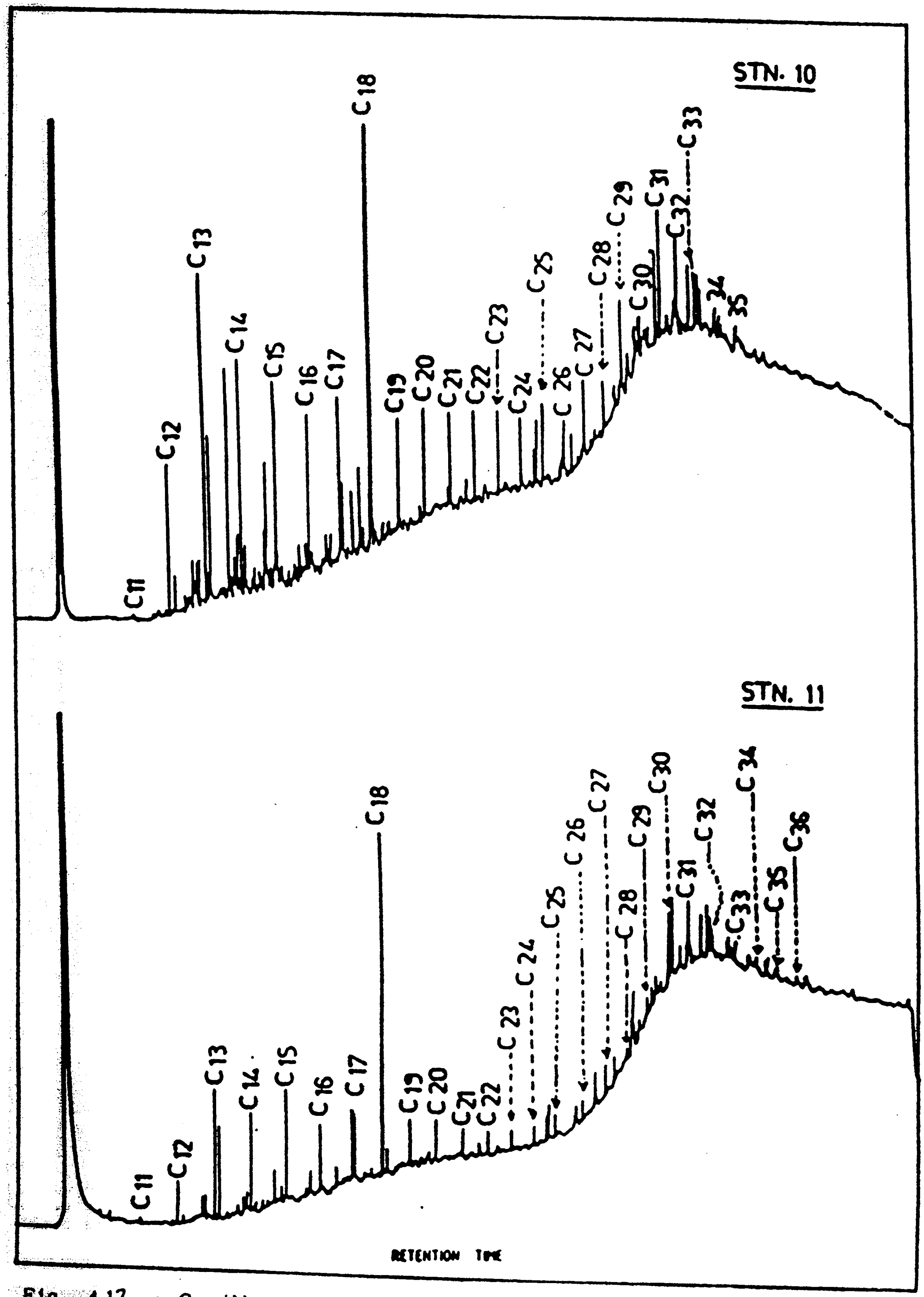

Fig. 4.17 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

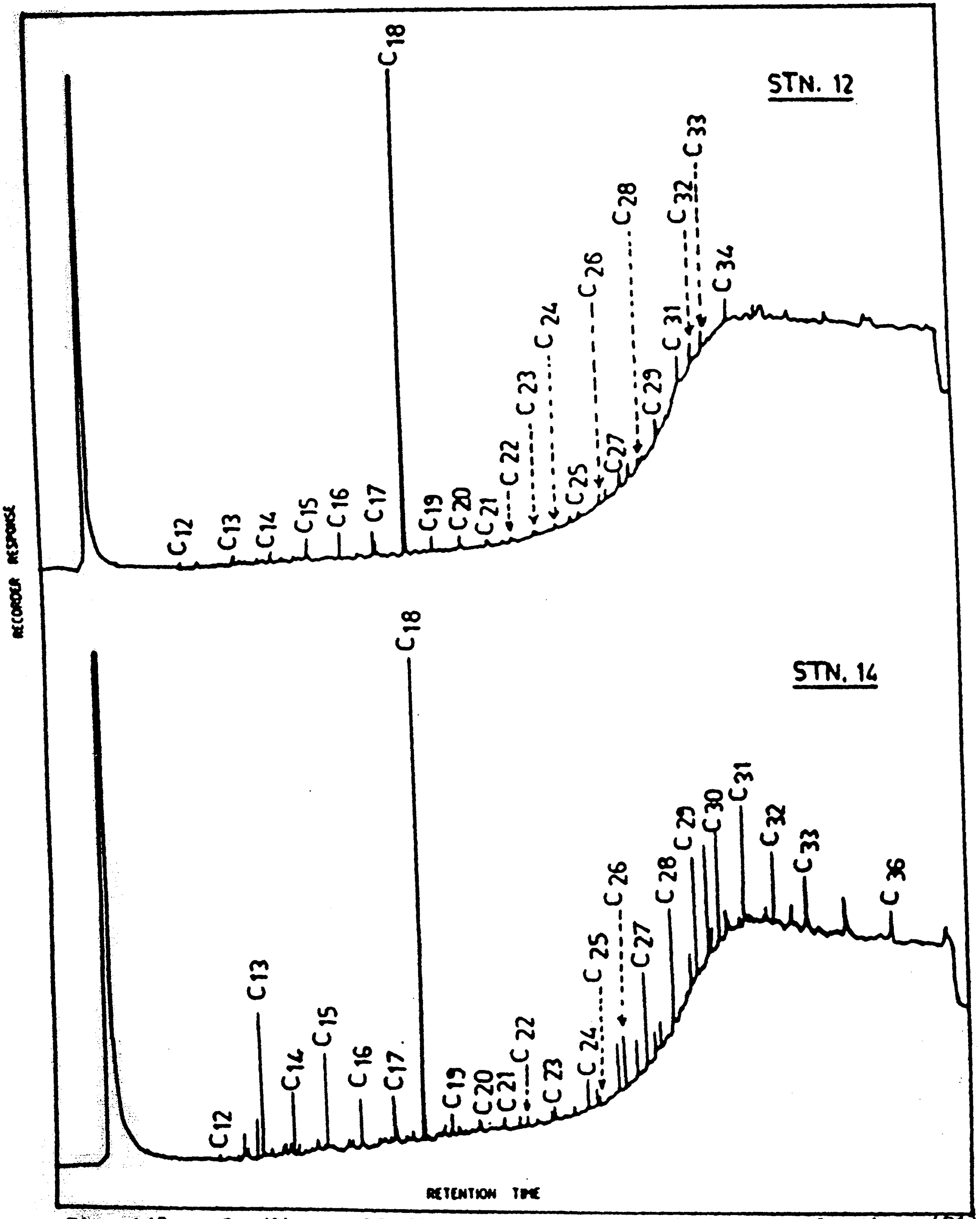

Fig. 4.18 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

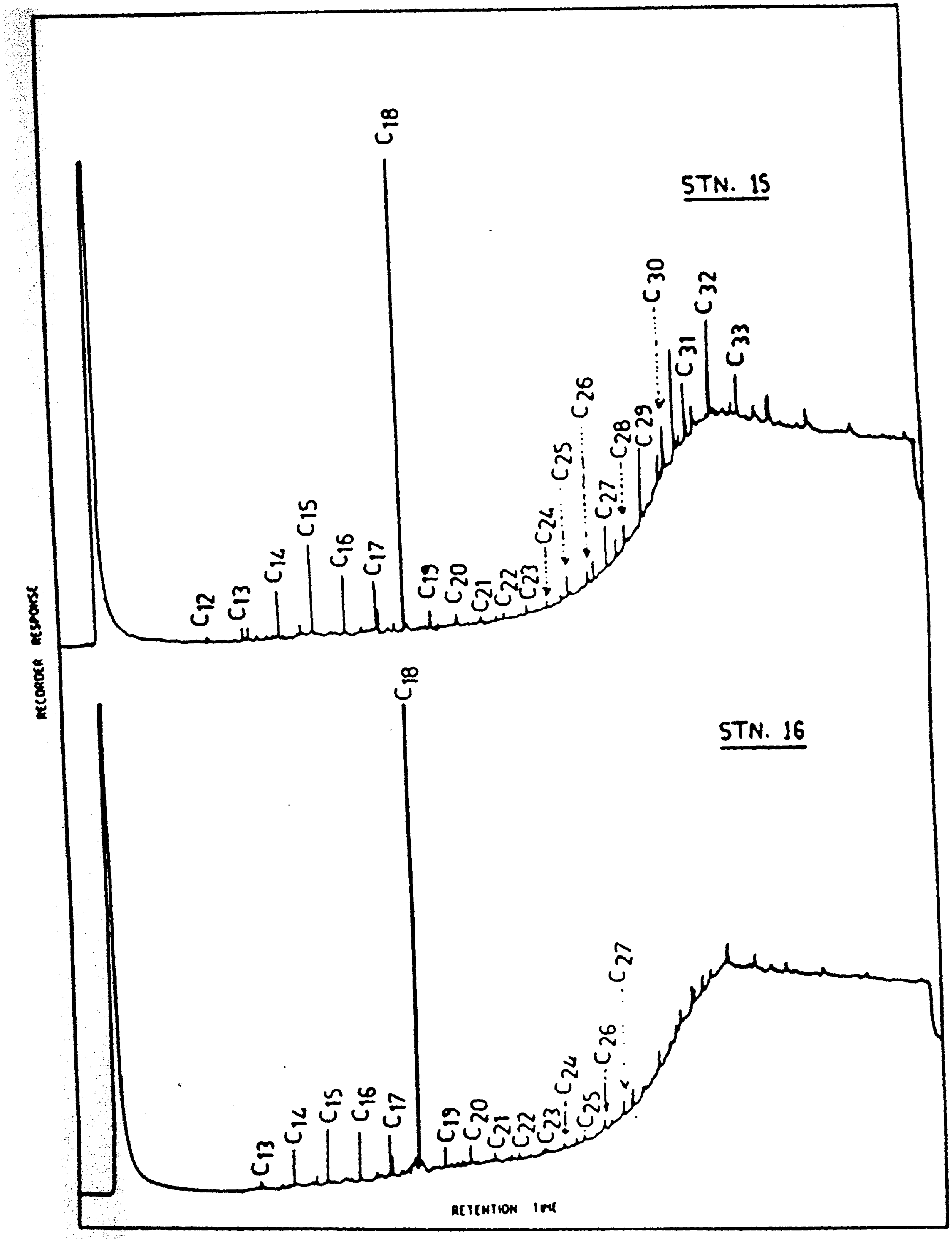

Fig. 4.19 : Capillary GC-FID chromatogram of hexane fraction (B1) of surface sediment extract from Thana Creek-Bombay Harbour.

characteristic pattern of several peaks overlying an unresolved envelop of a complex mixture of hydrocarbons while UCM was weak or absent in the chromatographs of stations 3, 4, 5, 12, 14, 15 and 16. As discussed earlier the region in which the stations of the former group were located was influenced by the wastewater from refineries in addition to other source and the UCM could be the characteristics of the influence of refinery waste. The stations of the other group (except for station 16) were along the eastern shores and mainly influenced by industrial wastewater from the Thana-Belapur belt and other sources. The presence of UCM in chromatographs of sediment extract has been attributed to highly degraded PHC (Meyers & Norishige, 1979; Bidleman et al, 1990; Readman et al, 1986; Farrington et al, 1977).

Sediment cores from Stations 1, 8, 18, 19, 20 and G 2595 were obtained in an attempt to construct geochemical record of the oil pollution history of the bay. As the harbour area was subjected to periodic dredging the cores from this locality were not considered of much use and hence were not studied. In order to obtain a good sedimentation rate record the area from which the core is taken should not be disturbed by physical mixing or by bioturbation and should have a constant rate of sedimentation over the period of interest. The Thana Creek/Bombay Harbour region was likely to be subjected to considerable frictional stress due to high tidal movements. The sediment was also known to be rich in benthic fauna. These factors were kept in view while interpreting the results of the cores.

The core 8 was recently investigated for sedimentation rate by ^{210}Pb dating technique (Sharma et al, 1993). The results indicated that the core throughout the length was fairly undisturbed and gave a sedimentation rate of 0.74 cm yr^{-1}. Thus, 100 cm long core which was studied for PHC retained the signature of the depositional environment in Thana Creek for about 130 years. Hence, the bottom of this core would represent the sedimentary environment of 1863 when there was no import of crude oil and petroleum products and petroleum based industries around the creek were not even established. Evidently, it was expected that the bottom portion of these cores would represent the baseline unless the PHC from the upper layers percolated downwards. The 106 cm long core (G 2595) from the nearshore waters of Bombay was also studied for ^{210}Pb dating and a sedimentation rate of 0.55 cm yr^{-1} was established (Sharma et al, 1993). Hence, this core was expected to have preserved the pollution history of the coastal depositional environment of about

186 years when exploitation of crude oil had not been begun, world wide.

Surficial sediment of cores 1 and 8 were analysed using wet sieving sedimentation method for particle size distribution. The station 1 sediment was reported to contain about 3 % sand (>63 µm), 80 % silt (2-63 µm) and 17 % clay (<2 µm) (Desai et al, 1986). While sediment at station 8 consisted of more or less equal proportions of clay and silt together forming more than 98 % of the total particles. The aluminium content of the sediment which could be roughly considered as representing clay fraction (Mackin and Aller, 1984) remained fairly uniform throughout the core lengths with minor perturbation indicating that the clay content has more or less remained the same in the sediment over the years (Sharma et al, 1993). Visual inspection of these cores also indicated absence of stratified bands or discontinuities except in the bottom section (90-95 cm) of the core 8. This section contained coarse, sand pebbles, rock pieces and broken shells along with clay and silt.

The moisture content of the surficial sediment (35-65 %) decreased gradually down the core attaining values of 25-40 % in the bottom sections except in core 8 in which an abrupt decrease was observed between 95 and 100 cm section attributed to the coarser sediment of this section as discussed above. Such a decrease in moisture content commonly observed in sediment cores is due to the decreasing porosity with depth because of sediment compaction by the burden of the overlying sediment (Engelhardt, 1977).

Core 1 indicated marginal enrichment in TOC in the top 10 cm and the concentration remained nearly constant around 1.7 % upto the bottom of the core. Core 8 on the contrary had uniform TOC of around 1.7 % upto a depth of 45 cm followed by a gradual decrease to attain a concentration 1.1 % at 95 cm depth. Sudden decrease further down the core was due to the occurrence of coarser sediment which had low absorbing capacity (Gundlach and Hayes, 1978). The cores G2595, 19 and 20 exhibited more or less similar concentrations of TOC throughout the lengths with minor perturbations (Figure 4.21). Core 18 however had high TOC of around 4 % throughout the length. Although, the Bay received considerable organic load, the TOC in the sediment did not seem to be affected appreciably possibly because the organic material deposited on the bed was efficiently consumed by the rich meiobenthos habitating these sediments (Govindan et al, 1976). Concentrations of total phosphorous were estimated in cores 18, 19 and 20. In core 18 the total phosphorous varied considerably between 1431 to

1781 ug g^{-1} with random variations throughout the core while in cores 19 and 20 the variations were in a narrow range at 766-1173 ug g^{-1} and the profile were roughly uniform similar to those of TOC.

The saponified material which was extracted, purified and weighed was considered to represent fatty acids (Meyers et al, 1979), the degradation products of hydrocarbons. It was evident from Figure 4.22 that the high fatty acid (FA) contents in the cores were associated with high concentrations of total hydrocarbons (THC) and although their variations were irregular, generally profile similar to those of PHC were evident in most cores with subsurface maxima coinciding with PHC maxima.

It was evident from Figure 4.20 that the cores obtained from the bay fall under three distinct categories. The cores 1 and 8 had high concentration (420 to 1180 $\mu g\ g^{-1}$) in the surface sediment which sharply decreased to 70-200 $\mu g\ g^{-1}$ at 20 cm depth followed by a gradual decrease upto the bottom with concentrations nearly constant (40 to 60 $\mu g\ g^{-1}$). In fact in core 8 the concentration remained constant at 15 $\mu g\ g^{-1}$ uniformly below 72 cm depth. Core 18 obtained from the nearshore region of Sewree mudflat had roughly constant concentration varying in 240-800 $\mu g\ g^{-1}$ range

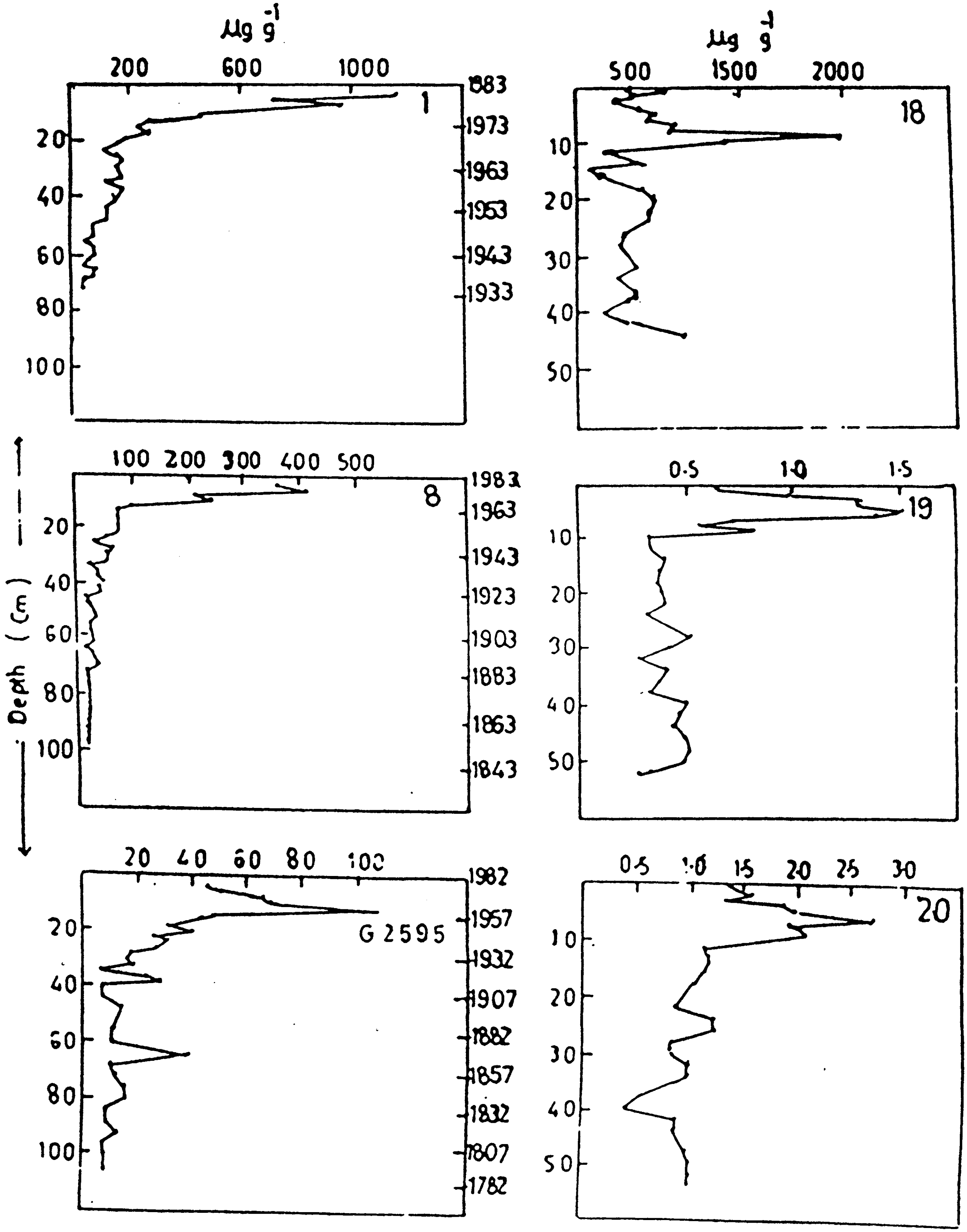

Fig. 4.20 : Depth profile of PHC in sediment cores at different stations.

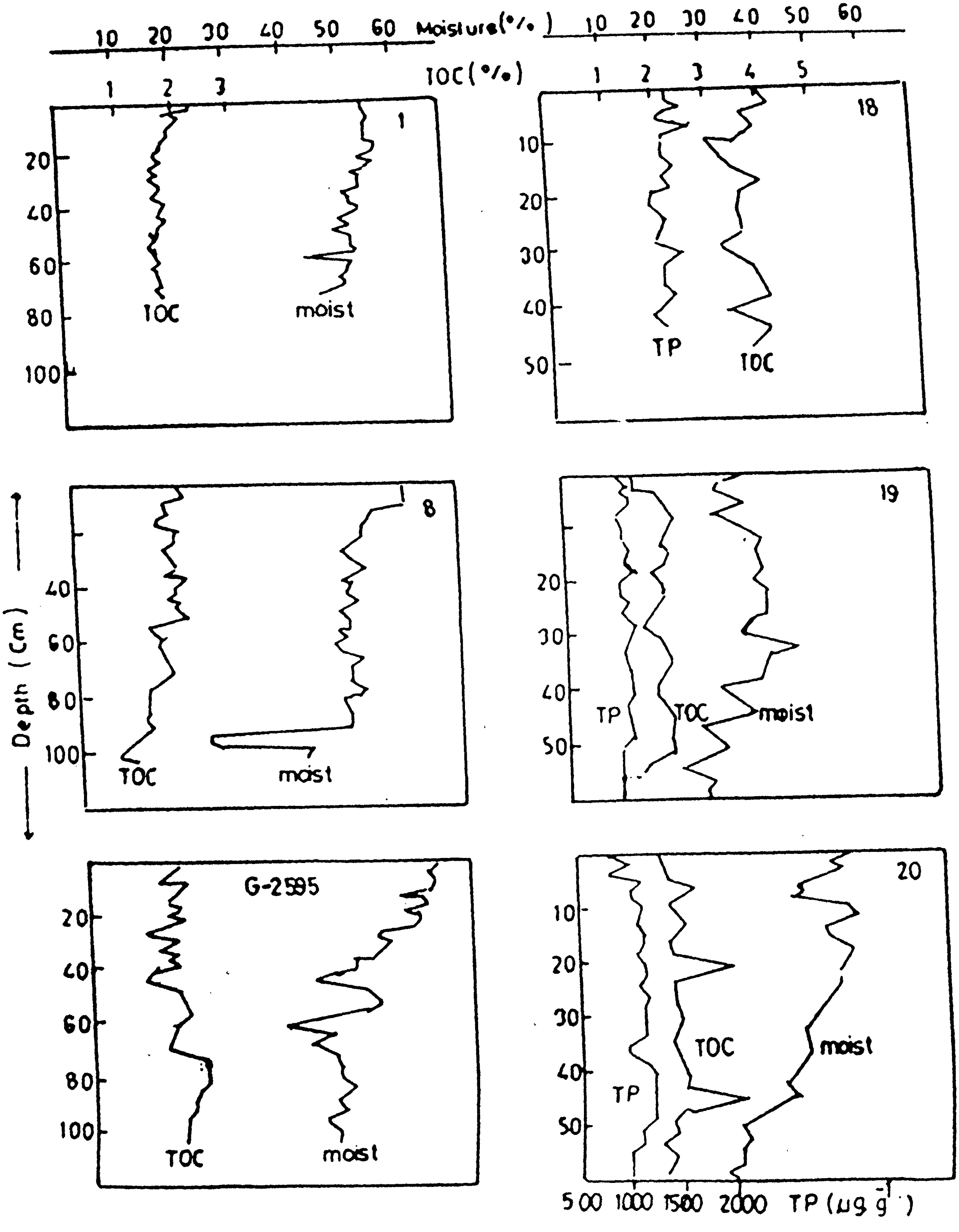

Fig. 4.21 : Depth profile of TOC, TP and moisture content in sediment cores at different stations.

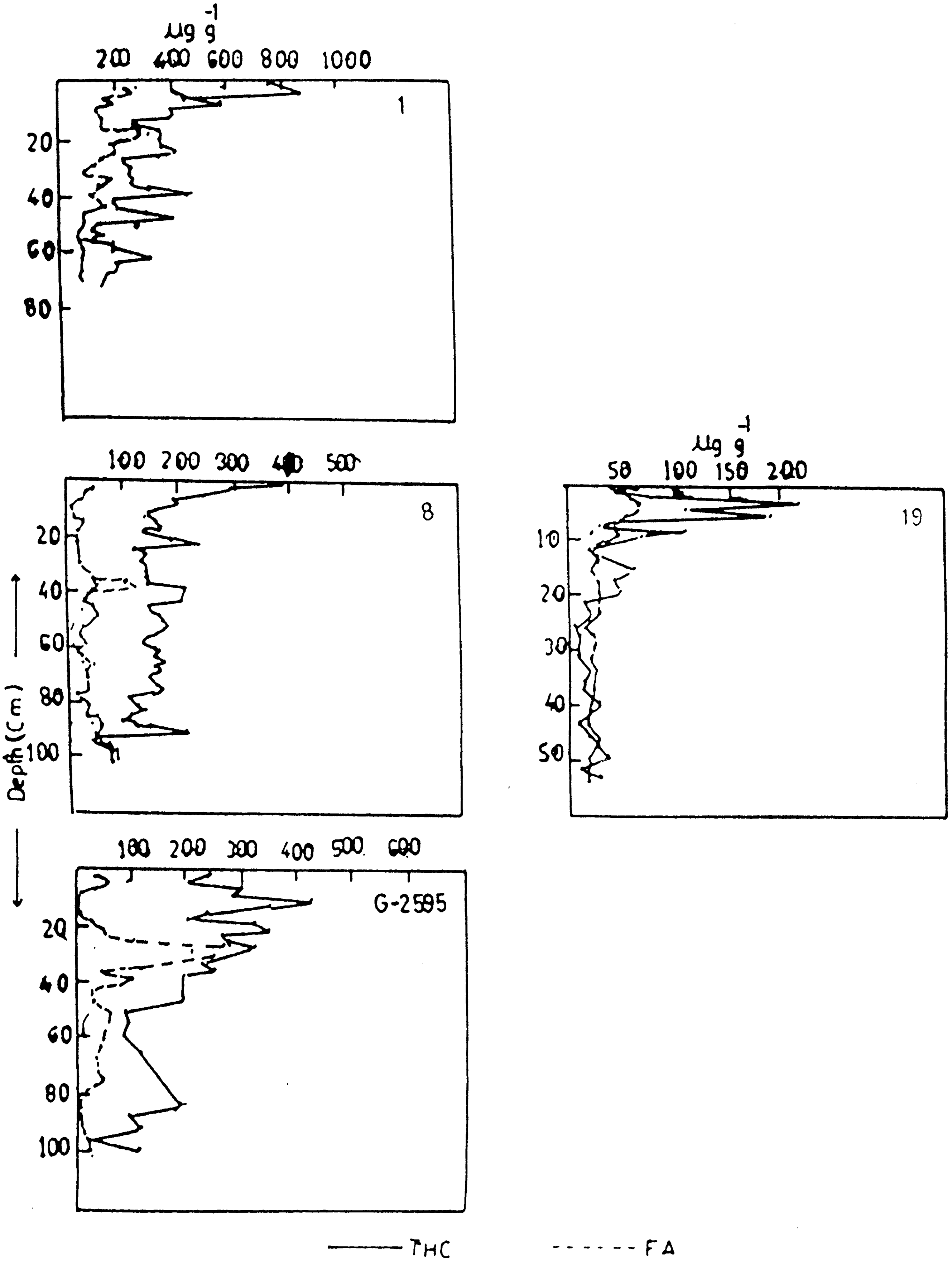

Fig. 4.22 : Depth profile of THC and FA in the sediment cores at different stations.

throughout the length except at 10 cm depth where PHC value sharply increased to 2000 $\mu g\ g^{-1}$. The cores 19 and 20 from Dharamtar creek although maintained similar profiles like cores 1 and 8 the concentrations were less than by atleast 2 orders of magnitude in these cores.

The bed sediment of Bombay Harbour-Thana Creek complex including Dharamtar creek is derived from the lithogenic flux from the adjacent basaltic terrain. Hence the gross composition of sediment in the region is similar and should have similar absorbing capacities. The PHC profiles in cores 19 and 20 indicated that the probable background concentration in these sediments were perhaps between 0.2 to 1 $\mu g\ g^{-1}$. This was in contrast to the concentration of 40 $\mu g\ g^{-1}$ in the bottom sections of core 1 and 15 $\mu g\ g^{-1}$ in core 8. As discussed above, the sediment below 95 cm would have deposited during the early nineteen twenties hence, it was unlikely that such high concentrations occurred through anthropogenic fluxes. Moreover, the concentrations of PHC in the bottom sections of cores from the Bay varied considerably which was not expected since this sediment would have deposited under similar environmental conditions. Hence, we presumed that the PHC deposited at sediment water interface was transported downward through interstitial water.

Transfer of PHC to lower sections of sediment has also been reported elsewhere (Blumer and Sass, 1972; Burns and Yelle, 1992; Burns et al, 1992).

From Figure 4.20 it was evident that the concentration in core 1 remained below 70 $\mu g\ g^{-1}$ before the 1950's and increased thereafter with an exponential increase in the nineteen seventies. Similar trend was also evident in core 8 with concentration remaining nearly constant at 15 $\mu g\ g^{-1}$ upto 1903 with a small but steady increase upto 1956 (50 $\mu g\ g^{-1}$) and then abrupt increase upto the top of the core. This increase in concentration after 1950's coincides with the setting-up of refineries at Chembur on the western bank of Thana Creek which released untreated oily wastewater in the Creek in the past that contributed substantially to the sediment burden of PHC.

The core G 2595 from coastal water of Bombay also revealed increase in PHC contamination in top 40 cm though the concentrations are markedly lower than that in the bay. The core below 40 cm (1907) had more or less similar concentration around 10 $\mu g\ g^{-1}$ which again suggested downward transport of PHC to account for these higher concentrations of PHC than expected for uncontaminated sediment earlier than 1850's.

From examination of PHC profiles in Figure 4.20 subsurface maxima centered around 10 cm depth were evident for cores 1, 18 and G 2595 and around 5 cm depth in cores 19 and 20. These maxima between 5 and 10 cm could be due to the transfer of sediment particles by the benthic organisms or some episodic event around 10 years ago calculated according to the sedimentation rate. The clay silt sediment at all these locations is known to have rich benthic fauna dominated by polychaetes (Govindan et al, 1976). These polychaetes are likely to feed on detritus contaminated with PHC at the sediment surface. Thus, the PHC contaminated particles pass through the gut of polycheate and are often ejected as fecal matter a few centimeters below the sediment-water interface. Again, the polychaetes are known for the uptake and depuration of PHC from petroleum contaminated sediment of the benthic environment (Aller, 1984; Lee, 1976; Lee et al, 1977). The subsurface maxima of PHC observed in the sediment could be due to the accumulation of excreted material by selected polychaetes at that depth.

There was no industrial development around Dharamtar creek prior to 1990. The Patalganga River which discharges in Dharamtar creek however has several industrial establishments including a petrochemical complex in the upper reaches about

35 km from the estuary mouth. Although these industries released the wastewater in Patalganga River, the levels of PHC in the sediment did not indicate severe contamination due to these sources. Dharamtar creek is fed by the water from the Bombay Harbour which ingresses the creek during high tide. Even during monsoonal freshwater flow through Amba and Patalganga Rivers, the influence of Bombay Harbour water in the creek is quite substantial. The freshwater discharge however becomes negligible after September and the creek essentially contains saline water with salinities exceeding 30 ppt after October. The high concentration of phosphate and nitrate in this creek also indicate the influence of Bombay Harbour water (NIO, 1990). Hence, the observed values of low levels of PHC in cores 19 and 20 indicated that the PHC entering the bay was effectively scavenged in the Bay itself and hence likely to be transported to the bed sediments.

4.2 Bombay High

4.2.1 Physico-chemical parameters.

Status of marine environment of Bombay High has gained considerable importance due to increasing exploitation of offshore petroleum. Fears were being expressed that the environmental quality of the region had deteriorated due to those activities. Levels of PHC in the surface sediments of Bombay High have recently been reported. The concentrations which varied in 0.01-0.3 $\mu g\ g^{-1}$ (chrysene equivalents) range indicated that the sediment contamination was not alarming. In order to establish the status of water quality and to evaluate temporal variability if any, two cruises were organised in the Bombay High region during 1982 (R.V.Gaveshani cruise no.115) and 1988 (R.V.Sagar Kanya cruise No.48) respectively. The results of these cruises were compared with those obtained during 1976 (R.V.Gaveshani cruise No.3) just prior to the commencement of full scale exploitation activities (NIO, 1976). Relevant data collected during 1980 from stationery production platforms (F, C, and SA) in Bombay High were also referred wherever required.

(a) Temperature

The available data (March 1976, March 1981, January 1982 and 1989) in conjunction with the present study indicated that the annual surface temperature showed a variation of about 6 ^{o}C from 30.6 ^{o}C in June to 24.7 ^{o}C in January. The highest surface temperature occurred in the summer monsoon months of June-July and decreased gradually to the lowest in January-February. Conspicuously this pattern was also followed by near bottom temperature

The thickness of the surface mixed layer varied considerably between 20 and 70 m during January and March (Table 4.3). Below this depth the temperature decreased rapidly resulting in a well marked thermocline during the period from May to December.

(b) pH

The pH of surface water varied widely in the range 7.7 to 8.2. The variation of pH in the water column was dependent on the occurrence of thermocline. While the pH was uniform from the surface to the bottom when the water mass was well mixed, a distinct decrease in pH occurred just below the thermocline (Figure 4.23).

The vertical profiles of pH and related total carbonate, bicarbonate and CO_2 components reflected the quasi-stationery state that existed at a particular locality. The forms of these profiles depend on the flux of the organic matter derived from the upper layers of the water column, its rate of oxidation and the rate of dissolution of carbonate. The vertical profile of bicarbonate indicated a small but steady increase upto 30 m followed by a considerable increase below the thermocline. The depth profile of carbonate however revealed a considerable decrease below the thermocline layer. Hence a decrease of pH below the thermocline layer may be due to an increase in CO_2 concentration (Figure 4.23).

(c) Dissolved oxygen

Dissolved oxygen is an important parameter to be determined since its decrease below the saturation value indirectly provides information about organic contamination of a water body.

The comparison of DO in the Bombay High region (Table 4.4) suggested that the DO had probable decreased in the surface layer from 1976 to 1988. Although this indicated possible increase in organic load in the water column perhaps due to offshore exploitation activities, a firm conclusion should not be drawn as levels of DO could be affected by several factors such as primary productivity, season and time of collection. Further studies are therefore required to confirm or otherwise, this observation. The vertical profiles of DO were dependent on the depth of occurrence of thermocline. The DO was more or less uniformly distributed with a marginal decrease with depth throughout the water column when the water body was well mixed vertically (Figure 4.23). A distinct decrease was however evident below the thermocline, when developed, because of the restricted mixing of water masses above and below the thermocline. The DO in the upper layer of the sea is influenced primarily by exchange with atmosphere and productivity of the euphotic zone. This oxygen rich water is restricted only to the well mixed layer above the thermocline. The transfer of oxygen below the thermocline was hindered and due to its consumption for the oxidation of organic matter settling through the water column, the DO decreased below the thermocline.

(d) Nutrients

Comparison of levels of NO_3^--N, NO_2^--N, NH_4^+-N and PO_4^{3-}-P at the surface did not reveal any systematic variations since the production activities had begun in Bombay High (Table 4.4). The overall distribution of nutrients along the central west coast of India however indicated a definite decrease from north to south and from east to west (Figure 4.24). The vertical profiles of nutrients at shallow stations (depths less than 50 m) were more or less uniform from the surface to the bottom. However, stations with depths exceeding 50 m revealed higher concentrations at the bottom perhaps due to the shoreward transport of low oxygen and nutrient enriched water confined between 100 to 500 m from the offshore (Sen Gupta et al, 1976; De Sousa and Singbal, 1986).

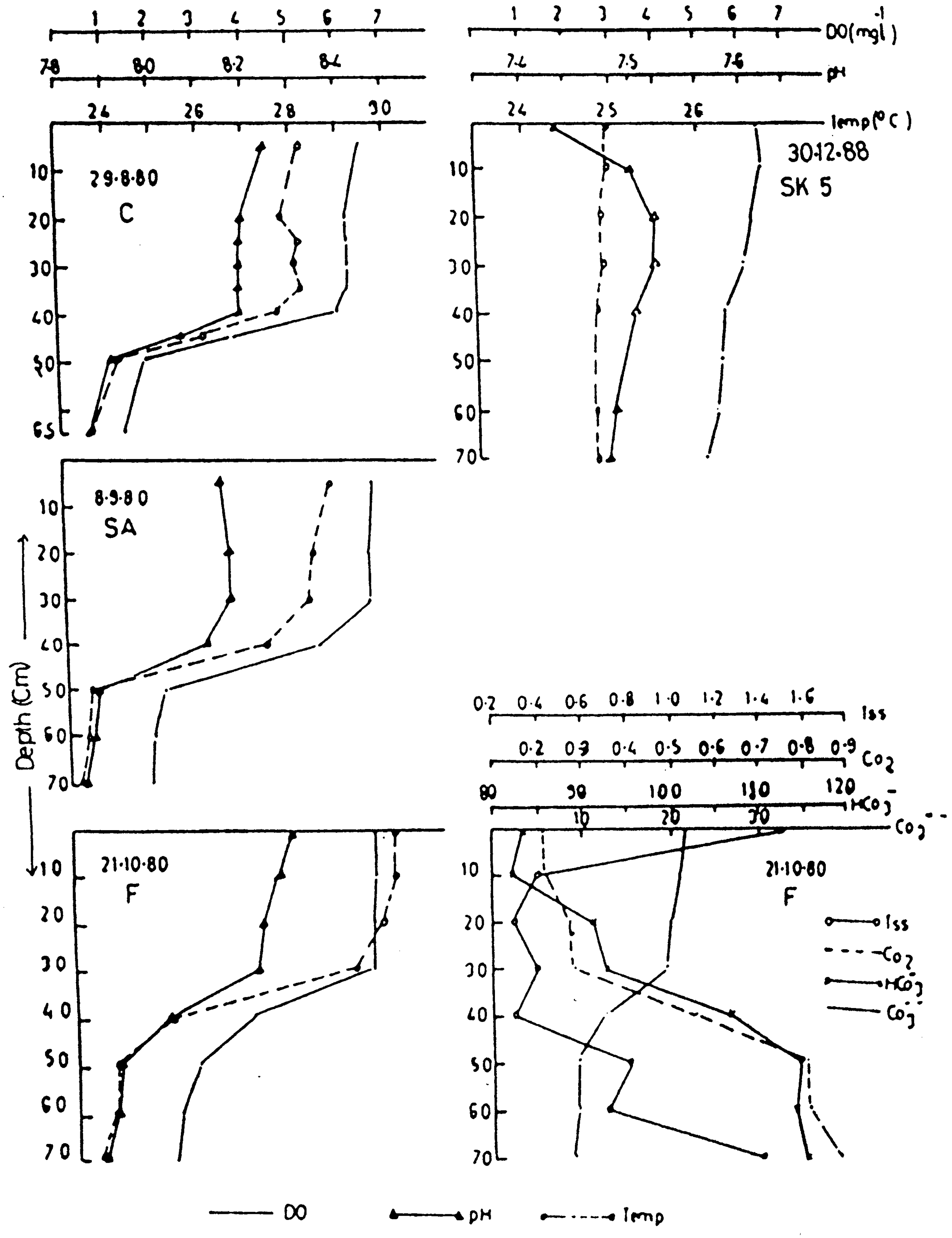

Fig. 4.23 : Depth profile of some physico-chemical parameters in the water column of Bombay High.

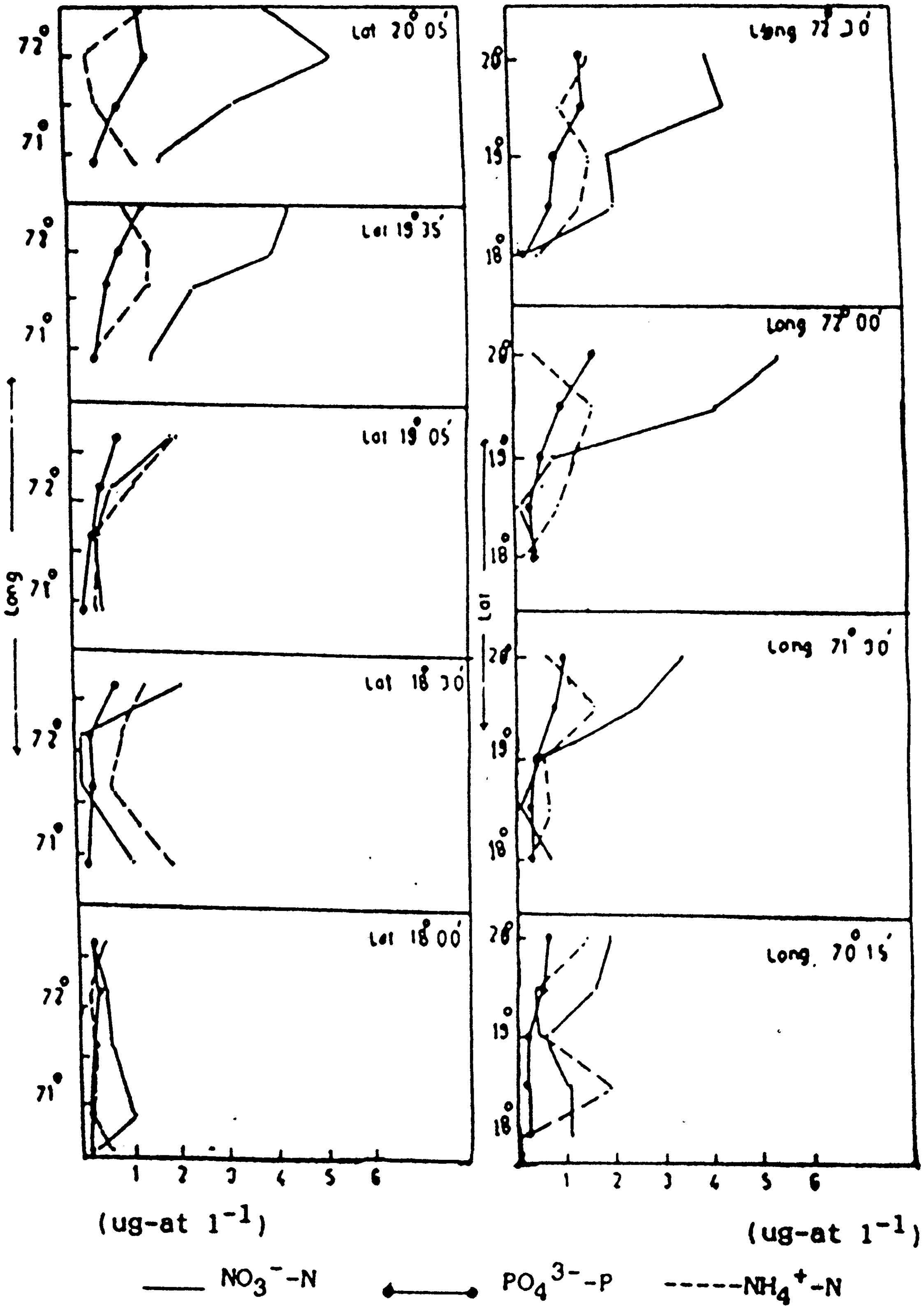

Fig. 4.24 : Lateral variation of NO_3^--N, PO_4^{3-}-P and NH_4^+-N in shelf waters off Bombay.

Table:4.3 Monthly variation of water temperature (^{o}C) with depth in Bombay High area during 1980-81

Depth (m)	Month							
	Mar	May	Aug	Oct	Nov	Dec	Feb	Jun
0	26.5	29.0	28.4	29.0	27.8	27.5	24.8	25.5
20	26.5	28.8	28.2	29.2	26.2	27.4	24.3	25.5
30	26.5	28.8	28.2	28.7	21.9	25.1	24.3	25.5
40	26.0	27.3	27.1	28.4	21.9	23.1	24.3	25.3
50	26.0	25.8	24.4	27.2	21.9	22.5	24.3	-
60	25.5	25.8	23.5	23.0	21.9	22.5	24.3	23.6
70	25.5	25.8	23.3	22.6	21.9	22.5	24.3	23.0

Table:4.4 Physico-chemical parameters at different stations in Bombay High area

Station	G 2	F	G 2581	SK 13
Latitude	19°22'	19°15'	19°20'	19°35'
Longitude	71°42'	71°25'	71°30'	71°38'
Period	March 76	March 81	Jan 82	Jan 89
Temp°C	26.0	26.3	-	25.3
S ($\times 10^{-3}$)	35.31	36.19	-	36.0
DO (mg l^{-1})	7.1	6.9	6.0	5.6
NO_3^--N (μg-at l^{-1})	2.3	-	1.4	2.5
NO_2^--N (μg-at l^{-1})	0.1	-	1.6	0.8
NH_4^+-N (μg-at l^{-1})	-	-	-	1.6
PO_4^{3-}-P (μg-at l^{-1})	0.7	-	0.5	0.8
PHC (μg l^{-1})	-	-	-	20

(e) **PHC**

Dissolved PHC along the west coast of India ranged from 7.5 to 87.7 $\mu g\ g^{-1}$. Levels of petroleum hydrocarbon in sediment along the central and north west coast of India varied in the range of 0.01 to 0.3 $\mu g\ g^{-1}$ wet wt crysene equilevent (Anirudh Ram and Kadam, 1991a, 1991b). Total lipid content in water varied from 165-293 $\mu g\ l^{-1}$ (Bhosle, et al, 1983).

4.3 Identification of oil spill

The discharge of petroleum products into marine waters has been a continuing environmental problem. It has been estimated that around 3.2 x 10^6 t of crude oil is spilled annually in the Sea through tanker traffic alone (ITOPF, 1987). Small spillages go unnoticed, since no visible environment degradation occurs. However, during oil spills when substantial quantities of oil enter the sea over a short time, large scale mortalities of some marine organisms and sea birds frequently occur. Transport of spilled oil on shores and beaches also causes considerable environmental problem. Localised pollution problems are often caused by tankers which discharge the bilge on high seas which under favourable coastal circulation and wind is frequently transported shoreward. In order to assign penalties for discharge and assess liabilities for clean up and restoration cost, it is desirable to trace the source of the spill and several efforts have been made for identifying the source of oil spills (Cubit et al, 1987; Bhosle et al, 1987; Jackson et al, 1989; Burns and Knap, 1989).

Identifying an oil spill to its source is however a difficult task in itself and is further complicated when the product is weathered or a mixture of two or more products is involved. A representative sample of the spilled oil is required to be characterised as a first step. Identification of the petroleum product then involves in demonstrating the sameness in the composition and the structure found in the spilled material when compared to the sample of the suspected source. Several methods of identification have been reported in the literature. Majority of these techniques are based on the infrared absorption characteristics of petroleum products (Kawahara, 1972; 1976; Brown et al, 1974).

Increasing transportation of crude oil and its products and offshore oil exploitation has rendered the marine environment around Bombay vulnerable to oil pollution. Although minor spillages of oil largely went unnoticed, a spill observed (19 August 1982) on the shore the

Napeansea area (South Bombay), attracted much attention by virtue of its occurrence within few days from the oil well blowout in the Bombay High region. It was feared that the source of the spill was the oil that might have spilled during the blowout. It was therefore of interest to investigate the spill to trace its source.

The spill on the rocky shore of Napeansea was reported on 19 August 1982. The first visit to the site was made on 26 August 1982. It was observed that a thick oily mass had spread along a 2 km stretch of the coastline covering rocky boulders and nearshore water. Visual inspection indicated that the spill was aged and was partly in the form of mousse. The representative specimens were obtained from different locations and pooled into a single sample for further study in the laboratory. This sample is hereafter termed as NS1. The collections were repeated subsequently on 23-9-1982, 15-10-1982, 10-11-1982, 9-12-1982, 13-1-1983 and these samples are identified by NS2, NS3, NS4, NS5, and NS6 in the discussion to follow.

The proton magnetic resonance spectra (PMR) of NS1 taken in the chloroform-D ($CDCl_3$) revealed a sharp and intense singlet at 1.2 delta and weak signals around 0.35 delta indicating its paraffinic character (Silverstein et al, 1981).

Complex pattern of several minor peaks around 1.4 to 3 delta was also noticed. This spectrum closely compared to the PMR pattern of paraffinic mixture isolated from crude oil. The IR spectra of NS (all samples as a group) showed several sharp and intense bands around 2900, 1462, and 1378 cm^{-1} and a sharp and prominent doublet around 730-720 cm^{-1}. The pattern of IR spectra indicated its crude oil origin (Lynch, et al, 1975). The doublet in particular was more significant as it reflected on the composition of the sample. This type doublet also observed in the IR of commercial white wax (Lynch, et al, 1975) and a number of petroleum products containing high wax residues arises from the methylene rocking vibrations due to alignment of n-paraffins into polymeric crystalline structure as in polyethylene (Lynch,et al, 1975). The presence of high waxy residue in NS as suggested by the doublet was confirmed by determining the wax content which was as high as 60 % in NS. The survey of literature (Brunnock, et al, 1968; Adlard, 1972) revealed that among the variety of all crude residues, generally a crude oil sludge discharge from tankers had high wax content. It was therefore presumed, as a first approximation that the spill was probably a crude oil sludge.

The technique of IR spectrophotometry has been extensively used for characterising unknown petroleum product specimens with respect to several known groups (Brown, 1974).In the present study representative IR bands were selected and their ratios were calculated for comparison. Another aim of the study was to critically investigate the usefulness of IR method as a tool for source identification of spilled oil.

For this purpose major crude oils imported through Bombay port were obtained through the courtesy of Bharat Petroleum Corporation Ltd, Bombay. The IR spectra of all these crudes were recorded along with the samples of the spill (Figure 4.25).

In one method the ratios of absorbance bands at 743, 769, 790 and 811 cm^{-1} with the band at 702 cm^{-1} were computed. These are given in Table 4.5. The other set of ratios of bands at 702, 743, 769 and 790 cm^{-1} with the band at 811 cm^{-1} were also calculated and included in Table 4.5. It is evident from Table 4.5 that the various ratios of different crudes are fairly close and the identification of the source on the basis of ratios alone is not unambiguous. It was also observed that the ratios were not always constant and repetition of spectra of crudes and samples indicated marked variations. However, comparison of ratios suggested that the NS was closely

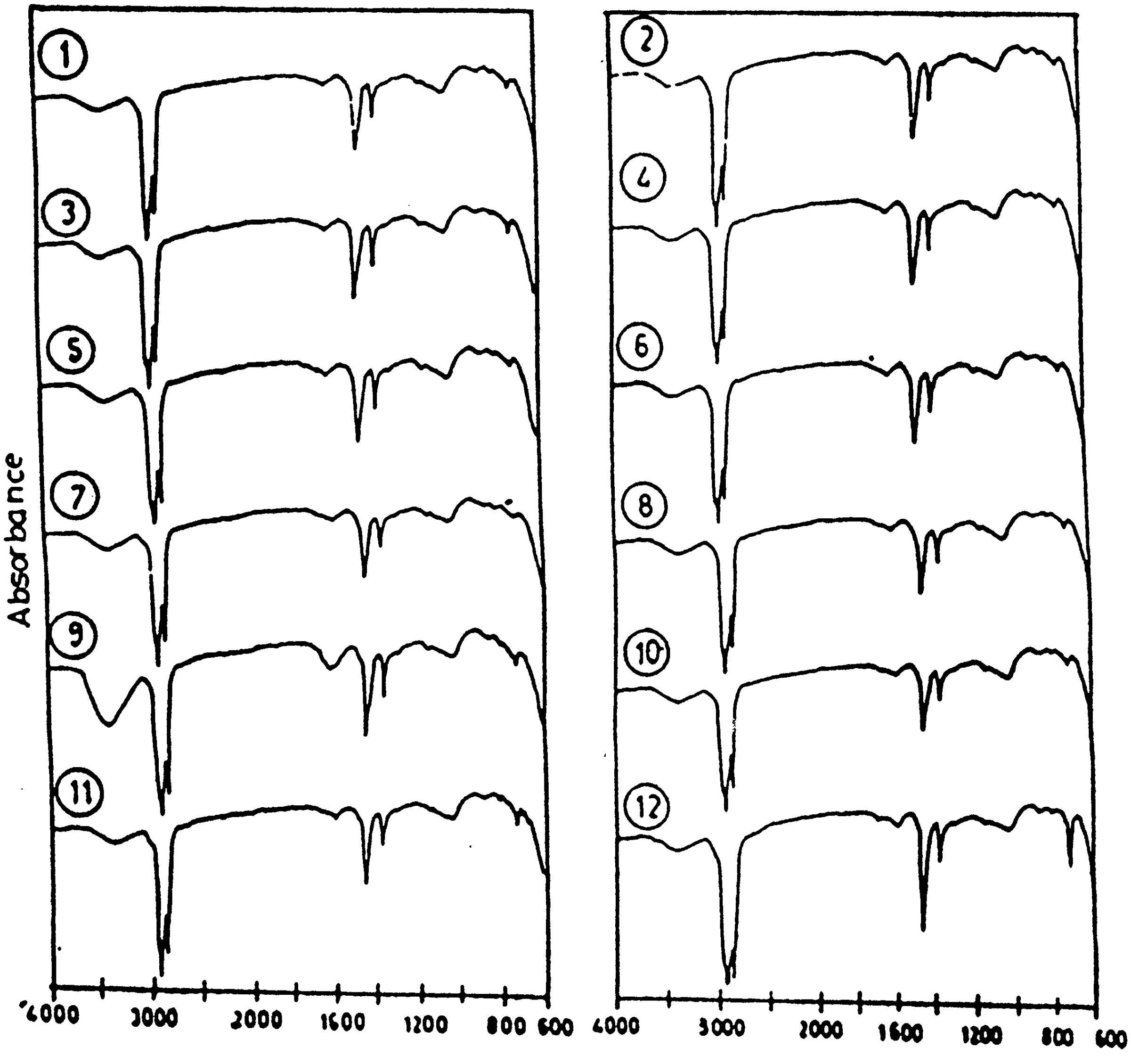

Fig.4.25 : IR spectra of various crude oils (1-11) and purified Napeansea oil spill (12)

Table:4.5 Ratios of IR absorbance

		Wave no (cm^{-1})							
	Type of crude	743/702	769/702	790/702	811/702	702/811	743/811	769/811	790/811
1	UMM shaif	1.6	1.5	1.2	1.4	0.7	1.2	1.1	0.9
2	Arabian mix	2.0	1.9	1.4	1.9	0.5	1.0	1.0	0.8
3	Basrah light	1.5	1.5	1.2	1.5	0.7	1.0	1.0	0.8
4	Arabian heavy	2.1	2.0	1.7	2.0	0.5	1.0	1.0	0.8
5	Iranian light	1.8	1.6	1.5	1.7	0.6	1.1	1.0	0.9
6	Iranian heavy	1.7	1.5	1.2	1.5	0.6	1.1	1.0	0.8
7	Rostam crude	3.5	1.7	1.4	1.7	0.6	1.2	1.0	0.8
8	Kirkuk crude	2.0	2.0	1.7	2.0	0.5	1.0	1.0	0.8
9	Arabian light	1.7	1.5	1.2	1.5	0.7	1.2	1.0	0.8
10	Salman crude	1.7	1.7	1.4	1.5	0.7	1.1	1.1	0.9
11	Bombay high	1.5	1.3	1.0	1.3	0.8	1.2	1.0	0.8
12	Napeansea spil (3-9-1982)	1.2	1.0	0.9	1.0	1.0	1.2	1.0	0.8
13	Bombay High (boiled)	1.5	1.3	1.1	1.5	0.7	1.0	0.8	0.7

comparable with the Bombay High crude. An attempt was also made to compare the ratios of Bombay High residue after removing the lighter fractions at 130 °C for 2 h. This was considered reasonable because the spill was reported on 19 August 1982 and the first sample was obtained after one week during which period considerable weathering was expected. However, the IR ratios of Bombay High residue did not improve the comparison with NS to conclusively assign the origin of the spill to Bombay High crude. In the method of Kawahara (Kawahara, 1976) the ratios of IR bands have also been utilised for the identification of the source of oil spill. This method was also applied in the present case. The results are given in the Table 4.6. It is evident from this table that the ratios of some bands in NS systematically changed in samples collected on different days. Thus for instance, the ratio 1.1 of 720/1375 bands in NS1 decreased to 1.0 in NS3. The ratios of other peaks on the contrary revealed a systematic increase with passage of time (Table 4.6). Once again although definite conclusions were not possible, the ratios were closer to the values obtained for Bombay High crude.

In the method suggested by Brown (Brown, et al; 1974) the intensities of IR absorbance bands were processed as follows

Table:4.6 Ratios of IR absorbance

		Wave no cm^{-1}					
	Type of crude	720/1375	3050/2925	810/1375	810/720	1600/1375	1600/720
1	UMM shaif	1.2	2.1	1.2	1.1	1.3	1.1
2	Arabian mix	1.2	2.4	1.3	1.1	1.3	1.1
3	Basrah light	1.2	2.0	1.3	1.1	1.3	1.1
4	Arabian heavy	1.2	2.5	1.4	1.1	1.4	1.1
5	Iranian light	1.2	2.3	1.3	1.0	1.2	1.0
6	Iranian heavy	1.5	5.9	1.6	1.1	0.6	0.4
7	Rostam crude	1.2	2.3	1.3	1.1	1.2	1.1
8	Kirkuk crude	1.4	8.0	1.6	1.1	1.7	1.2
9	Arabian light	1.2	2.4	1.3	1.1	1.3	1.1
10	Salman crude	1.5	3.7	1.4	1.0	1.4	1.0
11	Bombay high	0.9	0.6	0.7	0.8	0.6	0.7
12	Bombay high	1.1	-	1.3	1.1	1.2	1.0
13	Bombay high residue >135°C	1.1	-	1.1	1.0	1.1	1.0
14	Napeansea spill (3-9-1982)	1.1	0.6	0.6	0.5	0.4	0.4
15	Napeansea spill (15-10-1982)	1.0	0.5	0.6	0.6	0.8	0.8
16	Napeansea spill (10-11-1982)	0.9	-	1.2	1.4	1.2	1.3

(1) Ratios of absoptivity of each known to those of the unknown were calculated.

(2) Average ratios of each known to unknown were calculated,

(3) Ratios were divided by average to make average make one.

(4) Differences between ratios and 1.0 (the average) were calculated.

(5) The number of bands were listed.

The results obtained by applying this method are given in Table 4.7. As evident this method also did not provide conclusive evidence for the identity of the source.

Comparison of UV absorbance and UV fluorescence spectra were also used for the identification of oil spills as attempted by some workers (Bhosle, et al, 1987; Kiceniuk and Williams, 1987). However, they are of only limited use since absorbance bands of crudes are often closely comparable. The UV absorbance and fluorescence spectra of different crudes recorded under identical instrumental conditions along with the NS are illustrated in Figures 4.26 and 4.27. Although these spectra revealed closer resemblance of NS to the Bombay High crude, it was not possible to draw a definite conclusion through these comparisons.

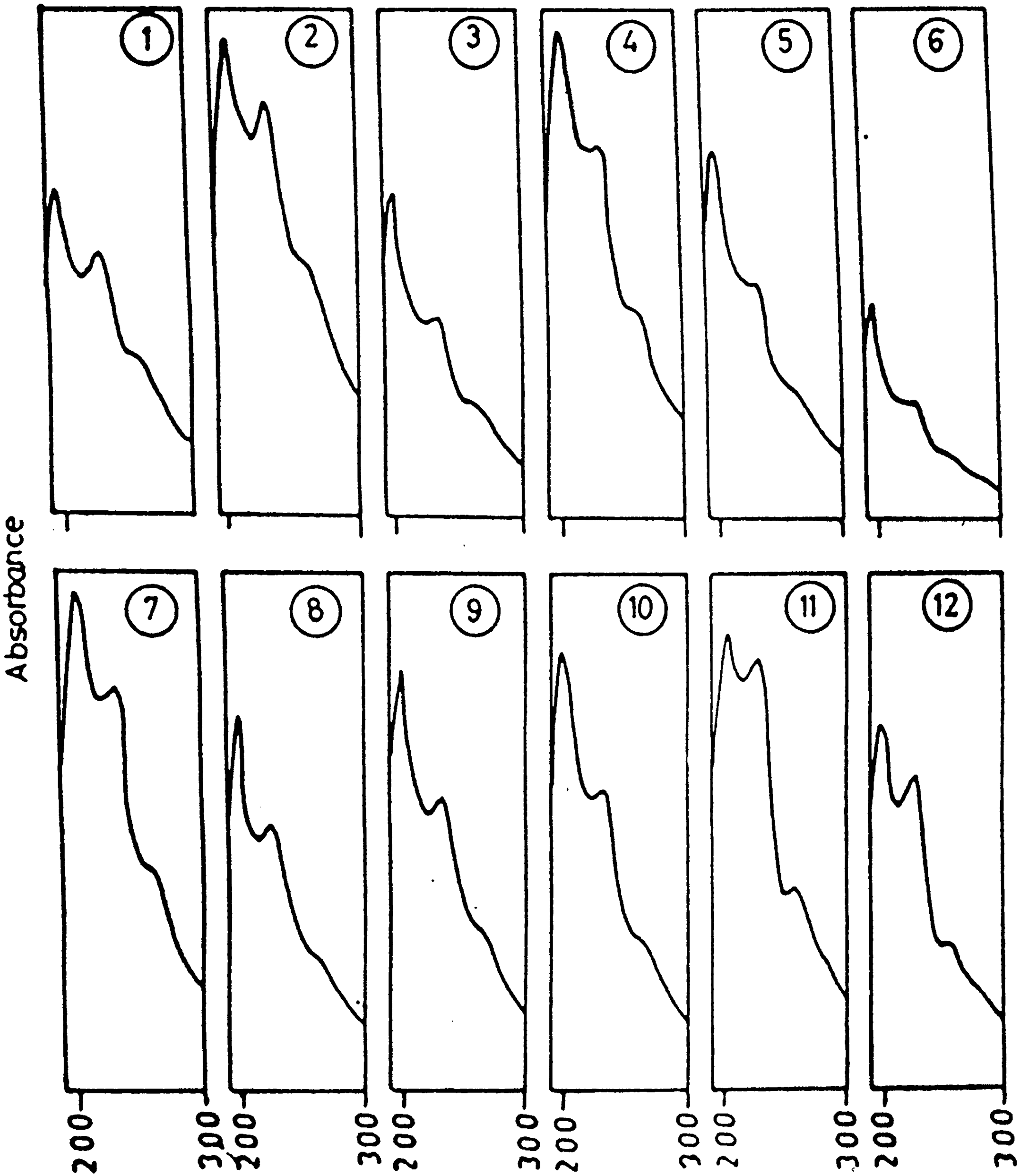

Fig. 4.26 : UV spectra of various crude oils (1-11) and Napeansea oil spill (12).

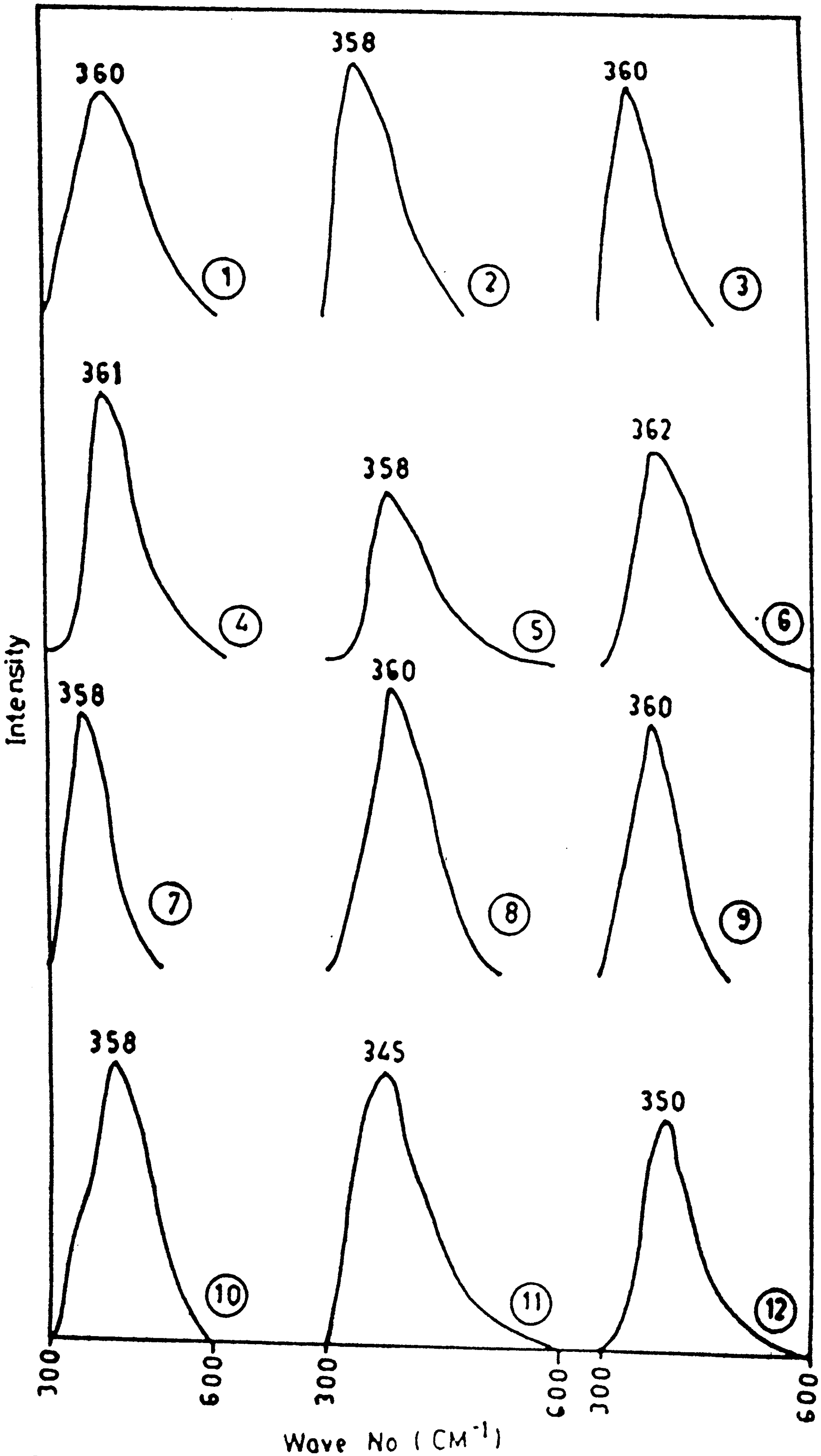

Fig.4.27 : Fl. spectra of various crude oils (1-11) and Napeansea oil spill (12).

Table: 4.7.

	Type of crude	Wave no (cm^{-1})	Abs	$\frac{\text{NS abs}}{\text{std abs}} = x$	mean	$\frac{x}{\text{mean}} = y$	1-y	mean 1-y
1	UMM shaif	722	0.23	3.70	2.53	1.46	-0.46	0.19
		732	0.31	2.58		1.02	-0.02	
		750	0.25	2.24		0.89	0.11	
		812	0.21	2.14		0.85	0.15	
		878	0.16	2.00		0.79	0.21	
2	Arabian mix	722	0.22	3.86	2.87	1.34	-0.34	0.22
		732	0.23	3.49		1.22	-0.22	
		750	0.21	2.62		0.91	0.09	
		812	0.20	2.27		0.79	0.21	
		878	0.15	2.13		0.74	0.26	
3	Basrah light	722	0.22	3.86	2.87	1.34	-0.34	0.23
		732	0.23	3.53		1.23	-0.23	
		750	0.22	2.56		0.89	0.11	
		812	0.20	2.31		0.80	0.20	
		878	0.15	2.11		0.74	0.26	
4	Arabian heavy	722	0.22	3.86	2.38	1.62	-0.62	0.29
		732	0.30	2.65		1.11	-0.11	
		750	0.27	2.03		0.85	0.15	
		812	0.23	1.83		0.76	0.24	
		878	0.21	1.56		0.65	0.35	

Table 4.7 ----- continued

5	Iranian light	722	0.22	3.86	2.13	1.81	-0.81	0.33
		732	0.36	2.20		1.03	-0.03	
		750	0.34	1.61		2.13	0.75	
		812	0.27	1.66		0.75	0.25	
		878	0.23	1.42		0.66	0.34	
6	Iranian heavy	722	0.29	2.98	2.41	1.23	-0.23	0.23
		732	0.25	3.24		1.34	-0.34	
		750	0.25	2.20		0.91	0.09	
		812	0.24	1.87		0.77	0.23	
		878	0.18	1.77		0.73	0.27	
7	Rostam crude	722	0.33	2.58	1.91	1.35	-0.35	0.24
		732	0.34	2.34		1.23	-0.23	
		750	0.33	1.69		0.88	0.12	
		812	0.30	1.52		0.79	0.21	
		878	0.23	1.40		0.73	0.27	
8	Kirkuk crude	722	0.22	3.86	1.91	1.55	-0.55	0.24
		732	0.28	2.83		1.14	-0.14	
		750	0.25	2.20		0.88	0.12	
		812	0.24	1.89		0.76	0.24	
		878	0.19	1,68		0.68	0.32	

Table:4.7 ----continued

9	Arabian light	722	0.29	2.93	2.42	1.21	-0.21	0.19
		732	0.26	3.05		1.26	-0.26	
		750	0.24	2.29		0.94	0.06	
		812	0.22	2.09		0.86	0.14	
		878	0.18	1.77		0.73	0.27	
10	Salman crude	722	0.20	4.25	2.53	1.68	-0.68	0.3
		732	0.30	2.69		1.06	-0.06	
		750	0.28	1.96		0.77	0.23	
		812	0.22	2.05		0.81	0.19	
		878	0.19	1.68		0.66	0.34	
11	Bombay high	722	0.58	1.46	1.22	1.19	-0.19	0.16
		732	0.54	1.47		1.20	-0.20	
		750	0.49	1.12		0.91	0.09	
		812	0.44	1.01		0.82	0.18	
		878	0.31	1.04		0.85	0.15	
12	Napeansea spill (3-9-82) NS	722	0.85					
		732	0.79					
		750	0.55					
		812	0.45					
		878	0.32					

Table:4.7 --- continued

Type of crude		Numbers of bands with a difference less than			
		+ 0.05	+ 0.1	+ 0.25	+ 0.5
1	UMM shaif	2	2	5	5
2	Arabian mix	2	2	4	5
3	Basrah light	2	2	4	5
4	Arabian heavy	2	2	4	5
5	Iranian light	2	2	4	5
6	Iranian heavy	2	3	4	5
7	Rostam crude	2	2	4	5
8	Kirkuk crude	2	2	4	5
9	Arabian light	2	3	4	5
10	Salman crude	2	2	4	5
11	Bombay high	2	2	5	5

GC of crudes and NS were obtained under identical conditions using capillary column and are reported in Figures 4.28-4.33. However, these records were not of much use for identification of the source of the spill, although from the nature of pattern of NS it appeared that the sample had considerably weathered (Figure 4.33) and that the GCs of NS and Bombay high crude were closely comparable.

All crude oils and fuel oils contain trace levels of a number of metals. Of these V and Ni are the only indigenous metals present in a crude oil in significant quantity and the variation before the residue length and the value from these elements is linear over the boiling range upto 200°C. V and Ni content of the spill sample can therefore provide useful additional indication of the source of the spill. Hence, various oils and NS2, NS3, and NS4 were analysed for V, Ni and Fe, the results of which are given in Table 4.8. Unfortunately due to lack of sample, Bombay High crude could not be analysed for V and Ni. The Ni and V contents of some crudes were very low and below the limit of detection of the analytical procedures used. Hence, the ratios could be determined only for a few crudes (Table 4.8). Ni was below the detection limit in NS2, NS3 and NS4 hence comparison of ratios was not possible. It is evident from the Table that NS had high

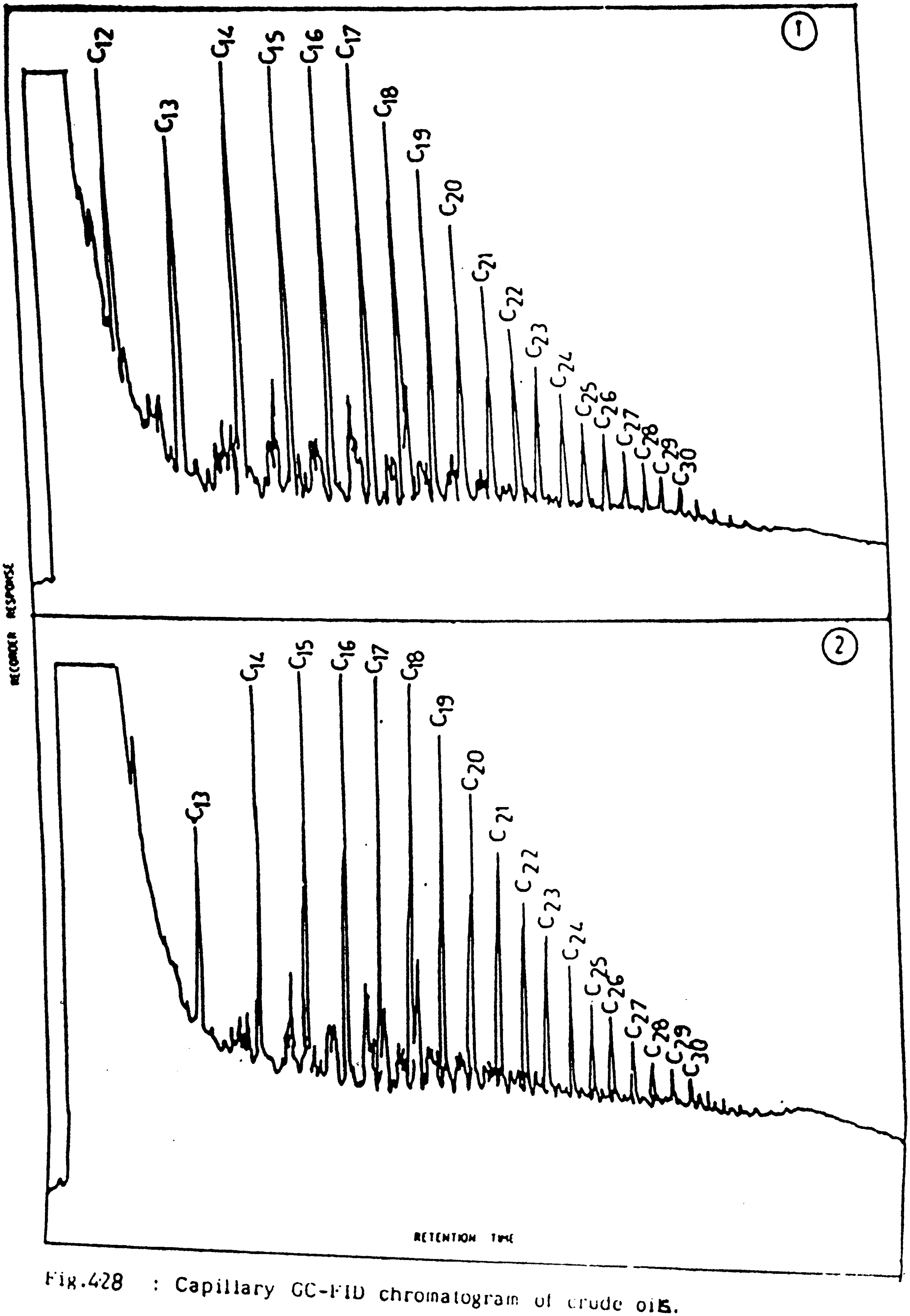

Fig.4.28 : Capillary GC-FID chromatogram of crude oils.

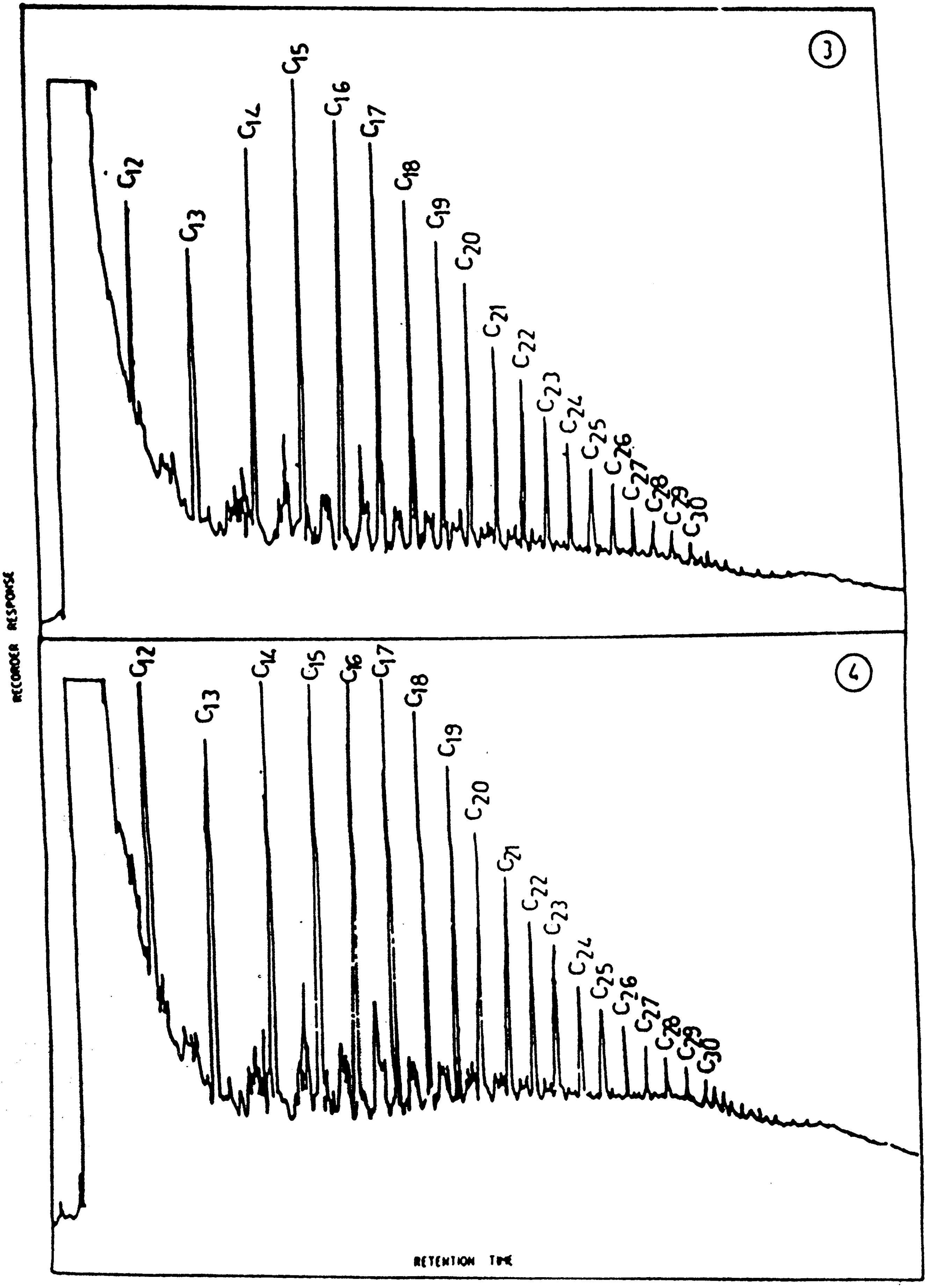

Fig.4.29 : Capillary GC-FID chromatogram of crude oils.

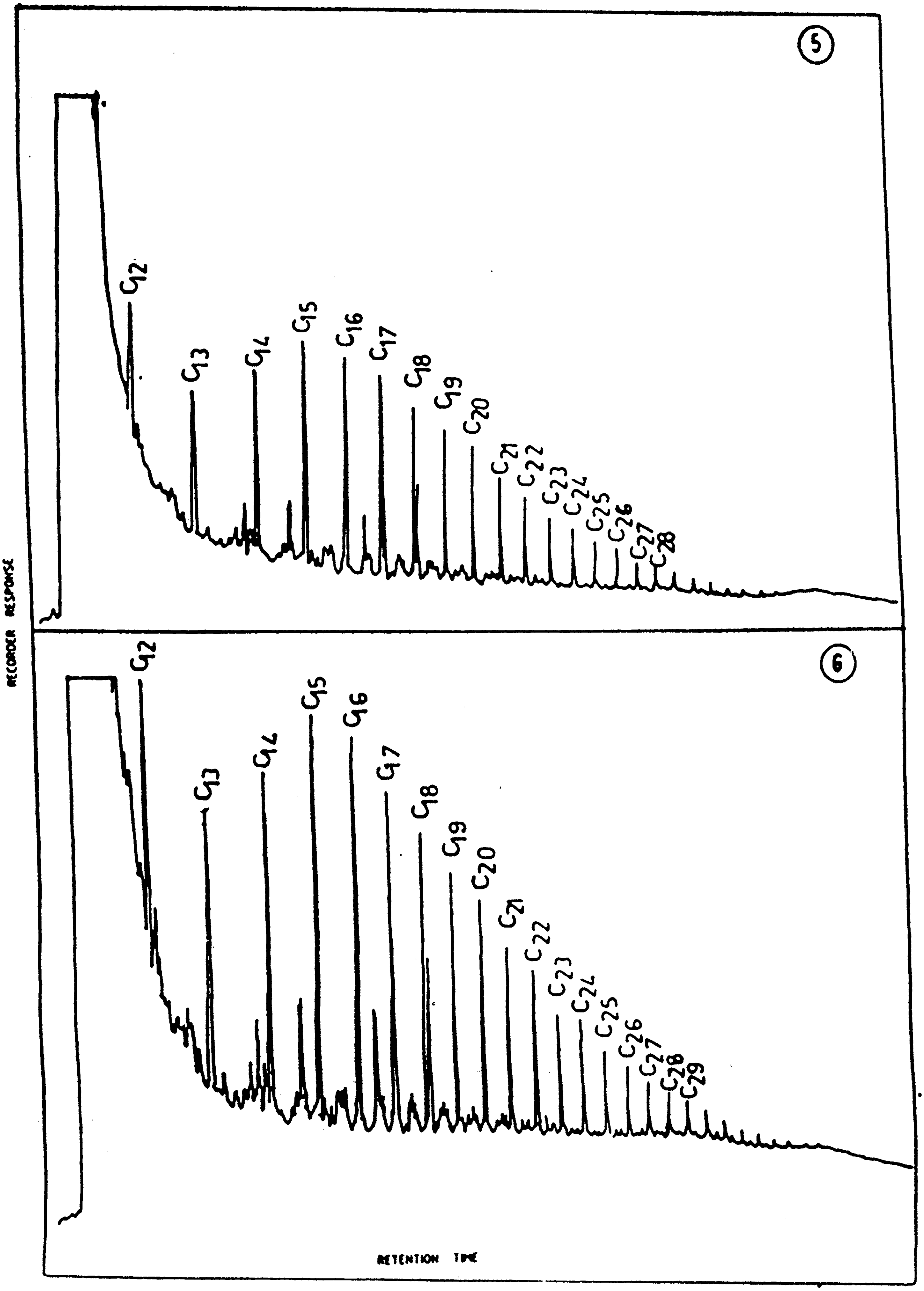

Fig.4·30 : Capillary GC-FID chromatogram of crude oils.

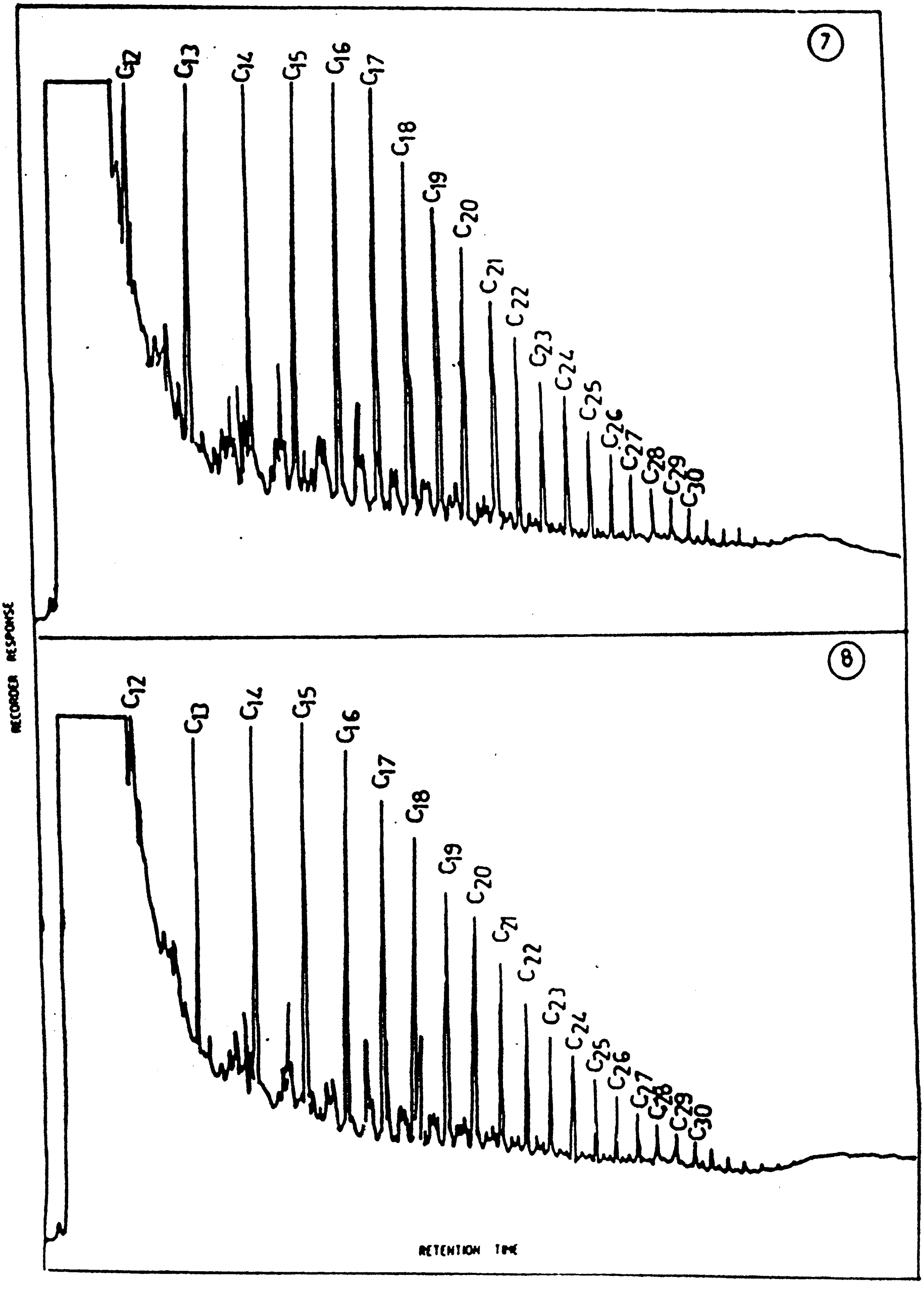

Fig.4·31 : Capillary GC-FID chromatogram of crude oils.

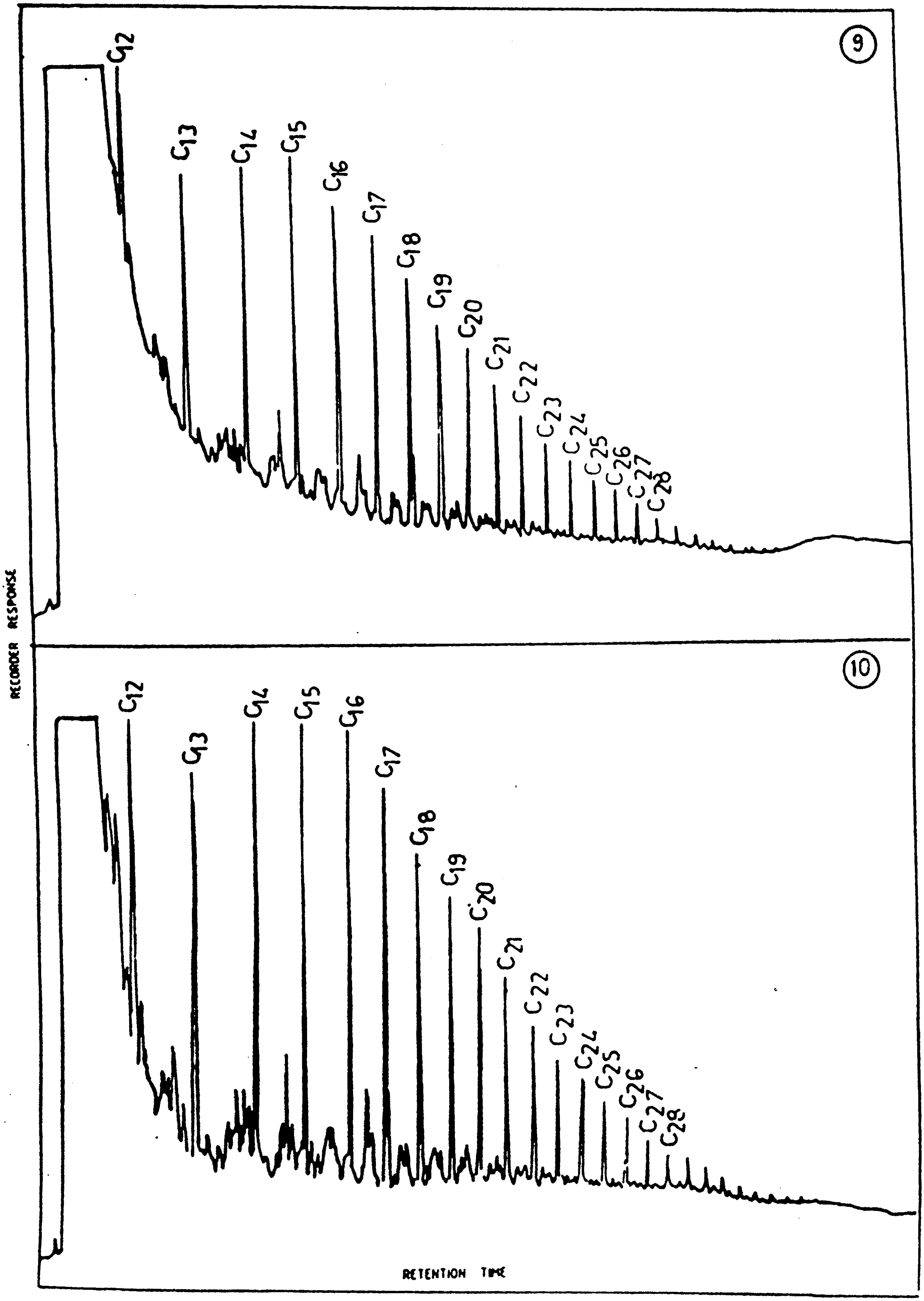

Fig.4·32 : Capillary GC-FID chromatogram of crude oils.

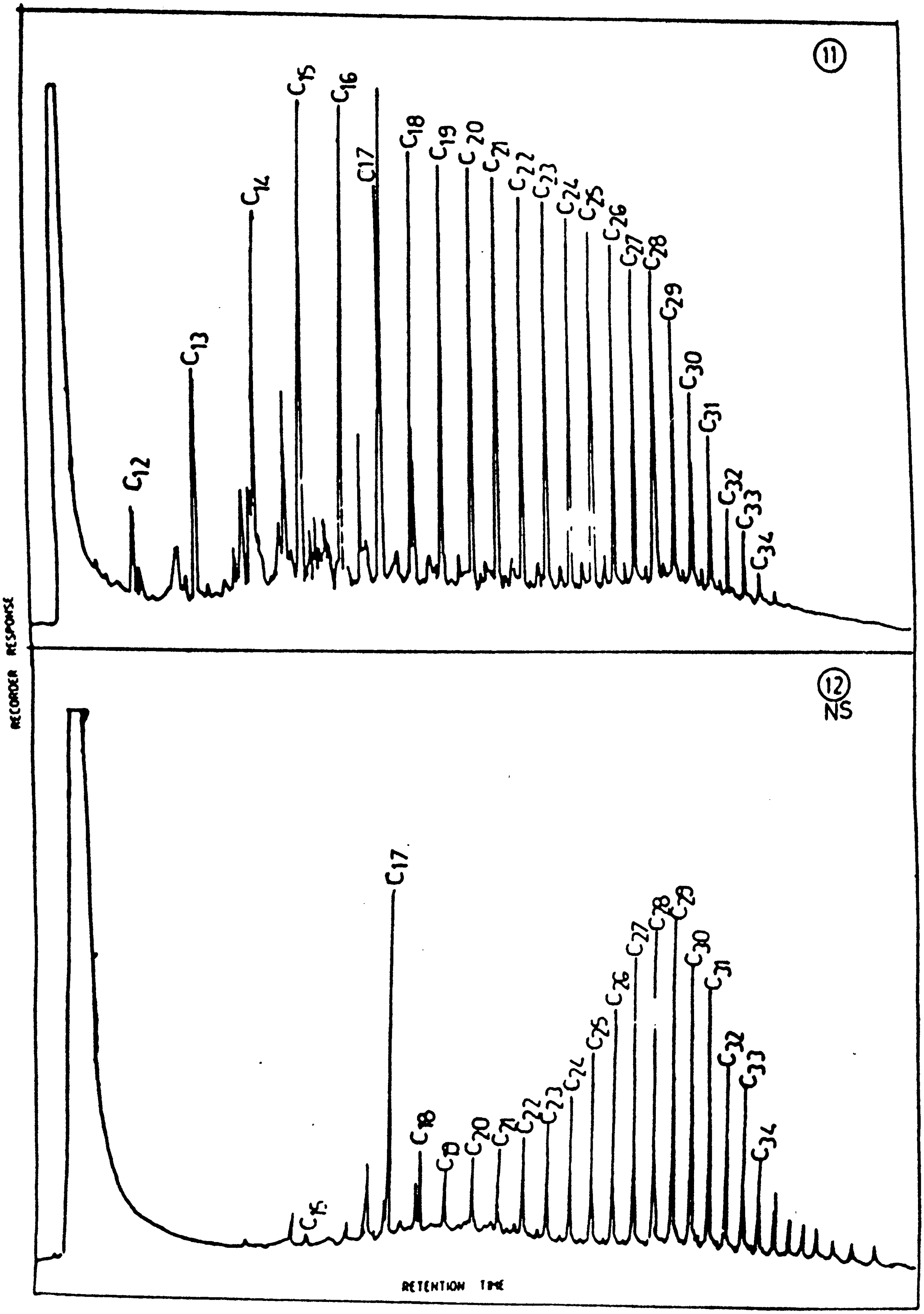

Fig.433 : Capillary GC-FID chromatogram of crude oils.

Table:4.8 Concentration of V, Ni, Fe and V/Ni ratios in different types of crudes.

Type of crude		V (ppm)	Ni (ppm)	Fe (ppm)	V/Ni
1	UMM shaif	4	ND	3	-
2	Arabian mix	8	8	5	1
3	Basrah light	21	7	2	3
4	Arabian heavy	32	13	5	2.5
5	Iranian light	33	11	3	3
6	Iranian heavy	58	9	2	6.4
7	Rostam crude	ND	6	4	-
8	Kirkuk crude	11	14	2	0.8
9	Arabian light	ND	ND	4	-
10	Salman crude	2	7	4	0.3
11	Bombay high	-	-	-	-
12	Napeansea spill (23-9-1982) NS2	48	ND	30	-
13	Napeansea spill (15-10-1982) NS3	28	ND	115	-
14	Napeansea spill (10-11-1982) NS4	40	ND	113	-

ND - not detectable.

concentration of Fe as compared to crude oils . For proper comparison the Fe content of crude should be adequately normalised since direct crude oils were used for analysis. If it was presumed that 50 % of the hydrocarbons had evaporated from NS prior to collection, Fe content should be doubled for comparison. It is evident that even if the concentrations are doubled the NS still maintains abnormal concentration of Fe . It has been reported that tanker sludge is generally expected to be contaminated with Fe due to its contact with metal in the bunker. Hence, it appeared that the spill was a tanker sludge. The high wax content of 60 % and the doublet in IR spectra between 730 and 720 cm^{-1} also supported this view.

Following the procedure of Kawahara and Ballinger (Figure 4.34) for the identification of the category of spills, the IR transmittance ratios of bands at 810 and at 1375 cm^{-1} for lubricating oils (Nos. 30 and 40), various crude oils, commercial white wax and NS were plotted as a function of the IR transmittance ratios of bands at 810 and at 720 cm^{-1} . NS lies far away from lubricating and crude oils and falls closer to commercial wax because of its high wax content.

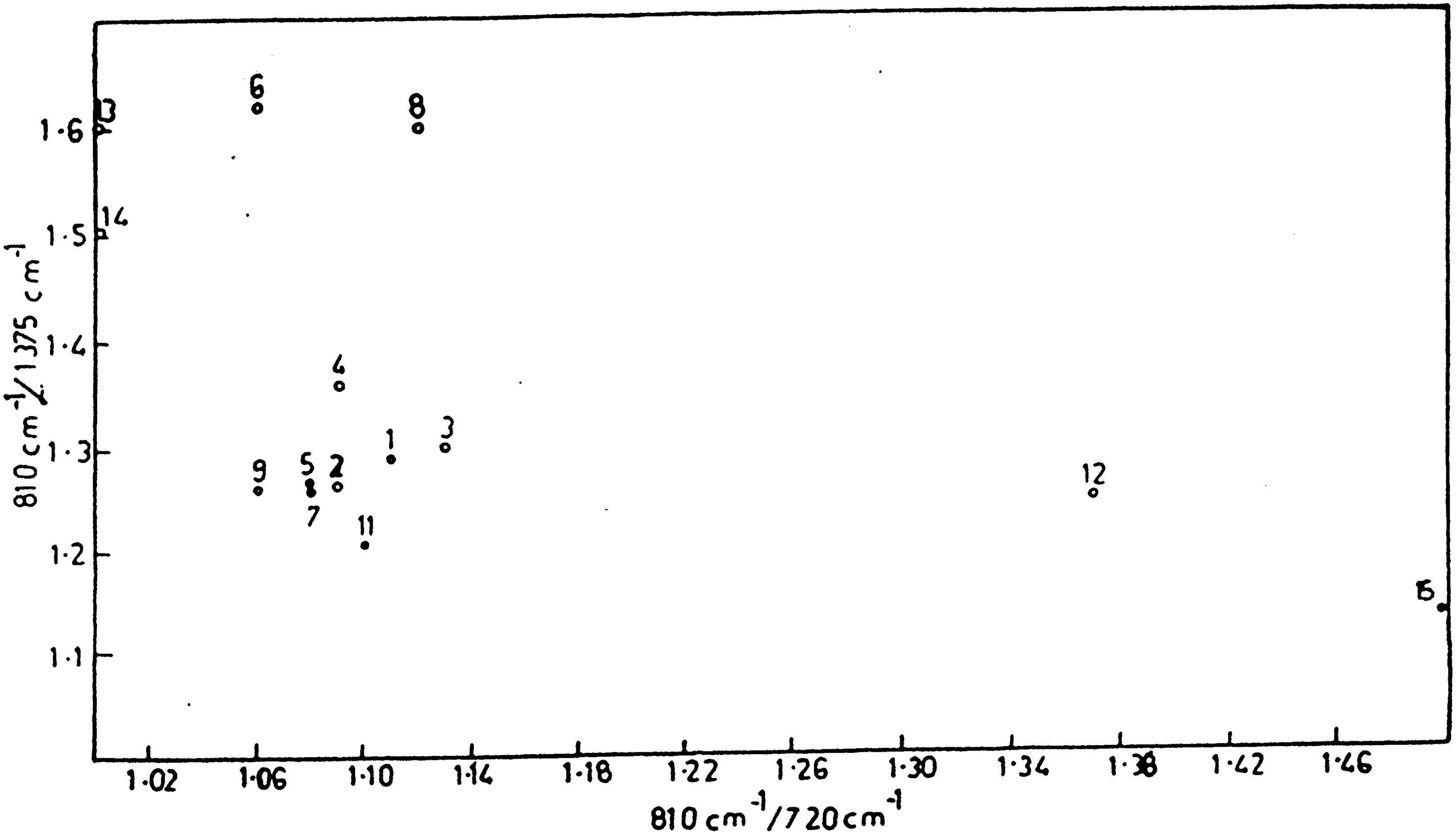

Fig.434 : Relation of various crude oils (1-11), Neapeansea oil spill (12), Lubricating oil No.30 (13), Lubricating oil No.40 (14) and commercial white wax (15) involving two ratios of IR.

As IR absorptions are very sensitive to even minor variations in the composition, the preparation of equivalent sample for matching is extremely difficult. Hence, the spectra of Bombay High crude and NS which was weathered could not be compared directly.

During the present investigation, rapid settling of sludge of Bombay High crude on the walls and the bottom of the container was observed. The virgin oil showed a weak doublet at 730-720 cm^{-1} in the IR spectra (Figure 4.25), the intensity of which varied after storing for a few days. Typically, the settled sludge yielded a stronger doublet in 730-720 cm^{-1} region (Figure 4.35) while it almost disappeared in the IR of the liquid portion.

From the foregoing discussion, it is considered that the spill was from a tanker sludge and the tanker was carrying Bombay High crude prior to the discharge of sludge. The spill did not seem to have originated from the oil well blowout for the following reasons. Studies on the probable movement of a hypothetical oil spill in Bombay High region have revealed (Gouveia and Kurup, 1977) that the oil would take 7 to 22 days (May to September) to reach the shore depending on the onshore component of the alongshore currents. Hence, any spill originating from Bombay High

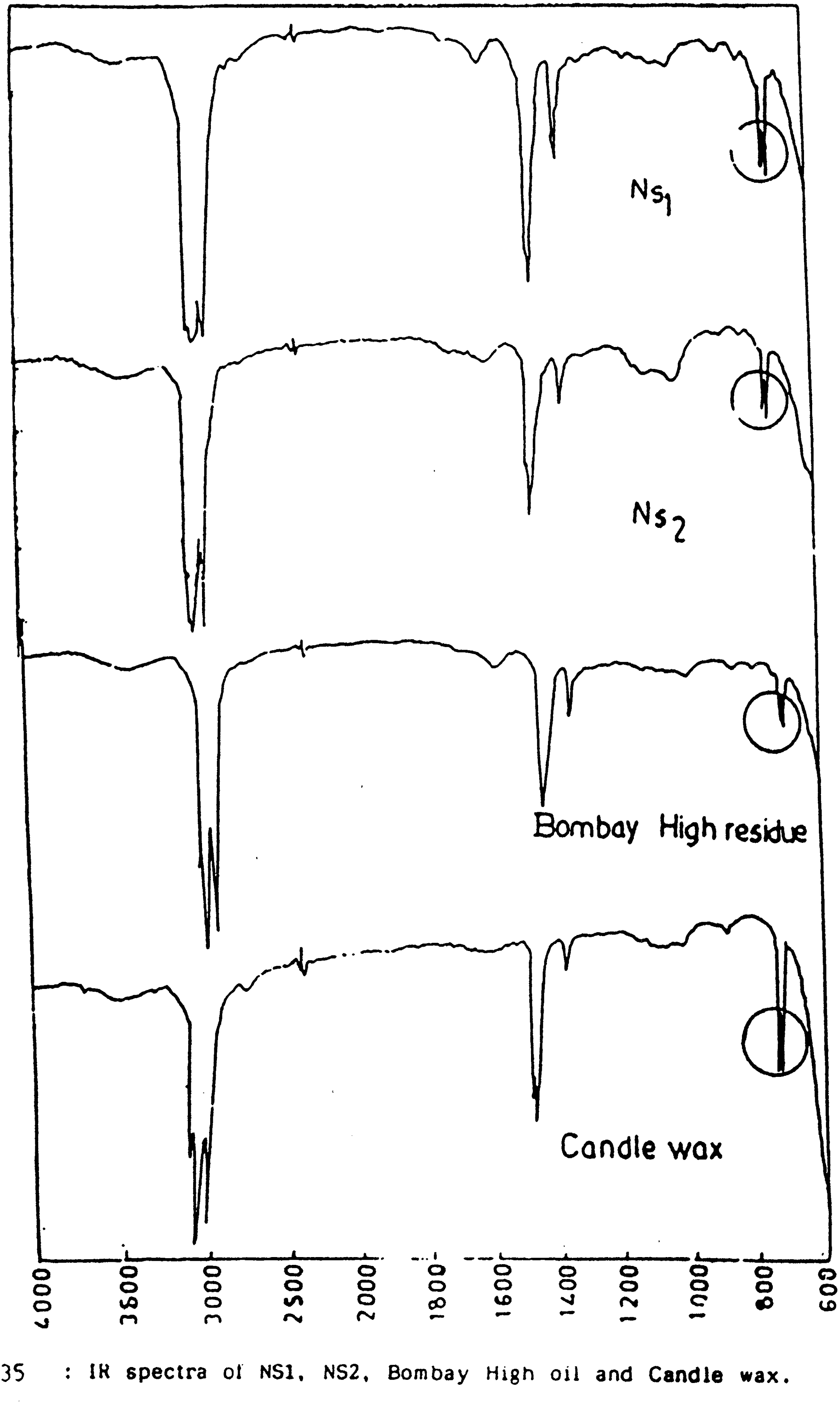

Fig.4·35 : IR spectra of NS1, NS2, Bombay High oil and Candle wax.

would be highly emulsified due to rough sea conditions during monsoon (June-August) and not likely to contain low boiling components (upto 250^0c) as the same were expected to have lost within a few days of the spill. Chemical changes were also expected due to the photo-oxidation of hydrocarbons transforming them into polar compounds containing hydroxyl and carbonyl groups. The sample of NS had lower ranges of boiling point (135^0c) and the absorptions around 1800-1700 cm^{-1} in the IR spectra pertaining to carbonyl compounds were either very weak or absent.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Unprecedented population growth and industrial development around Bombay Harbour and Thana Creek (Together termed as Bay) coupled with heavy port traffic and other port activities have imposed considerable strain on the aquatic environmental quality of the Bay. Studies undertaken in recent years to delineate effects of anthropogenic impacts on water quality, sediment quality and biological characteristics have revealed marked increase in nutrient concentrations, depletion in DO and enhancement of BOD in localised pockets, increase of levels of some toxic metals particularly in sediment, abnormally high phytoplankton production and high microbial contamination in water as well as the sediment.

Among the anthropogenic pollutants, petroleum hydrocarbons and their products (PHC) could be easily considered among the major contaminant in the Bay resulting from the fluxes associated with the wastewater from refineries set-up during the nineteen fifties, which until recently was only partially treated, the bilge discharges, the accidental spillages during loading and unloading operations and the domestic and industrial wastewaters from a wide variety of industries mainly discharging in the Thana Creek. A small fraction of the high volume of wastewater released into the Ulhas River is also considered to be flowing into the Thana Creek through its northern arm under favourable tidal conditions. Concentrations of dissolved and dispersed PHC in the water column were however surprisingly low and it was presumed that the high suspended load resulting from tidal dispersion of fine bed sediment into the water column of the Bay effectively scavenged the PHC, thus transporting them to the bed during tidal slacks when the suspended load gets partially settled. However, information regarding the extent of sediment contamination by PHC was largely lacking until the investigations reported in this thesis were undertaken. Water quality at a location in Bombay Harbour was also monitored to delineate changes if any with respect to the previously determined base line. The prevailing water quality of Bombay High a major offshore oil field, is also discussed in the thesis. An oil spill which occurred on the west coast of Bombay on 19 August 1982 was studied to identify its probable source.

PHC in Bay sediments

The surficial Bay sediment by virtue of its high adsorption capacity associated with fine grained silt-clay fraction that generally exceeded 80 % probably scavenged the PHC entering the Bay accounting for low PHC levels in the water column but eventually enriching the bed sediment. It was therefore not surprising to find (Table 2) high and variable concentrations of unsaponifiable residue (712-4456 $\mu g\ g^{-1}$ wet wt) in the surface sediment of the Bay. Markedly higher concentration in sediments along the western shores (1, 2, 6, 7, 8, 9, 10 and 11) and a decreasing trend towards the eastern bank (3, 4, 5, 12, 14 and 15) indicating that the wastewater from refineries was a major contributor to the sediment PHC which masked the fluxes through a variety of industrial discharges along the eastern shore. Evidently, the highest concentration of PHC was associated with the sediment from Sewree mud-flat in the discharge area of Mahul Creek through which a portion of the refinery wastewater is channeled to the Thana Creek.

Major unloading operation of crude oil in Bombay Harbour is generally confined to Butcher Island. The sediment in the vicinity, however, contained relatively low concentrations (461-556 $\mu g\ g^{-1}$ wet wt) of PHC perhaps because of prevailing strong tidal currents in the area which suppressed deposition of PHC enriched suspended load.

Aliphatic hydrocarbons constituted 30 to 40 % of the sediment extracts containing nonpolar lipids from nearshore stations and decreased to 10 to 20 % in the sediment at the midstream region (Table 2). Aliphatic and aromatic hydrocarbons and hydroxy compounds correlated very well with sediment total organic carbon (TOC) with correlation coefficients above 0.8. Such a correlation of fatty acids with TOC was however poor. Infrared spectra of nonpolar lipids indicated the presence of alkanes, cycloalkanes, monosubstituted aliphatic hydrocarbons, ketones and polyunsaturated hydrocarbons. Several sharp peaks overlying an unresolved envelope of complex mixture of hydrocarbons observed in the gas chromatograms of nonpolar lipids were typical of the weathered petroleum crude.

Geochemical record of oil pollution history of the Bay was evolved by analysing sediment cores a few of which were previously dated. Thus, the sedimentation rate of 0.74 cm yr^{-1} for a 100 cm core from Thana Creek (station 8) had the signature of the depositional environment of the past 135 years. Hence, the bottom section of this core represented the sediment deposited in 1848 when there was no import of crude oil and there were no industries discharging into the Bay. Likewise, the core from the coastal waters of Bombay (station G 2595) preserved the pollution history of the depositional environment of about 200 years. Though organic carbon and total phosphorous revealed only marginal enrichment in some instances, the PHC distinctly increased in the surficial sections. Thus, the two cores from the western portion of Thana Creek (station 1 and 8) had PHC concentration of 420-1180 μg g^{-1} (wet wt) in the top 10 cm of the sediment which sharply decreased to 70-200 µg g-1 (wet wt) at 20 cm depth followed by a gradual decrease to attain levels of 40-60 µg g^{-1} (wet wt) in the bottom sections (Figure 4.20). The cores obtained from Dharamtar Creek (station 19 and 20) which opens along the eastern shores of the harbour, though retains a similar profile, has very low concentrations of PHC with a maximum of 2.7 µg g^{-1} (wet wt) centered around 7 cm depth. It was therefore evident that the high anthropogenic influx of PHC to the Bay was effectively contained within the system and its influence was negligible in the adjacent Dharamtar Creek. The subsurface maxima between 5 and 10 cm in majority of the cores could perhaps, be signatures of some episodic event about 10 years ago.

Water quality of Bombay harbour - Thana creek (Bay)

Release of substantial qualities of domestic and industrial wastewater through point discharges resulted in enhanced concentrations of nitrate and phosphate but their assimilation to increase primary production was hindered perhaps by limitation of light penetration due to high suspended load. Average DO was generally above 4 mg l^{-1} but subnormal values were occasionally recorded probably due to the localised impact of the oxidizable waste. The BOD was below 2 mg l^{-1} indicating that the organic matter was effectively assimilated within the harbour.

Comparison of water quality of present

investigation with data-base established through extensive monitoring of the bay during 1976-77 indicated absence of gross changes over the years though most water quality parameters varied considerably over a tidal cycle.

Water quality of Bombay High

Water quality of Bombay High area evaluated during 1976 prior to the commencement of offshore oil exploitation was compared with the data obtained during 1982 and 1988. It was evident that the water quality had generally remained close to the baseline though the trend indicated probable decrease in concentration of DO. The PHC in water was low and compared well with the values observed for other regions of the Arabian Sea.

Oil spill on Bombay coast

A Spill that drifted and oiled the shore of the Napean Sea area (South Bombay) on 19 August 1982 attracted considerable attention by virtue of its occurrence within a few days from the well-blowout in the Bombay High region. It was feared that the spill had originated from the oil that was presumed to be spilled during the blow-out. Hence, in an attempt to identify the source, the spill was characterised through infrared, ultraviolet, proton magnetic resonance, fluorescence and chemical analyses through frequently employed methods for the identification of the source of the spill reported in the literature to facilitate reliable comparisons samples of several crude oils being imported through Bombay Port were also investigated through identical procedures. It was found that the reported spectroscopic methods for probable source identification gave ambiguous results and hence not reliable. However, application of combination of methods suggested that the spill probably was a tanker sludge and that the tanker was carrying Bombay High crude prior to discharge of sludge.

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