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MESA Special Report



Hydrocarbons in the Ocean

Edward P. Myers

Charles G. Gunnerson

April 1976

**U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
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Brown, R. A., T. D. Searl, and E. G. Prestridge (1975)

Measurement of volatile and nonvolatile hydrocarbons in selected areas of the Atlantic ocean. Report prepared for the U.S. Dept. of Commerce Maritime Administration (also issued as a NOAA/MESA Special Report).

Monaghan, P. H., D. E. Brandon, R. A. Brown, T. D. Searle, and J. J. Elliott (1974)

Measurement and interpretation of nonvolatile hydrocarbons in the ocean. Part I. Measurements in Atlantic, Mediterranean, Gulf of Mexico and Persian Gulf. Report prepared for the U.S. Dept. of Commerce Maritime Administration (also issued as a NOAA/MESA Special Report).

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Marine EcoSystems Analysis Program
Boulder, Colorado

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HYDROCARBONS IN THE OCEAN

Edward P. Myers and Charles G. Gunnerson

ABSTRACT

Measurements of hydrocarbons in ocean waters throughout the world are presented to supply baseline information. The data indicate that most surface and near-surface waters have from 1 to 10 parts per billion total hydrocarbons. Both biogenic and petroleum hydrocarbons appear to be ubiquitous, with some indications of more petroleum hydrocarbons in coastal waters and shipping lanes.

1. INTRODUCTION

A concern has evolved during recent years regarding the fate and effects of petroleum hydrocarbons in the world's oceans. Such concern is prompted by the increasing additions of these substances to the ocean environment, an environment that is an intimate part of the world ecosystem, and recognized as having finite carrying or assimilative capacities. The fact that the time scales involved in natural ocean processes are quite large, ranging from months to decades for coastal waters and from one hundred to one hundred million years for open ocean waters (24), intensifies the problem. This means that non-degradable fractions of toxic inputs to the oceans can remain for extremely long periods of time before finding their respective sinks. In such a system, it becomes imperative to detect small adverse changes from some baseline state if corrective action is to be taken.

Hydrocarbon measurements in ocean waters have been compiled in this report to indicate their current global distribution and to provide baseline information for the purpose of present and future comparisons. Most of these data were obtained through studies funded by the U.S. Maritime Administration (MARAD), the Marine Ecosystems Analysis (MESA) Program of the National Oceanic and Atmospheric Administration (NOAA), and the Exxon Corporation.

Samples were collected from Exxon tankers traveling on major tanker routes and from research vessels associated with the National Science Foundation's GEOSECS (Geochemical Section Lines) cruises in the Atlantic and Pacific.

Measurements were performed by the Exxon Research and Engineering Company in two phases:

Phase I. A study of hydrocarbons in waters of the Atlantic, Gulf of Mexico, Caribbean, Mediterranean, and Persian Gulf with support from MARAD and Exxon Corporation (10, 41).

Phase II. A study of hydrocarbons in waters of the Pacific, jointly supported by MARAD and NOAA (9).

During Phase I, surface and subsurface (-10 meters) samples were taken along tanker routes between the Gulf of Mexico and New York, between Caribbean ports and New York, between Libyan ports and other Mediterranean ports, and between the Persian Gulf and northern European ports. Surface, subsurface, and water column profile samples were also taken in the North and South Atlantic by scientific personnel associated with the GEOSECS cruises.

During Phase II, surface and subsurface samples were obtained on tanker routes between San Francisco and Cook Inlet, between San Francisco and Vancouver, B.C., between San Francisco and the Panama Canal, and between San Francisco and Singapore. Surface, subsurface, and water column profile samples were again provided from open Pacific waters through the courtesy of GEOSECS personnel aboard the R/V MELVILLE. This report also includes other measurements from the literature on hydrocarbons in near coastal and open ocean waters.

The referenced reports (9, 10, and 41) for Phases I and II of the Exxon studies are provided as micro-fiche inside the back cover of this report. In addition to containing the original data, these reports discuss sampling, preservation, and analytical techniques. ■

1.1 Sources of Petroleum Hydrocarbons in the Marine Environment

Inputs of petroleum hydrocarbons to the oceans are estimated to be about six million metric tons annually (43). Table 1 shows that 35 percent of this input is attributable to losses incident to the marine transportation of petroleum (Fig. 1). Other sources include river runoff (26 percent), natural seeps (10 percent), atmospheric inputs (10 percent), nonrefining industrial wastes (5 percent), urban runoff (5 per-

cent), municipal wastes (5 percent), coastal refineries (3 percent), and offshore production (1 percent). In order of decreasing contributions, the release of petroleum hydrocarbons associated with ocean transport activities is due to ballast water and tank washings, bilge water, dry docking activities, tanker accidents, non-tanker accidents, and terminal operations.

The return voyage of a tanker requires that the vessel carry seawater as ballast so that stability and control of the vessel are maintained. During the ballast voyage, residual oil from the previous loaded voyage mixes with the seawater ballast. In the past this oil, which can amount to about 0.4 percent of the loaded volume (43,44), and ballast water mixture was dumped at sea just before entering port. Although this procedure is still practiced, approximately 80 percent of tankers now use the Load On Top (LOT) procedure that essentially allows for gravity separation of entrained oil from seawater ballast. The separation is conducted in a slop-tank, and the separated seawater is pumped into the ocean before entering port. In port, fresh oil is taken on and is also "loaded-on-top" of the remaining oil in the slop-tank. Despite the large petroleum savings incurred through LOT, losses occur. Efficiency of the

procedure is dependent upon smooth seas and on trips taking enough time for separation to occur. Even under the best of conditions the wastewater contains 100 ppm of oil (46). The annual petroleum discharges due to ballast waters and tank washings are estimated at 0.3 million tons for LOT tankers and at 0.8 million tons for non-LOT tankers (43).

Tanker discharges of petroleum are also caused by machinery and pipe leakages to bilge waters. Unless a vessel is equipped with an oil-water separator, oily bilge waters are pumped to an onshore receptacle or, more frequently, directly to sea. The latter input of petroleum hydrocarbons is estimated to be about 0.5 million tons per year.

The input of hydrocarbons due to natural geological seepage is estimated from 0.2 to 1 million tons annually, with a best estimate of 0.6 million tons. The locations of known natural seeps and potential seep areas are shown in Fig. 2 (55). Also shown are the locations of potential inputs associated with major river systems, and the locations of offshore oil fields (39). A comparison of these locations with major water masses and current systems of the oceans can be made by examination of Figs. 3 and 4. ■

Table 1: Budget of petroleum hydrocarbons introduced into the oceans (from ref. 43)

Source	Input Rate (mta)* Best Estimate	Probable Range	Relative Percentage
Natural seeps	0.6	0.2-1.0	9.8
Offshore production	0.08	0.08-0.15	1.3
Transportation			
LOT tankers	0.31	0.15-0.4	5.1
Non-LOT tankers	0.77	0.65-1.0	12.6
Dry docking	0.25	0.2-0.3	4.1
Terminal operations	0.003	0.0015-0.005	0.1
Bilges bunkering	0.5	0.4-0.7	8.2
Tanker accidents	0.2	0.12-0.25	3.3
Nontanker accidents	0.1	0.02-0.15	1.6
Coastal refineries	0.2	0.2-0.3	3.3
Atmosphere	0.6	0.4-0.8	9.8
Coastal municipal wastes	0.3	—	4.9
Coastal, Nonrefining, industrial wastes	0.3	—	4.9
Urban runoff	0.3	0.1-0.5	4.9
River runoff	1.6	—	26.0
TOTAL	6.113		100

* million metric tons annually

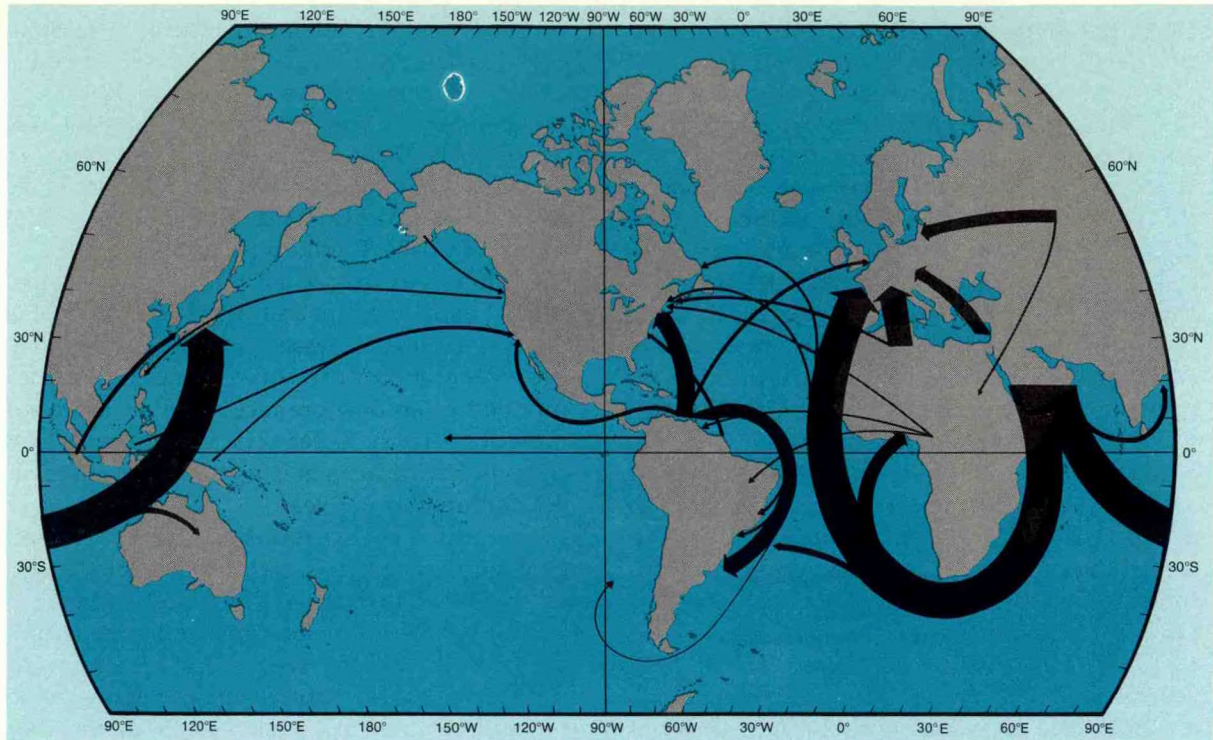


Figure 1. International Flow of Petroleum, 1971.

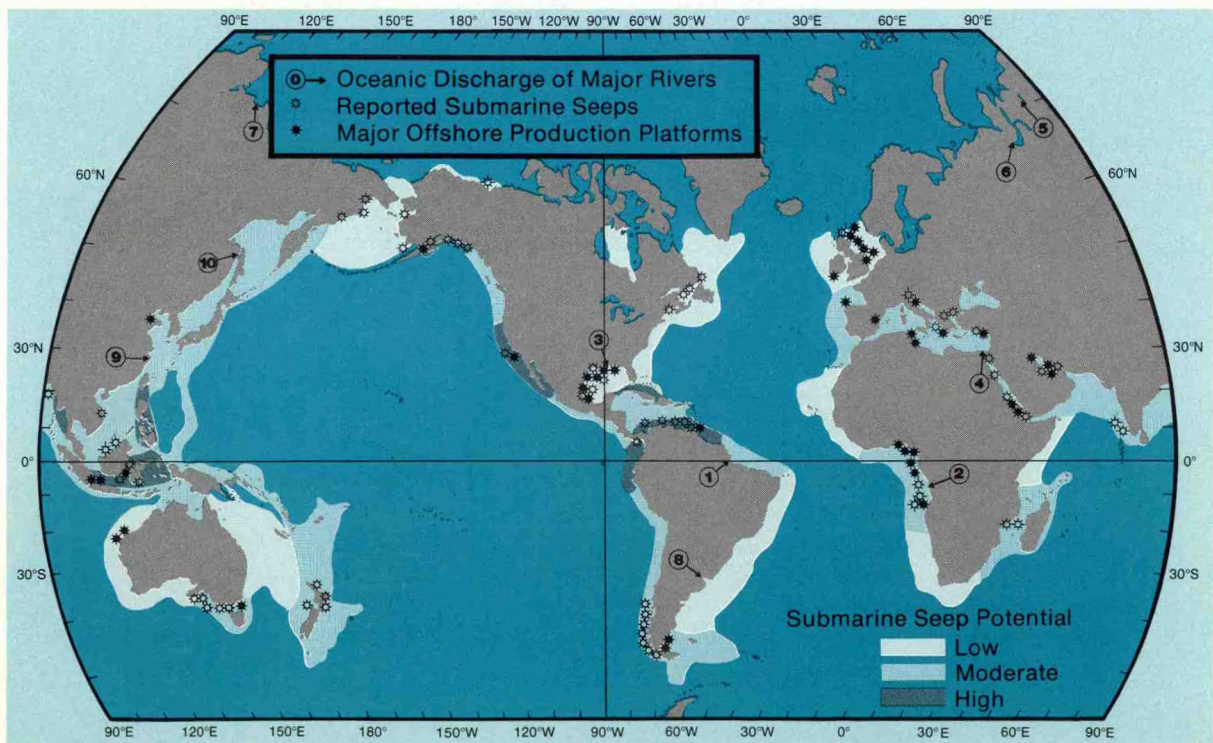


Figure 2. Locations of Potential Sources of Hydrocarbons Due to Seepage and River Inputs for Major Rivers: (1) Amazon, (2) Congo, (3) Mississippi, (4) Nile, (5) Yenisei, (6) Ob, (7) Lena, (8) Parana, (9) Yangtze, and (10) Amur.

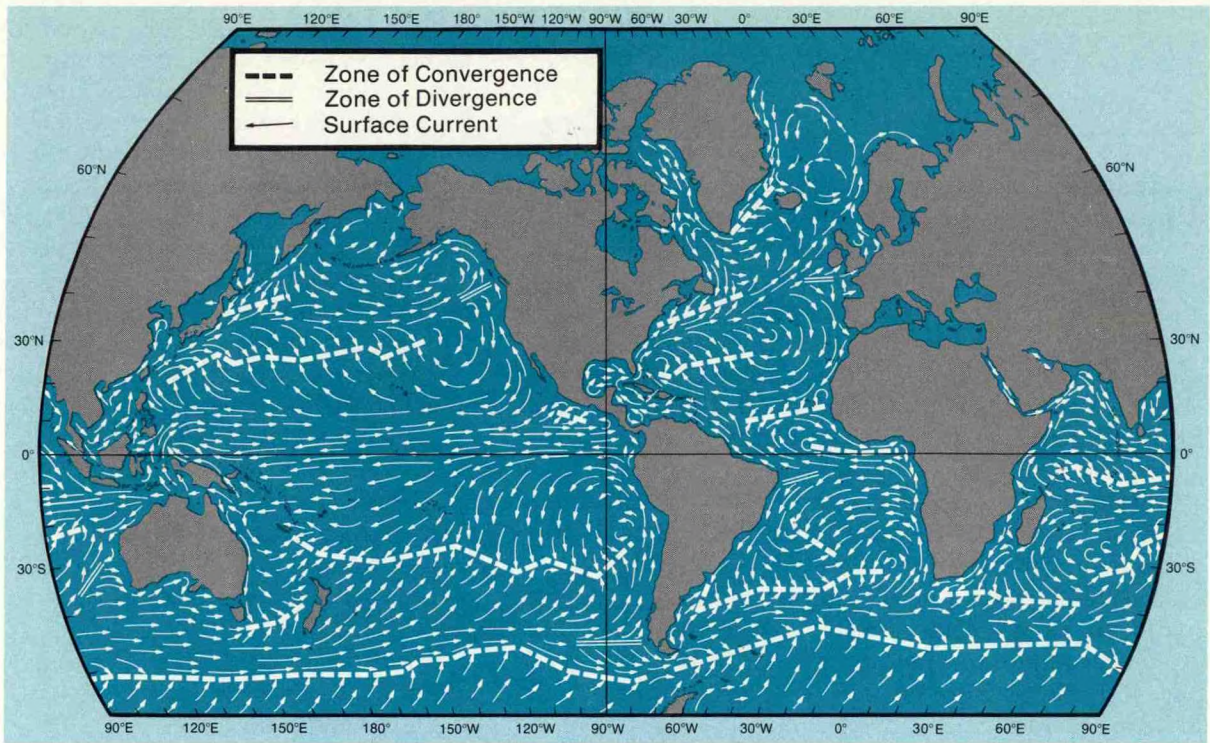


Figure 3. Surface Ocean Currents—Northern Summer. (from ref. 22)

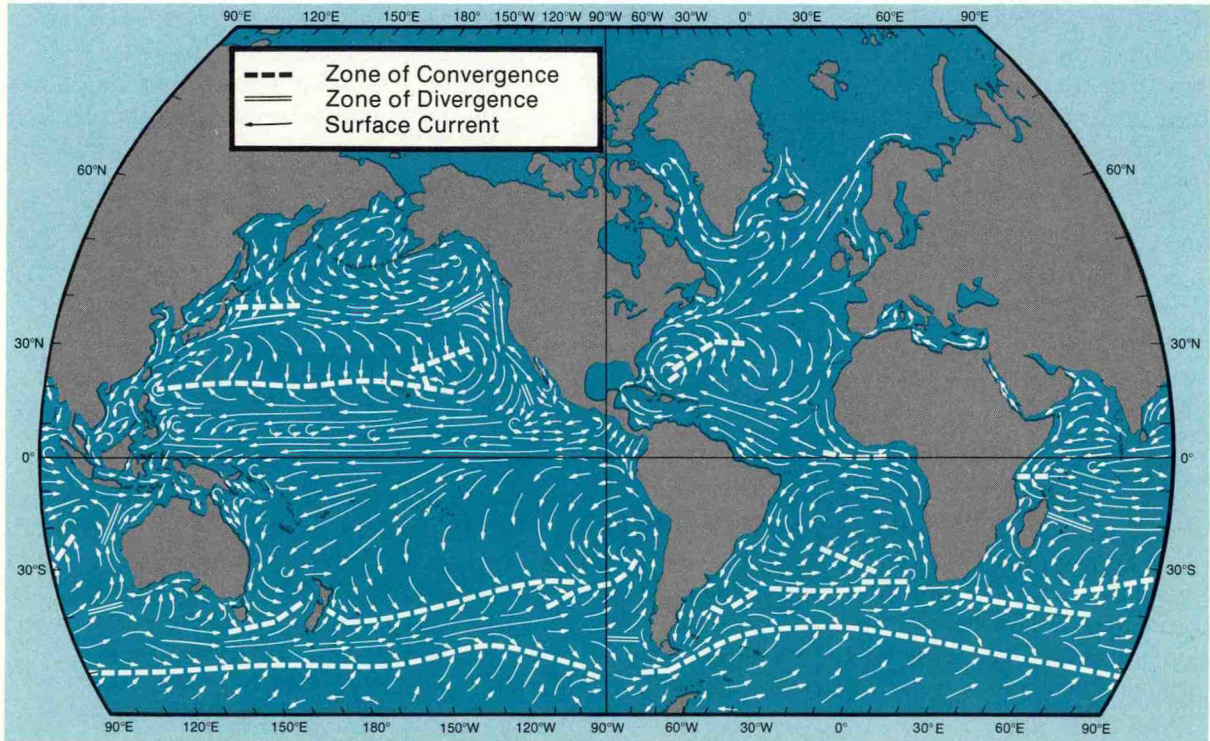


Figure 4. Surface Ocean Currents—Northern Winter. (from ref. 22)

1.2 Characteristics of Petroleum and Biogenic Hydrocarbons

Crude oils are complex mixtures of thousands of pure hydrocarbons, trace amounts of metals (primarily nickel, vanadium, and iron) complexed with organic chelates and porphyrins and with other organic compounds containing sulfur, nitrogen, and oxygen (48). The principal classes of hydrocarbons in crude petroleum are alkanes, cycloalkanes, and aromatics. The alkanes, commonly referred to as paraffins, are saturated straight or branched chain hydrocarbons having the general formula C_nH_{2n+2} . Cycloalkanes are saturated ring structures of the general formula C_nH_{2n} which may have alkyl groups substituted for certain hydrogen atoms. The aromatic hydrocarbons are unsaturated compounds primarily composed of one or more benzene ring structures that may also have alkyl substitutions.

Olefins, a fourth general class of hydrocarbons, are unsaturated compounds with two or fewer hydrogen atoms per carbon atom. Although they are found only in trace amounts in crude petroleum, they may account for as much as 30 percent of the weight of refined petroleum products such as gasoline.

Natural plant and animal hydrocarbons are ubiquitous in both terrestrial and aquatic environments. Normal alkanes in the C_{25} to C_{35} range predominate in plant waxes where molecules of odd numbers of carbon are in excess of those of even numbers by a factor of ten or more (32). Although there is a tendency of biogenic hydrocarbons to be characterized by an abundance of odd-carbon types (19), this is not a sufficient criterion for identifying a source as non-petroleum. For example, the sulfate-reducing marine bacteria *Desulfovibrio desulfuricans* produces a broad spectrum of unresolved hydrocarbons in the range of C_{16} to C_{25} with an even distribution of n-paraffins in the range of C_{25} to C_{35} (16). N-paraffins have also been detected in benthic, pelagic, and planktonic algae as well as in mixed plankton (14). The most frequently occurring n-paraffins were n- C_{15} and n- C_{17} .

The quantitative separation of hydrocarbons found in the ocean into those due to petroleum sources and those due to biogenic sources is nearly impossible with the present analytical

state-of-the-art. Part of the problem is due to the ubiquitous occurrence of plant and animal hydrocarbons and part is due to a lack of information regarding the eventual weathered products of both petroleum and biogenic hydrocarbons. Despite this, a number of approaches have been used to assess the relative presence of petroleum hydrocarbons in ocean samples. Farrington *et al.* (21) used the presence of the unresolved complex mixture signal in the hydrocarbon gas chromatograms as the initial criterion for the presence of petroleum contamination of marine samples. Lytle *et al.* (37) noted that a relatively high hydrocarbon to lipid ratio is very indicative of crude oils. Lipids are organic substances extractable by a nonpolar solvent such as carbon tetrachloride.

A National Academy of Sciences report (43) listed four characteristics considered indicative of petroleum sources:

- (1) Petroleum is a complex mixture of hydrocarbons with a wide range of molecular weights and structures.
- (2) Petroleum contains several homologous series (such as n-paraffins) with adjacent members present in nearly the same amounts.
- (3) Petroleum contains a greater variety of cycloalkanes and aromatics. Also the occurrence of alkyl-substituted ring compounds, characteristic of petroleum, has not been reported in marine organisms.
- (4) Petroleum contains naphtho-aromatic hydrocarbons that also have not been reported for marine organisms. ■

1.3 Fates of Petroleum Hydrocarbons in Marine Waters

The potential fates of petroleum hydrocarbons in the marine environment are numerous and dependent on the physical, chemical, and biological characteristics of the ambient environment and on the physical and chemical properties of the petroleum. Currents, tides, waves, and winds essentially control the advective and dispersive fate of petroleum in the ocean. The turbulence induced by these forces also prompts the formation of stable water-in-oil emulsions containing from 30 to 80 percent water. In the presence of natural or artificial emulsifiers, ocean turbulence can also induce

the formation of oil-in-water emulsions consisting of small droplets of oil dispersed in seawater. Such small oil droplets in water are more susceptible to weathering, adsorption to suspended organic and inorganic matter, consumption by zooplankton with incorporation of the oil into fecal pellets, and to hydraulic transport (23, 45). By adhering to suspended sediments of greater density, oil droplets dispersed in water may also find their way into bottom waters and sediments (15).

The most likely chemical reactions that hydrocarbons may undergo in the ocean waters are oxidative reactions that are photochemically or thermally initiated (45). The photo-oxidation of hydrocarbons is due primarily to ultraviolet light (UV) at wavelengths below 350 millimicrons (26, 45). Observations of the photo-oxidation of crude oils indicate that aromatics are preferentially degraded, followed by branched-chain paraffins and straight-chain paraffins (26). It is difficult to separate these reactions from other oxidative hydrocarbon reactions that occur in the ocean environment. Furthermore, the relative roles of these processes at any point in time depends on the chemical composition of the oil and its state of degradation as well as on environmental factors (5). Generally, under natural conditions, such reactions are estimated to be relatively slow (5, 26).

The solubility of hydrocarbons in pure water at room temperature varies from the parts-per-million (ppm) range for n-paraffins to the parts-per-thousand (ppt) range for some aromatics, olefins, and acetylenes (38). Factors that enhance the solubility are decreasing molecular weight and the presence of branching or ring formation. The solubility of hydrocarbons in seawater may be decreased somewhat from that in fresh water due to a salting-out effect (50). However, the presence of dissolved organic matter in seawater may act to increase the solubilities of n-paraffins by a similar magnitude (6).

Evaporation or weathering results in the greatest initial change in composition of most spilled oils. Examining the rates of evaporation of five *in situ* ocean spills of a South Louisiana crude, Harrison *et al.* (27) concluded that aliphatics and aromatics with lower boiling points disappear in an order of hours. Estimates of evaporative losses from a light Arabian crude spilled on August 9, 1974, in the

Strait of Magellan from the supertanker METULA ranged from 15 to 35 percent (3). Considering that evaporation losses are normally limited to those fractions boiling below 300°C (11), the preceding estimates are consistent with the physical properties of such crudes (44).

The capability of microorganisms to metabolize petroleum hydrocarbon fractions is well established. However, the chemical composition of an oil is a controlling factor with regard to the types of bacteria that will metabolize it. As a consequence, the microbial species composition that is attacking an oil changes as degradation proceeds (53). The extent of microbial degradation of crude oils is generally the same for the different temperatures occurring in ocean waters; however, the rate of microbial utilization is slightly slower in colder waters (1, 54). Lag periods before the onset of significant microbial activity are also observed in colder waters and may be due to reduced evaporation rates of specific volatile toxic fractions that, when removed, allow microbial degradation to proceed (1). Other factors possibly limiting microbial utilization of oil include the availability of nutrients and oxygen (2).

The biological fate of petroleum hydrocarbons due to uptake from waters or to predation is one of the severest consequences of petroleum contamination because of its toxic nature. The toxic effects of petroleum are numerous and include the mechanical clogging or blanketing ability of adsorbed oil, the resulting irritation to mucous membranes and other surfaces active in respiratory exchange and in the exchange of salts and water, the interference with chemical and neurological senses, and the alteration of ecological balances such as predator-prey and reproductive relationships (20, 44).

Marine organisms assimilate petroleum hydrocarbons by adsorption of dissolved or adhering fractions, by the ingestion of oil particles, and by the ingestion of other particles or prey that have had contact with hydrocarbons. Lee *et al.* (34) showed experimentally that the pathways of hydrocarbons in several fish species included uptake across gill membranes, metabolism in the liver, transfer of hydrocarbons and metabolites to the bile, and excretion via the urine or feces. It has been demonstrated on both invertebrates and vertebrates that the uptake rate of hydrocarbons by

exposed organisms is quite rapid, with trace quantities detectable in the order of minutes to hours (34, 35, 49).

This brief discussion of the potential fates of petroleum hydrocarbons in ocean waters emphasizes the fact that the pathways of these substances are varied and complex. Although much is known about the individual processes, there is still a great deal to learn regarding the relative roles and details of these processes in natural conditions and their long-term effects. ■

2. RESULTS

A large volume of data was obtained through the ocean hydrocarbon studies sponsored by MARAD, NOAA, and Exxon Corporation. The sampling locations are shown on Fig. 5. Other previous measurements of hydrocarbon levels in ocean water have been few and limited to certain locations.

2.1 Extractable Organic Matter and Nonvolatile Hydrocarbons

The measured spatial distributions of extractable organic matter (EO) and nonvolatile hydrocarbons (HC) are presented in Figs. 6 through 9. Since a relatively high density of data was obtained along the west and east coasts of the United States, only representative data for these waters is depicted.

Several generalizations can be made regarding the spatial distributions of EO and HC:

- (1) Levels of EO and HC in surface and subsurface waters are higher in coastal waters.
- (2) The subsurface (-3 and -10 meters) measurements of EO and HC in open ocean waters tend to be somewhat lower than detected in surface waters; however, this tendency was not as evident in the sampled coastal waters.
- (3) Measurements of HC tend to indicate higher levels in the Atlantic and Mediterranean (particularly along the tanker routes) than in the Pacific.

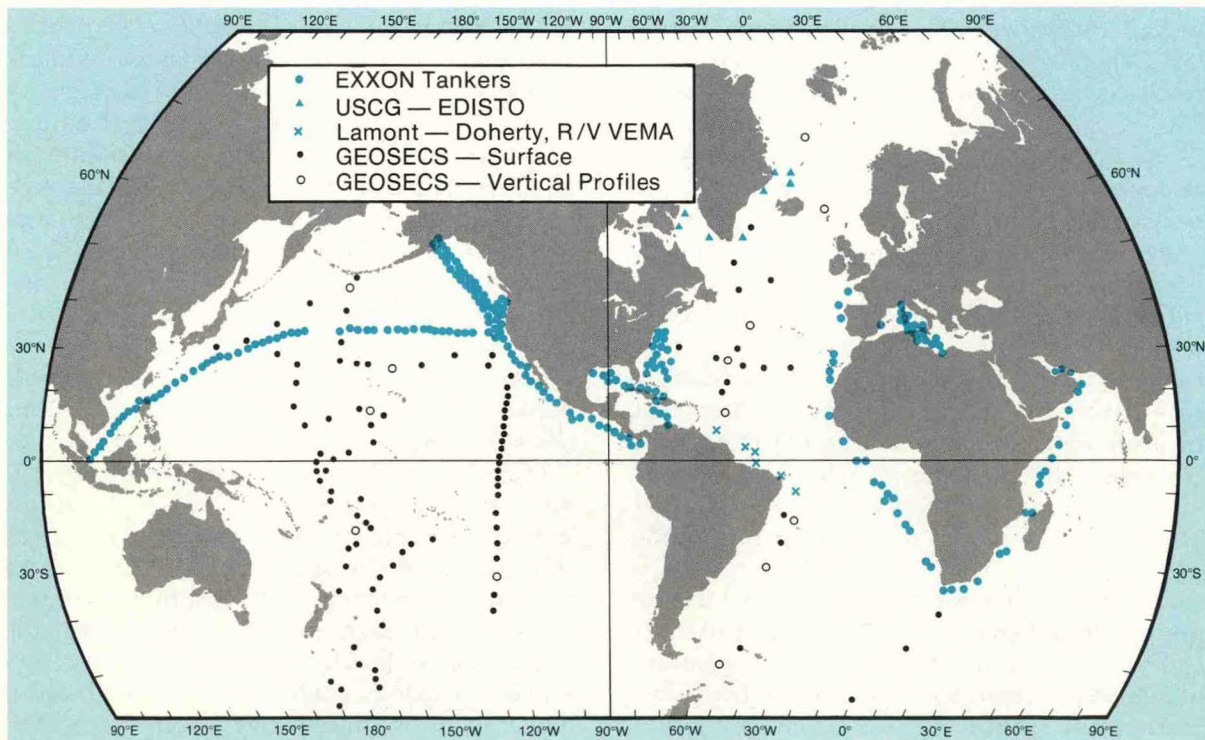


Figure 5. Sample Locations in Exxon Studies.

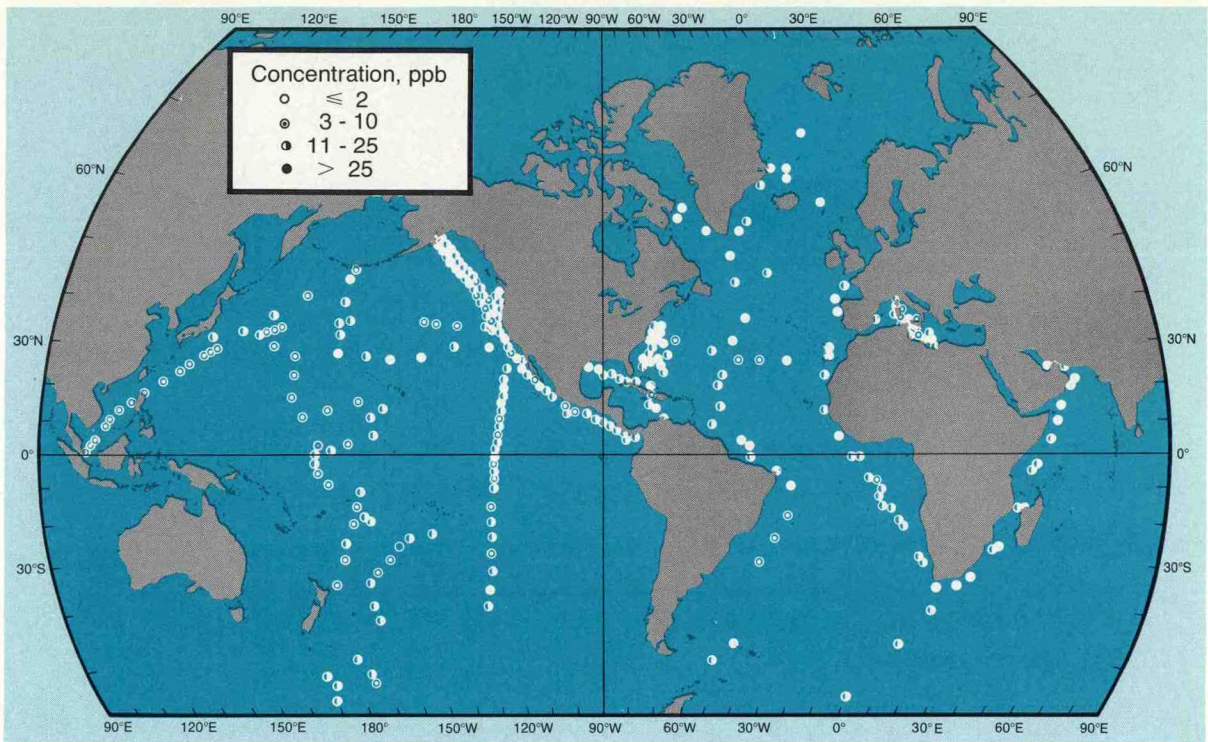


Figure 6. Extractable Organics in Surface Waters.

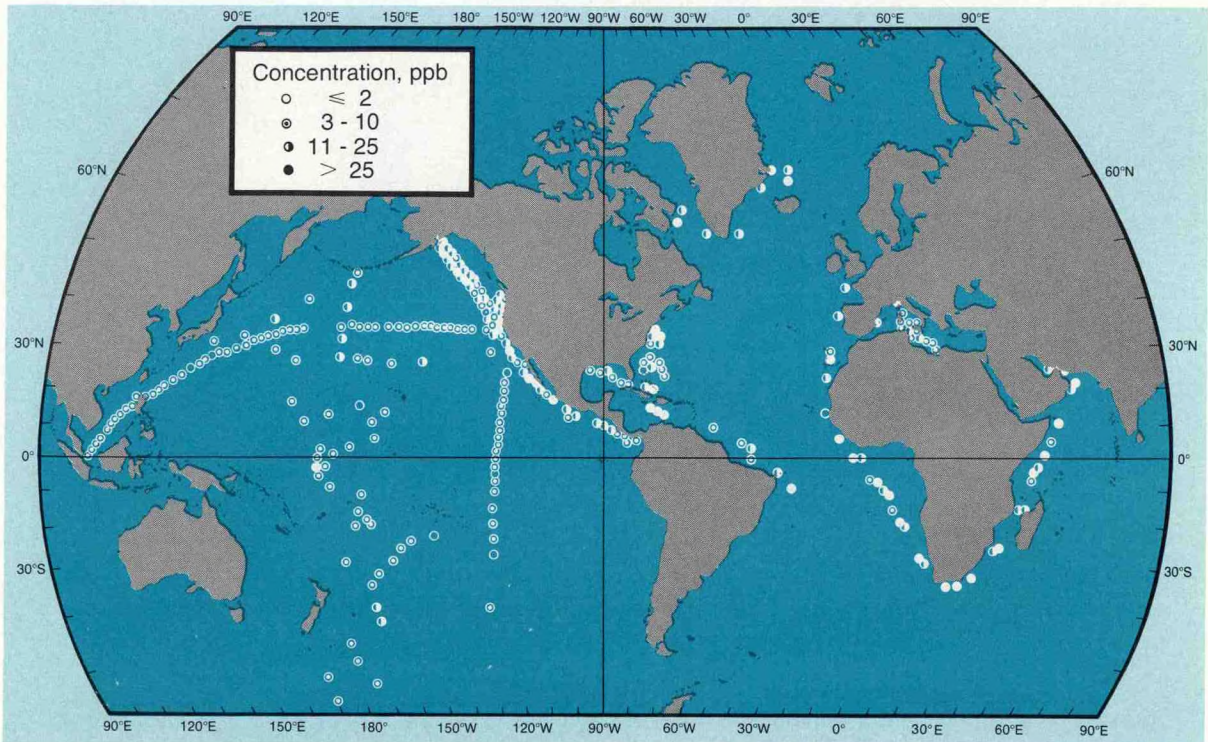


Figure 7. Extractable Organics in Subsurface Waters.

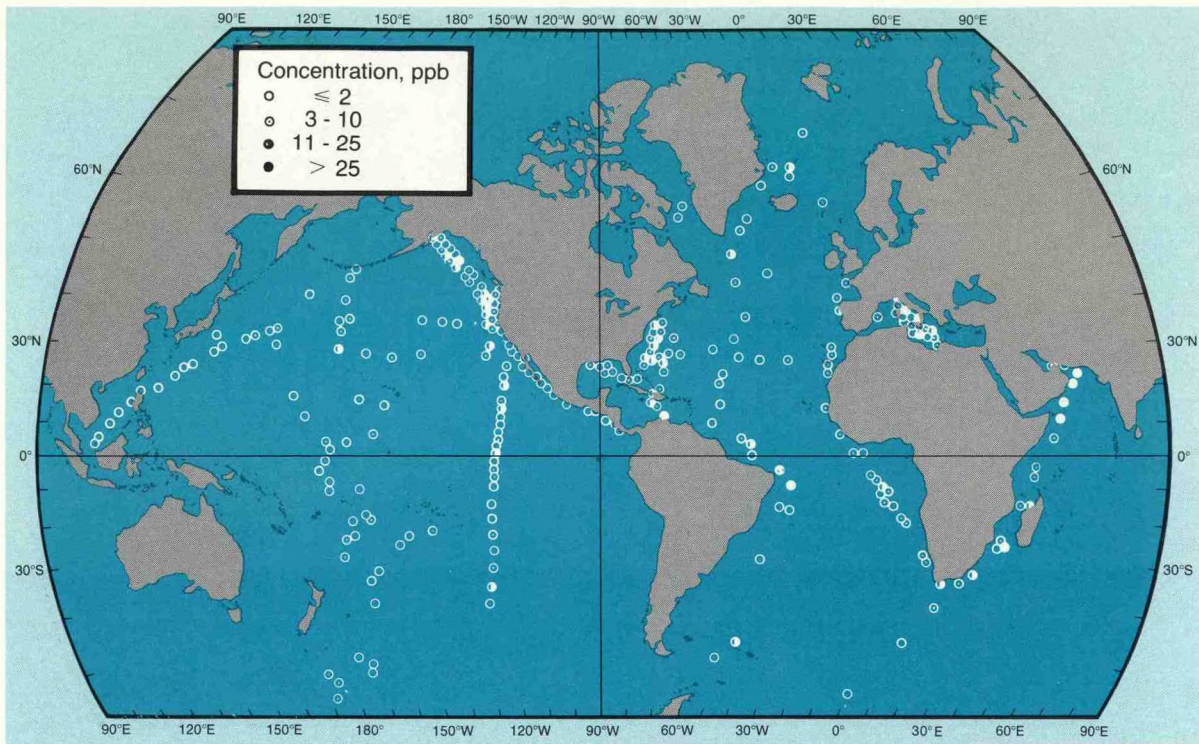


Figure 8. Non-Volatile Hydrocarbons in Surface Waters.

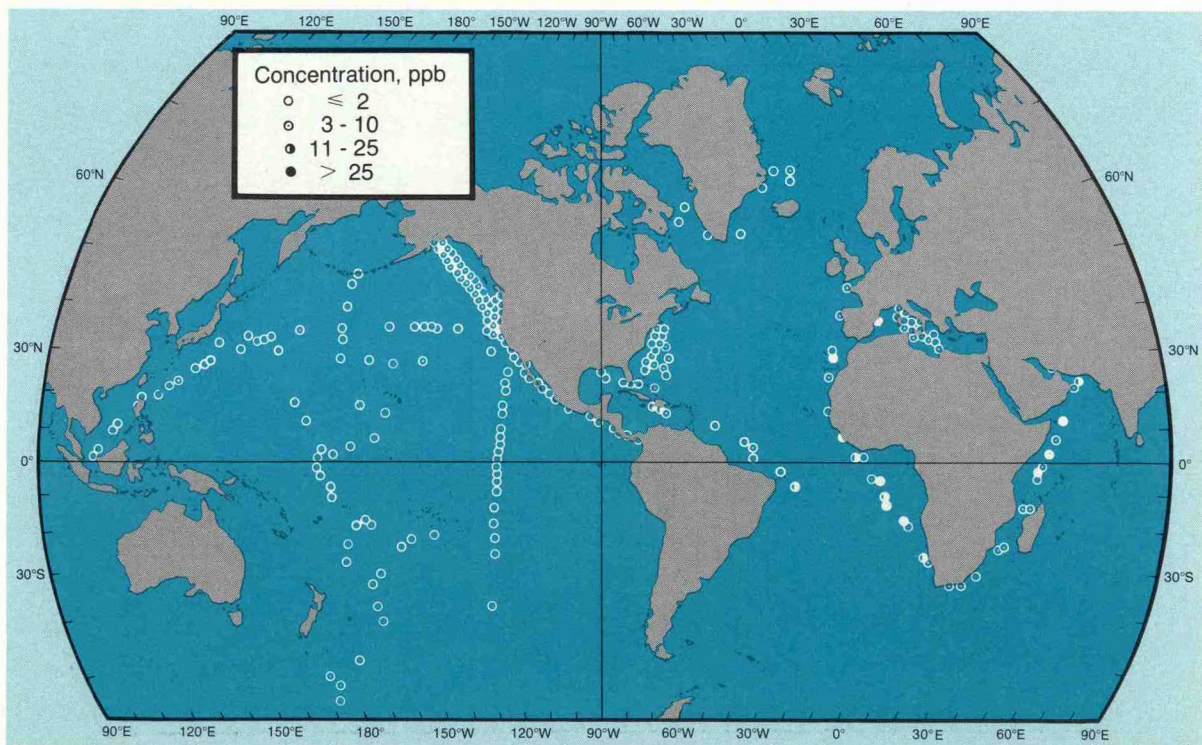
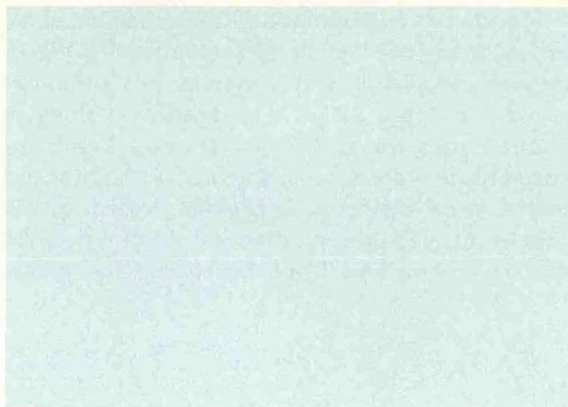


Figure 9. Non-Volatile Hydrocarbons in Subsurface Waters.

The preceding observations are further exemplified in frequency histograms of EO and HC measurements for the different routes (Figs. 10-13). The histograms of EO measurements depicted in Figs. 10 and 11 indicate values ranging over several orders of magnitude, from about 1 to 500 ppb with medians in the range of 10 to 20 ppb. With one exception, the distributions indicated for the different routes are similar. The one exception is the San Francisco to Singapore tanker route for which median values for surface and subsurface waters were 6 and 4 ppb, respectively.



Frequency histograms of the measurements of HC along the Pacific and Atlantic GEOSECS cruises and along the different tanker routes are shown in Figs. 12 and 13; median values of about 2 ppb for surface waters and 1 ppb for subsurface waters are indicated for open and near-coastal waters of the Pacific. Exceptions to this trend were the median values of 4 ppb for surface waters and 3 ppb for subsurface waters

on the San Francisco to Cook Inlet tanker route. The histogram of HC measurements for this latter route is based on measurements from two different round trips, one in February 1974 and the other in September 1974. The higher median values indicated for this route were due to higher levels of HC encountered during the February 1974 trip. The measured differences in HC levels for these two trips account for the

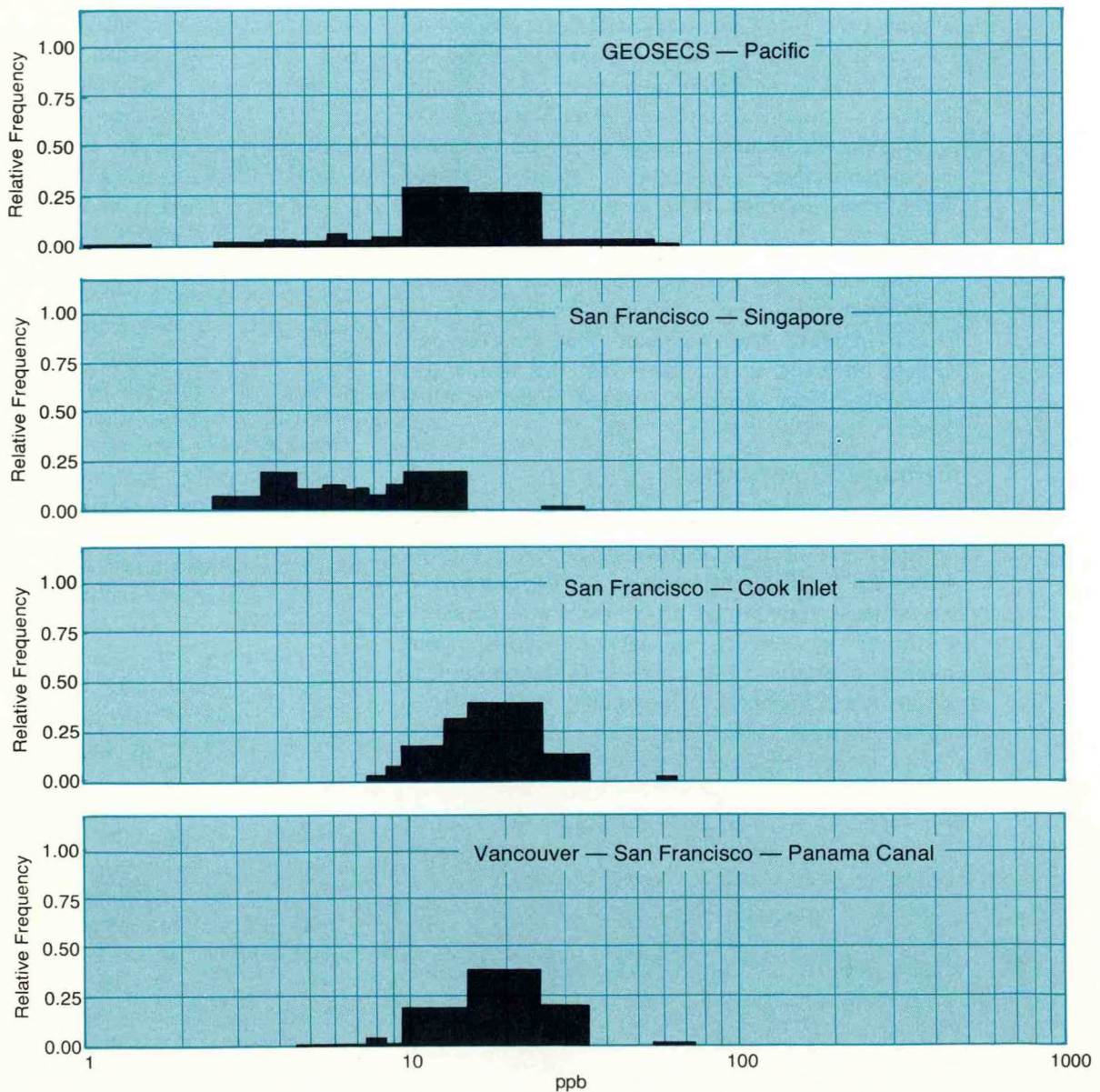


Figure 10a. Frequency Histograms of Extractable Organic Measurements in Surface Waters.

somewhat bimodal character of the depicted histogram.

A rather obvious feature of the HC histograms depicted in Fig. 12 is the higher median values indicated for tanker routes of the Atlantic and Mediterranean: New York to the Gulf of Mexico and Caribbean (5 ppb, surface; 2 ppb, subsurface), Persian Gulf to Europe (6 ppb, surface; 5 ppb, subsurface) and the

Mediterranean (3 ppb, surface; 2 ppb, subsurface). The higher values of HC along these routes appear to be indicative of HC contamination associated with more intense tanker activity (Fig. 1).

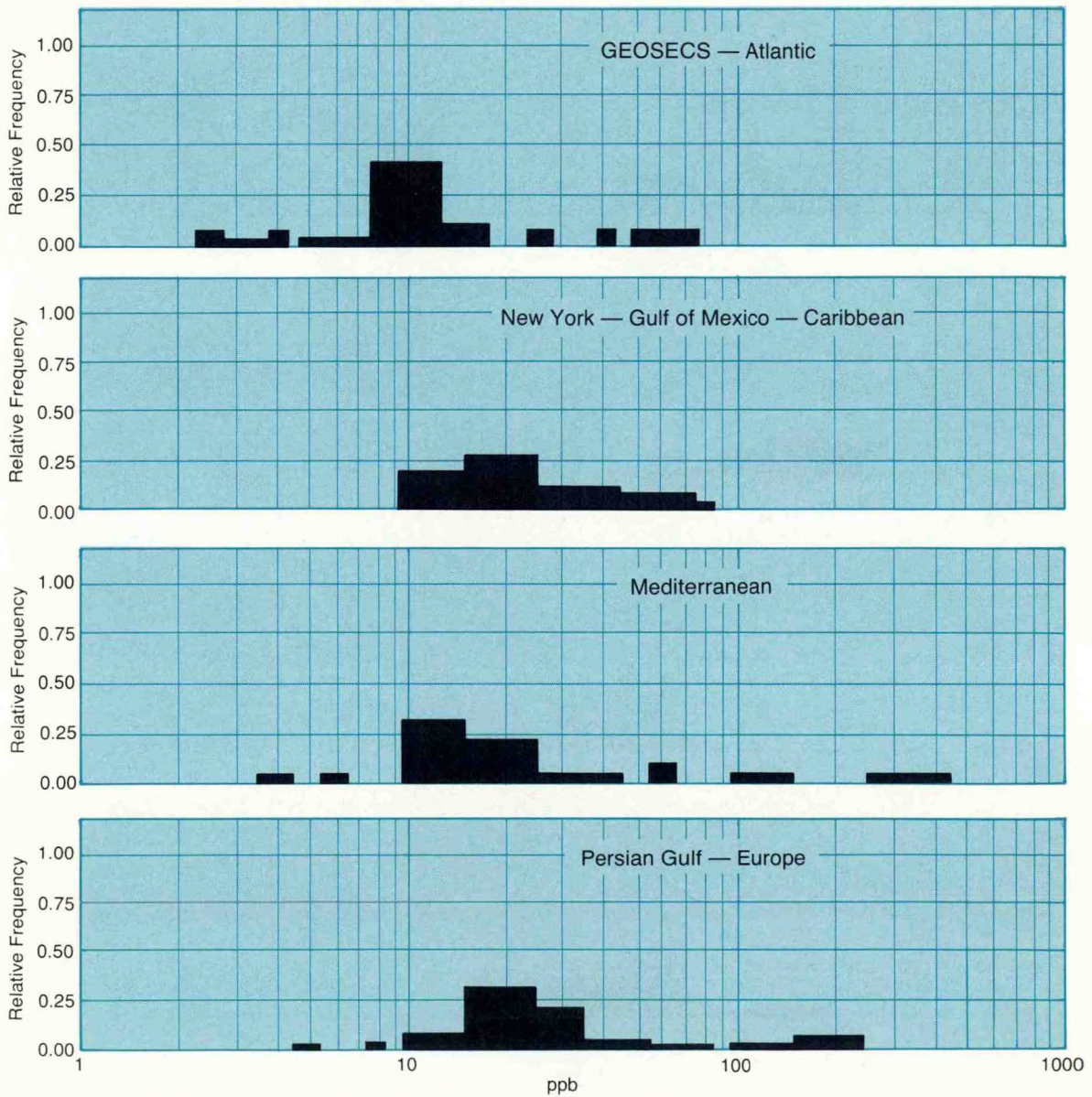


Figure 10b. Frequency Histograms of Extractable Organic Measurements in Surface Waters. (Continued.)

Compositional information, obtained by gas chromatography and mass spectrometry, was also determined for some of the hydrocarbon samples in order to characterize types and possible origins (i.e., biogenic or petroleum). As shown in Fig. 14, cycloparaffins were the dominant hydrocarbon type for all sampling cruises. Since cycloparaffins have not been reported as being ubiquitous in marine or-

ganisms, their presence would tend to suggest a petroleum source.

The relative contents of normal- and iso-paraffins and of aromatics showed the greatest variation on the sampling cruises. This variation was possibly due to differences in the degradation of these hydrocarbon types as well as to differences in source types. As shown in Fig. 14 the normal paraffins typically accounted for

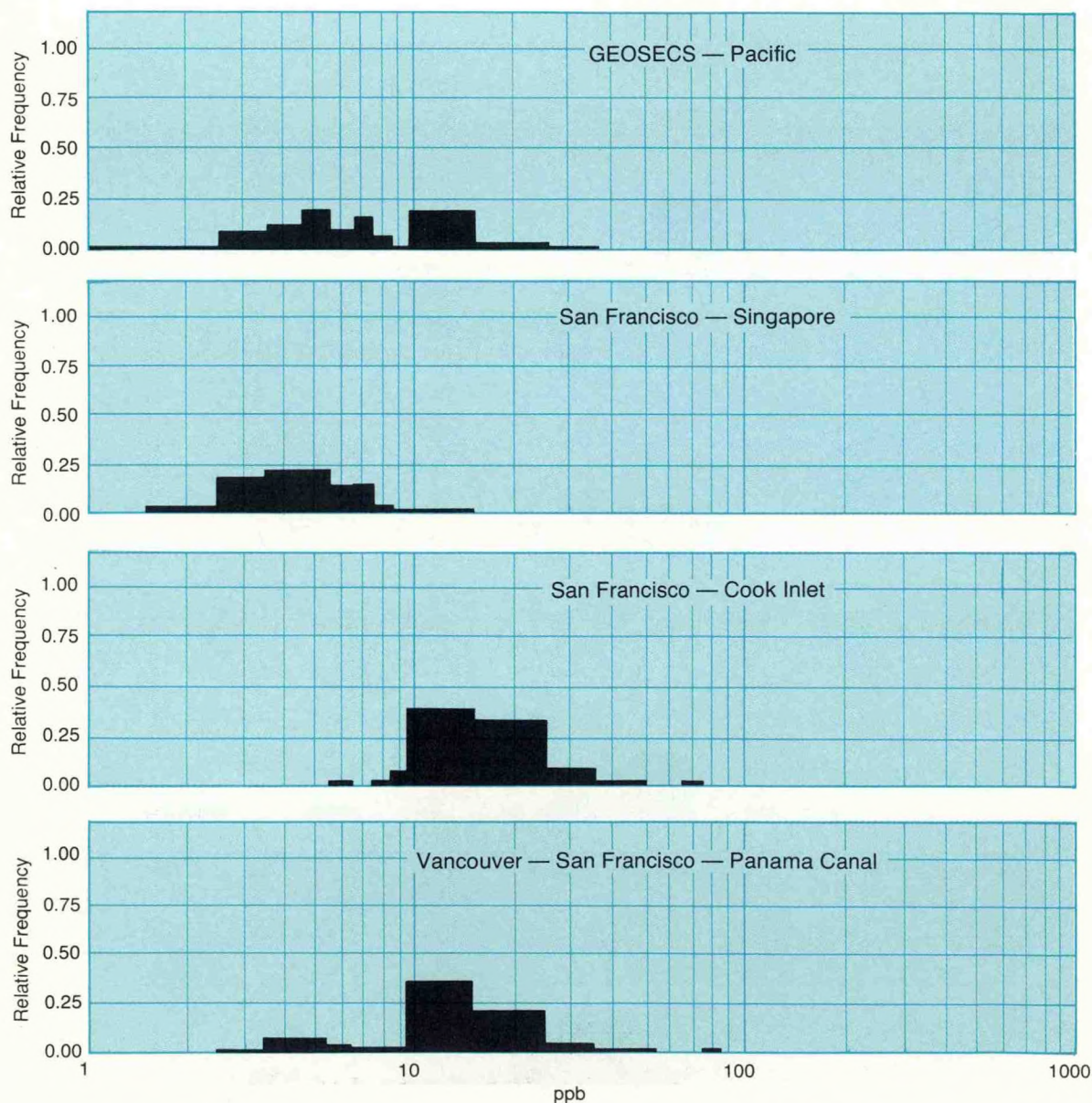


Figure 11a. Frequency Histograms of Extractable Organic Measurements in Subsurface waters.

only a small percentage of the total hydrocarbons. However, exceptions did occur; normal-paraffin values as high as 15-percent were detected for some of the samples taken on the GEOSECS Pacific cruise. Some notably high values, to 23-percent, were also observed on the lower portion of the tanker route to the Panama Canal. Since normal-paraffins are usually

weathered quite readily in ocean waters, these high values may be indicative of fresh biogenic sources.

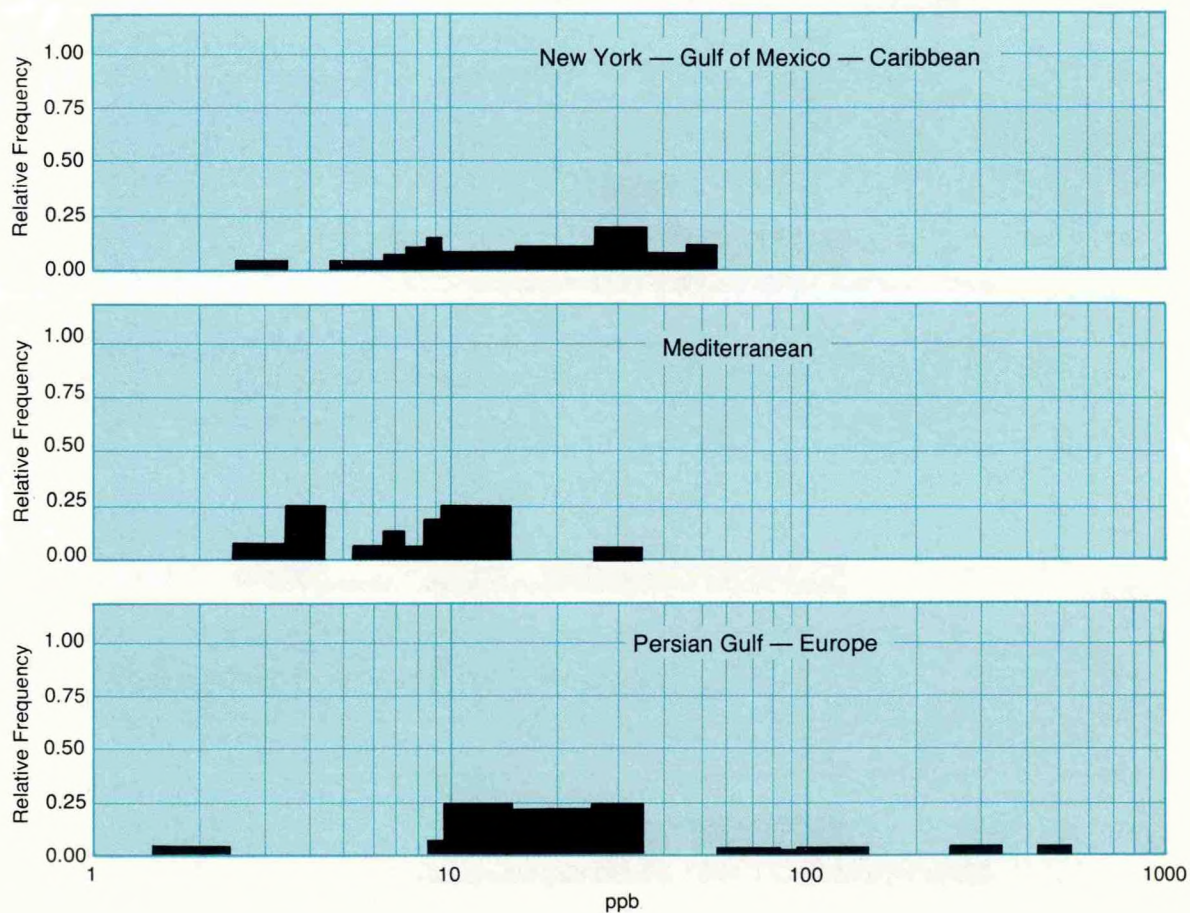


Figure 11b. Frequency Histograms of Extractable Organic Measurements in Subsurface Waters. (Continued.)

With the exception of a few crudes, such as Cook Inlet crude, the majority of crude petroleum have high aromatic contents as is evident in Fig. 14 for Middle East and Venezuelan crudes. An observed relatively lower occurrence of aromatics in the sampled waters may thus be due to a preferential degradation, such as photo-oxidation, of the aromatic fraction in ocean waters. It may also be due to other

sources of specific hydrocarbon types such as biogenic paraffins and olefins, which would reduce the relative content of the aromatic fraction (8).

Both petroleum hydrocarbons and the biogenic hydrocarbons formed by marine organisms are found in the sea. There is a wide variety of marine physical and biochemical activities that degrade and transform these dis-

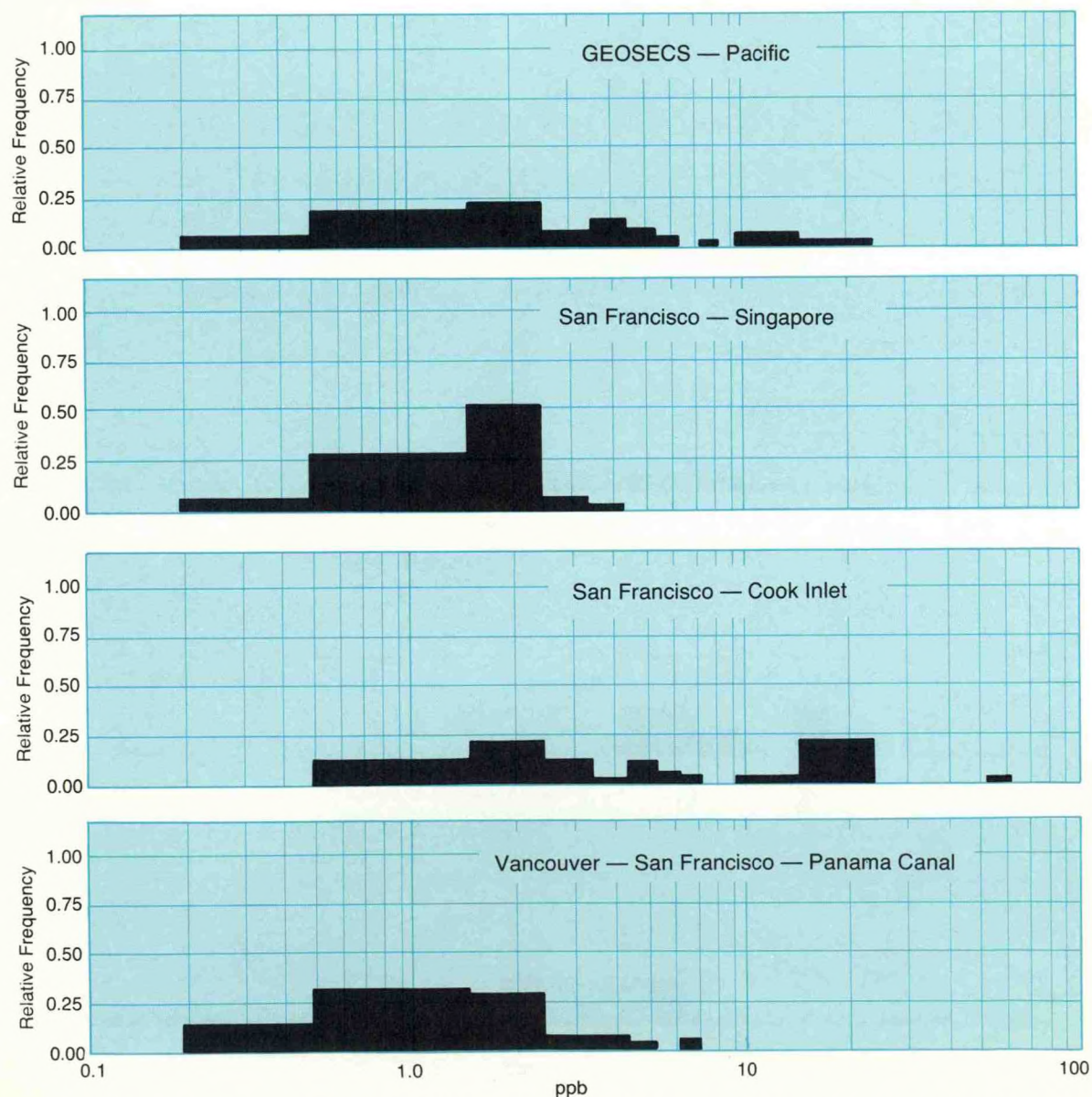


Figure 12a. Frequency Histograms of Non-Volatile Hydrocarbon Measurements in Surface Waters.

similar hydrocarbon types at different rates and with varying intermediate and/or end products. All of these factors introduce a high degree of uncertainty into quantitative estimates of petroleum hydrocarbon concentrations in a given sample. Qualitative assessments can be made based on extensive GC results presented in the original reports and on the ratios of hydrocarbons to total extractable organics.

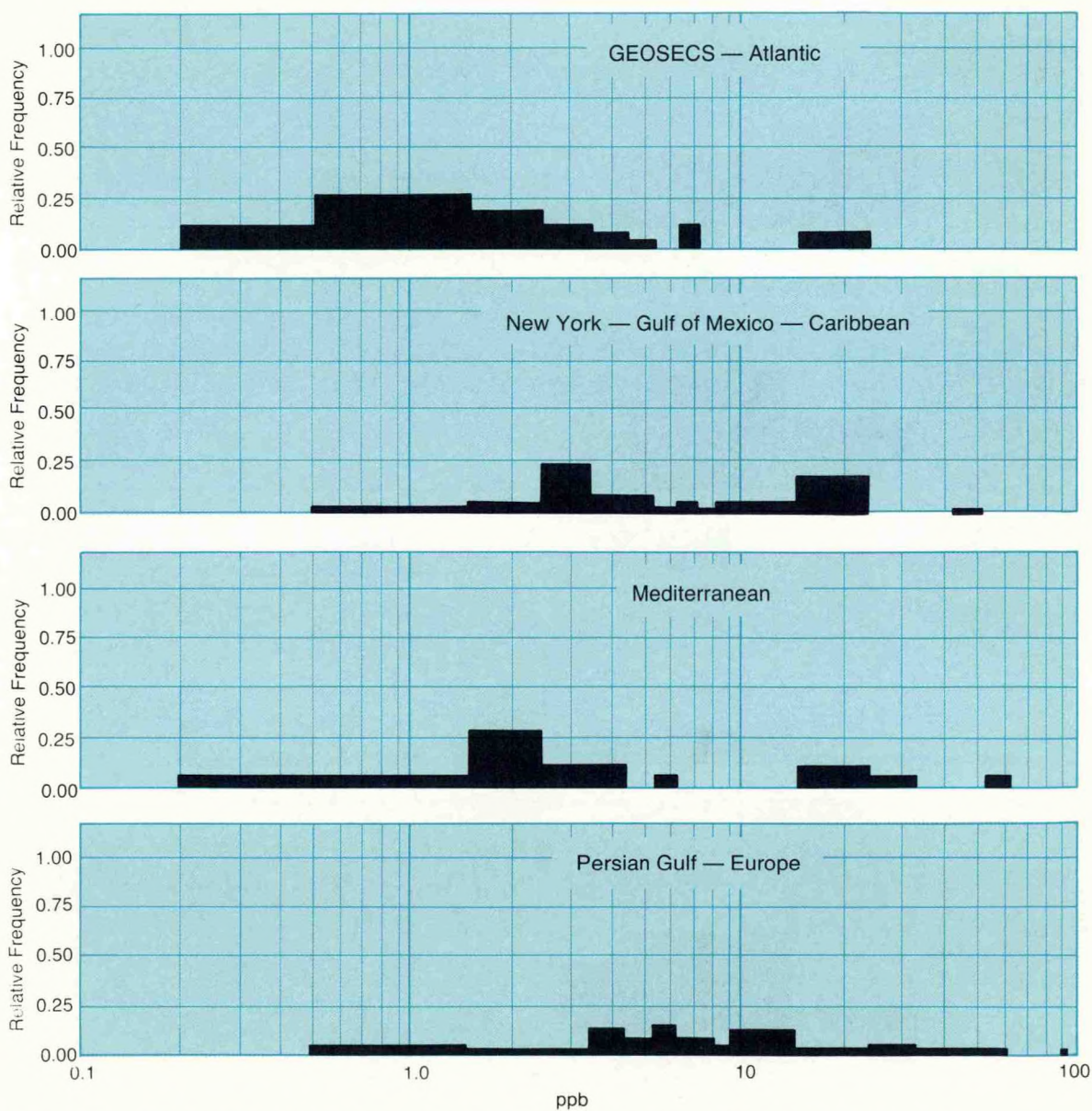


Figure 12b. Frequency Histograms of Non-Volatile Hydrocarbon Measurements in Surface Waters. (Continued.)

Most of the gas chromatograms displayed unresolved base envelopes very similar to those of crude oils. Typical examples are shown in Fig. 15, which may be compared with those of two crude oils depicted in Fig. 16. Although the sample chromatograms have unresolved envelopes suggestive of petroleum sources, they also display peaks considered characteristic of biogenic hydrocarbon types, most notably the predominant n-paraffin peak at C₁₅ and the

fractional carbon peak between C₂₀ and C₂₁. Normal paraffins in this carbon number range would normally be weathered, as indicated by other nearby n-paraffin peaks; the fact that the n-C₁₅ peak is not as weathered is indicative of a recent biogenic source. Large intermediate fractional carbon number peaks in these traces are suspected to be due to biogenic olefins. Such GC-traces, showing strong indications of biogenic hydrocarbon contribution, were most

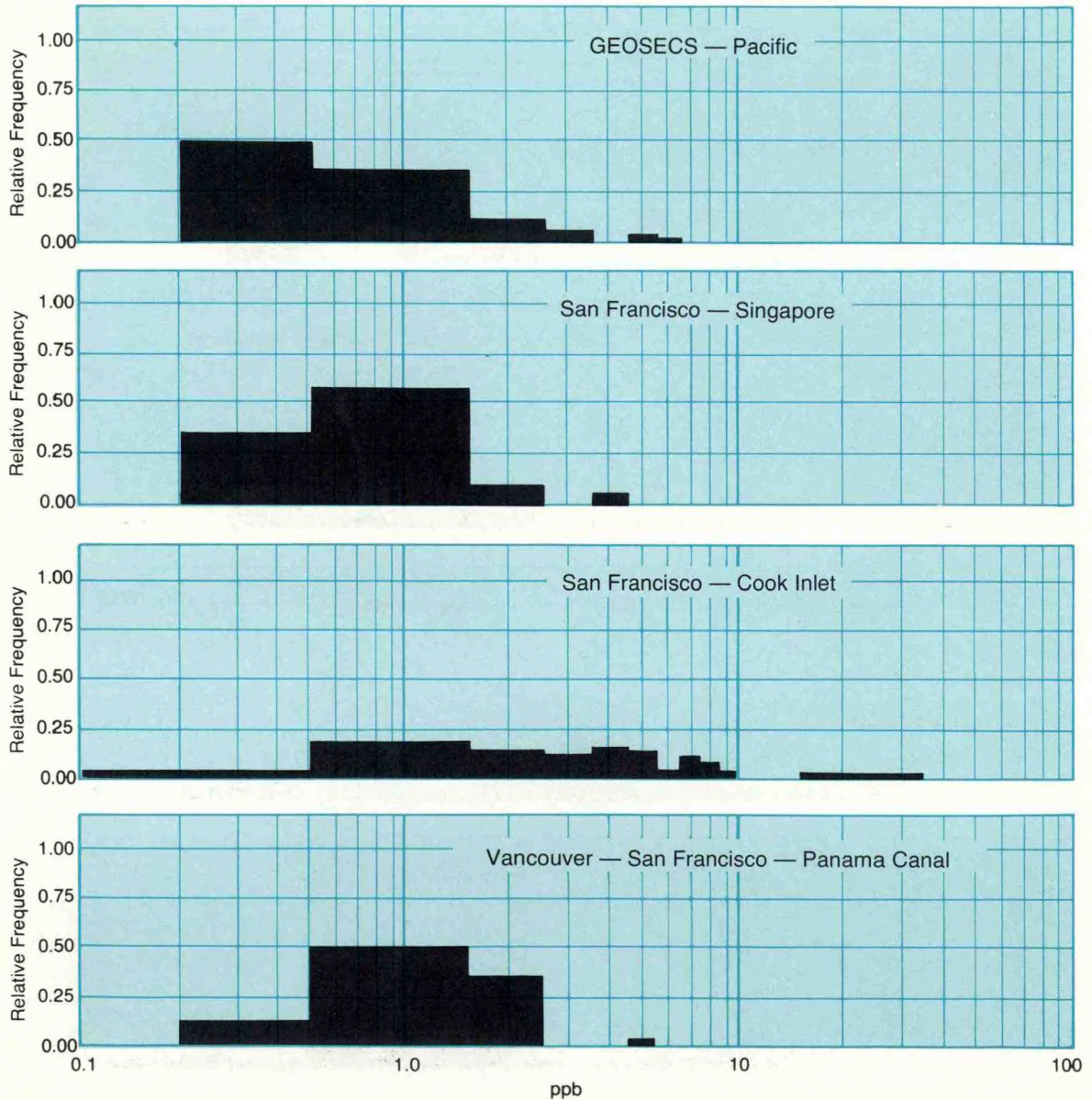


Figure 13a. Frequency Histograms of Non-Volatile Hydrocarbon Measurements in Subsurface Waters.

often associated with samples collected in open ocean waters and along less frequently traveled tanker routes.

At the present state-of-the-art, the relatively high hydrocarbon to lipid ratio that is characteristic of crude oils is a reasonable indicator of petroleum contamination (37). Ratios of total hydrocarbons to total chloroform extractable material (primarily hydrocarbons and lipids) have thus been plotted in Figs. 17 and 18. Pre-

sented in this manner, the data suggest petroleum contamination in near-coastal areas where there is more tanker activity and where there is also a greater potential for inputs from seeps, rivers, outfalls, etc. (Fig. 2). ■

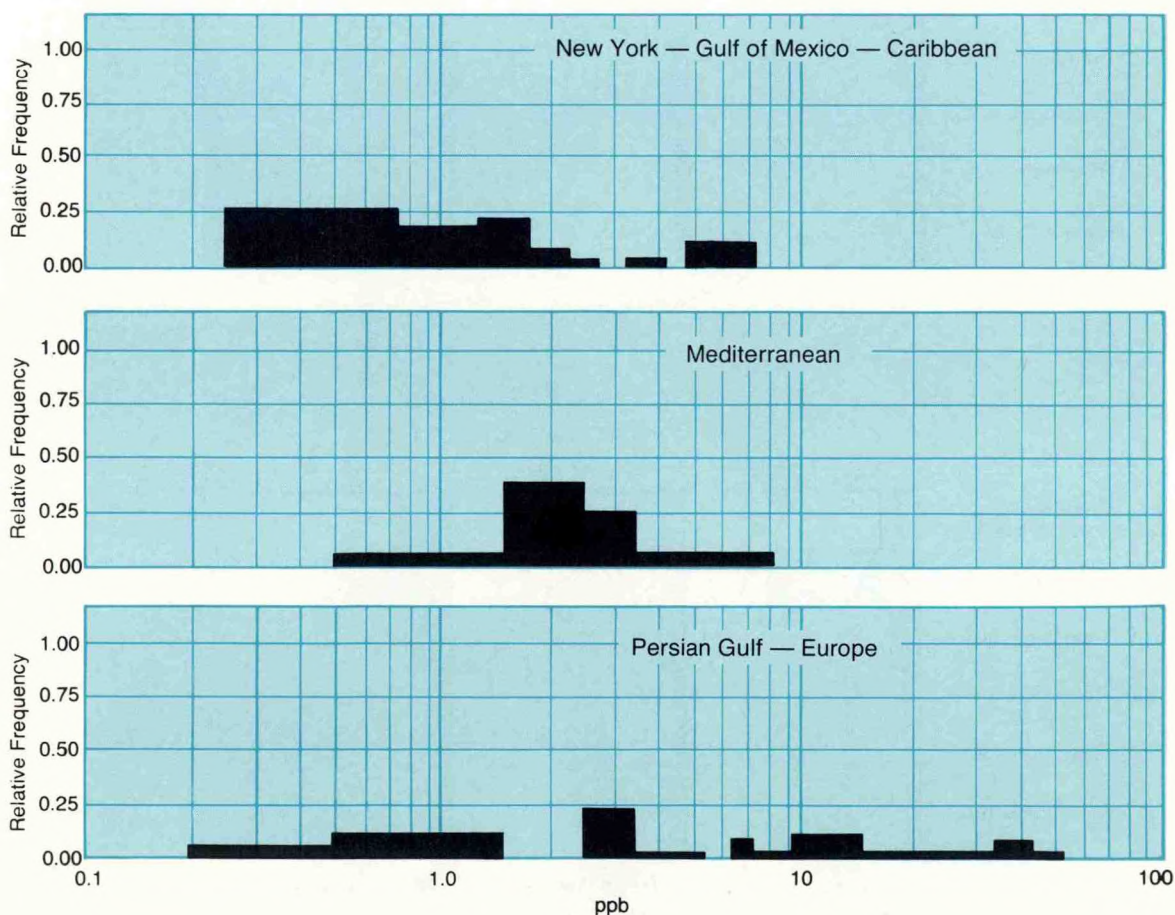


Figure 13b. Frequency Histograms of Non-Volatile Hydrocarbon Measurements in Subsurface Waters. (Continued.)

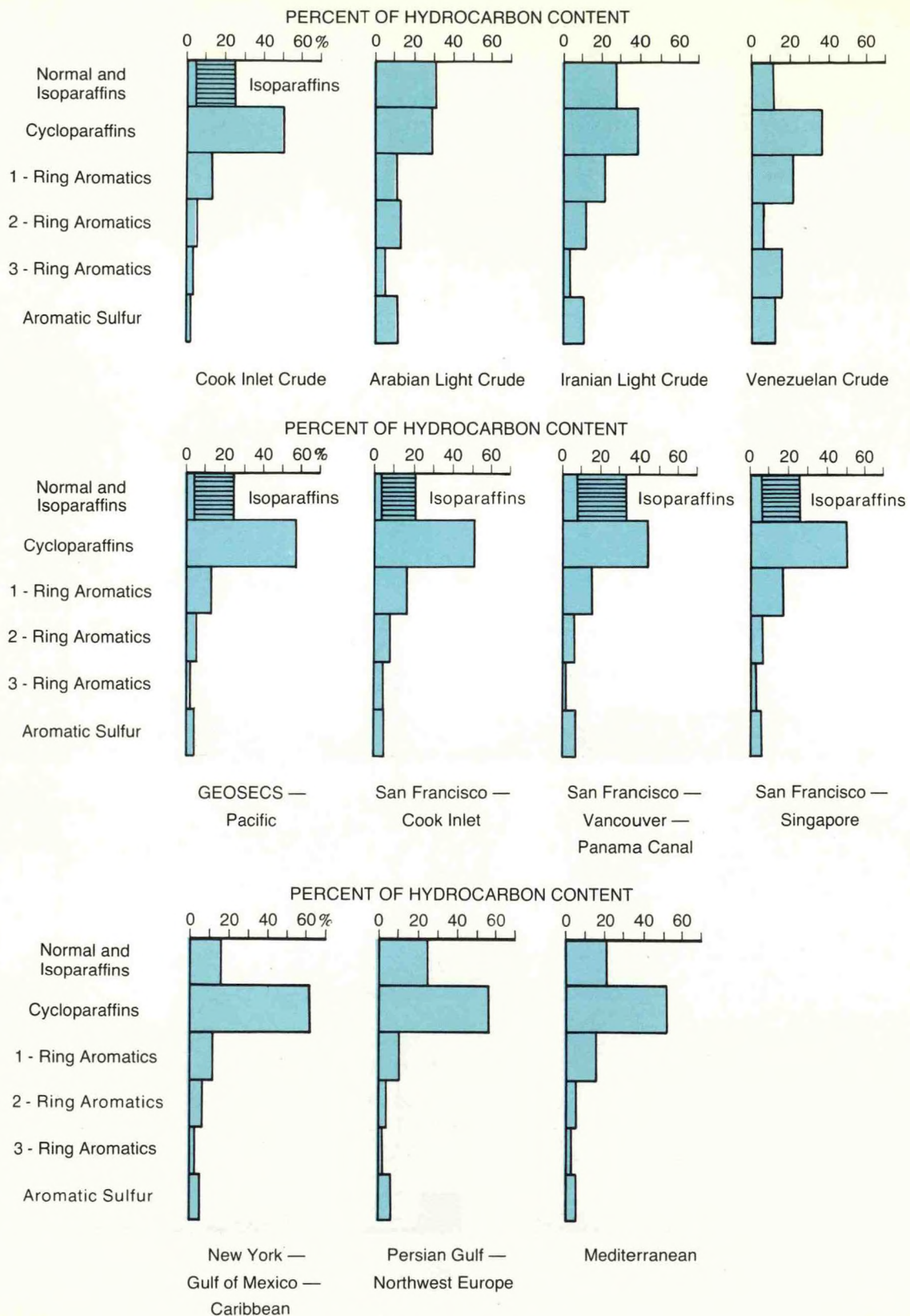


Figure 14. Compositions of Hydrocarbons Extracted from Ocean Waters.

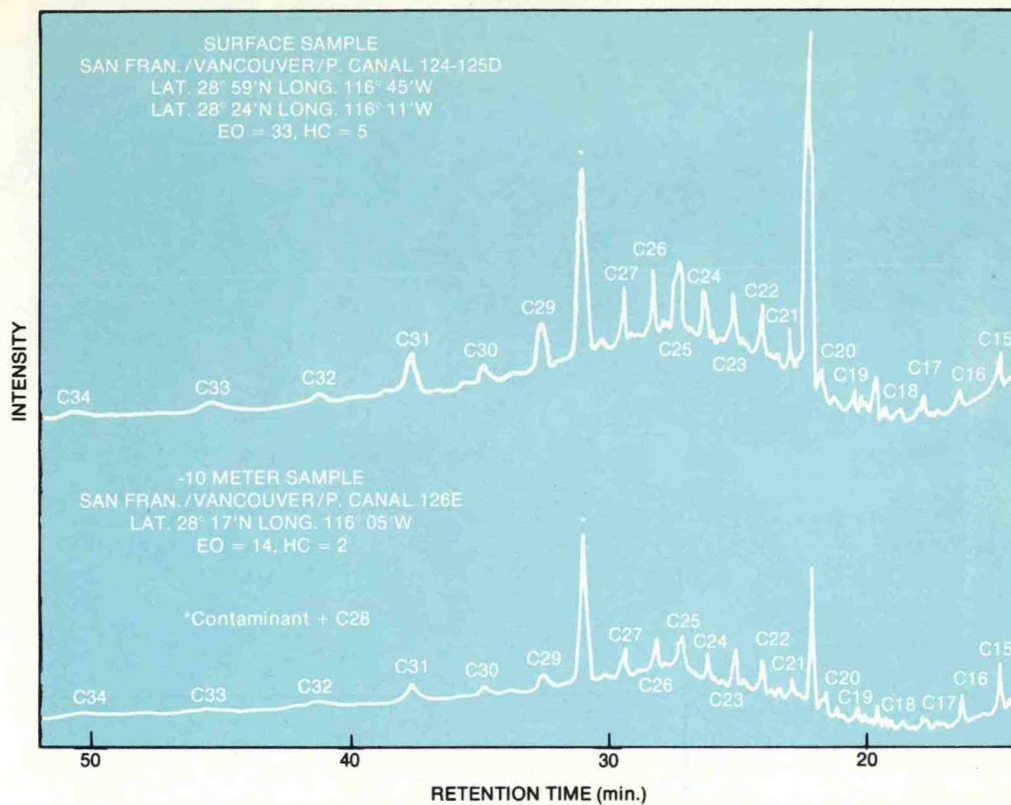


Figure 15. Gas Chromatograms of Typical Hydrocarbon Samples.

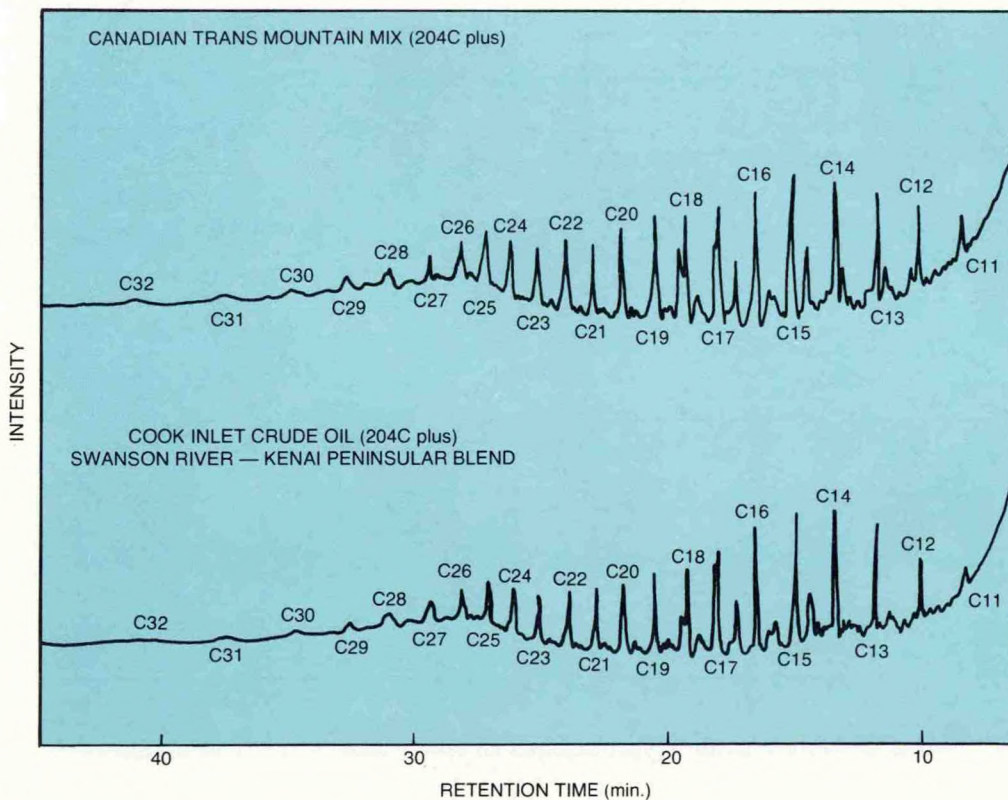


Figure 16. Gas Chromatograms of Two Crude Oils.

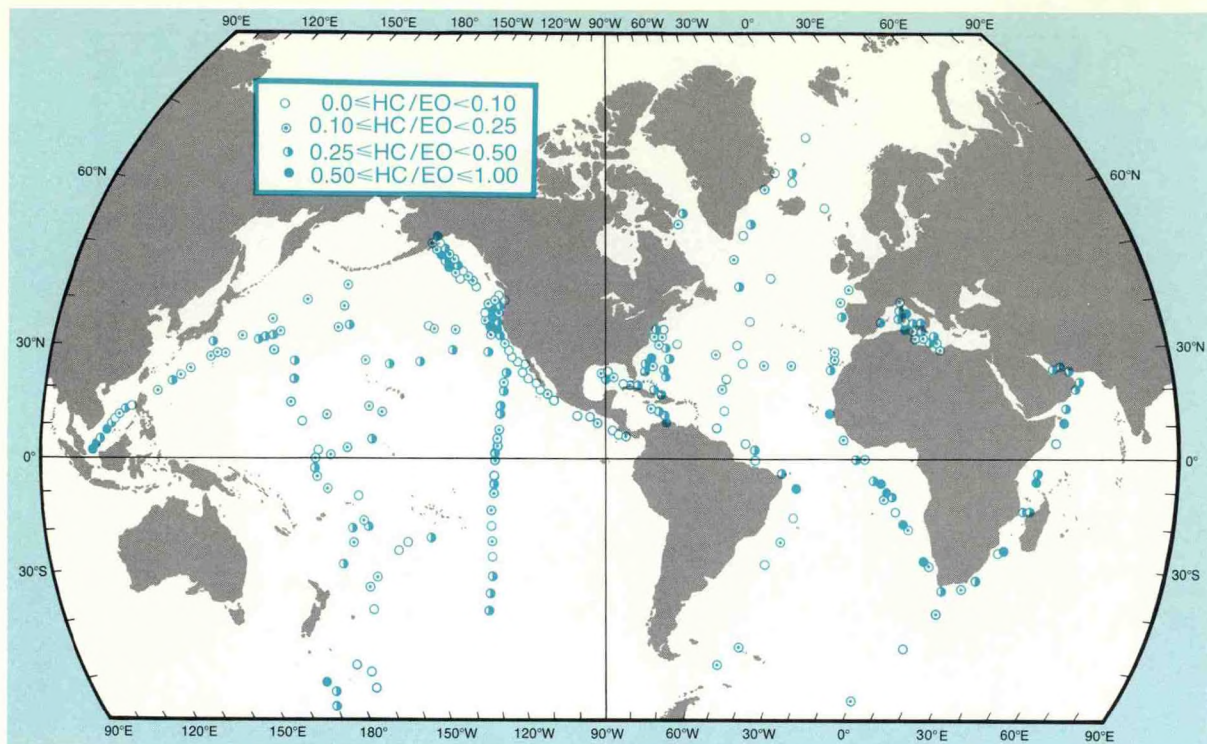


Figure 17. Ratios of Non-Volatile Hydrocarbons to Extractable Organics for Surface Waters.

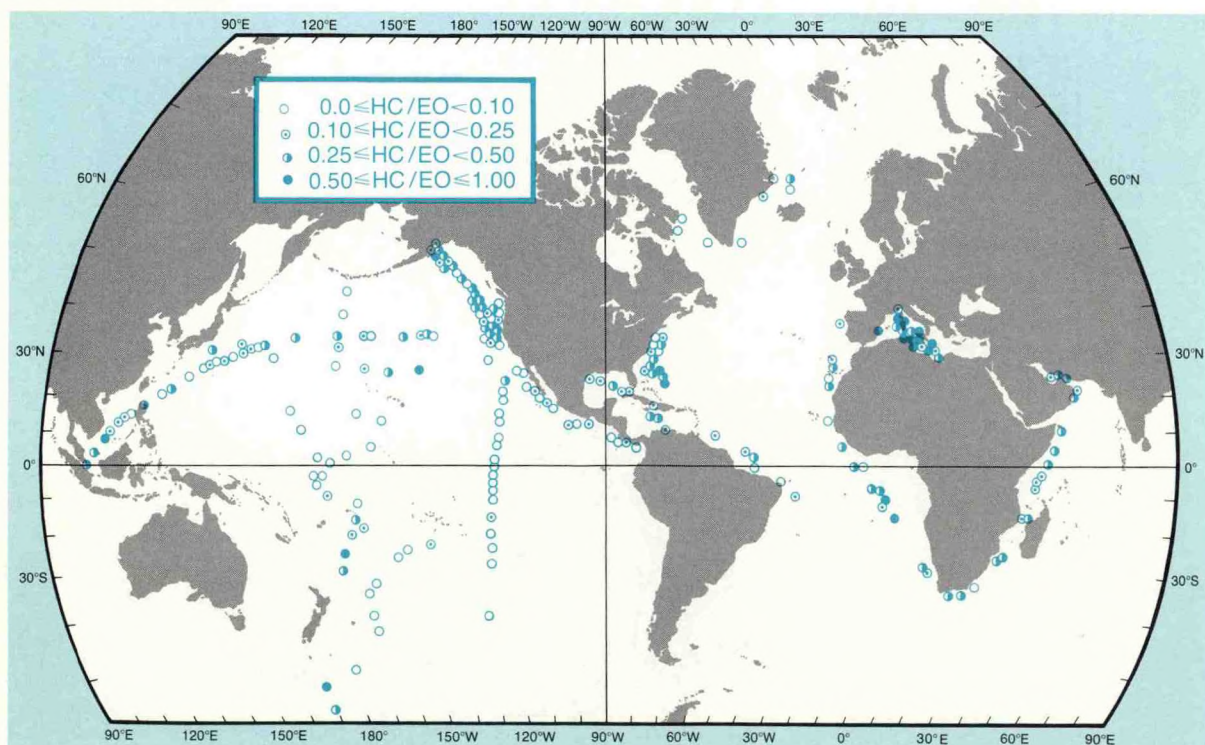


Figure 18. Ratios of Non-Volatile Hydrocarbons to Extractable Organics for Subsurface Waters.

2.2 Volatile Hydrocarbons

Volatile hydrocarbon determinations for the carbon number range of C₄-C₈ were made on many of the Pacific Ocean samples, but only a few such measurements were performed in the Atlantic study. The results of these measurements are depicted in Fig. 19 for surface waters and in Fig. 20 for subsurface waters. Frequency histograms of these measurements are presented in Fig. 21. The measured range of values for volatile hydrocarbons in Pacific waters varied from 0.01 ppb (lower detection limit) to about 4 ppb. Median values for subsurface (-3 or -10 meters) waters along the GEOSECS cruises and along the San Francisco to Singapore tanker route were about 0.1 ppb. Surface values for the GEOSECS cruises indicated a median value between 0.1 and 0.2 ppb.

Due to the limited number of volatile hydrocarbon measurements along the west coasts of the U.S. and Central America, the measurements from the San Francisco-Cook Inlet and the San Francisco-Vancouver-Panama Canal tanker routes were combined to form the histogram of Fig. 21. This histogram indicates a median of 0.3 ppb for surface samples, and is based almost solely (7 out of 8 measurements) on measurements along the San Francisco-Cook Inlet tanker route. On the other hand, a lower median value of less than 0.05 ppb for subsurface coastal waters along these routes is weighted by consistently low measurements off the coast of Central America.

Only a few volatile hydrocarbon analyses were made in the Atlantic study and these were on waters sampled along the New York-Gulf of Mexico tanker route. Surface values ranged from 0.08 to 1.2 ppb with a median of about 0.1 ppb; subsurface values ranged from 0.1 to 2.4 ppb with a median of about 0.3 ppb.

Considered together, volatile hydrocarbons in the C₄ to C₈ carbon number range were predominantly composed of aromatics with benzene, toluene and xylenes typically accounting for about three-fourths of the volatiles.

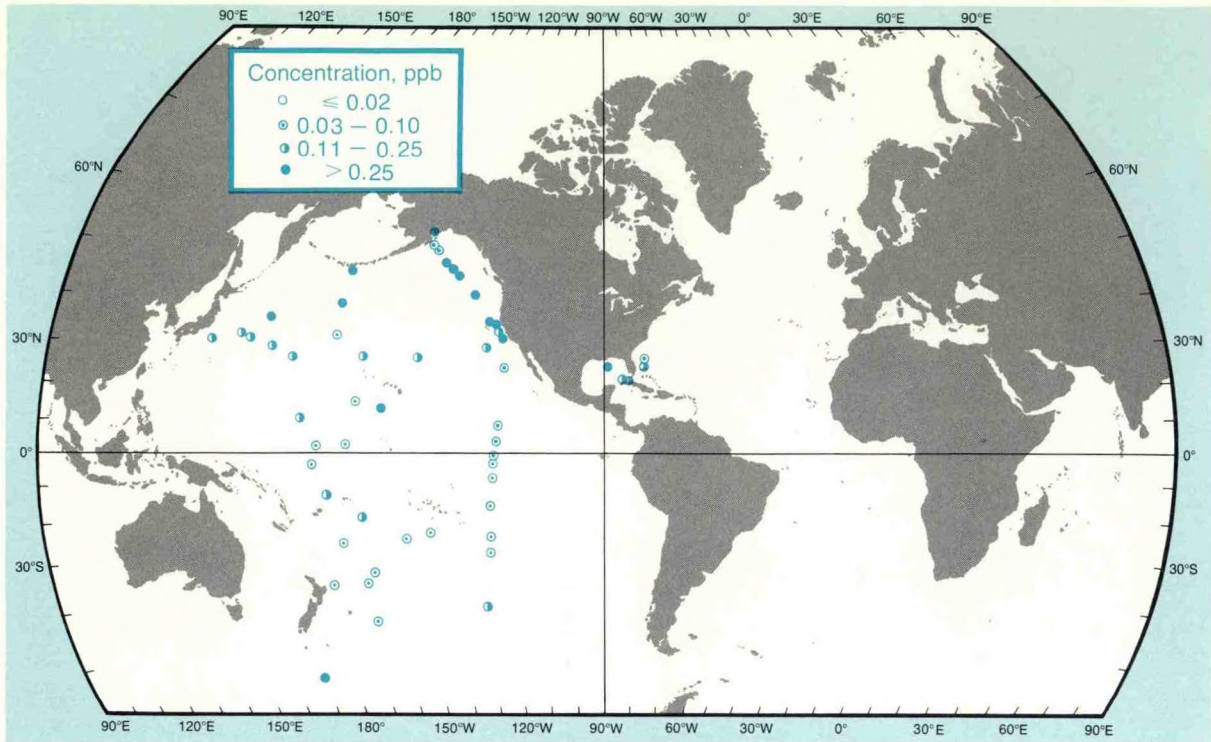


Figure 19. Volatile Hydrocarbon Measurements in Surface Waters.

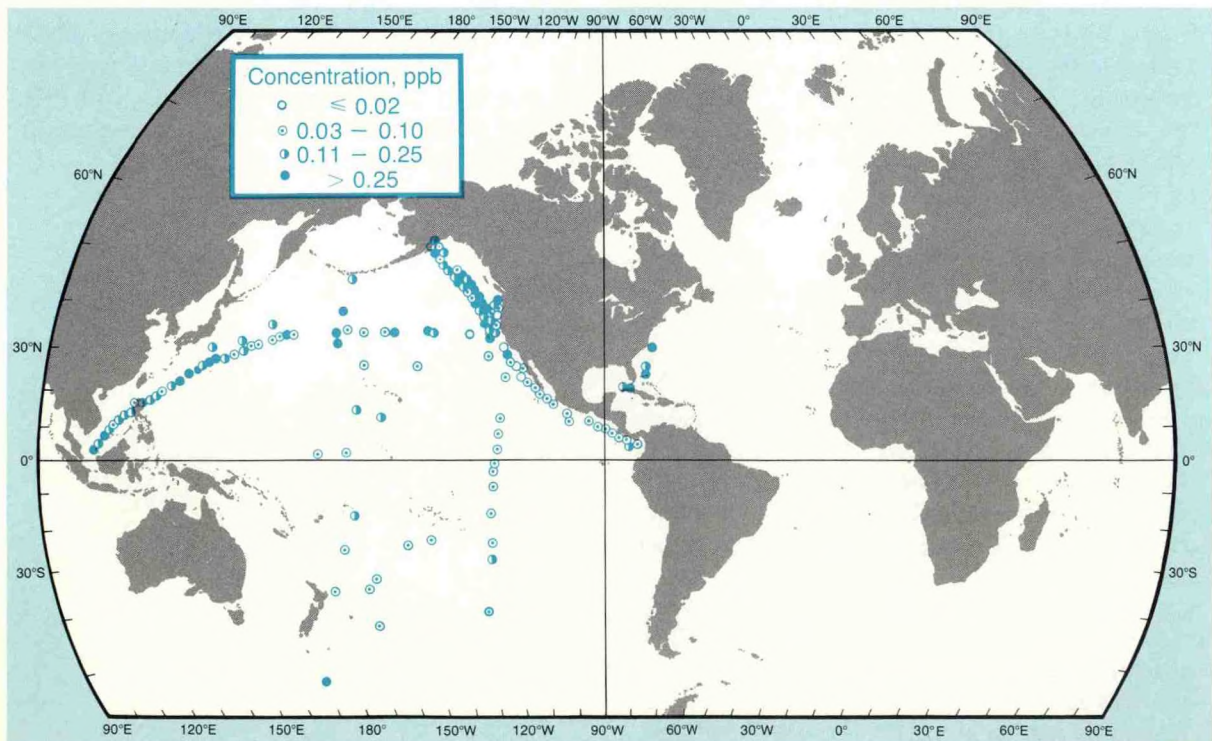


Figure 20. Volatile Hydrocarbon Measurements in Subsurface Waters.

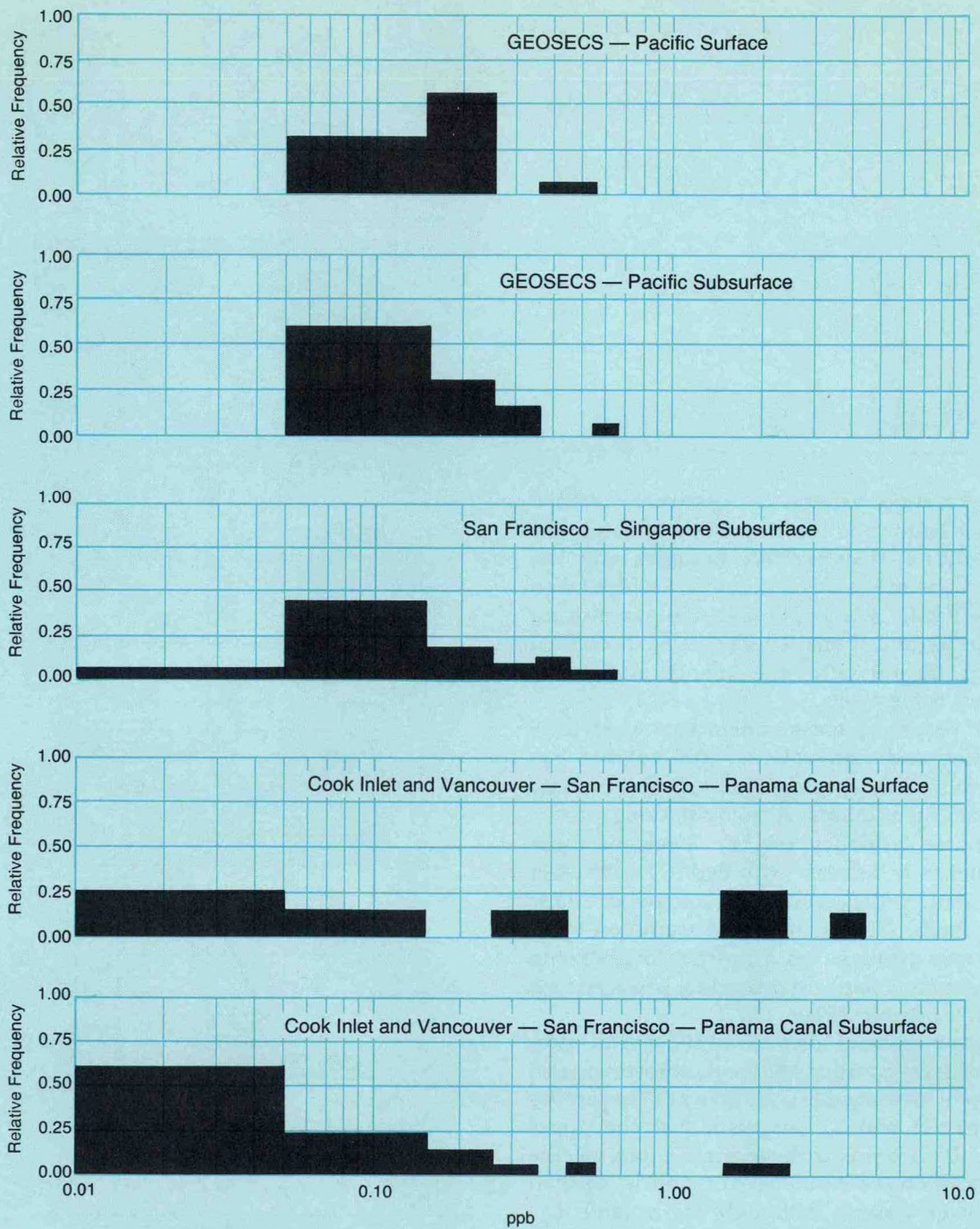


Figure 21. Frequency Histograms of Volatile Hydrocarbon Measurements.

Legend for Figure 22

- Extractable Organics
 - Non-Volatile Hydrocarbons
 - △ Volatile Hydrocarbons
 - Temperature
- HC/EO Ratios
- $0 \leq HC < 0.10$
 - ◐ $0.10 \leq HC < 0.25$
 - ◑ $0.25 \leq HC < 0.50$
 - $0.50 \leq HC \leq 1.00$

Shaded areas are estimates of thermocline (from Ref. 51)

2.3 Vertical Profiles

A number of vertical profiles were obtained in the Atlantic and Pacific studies to define the distribution of extractable organics and hydrocarbons in the water column. Profiles taken in the Pacific study also included samples for volatile hydrocarbons. These data are presented in Figs. 22 and 23 for the Atlantic and Pacific studies, respectively.

The results of measurements of extractable organics and non-volatile and volatile hydrocarbons in the water column do not indicate any consistent trends. At some stations there is a definite tendency for the levels of these parameters to decrease with depth; however, at other stations the results were somewhat erratic with depth. One characteristic common to all measured profiles was a positive relationship between nonvolatile hydrocarbon levels and extractable organic levels.

A comparison of the vertical HC and EO profiles with the positions of the thermoclines, also shown or estimated (51) for many of the profiles in Figs. 22 and 23, suggests that the upper mixed layer tends to have higher non-volatile hydrocarbon and extractable organic levels than the lower waters. Although the volatile hydrocarbon data are fewer, there is some indication of higher levels at about the position of the thermocline. This is a potentially interesting feature that deserves more study. It may be that a vertical transport of volatile components from lower water masses and sediments is somewhat

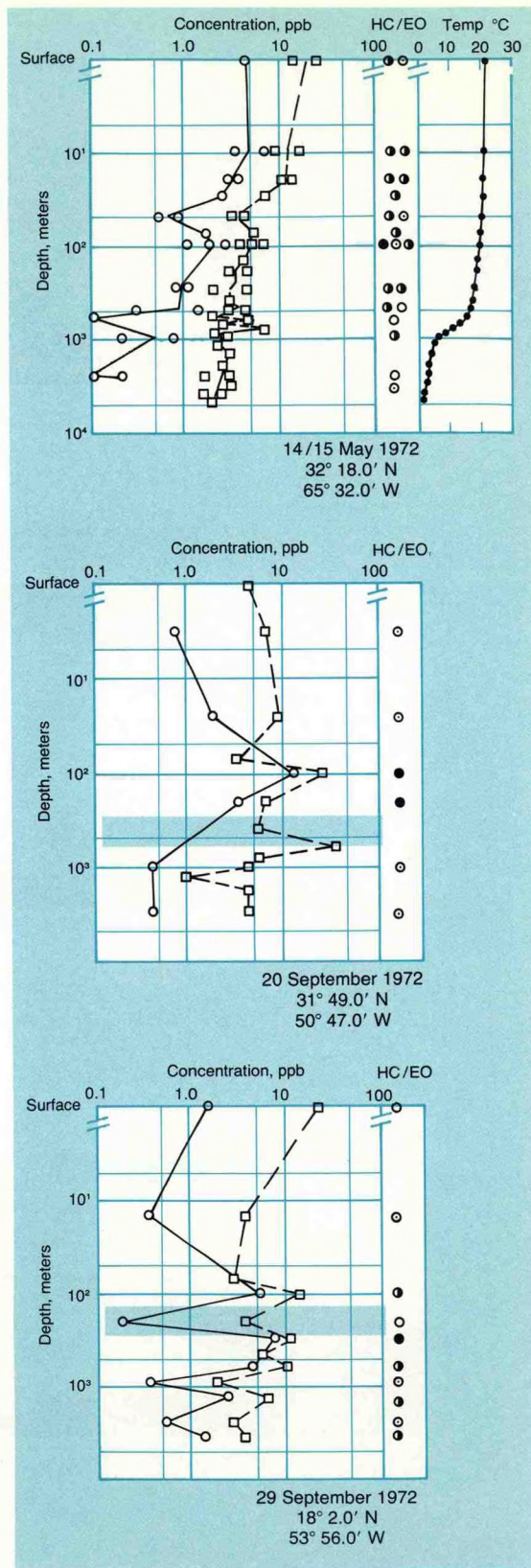


Figure 22a. Water Column Profiles of Extractable Organic and Hydrocarbon Measurements in the Atlantic.

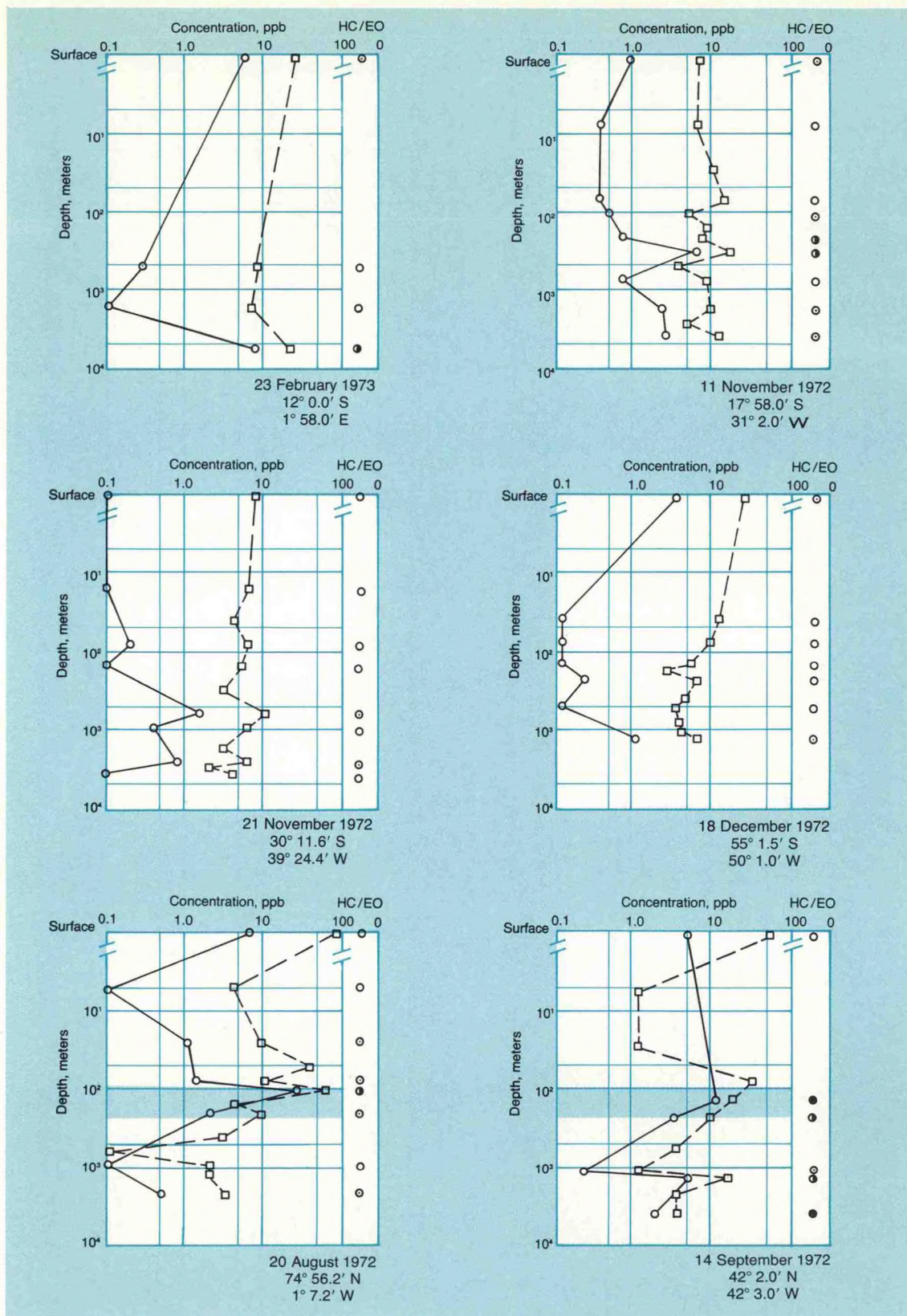


Figure 22b. Water Column Profiles of Extractable Organic and Hydrocarbon Measurements in the Atlantic. (Continued.)

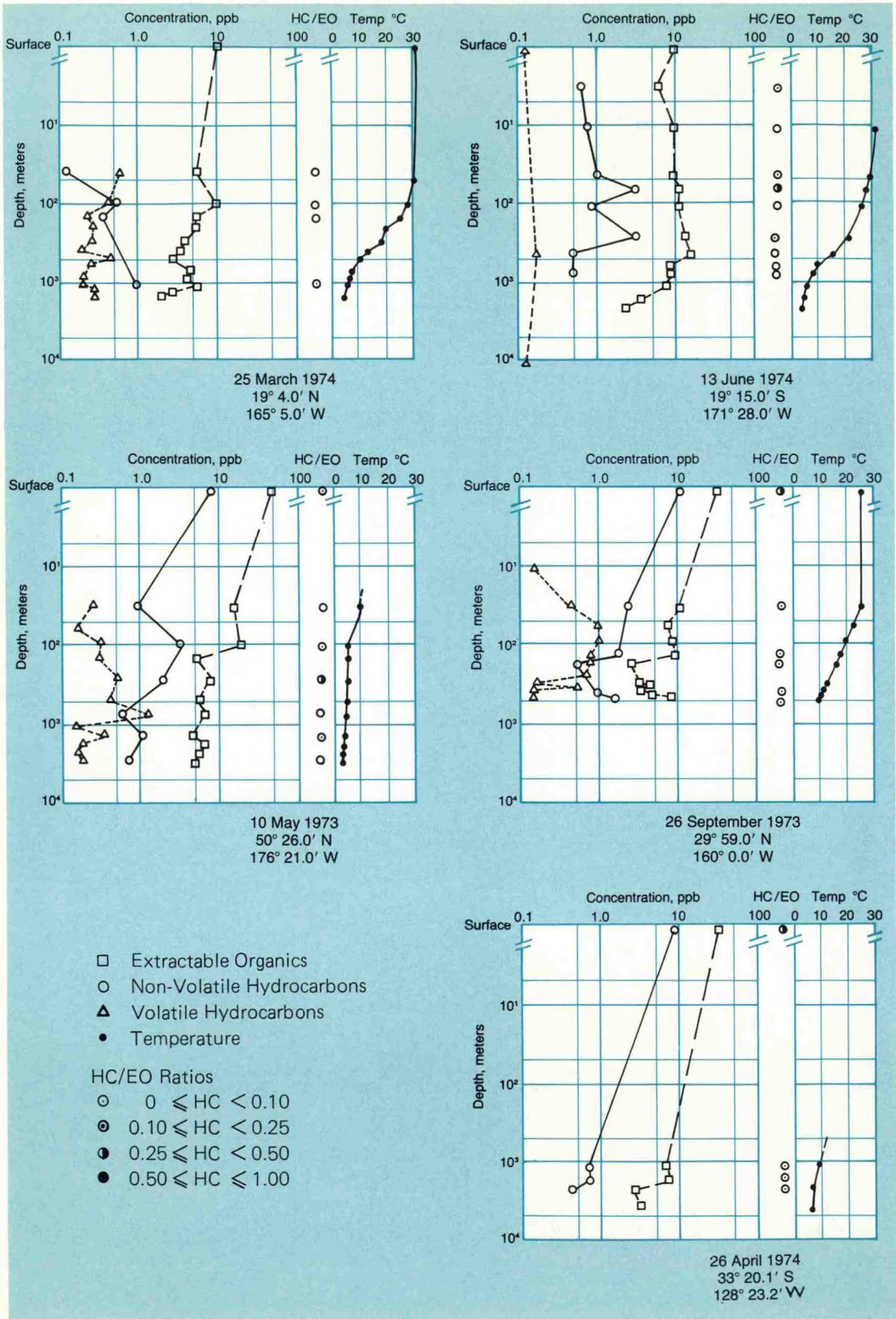


Figure 23. Water Column Profiles of Extractable Organic and Hydrocarbon Measurements in the Pacific.

inhibited or slowed at the thermocline, resulting in a relative accumulation of volatile substances. These maximums may also be the result of plant or animal metabolism or the decomposition of organic matter in the water column, as was suggested by Brooks and Sackett (7) for measured maximums of methane and some other light hydrocarbons in the Gulf of Mexico at depths of 50 to 200 meters.

The relative ratios of non-volatile hydrocarbons to extractable organics have also been indicated on Figs. 22 and 23. Although exceptions occur, the majority of these ratios are low and suggest that the principal sources of hydrocarbons in the lower part of the water column are biogenic. ■

2.4 Other Data

Other data on levels and types of hydrocarbons in ocean waters are relatively scarce and geographically limited. Such data as could be readily obtained are presented in Figs. 24 through 27.

Wade and Quinn (52) measured total hydrocarbons in the surface microlayer of the Sargasso Sea (Fig. 24) at levels ranging from 14 to 559 ppb with a median value of 105 ppb. Sub-surface values, taken 20-30 cm beneath the surface, ranged from 0.13 to 239 ppb with a median of 60 ppb. In 5 of 17 analyzed samples, the surface microlayer contained greater levels of hydrocarbons than did the subsurface waters.

Barbier *et al.* (4) reported dissolved hydrocarbon levels at two stations offshore of the west coast of Africa, at two stations on the north coast of France (Brest and Roscoff) and at one station on the south coast of France (Villefranche). The levels of dissolved hydrocarbons measured at an open ocean station off west Africa varied from 43 ppb at 50 m to 19 ppb at 500 m, 10 ppb at 2000 m and 37 ppb at 4500 m (a few meters above the bottom). It was of interest that the hydrocarbons in samples from water depths of 500, 2000, and 4500 m gave approximately the same GC and MS results. This is in agreement with results indicated by the Exxon

data and "indicates a certain permanence of the structure of hydrocarbons in the sea" (4). Levels of dissolved hydrocarbons detected at Brest and Roscoff, both surface samples, were 137 ppb and 46 ppb, respectively. The Villefranche sample was collected at 50 m and indicated a dissolved hydrocarbon concentration of 75 ppb.

Zsolnay (56) reported measurements on particulate and dissolved non-olefinic hydrocarbons in the Gotland Deep of the Baltic. His data showed no significant differences in the variation of these hydrocarbon levels with depth. Values were measured in the range of 0.5 to 2.3 ppb for particulate non-olefinic hydrocarbons, and in the range of 48 to 64 ppb for dissolved non-olefinic hydrocarbons.

Iliffe and Calder (29) reported hydrocarbon measurements for the Florida Strait, the Gulf of Mexico, and the Yucatan Strait. Although they measured higher levels in the Florida Strait (an

average of 47 ppb) than in the mid-Gulf (an average of 12 ppb) and Yucatan Strait (an average of 12 ppb), the vertical distributions of these hydrocarbons to depths of 500 m did not vary greatly at any one station. Furthermore, they also observed a similarity in the hydrocarbon GC-traces for samples from different stations and at different depths.

Other data indicated in Fig. 24 include those reported for Narragansett Bay and for waters between Halifax and Bermuda. Duce *et al.* (17) reported a value of 8.5 ppb for surface waters of Narragansett Bay and a value of 5.9 ppb for subsurface waters. Gordon and Keizer (25) reported the following mean values for waters from different depths between Halifax and Bermuda: 1-5 m, 9.3 ppb; 1 m, 0.6 ppb; 5 m, 0.4 ppb; and 10-1000 m, 0.8 ppb.

Levy (36) measured the concentration of oil in Chedabucto Bay, Nova Scotia, several months

Figure 24a.

Other Hydrocarbon Measurements (from Refs. 4, 17, 25, 29, 52, and 56). Concentrations: ○, ≤2; ⊙, 3-10; ⊕, 11-25; and ●, > 25 ppb.

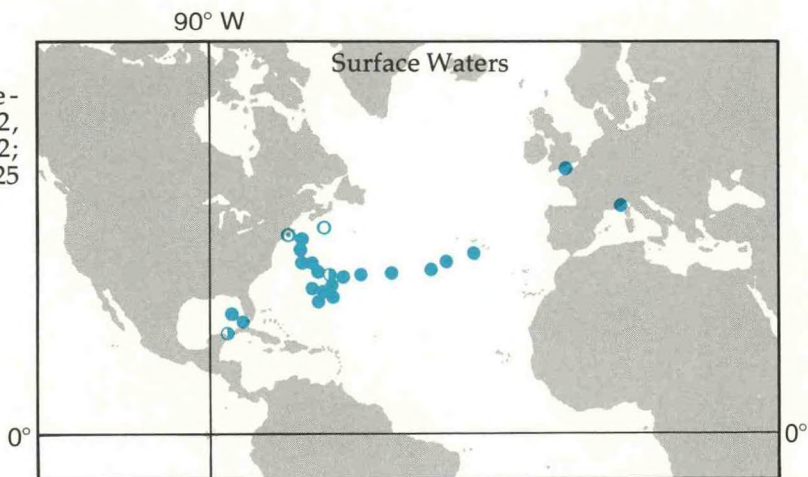
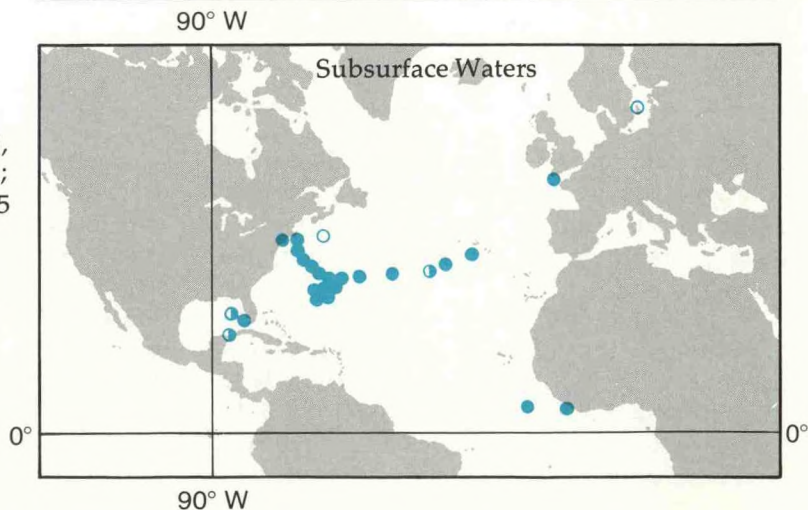


Figure 24b.

Other Hydrocarbon Measurements (from Refs. 4, 17, 25, 29, and 56). Concentrations: ○, ≤2; ⊙, 3-10; ⊕, 11-25; and ●, > 25 ppb.



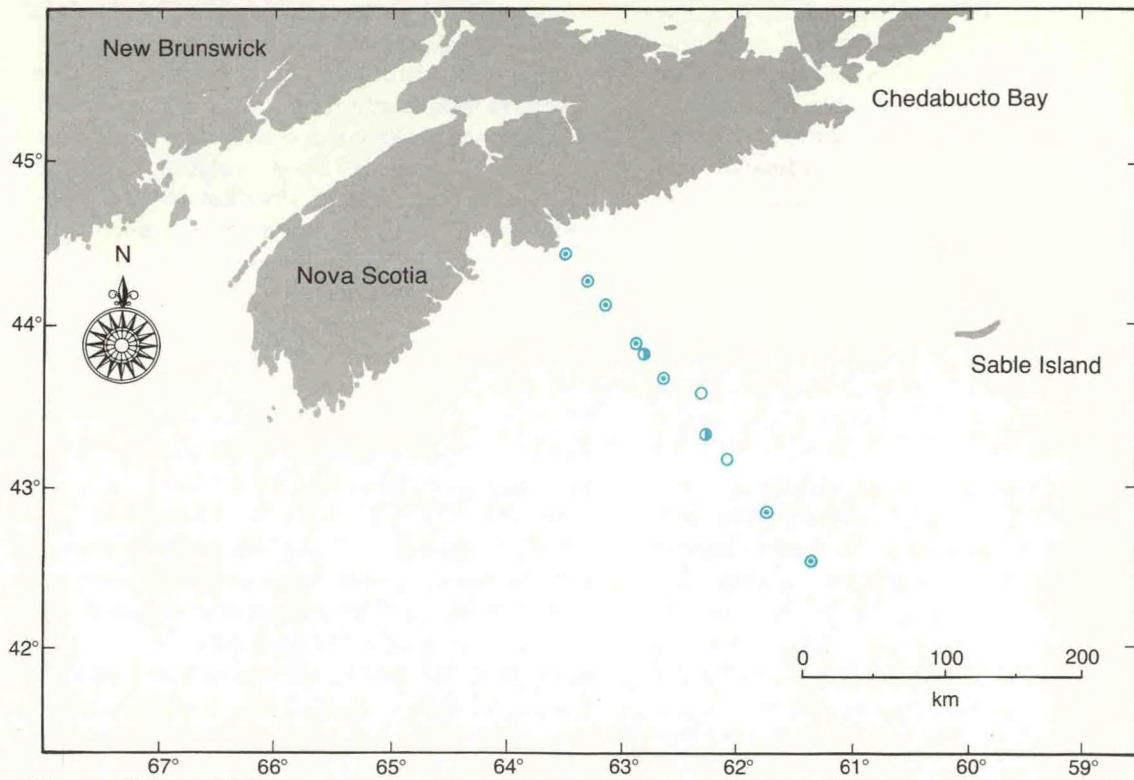


Figure 25 a. 2 Meter Depth Hydrocarbon Measurements Offshore of Nova Scotia (from Ref. 36). Concentrations: ○ , ≤2; ◌ , 3-10; ◐ , 11-25; and ● , > 25 ppb.

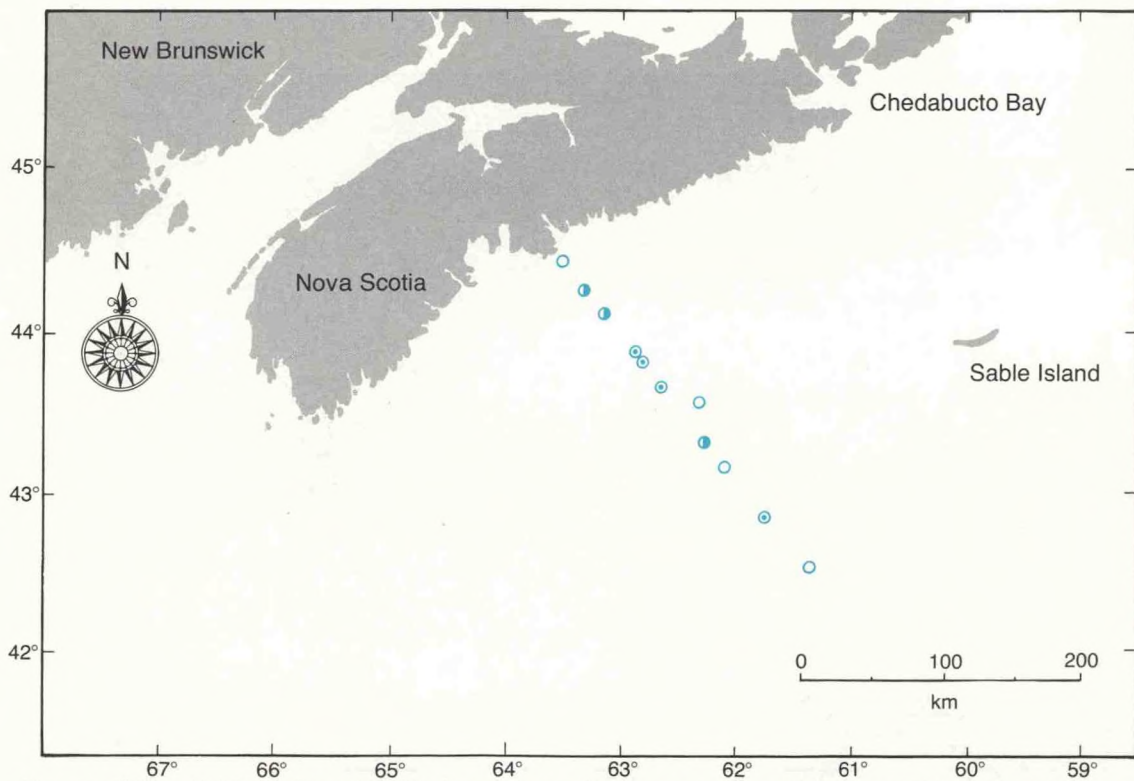


Figure 25 b. 10 Meter Depth Hydrocarbon Measurements Offshore of Nova Scotia (from Ref. 36). Concentrations: ○ , ≤2; ◌ , 3-10; ◐ , 11-25; and ● , > 25 ppb.

after the February 1971 spillage of oil in these waters from the tanker ARROW. Concentrations of particulate oil, which was filtered by a 0.45 micron filter, were observed in the range of 16 to 41 ppb. Further analyses of the filtrates of water collected within the bay indicated that the concentration of oil passing through the filter could be as large as 131 ppb. Other measurements of hydrocarbons in the outer reaches of Chedabucto Bay, in the Gulf of St. Lawrence, in the St. Lawrence River, and in the Atlantic offshore from Halifax included both dissolved and particulate hydrocarbons. The measurements for total non-volatile hydrocarbons in the outer reaches of the bay ranged from 7 to 106 ppb in surface waters (1 meter) and from about 7 to 20 ppb in deeper waters (20 to 140 meters). Measurements in the Gulf of St. Lawrence and the St. Lawrence River ranged from about 1 to 6 ppb and did not show any depth dependence. Values measured offshore from Halifax (Fig. 25) ranged from 2 to 13 ppb (median = 5 ppb) at the 2 meter depth, and from 2 to 14 ppb (median = 8 ppb) at 10 meters. The results indicated that the water of Chedabucto Bay still showed residuals of the spilled oil several months after spillage.

Koons and Brandon (33) presented the results of measurements on total volatile and non-volatile hydrocarbons in marine waters off Coal Oil Point near Santa Barbara, California. This area, known for its natural submarine oil seeps, contained higher levels of volatile hydrocarbons in surface waters (median of 5 samples equal to 0.07 ppb) than at a control area off Pt. Dume, some 100 kilometers to the southeast. Both surface measurements were less than 0.02 ppb and, with the exception of one sample, all subsurface measurements (six) were less than 0.02 ppb, barely above the detection limit of 0.01 ppb. Levels similar to those detected in the vicinity of Coal Oil Point were also measured offshore from Gaviota. These latter stations were about 2.5 kilometers to the west of Coal Oil Point in an area where considerable drilling activity has occurred. Measured values ranged from 2 to 45 ppb for extractable organics and from 0.2 to 16 ppb for non-volatile hydrocarbons (Fig. 26). Many of the non-volatile hydrocarbon data indicated low hydrocarbon to extractable organic ratios, suggesting biogenic sources.

As part of an environmental assessment of the northeastern Gulf of Alaska, Shaw (47) mea-

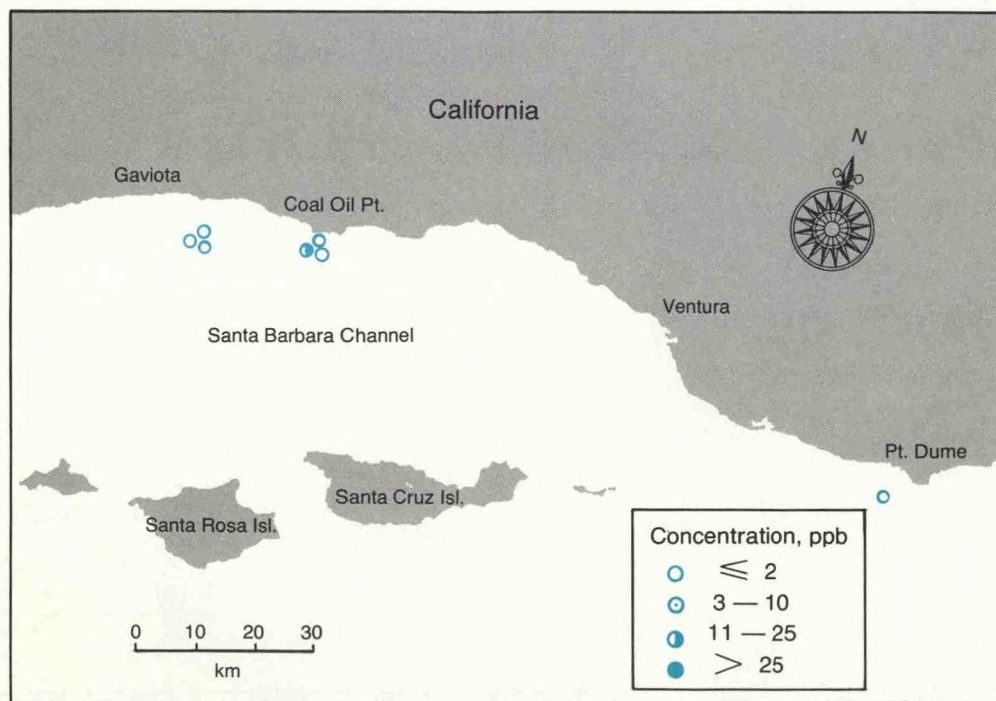


Figure 26a. Non-Volatile Hydrocarbon Measurements in Subsurface Waters of Santa Barbara Channel.

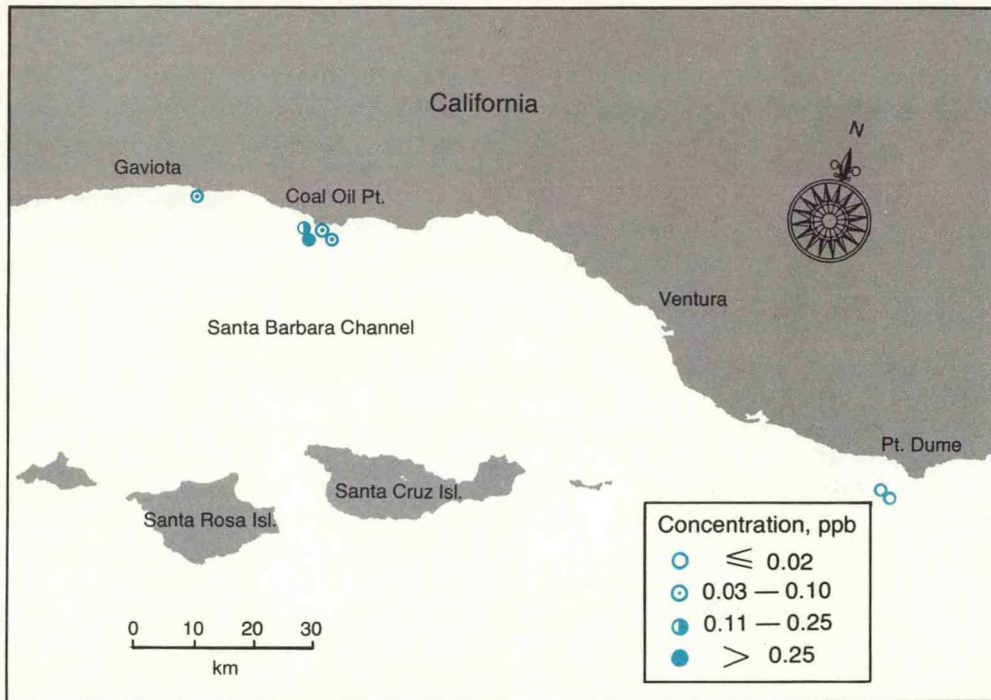


Figure 26b. Volatile Hydrocarbon Measurements in Surface Waters of Santa Barbara Channel.

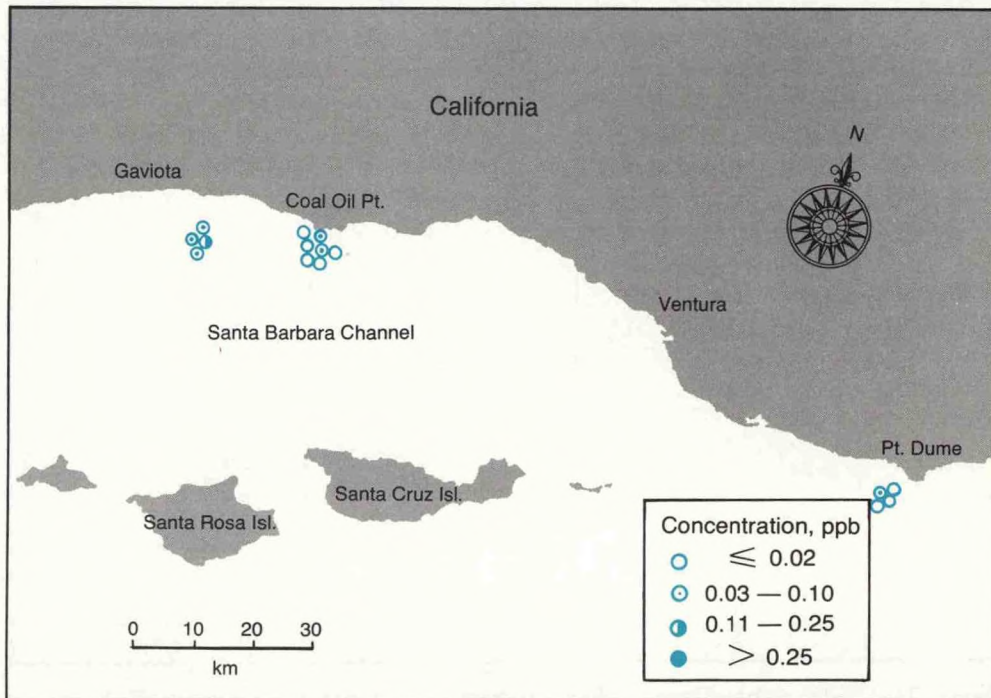


Figure 26c. Volatile Hydrocarbon Measurements in Subsurface Waters of Santa Barbara Channel.

sured surface extractable organic and hydrocarbon levels at several locations (Fig. 27). Levels of carbon tetrachloride extractable organic matter in sixteen samples ranged from less than 1 ppb to 54.2 ppb (a sample suspected of being contaminated). Ten of these samples were collected from the NOAA ship OCEANOGRAPHER during February 1975 and, with the exception of one sample (the 54.2 ppb value), all showed values less than 1 ppb. Six of the samples were collected in May 1975 from the NOAA ship TOWNSEND CROMWELL and indicated values in the range of 9.7 ppb to 19.7 ppb with a median of about 13 ppb. The large differences encountered between the two cruises were suspected of being due to a greater biological activity in May 1975. Only five samples were analyzed for non-volatile hydrocarbons; these values ranged from 1.1 ppb to 9.2 ppb with a median of 4.7 ppb.

Hertz *et al.* (28) also measured total hydrocarbons in the Gulf of Alaska area. These data, also included in Fig. 27, ranged from 2.7 ppb to 14.9 ppb for surface waters, and from 0.95 ppb to 30.5 ppb for subsurface waters. Median values were about 5 ppb for surface waters and 4 ppb for subsurface waters.

Although tar balls were excluded from samples obtained during the Exxon studies, a brief mention of their occurrence is appropriate. The occurrence of tar balls, or pelagic tar, has been frequently observed in the major oceans of the world as well as on beaches (12, 13, 18, 30, 40). The most publicized observations of pelagic tar have been those of Thor Heyerdahl and his crew during their crossings of the Atlantic by raft in 1969 and 1970. However, as noted by Butler (12), the first observations of pelagic tar at sea date back to at least 1954. Butler estimates that the present amount of tar on the surface of the oceans is about 700,000 tons. Analysis of these tars suggest that their source is tanker ballast wastes containing waxy fractions of crude oils. The waxy sludges adhere to the walls of tankers and are discharged with ballast before loading fresh cargo. The eventual fates of this tar, estimated to have a residence time in the sea of about a year, include (1) breakdown to smaller particulates that disperse in the water column, (2) deposition in sediments, and (3) oxidation to carbon dioxide.

The preceding data are representative of those that could be readily obtained from the literature; other data undoubtedly exist and

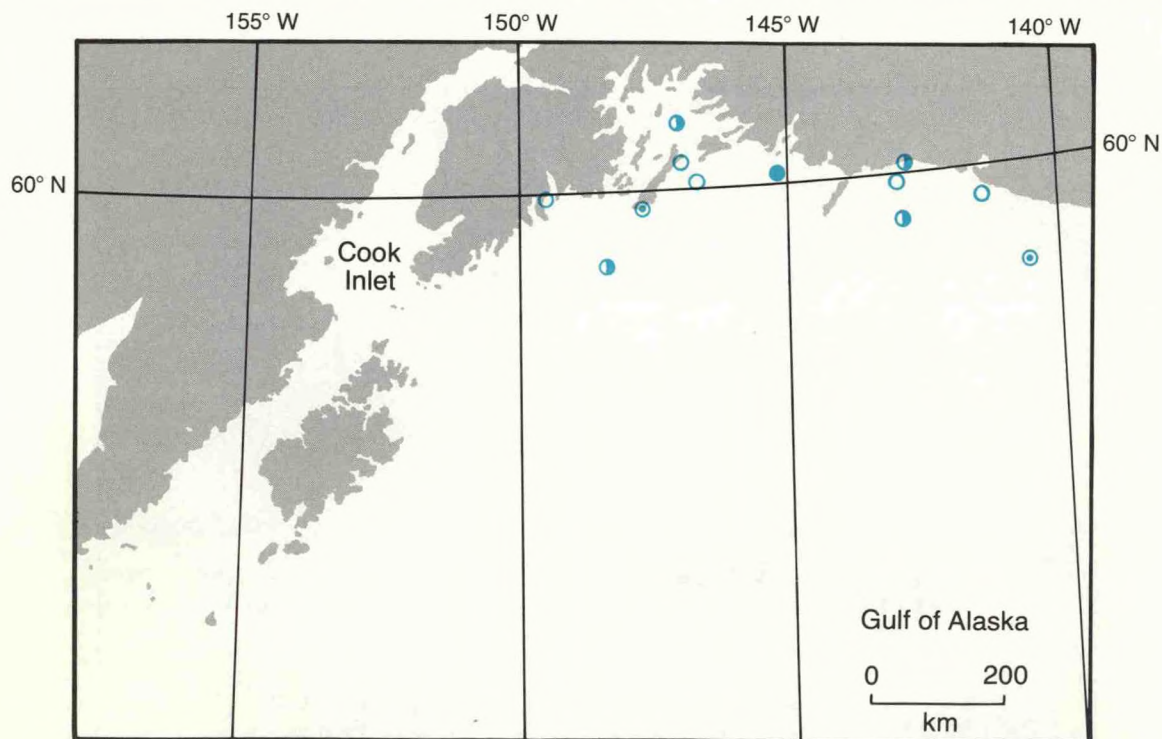


Figure 27a. Extractable Organic Measurements in Surface Waters of Gulf of Alaska (from Ref. 47). Concentrations: ○, ≤ 2; ◐, 3-10; ◑, 11-25; and ●, > 25 ppb.

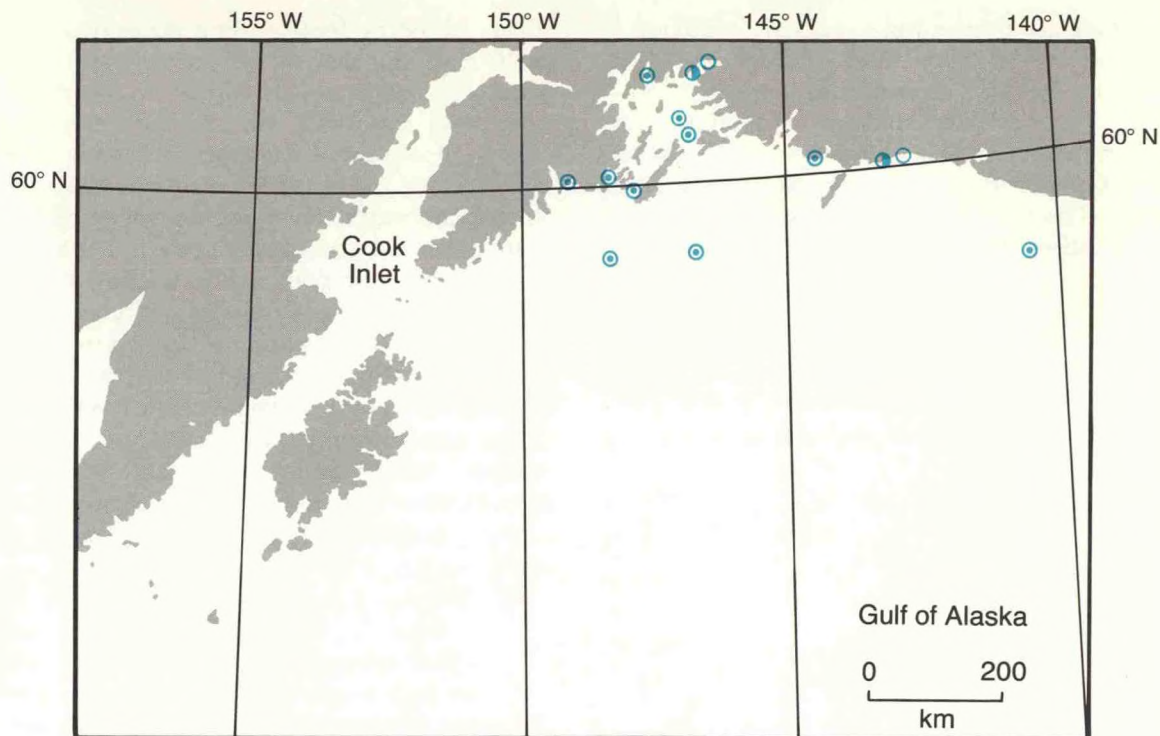


Figure 27b. Non-Volatile Hydrocarbon Measurements in Gulf of Alaska Surface Waters (from Refs. 28 and 47). Concentrations: ○, ≤ 2; ◐, 3-10; ◑, 11-25; and ●, > 25 ppb.

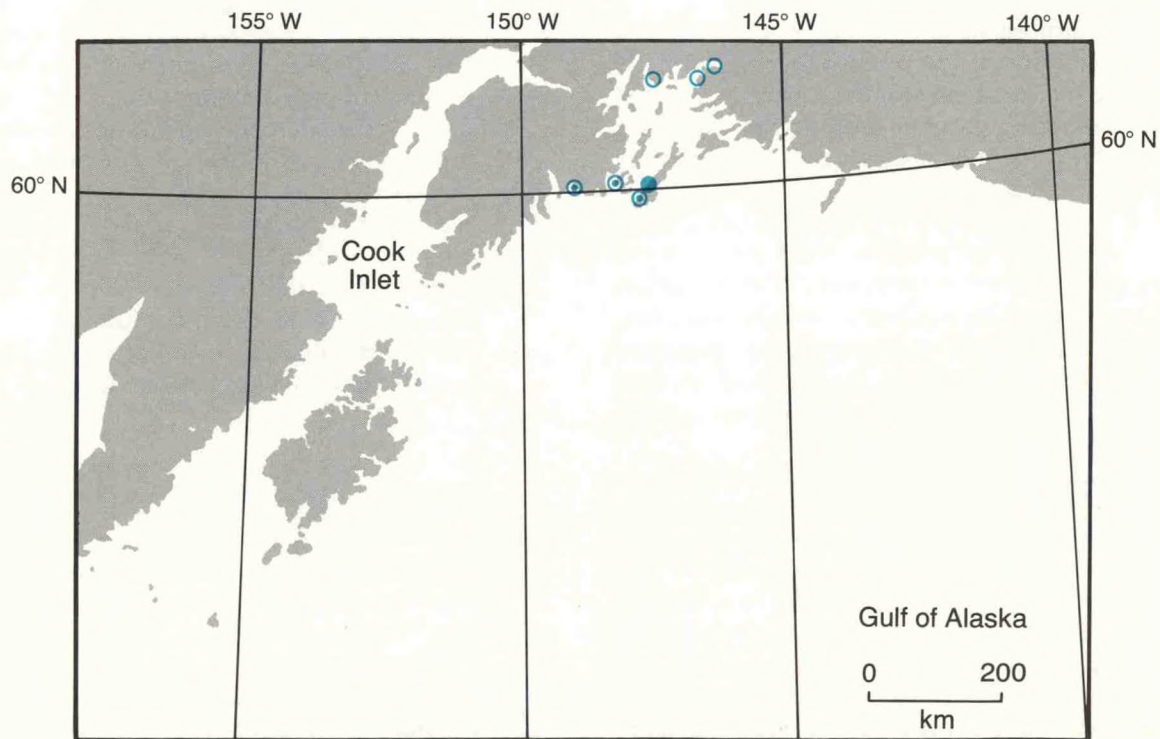


Figure 27c. Non-Volatile Hydrocarbon Measurements in Gulf of Alaska Subsurface Waters (from Refs. 28 and 47). Concentrations: ○, ≤ 2; ◐, 3-10; ◑, 11-25; and ●, > 25 ppb.

new data are continuing to appear. Although a comparison of these latter hydrocarbon data with the Exxon data indicates a general compatibility, the Exxon data are generally lower than many others. The differences that exist are probably due to actual variations in the waters sampled as well as to differences in sampling, preservation, and analytical techniques. ■

3. CONCLUSIONS

The purpose of this report is to summarize available information on baseline levels of hydrocarbons in ocean waters. The data indicate that, although hydrocarbon concentrations vary over several orders of magnitude, the majority of surface and near-surface measurements are in the range of about 1 to 10 parts per billion. Compositional information indicates that cycloparaffins are the predominant hydrocarbon type, followed by iso-paraffins and aromatics. The measurements of hydrocarbons in deeper ocean waters generally indicate levels less than measured in surface and near surface waters, with many values less than 1 ppb.

In general, coastal waters, for which there are greater potentials for hydrocarbon inputs, exhibit slightly higher levels than are detected in open ocean waters. Open ocean waters that are frequented by tanker traffic also exhibit slightly higher levels than are measured for less frequently traveled ocean waters. The hydrocarbon measurements on ocean waters indicate a pervasive distribution of both petroleum and biogenic hydrocarbons; however, the relative presence of biogenic hydrocarbons is more apparent in open ocean waters.

The preceding hydrocarbon range of about 1 to 10 ppb, measured for surface and near-surface ocean waters, is some 2 to 3 orders of magnitude less than the ppm concentrations used in most acute toxicity experiments. However, soluble fractions of petroleum hydrocarbons at concentrations near the ppb level have been observed to inhibit certain behavioral traits, such as the response to feeding stimuli, that are normal characteristics of some marine species (31). More research is needed to predict effects and risks associated with present and future levels of hydrocarbons in the oceans.

The data presented in this report and the necessity for an accurate assessment of fates and effects of petroleum hydrocarbons in the oceans, indicate the following additional research needs:

- (1) There is a need, as emphasized in Appendix A, to establish standard, officially recognized techniques of sampling, storage, preparation, and analysis for hydrocarbons in water, sediments, and biota. As emphasized by the National Science Foundation (42), such needs also extend to other trace contaminants.
- (2) Suitable models describing the probable history of individual hydrocarbon samples are needed. These should be developed in coordination with the Coast Guard's research and operations involving the "fingerprinting" of spilled oil.
- (3) A global conceptual model which includes the sources, transport mechanisms, and fates of petroleum hydrocarbons in the oceans should be developed. This model should define critical information gaps so that a complete predictive model can be assembled. ■

4. ACKNOWLEDGMENTS

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APPENDIX

NEED FOR STANDARDIZED TECHNIQUES IN HYDROCARBON ANALYSIS

The fact that hydrocarbon levels in sediments, biota, and waters of the oceans range over many orders of magnitude stresses a need for versatile and precise analytical hydrocarbon techniques if associated impacts are to be adequately assessed. The need for standard analytical techniques, approved by intercalibration exercises of the type reported by Farrington *et al.* (1), was emphasized in a paper presented at a Workshop on Standard Reference Materials for Offshore Drilling — Petroleum (2). The following is essentially an excerpt from that paper.

During 1975, the MESA (Marine Ecosystems Analysis, NOAA) Program Office funded hydrocarbon measurements in sediments and organisms contaminated by the August 1974 METULA oil spill in the Strait of Magellan (3, 4). The majority of measurements were performed by Battelle Columbus Laboratories using gas chromatography (GC) for determination of hydrocarbons in biological tissues, and infrared (IR) and gravimetric (GR) techniques for determination of carbon tetrachloride extractables in sediments (primarily hydrocarbon components at these concentrations). Splits of five of the samples (one tissue and four sediment samples) were sent to the National Bureau of Standards (NBS) for petroleum contamination determinations by gas chromatography, liquid chromatography (LC) and gravimetric analysis.

Interlaboratory and intralaboratory comparison of the results from both labs are depicted in Figs. A1 and A2. This representation of the data indicates that consistent results were obtained by Battelle to 1 part in 10^5 , and by the NBS to 1

part in 10^3 . The tendency for lower hydrocarbon determination by GC, as compared to LC, may be due to some weathering of the n-C₁₅ to n-C₁₈ fractions (assumed not to weather) used for GC quantification. It is also observed (Fig. A2) that the measurements obtained by each laboratory on the split samples are quite compatible above the parts per thousand level. Differences at and below this level are partly due to differences in specificities of the individual techniques. For instance, the gravimetric and IR determinations are for total carbon tetrachloride extractables and include some non-petroleum organics. The results of the gravimetric and IR measurements would thus tend to overestimate the hydrocarbon contents, particularly at the lower petroleum contamination levels. Other differences in the results may be due to local inhomogeneities of samples, weathering effects, differences in internal standards, and differences associated with the storage, handling, and preparation of samples.

These comparisons indicate a need for establishing standard methods of obtaining, storing, preparing, and analyzing such samples. This is particularly true if the subtle effects of hydrocarbon contamination are to be determined accurately.

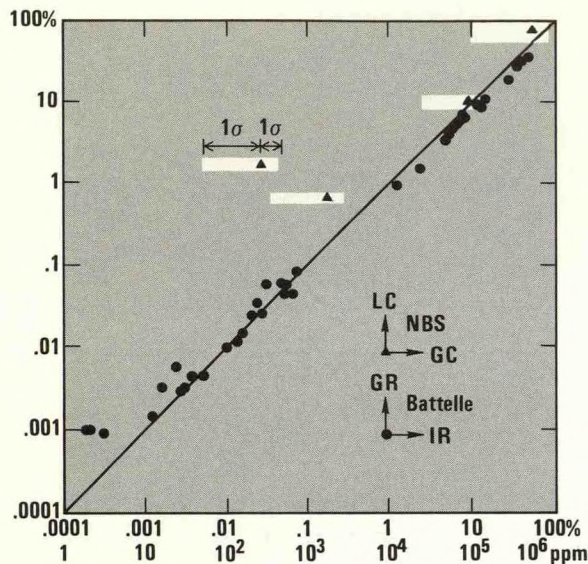


Figure A1. Intralaboratory comparisons of different methods of Hydrocarbon analysis of METULA oil spill samples.

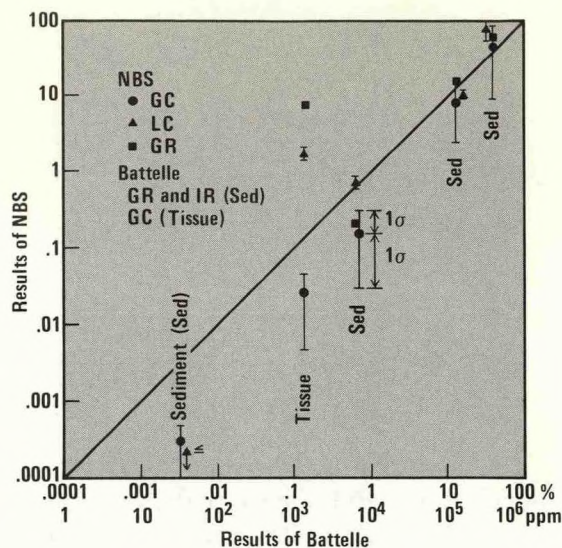


Figure A2. Intralaboratory comparisons of Hydrocarbon determinations on Metula oil spill split samples.

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The mission of the Environmental Research Laboratories (ERL) is to conduct an integrated program of fundamental research, related technology development, and services to improve understanding and prediction of the geophysical environment comprising the oceans and inland waters, the lower and upper atmosphere, the space environment, and the Earth. The following participate in the ERL missions:

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- OCSEA** *Outer Continental Shelf Environmental Assessment Program.* Plans, directs, and coordinates research of federal, state, and private institutions to assess the primary environmental impact of developing petroleum and other energy resources along the outer continental shelf of the United States.
- WM** *Weather Modification Program Office.* Plans, directs, and coordinates research within ERL relating to precipitation enhancement and mitigation of severe storms. Its National Hurricane and Experimental Meteorology Laboratory (NHEML) studies hurricane and tropical cumulus systems to experiment with methods for their beneficial modification and to develop techniques for better forecasting of tropical weather. The Research Facilities Center (RFC) maintains and operates aircraft and aircraft instrumentation for research programs of ERL and other government agencies.
- AOML** *Atlantic Oceanographic and Meteorological Laboratories.* Studies the physical, chemical, and geological characteristics and processes of the ocean waters, the sea floor, and the atmosphere above the ocean.
- PMEL** *Pacific Marine Environmental Laboratory.* Monitors and predicts the physical and biological effects of man's activities on Pacific Coast estuarine, coastal, deep-ocean, and near-shore marine environments.
- GLERL** *Great Lakes Environmental Research Laboratory.* Studies hydrology, waves, currents, lake levels, biological and chemical processes, and lake-air interaction in the Great Lakes and their watersheds; forecasts lake ice conditions.
- GFDL** *Geophysical Fluid Dynamics Laboratory.* Studies the dynamics of geophysical fluid systems (the atmosphere, the hydrosphere, and the cryosphere) through theoretical analysis and numerical simulation using powerful, high-speed digital computers.
- APCL** *Atmospheric Physics and Chemistry Laboratory.* Studies cloud and precipitation physics, chemical and particulate composition of the atmosphere, atmospheric electricity, and atmospheric heat transfer, with focus on developing methods of beneficial weather modification.
- NSSL** *National Severe Storms Laboratory.* Studies severe-storm circulation and dynamics, and develops techniques to detect and predict tornadoes, thunderstorms, and squall lines.
- WPL** *Wave Propagation Laboratory.* Studies the propagation of sound waves and electromagnetic waves at millimeter, infrared, and optical frequencies to develop new methods for remote measuring of the geophysical environment.
- ARL** *Air Resources Laboratories.* Studies the diffusion, transport, and dissipation of atmospheric pollutants; develops methods of predicting and controlling atmospheric pollution; monitors the global physical environment to detect climatic change.
- AL** *Aeronomy Laboratory.* Studies the physical and chemical processes of the stratosphere, ionosphere, and exosphere of the Earth and other planets, and their effect on high-altitude meteorological phenomena.
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