

Dissolved hydrocarbons in the eastern Gulf of Mexico Loop Current and the Caribbean Sea

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Abstract—Concentrations of dissolved non-polar hydrocarbons extracted from waters taken at several stations and depths in the Gulf of Mexico and Caribbean Sea ranged from traces to $75 \mu\text{g l}^{-1}$, with the highest occurring in the Florida Strait. In all cases except in the Florida Strait, this fraction was characterized by relatively large amounts of n-alkanes having between 15 and 20 carbon atoms and relatively small amounts of n-alkanes with more than 20 carbon atoms. In the Florida Strait there were much larger concentrations of n-alkanes above C_{20} . There was an unresolved envelope in the gas chromatograms of all the samples that extended approximately from the C_{15} to the C_{30} position, with the maximum between the C_{20} and C_{23} positions.

INTRODUCTION

THERE have been few studies of the dissolved hydrocarbons in seawater. BLUMER (1970) reported carbon numbers ranging from C_{14} to C_{33} for n-alkanes in surface seawater. The maxima occurred at C_{25} to C_{28} and there was no preference for odd nor even numbers. PARKER, WINTERS and MORGAN (1972) reported concentrations of n-paraffins of $1 \mu\text{g l}^{-1}$ or less and a range of C_{15} – C_{36} for surface water samples from the Gulf of Mexico and the Caribbean Sea. More recently, BARBIER, JOLY, SALIOT and TOURRES (1973) examined the hydrocarbon content of coastal and open waters from the eastern Atlantic Ocean. N-Alkanes comprised about 12% of the total extracts and ranged from C_{14} to C_{37} with a maximum between C_{27} and C_{30} . Hydrocarbons are among the most stable organic molecules and, in sediments, can persist for geologically long periods of time. Because of their stability, dissolved hydrocarbons may be useful indicators of the history of a water mass. However, it is not now known how rapidly dissolved hydrocarbons can be degraded or modified by natural *in situ* processes. Detailed studies of the dissolved hydrocarbons in many different waters would be needed to provide this information. As a first step, we present preliminary information on non-polar hydrocarbon concentrations and composition in an identifiable water mass and differences among water masses.

THE LOOP CURRENT

A major circulation feature in the Gulf of Mexico is a Caribbean-derived tongue of warm water, the Eastern Gulf Loop Current. This current was defined by NOWLIN and MCLELLEN (1967) as a surface and subsurface flow, originating in the Caribbean Sea and flowing northward toward the northwest Florida coast, then turning east, and, in the region of the West Florida Escarpment, turning southward until it joins the

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Florida Current. Beginning in the spring and intensifying through the summer, the current forms a pronounced loop into the northern Gulf of Mexico. By late summer, the loop may detach from the current and become a separate westward drifting eddy. In the main current, speeds range from 50 to 200 cm s⁻¹ and transport about 30×10^6 m³ s⁻¹ (SACKETT, 1972). LEIPPER (1970) found the 22°C isotherm to be present all year in the Loop Current. The velocity core of the current was generally in the region of maximum slope of the 22°C isotherm.

Water entering the Gulf of Mexico through the Yucatan Channel is derived from at least three different water masses (WÜST, 1963). Deep water is a mixture of low salinity Subantarctic Intermediate Water (SIW) and oxygen-rich North Atlantic Deep Water (NADW). High salinity Subtropical Under Water (SUW) is found from 100 to 200 m.

SAMPLING

Three stations in or near the velocity core of the Loop Current were the basis for this study. Each consisted of a hydrocast with sampling at 1 m below the surface, at intermediate isotherms and at 500 m (Table 1). Other samples were obtained from

Table 1. *Samples and fraction concentrations.*

Station	Depth (m)	Temp. (°C)	Volume extracted (l.)	DEM (µg l ⁻¹)	Non-polar hydrocarbon (µg l ⁻¹)	N-p HC (% of DEM)
Florida Strait*	1	28.5	18.98	—	52	—
	107	25	16.34	291	38	13
	144	22	17.45	180	75	42
	213	18	18.99	196	16	8
	269	16	18.61	117	54	46
	500	10	19.46	121	trace	—
			Average:	181	47	26
Mid-Gulf†	1	25.2	19.18	84	12	14
	75	20.5	19.31	318	—	—
	150	16.4	19.36	78	7	9
	225	12.4	19.24	215	18	8
	500	—	19.23	75	13	17
			Average:	154	12	8
Yucatan Strait‡	1	28.0	19.15	210	24	11
	100	24	19.14	358	trace	—
	128	22	19.04	202	trace	—
	200	18	18.71	279	4	1
	500	10	18.82	224	9	4
			Average:	255	12	5
Cariaco Trench§	900	16.9	18.44	357	5	1
Caribbean	200	—	18.56	124	8	6

*24°06'N, 83°16'W, R.V. *Bellows*, 30 and 31 August, 1971.

†25°16'N, 84°34'W, R.V. *Tursiops*, 1 March, 1972.

‡21°58'N, 85°59'W, R.V. *Oregon II*, 9 November, 1971.

§10°37.5'N, 65°45.5'W, U.S.N.S. *Mizar*, 9–11 March, 1972.

||13°20'N, 66°48'W, U.S.N.S. *Mizar*, 9–11 March, 1972.

900 m in the anoxic Cariaco Trench off Venezuela and from 200 m in the central Caribbean Sea.

Niskin water sampling bottles (30-l.) were used. Each had been rinsed with redistilled chloroform before sampling. Depths of the desired isotherms were found from the expendable bathythermograph (XBT) traces for the station. Auxiliary data, such as salinities, STD traces, etc. were obtained when possible.

Water samples were removed from the Niskin bottles through Teflon tubing to avoid contamination. They were then filtered through Whatman No. 1 filter paper (previously extracted with CHCl_3) under vacuum to remove particulate matter. The samples were then poisoned with copper and mercury salts and stored in glass bottles. On the *Mizar* and *Oregon II* (Table 1), samples were stored under refrigeration. Samples were stored at ambient temperature on the *Bellows* and *Tursiops*.

Plankton samples were obtained in both the Florida and Yucatan straits in November, 1971 using 0.5-m nets with 0.33-mm mesh. The samples were placed in sterile containers and half of them were frozen immediately. Inorganic nutrients were added to the other half to stimulate microbial growth, and the samples were allowed to decompose aerobically in the dark for one month in seawater.

METHODS

Organic solvents were redistilled in an all glass still from reagent grade solvent. The dissolved lipids were extracted using a separatory funnel with three 50-ml portions of chloroform for each 1500 ml of seawater. The samples were adjusted to pH 2 with concentrated HCl. BLUMER (1970) demonstrated that this procedure, using pentane as the solvent, produces quantitative results after four extraction steps. We added ^{14}C -labelled hexadecane to 1.5 l. of seawater and extracted successively with 50-ml portions of chloroform. Of the recovered ^{14}C -hexadecane, 83% was in the first extraction, 12% in the second, 4% in the third, and 1% in the fourth. Three extractions were judged sufficient for the water samples. Plankton samples were homogenized in a high-speed blender before being extracted with 1:1 chloroform-methanol while exposed to ultrasonic energy. Water and plankton extracts were evaporated to dryness under a stream of nitrogen at room temperature and weighed. The total extract was saponified for 6 h with 10 ml of 0.5-N KOH in methanol. The saponification mixture, with 5 ml of distilled water added, was extracted with hexane to yield the non-saponifiable fraction. The methanol-water fraction was saved for analysis of fatty acids. The non-saponifiable fraction was applied to a silica gel column and the non-polar hydrocarbons were eluted with hexane. The hexane was evaporated under nitrogen at room temperature, and the solvent-free eluate was weighed.

Non-polar hydrocarbons were identified by gas chromatography using 5% Dexsil 300 GC on Chromosorb G (acid washed, dimethyldichlorosilane treated, 60/80 mesh) in a 2 m \times 2 mm i.d. stainless steel column. Conditions for gas chromatography were as follows: single flame ionization detector; prepurified nitrogen carrier gas, flow controlled at 20 ml min^{-1} ; hydrogen 30 ml min^{-1} ; air 300 ml min^{-1} ; column oven temperature programmed from 100 to 350°C at 8° min^{-1} with no initial hold; electrometer sensitivity variable from 1×10^{-11} to 1×10^{-10} A full scale; 1 mV chart recorder. Because of the small quantities of material available, high sensitivity (low attenuation) settings on the electrometer were necessary to produce useful spectra. Because of the

high sensitivity required, it was necessary to use a column packing with high thermal stability and low bleed characteristics. The only liquid phase meeting these requirements was Dexsil, although it lacks the resolving power of other liquid phases such as Apiezon L. Compounds were identified by comparison of their retention times with those of standards or by plotting retention times versus carbon number.

Two liters of CHCl_3 were evaporated to dryness under nitrogen and subjected to saponification and all other procedures to produce a non-polar hydrocarbon fraction. Analysis of this fraction indicated no contaminants with retention times greater than that of $n\text{-C}_{15}$. All possible precautions were taken to exclude contamination during collection. The similarity of non-polar hydrocarbon GC spectra from surface and from deep water samples (see Discussion) indicates indirectly that our sampling procedure avoided any contamination of the surface by the ship.

RESULTS AND DISCUSSION

The dissolved extractable matter (DEM) ranged from 75 to 360 $\mu\text{g l}^{-1}$ in open ocean waters (Table 1). This material includes all the chloroform-soluble lipids, and in addition to non-polar hydrocarbons, should contain the more polar aromatic hydrocarbons, long-chain acids, alcohols, esters, and other compounds similarly soluble. The non-polar hydrocarbon fraction was an average of 5% of the DEM in the Yucatan Strait and 8% in the mid-Gulf region. The absolute concentration of non-polar hydrocarbons averaged 12 $\mu\text{g l}^{-1}$ in the Yucatan Strait and the mid-Gulf station. In the Florida Strait, the non-polar hydrocarbon fraction was 26% of the DEM with an average concentration of 47 $\mu\text{g l}^{-1}$, or almost four times that at the other two Loop Current stations.

Our values are all greater than those reported by PARKER, WINTERS and MORGAN (1972). This difference is probably a reflection of different methods. They summed GC peak areas for the n -paraffins and converted areas to weight, while we weighed the total hexane eluate from silica gel. The concentrations reported by BARBIER, JOLY, SALIOT and TOURRES (1973), who also used gravimetric methods, are similar to ours.

Gas-liquid chromatographic (GC) spectra for the Caribbean and Loop Current samples (Figs. 1, 2 and 3) show that normal alkanes in seawater ranged from C_{14} to C_{40} . An envelope of unresolved components extending from about C_{15} to C_{30} with a maximum between the C_{20} and C_{23} positions was found in every chromatogram from seawater samples. In general, there were relatively large concentrations of n -alkanes from C_{15} to C_{20} and relatively low concentrations of n -alkanes above C_{20} (except in the three shallowest samples from the Florida Strait, which contained larger quantities of higher molecular weight n -alkanes). This distribution is similar to that found in marine phytoplankton in which the major alkanes have 21 or fewer carbon atoms (BLUMER, GUILLARD and CHASE, 1971). The similarity of the hydrocarbon spectra from the Caribbean, Yucatan Straits and mid-Gulf at all depths indicates that local processes exert little influence on the non-polar hydrocarbon composition of seawater. Even in the Cariaco Trench the hydrocarbon spectrum was similar to that from oxygenated surface water.

The vertical distribution from the mid-Gulf clearly points out that near-surface processes have no detectable effect on the non-polar hydrocarbon content of seawater; GC spectra are virtually identical from the surface to 500 m. There is no indication of

increased biological production of hydrocarbons at the surface. The evidence (Figs. 1 and 2) indicates that the non-polar hydrocarbon content of open ocean water must be controlled by long-term non-local processes. This conclusion is corroborated by comparison of dissolved non-polar hydrocarbons (Figs. 1 and 2) with those from net plankton and their decomposition products (Fig. 4). The plankton did not contain the envelope of unresolved components found in seawater, and the series of n-alkanes above C_{20} that appeared in both plankton and their aerobic decomposition products was not apparent in seawater. Planktonic organisms constitute the bulk of the biomass of the oceans, yet they apparently do not make a recognizable contribution to the dissolved non-polar hydrocarbons in seawater. Thus, the non-polar hydrocarbon composition of the water samples described in Figs. 1 and 2, is apparently controlled by long-term biological and physicochemical activity.

The hydrocarbon spectra from 1, 107 and 213 m in the Florida Strait depart from the

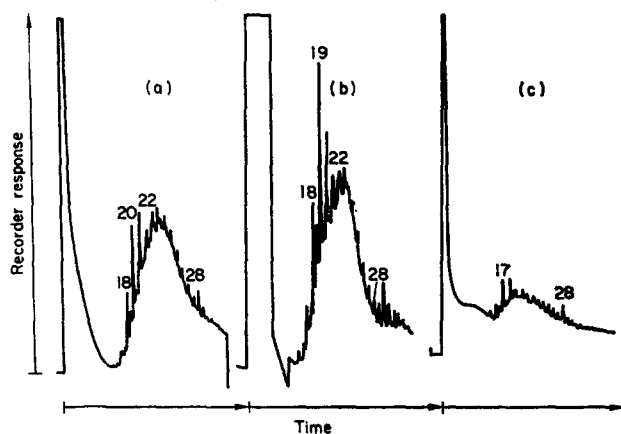


Fig. 1. GC spectra of the non-polar hydrocarbon fraction from (a) Caribbean station, 200 m, (b) Cariaco trench, 900 m, (c) Yucatan Strait, 200 m.

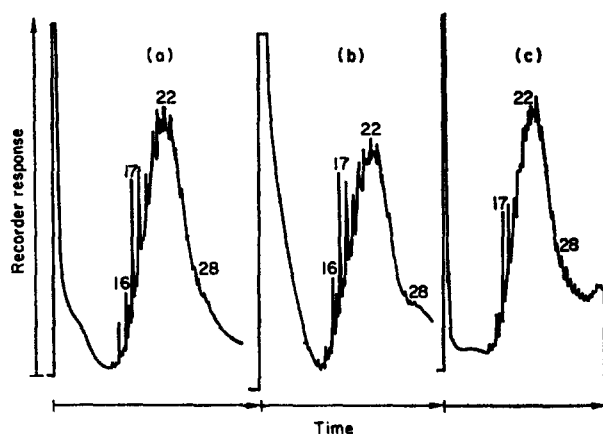


Fig. 2. GC spectra of the non-polar hydrocarbon fraction from the mid-Gulf station. (a) 1 m, (b) 150 m, (c) 500 m.

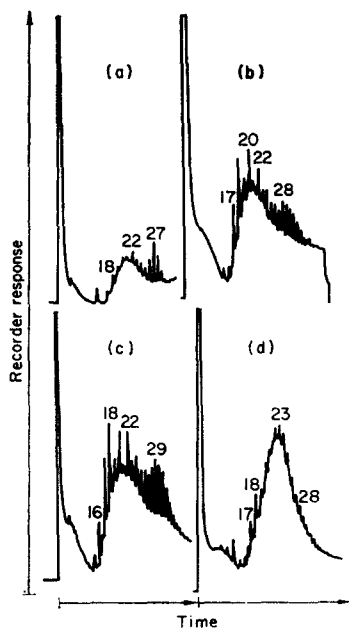


Fig. 3. GC spectra of the non-polar hydrocarbon fraction from the Florida Strait station taken at (a) 1 m, (b) 107 m, (c) 213 m, (d) 269 m.

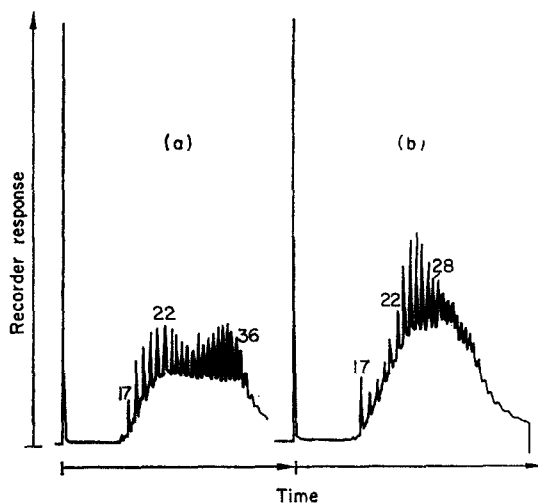


Fig. 4. GC spectra of the non-polar hydrocarbon fraction from (a) net plankton from the Yucatan Strait, (b) decomposed net plankton from the Florida Strait.

generalizations stated above in that there are higher concentrations of n-alkanes above C₂₀ (Fig. 3). There is also an increase in total non-polar hydrocarbon concentration in these waters (Table 1). The potential sources for the additional hydrocarbons are increased productivity or input from outside sources. Net plankton and their aerobic decomposition products could provide higher molecular weight n-alkanes (Fig. 4). If plankton production is the source of these alkanes, the primary production in the Florida Strait should be significantly greater than in the mid-Gulf and Yucatan Strait areas, but available literature does not confirm this. BELOUSOVA, IVANOV, PASTERNAK, RASS and ROSOV (1966) report productivity in the Florida Strait to be generally low and not greater than elsewhere in the southeastern Gulf of Mexico. Therefore, increased productivity cannot confidently be invoked to explain the greater alkane content of the water in the Florida Strait.

In regions where the rate of primary productivity is high relative to the background of dissolved organic matter, one may find a correlation between dissolved hydrocarbons and biologic activity. A recent report by ZSOLNAY (1973), demonstrated a positive correlation between relative amounts of non-aromatic hydrocarbons and chlorophyll-*a* concentrations in a zone of upwelling off the West African coast.

It has been postulated that atmospheric fallout may be a major route for the introduction of hydrocarbons into the oceans (*Study of Critical Environmental Problems*, 1970, pp. 140–141). Such a mechanism could be responsible for the greater non-polar hydrocarbon content of the near-surface waters in the Florida Strait. However, the GC spectra from the mid-Gulf station (Fig. 2) clearly demonstrate that atmospheric fallout has not altered the surface hydrocarbon distribution relative to deep water distribution and this is probably not an important factor in the Florida Strait.

The Florida Strait is a major tanker route. Approximately 400,000,000 barrels of oil are transported through the Strait annually (GILMORE, SMITH, RICE, SHENTON and MOSER, 1970). It is estimated that tankers lose about 0.05% of their cargo during routine operations (*Study of Critical Environmental Problems*, 1970, pp. 266–267) plus an additional amount by accidents. Thus tanker traffic through the Straits is a large potential source of hydrocarbons.

There is heavy tanker and other ship traffic in the Caribbean Sea and Gulf of Mexico. It is possible that the dissolved hydrocarbons from these waters are primarily the result of chronic petroleum additions. This would be consistent with the general uniformity of the GC spectra and the unresolved envelope in Figs. 1–3. If so, this implies that marine organisms to depths of several hundred meters are exposed to elevated concentrations of aromatic petroleum hydrocarbons as well as to the non-polar hydrocarbons.

It is not possible to determine from our data the source for the higher concentration of dissolved non-polar hydrocarbons in the Florida Strait. Clearly, more detailed investigation would be required to resolve this important question. If pollution is responsible for the hydrocarbon levels in the Florida Strait, one must be concerned about possible harmful biological effects. If natural processes are responsible, the biology of the Florida Strait must differ in some significant fashion from that of the southeastern Gulf of Mexico.

The work of BARBIER, JOLY, SALIOT and TOURRES (1973) is most directly comparable to ours. The concentrations of total extract and of hydrocarbons they determined are similar to those reported here. With the exception of the unresolved envelope, our

spectra from the Florida Strait surface (Fig. 3a) correspond to most of their spectra. However, there are significant qualitative differences apparent in the remainder of our gas chromatograms. In their work, the dominant n-alkanes were generally above C₂₂ with minor quantities of the C₁₅ to C₂₀ n-alkanes. This is opposite to most of the distributions we observed. The reason for this significant difference is not readily apparent. Their spectra correspond more closely to the alkane composition of mixed marine plankton (CLARK and BLUMER, 1967, and Fig. 4a). It is possible that their water samples contained relatively young n-alkanes whereas the n-alkanes in our samples may have been older and more highly modified by *in situ* processes.

This preliminary report and the existing literature indicate that the chemistry of dissolved hydrocarbons in seawater may yield valuable information regarding the bio-organic history of a water mass. In particular, there are significant differences in the n-alkane composition of waters from the Florida Strait and of other waters from the Gulf of Mexico and Caribbean Sea. Waters from the eastern Atlantic Ocean have yet a different n-alkane distribution.

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