HYDROCARBONS AND FREE FATTY ACIDS ASSOCIATED WITH THE AIR/WATER INTERFACE, SEDIMENTS, AND BEACHES OF THE TIMBALIER BAY AND OFFSHORE LOUISIANA AREA

by J. L. Laseter and E. J. Ledet

ABSTRACT

Some 5,800 compounds were isolated and analyzed from 224 sediment and air/water interface samples taken during the Offshore Ecology Investigation. The objective was to characterize the nature and distribution of hydrocarbons and related organic substances and to distinguish them from pollution-derived hydrocarbons resulting from petroleum activity in the area. The results of these investigations, including the sampling methods developed and the results of the air/sea interface studies, were published in three papers. These papers are reprinted herein, with minor changes, as they originally appeared in *Analytical Chemistry, Analytical Letters,* and *Science*. The authors and the Gulf Universities Research Consortium are grateful to the original publishers for permission to reprint the papers.

I. NEW SAMPLING DEVICE FOR THE RECOVERY OF PETROLEUM HYDROCARBONS AND FATTY ACIDS FROM AQUEOUS FILMS

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Replacement of coal by petroleum as the major world source of energy has resulted in increasing amounts of petroleum products being released into the environment. The need to quantify and to identify petroleum hydrocarbons in natural waters has presented methodological difficulties—especially with hyrocarbon films at the air/water interface. Since petroleum spills generally result in surface slicks of non-uniform thickness that can cover relatively large areas, a surface film sampler was required that would permit rapid, consistent, and efficient retrieval of surface hydrocarbons.

We have developed an inexpensive sampler which fulfills these requirements, and which can be operated under moderately rough surface conditions. Field comparison of this sampler with the screen technique (Garrett 1965) and the sorbent-in-a-can sampler (Estes et al. 1973) showed it to be easier to use and to require less sampling time. While we have used this sampler for both inshore and offshore field work for the past year under a variety of sea surface conditions, the purpose of this report is to discuss laboratory studies performed to determine the selectivity of the sampler for hydrocarbons and related compounds as a function of molecular structure, and the efficiency of recovery for petroleum films of varied thicknesses.

EXPERIMENTAL

Sampling apparatus and procedure

The surface film sampler (figure 1) consists of a disc of 2-mm Teflon attached to a 4-mm marine aluminum backing by means of 24 aluminum countersunk bolts. The original prototype tested by one of us (Miget) utilized a "heat cured" epoxy coated wooden backing plate. It was later found, however, that the epoxy would contribute small quantities of aromatic compounds in the 220- to 524-molecular weight range to the samples collected. Substitution of marine aluminum eliminated the contamination problem and produced a stronger and lighter weight device. A unidirectional hinge is located in the center of the backside of the aluminum disc. For field use, a wooden pole is attached to the hinge at such an angle that the Teflon face and water surface are parallel.

In order to collect a sample, the device is first touched to the water surface as lightly as possible, and the disc is then rested vertically on a large glass funnel. Organics adhering to the disc are then washed through the funnel into a container by a gentle stream of CCl_4. The sampler is slowly
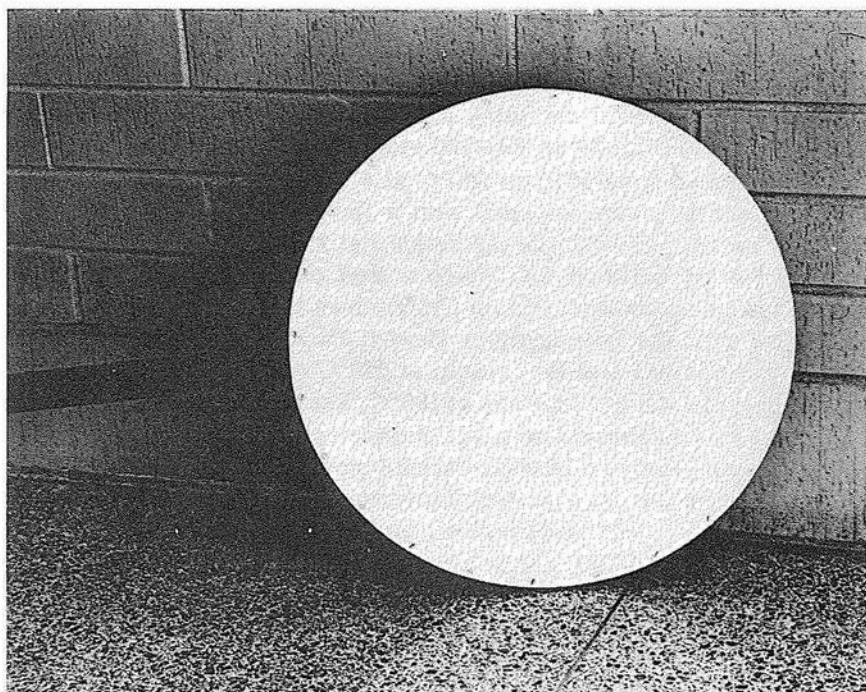
FIG. 1. PHOTOGRAPH OF THE SAMPLING DEVICE.

rotated and CCl₄ applied in a fine stream from the center of the disc downward to the washed surface. A 30- to 40-ml solvent rinse is generally sufficient, although unusually thick films require more solvent. When crude oil slicks are sampled, the dark oil contrasts against the white Teflon, aiding in an efficient removal. Other than for allowing the solvent to dry, no additional treatment of the Teflon surface is required before taking the next sample. Thus, several samples may be collected at the same site and washed into the same tube for a pooled sample. Further treatment of the samples for qualitative and quantitative analysis will be described in the following sections.

Gas chromatography and mass spectrometry

Gas chromatographic separation of both the paraffinic hydrocarbons from Louisiana crude oil and paraffinic standards was achieved using a stainless steel capillary (270-m × 0.05-cm i.d.) column: initial 100 m coated with 3% Apiezon L and the remainder with 3% OV-17. The column was programmed from 125°C to 280°C/min with an initial hold of 15 min. and a final hold for 45 min. The flow rate of 5-6 ml/min was measured

at 125 °C. A 7620A Hewlett-Packard gas chromatograph equipped with a flame detector was employed. The injector was at 250 °C and the detector was at 350 °C. No injection split was used. Separation of the aromatic compounds was carried out using a 3.25-m × 2-mm i.d. glass column employing 1% GE SE-30 on 800/100 mesh Chromosorb Q and temperature programmed from 50 °C to 200 °C at 4°/min. A 5750 Hewlett-Packard gas chromatograph equipped with a flame detector was employed. The injector was at 250 °C and the detector at 350 °C.

A 9.5-m × 0.318-cm i.d. stainless steel packed column employing ethylene glycol succinate (12%) on Chromosorb P at 180° isothermal was used to separate the fatty acids. A Hewlett-Packard 5750 gas chromatograph was employed with the injector at 250 °C and the flame detector at 350 °C. The flow was at 18 ml/min at 180 °C. The identity of each recovered compound was determined with gas chromatography-mass spectrometry. The system consisted of a Hewlett-Packard model 5750 gas chromatograph connected by means of a jet-type separator to a model 21-491 duPont double focusing mass spectrometer as described previously (Laseter, Lawler, and Griffin 1973). The transfer line and separator were maintained at temperatures of 225° to 250 °C. All spectra were taken at 70 eV and recorded by use of an oscillographic recorder and a Digital Equipment Corporation PDP-12 LDP computer. Identifications were made by comparison with authentic laboratory standards. Pristane was obtained from K & K Labs., Inc. (Plainview, N.Y.), whereas phenanthrene and diphenylmethane were obtained from Aldrich Chemical Company (Milwaukee, Wis.). All other standards were purchased from Applied Science Laboratories (College Park, Pa.). Spectrograde solvents were obtained from Matheson Coleman & Bell (Norwood, Ohio).

Qualitative recovery of petroleum paraffinics

The crude oil employed was obtained from the 5380-m depth production zone of a Louisiana offshore well operated by Exxon, located in South Timbalier Block 54 approximately 16 km southwest of Grand Isle, La., at latitude 28.5 N, longitude 90.3 W. The petroleum is typical of the lighter crudes produced in the Southern Louisiana area. Crude oil (0.1 ml) was carefully pipetted onto deionized water (27 °C) contained in a stainless steel tray. The water was left undisturbed for 20 minutes prior to sampling, during which time the petroleum spread to form a thin film.

The Teflon surface of the sampler was then gently placed in horizontal contact with the water surface and immediately removed. The petroleum was washed from the disc using spectrograde CCl_4. The solvent was evaporated under reduced pressure at 40 °C and the residual material taken up in 5 ml of n-heptane for fractionation on silica gel (activated at 250 °C for 24 hours) in a 1- × 20-cm column. Prior to use, the column was washed

with three column volumes of n-heptane. The paraffinic hydrocarbons were eluted with 40 ml of n-heptane. The resulting fraction was taken to dryness under a stream of purified nitrogen. A duplicate 0.1-ml volume of crude oil used as a control was taken up in 100 ml of CCl_4 and treated as above, with the exception that the sampler was not employed. In both cases, the residues were dissolved in 50 μl of n-pentane and injected directly on a capillary column for gas chromatographic analysis (figure 2).

Qualitative recovery of unsaturated and branched chain paraffins, aromatics, and free fatty acids

Pristane (2, 6, 10, 14-tetramethylpentadecane), 1-hexadecane, n-hexadecane, 3-methylhexadecane, and 2-methylhexadecane were dissolved in n-hexane. Aliquots containing from 50 to 100 μg of each hydrocarbon were carefully pipetted onto the water surface and recovered using the sampler. Following solvent removal as described above, the residue was injected onto a capillary column (figure 3). An aliquot of the original mixture was used as the non-sampled control. Recovery of aromatic hydrocarbons was likewise tested using diphenylmethane and phenanthrene with n-octadecane as an internal standard. After solvent removal, the organics in the recovered residue were dissolved in benzene and injected directly onto a packed column which employed 1% GE SE-30 (figure 4). An aliquot of the original mixture was chromatographed as the control. Approximately 250-750 μg each of free stearic, oleic, and linoleic acids along with n-eicosane were also recovered from the water surface using the sampler. The recovered residue after solvent removal was taken up in 3 ml of BF_3-methanol and methylated (Laseter, Lawler, Walkinshaw, and Weete 1973). The methyl esters and n-C_{20} standard recovered from the methylation procedure were taken up in 50 μl of benzene and samples directly injected onto a packed gas chromatographic column employing 12% ethylene glycol succinate (figure 5). A portion of the original fatty acid-alkane mixture was methylated directly and served as the control.

Quantitative recovery of a Louisiana crude oil

The crude oil was artificially "weathered" by evaporation under low heat (50°C) for 2 hours. This process essentially removes all compounds with boiling points below n-C_{16}. A small volume of the "weathered" petroleum (0.1 ml) was mixed with 5 ml of benzene. The oil in 50 μl of this mixture formed an incomplete sheen on distilled water contained in an aluminum pan (30-cm diam. × 20-cm deep) after the benzene evaporated. A 100-μl aliquot left a slightly broken sheen, whereas the oil in 200- and 300-μl aliquots covered the water surface with a continuous film. A sampler with the same diameter as the pan was used to recover the oil so that the uneven distribution of the films would not affect the
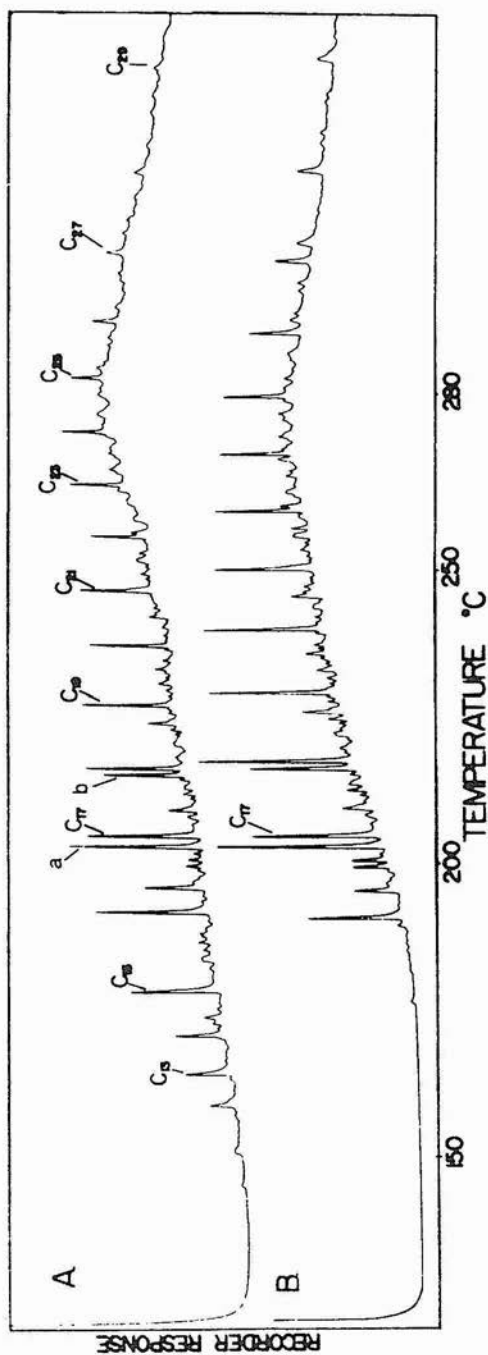
FIG. 2. GAS CHROMATOGRAPHIC SEPARATION OF THE PARAFFINIC HYDROCARBONS from Louisiana crude oil (Trace A) and from the same crude recovered from water surface by means of the sampling device (Trace B). Pristane and phytane are indicated by 'a' and 'b,' respectively.
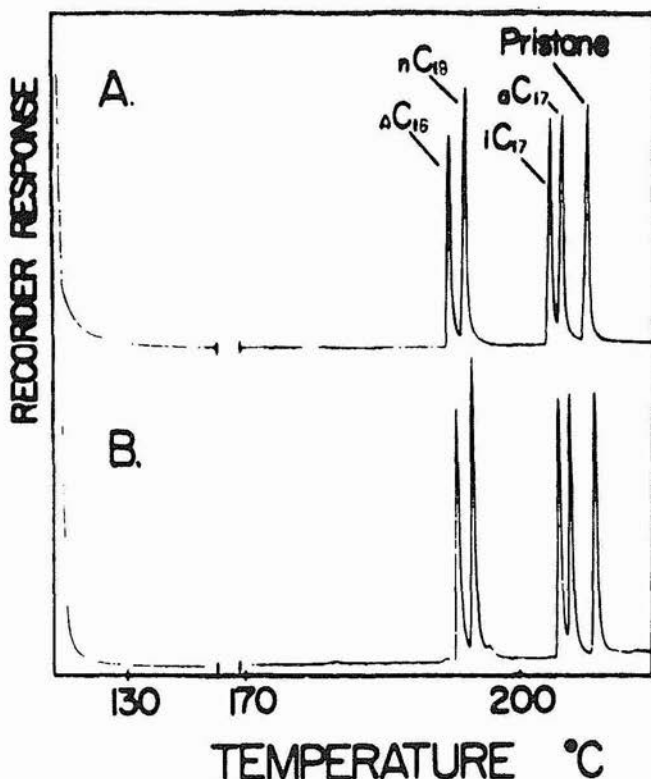
FIG. 3. GAS CHROMATOGRAPHIC SEPARATION OF STANDARD MIXTURE of
n-hexadecane, 1-hexadecane, 2-methylhexadecane (ISO-C_{17}), 3-methyl-
hexadecane (ANTEISO-C_{17}) and pristane (Trace A) and the same mixture
following recovery from the water surface by means of the sampling device
(Trace B).

recovery efficiencies. Sets of eight replicate samples for each of four
selected film thicknesses were collected. The pan was washed with soap
and repeatedly rinsed with cold water between samples. For controls,
identical quantities of "weathered" oil from each set were carefully
added directly to the Teflon disc using a 50-μl syringe, the solvent was
allowed to evaporate (20°C) and the residual crude washed off with CCl_4
using the recovery procedure described.

Each CCl_4 washing was collected in a glass test tube, the water
drawn off the top with a glass pipet, and the solvent plus oil carefully
transferred to a tared aluminum weighing dish. The solvent was slowly
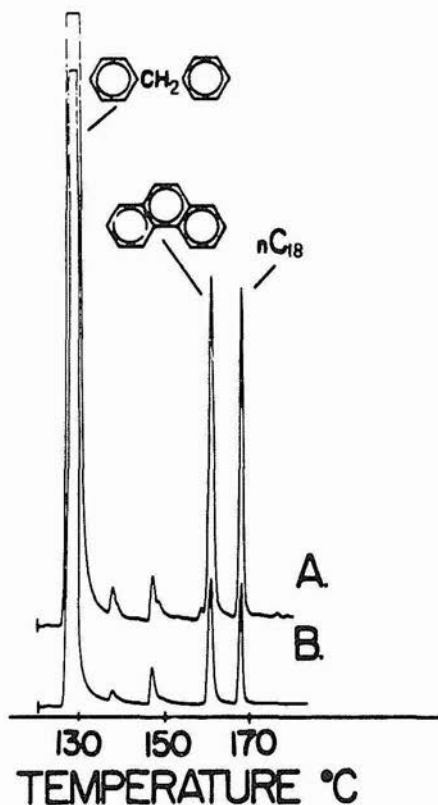evaporated (from the dish) on a heating tray (40°C) in a fume hood.

FIG. 4. SEPARATION OF DIPHENYL-METHANE, PHENANTHRENE, AND n-C_{18} STANDARD MIXTURE (Trace A) along with that same mixture following recovery from the water surface by means of the sampling device (Trace B).
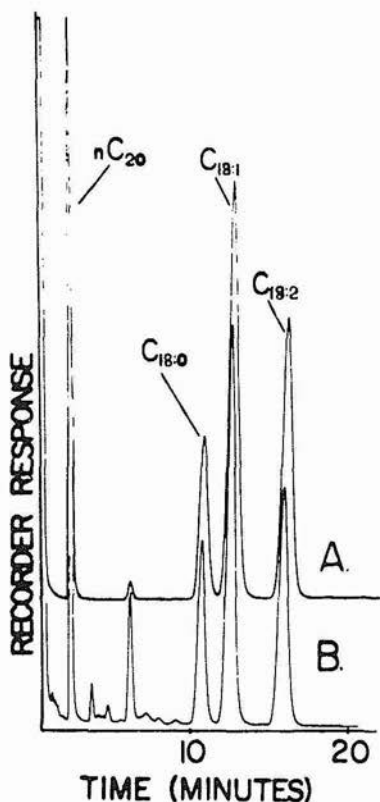
FIG. 5. SEPARATION OF A STANDARD MIXTURE of stearic ($C_{18:0}$), oleic ($C_{18:1}$), and linoleic ($C_{18:2}$) fatty acid methyl esters plus n-eicosane (Trace A) and the same mixture recovered from the water surface by means of the sampling device (Trace B).

After the solvent evaporated, the dishes were placed in a desiccator and weighed until constant weights were obtained. Blanks using CCl_4 were run by evaporating 50 ml of solvent (approximate amount used for each wash) in tared dishes. In a similar experiment, three sets of relatively thicker oil films were quantitatively collected using the sampler. After evaporating the solvent under reduced pressure at 40°C, each residue was taken up in exactly 100 μl of n-heptane and analyzed using gas chromatography. Analysis was carried out using a Hewlett-Packard 7620A Gas

Chromatograph with flame ionization detectors and 1/8-in. × 6-ft. stainless steel columns packed with 10% UCCW-982 on Chromosorb W. N_2 carrier flow was 40 ml/min. Temperature was programmed from 100° to 300°C at 4°C/min. Peak heights of n-paraffins from n-C_{17} to n-C_{26} were measured, corrected for attenuation factor, and summed. Controls again consisted of oil added directly to the sampler. The efficiency of recovery was calculated using the following formula:

% Efficiency =

$$\frac{\text{Av. } \Sigma \text{ peak heights of recovered oil}}{\text{Av. } \Sigma \text{ peak heights of control oil}} \times 100$$

RESULTS AND DISCUSSION

The ability of the sampler to recover crude oil compounds from aqueous surface films is illustrated in tables I and II and figure 2. Not included in table I is the information from control experiments where the weathered crude oil was added directly to the disc surface (100 μl) with an equal volume of oil added to a weighing pan containing approximately 50 ml of CCl_4. The oil was collected from the disc in the usual manner. Following evaporation of the solvents in both cases, the weight of residual oil in the weighing pan and that recovered from the disc were found to be essentially the same, considering the limits of error of the microliter syringe used. The chromatograms in figure 2 clearly demonstrate that low molecular weight alkanes below n-C_{16} are not recovered efficiently by the sampler. However, there appears to be no discrimination on either a qualitative or quantitative basis with respect to alkanes above n-C_{16}. All major compounds were identified by mass spectrometry.

Figures 3, 4, and 5 respectively illustrate the ability of the sampler to recover normal alkanes, aromatics, and free fatty acids. In each of these experiments, a normal alkane was included as an internal standard to determine if there was selective discrimination between it and the other organics being evaluated by the Teflon surface. The data suggest that the sampler does not discriminate with respect to branching, saturation, or aromatic nature of the hydrocarbons tested. Also, the presence of a carboxyl group on a hydrocarbon chain containing one, two, or no double bonds does not appear to influence the recovery of the compound. In all instances, the quantitative recovery of the various classes of organics tested in the experiments ranged from 87% to 96%. It should be noted that extensive secondary washing of the Teflon surface did not yield additional organics.

Table I. Retrieval Efficiency of the Surface Film Sampler Using a "Weathered" Louisiana Crude Oil—Gravimetric Analysis

Amount of oil added, mg, control	Calculated film thickness, nm[a]	Appearance	Amount of oil retrieved, mg	Std dev, mg	Efficiency, %
0.623	10.4	Partial sheen	0.551	±0.035	88
1.216	20.2	Continuous sheen	1.110	±0.045	91
2.532	42.2	Dull sheen	2.165	±0.114	85
4.181	69.6	Continuous film	3.596	±0.251	86

[a] Density = 0.85 g/ml.

Table II. Retrieval Efficiency of the Surface Film Sampler Using a "Weathered" Louisiana Crude Oil—Gas Chromatographic Analysis

Amount of oil added, control, mg	Calculated film thickness, nm[a]	Appearance	Peak height control	Peak height retrieved	Std dev	Efficiency, %
4	66.6	Continuous film	158	130	±7.77	82
13	216.5	Continuous film	309	277	±13.43	89
30	499.6	Continuous film	232	205	±9.19	88

[a] Density = 0.85 g/ml.

Table I shows the quantitative recovery of a "weathered" Louisiana crude oil using the sampler. The chromatograms in this experiment were similar to those in figure 2 and revealed no discrimination in the recovery of alkanes above n-C_{16}.

These laboratory studies indicate that the sampler should prove to be valuable for both quantitative and qualitative retrieval of surface film paraffins, aromatics, and fatty acids in the environment. The sampler has been employed in actual field exercises to collect surface organics from offshore Louisiana, offshore Florida, and Lake Pontchartrain. Analogously, the ability of the sampler to collect petroleum-type organics suggests that it will also be useful in collecting related surface film organics such as pesticides.

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II. A COMPARISON OF TWO SAMPLING DEVICES FOR THE RECOVERY OF ORGANICS FROM AQUEOUS SURFACE FILMS

by Enoch J. Ledet and John L. Laseter

INTRODUCTION

Observance of monomolecular films associated with the air-sea inter-face have been described by investigators for a number of years. It has been established that organics at an interface will exert an influence on many important exchange processes with the atmosphere by changing the surface potential, tension, and viscosity (Garrett 1972). The need to quantify and identify petroleum hydrocarbons in natural waters has presented method-ological difficulties—especially with hydrocarbon films at the air-water in-terface. Both laboratory and offshore studies have been performed to deter-mine the selectivity of a Teflon disc sampler for hydrocarbons and related organics and the efficiency of recovery for petroleum films of varied thick-nesses (Miget et al. 1974; Ledet and Laseter 1974). Methods for removal of monolayers of oleic acid, stearic acid, and oleyl alcohol from the surface of both distilled water and synthetic sea water by using a screen sampling tech-nique have also been reported (Garrett 1965). Reports describing the use of a wire screen device to recover pesticides, hydrocarbons, and fatty acids from the air-sea interface have recently been published (Duce et al. 1972; Bioleman and Olney 1974).

This paper will report on a preliminary comparison between the Teflon disc and wire screen techniques on the basis of consistency, efficiency, and general utility of each for retrieval of typical organics at the air-sea inter-face.

EXPERIMENTAL

Apparatus

Gas chromatographic analyses were carried out with a Hewlett-Pack-ard 7620A chromatograph equipped with a flame ionization detector, con-nected to a Hewlett-Packard 3370A integrator. Separation of hydrocarbons collected from surface films was achieved on a 243m × .05 cm steel capillary coated with 3% Apiezon L (Applied Science, College Park, Penn-sylvania). The column was programmed from 155° to 285°C at 2°/min. with a post-injection hold of 10 minutes and a final hold of 45 minutes. The flow rate measured at 150°C was 6 ml/min. The chart speed of the recorder was set at 0.63 cm/min. The injection port was maintained at 250°C while the flame detector was set at 325°C. Separation of aromatics and fatty acid methyl esters was accomplished on 2.3 m × 0.33 cm steel column coated with UCW-98 (Hewlett-Packard, Avondale, California) programmed from 85° to 230°C at 6°/min. with an initial flow rate of 40 ml/min. The injec-tion port and detector were maintained at 250°C and 325°C respectively.

Sampling devices and procedures

Surface samples from Lake Pontchartrain (a large, brackish body of water opening to the Gulf of Mexico) were obtained concurrently at six different locations by means of a Teflon disc and a 16-mesh stainless steel screen, measuring 27.9 cm in diameter, incorporated in a circular aluminum frame. A 16-mesh size screen was selected because of the high recovery efficiencies reported for monomolecular layers of oleic acid on synthetic sea water (Garrett 1965). Both disc and screen devices were touched to the water's surface as lightly as possible and then rested vertically on a large polyethylene funnel. Organics adhering to the surface of both devices were washed through the funnel and collected in two separate screw top 500 ml narrow-neck glass bottles by a gentle stream of CCl_4 from a polyethylene squeeze bottle. Details of construction and the sampling procedure using the Teflon device are reported in the preceding reprint from *Analytical Chemistry*.

Laboratory recovery experiments consisted of pipetting, either independently or as a mixture, 300 to 500 μg of dodecane, hexadecane, octadecane, palmitic acid, stearic acid, oleic acid, napthalene, and phenanthrene onto deionized water (27 °C) contained in a stainless steel tray (53.3 cm $\times$ 47.7 cm $\times$ 3.0 cm deep). Benzene was used as the solvent. Each experiment was repeated in triplicate. The disc covered approximately 53% of the tray's surface area while the screen covered approximately 25%. The water was left undisturbed for 20 minutes prior to sampling, during which time the organics spread to form a thin film. Sampling and collection procedures for the laboratory were the same as those described above for the field work. After each collection had been accomplished, the solvent was evaporated under reduced pressure at 40 °C and the residual material taken up in 2 ml of *n*-heptane for fractionation on silica gel (activated at 250 °C for 24 hours and washed with 3 volumes of *n*-hexane prior to use) in a 1 $\times$ 20 cm column. Hydrocarbons, aromatics, and free fatty acids were eluted with 40 ml of *n*-hexane, benzene solvent, and methanol respectively. An aliquot of each of the experimental compounds dissolved in benzene was used as a control. The solvent was removed and the residue taken up in 150 ml of CCl_4 and treated as above with the exception that the sampling devices were not employed. Free fatty acids were methylated prior to injection into the gas chromatograph (Morrison and Smith 1964).

In both cases, the residues collected by each device were dissolved in 10 μl of *n*-heptane and injected directly onto a capillary or packed steel column for gas chromatographic analysis. Differences between the chromatograms of the control and collected samples would demonstrate the extent of selectivity of each device for the various organics employed. Percentage of recovery was based upon the contact surface area for each of the sampling

TABLE I

ORGANICS RECOVERED FROM THE SURFACE FILM FOR LAKE
PONTCHARTRAIN $(mg/m^2)^a$

Sampling Device	Hexane Eluate	Benzene Eluate	Methanol Eluate
Screen	0.50	0.14	0.22
Teflon Disc	0.45	0.28	0.56

[a]Averages of six concurrent sample collections for each device.

devices. The Teflon disc was approximately 2.12 times greater in diameter than the screen and therefore a compensation factor was taken into account when percentage of efficiency was calculated.

RESULTS AND DISCUSSION

Both the Teflon disc and wire screen were relatively easy to operate. Field and laboratory comparisons between the two collection devices, however, showed the disc to require substantially less sampling time. A longer time period was necessary with the screen in order to prevent sample loss and spillage.

The information in table I suggests that the screen is approximately as effective as the Teflon disc in the recovery of hydrocarbons from the air-sea interface. However, care must be taken in placing a strict interpretation on this observation due to the fact that elemental sulfur will also appear in the n-hexane fraction. It therefore becomes necessary to inspect the n-hexane fractions in chromatographic detail in order to determine if any qualitative differences exist in the hydrocarbons collected. A typical chromatographic separation is shown in figure 1. One will note that initially there is marked discrimination of the n-alkanes in the low molecular weight portion of the sample collected by the Teflon disc. This observation was reported previously (Garrett 1972). The screen does not appear to be as restricted with respect to n-alkanes below 16 carbons. The screen shows hexadecane as the major n-alkane, whereas it is octadecane for the Teflon disc. Table II supports these observations derived from the field samples. For example, the screen is 3 times more effective at retrieval of dodecane, whereas the Teflon disc is over twice as efficient as the screen at recovery of octadecane.
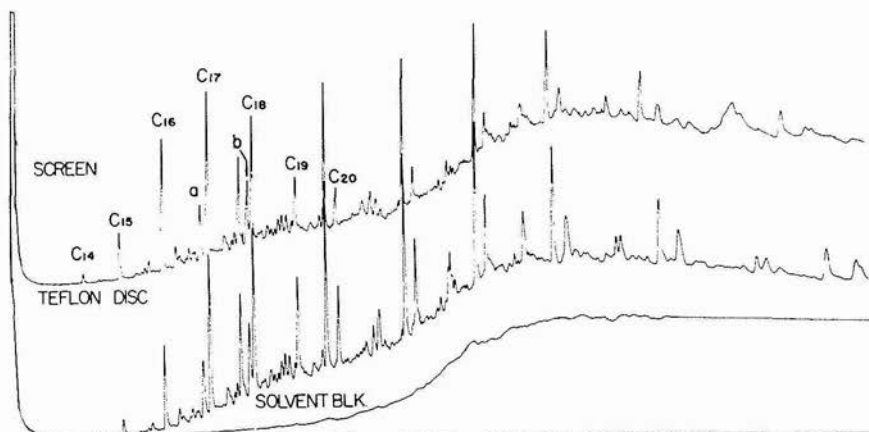
FIG. 1. GAS CHROMATOGRAPHIC SEPARATION OF HYDROCARBONS found in the *n*-hexane eluate from a typical surface sample collected by the screen (upper trace) and Teflon disc (middle trace). Details of chromatographic operation are described in the text. Pristane is indicated by 'a' and phytane by 'b.'

Also of interest is the retrieval capacity of normal alkanes with respect to the methyl branched alkanes. Pristane (2, 6, 10, 14-tetra-methylpentadecane) and phytane (2, 6, 10, 14-tetramethylhexadecane) ratios appear to be about the same in each case, as is their respective

TABLE II

PERCENT EFFICIENCY FOR RECOVERY OF ALKANES, AROMATICS, AND FREE FATTY ACIDS FROM SURFACE FILMS ON DEIONIZED WATER

Compound Recovered	%Efficiency[a]	
	Wire Screen	Teflon Disc
Alkanes		
n-dodecane	6.80	2.20
n-hexadecane	7.98	8.90
n-octadecane	25.05	60.89
Aromatics		
napthalene	4.50	12.80
phenanthrene	32.99	29.45
Fatty Acids		
palmitic	65.95	99.53
stearic	87.31	71.64
oleic	44.08	71.47

[a]Values represent an average of triplicate experiments.

relationship to hexadecane. Sampling devices used to study the environment must provide an accurate picture of such ratios. This is because significance is frequently attached to such ratios as an aid in differentiating between petroleum-derived and indigenous alkanes.

It is of interest to note in table I that the efficiency of the recovered organics from the surface of Lake Pontchartrain, in which the Teflon disc was employed, increased in relationship to increased polarity of the test compound. Table II shows that for the aromatics employed in this study, napthalene is recovered approximately 3 times more efficiently by the Teflon sampler. No significant difference was noted between the two devices for phenanthrene. In the case of the free fatty acids, however, the Teflon disc was more efficient at recovering the saturated acids. There appears to be a relationship between chain length and the efficiency of recovery with both sampling devices. One *cis* double bond markedly improves the ability of the wire screen to retrieve a free acid when compared to a saturated acid of equal carbon number. No significant difference in efficiency between oleic and stearic acids was observed when the disc was employed.

In summary, it appears that the wire screen sampling device is more effective in recovering low molecular weight ($< C_{16}$) *n*-alkanes from surface films in the concentrations employed in this study. Little discrimination is observed in higher molecular weight normal or methyl branched alkanes by either device. Both samplers are somewhat limited in their ability to recover polycyclic aromatics. The Teflon disc is superior at recovering saturated free fatty acids, whereas both devices were about equal with respect to their ability to recover oleic acid. The values observed for percentage of efficiency of oleic acid from synthetic sea water were similar to those reported previously for a 16-mesh screen (Garrett 1965).

Our findings suggest that care should be exercised in selecting any device for environmental sampling of organics associated with aqueous surface films. Because of the ease of operation and ruggedness of the Teflon disc, it appears to have several advantages over the wire screen used in this study. However, in any study of the organics at the air-water interface the particular device employed should be calibrated for the compound or compounds to be collected in order to ensure as much sampling accuracy as possible.

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III. ALKANES AT THE AIR-SEA INTERFACE FROM OFFSHORE LOUISIANA AND FLORIDA

by Enoch J. Ledet and John L. Laseter

In recent years there has developed considerable interest in the distribution and impact of hydrocarbon residues introduced into the marine environment by petroleum production and maritime activities. Studies of the C_1 to C_5 hydrocarbons dissolved in the surface waters of the Gulf of Mexico show that the highest concentrations are apparently associated with shipping and petroleum activities (Brooks et al. 1973). The presence of dissolved paraffins of higher molecular weights has also been reported in the Gulf of Mexico (Parker et al. 1972). Koons and Monaghan (1973) concluded that the hydrocarbon content of the water in the northern Gulf of Mexico is probably less than 7 $\mu g/l$. Concentrations of total dissolved hydrocarbons in the area of the east central Atlantic vary from 10 to 140 $\mu g/l$ (Barbier et al. 1973), and 2 to 13 $\mu g/l$ is reported for the Nova Scotia vicinity (Levy 1971). In the last case alkanes from C_{14} to C_{37} were present, and there was no preference for odd or even carbon numbers.

Garrett (1967), using both a screen technique to sample the air-sea interface and a bucket sample, found that a variety of organics was

present at a number of locations. More recently, samples collected at the air-sea interface in the area of the Sargasso Sea by use of a stainless steel screen were found to contain a variety of chlorinated hydrocarbons, and the highest concentrations were associated with the surface microlayer (150 μm) (Bidleman and Olney 1974). Duce et al. (1972), using similar techniques, showed that hydrocarbons and fatty acids, as well as pesticides, are more concentrated in the surface microlayer of Narragansett Bay than in water as deep as 20 cm below the surface.

It has been established that organics affect the physical properties of the ocean surface and many important exchange processes between the ocean and the atmosphere (Garrett 1968). For example, they reduce the capillary wave spectrum and thereby contribute to the production of sea slicks. Also, during any type of petroleum-related accident or oil spill it is the surface layer that is initially disrupted. Because of the importance of this microlayer and the general lack of qualitative and quantitative data, it is important to characterize the indigenous chemical components found at the air-sea interface. This report deals with the nature and distribution of alkanes at the air-sea interface in selected areas of Timbalier Bay and offshore Louisiana and Florida. Samples were collected at five intervals between August 1972 and July 1973.

An aluminum-backed Teflon disc was employed for sample collection. Approximately 90% of weathered crude can be recovered by this technique, and there appears to be little or no discrimination in retrieving petroleum paraffins above C_{15} (Miget et al. 1974). Residues collected were fractionated by using a silica gel column (Laseter, Lawler, and Griffin 1973; Laseter, Lawler, Walkinshaw, and Weete 1973), and the alkanes were eluted with n-heptane. After removal of the solvent under a stream of purified nitrogen, the residue was weighed and further fractionated by gas chromatography. A portion of each sample eluted from the gas chromatographic column was passed through a DuPont 21-491 mass spectrometer attached to a PDP-12 computer. Alkanes from local production facilities and fuel and lubrication oils from the ships used to collect samples were also analyzed as possible sources of sample contaminants. The average (dry) weight of the n-heptane eluate was 0.70 mg per square meter of sea surface for residues collected from offshore Louisiana during five field experiments, whereas the 43 samples from the two exercises in Timbalier Bay averaged 0.36 mg/m^2.[1] Similar fractions averaged 0.18 mg/m^2 for Florida, while ten samples collected at the same time from Louisiana averaged 0.21 mg/m^2. No significant relation between proximity to a drilling or production platform and the quantity of alkanes at the surface was noted.

Figure 1 illustrates a typical distribution of compounds observed in a surface sample; more than 90% of the compounds are alkanes, and 118
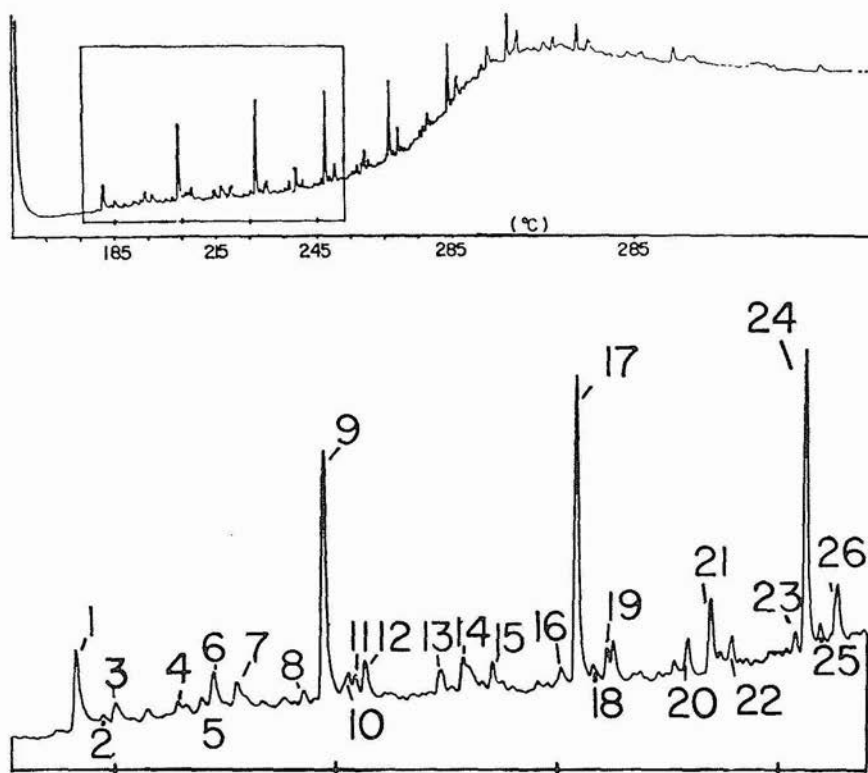
FIG. 1. GAS CHROMATOGRAPHIC SEPARATION OF A TYPICAL PARAFFIN FRACTION collected from the air-sea interface of offshore Louisiana in October 1972. Separation was on a stainless steel capillary column 250 m long, 0.5 mm in inner diameter, and coated with Apiezon L. A flame detector was used. The chromatograph was held at 155 °C for 10 minutes and programmed from 155° to 285 °C at 2 °C per minute. The injector was at 250 °C and the detector at 325 °C. Numbered components are identified in table 1.

such samples were analyzed. Samples obtained during a single collection trip showed only minor variations in the distribution of alkanes, qualitatively or quantitatively. Treatment with a molecular sieve to remove normal alkanes followed by hydrogenation to remove the unsaturated compounds failed to alter significantly the observed chromatographic pattern. The sample represented in figure 1 contained about 70% branched alkanes, of which 50% by weight are 3-methyl branched, 13% are cycloalkanes, and 3% are normal alkanes. The components num-

Table 1. Mass spectrometric identification of
the components in Fig. 1.

Chromatogram peak number	Compound
1	3-Methylpentadecane
2	Nonadecylcyclohexane
3	n-Hexadecane
4	3-Methylhexadecane
5	Decylcyclohexane
6	Pristane
7	2,6-Dimethylpentadecane
8	Dimethyloctadecane
9	3-Methylheptadecane
10	Undecylcyclohexane
11	Phytane
12	n-Octadecane
13	3-Methyloctadecane
14	Dodecylcyclohexane
15	2,6-Dimethylheptadecane
16	Dimethyleicosane
17	3-Methylnonadecane
18	Tridecylcyclohexane
19	Dimethyleicosane
20	3-Methyleicosane
21	Tetradecylcyclohexane
22	2,6-Dimethylnonadecane
23	Dimethyldocosane
24	3-Methylheneicosane
25	Pentadecylcyclohexane
26	Dimethyldocosane

bered in figure 1 are identified in table 1. To date, some 50 compounds ranging from C_{16} to C_{36} in carbon number have been identified by mass spectrometry. When normal alkanes were present and in sufficient concentration to be detected, they usually ranged from C_{16} to C_{21} and exhibited no odd-even carbon preference. In only a few samples, collected during August 1972 from offshore Louisiana and during October 1972 from Timbalier Bay, did the quantity of normal alkanes exceed 20% by weight of the paraffinic fraction. Samples collected at approximately the same time and location from a 10-m depth were found to contain predominantly normal alkanes from C_{14} to C_{36} (Oppenheimer et al., unpublished). Tar ball samples from the Gulf of Mexico, even though they vary considerably in chemical composition, show substantial proportions of normal alkanes (Koons and Monaghan 1973).

Our data suggest that the branched and cyclic paraffins comprise the bulk of alkanes at the air-sea interface, whereas the normal paraffins accumulate in the water column. There are several possible explanations for this enrichment, such as selective removal by autooxidation or photooxidation, emulsification by wave action, and adsorption on particulate

matter. However, one of the more important factors may be biological. Marine bacteria preferentially oxidize normal alkanes (Kator 1972; Jobson et al. 1972), and microbial attack is most effective against oil in thin films or adsorbed on solid particles (Miget et al. 1969). The pristane/phytane ratio in the alkane fraction at the air-sea interface (which varies from 1.5 to 2.3) and the presence of a large number of dimethylalkanes suggest that crude oil or petroleum products may serve as the hydrocarbon precursor pool. If so, however, it is difficult to explain the presence of such high concentrations of 3-methyl branched alkanes with even carbon numbers. Certain plants contain substantial quantities of 3-methyl branched alkanes with even carbon numbers ranging from C_{28} to C_{34} (Weete et al. 1971), and it has been suggested that such alkanes occur in marsh plants that are common to the Gulf Coast (Lytle et al. 1973). We suggest that the alkanes at the air-sea interface are probably entering the marine environment from a wide variety of biological sources as well as from petroleum released by natural seeps and man's activities, and that branched and cyclic alkanes accumulate at the interface as a result of a complex combination of physical and biological influences. The data that have been collected so far show that the types and amounts of hydrocarbons in the surface film along the northern Gulf Coast have remained fairly constant during the study period.

NOTE

1. Gas chromatographic methods revealed that the alkanes present in the heptane eluate averaged 35 $\mu g/m^2$. This apparent discrepancy with the total weight values reported for this fraction is probably due to a number of factors: (i) a substantial portion of the alkanes present are not chromatographically resolved and are expressed as a base-line "hump"; (ii) some of the components may have molecular weights above C_{40} and do not emerge below 280°C; and (iii) elemental sulfur (produced in large amounts in the vicinity) will concentrate in the heptane eluate.

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