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The Organic Chemical Composition of the Ocean Surface

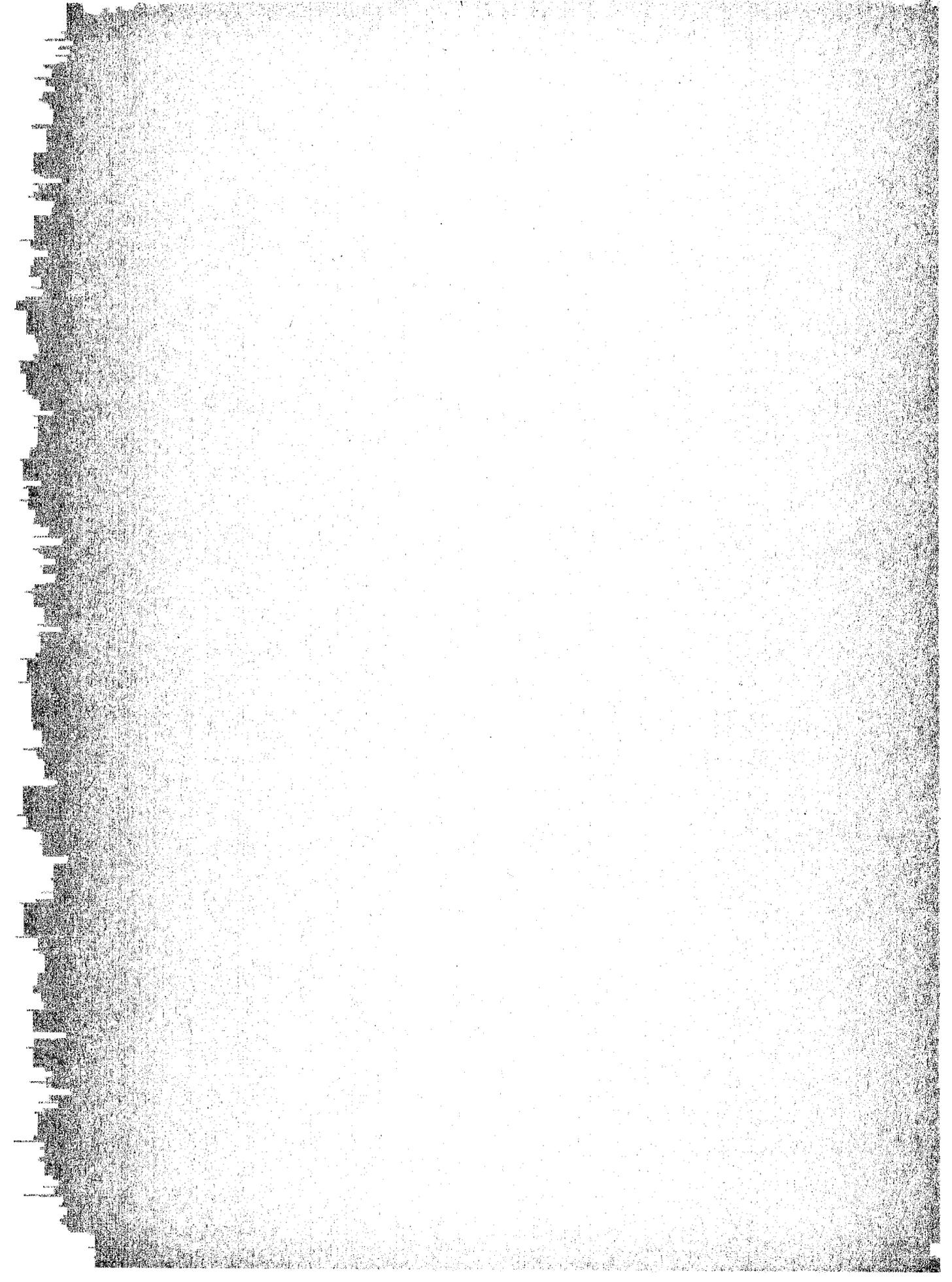
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ABSTRACT

An analytical survey has been conducted to determine the organic chemical constitution of the sea. Special emphasis was placed upon the nature of the surface-active water-insoluble components present in the sea surface. Samples were collected under various oceanographic conditions from the Atlantic and Pacific Oceans, the Gulf of Lower California, the Gulf of Mexico, and the Bay of Panama. The water-insoluble organic constituents were isolated from these samples and were analyzed by infrared spectroscopy, microelemental analysis, and various gas chromatographic techniques.

The following conclusions were drawn from a comparison of the analytical data with the sea conditions which existed at the time the samples were taken. The major water-insoluble organic constituents of the sea are fatty esters, free fatty acids, fatty alcohols, and hydrocarbons. These chemical types are general to all areas sampled, but specific differences within these classes exist from one location to another. For example, the distribution of the various fatty acids and alcohols varies according to the meteorological and oceanographic conditions prevalent at a particular location. A competition for adsorption sites exists at the surface between the various chemical species. The higher molecular weight and less water-soluble fatty acids and alcohols are the most surface-active and likely to be found adsorbed at the surface while the more water-soluble or less surface-active entities are excluded from the surface by the fatty material when competitive adsorptive processes occur.

Surface-active substances were found in all areas of the ocean in sufficient quantity to account for the observed alterations of the sea surface by monomolecular films. This does not mean that the entire surface of the ocean is always under modification, but that a chemical potential exists whereby such surface alterations can occur when conditions are suitable for the adsorption and compression of the surface-active molecules at the air/water boundary.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C02-18
BUWEPS Task No. RUDC-4B-000/652-1F001/99-01-231-3

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THE ORGANIC CHEMICAL COMPOSITION OF THE OCEAN SURFACE

INTRODUCTION

Many properties of the air/water interface may be extensively modified through the adsorption of surface-active organic matter at the ocean surface. At any particular time there is some material already present in the surface and additional surface-active substances will reach the sea/air boundary by diffusion from below. The adsorbed film may alter the surface temperature of the sea to a small extent and also interrupt the normal mass and thermal convection processes occurring just beneath the air/water interface (1). Another important surface effect of an adsorbed film is the damping of capillary surface waves. It has been demonstrated that this damping of surface waves can be caused by a monomolecular layer of surface-active materials at film pressures of less than one dyne/cm (2). Such a manifestation of the wave-damping process on the ocean is called a "sea slick" which represents an area of the ocean with significantly different light reflectance from that of the surrounding sea since the average wave slope has been decreased by the damping action of the monomolecular film.

These surface-active materials may be organic products of the marine biosphere or they may originate from manmade sources. Whatever their origin, little analytical data exists which details the chemical species to be found at or near the ocean surface, although some information exists on the organic composition of the bulk ocean. Several investigators have measured the concentration of organic oceanic material at various locations and depths (3,4). Gas and paper chromatography have recently been used to analyze specific components of the organic mixtures from the ocean. Williams (5) isolated fatty acids from sea water and determined the specific methyl esters present by gas chromatography. Six saturated fatty acids and three unsaturated fatty acids with carbon chain lengths of from 12 to 22 were identified and determined quantitatively. There has also been some interest in the water-soluble organic substances. A number of amino acids were found in the acid hydrolyzates of dissolved organic material from sea water (6,7). Carbohydratelike materials were first reported by Collier (8), and Lewis and Rakestraw (9) found soluble substances in Pacific Coastal waters which responded to the anthrone or N-ethyl carbazole tests for carbohydrate. Pure hydrocarbon material (not surface active) has been shown to be a likely resident of the sea. Blumer, Mullin, and Thomas (10) report that from 1% to 3% of the body fat of certain planktonic crustaceans consists of pristane (2,6,10,14-tetramethyl pentadecane). Other hydrocarbon sources include ship discharges and oil seeps through geological faults where liquid and gaseous hydrocarbons from submarine oil fields are released into the sea (11).

Pure hydrocarbons have no surface activity and do not contribute significantly to sea surface effects. Although some soluble carbohydrate and proteinaceous substances are surface active, they are of secondary importance when compared to the very active water-insoluble fatty compounds. This is due to the fact that the fatty acids, esters and alcohols are strongly adsorbed at the water surface and can exclude the water-soluble materials by competitive adsorption. For example, as the components of the sea surface are compressed by the action of wind, sea currents, or Langmuir circulation cells (12), certain of the less strongly adsorbed molecules may be displaced upwards from the surface while the more water soluble will be redissolved into the sea. For this reason, the major emphasis will be concentrated on the water-insoluble surface-active constituents of the sea although the less active species were also studied.

A preliminary report on the constitution and surface-chemical properties of the sea surface (13) outlined the analytical program being followed at this Laboratory to answer the following questions:

1. What is the chemical nature of the organic surface-active substances in the ocean?
2. Are these materials uniformly distributed or is the composition of the sea varied by local conditions?
3. From what sources and in what quantities do these materials arise?

Samples of surface water were collected from both sea slick and nonslick areas of the Bay of Panama. Small quantities (10-20 milligrams/5 gallon sample) of organic waxes and oils which had been freed of salt, water and solvents were isolated and partially identified. Both the slick and nonslick covered surface waters contained a somewhat similar mixture of surface-active materials as indicated by infrared analyses, surface viscosity, surface-potential measurements, and film-balance studies. Isolated substances were identified generally as fatty acids, lipids, and nonpolar hydrocarbons. Chemical unsaturation existed to a small extent in the hydrocarbon portions of the organic molecules.

The preliminary work has since been extended, and the present report is an up-to-date account of the results of an analytical survey of the organic composition of the sea with specific emphasis on composition of the material found in the ocean surface. Samples collected in the Atlantic and Pacific Oceans, the Gulf of Lower California, the Gulf of Mexico, and the Bay of Panama were examined in detail to identify the specific chemical compounds present. A portion of the analytical data presented was produced recently by F. Ellison and E. Klemm (14) of the Evans Research and Development Corporation.

SAMPLING METHODS AND LOCATIONS

Sea water collections (designated as surface samples) were obtained by the screen technique described by Garrett (15). This method utilizes a metal screen which is placed into the water parallel to the surface, withdrawn, and drained into a 5-gallon polyethylene collection vessel. It was demonstrated that this method removed a 0.15-mm-thick film of surface water, and since the method was nonselective, all of the organic constituents of the water were efficiently collected.

Samples beneath the surface were taken with a 16-liter Van Dorn-sample collection bottle constructed of polyvinyl chloride. While being lowered to depth on an oceanographic wire this device remains in an open condition and flushes continuously since it offers virtually no restriction to the flow of water through it. When the closure mechanism is tripped by a messenger released from the surface vessel, neoprene force cups are released and snap tightly into each end of the sampler. Upon return to the surface the entrapped sample was transferred to a 5-gallon polyethylene carboy. The organic material collected in this manner was concentrated by the precipitation of a ferric hydroxide sol within the carboy. The organic constituents were occluded and adsorbed by the gelatinous precipitate which, after settling, was separated from the sea water. A few milliliters of chloroform was added to the concentrate to halt biological activity. This mixture, which contained the organic sea matter in aqueous suspension, was frozen and packed in dry ice for shipment from the collection site to the Naval Research Laboratory at Washington, D.C. Upon receipt, the samples were thawed and portions of the organic materials were extracted with purified chloroform by the procedures described by Garrett, Timmons, and Jarvis (13). The remaining aqueous solutions were reserved for analysis of water soluble components.

Table 1
Sampling Locations and Conditions

Sample Designation	Date	Condition of Surface	Sampling Depth	Sea Conditions	Location
N-1	June 62	75% slick-covered	surface	calm	1 mi S, Narragansett Bay
N-2	June 62	75% slick-covered	surface	calm	1 mi S, Narragansett Bay
N-3	June 62	75% slick-covered	surface	calm	19 mi S, Block Island, R.I.
N-4	June 62	75% slick-covered	surface	calm	19 mi S, Block Island, R.I.
B-1	July 62	no visible slicks	surface	slight swell	North Atlantic, 56°N, 51°W
B-2	July 62	no visible slicks	surface	moderate swell	North Atlantic, 56°30' N, 51°W
A-1	Aug 62	no visible slicks	surface	choppy	200 mi E, Atlantic City, N.J.
A-2	Aug 62	no visible slicks	surface	choppy	200 mi E, Atlantic City, N.J.
A-3	Aug 62	no visible slicks	surface	calm	200 mi E, Atlantic City, N.J.
A-4	Aug 62	no visible slicks	surface	calm	200 mi E, Atlantic City, N.J.
B-3	Oct 62	no visible slicks	surface	-	Mid Atlantic, 47°W, 35°N
P-10	Nov 62	20% slick-covered	surface	swell, no chop	8 mi W, San Diego, Calif.
P-11	Nov 62	20% slick-covered	surface	swell, no chop	8 mi W, San Diego, Calif.
P-12	Nov 62	20% slick-covered	surface	swell, no chop	8 mi W, San Diego, Calif.
P-13	Nov 62	20% slick-covered	surface	swell, no chop	8 mi W, San Diego, Calif.
G-10	Nov 62	slicks sampled	surface	calm	Gulf of Lower California
G-11	Nov 62	no visible slicks	surface	choppy	E. Bahia de Los Angeles
G-20	Nov 62	no visible slicks	surface	choppy	30 mi SW, Key West, Fla.
G-21	Nov 62	no visible slicks	surface	choppy	30 mi SW, Key West, Fla.
G-22	Nov 62	no visible slicks	surface	choppy	30 mi SW, Key West, Fla.
G-23	Nov 62	no visible slicks	surface	choppy	30 mi SW, Key West, Fla.
G-9	Jan 63	slick associated with Planktonic Bloom		calm	8 mi SE, Galveston, Tex.
P-20	Apr 63	slicks present	12 ft	calm	10-15 mi S. Panama City, Bay of Panama
P-21	Apr 63	slicks present	36 ft	calm	10-15 mi S, Panama City, Bay of Panama
P-22	Apr 63	no visible slicks	12 ft	choppy	10-15 mi S, Panama City, Bay of Panama
P-23	Apr 63	no visible slicks	24 ft	choppy	10-15 mi S, Panama City, Bay of Panama
P-24	Apr 63	no visible slicks	36 ft	choppy	10-15 mi S, Panama City, Bay of Panama
P-25	Apr 63	slicks present	24 ft	choppy	10-15 mi S, Panama City, Bay of Panama
P-26	Apr 63	slicks present	surface	choppy	10-15 mi S, Panama City, Bay of Panama
W-3	June 63	no slicks	24 ft	choppy	5 mi E, Ft. Lauderdale, Fla.
W-4	June 63	no slicks	surface	choppy	7 mi E, Wilmington, N.C.
P-31	Dec 63	20% slick-covered	40 ft	choppy, well mixed	15-20 mi S, Panama, Bay of Panama
P-32	Dec 63	20% slick-covered	80 ft	choppy, well mixed	15-20 mi S, Panama, Bay of Panama
P-33	Dec 63	20% slick-covered	surface	choppy, well mixed	15-20 mi S, Panama, Bay of Panama
P-34	Dec 63	20% slick-covered	80 ft	choppy, well mixed	15-20 mi S, Panama, Bay of Panama
P-39	Dec 63	20% slick-covered	80 ft	choppy, well mixed	10 mi S, Panama, Bay of Panama
P-40	Dec 63	20% slick-covered	40 ft	choppy, well mixed	10 mi S, Panama, Bay of Panama

The oceanographic conditions observed at each sampling station are listed in Table 1. A number of areas of the Atlantic and Pacific Oceans, the Gulfs of Mexico and Lower California and the Bay of Panama were sampled between June 1962 and December 1963. Almost all of the samples were surface collections made under various sea conditions such as the presence or absence of slicks and the degree to which the water had been mixed by wind or wave action. Twelve samples representing subsurface water from various depths were collected with the Van Dorn bottles. The areas sampled represent coastal waters a few miles from shore as well as deep sea conditions several hundred miles from land. During all collection operations, an effort was made to avoid areas contaminated by ships or other sources capable of contributing substances not native to the ocean.

INFRARED STUDIES

Infrared spectra of the water-insoluble materials extracted from these samples with chloroform were obtained with a Beckman IR-5 spectrophotometer equipped with NaCl optics. The spectral region studied was from 2 to 16 microns. The materials were examined by spreading a small portion on the surface of a sodium chloride plate. The plate was then placed at the focus of a beam condensing unit in order to reduce the sample area needed to fill the radiation beam of the spectrometer. Each sample displayed strong absorption in the spectral bands characteristic of CH_2 and CH_3 groups, while varying amounts of carboxyl (COOH) and esterified carboxyl (COOR) groups were indicated for most collections. The evidence for alcohol and chemical unsaturation was inconclusive due to masking by adjacent bands. Nitrogen-containing functional groups were not indicated. The infrared spectra were, therefore, interpreted to indicate the presence of a complex mixture of long hydrocarbon-chain molecules with polar functional groups. Nonpolar materials such as nonpolar hydrocarbons were also postulated to be present in many of the samples from the intensity of the CH_2 and CH_3 bands compared to that of the other functional group absorption bands. From these data the water-insoluble slick constituents appeared to be largely lipids, free fatty acids, and nonpolar entities, although alcohols and sterols might be present. Qualitative spot tests performed subsequently showed no significant quantities of unsaturated sterols or carotenoid-type hydrocarbons in the water-insoluble fraction. In general, samples from both slick and nonslick areas of the sea surface yielded similar infrared spectra indicating that the same chemical groups existed in the sea surface regardless of whether the surface-active components had been sufficiently compressed to form slicks or whether they had come from relatively "clean" surface areas.

All samples contained a relatively high abundance of CH_2 and CH_3 absorption bands which represents the fatty segment (hydrocarbon portion) of the polar molecules. A few samples from the Bay of Panama (G-30 through G-35) were extremely rich in these hydrocarbon absorption bands although the polar functional groups bands were extremely weak. It was, therefore, concluded that these samples were primarily aliphatic hydrocarbons with a low percentage of polar aliphatic compounds.

Microelemental analysis for N and S were performed on the chloroform-extracted fatty materials from six of the samples. No nitrogen or sulfur was found. Thus, if any organic compounds containing these elements existed in the unprocessed samples, they were not extracted by the chloroform and would be found in the aqueous portion.

SPECIFIC FATTY COMPOUNDS

The water-insoluble mixture of fatty compounds was methylated by the method of Stoffel, Chu, and Ahrens (16) to convert the free and combined acids (as glyceryl esters) to their corresponding methyl esters. Since small samples (5 mg and up) could be treated by this procedure, it was most suitable for this study. The only important modification of the method was that the distillation of the methyl esters was carried out for 1.5 hours per 5 mg of original sample to insure completeness of the distillation.

The distilled methyl ester fraction was analyzed for its components by gas chromatography (Wilkins Instrument Co. Aerograph A-350 with a Wilkins Instrument A-500-B Hydrogen Flame Ionization Detector Kit). Two separate columns were calibrated with more than twenty known methyl esters, five fatty alcohols, and pristane ($\text{C}_{19}\text{H}_{40}$). The first column was six feet in length with an outside diameter of 1/8 inch and was packed with 3% ethylene glycol succinate on Gas Chrom P. This column was temperature programmed at a high sensitivity setting such that 1/2 of a microgram of a methyl ester was readily detected. The second column was five feet in length with an outside diameter of 1/8 inch and was packed with 20% diethylene glycol succinate on firebrick. This column was

operated isothermally at 200°C and, although it did not possess as high a sensitivity as the first column, it was used to insure correct identification of the C₁₄ to C₁₈ esters through the relative correspondences of peaks between columns. Thus, to be positively identified, an unknown peak must match a particular known peak on both columns.

Table 2 lists the percentage distributions of chromatographic peaks for the saturated and unsaturated fatty acid esters and fatty alcohols. Although pristane was considered to be a possible component of the water-insoluble fractions, none of the chromatographic peaks obtained from these samples corresponded to the known peak for this hydrocarbon. The relative areas of the peaks were good indications of the relative amount of the methyl esters present, since it has been reported (17) that equal weights of different methyl esters gave the same response when the hydrogen flame detector was used. The amount of fatty material determined by this method relative to the original water-insoluble sample is shown at the bottom of the table. The average number of carbon atoms per molecular chain calculated from the relative methyl ester percentage is also given.

Table 2 also contains values which correspond to unidentified chromatographic peaks. Known compounds were not found to establish definitely the identity of these undefined areas. They may be due to unusual branched or unsaturated hydrocarbon chains of fatty acids or alcohols, or they may represent a pure hydrocarbon which was sufficiently volatile to distill with the methyl esters. For example, an undefined peak was found to fall between the peaks for methyl arachidonate and methyl docosanoate. This unknown was found in eight samples and was the major water-insoluble component of sample P-11.

Although some dodecanol was found in most samples in varying amounts, cetyl alcohol appeared in only ten samples in small quantities. Oleyl and stearyl alcohols were essentially absent.

FREE FATTY ACIDS

Eleven of these samples were examined for free fatty acids to determine what percentage of the original fatty material was not combined in the form of fatty acid esters. Whereas the method described in the previous section analyzed both free and combined acids, the following procedure measured only the free or unesterified fatty acids. Using ether as solvent, the sample was chromatographed using the hydrogen flame detector. The column measured four feet in length by 1/8 inch outside diameter and was packed with 20% ethylene glycol succinate plus 3% phosphoric acid on alkaline washed Chromosorb W. The column was operated isothermally at 200°C. Since the hydrogen flame detector does not give the same response for equal amounts of different free acids, the relative areas of the peaks on the chromatograms were not an indication of the relative amount of each free acid present. Consequently, the results expressed in Table 3 are only qualitative. The table lists the acids detected in each sample along with a comment on the approximate ratio of the quantity of free acid to that of the original sample. The outstanding feature of Table 3 is the appearance of the more volatile lower molecular weight fatty acids with 8-10 carbon atoms. Since these acids were not found as methyl esters, it is possible that the procedure used for free and combined acids does not efficiently esterify the low molecular weight acids.

NONPOLAR SUBSTANCES

The possibility that the water-insoluble organic mixtures contained nonpolar or hydrocarbon materials was suggested (13) on the basis of infrared data and surface chemical studies. Similar indications were obtained for the samples reported in Table 1. Since several of the samples did not yield large amounts of distillable materials under the conditions of the methyl ester distillation step (Table 1), the presence of high molecular

Table 2
Methyl Esters and Alcohols Obtained from Water-Insoluble Samples

Alcohols or Methyl Esters of Fatty Acids (Carbons: Double Bonds)	Relative Quantities* (percent)																				P-31, P-32, P-33			
	N-3	N-4	B-2	A-1, A-3	A-2, A-4	B-3	P-11	P-12	G-10	G-20	G-21	G-22	G-23	G-9	P-20	P-21	P-22	P-23	P-25	P-26		W-4	P-39	P-40
11:0	-	0.6	0.7	-	-	0.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12:0	-	-	1.0	0.7	1.0	0.9	0.5	-	1.5	-	-	-	-	0.3	-	0.5	0.8	2.1	-	-	-	-	-	-
Dodecanol	12.4	54.4	2.2	2.7	10.3	4.3	2.3	0.8	3.1	-	2.6	-	3.2	1.8	-	19.5	6.9	14.7	11.0	2.3	10.5	5.9	11.0	-
14:0	-	-	-	-	-	-	-	2.0	-	-	-	-	-	1.1	-	-	-	-	-	0.5	-	-	-	-
14:1	16.5	2.3	-	2.0	5.2	9.9	-	-	13.4	3.7	2.6	2.8	3.2	-	11.2	4.7	4.6	3.2	8.0	4.2	8.9	4.6	5.5	-
15:0	4.1	1.2	0.8	-	2.1	1.3	-	-	-	-	-	-	-	-	4.8	-	-	-	-	-	5.8	-	-	-
-	-	-	-	-	-	2.6	-	-	2.3	-	-	-	-	3.2	-	1.6	1.7	0.5	4.0	2.4	-	2.4	2.3	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.4	-	-	-	-	-	-	-	-
16:0	-	-	-	-	-	-	-	-	2.3	-	-	-	-	-	5.9	7.9	5.8	-	-	-	-	-	-	-
16:1	25.7	14.4	26.7	29.5	37.1	31.3	7.9	27.2	34.9	38.2	{44.7}	{48.6}	29.0	25.1	20.0	29.8	21.0	{32.6}	32.8	31.0	15.9	34.6	30.2	-
Cetyl Alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17:0	-	0.6	-	-	-	-	-	1.2	-	3.7	-	-	-	3.1	-	1.1	-	1.1	2.1	1.0	-	-	-	-
-	6.0	1.2	0.8	-	-	3.8	-	-	2.3	8.5	-	5.7	1.6	-	2.7	-	-	7.4	5.0	1.7	1.7	{2.8}	2.3	-
18:0	11.1	-	0.7	-	-	-	3.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18:1	11.0	9.8	5.9	18.7	20.6	19.0	-	4.5	12.2	22.3	{29.0}	{28.6}	30.3	2.8	17.6	17.4	27.0	18.6	19.0	29.4	9.6	16.4	18.0	-
18:2	4.6	3.6	18.8	6.3	10.3	13.6	-	21.0	7.0	15.5	-	-	17.3	18.8	19.8	8.7	21.4	14.0	9.0	15.1	12.7	5.6	-	-
Stearyl Alcohol	1.1	2.6	38.4	40.1	4.1	0.9	-	42.5	1.5	-	5.3	-	-	48.7	5.3	3.3	4.0	3.2	-	5.3	25.5	1.3	1.4	-
19:0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6	-	-
18:3	3.0	1.4	1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	{1.8}	{0.5}	-
-	-	-	-	-	-	-	-	-	1.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	1.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
20:0	2.1	1.2	-	-	-	-	-	-	1.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
20:4	-	-	-	-	-	2.6	-	-	-	-	5.3	-	-	-	-	-	2.3	2.1	-	4.2	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.9	-	-	-	-	-	-	-
22:0	2.4	3.2	2.0	-	6.2	-	81.4	-	4.2	-	-	-	-	-	-	-	-	-	-	-	-	2.4	2.8	-
-	-	-	-	-	-	-	-	-	-	10.5	14.3	-	-	-	-	-	-	-	-	-	-	10.5	22.6	-
Estimated Yield of Methyl Esters	>75	>75	>75	>75	>75	50	>75	>75	50	<10	5	5	10	>75	10	25	50-75	10	10	75-100	75	10	10	-
Average Carbon - Chain Length	16.0	14.8	17.2	17.2	16.5	16.2	19.3	17.3	17.2	16.8	16.2	15.6	16.7	17.3	16.5	15.6	16.9	16.1	16.0	16.9	16.2	16.7	15.7	-

No peaks observed

*Percent of total area occupied by a particular peak. A few minor peaks were omitted as unimportant.

Table 3
Fatty Acids Detected in Water-Insoluble Samples

Sample No.	Fatty Acids (Carbon: Double Bonds)									Estimated Percent of Sample as Free Fatty Acids
	8:0	9:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	
G-20	-	-	-	-	-	+	-	-	-	<1
G-23	-	-	-	-	-	+	-	-	-	<1
P-20	-	-	-	-	+	+	+	+	+	10
P-25	-	-	+	-	+	+	-	-	-	3
P-26	+	-	+	+	+	+	+	+	-	25
G-10	-	-	-	-	+	+	-	-	-	1
P-39	-	-	-	-	-	+	+	-	-	5
P-40	+	-	+	-	+	+	-	-	-	5
P-31	} No acids detected									-
P-32										-
P-33										-

weight compounds was indicated. Much of this undistilled residue was shown to be non-polar material on the basis of film pressure vs area per molecule graphs plotted from film balance studies. Of particular interest were samples P-30 through P-35 which were collected at various depths as well as at the surface in the Bay of Panama. All of these samples were collected in an area of fish feeding and high biological activity. Their yield of water-insoluble organic matter was quite large (approximately 100 mg/5-gallon sample), little of which proved to be surface active. In spite of the relatively large quantities obtained, there was no chromatographic results for any free or combined fatty acids or fatty alcohols.

Several of these samples dissolved completely in freshly distilled petroleum ether. They were then passed through a column of adsorption-grade alumina several times to remove the small amounts of surface-active substances present. Sample P-34, when treated in this manner yielded 77% of its original weight as a clear, white viscous liquid with a refractive index, $n_D^{20} = 1.477$. When this liquid was placed on clean distilled water it remained as a lens and did not spread. This result indicates the complete removal of the surface-active components by the adsorption column. Furthermore, its infrared spectra did not contain any carbonyl absorption bands. Elemental analysis gave 13.12% of H and 86.46% of C which when coupled with a molecular weight of 400 g/mole corresponded to a possible molecular formula of $C_{29}H_{52}$.

An attempt was made to determine more specifically the components of this purified hydrocarbon substance. A high temperature gas chromatographic column was prepared with SE-30 Silicone Gum Rubber on Gas Chrom P and run isothermally at 250°C. The retention of four pure compounds on this column was as follows:

Methyl arachidate	3.8 minutes
Squalene	13.0 minutes
Cholestane	15.1 minutes
Cholesterol	25.6 minutes

Unfortunately, no significant peaks resulted when the components of P-31 through P-34 were gas chromatographed for several hours on the 250°C column. Further studies will be made to elucidate some of the major constituents of this nonpolar fraction.

ISOLATION OF WATER-SOLUBLE COMPONENTS

Since these samples had been concentrated by a ferric hydroxide precipitation technique, they contained a concentrated salt solution along with the small quantities of soluble organic materials. To effect the difficult isolation of these soluble organics for further analysis, the following series of separations were performed. The concentrate was first acidified to dissolve the ferric hydroxide sol. The resulting mixture was then passed over a Chelex 100 resin column to remove the large quantity of iron. The effluent was percolated through a column of Sephadex G-25, a highly cross-linked dextran gel with an exclusion limit of about 5000 (molecular weight units). The higher molecular weight proteinaceous and carbohydrate materials which were present were excluded by the gel and eluted from the column first while the smaller salt ions were detained for a time within the gel pores. Various fractions taken from the Sephadex column responded to qualitative tests for polypeptides or amino acids (ninhydrin) and for carbohydrates (anthrone reagent). These fractions were lyophilized to obtain dried solids which contained a mixture of organic material and some salt. An ion retardation resin was unsuccessfully employed in an effort to remove the salt from the low molecular weight organic material. The lack of success with this resin was most probably due to the high concentration of salt present. Removal of salt and analysis of the specific organic fragments present by paper chromatography are in process.

In general, the anthrone reactive material (carbohydrates) was more prevalent in the higher molecular weight fractions than the proteinaceous substances. The first fraction off the column contained the anthrone reactive substances while the ninhydrin reactive species eluted at a later time were accompanied by large amounts of salt. Very roughly about 2 to 5 mg of anthrone positive material (calculated as glucose) and about the same quantities of ninhydrin positive material (calculated as leucine) was estimated for these samples from the intensities of the color reactions.

DISCUSSION

This analytical program has sought to determine the general chemical classes and the specific compounds within these classes which are responsible for the modification of the sea surface. In addition, other classes (nonpolar or highly water soluble) which do not contribute substantially to the surface effects were studied because of their coexistence in the ocean with the surface-active species.

Preliminary studies using infrared spectroscopy revealed the existence of fatty substances among the water-insoluble constituents of the sea surface. The presence of adsorption bands representative of COOH, COOR, OH as well as strong CH₂ and CH₃ bands indicated fatty acids, lipids, and fatty alcohols. Subsequent spot tests for sterols or carotenoid hydrocarbons were usually negative. The infrared data as well as surface-chemical studies reported elsewhere (18) strongly suggested that in most samples there was nonpolar organic materials, i.e., hydrocarbons.

Specific fatty acids and alcohols were characterized by gas chromatography as their methyl esters. Individual free fatty acids in the water-insoluble fraction were also determined by an alternate gas chromatographic technique. Both saturated and unsaturated hydrocarbon chains were present in the fatty compounds with the saturated structures usually but not always predominating. The number of carbons per fatty acid varied from 8 to 22 and averaged from 16 to 17 for the entire distribution from any one sample. Since in

some cases the amount of material accounted for by the gas chromatograms was small with respect to the quantity of the entire water-insoluble sample, it appeared that there was high molecular weight material present. These molecular weights were about 400 or greater, and for several of the samples the high molecular weight material was largely hydrocarbon in nature.

Some water-insoluble organic material was found in all areas sampled (5 to 100 mg/5 gal) whether the sea was biologically rich or relatively sterile. Although the more bioactive regions yielded the greatest quantities, even the inactive waters contained some surface-active organic matter. Generally the same classes of chemicals were found whether the samples had been collected in or out of a surface slick or at depth. However, in the fine detail developed by the gas chromatograms, there are variations in the specific chemicals which relate to the events taking place locally in the ocean. Some of the events which could be followed by variations in fatty acid distribution might be (a) the mixing of the upper layers of water by wind, (b) local chemical enrichments as a result of currents or biological blooms, or (c) manmade effects such as the passage of a ship.

One of these localized situations is described by the fatty acid distributions of samples N-3 and N-4. At the time of sampling the sea was calm and had been in that condition for several hours. The surface was approximately 75% slick covered. Surface-chemical studies (18) showed that the material taken from this surface (N-3) acted nearly like a pure surface-active compound giving a spread film of monomolecular dimensions. On the other hand, water taken from the same locale, but from beneath the surface (N-4), yielded spread films many molecules thick which were fragile and difficult to reproduce. This led to the conclusion that this sample contained nonpolar material and/or water-soluble substances which had been forced out of the water surface by the more surface-active molecules. The fatty acid distributions show larger amounts of dodecyl alcohol in the subsurface sample which accounts for the shorter average carbon-chain length for this sample and perhaps for its surface-chemical properties. If this is the case, the analytical data are consistent with the sampling situation. That is, the surface sample contained molecules which were less soluble, had longer hydrocarbon chains, and were consequently more permanent residents of the surface. The subsurface water on the other hand contained species having shorter carbon chains and greater solubility.

Another oceanographic event noted at the time of sampling involved sample G-9 which was collected during a bloom of the plankton *Skujella* in the Gulf of Mexico, east of Galveston, Texas. The spectrum of fatty acids shows a larger proportion of the unsaturated C₁₈ acids (linoleic and linolenic acids) than in most of the other samples. It is possible that this distribution is due in part to the planktonic species present in the water. Sample B-2 is similar to G-9 in this respect even though it was a nonslick surface collection made about 150 miles east of Labrador in the North Atlantic Ocean. The biological properties of this water were not known.

The collection of large amounts of high molecular weight hydrocarbons in a fish feeding area of the Bay of Panama has been previously discussed under Nonpolar Substances. An event such as this was observed but once during the course of this program. The large yields of hydrocarbon were obtained in all of the samples from the area even though they were taken from the surface and to depths of 80 feet.

While this was of a localized event, a more general correlation can be made with regard to the nonpolar constituents of the sea. A comparison of the estimated yields of methyl esters (Table 2) with the type of sample taken (Table 1) reveals that in general the surface samples contained higher percentages of volatile fatty material than did those samples taken from beneath the surface. Thus, it may be that the nonpolar high molecular weight substances had been eliminated from the surface by the more permanent residents of the sea surface, the more surface-active fatty acids and alcohols, when slick-forming conditions existed.

Relationships of this kind may be obtained from a knowledge of the organic constitution of the sea. More definitive answers to the processes taking place in the ocean could be obtained through intensive sampling and analysis at a particular location. The major objective of this study, however, was to survey the organic constitution of the sea at various sites to determine the general classes of chemicals present and their distribution.

CONCLUSIONS

The following statements summarize the conclusions drawn from these data about the water-insoluble organic components of the ocean.

1. The major water-insoluble organic constituents of the sea are fatty esters, free fatty acids, fatty alcohols, and hydrocarbons.
2. These chemical types are general to all areas sampled but specific differences within these classes exist from area to area.
3. For example, the distribution of fatty acid carbon-chain lengths and chemical unsaturation varies according to the meteorological and oceanographic conditions prevalent at a particular location.
4. Competitive chemical adsorption exists at the surface between the various chemical species. The higher molecular weight and less water-soluble fatty acids and alcohols are the most surface active and likely to be found adsorbed at the surface while the more water-soluble or less surface-active entities are excluded from the surface by the fatty material when competitive adsorptive processes occur.
5. A sufficient quantity of surface-active substances was found in all areas of the ocean examined to account for alterations of the sea surface by monomolecular films. This does not mean that the entire surface of the ocean is always under modification, but that a chemical potential exists whereby such surface alterations can occur when conditions are suitable for the adsorption and compression of the surface-active molecules at the air/sea boundary.

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13. ABSTRACT An analytical survey has been conducted to determine the organic chemical constitution of the sea. Special emphasis was placed upon the nature of the surface-active water-insoluble components present in the sea surface. Samples were collected under various oceanographic conditions from the Atlantic and Pacific Oceans, the Gulf of Lower California, the Gulf of Mexico, and the Bay of Panama. The water-insoluble organic constituents were isolated from these samples and were analyzed by infrared spectroscopy, microelemental analysis, and various gas chromatographic techniques. The following conclusions were drawn from a comparison of the analytical data with the sea conditions which existed at the time the samples were taken. The major water-insoluble organic constituents of the sea are fatty esters, free fatty acids, fatty alcohols, and hydrocarbons. These chemical types are general to all areas sampled, but specific differences within these classes exist from one location to another. For example, the distribution of the various fatty acids and alcohols varies according to the meteorological and oceanographic conditions prevalent at a particular location. A competition for adsorption sites exists at the surface between the various chemical species. The higher molecular weight and less water-soluble fatty acids and alcohols are the most surface-active and likely to be found adsorbed at the surface while the more water-soluble or less surface-active entities are excluded from the surface by the fatty material when competitive adsorptive processes occur. Surface-active substances were found in all areas of the ocean in sufficient quantity to account for the observed alterations of the sea surface by monomolecular films. This does not mean that the entire surface of the ocean is always under modification, but that a chemical potential exists whereby such surface alterations can occur when conditions are suitable for the adsorption and compression of the surface-active molecules at the air/water boundary.			

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