



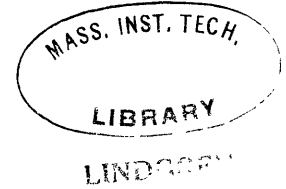
SATURATED HYDROCARBONS IN MARINE PLANTS AND SEDIMENTS

by

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ABSTRACT

Twelve species of algae from the Northeast coast of the United States, three species of planktonic algae grown in the laboratory, a pelagic algae, a recent sediment and a sample of mixed marine plankton were analyzed for normal alkane hydrocarbons over the range $C_{14}H_{30}$ to $C_{32}H_{66}$.

The samples were extracted in a Soxhlet extractor using a benzene:methanol mixture; the saturated hydrocarbons were first isolated from the organic extract by silica gel column chromatography and the normal paraffins were identified by gas chromatography.

The results:

1. The benthic algae and mixed plankton exhibit a slight odd carbon predominance.
2. The planktonic algae (Syracosphaera, Cryptophyceae and Skeletonema) grown under controlled laboratory conditions had a slight odd carbon predominance.
3. The recent sediment sample from Tarpaulin Cove, Mass., shows a pronounced odd carbon predominance.
4. Definite differences in hydrocarbon distribution between classes were found. The red algae (Corallina, Chondus, Polysiphonia and Rhodymenia), the green algae (Chaetomorpha) and the mixed marine plankton show a strong predominance of n-heptadecane. In the brown algae n-pentadecane predominates; the Fucules (Fucus and Ascophyllum) have a higher ratio of n-pentadecane to n-heptadecane than the Laminariales (Agarum and Laminaria) and Sargassum.
5. All plant samples show a hydrocarbon minimum in the n- $C_{18}H_{38}$ to n- $C_{21}H_{44}$ region and a moderate maximum in the n- $C_{27}H_{56}$ to n- $C_{30}H_{62}$ region.

6. Pristane was found in several samples but phytane was not detected.

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STATEMENT OF ASSOCIATION

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The advisory committee for the research consisted of Dr. Max Blumer, Profs. Dayton Carritt and John W. Winchester.

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INTRODUCTION

Straight chain saturated hydrocarbons (n-alkanes or n-paraffins, C_nH_{2n+2}) are minor but ever-present compounds in the marine environment. They occur in marine organisms, in sediments and in the sea water itself. Two principal sources contribute to the marine environment: fossil fuels and recent organisms.

Fossil hydrocarbons of ancient sediment and petroleum are introduced into the sea by pollution, by marine seepage and by sedimentary compaction. The hydrocarbon distribution in petroleum and products derived from fossil fuels is well documented. Fossil hydrocarbon mixtures tend to show a little odd carbon predominance. (See Appendix II).

Our knowledge of the recent biogenic hydrocarbons is much more limited. Selected land plants have been investigated systematically for their straight chain hydrocarbon content. These hydrocarbons, usually found in the waxy coating of stems, leaves, flowers and fruit, cover the range from methane (CH_4) to at least n-dohexacontane ($C_{62}H_{126}$) (See Appendix II).

Various authors associated with the petroleum industry have investigated the content and distribution of hydrocarbons in recent sediments in connection with the problem of the origin of petroleum. According to Bray and Evans²¹² recent sediments exhibit pronounced predominance of odd carbon normal paraffins over the even numbered members of the homologous series.

The recent sediments presumably reflect the odd carbon predominance pattern already present in the organisms which contribute their organic matter to the formation of the sediments. Large marine organisms have been analyzed to a limited extent for the presence of hydrocarbons but the marine algae and zooplankton have not been studied systematically. These organisms represent the bulk of the marine biomass¹⁹²; thus the dominant planktonic plants and animals are of special interest as potential sources of a large fraction of the marine hydrocarbons.

The organisms responsible for the odd carbon predominance found in recent sediments have not yet been identified.

Normal paraffins are relatively stable in the marine environment, therefore their residence time in the ocean should be longer than that of most nutrients. As compounds which are not easily metabolized the normal paraffins may be passed unaltered through the marine food chain. Thus, all marine organisms might contribute some hydrocarbons to the sediment on the ocean floor and eventually to petroleum.

The objectives of this investigation were:

- 1) An analysis of the principal marine seaweeds for normal paraffins in the C_{14} to C_{32} range.
- 2) A search for an odd carbon predominance or other distinguishing features in the hydrocarbon composition which might be reflected in sediments of recent and ancient age.
- 3) A search for differences in the hydrocarbon distribution pattern of different genera or species of algae; such differences might be of taxonomic and geochemical importance.

For this study twelve species of Northeast Atlantic intertidal zone seaweeds and one free-drifting pelagic seaweed were analyzed. While their contribution to the world ocean biomass is much less than the unicellular planktonic algae, they are easy to collect and their importance to inshore recent sediments might be appreciable.

Planktonic algae on the otherhand can not be easily collected in a pure or uncontaminated form from the ocean. Therefore, three species of planktonic algae were analyzed from pure cultures grown in an artificial medium excluding hydrocarbons.

Recent sediment and mixed plankton samples were collected in the same location as the benthic algae. Both were analyzed for their normal paraffin content.

EXPERIMENTAL

1. Laboratory Culture of Algae

Culture Assembly

Hydrocarbons had to be excluded from the culture system if the analysis for normal paraffins was to be meaningful. Thus all the culture equipment consisted of glass, Teflon or silicone rubber. The reagents and CO₂ necessary for algal growth were purified and artificial sea water was used.

The culture assembly consisted of an air purification train, the culture chamber and a light source. The air was filtered in succession through glass wool (Pyrex) and indicating silica gel (activated 24 hours at 240°C) in a two liter bottle by an air-cooled diaphragm air pump (Neptune Dyna-Pump, Model 3). The air was then pumped through an activated silica gel bed in a 90 x 3 cm glass tube and an activated alumina bed in a 15 x 3 cm tube to the distribution manifold. All the connections beyond the pump were glass, Teflon or baked silicone rubber.

Each culture chamber was supplied with air through a 12/5 ball and socket joint; a liquid seal of artificial sea water served as a grease-free seal. Before bubbling into the bottom of the culture chamber the air was again filtered through a glass wool plug. A Teflon stopcock below the cotton wool could be closed during autoclaving so that the wool would not become saturated with water. The culture chambers were 10 liter glass carboys or 2800 ml Fernbach flasks sealed with baked silicone rubber stoppers (Dow Corning RTV 502). From the top of the chamber the waste air bubbled into a check vial filled with artificial sea water. A siphon from the bottom of the chamber was used for harvesting the algae.

Two banks of four 1.2 m Sylvania VHO Powertubes spaced 9 cm were placed 5-10 cm from the chambers. The heat generated by the lights made cooling of the cultures necessary.

Water at 14-16°C was circulated over the chambers by sprinkler-type tubes fitted around the necks of the flasks. The water was cooled by a portable refrigeration unit (Model PCG-4; Blue M Electric Co: Blue Island, Ill.) and cycled by a centrifugal pump.

Artificial Sea Water Medium

Various artificial culture media have been reported^{7,33,160,192}. A compromise formula (See Table 1) was adapted to provide the various planktonic algae with the maximum number of micronutrients and, hence, the greatest chance for growth in common artificial medium.

Reagents

All reagents came from fresh stock bottles. The major reagents (used in quantities greater than 10^{-3} g) which could be heated without decomposition were dried at 500°C in porcelain crucibles for not less than 20 hours in a Muffle furnace (Hoskins Electric Type FD 204C; Hoskins Mfg. Co; Detroit, Michigan) in order to eliminate volatile organic compounds. The reagents were cooled in a large desiccator over freshly-activated silica gel.

Hydrated solids were dried over activated silica gel in a desiccator at atmospheric or reduced pressure. The distilled water was prepared in an all-glass water distillation apparatus (Model AG-2; Corning Glass Co; Corning, N.Y.) from tap feed water and was collected in a freshly cleaned and distillate-rinsed 20-liter glass carboy. All solutions were stored in Pyrex glass-stoppered reagent bottles.

Artificial sea water medium was prepared from the following reagents; the aliquot volumes are for one liter of medium.

Sodium chloride (NaCl), analytical reagent, crystal (Baker and Adamson: Allied Chemical Co; Morristown, N.Y.) was dried at 500°C for 20 hours and stored in a wide-mouth reagent bottle. It was added directly (26.726 g) to the flasks.

Magnesium chloride ($MgCl \cdot 6H_2O$), certified reagent, crystal (Fisher Scientific Company) was dried in a desiccator over silica gel at 23 mm Hg for four days. A stock solution was

TABLE 1

ARTIFICIAL SEA WATER MEDIUM

(Grams per liter of medium)

Compound	SW 1 Ref. 160	ASP - 2 Ref. 160	ASP - 6 Ref. 160	McClendon Ref. 192	This Work
NaCl	15	18	24	26.73	26.73
MgCl ₂ ·6H ₂ O	2.5	-	-	4.82	4.82
MgSO ₄	-	2.50	4.00	3.25	3.25
CaCl ₂ ·6H ₂ O	0.65	0.55	0.82	2.28	2.28
KCl	400 mg	600 mg	700 mg	720 mg	720 mg
NaHCO ₃	-	-	-	190 mg	190 mg
KBr	33 mg	97 mg	97 mg	87 mg	67 mg
H ₃ BO ₃	-	6 mg	2 mg	58 mg	85 mg
Na ₂ SiO ₃ ·9H ₂ O	100 mg	150 mg	70 mg	2 mg	7 mg
K ₂ HPO ₄	10 mg	5 mg	-	4 mg	1 mg
AlCl ₃ ·6H ₂ O	250 mg	4.5 mg	4.5 mg	23 mg	440 mg
NH ₄ Cl	-	-	-	6 mg	6 mg
LiCl	36 ug	600 ug	600 ug	800 ug	800 ug
SrCl ₂ ·6H ₂ O	12 mg	4 mg	4 mg	-	4 mg
RbCl	.85 ug	.28 ug	.28 ug	-	.28 ug
ZnSO ₄ ·7H ₂ O	10 mg	660 ug	2.2 mg	-	2.2 mg
MnCl ₂ ·4H ₂ O	2.3 mg	4.3 mg	3.6 mg	-	810 mg
Na ₂ MoO ₄ ·2H ₂ O	500 ug	-	1.3 mg	-	130 ug
CoCl ₂ ·6H ₂ O	25 ug	12 ug	40 ug	-	23 ug
CuCl ₂ ·2H ₂ O	3.5 ug	3.2 ug	2.7 ug	-	11 ug

Compound	SW 1	ASP - 2	ASP - 6	McClendon	This Work
NaNO ₃	84 ug	5 mg	30 mg	-	10 mg
NaFeEDTA	26 mg	40 mg	-	-	10 mg
TRIS	500 mg	1.0 g	1.0 g	-	500 mg
Thiamine - HCl	10 mg	50 ug	200 ug	-	200 ug
Vitamin B ₁₂	100 ug	2 ug	0.5 ug	-	1 ug
Biotin	-	0.1 ug	0.5 ug	-	1 ug
KI	26 ug	65 ug	65 ug	-	88 ug

Distilled water to make one liter.

made up to contain 4.826 g per 10 ml.

Magnesium sulfate (MgSO_4), certified reagent, anhydrous (Fisher Scientific Co.) was dried at 500°C for 20 hours. A stock solution was made up to contain 3.2484 g per 25 ml.

Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), certified reagent, crystal (Fisher Scientific Co.) was dried in a desiccator over silica gel at 23 mm Hg for four days. A stock solution was made up to contain 2.276 g per 10 ml.

Potassium chloride (KCl), test purity reagent (Fisher Scientific Co.) was dried at 500°C for 20 hours. A stock solution was made up to contain 0.721 g per 10 ml.

Sodium bicarbonate (NaHCO_3), analytical reagent, powder (Mallinckrodt Chemical Works; St. Louis, Mo.) was dried in a desiccator over silica gel at 23 mm Hg for four days. A stock solution was made up to contain 0.198 g per 5 ml.

Potassium bromide (KBr), analytical reagent, crystal (Mallinckrodt) was dried at 500°C for 20 hours. A stock solution was made up to contain 0.0673 g per 1 ml.

Boric acid (H_3BO_3), analytical reagent, granular (Mallinckrodt) was used directly to make up a stock solution containing 0.0581 g per 10 ml.

Sodium phosphate monomasic ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), analytical reagent, granular (Mallinckrodt) was used directly to make up a stock solution containing 9.992×10^{-4} g per 1 ml.

Aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), certified reagent, crystal (Fisher Scientific Co.) was dried at 23 mm Hg over silica gel. A stock solution was made up to contain 4.448×10^{-4} g per 1 ml.

Ammonium chloride (NH_4Cl), analytical reagent, granular (Mallinckrodt) was used directly to make up a stock solution containing 6.2987×10^{-3} g per 1 ml.

Lithium chloride (LiCl), analytical reagent, granular (Mallinckrodt) was dried at 500°C for 20 hours. A stock solution was made up to contain 8.026×10^{-4} g per 1 ml.

Strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), analytical reagent, granular (Mallinckrodt) was dried over silica gel in a desiccator for four days. A stock solution was made up to contain $3.959 \times$

10^{-3} g per 1 ml aliquot.

Rubidium chloride (RbCl), certified reagent, purified (Fisher Scientific Co.), was dried at 500°C for 20 hours. A stock solution was made up to contain 2.9696×10^{-5} g per 1 ml.

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), analytical reagent, granular (Mallinckrodt), was used directly to make up a stock solution containing $2,220 \times 10^{-3}$ g per 1 ml.

Manganese chloride ($\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$), analytical reagent, crystal (Mallinckrodt), was dried over silica gel in a desiccator for four days. A stock solution was made up to contain 8.496×10^{-4} g per 1 ml aliquot.

Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), analytical reagent, crystals (Mallinckrodt), was used directly to make a stock solution containing 1.264×10^{-4} g per 1 ml.

Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), analytical reagent, crystals (Mallinckrodt), was used directly to make up a stock solution containing 2.289×10^{-5} g per 1 ml.

Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), certified reagent, crystals (Fisher Scientific Co.), was used directly to make up a stock solution containing 1.352×10^{-5} g per 1 ml.

Sodium nitrate (NaNO_3), certified reagent, crystals (Fisher Scientific Co.), was dried at 220°C for four days. A stock solution was made up to contain 0.010 g per 1 ml.

Potassium iodide (KI), certified reagent, crystal (Fisher Scientific Co.), was dried at 500°C for 20 hours. A stock solution was made up to contain 6.66×10^{-6} g per 1 ml.

TRIS (2-amino-2-hydroxymethoxy)-1,3-propanediol, certified reagent (Fisher Scientific Co.), was dried overnight over silica gel at atmospheric pressure. A stock solution was made up to contain 0.4993 g per 7 ml.

Sodium meta-silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), analyzed reagent, crystal (Baker and Adamson), was dried overnight over silica gel under reduced pressure. A stock solution was made up to contain 7.122×10^{-3} g per 1 ml.

Sodium iron salt of ethylene-diaminetetraacetic acid was prepared according to Provasoli¹⁶⁰. Sodium hydroxide, pellets (4.00g) (Baker and Adamson), was dissolved in distilled water (50 ml)

and added with stirring to purified, sublimed, anhydrous ferric chloride (1.6221 g) (Fisher Scientific). The red brown precipitate was collected in a large Buchner funnel and rinsed with distilled water. The precipitate was then washed into a 2-liter beaker containing disodium ethylenediaminetetraacetate (3.772g) (Fisher Scientific Co.) and distilled water (1000 ml). The resulting yellow solution was filtered through a #31 Whatman filter into a glass-stoppered bottle. A 1 ml aliquot contained 4.05×10^{-3} g of NaFeEDTA.

The vitamins, sealed in ampoules were provided by R. Guillard. A 1 ml ampoule contained approximately 2×10^{-4} g thiamine hydrochloride, 1×10^{-6} g vitamin B₁₂ and 1×10^{-6} g biotin.

Culture Procedure

The artificial medium was prepared fresh for each culture. First the distilled water was added to the flask; this was followed by sodium chloride and the remaining inorganic reagents, except phosphate, in the order given in Table 1.

The vitamin ampoule, stored in the freezer, was rinsed with methanol, its tip flamed and broken and the solution was added to the medium. Two ampoules were sufficient for 10 liters of medium while one ampoule was used on volumes to two liters. The culture chamber was then stoppered with the silicone rubber plug equipped with the air input (stopcock closed), outflow tube and siphon (stopcock closed). The whole unit was autoclaved at 15-18 psig at 130°C for 20 minutes and cooled to room temperature over-night.

The EDTA and phosphate solutions were added quickly by pipette through the outflow tube joint. The pure phytoplankton culture (50 ml, provided by R. Guillard) was added after flaming the outflow joint of the chamber and the neck of the small culture flask. The culture chamber was then mounted in the growing assembly and one bank of lights was turned on immediately; the second was turned on after a day's growth. The cultures were allowed to grow for three to five days.

Harvesting was accomplished by removing the culture chamber from the assembly and by siphoning the phytoplankton medium into 250 ml centrifuge bottles. After capping with aluminum foil the bottles were centrifuged at 2000 rpm (International Centrifuge, Size2); the supernatant liquid was decanted. The phytoplankton was finally concentrated into a minimum amount of medium and quickly frozen at -20°C . Some of the supernatant liquid from each culture was filtered through a benzene-washed 0.45 micron Millipore filter (Millipore Corp; Waltham, Mass.) and reserved for later analysis.

Planktonic Algae

Cultures successfully grown in this artificial sea water medium are given in Table 2. Only three were analyzed for their normal paraffins content and distribution.

TABLE 2

Planktonic Algae Cultures Grown in Artificial Sea Water Medium

Clone Symbol	Name	Original Isolation (Person; place; date)	Culture Volumes
CHRYSOPHYCEAE			
Iso	<u>Isochrysis galbana</u>	M. Parke	50 ml
*Cocco II	<u>Syracosphaera carterae</u>	I. J. Pintner; Woods Hole 1958	50 ml 2 & 10 l.
CRYPTOPHYCEAE			
*3C	Undetermined cryptomonad (Rhodomonas ?)	R. Guillard; Milford Harbor Conn.; 1957	50 ml 10 l.
DINOKONTAE			
Amphi 1	<u>Amphidinium carteri</u>	R. Guillard; Falmouth Great Pond; 1954	50 ml
Peri	<u>Peridinium trochoideum</u>	M. Parke	50 ml
BACILLARIOPHYCEAE			
Ch 1	<u>Chaetoceros sp.</u>	J.H. Ryther; Woods Hole	5,7 & 8 l.
13-1	<u>Cyclotella nana</u>	R. Guillard; Sargasso Sea 33°11'N, 65°15'W; 1958	50 ml
*Skel	<u>Skeletonema costatum</u>	R. Guillard; Long Island Sound; 1956	2,7 & 8 l.
CHLOROPHYCEAE			
Pyr 2	<u>Pyramimonas sp.</u>	I. J. Pintner; Great South Bay, Long Island; 1958	50 ml
Nep	Undetermined flagellate	R. Guillard; Gulf Stream 37°10'N, 68°30'W; 1958	50 ml 2 & 5 l.

* Planktonic algae analyzed for normal paraffin content and distribution. Grown and harvested September, 1963.

B. Collection of Marine Algae and Sediments

Collection

Polysiphonia sp. was collected and identified 9 February 1966 by R. Stone at extreme low tide from Jaffery Point on New Castle Island, New Hampshire (43° 03'42" N, 70°42' 40"W), at the entrance to Portsmouth Harbor. The sample was placed in a stainless steel canister ("Bain Marie" type, 2-1/16 quart) with matching cover and stored eleven days at -20°C before using. The frozen sample was separated from Chaetomorpha prior to extraction.

Corallina officinalis was collected and identified 6 March 1966 by R. Stone at Jaffery Point. It was stored overnight at 10°C and cleaned while wet before freezing for five days.

Rhodymenia palmata was collected and identified 6 March 1966 by R. Stone at Jaffery Point. This young epiphyte was separated from Ascophyllum while fresh and was frozen at -20°C for nineteen days.

Chondus crispus (N. Hampshire) was collected and identified 9 February 1966 by R. Stone at Jaffery Point. Stored seventeen days at -20°C, this sample was separated from two large mussels.

Chondus crispus (Falmouth) was collected 4 March 1966 at low tide on a groin close to the outflow of Salt Pond into Vineyard Sound in Falmouth, Mass. (41° 32'19" N, 70° 38'01"W) by J. Sass and identified by R. Stone. Excess water was shaken off and the sample was placed directly into the Soxhlet extractor.

Ascophyllum nodosum was collected and identified 6 March 1966 by R. Stone at Jaffery Point. It was stored overnight at 10°C and separated from an epiphytic Rhodymenia before freezing for five days.

Sargassum sp. was collected during the summer of 1963 in the northern Sargasso Sea and stored at -20°C wrapped in aluminum foil. Almost all the water had sublimed, leaving the sample brittle.

Fucus sp. (Woods Hole) was collected 5 November 1965 at low tide at the head of Little Harbour, Woods Hole, Mass. (41° 31'33" N, 70°40'02"W). Excess water was shaken off and the sample quick frozen at -20°C in a stainless steel canister. It was stored for three months before using.

Fucus sp. (New Hamp.) was collected and identified 9 February 1966 by R. Stone at Jaffery Point. It was stored seventeen days frozen before using.

Fucus sp. (Falmouth) was collected in vegetative stage in the same location as the Chondus in Vineyard Sound and was used immediately.

Agarum cribrosum was collected and identified 9 February 1966 by R. Stone at Jaffery Point. It was stored frozen four days before using.

Laminaria digitata was collected and identified 9 February 1966 by R. Stone at Jaffery Point. It was stored in a stainless steel canister overnight at 10°C before using.

Chaetomorpha linum was collected and identified 9 February 1966 by R. Stone at Jaffery Point. This sample was kept eleven days before using and was separated from Polysiphonia before extraction.

Sediment sample (81g wet weight) was collected 30 March 1966 with a pipe dredge during a fifteen minute tow in 6-9 meters of water in Tarpaulin Cove, off Naushon Island, Mass. (41°28'24"N, 70°45'25"W). The brown-grey sediment was stored overnight in a refrigerator in a wide-mouth, glass-stoppered bottle.

Mixed marine plankton sample was collected (36 g. wet weight) 30 March in the surface water in Tarpaulin Cove using a 3/4-meter open #2 mesh nylon plankton net towed at 4 knots for 25 minutes. The sample was stored overnight in a refrigerator in a wide-mouth, glass-stoppered bottle.

Preparation of Sediment for Carbonate Analysis

The sediment was dried for 48 hours at 140°C and ground to pass a 200 mesh US Standard Sieve. Duplicate samples (1.8g) were prepared for carbonate analysis using a volumetric technique.

C. Analytical Procedures

Solvents

All solvents were distilled through a 50 x 2 cm glass column packed with glass Raschig rings. After this distillation the apparatus was steam cleaned by distilling over at least 500 ml water; solvents collected after several distillations without steam cleaning of the unit possessed a contamination level of high boiling (n-C₂₄ to n-C₂₈ range) compounds. By passing steam through the column periodically most of these contaminants can be stripped off and the background level substantially reduced. The solvents were then redistilled through the cleaned column and stored in brown glass bottles or in glass-stoppered flasks.

Methyl alcohol, anhydrous (Mallinckrodt Chemical Works, St. Louis, Mo.) after two distillations contained less than 2.5×10^{-6} g/l of n-octacosane and less than 6×10^{-7} g/l of n-tetracosane the major contaminants.

Benzene, thiophene free (Mallinckrodt) after two distillations contained less than 3×10^{-7} g/l of n-octacosane and less than 1.5×10^{-7} g/l of n-tetracosane.

Pentane, 99 Mol %, pure grade (Phillips Petroleum Co, Bartlesville, Okla.) was distilled and then stored overnight over 5A Molecular Sieves (1/16" pellets, Union Carbide Corp., Linde Division; Buffalo, New York). The second distillation was through a previously steam-cleaned 115 x 2 cm glass column packed with ceramic Berl saddles; distillates containing more than 2×10^{-6} g/l of n-octacosane were discarded.

Reference Compounds and Solutions

The following reference compounds were used: normal tetradecane (Matheson, Coleman and Bell; Norwood, Ohio); normal pentadecane (Aldrich Chemical Co, Inc., Milwaukee, Wis.); normal hexadecane (Matheson, Coleman, and Bell); normal heptadecane (Aldrich); normal octadecane and normal eicosane (Matheson, Coleman and Bell); normal tetracosane, normal octacosane and normal dotricontane (Humphrey-Wilkinson, Inc; North Haven, Conn.) Pristane (2,6,10,14-tetramethylpentadecane, Robeco Chemicals, Inc; New York) was

chromatographed on silica gel by frontal elution.

The primary reference was made up of the following saturated hydrocarbons: $n\text{-C}_{14}$ (7.432×10^{-6} g/ul), $n\text{-C}_{18}$ (8.108×10^{-6} g/ul), $n\text{-C}_{20}$ (8.676×10^{-6} g/ul plus $n\text{-C}_{21}$ at 1.159×10^{-6} g/ul), $n\text{-C}_{24}$ (8.020×10^{-6} g/ul), $n\text{-C}_{28}$ (8.000×10^{-6} g/ul) and $n\text{-C}_{32}$ (8.056×10^{-6} g/ul) in CS_2 (25 ml). The solution was stored in a ground glass-stoppered volumetric flask in the dark.

A secondary reference was prepared by transferring 50 ul of the primary standard (100 ul Hamilton Gas-Tight syringe) to 10 ml of CS_2 (volumetric pipette) in a vial sealed with a Teflon-lined screw cap. Fresh secondary standards were made up for each series of analyses to reduce errors due to evaporation from the vials.

For calibration of the large $n\text{-C}_{15}$, pristane and $n\text{-C}_{17}$ peaks present in some samples a primary reference was prepared to contain $n\text{-C}_{15}$ (7.400×10^{-6} g/ul) and $n\text{-C}_{17}$ (7.392×10^{-6} g/ul) in CS_2 (25 ml). A secondary solution was made up by transferring 50 ul of primary standard to 10 ml of CS_2 .

To check the pristane content on the polar gas chromatograph column, a primary standard of pristane was made up (7.87×10^{-6} g/ul).

Extraction

Large all-glass Soxhlet extraction apparatus with Allihn condensers were used for all extractions. The large seaweeds were extracted without thimbles by inserting a tightly-coiled ball of #28 Nichrome wire (which had been flamed) into the siphon arm. The unicellular algae and sediment were extracted in double thickness extraction thimbles (Whatman #4965, Fat Extracted). The thimbles were cut so that the top edge was just below the highest point of the siphon arm. They were extracted for at least 72 hours in refluxing methanol, benzene and methanol:benzene; six or more changes of solvent were necessary. Blanks were run on each set of thimbles simultaneous with the extraction of the algae and

and sediment. Final results reflect blank corrections where necessary (never greater than 6×10^{-7} g per thimble for n-hexacosane, the major contaminant).

The apparatus was rinsed with twice-distilled methanol prior to use as were the boiling chips (regular granules, Hengar Co; Philadelphia, Pa.). The round bottom boiling flasks (300 ml) were filled with methanol: benzene (210 ml, 1:1 vol/vol mixture) and three boiling chips were added.

The fresh or frozen seaweeds were weighed in a clean glass beaker and then transferred to the Soxhlet extractor. The frozen algae from laboratory culture and the wet sediment were placed in the paper thimble for weighing on the Mettler balance prior to insertion into the extracting chamber.

The samples were extracted for 10-20 hours. The extraction was stopped just before the liquid in the extractor started to drain. The benzene:methanol extract was transferred to a 500 ml separatory funnel and the flask rinsed with 10 ml tap water and 10 ml n-pentane. Fresh benzene and boiling chips were then added to the flask and the sample refluxed for an additional 24-36 hours. The extraction was considered terminated when the extracting liquid became clear and colorless.

The solution was transferred from the flask to the separatory funnel and the flask was washed with 25 ml tap water and 25 ml n-pentane. The organic phase in the separatory funnel was washed with 25 ml tap water at least three times.

Several samples were extracted a second time by fresh benzene (210 ml); recoveries up to 5% additional hydrocarbons resulted. Because of the increase in time, exposure and background contamination the second extraction was not performed routinely.

The benzene: methanol extract was concentrated on a rotary evaporator (Calab Co; Berkeley, Calif.) connected to an oil vacuum pump (Precision Scientific Co; Chicago, Ill.). The aqueous phase was washed a second time with 25 ml fresh n-pentane and the two organic phases combined. The solvent was evaporated in a round bottom flask (100 ml) at room

temperature to near dryness and the concentrate transferred in a minimum amount of n-pentane (3-5 ml) to a clean, weighed vial sealed with a Teflon-lined screw cap. The solvent was evaporated at room temperature under a stream of filtered nitrogen; the final evaporation was carried out on the rotary evaporator. When necessary the concentrate was stored in the dark in a refrigerator.

Solvent blanks were run during each extraction; the same volumes and apparatus were used and each step in the extraction was duplicated. Solutions were transferred in acetone- and pentane-rinsed disposable glass pipettes.

The residue from the extraction chamber or the thimble was air-dried at room temperature to constant weight. This residue weight (called the "extracted dry residue weight") was added to the total organic extract weight to obtain the "Dry Extracted Weight" (Tables and figures). The water-soluble portions of the extract were not considered.

Column Chromatography

The saturated hydrocarbons were isolated by silica gel chromatography of the organic extract. Silica gel (Davison Grade 922, 200 mesh; the Davison Chemical Co; Baltimore, Md.), activated at 220°C and then partially deactivated by adding 5% (vol/vol) tap water, was dry packed by vibration into a 30 mm O.D. chromatography column with a Teflon stopcock. The tip of the column was plugged with a small benzene-extracted glass wool plug and about 0.01 ml microbeads.

For extracts smaller than one gram 100 ml of silica gel was used. Normal pentane (400 ml) was forced into the column under pressure and the liquid level was adjusted to the top of the adsorbent. Pentane (50 ml) was run through the column and collected as a background check. The liquid was again adjusted to the adsorbent level. The organic extract was dissolved in a minimum amount of pentane (4-6 ml), transferred with a disposable glass pipette to the top of the adsorbent and forced into the column. Vial and pipette were washed several times and each addition was forced into the column. For extracts between one and two grams the amounts of silica gel and solvents were doubled.

Five fractions of 50 ml pentane were collected in 100 ml round bottom flasks; the solvent was then evaporated to near dryness on the rotary evaporator and the concentrate was transferred in pentane to a weighed vial with a disposable pipette. The solvent was evaporated to dryness under a stream of filtered nitrogen.

In several instances polar compounds including pigments were eluted from the column together with the saturated hydrocarbons. In these cases 75 ml silica gel packed beneath 25 ml alumina (activated at 220°C, Al-0102-P, Harshaw Chemical Co., Cleveland, Ohio) was used for the final separation.

Sulfur Removal

The sediment sample contained free sulfur which interfered with the gas chromatography. After chromatography of the organic extract on silica gel the sulfur was removed by percolation through a column of active copper powder according to the method of Blumer¹⁵.

Gas Chromatography

The gas chromatographic apparatus employed consisted of a Model 600 Hi-Fi Aerograph equipped with a hydrogen flame ionization detector and a Model 325 linear temperature programmer (Wilkins Instrument and Research, Inc., Walnut Creek, Calif.). The signal was fed through a Model 50 automatic attenuator (F & M Scientific Corp; Avondale, Pa.) to a 1 mv full scale recorder (Leeds & Northrup Co; Philadelphia, Pa.) with a chart speed of 30 inches per hour.

The columns were 1.8 meter by 0.3 cm O.D. stainless steel. The solid support was 80/100 mesh Chromosorb G, acid washed, dichlorodimethylsilane treated (Johns Mansville; New York). The nonpolar stationary phase was 1.5% Dow Corning RTV 502 silicone rubber (weight based on silicone rubber after removal of filler by centrifugation in benzene) coated from a chloroform solution. The columns were conditioned according to the method of Wotiz and Chattoraj²⁶⁹. Plate efficiencies varied from 600 to 1200 plates per meter measured at 200°C with n-tetracosane (retention time ca. 40 minutes); when the number of theoretical

plates dropped below 600 per meter the columns were discarded. The polar phase was 3.5% Carbowax 20M coated from a chloroform solution.

The chromatograph was operated at an input impedance of 10^9 , output sensitivity IX, attenuation 1 and the injection temperature 200°C. The gas flow for nitrogen was 21-24 ml per minute and 17 ml per minute for the hydrogen. Samples were injected in carbon disulfide onto a cooled column (60°C) with a microsyringe (Hamilton 100 ul Gas-Tight syringe) and programmed from 100° to 320° at 3°C per minute. Occasional cleaning of the column by injections of 0.025 ml water at 250°C prolonged its useful life.

The silica gel chromatographic fractions were dissolved in 0.100 ml, 0.250 ml, 0.500 ml or 1.000 ml of CS₂ depending on the weight of sample in the vial. Chromatograms of all samples were repeated with the addition of reference solutions in order to permit the calculation of retention indices of the eluted peaks according to the method of Kovats and Keulemans²⁷¹. The quantities of individual normal paraffins determined from peak areas (peak height times the width at half height) were added for all five silica gel fractions. The sum of the blank corrections (solvent plus thimble, where applicable) was subtracted from the sum of the individual silica gel normal paraffin quantities to get the content at each carbon number. The blank correction for each normal paraffin was normally 0-10% of the paraffin weight (10^{-6} g level), although occasionally it would be as high as 30% for samples with low hydrocarbon content.

C. RESULTS

1 Data

Table 3 summarizes the following analytical data: weight of organic extract, hydrocarbon content, major normal paraffin and antimony content relative to the combined weights of the extraction residue and the organic extract. The antimony data on some of the same species were furnished by H. Smith²⁷⁴. Table 4 lists the analytical data of a recent sediment and a sample of mixed marine plankton. The sulfur value was obtained by weighing the free sulfur collected from the five gel chromatography fractions. The actual value in the sediment might be larger.

The gas chromatographic analyses, tabulated in terms of individual normal paraffins from C₁₄ to C₃₂, are given in Appendix 1 and Figures 1-7. The carbon preference index (CPI: see footnote of Table 5) over the range n-C₂₀ to n-C₃₂, the retention index of the presumed pristane peak and the ratio of its area to the area of the n-C₁₇ peak are given in Table 5.

11 Discussion

The red algae have large concentrations of n-C₁₅ and n-C₁₇ with a minimum near n-C₂₁ and the general increase in normal paraffin content to a secondary maximum in the n-C₂₇ to n-C₃₁ region. See Figures 1 and 2. In addition to the extreme odd predominance at n-C₁₅ and n-C₁₇, a definite odd predominance can be seen in the n-C₂₀ to n-C₃₂ region for Corallina (CPI = 1.3) and Polysiphonia (CPI = 1.2) while Rhodymenia had less of an odd predominance (CPI = 1.1) and Chondus exhibited an even carbon predominance (CPI = 0.9 for the New Hampshire sample and 0.4 for the Falmouth sample). The two Chondus samples, though collected at the same period represent different growth stages; the New Hampshire sample was somewhat weather-beaten from winter storms while the Falmouth sample had started to vegetate with the warming of the water. This fact might account for some of the difference between the organic extract and the hydrocarbons content; the New Hampshire

TABLE 3

ALGAE ANALYSES

(in ppm Dry Extracted Weight)¹

	Organic Extract	Hydrocarbon Content	Major Component	Antimony Content ²
CHLOROPHYCEAE				
<u>Chaetomorpha linum</u> (N. Hamp.)	28,000	12.7	C ₁₇ 35.5%	-
RHODOPHYCEAE				
<u>Corallina officinalis</u> (N. Hamp.)	-	-	C ₁₇ 76.3%	-
<u>Polysiphonia sp.</u> (N. Hamp.)	5,600	54.9	C ₁₇ 86.1%	0.01
<u>Rhodymenia palmata</u> (N. Hamp.)	6,700	93.8	C ₁₇ 79.0%	0.06
<u>Chondus crispus</u> (N. Hamp.)	14,500	28.2	C ₁₇ 57.7%	-
<u>Chondus crispus</u>	8,400	54.4	C ₁₇ 95.2%	-
PHAEOPHYCEAE				
Fucales:				
<u>Ascophyllum nodosum</u> (N. Hamp.)	40,500	57.1	C ₁₅ 98.4%	0.16
<u>Fucus sp.</u> (N. Hamp.)	41,000	28.3	C ₁₅ 94.7%	0.15
<u>Fucus sp.</u> (Falmouth)	69,700	110.3	C ₁₅ 96.9%	-
<u>Fucus sp.</u> (Woods Hole)	75,000	122.5	C ₁₅ 97.9%	-
<u>Sargassum sp.</u> (Sargasso Sea)	15,000	8.4	C ₁₅ 54.9%	-
Laminariales:				
<u>Agarum cribrosum</u> (N. Hamp.)	29,000	10.1	C ₁₅ 28.3%	0.08
<u>Laminaria digitata</u> (N. Hamp.)	49,000	13.2	C ₁₅ 77.1%	0.07

	Organic Extract	Hydrocarbon Content	Major Component	Antimony Content ²
PLANKTONIC ALGAE				
Chrysophyceae				
<u>Syracosphaera carterae</u>	120,000	33.9	C ₁₇ 45.5%	-
Cryptophyceae				
Undetermined cryptomonad	305,000	33.5	C ₂₉ 11.3%	-
Bacillariophyceae				
<u>Skeletonema costatum</u>	480,000	120.7	C ₂₉ 10.5%	-

¹Dry Extract Weight was the sum of the extracted dry residue weight plus the organic extract weight.

²Unpublished results, Harvey Smith, Master's Thesis, Clark Univ., 1966.

TABLE 4

SEDIMENT AND PLANKTON ANALYSES

(In ppm Dry Extracted Weight)

	Organic Extract	Hydrocarbon Content	Major Paraffin	CaCO ₃	Sulfur
Recent Sediment (Tarpaulin Cove)	2,800 ppm	1.68 ppm	n-C ₁₇ 14 % n-C ₂₅ 14 %	3.18 %	250 ppm
Mixed Marine Plankton (Tarpaulin Cove)	150,000 ppm	102.0 ppm	Pristane 21 % n-C ₁₇ 9 %	-	-

TABLE 5

CARBON PREFERENCE INDEX¹ (n-C₂₀ to n-C₃₂)
AND PRISTANE/n-HEPTADECANE RATIO

	CPI	Retention Index	Pristane/n-C ₁₇ Ratio
CHLOROPHYCEAE			
<u>Chaetomorpha linum</u>	1.0	1669	1/130
RHODOPHYCEAE			
<u>Corallina officinalis</u>	1.3	1671	1/1300
<u>Polysiphonia sp.</u>	1.2	1669	1/4500
<u>Rhodomenia palmata</u>	1.1	1664	1/1000
<u>Condus crispus</u> (N. Hamp.)	0.9	1666	1/2000
<u>Chondus crispus</u> (Falmouth)	0.4	1664	1/3300
PHAEOPHYCEAE			
Fucales:			
<u>Sargassum sp.</u>	1.5	1674	1/285
<u>Ascophyllum nodosum</u>	1.4	-	<1/5000
<u>Fucus sp.</u> (Woods Hole)	1.1	1670	1/34
<u>Fucus sp.</u> (Falmouth)	1.0	-	<1/10,000
<u>Fucus sp.</u> (N. Hamp.)	0.8	1673	<1/5000
Laminariales:			
<u>Agarum cribrosum</u>	1.0	1667	1/20
<u>Laminaria digitata</u>	0.7	1671	1/14
PLANKTONIC ALGAE			
<u>Skeletonema costatum</u>	1.2	1672	1/1.6
<u>Syracosphaera carterae</u>	1.1	1672	1/2.2
Cryptophyceae	1.1	1671	1/5
MIXED MARINE PLANKTON	1.2	1668	1/1.4
RECENT SEDIMENT (Tarpaulin Cove)	4.0	1770	1/3.5
RECENT SEDIMENT (Santa Barbara Basin ²⁶⁸)	2.4	-	-

¹According to Cooper and Bray²²⁰ the Carbon Preference Index is calculated over the range n-C₂₀ to n-C₃₂:

$$\text{CPI} = \left[\frac{\sum_{n=21}^{n=31} \text{HC}_{\text{odd}}}{\sum_{n=22}^{n=32} \text{HC}_{\text{even}}} + \frac{\sum_{n=21}^{n=31} \text{HC}_{\text{odd}}}{\sum_{n=20}^{n=30} \text{HC}_{\text{even}}} \right] \times \frac{1}{2}$$

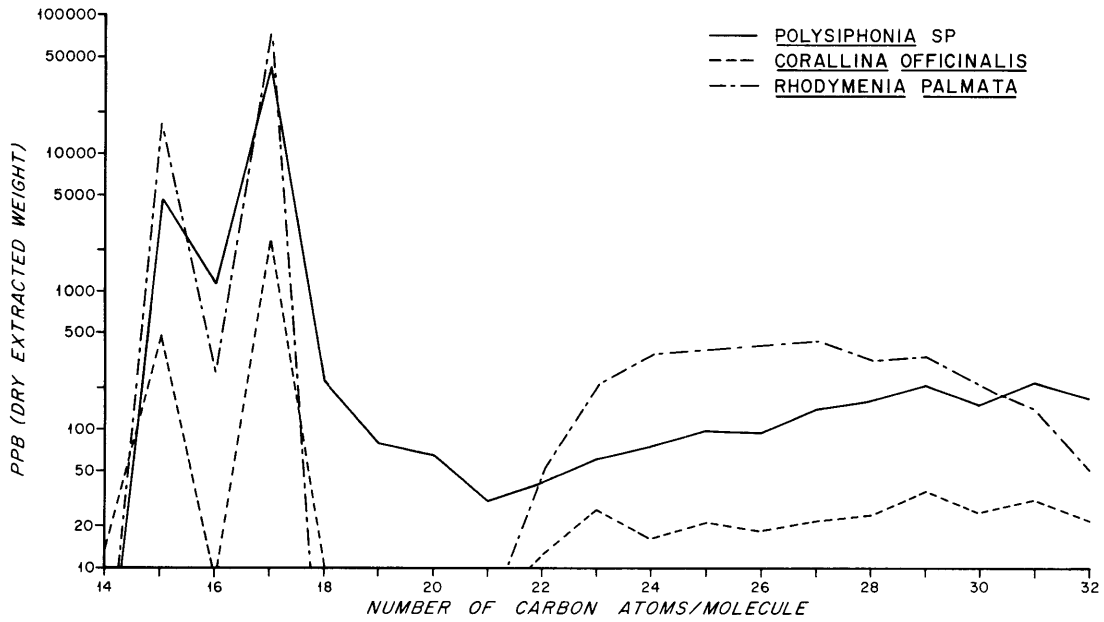


FIGURE 1 NORMAL ALKANE CONTENT OF RED ALGAE

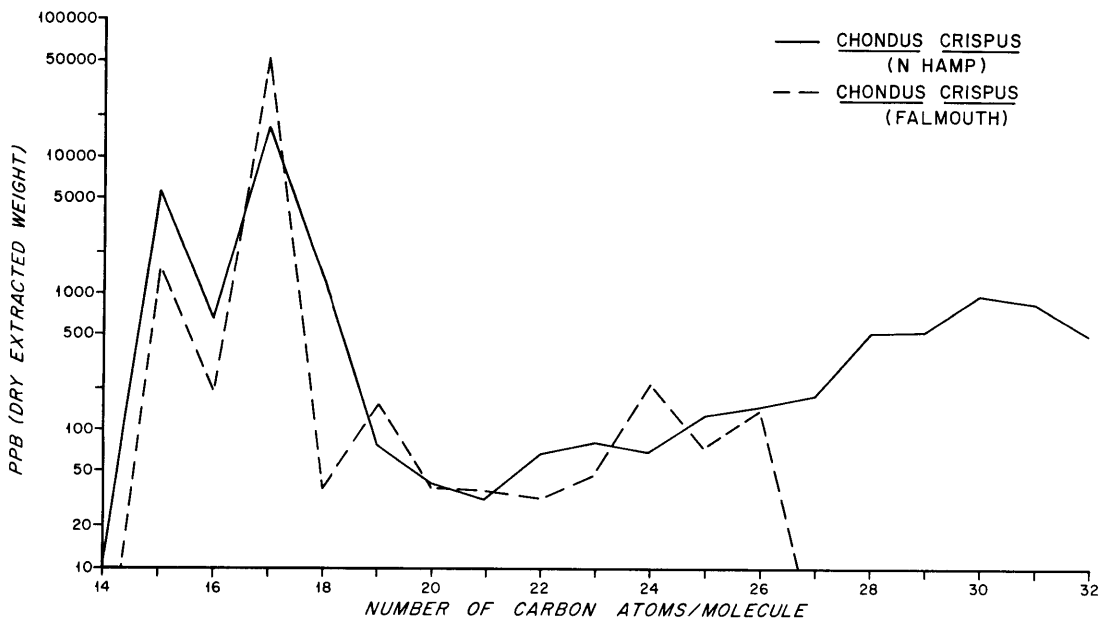


FIGURE 2 NORMAL ALKANE CONTENT OF RED ALGAE (CHONDUS)

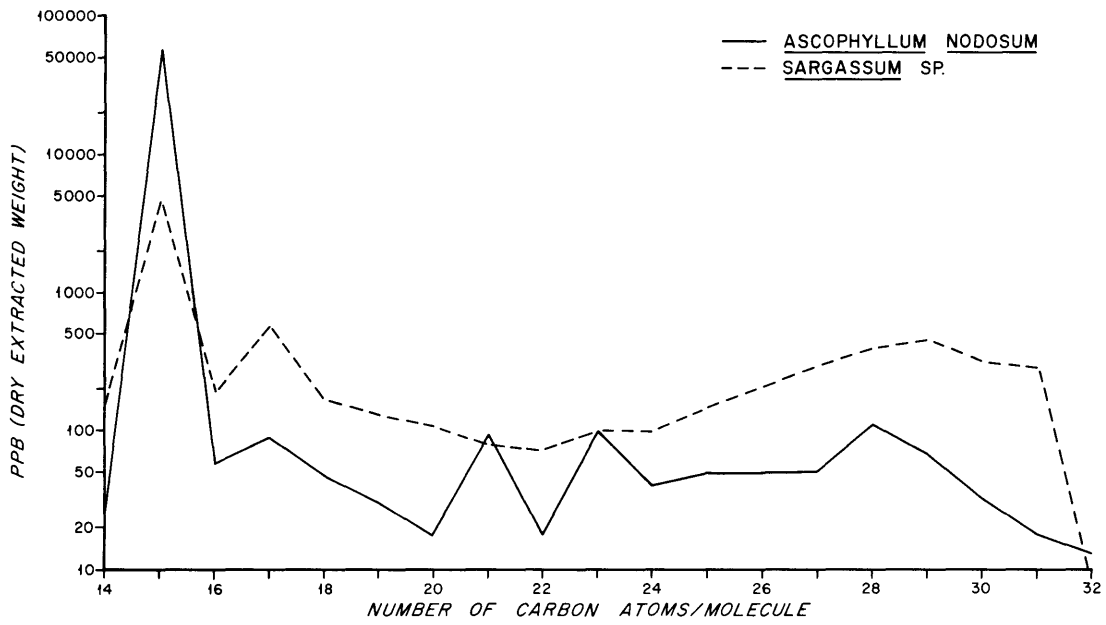


FIGURE 3 NORMAL ALKANE CONTENT OF BROWN ALGAE

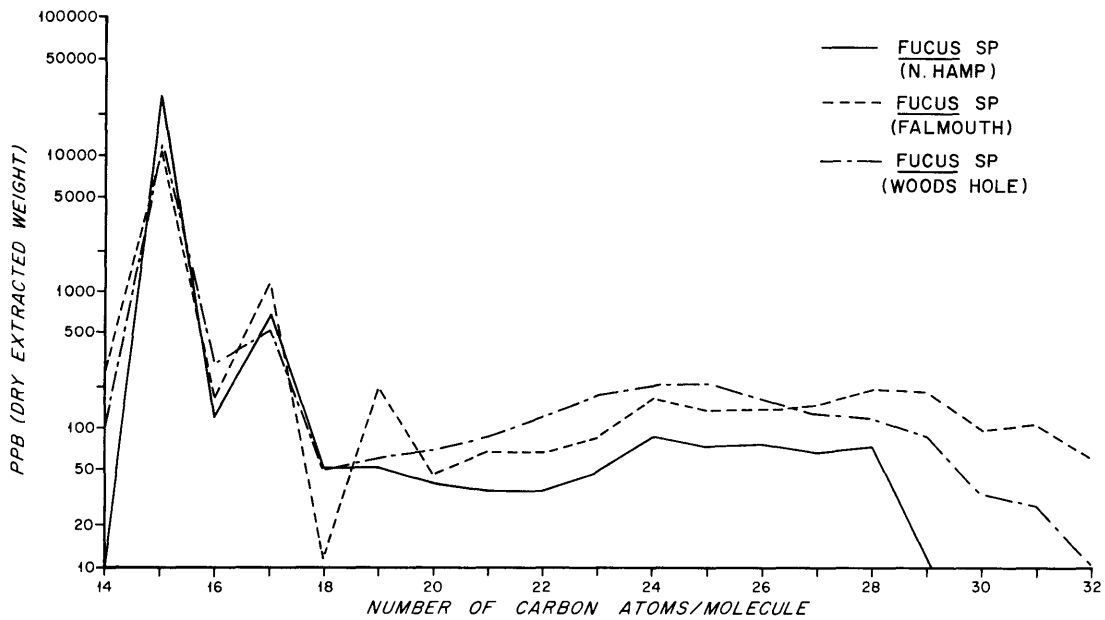


FIGURE 4 NORMAL ALKANE CONTENT OF BROWN ALGAE (FUCUS)

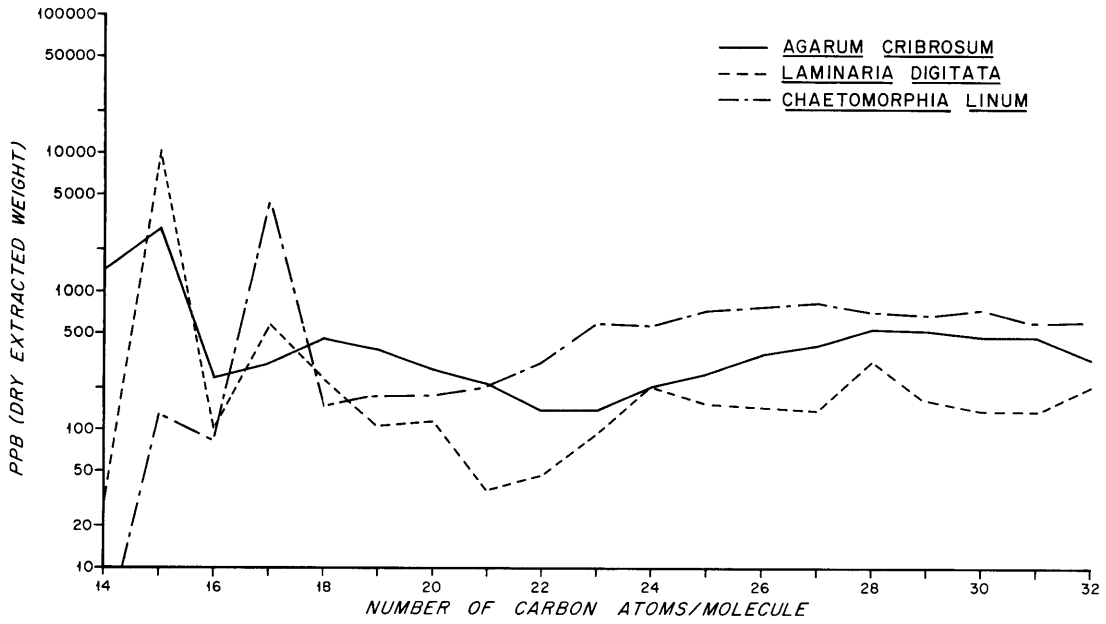


FIGURE 5 NORMAL ALKANE CONTENT OF BROWN AND GREEN ALGAE

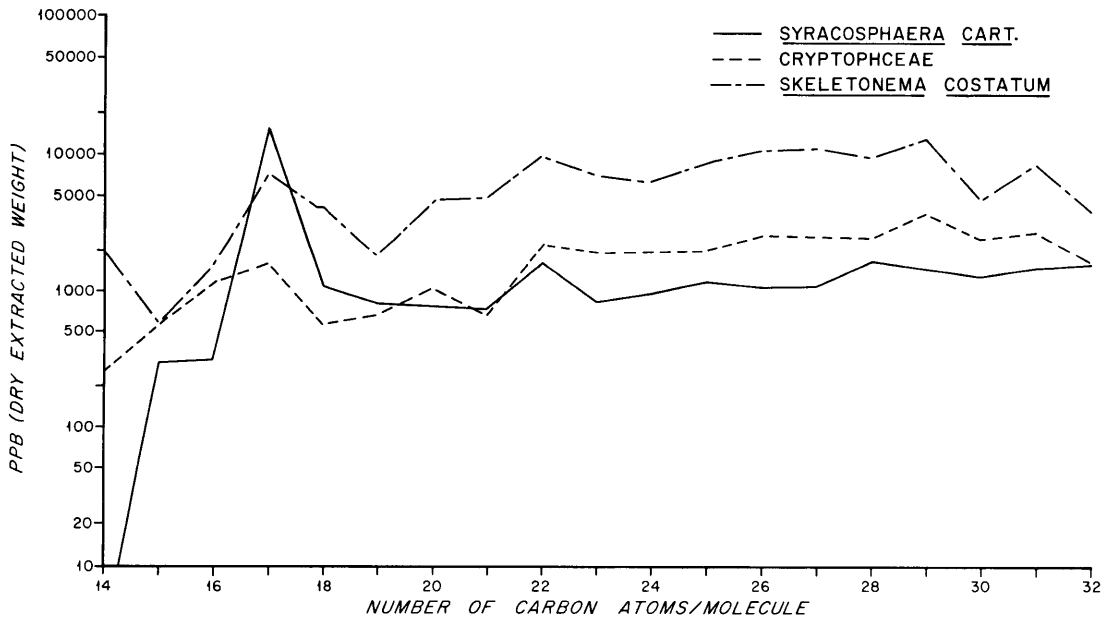


FIGURE 6 NORMAL ALKANE CONTENT OF PLANKTONIC ALGAE

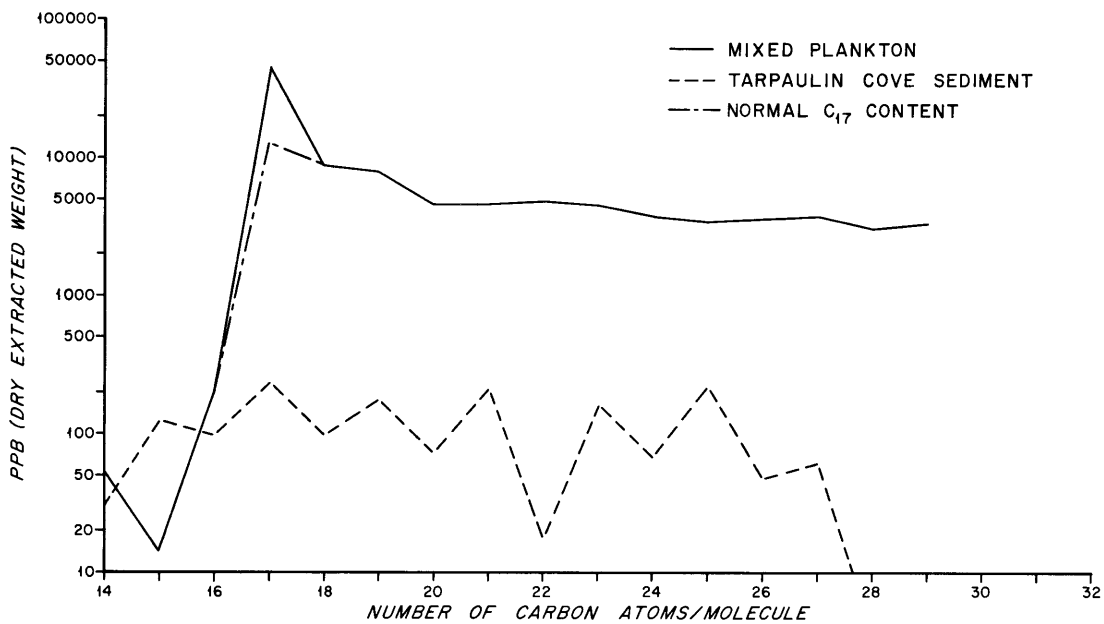


FIGURE 7 NORMAL ALKANE CONTENT OF SEDIMENT AND PLANKTON

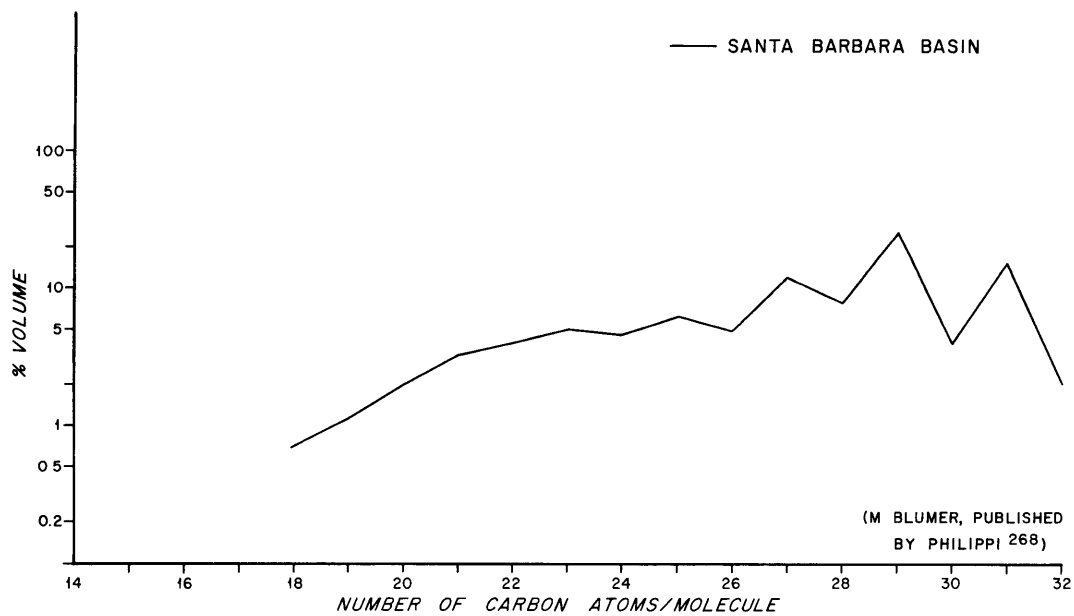


FIGURE 8 NORMAL ALKANE CONTENT OF A RECENT SEDIMENT

sample had a greater organic extract with a smaller hydrocarbon content (57.7% of the normal paraffins was C₁₇) compared to the Falmouth sample (95.2% of the paraffins was n-C₁₇).

Normal pentadecane was the predominant compound in the Fucales family of brown algae (Figures 3 and 4). Fucus and Ascophyllum have more than 94% of the normal paraffins as n-C₁₅ with the n-C₁₇ the next most important paraffin. Sargassum, however, had a lower content of n-C₁₅ compared to the other normal paraffins but its CPI was the largest of the family (CPI = 1.5). Ascophyllum had an odd carbon predominance (CPI = 1.4) but the Fucus sample did not have significantly odd predominance; the New Hampshire sample even showed a slight even carbon predominance. The minimum in the n-C₁₈ to n-C₂₁ region was present with a moderate maximum near n-C₂₅ to n-C₂₈.

Another family of brown algae, the Laminariales resemble the Fucales though the n-C₁₅ predominance is less (Figure 5). The minimum is at a higher carbon number than the Fucales' being near n-C₂₁ and the secondary maximum is shifted to n-C₂₈. The Agarum showed no odd carbon predominance in the n-C₂₀ to n-C₃₂ region (CPI = 1.0) while the Laminaria had a slight even predominance (CPI = 0.7).

The one green seaweed of the study, Chaetomorpha, had n-heptadecane as its major normal component (35% of the paraffins) and a minimum at n-C₁₈ (Figure 5). A carbon preference index of unity indicated no predominance and the secondary maximum appeared at n-C₂₇.

The planktonic algae from laboratory cultures (Figure 6) displayed a normal paraffin distribution different from the benthic seaweeds. While each phytoplankton had a slight predominance of n-C₁₇ over the adjacent homologs, the n-heptadecane was the major normal paraffin in *Syracosphaera* (45%) only. A slight odd predominance existed for all three and they had a trend toward a maximum near n-C₂₉.

The mixed plankton (Figure 7) had pristane and $n\text{-C}_{17}$ as the major components with a slight odd carbon predominance (CPI = 1.2) over the $n\text{-C}_{20}$ to $n\text{-C}_{32}$ region but no maximum above $n\text{-C}_{19}$.

The recent marine sediment exhibited the marked odd carbon predominance (CPI = 4.0) usually associated with recent sediments. Neither $n\text{-C}_{15}$ nor $n\text{-C}_{17}$ has much predominance over the other odd carbon homologs. For comparison the normal paraffin content of the Santa Barbara Basin was given in Figure 8 from the data of Blumer published by Philippi²⁶⁸. The odd carbon predominance (CPI = 2.4) was less pronounced than the Tarpaulin Cove sediment.

Pristane (2,6,10,14 - tetramethylpentadecane) has been reported to occur in some algae mats²⁷⁰. Since a silicone rubber column (1.5% RTV 502) does not significantly resolve $n\text{-heptadecane}$ from pristane, a polar column (3.5% Carbowax 20M) was used for this separation (retention index of pristane = 1671). The major paraffin fraction eluted from silica gel for each extraction was rechromatographed on the polar column. The area of the peak of approximate retention index of 1670 was measured and compared to that of $n\text{-C}_{17}$; however, the identity of this peak as pristane remains to be established. Thus, the pristane/ $n\text{-C}_{17}$ ratios of Table 5 represent maximum values.

No peak at the retention index of phytane (RI = 1786) was observed. It is estimated that phytane would have been detected if the ratio of phytane to $n\text{-C}_{18}$ had been larger than 1/1000.

D. CONCLUSIONS

The objectives of this work were threefold:

- 1) An analysis of the principal marine seaweeds for normal paraffins in the C₁₄ to C₃₂ range.
- 2) A search for an odd-carbon predominance or other distinguishing features in the hydrocarbon composition which might be reflected in sediments of recent or ancient age.
- 3) A search for differences in the hydrocarbon distribution pattern of different genera or species of algae.

1) In regard to the first goal it has been definitely established that the sixteen marine algae studied do contain normal saturated hydrocarbons. The planktonic algae contain much extractable material (12 to 48% of the Dry Extracted Weight) but the hydrocarbon content is only 34-120 ppm. The benthic algae on the other hand produce less organic extract (0.67 to 7.5% by weight) while the hydrocarbon content (10-120 ppm) is similar to that of the planktonic algae. The one pelagic seaweed analyzed, Sargassum, contains relatively little extractable material (1.5% by weight) as well as a low normal hydrocarbon content (8 ppm).

The range of paraffin concentration encountered in marine algae (8-120 ppm) is difficult to compare to land plants because of the great diversity of terrestrial plants and the limited number of analyses. Whole fresh apples contain 70 ppm normal paraffins¹²⁴ while dry shredded tobacco leaves have 1700 ppm normal paraffins¹³³ and in an Australian cane grass (Leptochloa digitata) up to 1% of the weight of the air-dried stems is normal paraffins¹⁰².

2) The analysis of a recent sediment from Tarpaulin Cove confirms the predominance of odd-carbon number paraffins in an area for which no earlier analyses are available. The odd-carbon predominance (CPI = 4.0) is well within the range (CPI = 2.4 to 5.5) found in other areas²²⁰. The source for the odd-carbon predominance in the sedimentary organic material has to be sought in organisms living in the water column, on the surface of the sediment or within the sediment.

The analyses of planktonic algae show only a minor odd-carbon predominance (1.1 to 1.2). A similar, insignificant odd-carbon predominance has also been found in mixed marine zooplankton (M. Blumer, unpublished data). The mixed marine plankton sample from Tarpaulin Cove had a slight odd-carbon predominance (1.2). Further, the odd-carbon predominance of a pelagic seaweed (1.5) and of benthic algae (0.4 to 1.4) is found to be minor.

Thus, the odd-carbon predominance of recent sediment does not appear to reflect the hydrocarbon composition of planktonic and benthic algae. Rather it resembles that found in many land plants, the extent of which can be seen from the following carbon preference indices: cane grass¹⁰² 4.2; maize²²⁰ 5.1; barley²²⁰ 7.2; sugar cane¹⁰¹ 7.3; oats²²⁰ 9.2; tree leaf (Aeonium virgineum)⁴⁷ 11; and Italian rye grass⁴⁷ 36. This suggests, that the source for the sediment paraffins should not be sought in marine planktonic or benthic algae; rather, it may lie within the sediment itself or in detrital terrestrial plant material.

The benthic algae contain high concentrations of n-pentadecane and n-heptadecane. Further, all algae analyzed have a definite minimum in their normal paraffin content between C₁₉ and C₂₁ and a secondary maximum near C₂₇ to C₃₀. These characteristic features are not encountered in the recent marine sediment. This is an additional indication that the benthic and planktonic algae are not likely to be the major sources for the sedimentary normal paraffins.

3) Different genera of algae had different hydrocarbon distribution patterns, especially in the C₁₅-C₁₇ molecular weight range. The benthic algae can be grouped into two categories: 1) In red and green algae the n-heptadecane predominates (36 to 95% of the paraffins); 2) in the brown algae the n-pentadecane predominates (to 98% of the normal paraffins). Of the planktonic algae only one species (Syracosphaera) shows a moderate n-C₁₇ predominance.

The red and brown algae analyzed here live in close physical association. Thus, the predominance of a single paraffin probably reflects a taxonomic difference rather than the concentration of an external hydrocarbon, e.g. from marine pollution. If confirmed in specimens from other areas, such a chemical difference between algae may have important taxonomic implications. It would be especially useful in a class like the red algae where complete agreement about the taxonomy has not yet been reached.

The possibility of external contamination cannot be ruled out in the case of two samples (Chondus and Fucus) collected at the same location in Falmouth. Here, n-C₁₉ has a four-fold predominance over that found in the same or different species at other locations.

The origin of the normal paraffins in benthic algae remains uncertain. It is not possible to rule out the idea that the algae concentrate paraffins from the sea water. On the other hand it has been suggested²²⁰ that paraffins are biochemical products of the decarboxylation of the saturated normal fatty acids. However, it is difficult to understand the high concentrations of normal pentadecane and heptadecane on this basis. Published analyses of benthic algae do not reflect a similar predominance of the normal hexadecanoic and octadecanoic acids²⁷⁵. A decarboxylation process of great molecular selectivity would be required to create the paraffin distribution observed in red and brown algae.

The presence of normal paraffins in the three species of planktonic algae grown under clean conditions supports the assumption that algae are capable of producing such compounds.

Isoprenoid hydrocarbons, especially phytadienes, pristane and related C₁₉ mono-, di- and triolefins are abundant in the marine environment^{276, 278, 279, 280}. Pristane occurs in recent sediments²¹⁶ and both pristane and phytane have been isolated from petroleum²⁷⁷ and from oil shales²²¹ as well as in Precambrian sediments^{245, 246}. It is believed that zooplankton convert ingested phytol to pristane and that this represents the principal source for the pristane found in other marine animals²⁷⁶.

The presence of pristane and phytane in marine algae has been reported by Oró and Nooner²⁷⁰. If confirmed, this finding may have important implications for the biogeochemistry of isoprenoids. The analyses reported here are in partial agreement with Oró and Nooner. Pristane appears to be present in the samples analyzed except for the red algae, the Ascophyllum, and the Fucus collected in the spring of 1966 (Falmouth and New Hampshire). Its identification is based solely on the appearance of a peak at the proper retention index on a Carbowax 20M gas chromatograph column; therefore, it must remain tentative. Relative to n-C₁₇, planktonic algae appear to contain one to two orders of magnitude more pristane than benthic algae (See Table 5.). Among the benthic algae the Laminariales appear to have the largest pristane content. With the exception of a Fucus sample (Woods Hole) the remaining benthic algae contain less than 1%, in most cases less than 0.1%, pristane relative to n-C₁₇.

In contrast to the results of Oró and Nooner, phytane was not identified in the algal specimens or in the marine sediment sample. It is estimated that phytane would have been detected at a level two orders of magnitude lower than that of pristane.

An independent study of antimony in identical seaweed samples shows definite similarities within members of a family but differences between families and classes

(Table 3, H. Smith). This again supports the potential usefulness of chemical analyses - inorganic and organic - for the taxonomy of marine organisms.

Questions raised by this investigation open up the following areas for further normal hydrocarbon research:

- 1) A search for possible sources, such as bacteria, of the odd-carbon predominance within the recent sediment.
- 2) Analyses of the filtered sea water medium used for the planktonic algae cultures to see how much hydrocarbon material is lost by the organisms.
- 3) Analyses of bulk marine planktonic algae collected in natural sea water.
- 4) Development of sampling and analytical techniques to the point of practical application to the analysis of natural sea water.
- 5) Analyses of major shoreline terrestrial plant sources which might contribute to the odd-carbon predominance found in recent sediments.
- 6) Continuation of the search for differences in the hydrocarbon distribution pattern of algal species for chemical taxonomy purposes.
- 7) Extension of chemical taxonomic techniques to higher marine organisms, such as zooplankton and fish.

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APPENDIX I

NORMAL ALKANE CONTENT IN SAMPLES

(In **ppb** Dry Extracted Weight)

RHODOPHYCEAE

(In ppb Dry Extracted Weight)

	<u>Corallina</u> <u>officinalis</u> (N.Hamp.)	<u>Chondus</u> <u>crispus</u> (N.Hamp.)	<u>Chondus</u> <u>crispus</u> (Falmouth)	<u>Polysiphonia</u> <u>sp.</u> (N.Hamp.)	<u>Rhodomenia</u> <u>palmata</u> (N.Hamp.)
Organic Extract	-	14,000 ppm	8,400 ppm	5,600 ppm	6,700 ppm
Total Hydrocarbons	-	28.2 ppm	54.4 ppm	54.9 ppm	93.8 ppm
Dry Extracted Wt.	0.0999	10.43 g	39.09 g	14.04 g	3.65 g
<u>Normal Hydrocarbons</u>					
14	14 ppm ¹	12 ppb	1 ppb	0	2 ppb
15	456	5,720	1,610	4,700	16,500
16	8	670	190	1,100	250
17	2,460	16,300	51,800	47,000	74,100
18	11	1,330	38	220	<1
19	7	79	160	78	<1
20	8	42	38	65	<1
21	7	32	37	30	<1
22	12	68	32	41	60
23	26	83	48	61	210
24	16	70	220	75	350
25	21	130	76	97	380
26	18	150	140	93	410
27	21	180	19	140	440
28	24	520	7	160	320
29	36	530	1	210	340
30	25	970	1	150	210
31	31	850	1	220	140
32	22	500	2	170	51

¹As ppm total organic extract since the sample was not quantitative on a dry weight basis.

PHAEOPHYCEAE (Brown Algae)

(In ppb Dry Extracted Weight)

	<u>Ascophyllum</u> <u>nodosum</u> (N.Hamp.)	<u>Fucus</u> <u>sp.</u> (N.Hamp.)	<u>Fucus</u> <u>sp.</u> (Falmouth)	<u>Fucus</u> <u>sp.</u> (Woods Hole)	<u>Sargassum</u> <u>sp.</u>
Organic Extract	40,500 ppm	41,000 ppm	69,700 ppm	75,000 ppm	15,000 ppm
Total Hydrocarbon	57.1 ppm	28.3 ppm	110.4 ppm	122.5 ppm	8.4 ppm
Dry Extracted Wt.	39.81 g	36.99 g	20.85 g	34.29 g	14,90 g
<u>Normal Hydrocarbons</u>					
14	25 ppb	10 ppb	250 ppb	97 ppb	150 ppb
15	56,200	26,800	107,000	120,000	4,610
16	58	120	170	300	190
17	90	690	1,200	530	570
18	47	52	12	51	170
19	31	53	200	63	130
20	18	41	47	72	110
21	95	36	69	89	81
22	18	36	68	123	75
23	99	49	90	180	100
24	40	89	170	210	100
25	50	75	140	220	150
26	50	78	140	170	210
27	51	68	150	130	300
28	110	76	200	120	400
29	68	12	190	90	460
30	33	5	100	34	320
31	18	9	110	28	280
32	13	7	65	11	<1

PHAEOPHYCEAE (Brown Algae)

(in ppb Dry Extracted Weight)

	<u>Agarum</u> <u>cribrosum</u> (N.Hamp.)	<u>Laminaria</u> <u>digitata</u> (N.Hamp.)
Organic Extract	29,000 ppm	49,000 ppm
Total Hydrocarbons	10.1 ppm	13.2 ppm
Dry Extracted Wt.	19.24 g	14.07 g
<u>Normal Hydrocarbons</u>		
14	1,450 ppb	30 ppb
15	2,870	10,200
16	240	100
17	310	600
18	470	240
19	390	110
20	280	120
21	220	38
22	140	48
23	140	96
24	210	210
25	260	160
26	360	150
27	420	140
28	550	320
29	540	170
30	480	140
31	480	140
32	330	210

GREEN AND PLANKTONIC ALGAE

(In ppb Dry Extracted Weight)

	<u>Chaetomor-</u> <u>phia linum</u> (N. Hamp.)	<u>Syracosphaera</u> <u>carterae</u> (Culture)	Cryptophyceae (Culture)	<u>Skeletonema</u> <u>costatum</u> (Culture)
Organic Extract	28,000 ppm	120,000 ppm	305,000 ppm	480,000 ppm
Total Hydrocarbons	12.7 ppm	33.9 ppm	33.5 ppm	120.7 ppm
Dry Extracted Wt.	5.08 g	0.7446 g	0.4587 g	0.0417 g
<u>Normal Hydrocarbons</u>				
14	2 ppb	<1 ppb	260 ppb	2,000 ppb
15	130	300	570	600
16	87	320	1,160	1,600
17	4,500	15,400	1,660	7,400
18	150	1,100	590	4,200
19	180	820	680	1,900
20	180	780	1,090	4,700
21	210	750	680	5,000
22	310	1,650	2,240	9,730
23	600	850	1,990	7,070
24	580	980	1,990	6,430
25	740	1,200	2,060	8,750
26	800	1,090	2,640	10,600
27	840	1,110	2,640	11,200
28	720	1,700	2,550	9,660
29	680	1,490	3,790	12,700
30	760	1,280	2,460	4,710
31	600	1,480	2,790	8,470
32	610	1,500	1,660	4,000

SEDIMENT AND BULK PLANKTON

(In ppb Dry Extracted Weight)

	Tarpaulin Cove Sediment	Tarpaulin Cove Plankton
Organic Extract	2,800 ppm	150,000 ppm
Total Hydrocarbon	1.68 ppm	102.0 ppm
Calcium Carbonate	3.18 %	-
Sulfur	250 ppm	-
<u>Normal Hydrocarbons</u>		
14	31 ppb	56 ppb
15	130	15
16	100	210
17 + Pristane	240	45,000
18	100	8,750
19	180	8,000
20	76	4,660
21	220	4,660
22	18	4,390
23	170	4,660
24	71	3,780
25	230	3,420
26	49	3,650
27	63	3,800
28	<1	3,050
29	<1	3,350
30	<1	<1
31	<1	<1
32	-	<1

APPENDIX II

TABLES OF OCCURRENCES OF HYDROCARBONS IN NATURE

Per cent paraffin content compared to total normal paraffin reported:

x	Presence indicated
T	Trace
M	Major component
m	Maximum value of several
—	Estimated content from a graph

Normal Paraffins in Land Plants and Products

Occurrence	Normal Paraffins (%)									Ref.
	1	2	3	4	5	6	7	8	9	
Apples		x	x							123
<u>Araucaria cunninghamii</u>									x	57
Cigarette smoke	x	x	x	x	x	x				156
<u>Hypericum</u> sp.							x			118
Lime Oil								55		100
Lodgepole pine oleoresin							T			186
Petroleum nut							x			60
Pineweed (<u>Sarothra</u> sp.)									x	16
<u>Pinus ayacahuite</u>							x			126
" <u>jeffreyi</u>							x			178
" <u>montezumae</u>							x			72
" <u>monticola</u>							x			128
" <u>occidentalis</u>							x			131
" <u>reflexa</u>							x			127
" <u>sabiniana</u>							x			178
" <u>torreyana</u>							x			62
<u>Pittosporum eugenoides</u> , oil									x	27
<u>Populus siminii</u>	x	x	x	x						171
" <u>sosnowskyi</u>	x	x	x	x						171

Occurrence	Normal Paraffins (%)									Ref.	
	19	20	21	22	23	24	25	26	27		
<u>Acaena anserinifolia</u>								x	1	4	48
<u>Acaria farnesiana</u>		x									105
Apple Skin wax	0.1	0.1	0.2	0.2	0.7	0.4	5.6	0.9	30.2		124
" " "					T		T		0.5		120
<u>Astemisia annua</u>								x			143
" <u>maritima</u>		x									17
Banana leaf	x	x	x	x	x	x	x	x	x	x	140
Barley						3	7	3	16		220
Brussels sprout leaf		x									60
" " "									0.4		202
Cabbage leaf				x	x	x	x	x	x	x	161
Canary dragon tree wax					1	2	4	5	12		47
Carnauba wax (palm tree)										x	44
<u>Centaurium umbellatum</u>										x	157
<u>Ceropedia woodii</u>										x	168
<u>Chamaecyparis obtusa</u>	x	x									55
Chrysanthemum flowers							x				198
Cidar eucalyptus leaf										x	44
Cigarette smoke						0.1	0.6	0.4	6.3		26
" "				0.2	0.8	1.5	4.0	2.2	10		99
Clover, red	3.5	2.8	4.5	7.3	13.8	17.3	45				205
" , spotted bur	x	x	x	x	6	.5	x	.5	7		151
<u>Coryline australia</u>							21	2	42		48
<u>Euphorbia balsimifora</u>					2	1	4	1	51		47
Fern leaf oil										x	19
Fig leaf					x						54
<u>Gaultheria subcorymbosa</u>								4	3		48
<u>Gleditschia horrida</u>										x	48
Grass, Cocksfoot									1.3		202
" , <u>Leptochloa</u> , stem				0.6	0.8	2.2	2.0	4.9			102
" , Rye									6.5		202

Occurrence	Normal Paraffins (%)									Ref.
	19	20	21	22	23	24	25	26	27	
Grass, Italian rye					T	T	20	1	7	47
<u>Hebe odora</u>					x	1	2	2	10	48
" <u>stricta</u>							x	1	2	48
Hemp, <u>Cannabis indica</u>									x	29
Hop Cone wax	0.7	.09	0.3	0.3	1.4	0.6	3.1	0.6	0.8	209
Hsiang-p'u seed oil							x			177
Laural berry oil		x								44
Maize						<u>7</u>	<u>13</u>	<u>5</u>	<u>33</u>	220
<u>Manilkana bidentata</u>	19.3	18.7	12.3	11.6	4.7					38
Marigold flowers								2.1	0.5	191
Mint leaf					x					58
<u>Nothopanax simplex</u>					x		x		x	138
Oats						<u>2</u>	<u>18</u>	<u>2</u>	<u>22</u>	220
Ouricuri wax							x		x	173
" "						x				182
Parsley seed oil		x								44
Peanut oil	x	x	x	x	x	x	x	x	x	203
<u>Phormium tenax</u>						2	9	4	16	48
<u>Pimelea prostrata</u>							3	2	13	48
<u>Piper longum</u>	23.3	18.9	9.9							63
Pollen, Alder									x	149
" , Corn							x			149
" , Hazel					x					190
" , <u>Lilium candidum</u>									x	194
<u>Pseudowintera colorata</u>					x		x			41
Pyrethrum flowers						0.5	m.9	m.7	m31	204
Red-berry bryonia oil		x								51
Rose wax			6.5		16.5		17.5		23.1	30
" "		x								49
" "	x	x	x	x	x		x			77,78
" "	2.6	0.4	3.6	0.2	2.9	0.4	2.7	0.7	17.7	208

Occurrence	Normal Paraffins (%)									Ref.
	19	20	21	22	23	24	25	26	27	
Runner bean leaf									3.3	202
<u>Sempervivoideae</u> leaf							m2	m1	m8	47
<u>Sphaeranthus indica</u>							x			195
Skunk cabbage			T	T	2	0.5	34	3	53	67
String bean wax								1.9	3	204
Sugar cane cuticle wax	0.4	0.4	0.4	0.8	1.1	7.0	4.9	56		101
Swede-turnip								1.3		202
Tobacco, Argentine ferment.							0.3	4.4		26
" , Bright						2.9	1.4	8.0		133
" , Burley						1.9	0.9	8.3		133
" , Commercial blend						2.7	1.3	12.3		133
" , green leaf						0.5	0.3	7.5		26
" , Turkish						2.0	1.0	12.4		133
<u>Ulex europeaus</u>	x	x	x	x	x	x				39
Vegetable oils	x	x	x	x	x	M	x	x	x	23
White mustard leaf								0.7		202
Wisteria flowers								x		25
Wood, Douglas fir		x		x		x				37
" , tall oil				x	x	x	x	x		13
<u>Zanthoxylum alatum</u>					x					148

Occurrence	Normal Paraffins (%)									Ref.
	28	29	30	31	32	33	34	35	36	
<u>Chrysanthemum cincerari.</u>	x	x		x						56
" flowers	x									198
Cider eucalyptus leaf		x								44
<u>Citrullus colocynthis</u>				x						2
Cigar smoke				x						176
Cigarette smoke	1.1	7.4	3.8	43.4	13	22.8	1.1			26
" "	2.8	10	5.2	36	7.6	15	1.9	1.5	.08	99
Clover, crimson				x						164
" , spotted bur	<u>.7</u>	<u>23</u>	<u>7</u>	<u>38</u>	<u>3</u>	<u>8</u>	<u>.5</u>	x		151
Coffee oil		x								146
<u>Cordyline australia</u>	3	15	3	10						48
Corn (<u>Zea mays</u>) wax				x						44
Cotton plant	x			x		x				167
" "								x		159
Coniferae: <u>Chamaecyp.</u>		x						x		85
<u>Cycas revol.</u>		x								86
<u>Diplorterygium</u>		x						x		84
<u>Ginkgo biboba</u>		x								4
<u>Crotalaria medicagina</u>								x		121
Cryptostegia leaf		x		x		x				206
<u>Daemia extensa</u>				x						162
<u>Diplorrhynchus angol.</u>				x						170
Doveweed				x						142
<u>Euphorbia balsimifera</u>	1	24								47
" <u>hirta</u>				x						50
<u>Evodia micrococca</u>				x						22
<u>Evolvulus alsinoides</u>			x					x		122
Fig leaf	x									54
<u>Firmiana simplex</u>				x						95
<u>Fumaria officinalis</u>								x		3
" <u>parviflora</u>								x		201

Occurrence	Normal Paraffins (%)								Ref.	
	28	29	30	31	32	33	34	35		36
Fungi	x									207
<u>Gardenia jasminoides</u>		x								31
<u>Gaultheria subcorymbosa</u>	1	16	3	56	4	7				48
<u>Gleditschia horrida</u>		x								48
Grapefruit peel		x		x						115
Grape pomace		x		x						117
Grass, Cocksfoot	1.5	35.2	3.5	48.8		9.7				202
" , <u>Leptochloa</u> , stem	4.5	9.6	12	58.1	T	6.1				102
" , Rye	1.2	40.2	4.6	39.2		8.3				202
" , Italian rye	1	42	1	40		3				47
<u>Grindelia squarrosa</u>				x						103
<u>Hebe odora</u>	3	32	2	25	2	3				48
" <u>stricta</u>	2	10	4	24	1	37	1	16		48
<u>Helichrysum arenarium</u>				x						81
Hemp, <u>Cannabis indica</u>		x		x		x				29
Hop Cone wax	2.8	51.6	3.5	21.8	0.9	1.3				209
Horse chestnut seed			x							6
<u>Hypericum laxinsculum</u>	x									169
" <u>perforatum</u>	x		x							119
<u>Kopsia longiflora</u>				x						32
<u>Landolphia laurebtii</u>					x					168
<u>Lobelia sessilifolia</u>		x								173
<u>Luffa echinata</u>				x						91
Maize	<u>4</u>	<u>27</u>	<u>2</u>	<u>4</u>	<u>2</u>	<u>2</u>	<u>1</u>			220
Marigold flowers	16.4	3.0	33.8	3.2	29.9	3.9	7.3			191
<u>Matricaria chamomilla</u>			x							184
Mogusa wax				x						53
<u>Musa sapientum</u>		x								24
Nim blossoms		x								132
<u>Nothopanax simplex</u>		x		x						138
<u>Nyctanthes arboretris</u>				x						183

Occurrence	Normal Paraffins (%)								Ref.		
	10	11	12	13	14	15	16	17		18	
Algae, <u>Chlorella</u>							x			80	
" , <u>Scenedesmus</u>							x			79	
" , Blue-green, mat							x	M	x	270	
Ant volatile oil	x									175	
Bacteria, <u>Sarcina lutea</u>							1.8	2.3	0.9	5	
Bronze orange bug			2.5	97.5						154	
Coral, fossil					x	x	x	x	x	155	
" , living							x	x	x	155	
Cricket cuticle wax			x	x	x	x	x	x	x	9	
Herring oil					0.3	7.5	0.6	9.0	1.7	106	
Horned citrus bug			x	x						154	
Housefly, adult							1	1	1	109	
Human femoral tissue									x	59	
Mandibular gland, insect		x								60	
Rice stink bug				x						14	
Sanna oil						x				144	
Sardine oil								x		196	
Silkworm papa odor	x									172	
Wool wax				T	0.4	0.6	2.5	3.7	6.6	45	
" "				T	0.5	0.7	0.9	1.9	4.2	6.7	134

Occurrence	Normal Paraffins (%)									Ref.
	19	20	21	22	23	24	25	26	27	
Algae, <u>Chondus ocellatus</u>							x			135
" , <u>Enteromorpha</u>			x							5
" , Blue-green, mat	x	x	x	x	x	x	x	x	x	270
Bacteria, <u>Sarcina lutea</u>	1.0	1.5	1.9	1.8	3.7	9.9	9.9	12.6	11.7	9
Beeswax, <u>Apis mell.</u> (Rural)	x	x	0.8	0.3	3.7	0.6	7.5	1.2	30.1	46
" , " " (Subur.)	x	x	0.8	0.2	3.7	0.4	8.5	1.0	26.8	46
" , Yellow									x	44
Chrysalis oil, <u>Bombyx mori</u>				x		x		x		152
Coral, fossil	x	x	x	x	x	x	x	x	x	155
" , living	x	x	x			x	x	x	x	155
Cockroach, American							x			10
Cricket cuticle wax	x	x	x	x	x	x	x	x	x	9
Herring oil	10.5	0.3	6.0	0.3	0.8	0.3	9.5	T	33	106
Housefly, adult	1	1	2	2	16	2	21	2	26	109
Insect wax, Chinese									x	44
" " , Ghedda									x	44
" " , lac							x			44
Liver oil, pollack									x	197
Manure, cattle						<u>1</u>	<u>2</u>	<u>2</u>	<u>8</u>	151
Mollusk, <u>Nassa obsoleta</u>									x	92
Olive oil						x		x		44
Sperm, human									x	200
Sponge, <u>Terpios zeteki</u>						x	x	x	x	97
" , <u>Spheciospongia</u>									x	12
Urine, human pregnancy							x		x	65
Wool wax	9.6	14.0	10.6	7.5	5.5	5.0	4.8	5.8	5.2	45
" "	10	10	7.6	4.4	4.6	2.2	3.2	1.1	6.8	134

Occurrence	Normal Paraffins (%)									Ref.
	28	29	30	31	32	33	34	35	36	
Algae, <u>Cladophora sauteri</u>				x						66
" , <u>Fucus vesiculosus</u>				x						66
" , <u>Laminaria digitata</u>				x						66
" , <u>Nitella opaca</u>				x						66
" , <u>Oedogonium</u>				x						66
" , <u>Pelvetia canalicu.</u>				x						66
" , <u>Rhodomenia palmata</u>				x						66
" , Blue-green, mat	x	x	x	x	x					270
Bacteria, <u>Sarcina lutea</u>	16.2	8.5	5.7	4.2	3.2	2.1	0.9	0.7	0.3	9
Butter fat					x					136
Beeswax, <u>Apis mell.</u> (Rural)	1.3	16.5	0.9	19.0	1.5	15.5				46
" , " " (Subur.)	2.2	19.3	1.6	20.8	0.9	13.8				46
" , Stingless bee				x						44
" , Yellow				x						44
Chrysalis oil, <u>Bombyx mori</u>	x									152
" " , Silkworm	x									64
Coral, fossil	x	x	x	x	x	x	x	x	x	155
" , living	x	x	x							155
Cricket cuticle wax	x	x	x	x	x					9
Gorgonians									x	36
Herring oil	T	9	T	7	T	1				106
Housefly, adult	4	7	4	4	1	2	1	1		109
Insect wax, Coccidae				x						193
" " , Ghedda		x		x		x				44
" " , lac				x						44
Manure, cattle	<u>4</u>	<u>18</u>	<u>5</u>	<u>27</u>	<u>5</u>	<u>22</u>	<u>2</u>	<u>4</u>		151
Sponge, <u>Terpios zeteki</u>	x	x	x	x	x	x	x			97
Wool wax	4.9	4.9	2.7	3.0	0.5	0.7				45
" "	2.8	15.8	T	10.0	T	5.7	T	T		134

Normal Paraffins in the Geologic and Atmospheric Environment

Occurrence	Normal Paraffins (%)									Ref.
	1	2	3	4	5	6	7	8	9	
Boraciferous soffioni	x									254
Coal, Japan									.08	248
" , gas, Germany	x	x	x	x		x				232
Earth's atmosphere	x									231
Freshwater carbonate conc.	x	10.4	19.3	29.7	19.3	16.9	4.4		x	223
Marine sediment, G.Mex.	x	x	x	x	x	x				258
" " , Calif.		x	x	x	x					227
" " , USSR	m78	m.07	m.03	m.02	m.09					264
Mineral springs	x									253
Natural gas (dry), Okla.	85	9	4	2						252
" " (wet), "	45	25	17	5	4					252
Peat					x	x				218
Petroleum, Ponca City	x	x	x	x	x	8.8	11.3	9.3	8.8	266
" , Magallens	m91	m10	m6	x	x	x				211
Shale, tar							x	x	x	226
Soil, Germany		x	x	x	x					250
Volcanic glass	x									217
Volcanic mud			x	x	x					222

Occurrence	Normal Paraffins (%)									Ref.
	10	11	12	13	14	15	16	17	18	
Air-bourne particles						x	x	x	x	241
Coal, Japan	.07	0.3	0.7	1.3	2.5	4.7	5.7	5.8	6.5	248
" , tar							x	x	x	239
Devonian sediment, Top								<u>1</u>	<u>2</u>	265
" " , Bottom								<u>1</u>	<u>2</u>	265
Dust									x	240
Marine sediment, Calif.					<u>1</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>1</u>	237
Meteorites							x	x	x	244
"						x	x	x	x	247
Miocene sediment					x	x	x	x	x	255
Nonesuch calcite vein		x	x	x	x	x	x	x	x	225
Oil seep, Nonesuch				x	x	x	x	x	x	225
Petroleum, Ponca City	8.8	7.8	6.9	5.9	4.9	3.9	2.9	3.4	2.5	266
Precambrian, Gunflint							x	x	M	246
" , Soudan						x	x	M	x	245
" , S. Africa							x	x	x	234
Shale, Eocene, Non-marine								5	8	267
" , Green River					x	x	x	M	x	225
" , " " (Top)				0.1	0.8	2.8	3.9	15.1	6.3	251
" , " " (Bottom)		0.2	1.0	2.2	2.9	4.9	4.0	17.2	5.8	251
" , Mowry				x	<u>.3</u>	<u>1</u>	<u>1</u>	<u>3</u>	<u>3</u>	237
" , Thermopolis				<u>.1</u>	<u>1</u>	<u>3</u>	<u>4</u>	<u>7</u>	<u>6</u>	237
" , bitumin				x	x	x	x	x	x	221
Soil, Australian "green"					x	x	x	x	x	261

Occurrence	Normal Paraffins (%)									Ref.
	19	20	21	22	23	24	25	26	27	
Air-bourne particles	x	x	x	x	x	x	x	x	x	241
Coal, Japan	7.0	11.8	9.1	6.5	7.2	6.6	6.6	5.3	4.3	248
" , tar	x	x								239
Devonian sediment, Top	<u>4</u>	<u>7</u>	<u>9</u>	<u>12</u>	<u>14</u>	<u>13</u>	<u>12</u>	<u>10</u>	<u>7</u>	265
" " , Middle	<u>2</u>	<u>3</u>	<u>5</u>	<u>6</u>	<u>9</u>	<u>12</u>	<u>14</u>	<u>11</u>	<u>12</u>	265
Dust	x	x	x	x	x	x	x	x	x	240
Marine mud, G. Mexico				<u>3</u>	<u>6</u>	<u>5</u>	<u>8</u>	<u>5</u>	<u>14</u>	260
Marine sediment, Calif.	<u>2</u>	<u>1</u>	<u>2</u>	<u>2</u>	<u>4</u>	<u>2</u>	<u>5</u>	<u>2</u>	<u>11</u>	237
Meteorites	x	x	x	x	x	x	x	x	x	244
"	x	x	x	x	x	x	x	x	x	247
Miocene sediment	x	x	x	x	x	x	x	x	x	255
Nonesuch calcite vein	M	x	M	x	x	x	x	x	x	225
Oil seep, Nonesuch	x	x	x	x	x	x	x	x	x	225
Petroleum, Lacq(France)				x		x				229
" , Ponca City	2.1	1.8	1.6	1.4	1.2	1.1	1.0	0.9	0.9	266
Precambrian, Gunflint	x	x	x	M	x	x	x	x	x	246
" , Soudan	x	x	x	x	x	x	x	x	x	245
" , S. Africa	x	x	x	x	x	x	x	x	x	234
Shale, Chattanooga						<u>22</u>	<u>19</u>	<u>16</u>	<u>12</u>	212
" , Cretaceous						<u>14</u>	<u>13</u>	<u>11</u>	<u>12</u>	214
" , Eocene, Non-marine	<u>4</u>	<u>5</u>	<u>5</u>	<u>4</u>	<u>14</u>	<u>4</u>	<u>20</u>	<u>7</u>	<u>17</u>	267
" , Green River	x	x	x	x	x	x	x	x	x	225
" , " " Top	4.7	5.9	4.8	8.7	5.6	4.9	6.1	5.1	7.5	251
" , " " Bottom	4.6	5.0	4.6	6.2	5.4	5.1	5.6	5.1	5.9	251
" , Mowry	<u>4</u>	<u>4</u>	<u>6</u>	<u>6</u>	<u>7</u>	<u>6</u>	<u>9</u>	<u>5</u>	<u>12</u>	237
" , Thermopolis	<u>7</u>	<u>7</u>	<u>8</u>	<u>6</u>	<u>7</u>	<u>5</u>	<u>6</u>	<u>4</u>	<u>7</u>	237
" , Woodford				x	x	x	x	x	x	260
" , bitumin	x	x	x	x	x	x	x	x	x	221
Soil, Australian "green"	x	x	x	x	x	x	x	x		261
" , Continental				<u>4</u>	<u>6</u>	<u>5</u>	<u>11</u>	<u>6</u>	<u>11</u>	260

Occurrence	Normal Paraffins (%)						34	35	36	Ref.
	28	29	30	31	32	33				
Air-bourne particles	x									241
Coal, Japan	3.2	2.8	1.3	0.1						248
Devonian sediment, Top	<u>5</u>	<u>3</u>	<u>.1</u>							265
" " , Middle	<u>8</u>	<u>7</u>	<u>4</u>	<u>3</u>	<u>1</u>					265
Dust	x	x	x							240
Marine mud, G. Mexico	<u>6</u>	<u>25</u>	<u>5</u>	<u>21</u>	<u>2</u>					260
Marine sediment, Calif.	<u>3</u>	<u>25</u>	<u>3</u>	<u>15</u>	<u>1</u>	<u>8</u>	<u>1</u>	<u>2</u>		237
Meteorites	x									244
"	x	x	x							247
Miocene sediment	x	x	x	x	x	x				255
Nonesuch calcite vein	x	x	x	x	x	x	x	x		225
Oil Seep, Nonesuch	x	x	x	x	x					225
Petroleum, Ponca City	0.6	0.6	0.6	0.5	0.5					266
Precambrian, Gunflint	x	x	x	x	x					246
" , S. Africa	x	x	x							234
Shale, Chattanooga	<u>10</u>	<u>8</u>	<u>5</u>	<u>3</u>	<u>3</u>	<u>2</u>	<u>2</u>			212
" , Cretaceous	<u>9</u>	<u>11</u>	<u>8</u>	<u>9</u>	<u>5</u>	<u>5</u>	<u>3</u>			214
" , Eocene	<u>2</u>	<u>4</u>	<u>1</u>							267
" , Green River	x	M	x	M	x	x				225
" , " " Top	5.8	6.1	2.5	2.7	0.6	0.6				251
" , " " Middle	4.5	4.7	2.5	1.8	0.5	0.3				251
" , Mowry	<u>6</u>	<u>11</u>	<u>3</u>	<u>7</u>	<u>1</u>	<u>2</u>	<u>.3</u>			237
" , Thermopolis	<u>4</u>	<u>7</u>	<u>2</u>	<u>4</u>	<u>1</u>	<u>2</u>	<u>.5</u>	<u>1</u>		237
" , Woodford	x	x	x	x	x					260
" , bitumin	x	x	x	x	x	x				221
" , oil (Scotland)				x						219
Soil, Australian "green"	x	x	x							261
" , Continental	<u>5</u>	<u>21</u>	<u>4</u>	<u>24</u>	<u>3</u>					260
" , South Carolina				x						256
"						x		x		262

ERRATA

Pg	Par	Ln	Change from:	to:
2	1	2	pelatic	pelagic
2	2 (#2)	1	Cryptophyceae	Cryptophyceae
15	8	1	monomasic	monobasic
26	3	1	interferred	interfered
32		22	1/1.4	1/0.41
32		21	Cryptophyceae	Cryptophyceae
39	3	1	algae	algal
81		28	48	89
86		4	48	89