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BIOLOGICAL OIL SLICKS

Part I - Literature Examination

J. M. Leonard
CHEMISTRY DIVISION

July 1959

DEPARTMENT OF THE NAVY · OFFICE OF NAVAL RESEARCH

U. S. NAVAL RESEARCH LABORATORY
Washington, D.C.

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Part I. Literature Examination.

⑭ NRL-MR-955

⑩ by
J. M. Leonard
Organic and Biological Chemistry Branch
Chemistry Division

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ABSTRACT

It has been suggested that some of the films on the sea surface may be oils of marine biological origin. This report summarizes a survey of scientific literature relating to the distributions of oil-bearing marine plankton and the quantities of oil which may be available to form surface films. Analytical data on the composition of plankton oils indicate ample amounts of surface active substances. No definite mechanism by which the oil is liberated and comes to the surface is adduced; it is suggested that the fecal pellets of certain zooplankton provide a route by which sufficient quantities of oil could be dispersed in the sea.

PROBLEM STATUS

This is an interim report. Work on this problem continued.

AUTHORIZATION

NRL Problem C03-17

INTRODUCTION

The multitudinous flotsam of the sea include an enormous variety of materials and objects - some as gross as icebergs, others as subtle and evanescent as the various oil "slicks". Often the various oil slicks on the sea are simply petroleum products - the fuel, lubricant or cargo of a passing ship. Sometimes there are apparent surface films which are not so readily identifiable - they appear as patches, or zones discernible by very slight differences in reflective or radiative properties. Sometimes the differences are visible to the eye, more often they register only on the most sensitive instruments. When the "slick" is thick enough - a quarter wavelength or more - to give interference colors, there is no great problem in identifying it as a second oily phase spread upon the water. Films less than a quarter wavelength thick would alter optical properties; the patches do appear in places that belie any possible petroleum origin.

It has been suggested that these patches are indeed oily, having their immediate origins in the living organisms of the sea. It is the purpose of this report to discuss the suggestion in the light of available information about marine sources of natural oil, its concentrations and its compositions, and the possible means by which the oil could come to the surface.

Examination of the oceanographic literature has disclosed a considerable amount of heterogeneous information. So this study has become both review and interpretive.

The Plankton

As on land, the primary source of organic foodstuff in the sea is the green plants that use solar energy to convert carbon dioxide into their own tissues; and all the life in the sea is nourished by feeding on these green plants, directly or indirectly, through the mediation of one or more stages of the system whereby the little are eaten by the bigger. It is interesting to note that large marine plants, "seaweeds" and such, make an almost negligible contribution to the food-chains of the sea. The major contributors are the free-floating microscopic plants. Their photosynthetic output, by the way, is about four times that of all the forests, fields and jungles on earth. The term plankton (Greek, planktos, wandering) refers collectively to the floating and the weakly swimming plants and animals of the sea. Though the free-floating kelps such as occur in the Sargasso Sea, and animals like salps and jellyfish come within the definition, they are arbitrarily excluded here. The plankton community is composed of the phytoplankton (phyton-plant) and the zooplankton (zoion-animal); this discussion will be limited to the small members of the community (a few millimeters down to a few microns in some dimension).

Sverdrup (1, p. 295 et seq) groups all of the plants of interest here under the heterogeneous caption of "Yellow-Green Algae". This includes the diatoms (diatomos, cut in two) a large group, both by numbers and by bulk. Their characteristic is a translucent shell made of SiO_2. It is the fossil deposits of these shells that comprise diatomaceous earth. They vary greatly in physical appearance; under the microscope Coscinodiscus resembles a stack of coins, Chaetoceros, a hairy worm, Asterionella is delicately spiculated.

Of great importance to this study is that the diatoms synthesize oil in considerable quantity. To cite one example from many, Barg (2) describes microscopic examinations of many species of diatoms. He leaves no doubt that oil can be the major cell constituent. Most of the oils in the sea - even the familiar fish oils, originate with the phytoplankton, especially the diatoms. There is some evidence - by no means undisputed - that all of fatty acid synthesis in the sea is performed by phytoplankton. Hofler (3) offers a teleological "why" for fat synthesis by pointing out that the diatom is very permeable to sugar and that an insoluble oil can be more efficiently stored.

The group of next importance are the dinoflagellates (a truly hybrid term - from Greek <u>dinos</u>, whirling; and Latin, <u>flagellum</u>, whip). The characteristic is a pair of whip-like appendages or flagella which confers locomotive ability of a very rudimentary sort. Though there are some dinoflagellates which are more animal than plant-like, they will not concern us here. The dinoflagellates do not have the durable, inorganic armor of the diatoms or the coccolithophores. These latter are small in size, but they are important in the economy of the sea. There are other groups which at certain times and situations predominate in given plankton communities, but those mentioned are sufficient to the purposes of the discussion. Harvey (4, p. 98) gives the following rough estimates of size (gross volume) of the principal phytoplankton individuals as follows:

diatoms	20 to 20 million cubic microns
dinoflagellates	500 to 100 thousand cubic microns
flagellates	14 to 500 cubic microns
coccolithophores	14 to 500 cubic microns

Even the largest of these, please note, would make a sphere only 0.3 mm. diameter. Attention is directed also to the enormous ranges in the size distributions of the first two (and most important) groups; they greatly complicate the tasks of the marine biologist.

The phytoplankton are ubiquitous, but of course there are times and places in which they flourish better than others. In general, they favor cool waters; especially where there are upwellings of nutrient-rich waters from the deeps. It seems too, that the plankton are stimulated by an influx of fresh water into the sea; but the cause is more subtle than the simple decrease in salinity (8, 9). Being photosynthetic, the phytoplankton cannot survive in depths beyond the penetration of sunlight. The plants do not necessarily congregate at the surface either. Depending on the clarity of the water, the incident angle and intensity of the sunlight, and other factors, the optimum depth is perhaps 5 or 10 meters, the extreme depth 100 to 150 meters. To fall below this so-called "euphotic" zone is to disappear, most probably into the digestive tract of some zooplankton for natural disintegration is uncommon. Harvey (4, p.106) points out that the ocean bottom around Plymouth, England at least, has a negligible debris.

One may well ask how the allegedly non-motile diatoms manage to maintain themselves at favorable depths. The clear implication of Sverdrup (1, pp. 764-765) and others is that they do not - though they can't repeal Stokes' Law, they manage a fairly effective passive resistance. With their small size they have a high surface/volume ratio for maximum viscous drag; they are decidedly non-streamlined, even some long, slender species have curled ends so that they fall slowly, long axis horizontal, in great circles. Sverdrup (loc cit) mentions the presence of oil in diatoms and suggests that its low specific gravity may have a role in maintaining bouyancy.

Beklemishev (5) cites Skopintsev (6) that the settling rates of 20-50 µ phytoplankton are 0.2 to 1.2 meters/day in calm sea water at 12°C and that the organic matter of free-sinking, dying diatoms is decomposed in the first 100 meters. Beklemishev, too, concludes that between heavy grazing and decomposition, few diatoms indeed reach bottom, except in shallow water.

In their impressive paper Gross and Zeuthen (7) state unequivocally that the vegetative cells of diatoms do not sink, that bouyancy is maintained by keeping the concentrations of certain divalent ions in the cell sap lower than their concentrations in the sea; that spores do sink by expelling a cell sap of lower density than sea water.

Since the zooplankton do not photosynthesize, they are not bound to stay in the euphotic zone as the phytoplankton must. Since the animals are grazing on the plants, the two populations are often times well-mixed, but there is a tendency for the zooplankton to distribute generally below the phytoplankton and to make diurnal trips to and from the upper regions. Bogorov (10) compares these vertical migrations of zooplankton in temperate latitudes with their regular cycles of daylight and dark, to those in the Arctic, and its 24 hours of daylight. He concludes that the migrations are really phototactic responses, - efforts stay in strata of favorable light intensities.

The animals of the zooplankton community include most of the phyla or large groups of the animal kingdom. The "higher" phyla are represented by eggs, larvae and other developmental stages; these are the "temporary" plankton. The "permanent" membership of the zooplankton comes from the "lower" phyla. The protozoa (the single-celled) animals are undoubtedly an important group, but their small sizes make quantitative studies difficult. Noctiluca is fairly large (ca. 1 mm). Its flowering accounts for the occasional pink color of coastal waters. Sverdrup (1, p. 304) notes that the Noctiluca "masses may be blown into conspicuous windrows or patches resembling 'tomato soup'. Noctiluca are voracious feeders .....".

From the standpoint of bulk or gross weight, the crustaceans are easily the dominant element of the zooplankton. According to Sverdrup (1, p. 309) one group, the copepods alone usually comprise about 70% of the zooplankton. Sometimes another crustacean group, the Euphausiaca predominates. It is the "krill" of Antarctic waters where it forms the major food of whales. According to Sverdrup (1), the copepods are relatively small (0.3-8mm); the bottom-dwelling Euphausiaca sometimes are 50 mm long. It is scarcely surprising that they resemble somewhat their larger relatives, the crayfish and the shrimp. They feed by filtering particulate matter from the sea by ciliated mouth appendages. That diatoms are the principal food of copepods should need no extensive documentation; more than 35 years ago, Marshall (11) observed that diatoms were the major food of the most common copepod Calanus finmarchicus and there were no obvious signs of species "preference" in its dietary.

Sources of Surface Oil From the Plankton

It is natural that a diet of oil-rich diatoms should result in a zooplankton with a high oil content. Of special relevance here is the fairly common observation, e.g. Harvey (4, pp. 117, 119), Beklemishev (5)

Harvey et al (12) that the zooplankton are voracious eaters. Given an adequate food supply, they ingest far beyond their needs. The undigested excess is extruded as green fecal pellets, of practically the same composition as the ingested diatoms. This writer suggests that these oil-rich pellets, being rather friable, could be the major source of surface oil.

QUANTITATIVE DISTRIBUTION OF PLANKTON AND THEIR FATTY COMPOSITION

The rest of this study will be devoted to reviewing some of the literature data on the quantitative distributions of marine plankton, and their fatty compositions. The goal, of course, is estimates, crude at best, of the amounts of oil that could be available at various seasons and places for the formation of oil "slicks". Analytical data on the oils will be interpreted, so far as possible, in terms of surface activity and consequent film-forming tendencies.

The plankton-distribution phenomenon is exceedingly complex in itself. The situation at any given time, place, and depth is the result of interplay of many varying ecological and environmental factors not one of which is completely understood. The phytoplankton population, for example, at a given stratum at a given location depends on the dissolved nutrients of the water, carbon, nitrogen, phosphorus and trace elements too. These vary with the season and with the turbulence, which in turn is affected by temperature gradients. The phytoplankton at a given spot will vary with the water temperature, with the intensity of the sunlight, and with the extent of grazing by zooplankton whose numbers and activities are affected by other complexes.

In addition to difficulties inherent to the intricacies of the phenomenon itself, there are difficulties of method. No matter how the sea is sampled and the population of the sample determined, there is a nice question of "small-sample statistics" - how closely any sample taken represents its particular "whole".

Plankton are sampled in various ways. One is to tow a net of a given fineness of weave horizontally through the water at a given depth. In the most careful experiments, a flow-meter in the mouth of the net corrects for the clogging effect of the catch and permits a computing of the volume of water sampled. There are also oblique and vertical hauls which give different sorts of sample. The texture of the net of course, specifies the sample. Thus, "000" cloth (1 mm mesh)would pass most of the small zooplankton. Even the finest silk (#25) listed by Sverdrup (1, p. 378) with apertures of 0.064 mm would pass almost all of the phytoplankton. So phytoplankton are best collected by centrifuging or filtering an appropriate sample of sea water. And the precision is not very good even under the most favorable circumstances. For example, Goldberg et al (13) put duplicate 500 ml portions of sea water through molecular filters. One sample bulked 80% more than the other; even after a questionable "correction" the difference was still 30%. But one must not conclude that the situation is so complex as to defy analysis forever. Some investigators, notably Riley and his associates (15) and Riley (19) have made some excellent beginnings at formulating the most important environmental factors into useful mathematical expressions.

There is a great need, however, for more and better oceanographic data of every kind.

After the plankton have been collected and separated from their sea water, they must be measured or counted in some manner and the measurement must be converted to some useful term expressing concentration in the sea. Here arises a difficulty in making comparisons between different investigations. Some workers simply measure the gross volume of a settled mass of plankton; others report the dry weight; others, the weight of organic matter (difference between dry weight and weight of ash); others analyze and report the quantity of carbon, nitrogen, or phosphorus in the plankton sample. But some convenient approximate conversion factors among these various methods of expression are available (14). Perhaps the most common procedure of all is simply to count the organisms and to ignore the great differences in their sizes. This is a vexing practice indeed to one interested in quantities of plankton tissue rather than populations. Phytoplankton are frequently measured and reported in terms of the chlorophyll content of the sample. There are various ways too, of expressing the "quantity" of ocean sampled. Simple volumetric units - cubic centimeters, liters and cubic meters are common. It is frequently useful to express concentration of matter as the quantity underlying unit area of ocean surface. With the qualifying provisos in mind, let us examine some data on the planktonic composition of the sea. So far as possible, data from diverse sources will be put in comparable units.

The Plymouth (England) Marine Laboratory has closely studied the sea (50-70 m. deep) in its vicinity. Phytoplankton collections by net (41 x 52 μ) were almost zero except for the spring flowering which showed 0.5 to 3 grams of phytoplankton organic matter below 1 square meter of sea. Comparable samples of water through a membrane filter (0.9 μ pores) showed 10-12 grams plant organic matter below 1 m^2. (4) An adaptation of the summary data of Riley, Stommel and Bumpus (15, p. 23) for the Western North Atlantic is given in Table 1. The data exemplify several important items, viz., a flowering of phytoplankton during the spring, a summer subsidence, and a lesser burst in August or September. Population densities vary from place to place, the Maine coast is significantly richer than the waters off Plymouth; the comparative poverty of the Sargasso is unmistakable. Data elsewhere (16) indicate that Sargasso surface water to be only 5% (or even less than 1%) as rich in phytoplankton as surface water off the New England coast. From still other data (17) the following fluctuations in the phytoplankton of Georges Bank are calculated:

September	14	gm	phytoplankton	organic	matter/m^2
January	3	"	"	"	"
March	20	"	"	"	"
April	56	"	"	"	"
May	21	"	"	"	"
June	12	"	"	"	"

TABLE 1

SUMMARY DATA ON PHYTOPLANKTON OF THE WESTERN NORTH ATLANTIC

Grams of Plant Organic Matter/m^2*

Area	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept	Oct.	Nov.	Dec.
Gulf of Maine	1.4		9	10.5	19.6	7.8			9.0			
Georges Bank			11.1	29.1	17.1	6.6			9.0			
Coastal Water, Cape Cod, Montauk Point			7.4		1.4							3.2
Slope Water	4.0		9.2	59.	8.9	4.7			6.1			4.8
Sargasso Sea, N.W. of Bermuda					5.0							6.6
Sargasso Sea, Bermuda to Azores						1.6						6.7
Gulf Stream												
Florida Straits					7.7							
Carolinas					5.9							
Off Montauk Point					4.8							

* Based on conversion of the original plant pigment data, an operation of limited validity at best.

As mentioned, Harvey (4) feels that in the Plymouth area at least, practically all of the phytoplankton crop disappears in the grazing; very little deposition of organic debris takes place in spite of the abundant production of green fecal pellets by the plankton animals. Low counts preclude bacteria being considered as important planktonic scavengers. Moreover Waksman and his colleagues (18) have noted that bacteria can't feed directly on diatom plankton, even dying ones. To one recalling Miss Carson's beautiful chapter on "the long snowfall" of the ocean bottom, it seems that the absence of bottom debris must be exceptional, a feature of nutrient-poor waters perhaps.

It would surprise no one to learn that as a first approximation, where the phytoplankton abound, there too, will the herbivorous zooplankton be found. One might expect the population cycle of the animals to lag behind that of the plants. The work of Riley and Bumpus (17) and Riley (19) gives quantitative support for the view. Interestingly enough, it is phytoplankton production - not natural enemies - that exerts primary control over the population density of zooplankton. As noted already, the zooplankton are a mixed fauna, but from the standpoint of bulk the copepods predominate. See, for example, Harvey et al (12) whose censuses indicate the copepod group to be at least 80% of the zooplankton near Plymouth. In this group, the genus Calanus is easily the most prominent. So it is expected that no serious error would result from discussing a whole community in terms of its biggest family.

Harvey (4, p. 129) estimates the year-round quantity of phytoplankton near Plymouth as 4 gm. organic matter/m^2; of zooplankton, 1.5 gm./m^2.

Riley's (6) data on the deeper, more nutrient waters of Georges Bank calculated to the same basis indicate a maximum of about 45 gm. in May and a fairly steady 12 gm during most of the year. Elsewhere off New England the values were 1.4 to 7.3 grams; the Sargasso was consistently lower, 1.1 - 2.3 gm.

Thrailkill has reported on a series of annual zooplankton surveys of the California coast. His report (20) for 1956 is typical. A zone about 100 miles wide, extending the full length of California plus lower California was explored. Apparently all the tows were vertical - from the maximum depth right to the surface. From a welter of detailed data, certain generalizations emerge. Areas of maxima concentration were spotty - 10% or less of the total area. The "spotty" maximima calculate to 150 mg. dry plankton per <u>cubic</u> meter of water. Most of the remainder was 50-150 mg.; the waters of lower California were consistently poorer, 15-50 mg. Vinogradov (21) reports a zooplankton value for Bering Sea corresponding to 8.8 gm. dry zooplankton/m^2. Since the water was about 200 meters deep, the average density is low (44 mg/m^3) compared to Thrailkill's findings above.

The ravenous appetites of the copepods for phytoplankton has been mentioned already. Harvey (4, p. 117) states "If a Calanus is placed in a dense population of diatoms, it can be seen to extrude green faecal pellets at 20 min. intervals. For greed, voracity and wasteful feeding, many planktonic crustacea are unmatched. [During some net-censuses of phytoplankton] great numbers of such green faecal pellets were found in the water at the time and immediately after the population of the larger diatoms had risen to high values."

Harvey et al in another place (12) reiterate that not many diatoms reach bottom near Plymouth. They note that fecal pellets in the sea are at maximum in March and April and that the animals eat far in excess of their needs when food abounds. In the February-April period, pellet counts ran 1,000-50,000/m^3, the animal counts 3,000 to 30,000/m^3. The maximum ratio was 13 pellets per animal, 3 was the average.

Riley and Gorgy (16) suggest that the zooplankton of the nutrient-rich U. S. coastal waters are ingesting ten to thirty times their nutritional needs. Moreover, the fat content of zooplankton correlates well with the abundance of phytoplankton, e.g. the south Japan Sea and the Sargasso, both poor in phytoplankton, have a zooplankton poor in fat; the plant-rich waters off the northern U. S. have animals with abundant fat reserves. Beklemishev (5) cites data of Lucas (22) to show that one species, Eurytemova hirundoides eats 40% of its body weight in diatoms daily. Harvey (4, p. 119) estimates that zooplankton need food amounting to 11-14% of their body weight daily. Riley (19) notes that they eat 30% and assimilate only 10%. It appears, therefore, that a quantity of pellets containing slightly digested diatoms, amounting to 20-30% of the weight of the zooplankton population is cast out daily. The chemical composition of the pellets should resemble closely that of the diatoms eaten. But some ingenious laboratory experiments of Marshall and Orr (23) suggest that digestion may advance further than is ordinarily supposed. Calanus were fed phytoplankton containing radioactive P^{32}. By this index, the distribution of phosphorus between animal and feces, apparent absorption averaged around 80%. But it is entirely possible that phosphorus is selectively - and rapidly - absorbed. It is worth noting that even when the food intake is very low, e. g., 1% of the body weight, the phosphorus extruded is still about 20% of that ingested.

According to Moore and Druse (24), a Calanus pellet is 50 to 100 microns diameter by 200 to 400 microns long. Beklemishev's (5) cursory observations are in substantial agreement. To estimate the importance of Calanus pellets, some indication of their fragility would be helpful. Some undetermined fractions of the total number are sturdy enough to withstand netting from the sea. That they may, at times, be exceedingly frangible is indicated by Marshall and Orr (23). Speaking of pellets from Calanus fed on Chlorella they note

> "When the pellets are punctured or broken (and they seem to be particularly fragile) a cloud of cells emerges and the whole pellet soon disappears."

Skopintsev (6) and Kalle (25) too permit the inference that the pellets are somewhat unstable, viz., about 3/4 of the organic matter of a pellet should decompose within 1500 meters, or only 1/4 could reach deep bottom. This disintegration of a relatively large agglomerate of diatoms within 1500 meters is in harmony with evidence that a single, dying, free-sinking diatom would decompose within 100 meters.

What then is the composition of this fecal debris in terms of fatty or other surface-active material? As already noted, the composition of the diatom is a good index. Data of Clarke and Mazur (26) on various collections of diatoms are summarized as follows:

1. Lipid content, dry basis, 5-15% (7-22% basis of dry organic matter)

2. Free fatty acids* - 59-82% of the total lipid

A typical analysis of the free fatty acids

(a) Saturated, 60% palmitic, 36% stearic

(b) Unsaturated

	"Solid" Acids	"Liquid" Acids
C_{14}	7%	
C_{16}	29	26
C_{18}	7	13
C_{20}	20	19
C_{22-24}	37	31
C_{24}-30		11

3. Also present- sterol and a saturated, crystallizable hydrocarbon analyzing $C_{31}H_{64}$

Item 2, the high content of free fatty acids is most striking. In the first place it is unusual; in the second place it suggests great possibilities of surface activity. The investigators note that the lipid composition does not change much with season or the biological composition of the catch. Lovern (27) without stating the status of the fatty acids, whether free or combined, notes an unusual distribution, viz., C_{18} unsatd., 62.5%; C_{20} unsatd., 13.5%; C_{14} satd., 9.2%. The familiar palmitic and stearic acids together comprise less than 10% of the total.

---

* Free fatty acids decrease on standing in air; combined acids, alcohols and hydrocarbons increase.

Collin *et al* (28) studied the oils of both phyto- and zooplankton. The zooplankton oils from the several species were similar enough to warrant pooling. The phytoplankton study was impaired by the small sample. Analytical data are as follows:

TABLE 2

ANALYTICAL CONSTANTS OF PLANKTON OILS

Measurement	VALUE Phytoplankton Oil	Zooplankton Oil
Saponification No	182	123
Iodine No	141	126
Non-saponifiable	17.9%	28.2%
Iodine No of the non-saponifiable	67.7	60.5
Sapon. equiv. of the fatty acids	262.1	280.8
Iodine No of fatty acids	122.4	167-188
Saturated acids	15.5%	17.3%
Acids giving ether-insoluble "bromides"	2.1%	9.6%

The fatty acids of zooplankton oil resemble cod liver oil, according to these investigators. The zooplankton oil also contains cholesterol, an unidentified wax, squalene or some similar hydrocarbon, cetyl and eicosyl alcohols.

It is Lovern's (29) belief that zooplankton fat is the same as that of the phytoplankton; that fish fat in turn is about the same as that of the zooplankton, a view that the data of Table 2 would scarcely sustain. Differences among fish fats according to Lovern are traceable to effects of salinities on the phytoplankton. He gives the following data on *Calanus* (zooplankton) fat.

TABLE 3

ANALYSIS OF CALANUS OIL

Saponification Equivalent	457.5
Iodine No.	177.6
Saponifiable, percent	32.

Fatty acid composition (in mol percent)

C_{14} satd.	10.3	C_{14} (-2H)	2.
C_{16} satd.	11.7	C_{16} (-2.4H)	13.2
C_{18} satd.	1.3	C_{18} (-5.1H)	17.1
		C_{20} (-7.8H)	22.9
		C_{22} (-8.1H)	21.5

The fatty acid data given above calculate out to a saponification equivalent of 287, a good check with Collin's 280.8 for zooplankton oil of Table 2. This observer cannot reconcile the fatty acid data with the values given for saponification equivalent and the percent saponifiable. Perhaps "32"% for the latter is a misprint of 62%. It is regrettable that no estimation of free fatty acids can be made from the data.

Japanese workers (30) among others, are understandably sceptical of the view that fat is simply an item of transfer on the marine biological ladder. They note that _Calanus_ contains significant amounts of C_{20} and C_{22} acids even though the phytoplankton food of _Calanus_ contains very little. A portion of the Japanese analytical data on _Calanus_ follows:

TABLE 4

ADDITIONAL ANALYTICAL DATA ON *CALANUS* OIL

Oil content of Calanus (dry weight basis)	58.6%

PROPERTIES OF THE OIL

Acid value	11.4
Saponification value	103.2
Iodine value	159.7
Unsapon. matter	43.1%

MIXED FATTY ACID PROPERTIES

Neutralization value	188.8
Av. molec. wt	297.2
Iodine value	161.3

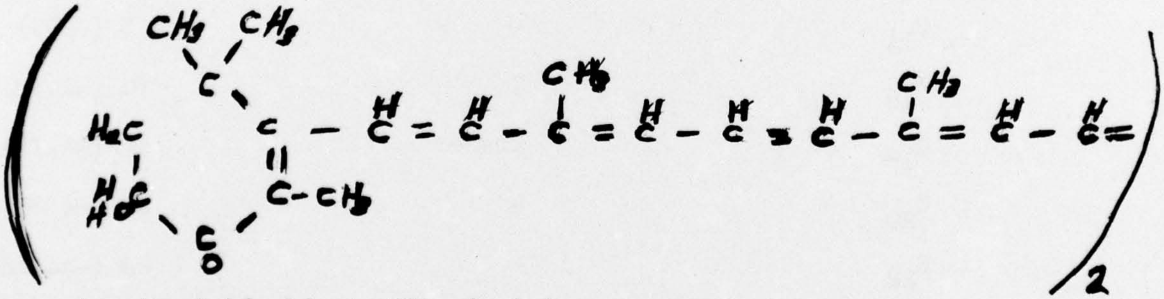
FATTY ACID DISTRIBUTION, WT. PERCENT

Acid	Saturated	Unsaturated
C_{14}	9	3 (-20H)
C_{16}	7	10 (-2.2H)
C_{18}	trace	14 (-4.7H)
C_{20}	-	29 (-4.2H)
C_{22}	-	28 (->4.2H)

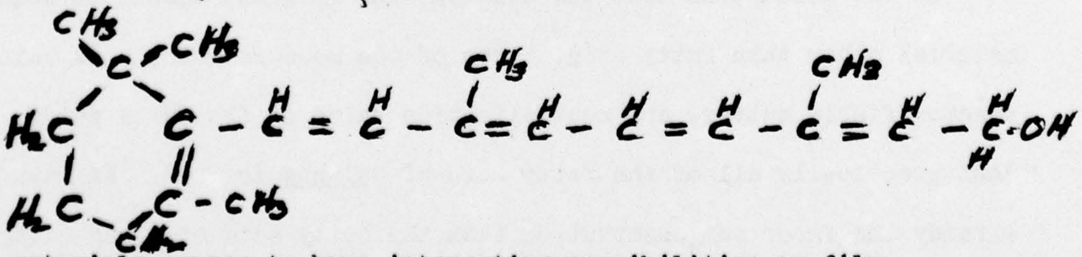
On the assumption that the oil contains no great amount of acidic material other than fatty acid, three of the measurements, acid value, unsaponifiable matter, and neutralization value of the fatty acids, demonstrate that practically all of the fatty acid of *Calanus* is free. We have noted already the important observation that the fatty acid of fresh diatom oil is largely uncombined. Even the presence of a considerable amount of astacin (see below) would not seriously compromise the implication of the Calanus data. These free fatty acids are excellent "prospects" as film-formers, so are the high molecular weight alcohols.

Among the non-saponifiables, substances related to Vitamin A should be mentioned; some could have considerable surface activity. One is the red pigment, astacin. Drummond and Macwalter (31) report that astacin is a constituent of the previously mentioned "krill", the zooplankton on which Antarctic whales feed. Astacin is poorly absorbed; it is found in whale feces. The writers are sure that the pink color of Calanus as well as Euphausia "krill" is due to astacin.

The naturally occurring form of astacin is astaxanthin (Karrer's "Organic Chemistry", Elsevier Press, 1938, p. 658-9). The formula, $C_{40}H_{52}O_4$:



Its close structural kinship to Vitamin A is apparent:



Both of these materials appear to have interesting possibilities as film formers.

RECAPITULATION

We have seen that the primary source of marine oil is the phytoplankton which on the basis of their organic content may contain from 5 to 50% lipoid; perhaps 15% would be a good median. The plant populations vary greatly with the season, the geographical location, the depth and other variables too. They range from 1 to 60 grams organic matter per square meter of sea, and 10 grams seems a reasonable median. So the total plant oil beneath the surface may range from .05 to 30 grams per square meter and the mid-value is perhaps 1.5 grams. Some - but not much - of this should be freed by the natural death and disintegration of the phytoplankton; the consensus indicates that few"die naturally"; animal grazing disposes of most of them.

The zooplankton population varies with its food supply, of course. It would be a fair general approximation to set the quantity of zooplankton tissue at any moment as one-third to one-half that of the phytoplankton, or 0.3 to 30 grams per square meter. The animals eat 10 to 50% of their body weight daily and "waste" 20-50% of all they ingest. This amounts to a minimum consumption of 30 mg. plants, with the ejection of 6 mg pellets containing 0.3 mg. oil. The corresponding maxima would be an intake of 15 grams with an output of 7.5 gm. pellets containing 3 or 4 grams of oil. The minimum value, 0.3 mg/m^2 is about 1/8 of the amount needed to make a continuous monolayer of fatty acid. Having defined the limits of available oil within 4 orders of magnitude, we now stumble; we can define neither the cohesive strength of the pellet nor the disruptive stresses of turbulence to which it might be subject.

In the oil itself, by whatever means it may reach the ocean surface, there is no lack of surface active materials - free fatty acids, long chain alcohols, sterols, astacin pigment and other substances allied to the carotenes.

In conclusion, it is very possible that some marine slicks are of biological origin. Sufficient amounts of insoluble but surface active material are excreted daily by animals commonly found in the plankton to be responsible. Further research on the sources and on the film-forming properties of the surface active materials excreted is recommended.

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