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THE WEST FALMOUTH OIL SPILL

Data Available in November, 1971

II. Chemistry

by

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TECHNICAL REPORT

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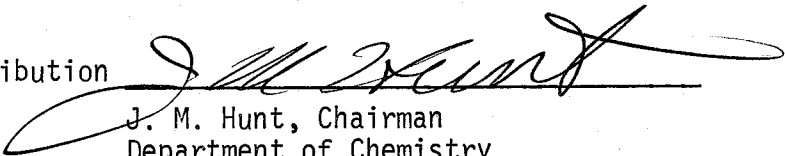

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INTRODUCTION

A spill of 650,000 to 700,000 liters of #2 fuel oil in Buzzards Bay, Mass., USA, on September 16, 1969, has severely polluted the coastal waters, the marshes, the offshore sediments and the shellfish resources of Falmouth and of Bourne, Mass. In preliminary publications and reports (Blumer et al. 1970, b,c,d, 1971a) we have discussed the chemical and biological data available during the first few months after the accident. The present report documents the continuation of our analytical effort; we include analyses of stations that had not previously been covered and present the data that were available by October, 1971.

Three distinct, though partly overlapping, series of events followed the spill. First, within the first few hours or days after the accident, there was a very heavy kill of those organisms which came into contact with the oil. It extended over all phyla and over benthic and intertidal organisms. Next, within weeks or months after the spill, the oil pollution spread to areas that had not been immediately affected; and the kill extended, though in some cases more slowly than the spread of the oil, to outlying areas. Oil entered the marine food web and made the shellfish resources of our area unacceptable to human nutrition. The oil showed an unexpected persistence in the sediments and in marine life, especially in view of its relatively low boiling range and of earlier assertions that fuel oil pollution was transitory in nature and without long-term consequences. For considerable time after the spill, the oil pollution of the sediments prevented the resettlement by the original fauna. Now, degradation of the oil has become evident. Biochemical and physical

processes lead to a gradual reduction of the oil content of the polluted sediments. Concurrent with the degradation, there has been a gradual reduction in the immediate toxicity of the oil in the sediments. This has permitted resettlement of the polluted region first by the most resistant opportunists and later by a more varied and more normal fauna. However, oil-derived hydrocarbons have remained at all stations during the entire two year span for which data are now available, and it appears that the life span of pollution, even by a low boiling fuel oil must be measured in terms of many years.

The eventual aim of this study is the documentation of the effects, the persistence and the eventual disappearance of pollutant hydrocarbons from a relatively small spill in a limited and previously clean coastal area. Of necessity, most of our analytical effort in the past was aimed at a survey of the extent of the oiling of the sediments and of some of the commercially important animals. As the degradation proceeds, we expect to devote a greater effort to a more detailed chemical analysis of the hydrocarbons remaining in the environment in order to define and understand the modes of degradation and to correlate chemical analyses with biological data. Parallel investigations on the weathering of different oils under other ecological and climatic circumstances are under way here and should, in combination with the West Falmouth study, give a more realistic assessment of the environmental hazard and persistence of crude oil than has been available until now.

METHODS

The methods used were essentially the same as those described in our previous reports. An effort was made to carry out all gas chromatograms on the same Apiezon L column in order to facilitate comparison between chromatograms. However, that column failed by mid-1971 and was replaced by a similar column. The resulting improvement in resolution is noted in the most recent chromatograms (e.g. Station 31, August 1971).

The aromatic hydrocarbon fraction of some sediment extracts was isolated by column chromatography. About 30-45 mg of total hydrocarbons that were recovered as described by Blumer et al., 1970 b,c,d, were separated on a 1 ml column of silica gel, deactivated with 5% water. Pentane was used as the eluent in fractions of 0.7, 0.5, 1, 2 and 2 ml, followed by 4 ml pentane with 10% benzene. Fraction 1, corresponding to the column dead-volume, was devoid of sample; fraction 2 contained saturated hydrocarbons; the aromatics were eluted in fractions 4 and 5. The mixed saturated-aromatic fraction 3 was rechromatographed on a column of the same dimensions with pentane (0.7, 0.5, 0.5, 0.5 ml) elution. Fractions 2 and 3 contained additional saturates while fraction 4 contained aromatics. The combined aromatics were subjected to mass spectral analysis (CEC-DuPont 21 - 104 mass spectrometer, magnetic scan, 1600 V accelerator voltage, beam current 40 ua, 8 V ionization potential).

In the low voltage mass spectra of the aromatic fraction, all peaks belonging to the benzene, naphthalene, tetrahydronaphthalin- and diphenyl-series were normalized to a total peak intensity of 1000. The plots

(Fig. 4) give the relative peak distributions within the aromatic-series, without resolving the individual isomers and without correction for different mass spectral sensitivities between and within series. The plots are comparable and can be interpreted in terms of relative concentrations and of changes in relative composition but not in terms of exact amounts.

THE DISTINCTION BETWEEN INDIGENOUS AND POLLUTANT HYDROCARBONS

The identification and quantitative determination of hydrocarbon pollutants is more difficult than that of purely synthetic chemical pollutants. There, eg. in the case of chlorinated hydrocarbon pesticides, pure chemicals can be isolated for which no natural background exists; therefore, the analytical measurement defines directly the pollution level.

This is not the case with hydrocarbons. All organisms and all recent geological samples contain hydrocarbons of biochemical origin. These have to be determined and an allowance has to be made for their presence in the identification of hydrocarbon pollutants. Failure to detect this natural hydrocarbon background in environmental samples usually suggests the use of samples or of methods which are inadequate for the detection of hydrocarbon pollutants at low concentration levels.

Fortunately, sufficient structural and compositional differences exist between biologically and pollution-derived hydrocarbons to permit the qualitative distinction and their detection in each other's presence.

The exact quantitative determination of petroleum pollution in environmental samples is further complicated by the compositional complexity of crude oil. In analytical separations of petroleum hydrocarbons, losses of low or high boilers are almost unavoidable and the separation of the more polar petroleum fraction from those biochemicals with which it overlaps in polarity is difficult. Fortunately, in the case of the #2 fuel oil spilled in Buzzards Bay these difficulties are minimized; the narrow structural and boiling point range permits an easy separation of the oil from the lipids and a recovery without substantial losses of high and low boilers.

The identification of the fuel oil contamination in the samples from West Falmouth is based on several simultaneous observations:

1. Hydrocarbon Concentration in the Sediments

Biologically derived hydrocarbons occur in all recent sediments in amounts which depend on the type of source material, the total organic content and the degree of preservation, among other factors. Because of the variability of the indigenous hydrocarbon concentrations, weights of hydrocarbon extracts are indicative of pollution only if they exceed significantly, in a particular area, the range of the normal environmental background.

The natural hydrocarbon background level in the sediments at Buzzards Bay can be estimated in two ways. Table I lists analyses of samples taken before the arrival of the pollution, outside of the polluted area or within the polluted area in a core at a depth where gas chromatography shows the absence of fuel oil hydrocarbons. The average hydrocarbon content of these samples is 7.1 mg/100 g dry sediment.

In many of the polluted samples analyzed in the course of this study, especially during the present year, gas chromatograms demonstrate the presence of pollutants at concentrations comparable to, or below that of the indigenous sedimentary hydrocarbons. In these cases, the total measured hydrocarbon content is but slightly higher than the hydrocarbon background level. An inspection of the data of Table II for the first part of 1971 suggests that the offshore stations, with the exception of the heavily polluted river stations and Stations 31 and 10, contain indigenous and pollutant hydrocarbons averaging about 5 mg/100 g sediment. Thus, the average hydrocarbon background in Buzzards Bay appears to lie close to 5-7 mg/100 g sediment and it seems to exceed rarely 10 mg/100 g dry sediment.

Because of the variability of the indigenous hydrocarbon content, hydrocarbon weights in the sediments at West Falmouth, if considered alone, are indicative of pollution only if they exceed 10 mg/100 g dry sediment, such as at the river stations, at the offshore Station 31, and in some samples, at Station 10.

In spite of these limitations, hydrocarbon weights, even at low levels, are important if used in conjunction with gas chromatography for the study of trends in the relative concentration of biologically and pollution derived hydrocarbons.

In terms of their environmental role and toxicity, the indigenous and the pollutant hydrocarbons must be considered separately. The indigenous hydrocarbons are normal components of a stable environment; few, if

100 ppm

any, are toxic, and recent research has suggested that some may have well defined biochemical roles. Most of the hydrocarbon pollutants in fossil fuels are foreign to the marine environment and numerous components are toxic to living organisms.

A polluted sediment contains indigenous and generally harmless hydrocarbons in addition to the generally harmful hydrocarbon pollutants. The toxicity of the fossil fuel component is largely independent of the presence and of the concentration of the indigenous hydrocarbons; the petroleum hydrocarbons retain their potential for adverse biological effect, even if they are present at levels below the natural hydrocarbon background. Thus, whether the pollutants are present at higher or lower concentrations than the indigenous hydrocarbons is principally irrelevant in consideration of the toxicity.

2. Boiling Point Distribution

The fuel oil spilled at West Falmouth has a boiling range of 170° - 370° C. The normal paraffins range from about n-decane to n-docosane with a maximum in the C_{14} - C_{15} region. A large number of isomeric and homologous hydrocarbons are present whose boiling points overlap; in the gas chromatograms, which are graphic expressions of the boiling point distribution, this results in a broad, unresolved background over which are superimposed the resolved or partly resolved peaks of the normal and iso-alkanes and of some other homologous series.

A similar boiling point distribution and predominance of complex homologous series from about C_{10} - C_{22} is observed in the polluted sediments and organisms in Buzzards Bay, but it is absent at greater distances

from the site of the spill.

Our identification of the fuel oil pollution in this area is based on several criteria, which are discussed in this section of the report. Among others, one of these criteria is the boiling point distribution of the sedimentary hydrocarbons within the fuel oil boiling range. In informal discussions it has been suggested to us that the existence of a hydrocarbon "envelope" (Figure 7) in the fuel oil boiling range might be a normal feature of the sedimentary hydrocarbons, rather than being associated with residues of fuel oil from this spill. This, then, would make doubtful the ability to recognize the fuel oil pollution in this area.

It would be of the greatest importance to petroleum geochemists to find in unpolluted recent sediments hydrocarbons which have all the characteristics of #2 fuel oil, including the restriction to the particular boiling range. In spite of world wide analyses of recent sediments, such evidence does not exist. Thus, there is no support for the suggestion that a boiling point envelope in the fuel oil boiling range is a normal feature of sedimentary hydrocarbons. We wish to summarize the additional evidence that leads us to reject this assumption, specifically for the Buzzards Bay sediments, but also for other recent marine sediments.

- 1) Hydrocarbons showing the 170 - 370⁰ boiling envelope are found within Buzzards Bay only within the area affected by the 1969 spill. This feature is absent in control samples collected during this investigation, as well as in earlier analyses from this area (Clark and Blumer, 1967).

- 2) The magnitude of the envelope decreases radially outward from the focal point of the heaviest pollution.

3). At one and the same station, the magnitude of this envelope decreases in time as weathering reduces the pollution level.

4). In the core taken at the heavily polluted Station 31, the 170 - 370°C boiling envelope occurs only in the uppermost three inches of sediment. Hydrocarbons are present below this level but show the boiling point distribution common to unpolluted recent sediments (Stevens et al., 1956).

5). Similarly, cores from the intertidal region of Wild Harbor River (Blumer et al., 1970d) show the envelope in the uppermost, but not in the lower section. The only exception comes from the coarse sand in the bottom section of core #2, which contains undegraded oil, whose major and minor components correlate with those present in the spilled oil.

6). The literature contains numerous analyses of hydrocarbons from recent marine sediments and from marine plants and animals. None show an exclusive hydrocarbon envelope in the 170 - 370°C boiling range.

7). The biochemical processes, which are responsible for the formation of the hydrocarbons contained in recent unpolluted sediments, are specific, aimed nonrandom processes. They generate a simple assemblage of products. In all cases where hydrocarbons of marine organisms or of recent (unpolluted) sediments have been studied by medium resolution gas chromatography (columns of about 3000 theoretical plates), the hydrocarbons in the range to at least C₂₂ have been resolved into individual compounds, no continuous unresolved background was found, especially not in the exact 170 - 370° boiling range. Above C₂₂ a more complex hydrocarbon mixture,

not fully resolved by medium resolution GC may be present, simply because of the rapidly increasing number of possible isomers; however, this has not been demonstrated conclusively for conditions that excluded sample contamination and the formation of artifacts.

8). On the other hand, the diagenetic processes involved in petroleum formation at depth randomize the sedimentary organic matter through inter- and intra-molecular scrambling and produce a hydrocarbon mixture of enormous complexity, which cannot be resolved completely by present medium or high resolution gas chromatography.

9). The medium resolution gas chromatograms of the sediment extracts from the affected areas in Buzzards Bay show the presence in the fuel oil boiling range of an incompletely resolved hydrocarbon mixture, containing among other components, extended series of homologous and isomeric branched, alicyclic and aromatic hydrocarbons. Thus, the hydrocarbon composition in these Buzzards Bay sediments, within this boiling range, is unlike that of recent unpolluted organisms or sediments; on the other hand, it corresponds in complexity to the hydrocarbon composition of all crude oils, formed from organic matter at depth.

3. Hydrocarbon Type Distribution

The hydrocarbons in living organisms are relatively simple and few in number; one or a few components may exceed all others by orders of magnitude. In general, normal and iso-alkanes and alkenes predominate, cyclo-alkanes, cycloalkenes and especially aromatics are in the minority.

If present, aromatic hydrocarbons occur in small amounts and are limited to a small number of unsubstituted rings or to compounds with a low degree of substitution.

Extensive analyses exist of the hydrocarbons in benthic and planktonic plants and animals of the Western North Atlantic (Blumer, 1967; Blumer and Thomas, 1965a,b; Blumer et al., 1963, 1964, 1969, 1970a; Clark and Blumer, 1967; Youngblood et al., 1971).

In contrast, crude oil and oil products are extremely complex mixtures, containing many homologous series with most adjacent members occurring at approximately the same concentrations. Olefinic hydrocarbons are absent in crude oil and in straight run distillates but they may be present in cracked products. Large amounts of varied substituted branched, cyclic and aromatic hydrocarbons exists, often with mixed structures.

Thus, a large number of potential parameters exists for the distinction between the indigenous hydrocarbons of recent sediments and the fossil fuels. Usually, the extent of the analytical effort rather than the number of inherent differences limits the analytical differentiation. A few of the parameters which distinguish the fuel oil from the indigenous hydrocarbons in the sediments of Buzzards Bay will be discussed:

a. Isoprenoid Alkanes: In recent marine organisms pristane predominates within the isoprenoid alkanes; phytane and farnesane may be present at lower concentrations, but the homologues below farnesane and from C_{16} - C_{18} have never been detected. In crude oil, on the other hand, an unbroken series extending to the C_{21} isoprenoid occurs; the ratios between individual members are variable and are characteristic for different crude oils. Correspondingly, the oil spilled at West Falmouth and the residual oil in the sediments contain the isoprenoid alkanes from C_{13} to at least C_{20} (the

C₂₁ homologue is not separated from n-nonadecane on our Apiezon L columns). The similarity in the relative abundance of the isoprenoid alkanes permits the correlation of the oil in the sediments with the spilled oil and confirms the identity of the oil remaining at the different stations for a long period after the spill.

b. Olefins: Attempts to hydrogenate the hydrocarbons recovered from the sediments with high hydrocarbon content lead to no observable changes in the gas chromatograms in the region below C₂₀. This demonstrates the absence of major olefinic contributors in these samples. In biogenic material, on the other hand, olefins would almost certainly be present in that range. Many chromatograms from the less polluted stations show, immediately above n-eicosane, one or several large components. That these exceed in amount the adjacent compounds by a large margin immediately suggests their biochemical derivation. That they are of an olefinic nature, as hydrogenation demonstrates, supports this.

c. Aromatic Hydrocarbons: Mass spectral analysis of the aromatic fraction from sediment extracts at low ionization potential shows the presence in fuel oil, in the polluted sediments and in contaminated shellfish, of continuous homologous series of substituted aromatics. Thus, we have identified in these samples benzenes substituted with 4 to 13 carbons, naph-

thalenes substituted with 0 - 9 carbons and diphenyls with 0 - 7 carbon atoms. These homologous series of substituted aromatics are common to crude oils and are not present in living organisms or in recent sediments. Again, this ties the hydrocarbons in the sediments at West Falmouth to the spilled oil.

4. Biologically and Pollution-Derived Hydrocarbons in a Core at Station 31:

Analyses of consecutive sections from a core taken at Station 31 in September 1971, two years after the spill, demonstrate particularly well the differences between pollutants and indigenous hydrocarbons and the persistence of their distinguishing features (Table III and Fig.5).

Chromatogram 'a' represents the uppermost inch of the core and agrees with the chromatograms from grab samples taken at the same station on and before September, 1971. The chromatogram shows the presence of partially degraded fuel oil; its boiling range still corresponds to that of the original oil. Within this boiling range, almost the entire straight chain hydrocarbon content has been depleted, presumably by biochemical processes. The large unresolved boiling point envelope is due to the presence of the many overlapping homologues and isomers, especially within the cyclic and aromatic hydrocarbons, which are characteristic of fossil fuels. Superimposed over this background are partially or fully resolved peaks; the most prominent ones are those of pristane, of phytane and of the homologous C_{18} isoprenoid, in order of decreasing amounts.

The secondary rise of the chromatographic envelope at carbon numbers above C_{25} in this and other highly polluted samples appears due, almost entirely, to column bleed. This is evident from chromatograms from the same

station run with relatively larger aliquots and at lesser recorder sensitivity. Thus, no such rise is evident in the chromatograms from Station 31 through August, 1971 (Figure 14).

Because of the rapid decrease in hydrocarbon content with depth, increasingly large aliquots of the total extracts of the deeper samples were chromatographed and a higher gas chromatographic recorder sensitivity was used; this explains the higher background, due to column bleed, in Figure 5 b, c and especially in d (Table III).

Chromatograms from the deeper section of the core (Figure 5c and d) show a picture that is typical for the indigenous hydrocarbons of recent marine sediments. The amounts of normal paraffins increase from n-heptadecane, whose presence is barely perceptible, to, and probably beyond, the analytical limit of the columns used here. Odd carbon-number paraffins predominate strongly; thus the C_{25} and C_{27} alkanes exceed the adjacent even carbon number homologues by a factor of five to six. (The conventional carbon preference index over the C_{20} to C_{32} range was not calculated because of the apparent mixed composition of some peaks). This odd carbon number predominance in the higher boiling paraffin range is characteristic of young marine sediments (Stevens et al., 1956), including those of Buzzards Bay (Clark and Blumer, 1967) and of plant waxes (reviewed by Clark, 1966); in crude oil it is found rarely and is much less pronounced. Chromatograms of the polluted sediments from West Falmouth within the first months after the spill show that no odd carbon predominance was present in the spilled fuel oil.

The paraffin concentration in the deeper section of the core increases steeply above C_{21} ; the boiling range of the fuel oil on the other hand lies below that. Numerous minor components are present, notably the principal low boiling peak just before n-heptadecane, possibly one of the $n-C_{17}$ olefins which are common in marine plants.

Below three inches depth this core apparently contains no, or only small amounts of fuel oil derived hydrocarbons. The principal arguments are:

1. The high odd carbon predominance which extends here throughout the entire boiling range of the sedimentary hydrocarbons. In the fuel oil, odd and even carbon number paraffins occur at comparable concentrations.
2. In this lower core section, hydrocarbons boiling above the fuel oil range predominate.
3. Pristane, the principal resolved component of the partly degraded fuel oil is a minor component of the lower core sections, if present at all.
4. The lower core sections, in contrast to the uppermost part, show no unresolved envelope in the boiling range of the fuel oil.
5. Within the fuel oil boiling range, the minor hydrocarbon peaks ("fingerprints") correlate poorly between the contaminated top and to the two bottom sections of the core.

The core sections from 1 - 3 inches (Figure 5b) shows mixed hydrocarbon derivation from recent biochemical sources and from fuel oil. It is intermediate also in terms of its hydrocarbon content (Table III). Again, the

principal arguments are:

1. Below C_{21} no strong odd carbon predominance is found and already $n-C_{22}$ is more abundant relative to the adjacent homologues than in the lower core sections. The presence of biologically derived hydrocarbons, on the other hand, is evident from the high odd carbon predominance above C_{22} .

2. Hydrocarbons within the fuel oil boiling range are more abundant here than in the lower core sections; also, they exceed in quantity the higher boiling biologically derived hydrocarbons.

3. Phytane from oil is a major component together with the adjacent C_{19} and C_{18} isoprenoids; as in the fuel oil, the pristane/phytane ratio is close to unity. In unpolluted sediments, pristane predominates.

4. This core section shows the unresolved hydrocarbon envelope which is characteristic of the fuel oil.

5. The correlation of the minor hydrocarbon peaks with those in the top section of the core and in the fuel oil is excellent.

The analyses show that fuel oil at Station 31 has penetrated the sediments only to approximately 3 inches. This suggests little if any sediment reworking by physical or biological agents. Greater penetration was found in the marshes. There, oil derived from the 1969 spill penetrated at least 5 feet below the surface (Blumer et al., 1970c). The greater penetration of the marsh sediments relative to those offshore is due to their greater permeability and to the fluctuations of the water table with tidal and weather cycles.

As in the marshes, bacterial degradation at Station 31 is slower below than at the surface. In view of the known slow rate of hydrocarbon degradation under anaerobic conditions, this is not unexpected.

The presence of less degraded oil just below the sediment surface has biological implications. In spite of the increasing degradation and gradual detoxification of the oil at the sediment surface, a reservoir of less degraded oil exists just below it. Even when the repopulation of the sediment surface becomes possible, burrowing organisms will still encounter a fresher oil at moderate depth.

Our routine offshore samples are collected with a grab which penetrates 4-6 inches of sediment. To obtain reproducible samples we retain only the uppermost inch of sediment for analysis. The agreement between the analyses of the uppermost core section and the grab samples at Station 31 demonstrates that remixing of the sediment does not occur during our routine sampling.

THE ENVIRONMENTAL ALTERATION OF SPILLED OIL ("WEATHERING")

Crude Oil or oil products spilled in nature are altered by evaporation, by dissolution and by bacterial and chemical attack. The gross effects of these four types of processes on the chemical composition of spilled oil can be predicted (Blumer et al., 1970d; Ehrhardt and Blumer, 1972). Conversely, the compositional changes in a spilled oil over an extended period of time can be interpreted in terms of the rates and of the processes that are active in the oil degradation. Thus, observations on spilled oil

samples can yield significant data on the environmental fate of oil; these would be difficult to gather in laboratory experiments.

The investigation at West Falmouth, now extends over more than two years. It provides the longest existing continuous series of observations on persistence and degradation of an oil under environmental conditions in a controlled area that had not been subjected to previous heavy oil pollution. Some of our analytical data will now be discussed in the light of the processes which affect the amounts and the composition of the oil in the polluted area:

1. Quantitative Changes in the Oil Content of the Sediments

The fuel oil in the bottom sediments at Station 31 still exceeds the indigenous hydrocarbon content by more than an order of magnitude, two years after the spill. Because of their high contamination level, these samples are well suited to a study of the quantitative trend in the pollution level.

The analyses (Fig. 1a and Table II) show, after an initial rise between September and October 1969, a stable oil content at Station 31 through December 1969. By March 1970, the oil content at that location had increased more than tenfold and, in spite of gradual degradation since then, it has remained above the 1969 level for two years. The rise in the oil content of the sediments at Station 31 during winter 1969/70 has been interpreted as the result of a heavy influx of undegraded oil from the same spill, most likely from the marshes and their aquifers.

After this event, the oil content at Station 31 decreased, rapidly at first and then more slowly. A cautious extrapolation of the trend at that station suggests that the fuel oil may remain above the detection level for at least another two years, and probably longer.

The quantitative hydrocarbon data alone do not permit deductions on the nature of the processes which are responsible for the depletion of the oil. However, the gas chromatograms (Blumer et al., 1970d) show that the rapid decrease in oil content of the sediments at Station 31 between March and May 1970, is not paralleled by similarly rapid changes in the chemical composition of the oil, which would result from dissolution or bacterial degradation. This suggests that the depletion of the oil in this initial stage is due primarily to release of unaltered oil in particulate form into the water column. Correspondingly, oil films were observed in the vicinity of this station for a considerable time after the spill (Blumer et al. 1969, that report contains an analysis of an oil film from Station 31; Blumer et al. 1970d).

The sediments of Buzzards Bay have a moderate total organic content (Clark and Blumer, 1967 quote a value of 1.1% for a sample taken outside the presently polluted area). Such sediments do not have a particularly great retentive capacity for hydrocarbons. Therefore, it is likely that the very heavy loading with fuel oil observed in March, 1970 (1.2% on dry weight basis) represents a supersaturation of the sediment with oil. At lower pollution levels, the oil can be expected to be retained more strongly by the organic and inorganic matrix of the sediment and depletion would then

result principally from the slower processes of dissolution and gradual biodegradation.

In Wild Harbor River, as at Station 31, the oil content exceeds considerably the level of the indigenous hydrocarbons. The scatter of the analytical data (Table II) is greater than at Station 31, probably because of the greater sediment inhomogeneity. Therefore, average data for River Stations II, IV and V were calculated (Fig.16), they show a similar trend of slowly decreasing oil content as offshore. Again, cautious extrapolation suggests that the oil will remain detectable for at least another two years. It is not clear, whether the apparent rise in oil content at Station IV, from September/October 1969 to December, 1969/April 1970 represents a redistribution of oil within the Wild Harbor River area or statistical scatter.

2. The Degradation of the Straight and Branched Chain Paraffins

Laboratory studies have shown that the degradation of normal paraffins by bacterial concentrates proceeds more rapidly than that of the corresponding branched isomers. Our field observations confirm this. In contrast to laboratory experiments which often show more rapid degradation, but which are difficult to interpret in terms of environmental events, our observations at West Falmouth provide a realistic time scale of the environmental persistence of different hydrocarbon types.

The ratio of n-heptadecane to pristane is a sensitive indicator of the incipient stages of bacterial degradation, at least as long as the multi-branched hydrocarbons (e.g. pristane) are not attacked (Blumer et al., 1970c).

This ratio ($n\text{-C}_{17}/P$) remained nearly constant at Station 31 during the first three months after the spill. (Fig.2). In contrast, at the less heavily polluted Stations 7 and 20, this ratio decreased more rapidly, during the same period. This suggests that - at least in the marine samples - noticeable bacterial attack is delayed in areas where heavy oiling has taken place. By December 1969, a decrease of $n\text{-C}_{17}/P$ is noticed at Station 31 and the gas chromatograms show the decrease of all n -paraffin peaks relative to the adjacent branched chain compounds.

By March 1970, concurrent with the considerable increase in oil content at Station 31, $n\text{-C}_{17}/P$ reverted to its initial value. There are several observations that suggest very strongly that this rise in oil content and the reversal in the extent of biodegradation is the result of repollution with the same fuel oil. No biological processes are known that would produce this specific hydrocarbon mixture. No new large spill was observed in this area during winter, 1969/1970. The chromatograms before and after this event show exact agreement in boiling range, boiling point distribution, and in the distribution of the major and minor components ("fingerprints"). In addition, a reversal in the trend of the $n\text{-C}_{17}/P$ values was observed during that winter and early spring at stations more distant from shore (e.g. Stations 7 and 20). In combination, these data point to a general seaward movement of the oil from the 1969 spill during the first winter. We note that undegraded fuel oil was still present at some locations in the marshes at and below the surface by February 1970 (in April 1970, River Station V had a $n\text{-C}_{17}/P$ of 1.65). Thus, the marshes and their aquifers may represent a source for the oil influx to Station 31 in early 1970.

After this event, as after the initial pollution, the heptadecane to pristane ratio at Station 31 did not decrease drastically for several months. The more rapid loss of the straight chain paraffins at less polluted stations and the occurrence of a lag time at the heavily oiled Station 31 suggest possibly an induction phenomenon rather than one due to climatic conditions.

In spite of the rapid decrease in n-paraffin concentration during Spring and Summer 1970, small amounts of straight chain hydrocarbons have remained in the sediments during the entire two years for which observations are available now.

No such delay in the bacterial attack on the straight chain hydrocarbons is noted in the marshes. This may reflect the greater permeability, better aeration and the higher redox potential of the marsh sediments relative to the offshore sediments. As in the absolute hydrocarbon concentrations, a greater scatter is noted between successive measurements of the n-C₁₇/P ratio in marsh samples than offshore; again, this reflects the greater inhomogeneity of the marsh sediments.

The branched chain hydrocarbons are also attacked, though at a slower rate than their straight chain homologues. A comparison of analyses from Sediment Station 31 (e.g., December 1969 and August 1971) shows a marked decrease of the amplitude of the pristane and phytane peaks relative to the unresolved background envelope.

3. The Pristane-Phytane Ratio

Bacterial degradation and physical processes, such as evaporation and dissolution change the ratios between hydrocarbons of different structural

