

FOREWORD

Marine contamination by petroleum, whether by natural seepage or by spills from ships at sea, by accidents in harbour or at offshore installations or by atmospheric or terrigenous input is by no means a new or rare phenomenon. In recent years however, the problems have been highlighted not only by the increased utilisation and marine transport of oil but also by a number of spectacular accidents which have raised questions about possible effects on the ecosystem. A number of detailed studies have been carried out in an attempt to answer these questions. The demands for such knowledge have been further increased by the various questions raised as a result of expansion of offshore exploration and exploitation for oil, particularly in environments hostile to these operations, in regions as far apart as the northern North Sea and the coast of Alaska.

Consequently, diverse aspects of the problem are being studied in several parts of the world by chemists and biologists who are often asking the same questions but using different approaches and sometimes producing conflicting views. Against this background, it seemed timely therefore to bring together a group of scientists from university, industry and government, actively engaged in such work, to examine and discuss common problems relevant to petroleum hydrocarbon contamination of the marine ecosystem and so a Work-

shop was sponsored by the International Council for the Exploration of the Sea, and held in Scotland at Aberdeen in September 1975.

The Workshop considered methodology, occurrence and fate in the environment, and effects on the ecosystem of petroleum hydrocarbons in the sea. Most of the papers presented and updated where necessary, are brought together in the present volume together with an edited version of the recorded discussion that followed each session. Of necessity, the reportage of the discussion is very brief although the proportion of time available for discussion compared favourably with that set aside for formal presentation of the papers. In preparing the discussion reports, the editors were assisted in particular by Dr R. Hardy, Dr R. Johnston, Mr P. R. Mackie and Dr I. C. White, and by comments from several contributors.

No attempt was made to produce specific recommendations but a study of the papers in this volume does give a clear indication of several lines of research which must be followed up before an adequate understanding can be reached of the effects of petroleum in the sea and it is evident that widespread monitoring operations will be fully effective only when the basis of our knowledge has been thus extended.

A list of participants to the workshop may be found in Appendix I.

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HYDROCARBONS AND PETROLEUM IN THE MARINE ECOSYSTEM - A REVIEW

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Various aspects concerning the presence of petroleum in the marine ecosystem are discussed. It is clear from a review of the literature that there is no simple method of determining accurately the amount of petroleum in the ecosystem, especially in the open seas where the concentrations are low. The subsequent fate of the petroleum components is not known although studies have shown that they may be removed or converted into other components by physical, chemical and biological (biochemical) means. Nevertheless, the amounts of petroleum compounds present in the environment appear to exceed the estimated annual input by several orders of magnitude. This may be a reflection of the size of other non-petroleum inputs, erroneous calculations of the size of the petroleum input and/or a greater stability of the petroleum-like components in the ecosystem. The effects caused by petroleum vary not only with the composition and concentration of the petroleum but also with the interacting component. Such effects can be observed most readily where large spillages have occurred. At lower input levels, especially at concentrations found in the open sea, the effects caused by the various petroleum components are not well known and merit a more detailed study.

INTRODUCTION

This brief review is intended primarily to provide some guidelines and background information for the ICES Workshop, "Petroleum hydrocarbons in the Marine Environment", and considers input, methodology, occurrence, fate and effects of hydrocarbons in the marine ecosystem.

INPUT

Estimates on the quantities of petroleum and petroleum-like compounds that have been and are being introduced into the marine environment vary quite markedly (Zobell, 1963; Blumer, 1970; MIT SCEP, 1970; Jeffrey, 1971; NAS, 1975) as does the size of the various individual source inputs; thus the NAS report estimates the aeolian input to be 6×10^5 tonnes/annum whereas the MIT SCEP report gives a figure of 9×10^6 tonnes/annum. Whatever the actual total input from all sources is, it is almost certainly very large, probably between 10^6 and 10^7 tonnes/annum, but estimates such as these can be misleading in that the emphasis is placed on the quantity of the input rather than its quality. Thus it may be argued that the aromatic hydrocarbons released from electrode wastes (Palmork et al., 1973), oils from coking plants (Zitko and Tibbo, 1971) and from the pyrolysis of municipal wastes (Gerstle and Kemnitz, 1967) are of far more concern than less toxic petroleum inputs.

Concern over the large input of petroleum is not new. In 1922 the US Congress requested the President

to convene an international conference on preventing oil pollution. Since that time fossil fuel utilization has increased manyfold and public concern has grown primarily because the effects of oil pollution are often visible, e.g. in the fouling of beaches and the frequent catastrophic effects on seabirds. In addition to these phenomena, scientists have been concerned with the less obvious but possibly more worrying aspects concerning the introduction of petroleum components, namely their accumulation in the environment and their effects both on the biomass and man's enjoyment of fish as food (Blumer, 1970; Evans and Rice, 1974; Sutterlin, 1974).

METHODOLOGY

SAMPLING AND ANALYSIS

The methodology used depends on the amount of oil present. Where the amounts are considerable (i.e. visible) the techniques of obtaining and isolating the oil are relatively simple and, indeed, several methods have been proposed for the remote assessment of oil slicks (Horvath et al., 1971; Wright and Wright, 1973). At lower levels one encounters a number of problems not least of which is the difficulty in preventing contamination (Blumer, 1970; Mackie et al., 1974), and it is for this reason that sampling devices made of plastic, with the possible exception of teflon, should not be used if they are to be washed or extracted with a solvent (Farrington et al., 1972).

Because of the variable density of petroleum or petro-

leum aggregates in the sea, it is desirable in estimating its presence to sample the surface, the water column and the sediment. Replicate samples should be taken (Ahmed, 1974) and, if storage is essential, then they should be either frozen (Zsolnay, 1973) or stored in the presence of a bactericide (IMCO, 1972; Mackie et al., 1974). A number of devices have been described and used for sampling the sea surface such as stainless steel screens (Garrett, 1965), teflon discs (Miger et al., 1974), filter paper (Edeline, 1964), plastic sponges (Chang and Jadamec, 1974) and stainless steel buckets to act as scoops (Carlberg, 1975). Collection of floating particulate matter is usually carried out with the aid of a neuston net (Morris, 1971; McGowan et al., 1974).

Water sampling presents few problems except at depths in excess of 20 m but care must be taken to prevent adventitious contamination (Mackie et al., 1974).

In open sea conditions, sediment sampling poses a number of problems especially in sampling the surface layer. Where the depths are not too great, divers can be used to obtain cores. At greater depths, however, mechanical devices operated from the ship have to be used thus incurring a greater likelihood of contaminating the sample. Particular care must be taken not to disturb both the sedimentary layers especially in samples where the sedimentation rates are low, and the flocculent surface sediment which might provide the most recent evidence of input.

In the collection of the biota it is often difficult to prevent surface contamination and it is recommended that where possible the samples should be skinned prior to analysis and, if storage is essential, then this should be carried out by freezing and holding at -30°C .

The methods used to extract the samples vary according to the amount of pollutant present, whether the sample is solid or liquid and finally on the subsequent analytical method that is to be used. Where pollutant levels are high, isolation of the oil by mechanical methods, e.g. centrifugation, offers many advantages. The oil is removed comparatively intact without the introduction of solvent, simplifying preparative procedures and permitting the analysis of low molecular weight components if desired (IMCO, 1972). When concentrations are low, e.g. samples obtained from unpolluted areas, some form of extraction and concentration must be used. Thus, gas-purging systems have been used for the isolation of low molecular weight compounds in sea water samples (Swinnerton and Linnenbom, 1967). Higher molecular weight compounds are normally extracted with either pentane, if the sample is to be analysed by gas liquid chromatography (GLC), or carbon tetrachloride if it is intended to use fluorescence methods (Keizer and Gordon,

1973). Such solvent systems are not efficient extractants for solid samples and it is better to use the solvents and techniques employed in tissue lipid analysis (e.g. Bligh and Dyer, 1959).

The complex and variable nature of petroleum prevents its accurate determination in all but a few well defined instances. Instead, it is usual to determine the concentration of a component or class of components and from this an estimate of the amount of petroleum present is made. This is a comparatively easy task when large amounts of petroleum are present in the sample and a wide variety of methods can be used not only to determine the amounts present but also to provide information on the source, e.g. GLC, Zafiriou et al. (1972); Zafiriou (1973a); fluorescence spectroscopy, Keizer and Gordon (1973); heavy metal analysis, Stuart and Branch (1970).

At low concentrations freedom of choice of method is restricted usually to the determination of the concentration of the major or most readily identifiable components of petroleum, such as the various hydrocarbon classes. This is unfortunate because single parameter measurements such as these are more difficult to interpret in that the relationship between their presence and that of petroleum cannot be extrapolated in a simple manner (Hardy et al., 1977).

The methods most commonly used can be sub-divided broadly into those that analyse for a specific function, e.g. IR, Carlberg (1975); UV, Lijinsky (1960); isotope ratio, Miller (1975), Zafiriou (1973b); fluorescence, Levy (1971) and those that rely on the identification and quantization of individual components, e.g. chromatography, Schaad (1970); GLC, Blumer (1970), Swinnerton and Linnenbom (1967); GLC/fluorescence spectroscopy, Freed and Faulkner (1972); GLC/MS, Giger and Blumer (1974).

The specific function methods are often very sensitive, requiring little additional work-up after extraction, and are often suitable for shipboard analyses. They are, however, subject to error. The assumption has to be made that the parameter being measured is due to the pollutant and is not a natural product of the ecosystem, e.g. the IR method detects both biogenic and petroleum hydrocarbons. To a lesser degree, this is true also of the analyses of single components. However, these measurements may be more desirable in that, although they do not necessarily provide a better measure of petroleum, they can give an exact measure of the concentration of individual components, e.g. the measurement of the carcinogenic components in the aromatic hydrocarbon fraction (Giger and Blumer, 1974). Such measurements, however, require more complex analytical procedures and are thus more subject to adventitious contamination. They are also expensive in materials, equipment and labour.

The analytical methods used in petroleum pollution studies identify hydrocarbons in some form or other and, on the whole, the presence of other components has been neglected and therefore much of the ensuing discussion is concerned primarily with hydrocarbons.

OCCURRENCE

IN THE ENVIRONMENT - SURFACE

Although estimates have been made on the quantity of hydrocarbons that is present in the air, little factual information has been published either on the aeolian hydrocarbon level over or input into the sea (Farrington, 1973; Duce et al., 1974; NAS, 1975; McAuliffe, 1973).

In the open sea or in areas where oil slicks are absent, the hydrocarbons present in the sea-surface have been studied by examining both the particulate oil concentration and the composition of the surface film and sea-surface layer. The particulate oil studies, which are unusual in the sense that the concentrations can be determined by gravimetric methods (Butler et al., 1973), have shown that these particles are widely distributed, often concentrating in the windrows produced by Langmuir surface currents (Sleater et al., 1974). Compositional studies indicate that they are introduced into the sea during the washing operations of the ballast tanks of tankers and the fuel tanks of ships and it has been estimated that there is about 7×10^5 tonnes present in the global marine environment (Brunnock et al., 1968; Butler et al., 1973).

Similar studies have been carried out on the hydrocarbon content and composition of the surface film and sea-surface layer. It is difficult to compare the results of the different groups since some are quoted in $\mu\text{g}/\text{unit area}$ (Mackie et al., 1974) and others in $\mu\text{g}/\text{unit volume}$ (Wade and Quinn, 1975; Gordon et al., 1974; Carlberg, 1977). The methods of sample collection and analysis are also quite different. In surface film measurements (Hardy et al., 1977) the *n*-alkane levels (C_{15} — C_{33}) were found to be within the range 20 to 160 $\mu\text{g}/\text{m}^2$. The values were not markedly different between areas where input was thought to be high and those where it was believed to be low. There was also no tendency for the values to decrease with increasing distance from the land. This latter observation is in agreement with analyses made on samples obtained off the Texas coast (GURC, 1974) but it is not in agreement with the findings of Quinn and Wade (1972). It is perhaps to be expected that the actual values obtained by the different groups vary widely, from 1.27 mg/100 g (GURC report, 1974) through 1.0 mg/litre (Simonov and Justchak, 1972), to 20.4 $\mu\text{g}/\text{litre}$ (Gordon et al., 1974). The two higher values could only have arisen from the introduction of particulate oil into the

sample, sampling an area covered with a film of oil or some other form of heavy contamination.

The lower levels quoted for surface film and surface layers would not give rise to a monolayer and, if integrated over the global marine surface, indicate a total petroleum content of 2×10^4 tonnes (Gordon et al., 1973) or an *n*-alkane level of 7 to 60×10^3 tonnes (Hardy et al., 1977). These estimated levels are relatively insignificant when compared with the figures for the particulate oil content of the marine environment. When spectro-fluorimetric methods were used in the analyses it was felt that the spectra obtained could be related directly to those of petroleum oil (Gordon et al., 1974; Levy, 1971). This was not the case in the *n*-alkane analyses which showed *n*-alkane patterns which were not typical of crude oil or its derivatives. It is not known whether this is indicative of a non-petroleum input or of physico-chemical/biochemical weathering.

WATER

A number of studies have been carried out on the levels of petroleum or hydrocarbons in the sea. As with the determinations carried out on the surface layer, the relationship between the levels and distribution of the hydrocarbons and the presence of petroleum is not always clear. Solubility studies on petroleum in sea water show that a surprising amount appears to dissolve (Freearde et al., 1971) especially when compared with the measured solubilities of alkanes in water (Klevens, 1950; Bell, 1973). This dissolution, in which the hydrocarbons are probably present in a particulate or micellar form, is related directly to the relative amounts of oil and water present, and degree of turbulence but inversely related to the temperature (Boehm and Quinn, 1973; Gordon et al., 1973). Except in close proximity to oil spills, the actual amounts present in the open sea rarely attain the high levels observed in the laboratory.

Low molecular weight alkanes have been measured in inshore waters and the levels were shown to increase near industrial sites ($\times 10^3$) and oil rigs where levels of 3.4×10^{-4} g of ethane/litre of water have been measured (Sackett et al., 1972; Brooks and Sackett, 1973; Sackett and Brooks, 1974). In general, the values measured ranged from 0.2 to 10 $\mu\text{g}/\text{litre}$.

Although a wide variety of methods are used in analyses for less volatile components, most methods incorporate a filtration stage to remove particulate material. Such filtration undoubtedly introduces errors (Peake and Hodgson, 1966) as does the transfer of samples from one vessel to another (Mackie et al., 1977). With the exception of the Mediterranean and Baltic Sea, the majority of the values obtained, albeit for alkanes, petroleum or aromatic hydrocarbons, lie within the range of 1 to 10 $\mu\text{g}/\text{litre}$ (NAS, 1975; Gordon et al., 1974; Hardy et al., 1977). Some authors

have noted a trend for the values to increase near the surface (Corner et al., 1975; Monaghan, 1973) and others have found higher levels in inshore waters than in the open sea (Jeffrey, 1966; Parker et al., 1972), although there is a report of this effect being reversed (Hardy et al., 1977). Detailed analysis of the hydrocarbon classes is not usual but Barbier et al. (1973) have shown the following distribution between the different hydrocarbons; normal and branched alkanes 51.5%, monocyclic naphthenes 5.5%, bicyclic naphthenes 9.5%, tricyclic aromatics 3.5%, polycyclic aromatics 2.5%. It is interesting to note that although the alkane levels found by Barbier et al. (1973) are higher than those observed by Hardy et al. (1977), the compositions are remarkably similar with the envelopes showing a maximum at the C₂₆ to C₂₈ alkanes. Thus, although the hydrocarbon classes showed a remarkable similarity to petroleum, the alkane fraction was not similar. This may indicate either an alternate input (naturally occurring hydrocarbons were identified by both groups) or reflect weathering by physicochemical/biochemical mechanisms.

Far more interest has been shown in the presence of the aromatic compounds in the sea, primarily one feels because of their carcinogenic properties and the availability of sensitive techniques that permit their estimation and, by extrapolation, that of petroleum (NAS, 1975; Keizer and Gordon, 1973). Although qualitative and quantitative analysis of individual components was not attempted in the majority of studies, several groups have done this at least in part (reviews by Andelman and Suess, 1970; Suess, 1972; Corner et al., 1976; Harrison et al., 1975). The source of the components is not attributable always to either a petroleum input or, indeed, man's activities (Andelman and Suess, 1970). Many of the hydrocarbons, especially the polynuclear aromatic hydrocarbons, are rapidly degraded by photochemical and auto-oxidative reactions (Andelman and Suess, 1970), suggesting that the input must be considerable to maintain the concentration. Depending upon the figures selected (1 to 10 µg/litre), the estimated amount of alkane/aromatic hydrocarbons/petroleum in oceanic waters lies between 1.4×10^9 and 1.4×10^{10} tonnes, assuming uniform distribution and a world oceanic volume of 1.4×10^{21} litres (Garrett, 1971).

SEDIMENT

The presence of hydrocarbons in the sediments is of interest to geochemists as well as ecologists and marine chemists and, as such, has received considerable attention (Meinschein, 1969; Degens, 1969; Andelman and Suess, 1970). The levels vary enormously from as low as 0.15 mg of *n*-alkanes/kg dry sediment (Hardy et al., 1977), through 0 to 4 mg of oil/kg dry sediment in very deep water (NAS, 1975) to over 1 g oil/kg in polluted

inshore waters (NAS, 1975). Assuming the deep sea water measurements are more representative of open sea conditions, then the amount of "petroleum" present in the top 1 cm layer of the ocean bottom is of the order of 5×10^6 tons. The alkane composition of these sediments except at certain inshore sites (Farrington and Quinn, 1973; Cooper et al., 1974) shows a marked odd carbon atom predominance (Meinschein, 1969; Clark, 1966; Whittle et al., 1974a) and superficially would not appear to be derived from petroleum. It must be realised, however, that although recent sediments are young in geological time they may be old in historical time, thus the effect of recent hydrocarbon deposition would be diluted out except where it is very large. The suppression of the odd carbon atom predominance in recent sediments has been used as an indicator of pollution from land based sources (Cooper et al., 1974) or of oil contamination (Blumer and Sass, 1972; Tissier and Oudin, 1973).

Summaries of the results of studies on sediment aromatic hydrocarbons are presented in the review papers of Andelman and Suess (1970), NBS (1974) and Harrison et al. (1975). Of particular interest in many of the studies quoted was the benzo[*a*]pyrene levels which sometimes were of the order of 1 mg/kg dry sediment. A number of sources of aromatic hydrocarbons have been suggested in the reviews and Jensen et al. (1975) have identified several relatively new inputs.

IN THE BIOTA

With the exception of marine bacteria, hydrocarbon analyses have been carried out on a wide range of marine organisms.

Considerable quantities of hydrocarbon were present in analyses of plankton, 10 mg alkanes/100 g wet weight (Mackie et al., 1974), but the major component was pristane. Laboratory studies have shown that these organisms contain a range of alkanes and alkenes (Lee and Loeblich, 1971; Oro et al., 1967; Youngblood and Blumer, 1973; Murray et al., 1977) although there are also some indications that they can concentrate them from the medium (Lee, 1975; Murray et al., 1977). It would seem therefore that although parts of the hydrocarbon envelope of wild plankton are of endogenous origin other parts may not be (Murray et al., 1977). Aromatic hydrocarbons have been found also in plankton and although the indications are that they are abiogenic in nature this is not absolutely certain (Andelman and Suess, 1970; Zobell, 1971).

Hydrocarbon levels in marine macro-organisms have been collated and published in a number of reports (Zobell, 1971; NBS, 1974; NAS, 1975; Mackie et al., 1974; Whittle et al., 1977). As with all the other analyses, intercomparison of the results is often difficult. There are indications that the levels present increase

with the levels in the environment (Lee et al., 1972; Ehrhardt, 1972; Howard and Fazio, 1969; Cahnmann and Kuratsune, 1957; Fossato and Siviero, 1974). This has not been observed, however, in all studies (Morris, 1972; Whittle et al., 1977). Perhaps it is to be expected that the alkanes are found in the highest concentration in lipid rich tissues and that the composition of planktonivorous species resembles that of their feed (Corner et al., 1976). This was not observed in cod. In many instances there were marked differences between the alkanes of the liver which have a pronounced odd carbon predominance and those of the muscle which have a relatively smooth hydrocarbon profile in the C₂₆ to C₂₈ region (Mackie et al., 1974; Whittle et al., 1974a; Whittle et al., 1977). None of the profiles resemble crude oil, the muscle *n*-alkanes being more akin to those found in the plankton and water and the liver components resembling those found in the sediment.

The aromatic hydrocarbons are found in greatest concentration in fish caught near highly industrialised coastal areas (Zobell, 1971); in some of the analyses benzo[*a*]pyrene levels as high as 400 µg/kg dry weight tissue were measured.

Estimates of the biomass of the marine environment vary and there are variations in the hydrocarbon levels of the biota. Thus, we have found it difficult to estimate the total amount of hydrocarbons in the biomass. However, Button (quoted by Koons and Monaghan, 1973) has postulated that there is 10⁷ tons present. If we accept this figure and the various other estimates we have made earlier, it would seem that the amounts present in the ecosystem greatly exceed the estimated petroleum input perhaps by three orders of magnitude.

It has been known for some time that petroleum can give rise to taints in fish (Deshimaru, 1971; Howgate et al., 1977). The components that confer the taints are possibly organo-sulphur compounds (Motohiro, 1962); higher molecular weight sulphur compounds are preferentially concentrated in the marine environment and it has been suggested that they can be more definitive of an oil source than the corresponding hydrocarbon fingerprint (Warner, 1975).

In many of the analyses on the ecosystem no direct relationship could be found between the components identified and petroleum. It has been suggested that specific and unique petroleum constituents such as phytane can be used as an indicator of its presence. This may be so but it is essential to establish that the compound is, first of all, unique. It is doubtful whether the measurement of any individual component will provide a quantitative measure of the input, or indeed of its presence, unless a considerable amount of information is known of the dynamics of the system. The same arguments would also apply to the proposed use of indicator organisms (Goldberg, 1975).

If petroleum pollution studies are to continue then it is essential to bring about some standardisation of methods. This has been attempted in part but the number of analysts involved was small and perhaps insufficient information was available on how and what analyses should be carried out (NBS report, 1974).

FATE

A number of reviews have been published on the fate of petroleum in the marine ecosystem (Zobell, 1963; Nelson-Smith, 1970; Jeffrey, 1971; Texas A and M, 1972; Corner, 1975; Anderson et al., 1974(a); Burwood and Speers, 1974).

If the assessments of the relative size of the inputs are correct (NAS, 1975), then the greater proportion of petroleum is introduced into the ocean either as a relatively thin film or as floating or suspended particles. Of course, some oil, as in tanker accidents and bilge and fuel tank clearing operations, does enter the sea "en masse". When this happens the oil spreads and becomes emulsified at a rate which is controlled by the density, viscosity and temperature of the oil as well as the interfacial tension (Otto, 1972; Hoult, 1972). In these various forms petroleum is dissipated or degraded by a number of interacting and competing processes that can be classified broadly into two types; those that redistribute the material and those that degrade it.

The most rapid of the redistributive processes are undoubtedly those of evaporation and dissolution but the extent to which these occur will depend upon the nature of the input, i.e. whether it is a gasoline fraction, a crude oil or a lubricating oil (Cochran et al., 1974) as well as climatic conditions. The action of the wind, the formation of sea-spray aerosols, the vertical mixing of the water by Langmuir circulation at the windrows and, perhaps to a lesser extent, the movement of the water are also important in this context (Otto, 1972; Garrett, 1971). During these processes it is considered that other particulate matter can adhere to the oil or vice versa thus increasing the density and causing the oil to sink (Beyaert, 1975). Living organisms can be involved in this latter process either by their accretion on the surface of the oil particle (Butler et al., 1973) or by ingestion of these and subsequent evacuation with the faecal material (Conover, 1971).

The role of degradative processes in which the chemical nature of the petroleum is changed is still a controversial subject. Thus, although it has been shown in the laboratory and in certain field trials that photo-oxidation (Feldman, 1973; Freegarde et al., 1971), microbial oxidation (Traxler, 1975; Rashid, 1974; Hughes and McKenzie, 1975; Floodgate, 1972), absorption, ingestion and metabolism by other marine

biota (Corner et al., 1976) can occur and in some cases very rapidly, it is not known to what extent this happens in the open sea (Berridge et al., 1968; Bridie and Bos, 1971; Floodgate, 1972; Blumer et al., 1973). There is some evidence that such processes degrade materials like beach tar, tar balls, and sedimented oil very slowly (Rashid, 1974; Butler et al., 1973).

Chemical degradation is a complex process in which various oxidative reactions occur sometimes assisted by heavy metals (Feldman, 1973; Burwood and Speers, 1974). It is postulated that the primary products are hydroperoxides which can initiate further reactions such as polymerisations or may degrade to give a wide variety of oxygenated products. Such products may assist solubilisation of the oil or alternatively make it even less soluble (Burwood and Speers, 1974; Pilpel, 1970).

The utilisation of oil by bacteria has been the subject of intensive study primarily because of the potential use of the process for the production of food. In the marine environment organisms are present which can metabolise oil albeit in low concentrations in the open sea (Mulkins-Philips and Stewart, 1974). Introduction of oil, especially in the presence of nutrients (Gibbs, 1975) and oxygen (Hughes and McKenzie, 1975), tends to increase the number of the organisms and the rate of metabolism of the oil. Given time it appears that bacteria can convert crude oil into metabolic products but they tend to utilise the lower *n*-alkanes up to C₂₀ most rapidly (Gatellier et al., 1973; Gibbs, 1975). The initial site of attack is usually via the oxidation of the terminal methyl group although methylene group oxidation does occasionally occur (Raymond et al., 1971).

In common with terrestrial plants and animals, marine biota can synthesise aliphatic hydrocarbons (Clark, 1966). The extent to which this explains their presence in the ecosystem is not known but there is evidence that many organisms can adsorb and/or absorb such components from their environment or food (Hardy et al., 1974). Such accretion is often very selective with little or no concentration along the food chain.

Subsequent catabolism of the aliphatic hydrocarbons in the biota has not received detailed study (Corner et al., 1976; Lee et al., 1972). There is a little more information concerning the catabolism of polynuclear aromatic hydrocarbons. It seems to parallel mammalian mechanisms to give a variety of hydroxy compounds and their conjugated derivatives (Corner et al., 1973; Corner, 1975; Corner et al., 1976).

As in the analytical work, there is a noticeable lack of information concerning the fate of the non-hydrocarbon components of oil even though they can be present in relatively large amounts (Jobson et al., 1972). Almost certainly some of these compounds induce tainting and it may be that many other compo-

nents of the oil pervade the ecosystem. Toxicity studies should help to identify the important substances of special concern. Appropriate measurements can then be made on the ecosystem to determine their concentration and possible effects.

It is interesting to note that each of the degradative processes seem to work best on complementary fractions of the hydrocarbons. Thus chemical oxidation works most effectively on branched chain alicyclic and higher aromatics. Bacteria, preferentially metabolise the lower *n*-alkanes and aromatics, and the biota tend to remove, and presumably metabolise, the long chain *n*-alkanes most readily.

EFFECTS

Petroleum oil is possibly the most universal, visually apparent pollutant of the marine environment and perhaps because of this more attention has been given to the effects produced when large amounts are present. Under these conditions it is aesthetically offensive, fouling fishing gear, detracting from the amenity value of beaches and the seashore, and causing immense damage to sea birds. Some of the immediate secondary effects of this are the cost of "clean-up" operations and the fall in value of the marine harvest. Oily layers on the surface of the sea can reduce the transmission of light and the diffusion of oxygen (Garrett, 1971) and might act as a concentrating medium for non-polar toxic materials (Corner et al., 1976). Light transmission is also reduced when there are high concentrations of oil in the water column (Lacaze, 1974) and, under such conditions, organisms can be entrapped and smothered. This latter effect is particularly noticeable on the sea bottom (Mayo et al., 1974; Spooner, 1975) into which the oil may diffuse (Nelson-Smith, 1972).

The toxicity of petroleum oils in the marine environment depends not only on the composition of the oils (Anderson et al., 1974(b)) but also upon whether the spillage occurs, either in the open sea, where the effects, at least in the water column, often appear to be minimal (Strachan, 1972) or in more sheltered areas where the effects can be more marked or even catastrophic (Spooner, 1974).

Marine bacteria are affected by oil. Thus, oil utilizing organisms multiply (Hughes and McKenzie, 1975; Atlas and Bartha, 1973) but other, less adaptive organisms decline in numbers (Walker et al., 1974). Marked, although not uniform, effects have been observed on plankton, eggs and larvae (Corner et al., 1976). Thus, some of these organisms appear to be relatively indifferent to the presence of oil whereas others show high mortality even at relatively low oil concentrations. This is true of the benthic community also; in this group the larger organisms seem more able to

withstand percentile concentrations of oil in the sediment (Howgate et al., 1977). There is a lack of information on the effects of petroleum on fish but it has been shown that mortality can be high amongst fish that have strong territorial claims (Spooner, 1975). Although petroleum induced acute toxicity is rare or has gone unnoticed in migratory fish, they are known to assimilate components of the oil. The long term effects of this have not been elucidated although evidence has been presented that the higher alkanes, a petroleum component that is not normally associated with toxic effects, are deposited in the neural tissues (Anderson et al., 1974a). There is little evidence that petroleum hydrocarbons are concentrated along the marine food chain and it thus appears unlikely that constituents, harmful to man, are concentrated in this manner (Whittle et al., 1974b). However, some species are able to assimilate from the environment relatively large amounts of polynuclear aromatic hydrocarbons and this is of some concern in human nutrition (Sullivan, 1974).

The effects of oil on shore life and estuaries has been the subject of detailed study by the oil pollution group at Orielson and they have shown that a number of deleterious changes are brought about especially in salt marshes (Baker et al., 1977).

The effects alluded to so far have been concerned mainly with large, concentrated inputs of petroleum. Unfortunately, there are few data on low level inputs. This is somewhat surprising since the estimates show that this is how most petroleum enters the marine environment. Perhaps this is justifiable if one accepts the argument that petroleum components have always been present and that the biota have thus developed the facility to tolerate low level inputs. Such a hypothesis requires proof and the work on chemoreception and sex pheromone communication (Kittredge et al., 1974), tainting (US Dept of Interior, 1973) and the toxic effects on eggs and larvae (Anderson et al., 1974b; Kühnhold, 1974) would seem to oppose such a view.

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