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 Workshop 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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EFFECT OF SURFACE FILMS ON GAS EXCHANGE ACROSS THE AIR–SEA INTERFACE

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By using a two-layer model of the air-sea interface, it is argued that the possible effect of surface films in modifying gas exchange across the interface should be much greater for gases whose transfer is controlled by processes in the gas phase (H_2O, SO_2, NO_2), than for those whose exchange is under liquid phase control (N_2, O_2, CO_2 and the inert gases). However, unless the film material is close packed into a coherent monolayer or consists of a thick multi-layer, significant transfer retardation is unlikely for gases of either type.

INTRODUCTION

In considering the possible effects of natural and artificial surface films in modifying gas exchange across the air-sea interface, it is useful to divide such effects into two types. There are what can be termed "direct (or static)" effects in which the film contributes an additional barrier, over and above those which exist when no film is present, to the passage of gas molecules across the interface. "Indirect (or dynamic)" effects are those in which the film alters the interface in such a way that factors affecting gas exchange are altered in magnitude. An example of such an indirect effect is the damping of wind-induced capillary waves, which promote gas exchange, where the water surface is covered by a thick film of oil. However, even in the absence of wind and hence capillary waves, such films can still substantially reduce the rate at which water evaporates from the surface; this being an example of the static role of films. In this case the oil film presents a direct diffusion barrier to water molecules moving between the liquid and gaseous phases.

This paper will be concerned mainly with direct effects of films, although two possible indirect effects will also be discussed, albeit briefly. Such a balance seems inevitable since, as far as the air-sea interface is concerned, considerably greater effort has been devoted to the study of direct rather than indirect effects.

DIRECT (STATIC) EFFECTS

These depend on: (i) the physico-chemical properties (solubility, chemical reactivity in the aqueous phase) of the gas, (ii) the chemical nature and properties of the surface film.

PHYSICO-CHEMICAL PROPERTIES OF THE GAS

These are adequately handled by use of a two-layer model of the interface. The model, first proposed by Whitman (1923), has found great utility in chemical engineering systems. In it the bulk of the phases on both sides of the interface are considered to be well mixed by turbulent processes. In each phase, the region close to the interface is thought of as a stagnant laminar layer through which gas transfer is by molecular processes only; the laminar layer constituting the principle barrier (resistance) to exchange. Although physically somewhat unrealistic, predictions based on such laminar layer models do not appear to differ appreciably from those derived from more sophisticated (and mathematically more complex) models (Danckwerts, 1970). Liss and Slater (1974) have applied the model to gas exchange at the air-sea interface and calculate the flux of the following gases across the interface: SO_2, N_2O, CO, CH_4, CCl_4, CCl_3F, MeI, $(Me)_2S$. When applied to most gas-liquid systems, including the air-sea interface, for any particular gas the resistance of one or other of the two interfacial layers tends to predominate. For gases which are sparingly soluble in water (e.g. N_2, O_2, CO_2 and the inert gases) the resistance of the laminar layer in the liquid phase is much greater than the equivalent resistance presented by the gas phase, so that exchange of such gases is under liquid phase control (Liss, 1973). In contrast, for very soluble gases (e.g. H_2O, SO_2, NO_2) which often show marked chemical reactivity in the aqueous phase, the gas phase laminar layer is all important and exchange is controlled by processes in the air (Liss, 1971; Liss and Slater, 1974).

The above discussion of the two-layer model has been

restricted to gas-liquid systems with no impurities/contaminants (surface active molecules, oil films, etc.) at the interface. In trying to assess the possible effects of such surface material on interfacial gas exchange, it is helpful to consider gases whose exchange is under gas and liquid phase control as two separate groups.

GASES WHOSE EXCHANGE IS UNDER GAS PHASE CONTROL

The most important gas in this class is water vapour. In considering the evaporation of water molecules from a clean surface it is usually argued that the air immediately in contact with the aqueous surface is saturated with water vapour. Exchange between this saturated air and the free atmosphere is then by diffusional processes in the gas phase. Hence, for a contaminant free interface, liquid phase resistance may be ignored for water vapour (Whitney and Vivian, 1949).

The presence of a continuous film of surface active material or oil will add a liquid phase component to the existing gas phase resistance, and very substantial decreases in evaporation rates would be expected in these circumstances. Such reduction in evaporation has been substantiated in various laboratory studies (e.g. Jarvis et al, 1962; Frenkiel, 1965; La Mer and Healy, 1965; Garrett, 1971). As pointed out by Jarvis et al (1962), if the film is a monolayer then the molecules must be linear and capable of close packing in a compressed film in order to be effective. The presence of double bonds, ionised polar groups, or branching of the hydrocarbon chain greatly reduces the ability of the film to reduce evaporation. The presence of 1 % of non-linear impurities in the monolayer can lower its ability to reduce evaporation by 90—99 % (La Mer, 1962).

GASES WHOSE EXCHANGE IS UNDER LIQUID
PHASE CONTROL

Here the resistance to gas transfer is normally envisaged as being caused by diffusional processes in the water close to the interface (Kanwisher, 1963). The effect of contaminants at the water surface will be to add an additional aqueous phase diffusion resistance to the one naturally occurring at the surface of the liquid. Moderate decreases in the rate of gas exchange might be expected provided that the impurity forms a continuous layer at the interface. Such effects have been demonstrated for a number of gases in laboratory experiments using a variety of surface active substances, e.g. long chain fatty acids, alcohols and detergents (Downing et al, 1957; Hawke and Alexander, 1962; Mancy and Okun, 1965; Boyd and Marchello, 1966; Sada and Himmelblau, 1967). A number of workers have noted that an appreciable decrease in the gas exchange rate is observed only under regimes of moderate

stirring of the liquid phase (Mancy and Okun, 1965; Downing, 1962). Under calm conditions the natural resistance of the aqueous phase masks any effect of the contaminant film. With very turbulent mixing the surface film is broken up and transfer is dominated by the vigorous stirring of the liquid phase. Hawke and Alexander (1962) and Garrett (1972) have pointed out that the film must be in a close-packed condition in order to offer any appreciable resistance to passage of gas.

Support for the idea that films have little or no effect on transfer of gases whose exchange is under liquid phase control comes from field experiments carried out by Kinsey (1973). He used a fenced off area in a small coastal coral reef to examine the effect of oil films of thicknesses between 0·1 and 0·7 mm on exchange of O_2 and CO_2 across the interface. It was found that the films produced a calming effect of the water surface, but no significant interference with interfacial transfer of either gas, other than that directly attributable to the calming effect.

NATURE OF FILMS AT THE SEA SURFACE

Surface tension

The surface tension of clean sea water is approximately 75×10^{-3} N m^{-1} at a salinity of 35 ‰ and a temperature of 10°C. The presence of surface films will lower the surface tension, the magnitude of the decrease being equal to the pressure exerted by the film. Thus measurements of surface tension will yield values for the film pressure and hence give some indication of the physical nature of the film.

The most widely used method for measuring surface tensions at the sea surface is the spreading drop technique devised by Adam (1937). Lumby and Folkard (1956) measured surface tension depressions in Monaco Bay which were consistently between 2 and 3×10^{-3} N m^{-1} in ruffled water, but in slick covered water, values sometimes exceeded 22×10^{-3} N m^{-1}. These very high film pressures are thought to result from input of land-derived material rather than from natural marine surface film. For highly productive areas of the Sargasso Sea, Sieburth and Conover (1965) found film pressures from less than 1 to just over 3×10^{-3} N m^{-1}; values in rippled water were somewhat less than those in slick covered regions. From measurements on a slick in Chesapeake Bay, Garrett (1965) found film pressures in the range $3—12 \times 10^{-3}$ N m^{-1}, with an average value within the slick of 5×10^{-3} N m^{-1}. Sturdy and Fischer (1966) measured surface tensions in and around kelp beds just off the Californian coast. Outside the area of the kelp beds surface tensions were near 70×10^{-3} N m^{-1} but decreased to between 50 and 60×10^{-3} N m^{-1} directly over the beds. The most comprehensive measure-

ments of film pressures using the spreading drop technique are those reported by Barger et al (1974). They made over 170 measurements of surface tension over a period of 9 days at a station 0·7 miles offshore from Mission Beach, San Diego. More than 150 of the observations were in clean water, and nearly all of these indicated film pressures of 1×10^{-3} N m^{-1} or less. Where visible slicks were present film pressures were higher, the greatest value recorded being 23×10^{-3} N m^{-1}.

All the film pressure observations reported in this section have been made in coastal waters or other areas of high biological production. Even under these conditions film pressures in excess of 1×10^{-3} N m^{-1} are uncommon, except in the presence of visible slicks. Although there are no measurements from typical open ocean situations, it would appear that film pressures in such areas are likely to be considerably less than 1×10^{-3} N m^{-1}. In order to obtain data to confirm this conclusion it will be necessary to devise a method of measuring *in situ* film pressures (under all sea states, if possible) with a sensitivity greater than that obtainable with the spreading drop technique (1×10^{-3} N m^{-1}).

Force-area behaviour

Another technique for examining film material from the sea surface is to measure its force-area behaviour. This is done by spreading some of the film material onto a tray of water in the laboratory. The tray is equipped with a movable barrier, which can be used to compress (or expand) the film, and an instrument for measuring the film pressure.

Barger et al (1974) have performed experiments of this type on material collected from the top few hundred microns of the sea just offshore from San Diego, California. The results show that considerable compression of the film must take place before there is any dramatic increase in film pressure. The low slope of the force-area curve at high film areas probably represents a squeezing out of the less surface active molecules as the film is compressed. As this takes place the concentration of surface active molecules increases until they form a close packed layer. Once this point has been reached, further decrease in area leads to a very rapid increase in film pressure. This change in behaviour occurs when the film pressure is approximately 1×10^{-3} N m^{-1}. The fact that surface material has to be considerably compressed in order to form a coherent film implies that in the samples examined by Barger et al (1974) there was insufficient material to form such a film. This conclusion is supported by the results of laboratory studies conducted by Jarvis (1967) on the rate of formation of films on samples collected from the Bay of Panama. He concluded that most samples contained insufficient surface active material to form a

close packed film, except when the molecules are compressed under the action of light winds or convergences of surface water.

Organic chemical composition of natural and anthropogenic films at the sea surface

The organic chemical composition of films from open ocean areas has been reviewed by Liss (1975). From the detailed work of Garrett (1967a) it appears that chloroform extracts of surface film material contain free and combined fatty acids (some of which are unsaturated) having from 11 to 22 carbon atoms, as well as a variety of higher aliphatic alcohols. Quinn and Wade (1972) have shown that surface samples from Narragansett Bay, New York Bight and the North Atlantic contain hydrocarbons, although at concentrations considerably lower than those of the fatty acids.

It has been argued (Liss, 1975) that techniques involving chloroform extraction determine, at most, 25 % of the total organic matter dissolved in sea surface samples. The composition of the remaining material ($> 75 \%$) is unknown, but MacIntyre (1974) cites evidence which indicates that glycoproteins and polysaccharides are the dominant dissolved components very close to the interface.

As indicated above, our knowledge of the organic chemistry of the sea surface is rather poor. However, it is very apparent that the organic material has a very mixed nature, consisting of a wide range of chemical compounds. Similarly, as Garrett (1972) has pointed out, the mixed chemical nature of petroleum products (Posthuma, this volume p. 7—16) means that such anthropogenic inputs will bring a whole range of compounds to the sea surface.

ABILITY OF SURFACE FILMS TO AFFECT GAS EXCHANGE

Earlier in the text it has been argued that in order to reduce rates of evaporation and gas exchange across the air-sea interface, the near surface organic molecules must be close packed in a compressed film. The following lines of evidence point to the conclusion that such films do not occur naturally over most of the open ocean or in many nearshore areas: (a) the mixed chemical nature of the organic compounds found at the sea surface is not conducive to their close packing into a coherent film: (b) force-area plots indicate that natural sea surface films require considerable compression in order to achieve a film pressure of 1×10^{-3} N m^{-1}, which appears to be that required for close packing: (c) surface tension measurements in open waters show that *in situ* film pressures are generally less than this critical value.

However, there are areas where the situation is not so clearcut. In regions of high biological production

surface tension depressions of greater than 1×10^{-3} N m^{-1} have been observed (page 121) and monomolecular films of petroleum products will exist in the vicinity of oil spills and also, possibly, shipping lanes. In these situations film pressures are such that it can be argued that evaporation and gas exchange could be retarded. A major question is whether the film, although compressed, has such a mixed chemical nature that there are sufficient "holes" in it so that passage of gas molecules is not impeded to any substantial degree.

Garrett (1972) has discussed the possible role of thick multilayer films, caused by major release of hydrocarbons into the marine environment, in retarding evaporation and gas exchange. It has been shown in the laboratory that in such situations evaporation rates can be substantially lowered, although at sea the effect will be reduced because the film is subject to bacterial and photochemical degradation, loss of lighter fractions by evaporation, as well as the dispersive effects of wind, waves and tides. Because of such processes it is argued that the coverage of the sea surface by oil is unlikely to be sufficiently complete for any major depletion of dissolved oxygen to be apparent.

Garrett's analysis is in agreement with the argument presented earlier in this paper, i.e. that if there are situations in which films interfere with gas transfer across the sea surface, then the magnitude of the effect should be substantially greater for gases whose exchange is under gas rather than liquid phase control.

INDIRECT (DYNAMIC) EFFECTS

The presence of capillary waves (wavelength $< 1\cdot7$ cm) appears important in bringing about gas exchange across water surfaces, at least for gases whose exchange is controlled by processes in the liquid phase (MacIntyre, 1971). It has been shown by Garrett and Bultman (1963) and Garrett (1967b) that in order for surface films to damp out capillary waves the film pressure needs to be in the region of 1×10^{-3} N m^{-1}, or more. As discussed previously this is the pressure at which the films seem to achieve a close-packed condition. Thus, where capillary waves are damped out by the surface film, the possibility exists for interfacial gas exchange to be affected by both direct and indirect effects. Films having sufficient pressure to damp capillary waves give rise to a change in light reflection properties of the water, such areas being known as "slicks". The presence or absence of slicks on the sea surface would thus seem to be a very sensitive indicator of conditions in which retardation of evaporation and gas exchange can potentially become important.

A second possible indirect effect arises from the suggestion of Quinn and Otto (1971) that evaporative cooling of a water surface and consequent convective mixing in the liquid laminar layer promote gas exchange across the interface. The presence of a film, sufficiently coherent to substantially affect the rate of evaporation, would lead to a diminution of such convective mixing and hence to a decrease in the rate of gas exchange.

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