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IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP
Joint Group of Experts on the Scientific Aspects
of Marine Environmental Protection (GESAMP)

THE SEA-SURFACE MICROLAYER AND ITS ROLE IN GLOBAL CHANGE

GESAMP REPORTS AND STUDIES No.59

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WMO
Geneva, 1995

NOTES

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FOREWORD

1. The present report was prepared by the GESAMP Working Group No. 34 on the Sea-Surface Microlayer established by the XXIIIrd session of GESAMP in April, 1993 with the following terms of reference:

   To prepare a report on current understanding of the physics, chemistry and biology of the sea-surface microlayer with particular reference to its role in global environmental change and as a marine habitat, including:

   - a review of physical processes in the microlayer and their relation to changes in heat, momentum and mass exchange;
   - a critical assessment of interaction of the biology and chemistry (including radiochemistry) in the microlayer including references to the effects on living marine resources;
   - a quantitative consideration of the effects of the sea-surface microlayer on air-sea exchange of gases;
   - an assessment of the effects of solar radiation and photochemical reactions on the chemistry and biology of the microlayer, and
   - an evaluation of existing and potential new techniques for investigating the surface layer of the ocean.

2. The WMO has been nominated as the lead agency for the Working Group which was co-sponsored also by UNEP, IMO, IOC, and IAEA.

3. The meeting of Working Group 34 was held in the form of a workshop from 20-24 February, 1994 at the Alton Jones Campus of the University of Rhode Island, RI, USA. The first version of the report developed during and after the meeting was submitted to GESAMP for discussion and consideration at its 24th session (New York, 21-25 March 1994). GESAMP agreed that a core group of WG34 should meet in summer 1994 to complete and revise the report taking into account the comments made by GESAMP.

4. The second draft of the report was considered at the 25th session of GESAMP (Rome, 24-28 April 1995) which revised and then adopted the Executive Summary and agreed that the report on the sea-surface microlayer and its role in global change be published as GESAMP Reports and Studies No. 59.

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EXECUTIVE SUMMARY

Concern has been expressed in international fora that the relative importance of the sea-surface microlayer may have been underestimated, both as a site of adverse biological effects and as a medium for the transfer of energy and material between the sea and the atmosphere. This review was prepared to provide a contemporary perspective regarding scientific understanding of the nature, properties and role of the sea-surface microlayer, with particular emphasis on its relative importance in the contexts of marine environmental protection and global change. The body of the report is in three parts (see Table of Contents):

- The physical nature of the microlayer and processes of air-sea exchange of trace gases;
- The chemical and biological nature of the microlayer and associated effects of chemical and radiative change; and
- The photochemistry of the microlayer and its role in radiation energy transfer.

Each part of the report contains conclusions specific to each of these subject areas. This summary presents the conclusions of the overall review in the context of marine environmental protection.

The sea surface of the ocean comprises a series of sublayers. These include a thin surface nanolayer ($< \sim 1\,\mu m$) enriched in surface-active compounds; the surface microlayer ($< \sim 1000\,\mu m$) containing high densities of particles and microorganisms; and the surface millilayer ($< \sim 10$ mm) inhabited by small animals and the eggs and larvae of fish and invertebrates. The sea-surface microlayer is operationally defined in this report as the uppermost $\sim 1000\,\mu m$ (1 mm) of the ocean surface. It, together with an overlying atmospheric layer of thickness 50-500 μm, constitutes the boundary layer between the ocean and atmosphere.

Natural surface-active substances (surfactants) are often enriched in the sea surface compared to subsurface water. These include amino acids, proteins, fatty acids, lipids, phenols, and a variety of other organic compounds. The biota of the underlying water column are the primary source of such naturally-derived organic materials. Plankton produce dissolved compounds as part of their metabolic processes. Air bubbles, rising through the water column, scavenge such chemicals and bring them to the surface. In addition, as plankton die and disintegrate some particles and many of the breakdown products (e.g., oils, fats and proteins) are either buoyant or are actively transported to the surface.

The accumulation of natural organic chemicals modifies the physical and optical properties of the sea surface. Thin organic films, invisible to the naked eye, are ubiquitous in aquatic systems. These films become concentrated in areas of physical convergence (e.g., at fronts). Under light and moderate wind conditions, areas of accumulated film dampen small (capillary) waves and become visible as 'surface slicks'. Strong surface tension forces exist in these films creating a boundary region where turbulent mixing is attenuated.

There is increasing evidence for the importance of surface films in the transfer of mass, heat and momentum across the air-sea interface. The viscoelastic modulus (a measure of surface tension) appears to be the most relevant variable to characterize the ability of films to modulate such transfers. The present global distribution of surfactants capable of affecting exchange processes is largely unknown, as are factors controlling future distributions. In relatively uncontaminated areas it is reasonable to assume that marine biological productivity will be the dominant source and provide a good first order estimate of the extent of films.

Material accumulated in the sea-surface microlayer is ejected into the atmosphere in an enriched form as part of the sea-salt aerosol produced by bursting bubbles. This provides a mechanism for the selective transfer of materials to terrestrial environments. Documented examples of such aerosol transport from sea-surface microlayers include bacteria, viruses, 'red

-tide' dinoflagellates and artificial radionuclides. In addition, production of these sea-salt aerosols provides an important mechanism for charge separation and electrification of the atmosphere.

As might be anticipated, lipophilic organic compounds of anthropogenic origin introduced by way of atmospheric transport or aqueous and particulate runoff should be enriched in the sea-surface microlayer. While this enrichment has been observed in some coastal environments, it has not been confirmed by reliable measurements made in the open ocean environment. Many studies of dissolved trace elements in the microlayer are now considered unreliable because of sample contamination. In particular, there are no reliable measurements for open ocean microlayers. Recent evidence from contaminated coastal areas suggests that trace metal enrichments are generally less than a factor of 10 rather than the several orders of magnitude reported in older literature. This is consistent with the strong likelihood that trace metals are passively enriched in the microlayer through association with surface-active organic matter.

The degree to which contaminants in the microlayer cause adverse biological effects depends on two factors - chemical exposures of organisms with time and the toxicities of the chemicals involved. The importance of biological effects in the microlayer in relation to effects in the entire water column and surficial sediments is related to the degree to which organisms are dependent on residence in the microlayer for part, or all, of their life-cycles. Virtually all information on the chemical and biological characteristics of the sea-surface microlayer pertains to coastal environments where the concentrations of contaminants in the water column and microlayer are expected to be enriched. It appears that particle-reactive and/or lipophilic substances, notably tributyl tin and some other organic chemicals having relatively high toxicity, probably do cause adverse effects on microlayer organisms in some contaminated coastal waters, particularly semi-enclosed basins and harbours. The environmental significance of these effects (which remain to be demonstrated by *in situ* studies) is largely unknown and should be assessed in the context of concomitant ecological hazards associated with the same contaminants occurring in the underlying water column and sedimentary environments. Whether toxic effects on neuston occur in offshore oceanic microlayers remains unknown.

A prognosis regarding the overall significance of microlayer enrichment would require, first, an identification of organisms inherently dependent upon the microlayer as habitat for portions of their life-stages, and, second, the concentrations and forms (and therefore bioavailability) of the chemical agents involved. Chemical studies would require state-of-the-art contamination-free sampling and analytical capabilities that are presently only available to a few research groups. As already stated, biological effects would need to be placed in the context of analogous effects of the same chemicals throughout the water column and sediments. At present, the ecological significance of anthropogenically induced change within the microlayer, relative to changes in other components of the marine environment, is a matter of speculation.

Available evidence suggests that photochemical processes in the microlayer may not differ substantially from those in the near-surface bulk waters. Assuming the presence of a 50 μm thick microlayer that is enriched in light-absorbing biological pigments by a factor of two relative to the underlying water, it is concluded that the fluxes of reactive intermediates appear to be too small to affect significantly the transfer of reactive species across the air-sea interface. Further, the flux resulting from photochemical production of gases from within the microlayer is insignificant in relation to the total flux originating from the water column and sediments.

There remains a number of outstanding deficiencies in contemporary scientific understanding of the sea-surface microlayer. These include the importance of the 'cool skin effect' for the exchange of gases such as CO_2 and the role of bubbles as a medium for gas exchange. Specific concerns in this latter context are the exchange properties of dirty versus clean bubbles and the role of carbonic anhydrase in enhancing CO_2 uptake at the ocean surface.

1. INTRODUCTION

The sea-surface microlayer has often been operationally defined as roughly the top 1 to 1000 micrometers of the ocean surface. There has been considerable new research on this area over the past 5-10 years. The microlayer is known to concentrate many chemical substances, particularly those that are surface active, and many organisms live and/or find food there. It is obviously the interface through which all gaseous and particulate material must pass when exchanging between the ocean and the atmosphere. It also plays a vital role in the transfer of various forms of energy (momentum, heat) between the two media.

It is now recognized that important physical, chemical, and biological processes near the air-sea interface are not restricted to what has been traditionally referred to as the "microlayer", but rather occur over gradients of varying thickness. Above the interface is an atmospheric boundary layer of 50-500 μm, where atmospheric turbulence is much reduced. Below the air/water interface the aquatic surface layer contains a series of sublayers. As defined by Hardy and Word (1986), these sublayers include the thin surface nanolayer ($< \sim 1$ μm), enriched in surface-active compounds; the surface microlayer ($< \sim 1000\,\mu$m), with high densities of particles and microorganisms; and the surface millilayer ($< \sim 10$ mm), inhabited primarily by small animals and the eggs and larvae of fish and invertebrates. The upper meter of the ocean supports a very diverse and abundant assemblage of the early life stages of commercially and ecologically important species. For purposes of this report, we have used the term "microlayer" in its operational meaning to refer to roughly the uppermost millimeter, where properties are most altered relative to deeper waters. We also utilize the following terminology throughout the report. A film refers to a surfactant-influenced surface and a slick refers to a visibly surfactant-influenced surface. The viscous sub-layer is roughly the top 1000 μm of the water surface. The thermal sub-layer is approximately the top 300 μm of the water surface, while the diffusion sub-layer refers to the top 50 μm.

Natural surface-active substances are often enriched in the sea surface compared to subsurface water. Amino acids, proteins, fatty acids, lipids, phenols, and a great variety of other organic compounds collect on the surface. The biota of the water column below are the source for most of the enrichment of natural (non-pollutant) chemicals. Plankton produce dissolved compounds as products of their metabolism. Air bubbles, rising through the water column, scavenge these organic materials and bring them to the surface. Also, as plankton die and disintegrate some particles and many of the breakdown products (oils, fats, and proteins, etc) float or are transported by active processes to the surface.

The accumulation of natural organic chemicals modifies the physical and optical properties of the sea surface. Thin organic films, invisible to the naked eye, are ubiquitous in aquatic systems. In areas where currents converge, films become more concentrated. Under light to moderate wind conditions, areas of accumulated film dampen small waves and become visible as "surface slicks". Strong surface tension forces exist, creating a boundary region where turbulent mixing is much reduced.

Of particular concern are processes occurring at the sea-surface microlayer that either affect or are affected by global change. For example, growing population and industrialization have resulted in increasing atmospheric transport of pollutant materials over the ocean. Atmospheric deposition of this material and of naturally occurring substances represents an important source of inorganic and organic chemicals to the sea-surface microlayer. Many of these substances are surface active and contribute to increased concentrations in the surface microlayer and could result in increasing incidence of coherent films or slicks as well as the concentration of some dissolved surface active substances at the ocean surface in both coastal and open ocean regions. High concentrations of toxic chemicals are also often found in the surface microlayer compared to the subsurface bulkwater in coastal environments.

Global decreases in stratospheric ozone resulting from CFC and halon releases have led to increased levels of solar ultraviolet-B (UV-B) radiation (280 to 315 nm) reaching the earth's surface. Because of the long residence times of different CFC compounds in the atmosphere (8 to 380 years), stratospheric ozone depletion and increases in UV-B radiation are expected to continue well into the 21st century.

These changes or potential changes have raised several important and interrelated questions concerning global marine impacts, including:

a) Could continuing or increased deposition of toxic chemicals and surface active agents, and/or increased UV-B radiation alter either physically or biologically mediated fluxes of radiatively active and atmospheric chemically important trace gases between the atmosphere and ocean and vice versa?

b) What is the likely impact of chemical enrichment of the sea surface, along with increased UV-B radiation, on the health of biological communities inhabiting the sea surface, including the egg and larval stages of many commercially important fish species?

To adequately address these and related issues we must address and review our understanding of the fundamental physical, chemical and biological processes in the surface of the ocean that may affect or be affected by global change. Much new information has been generated recently about the chemical composition and structure of the surface layer and the types and rates of reactions occurring there (particularly photochemical reactions, but not explicitly in the surface microlayer). This new information provides an important foundation on which to base an understanding of the importance of this issue. However, there are many processes which may be of global importance, but for which we still have incomplete or virtually no information. In addition, there has been no comprehensive review of our understanding of the surface microlayer for almost a decade. This lack of a comprehensive evaluation of the surface microlayer, its potential future changes, and the impact of this important region on global change processes were the primary motivation for the meeting of the GESAMP Working Group No. 34 held in the form of a Workshop on The Sea-Surface Microlayer and its Potential Role in Global Change on the W. Alton Jones Campus of the University of Rhode Island in the United States from 20-24 February 1994. The list of the participants in the preparation of this report is given in Annex I. The workshop itself was organized through working groups addressing three major issues:

1. Physical processes in the microlayer and their relation to changes in heat, momentum, and mass exchange, with particular emphasis on air-sea gas exchange.

2. Biological effects of chemical and radiative change in the microlayer.

3. Effects of solar radiation and photochemical reactions on the chemistry of the microlayer.

The following report is based primarily on the reports of those three working groups. Thirteen review papers on many aspects of the issues above were prepared by some of the participants. These papers as well as the reports of the three working groups will be published by Cambridge University Press as the peer-reviewed book The Sea Surface and Global Change in 1996.

2. PHYSICAL PROCESSES IN THE MICROLAYER AND THE AIR-SEA EXCHANGE OF TRACE GASES

2.1 Surface Films

Sources, sinks, and properties of surface films

Sea-surface films are derived from multiple sources, both in the sea and on land. The low concentrations of degraded natural biopolymeric and geopolymeric materials in the sea potentially contribute to surface accumulations of organic matter even in oligotrophic waters. Specific inputs during phytoplankton blooms and from neuston indigenous to the microlayer also contribute to the enrichment of surface-active matter at the interface. Terrestrial sources include both natural and anthropogenic contributions. Terrestrial plant-derived materials are either directly released to the atmosphere and introduced via dry and wet deposition, or enter the ocean environment via riverine inputs as decay products of vegetation. Anthropogenic contributions include point sources related to industrial processes, agricultural runoff, and spills of petroleum products (catastrophic and chronic). In addition, municipal wastewater discharges are frequently highly enriched in surfactants which enter coastal seas and sediments. In shallow coastal environments, resuspension of sediments and release of sediment pore water materials is another potential source of surfactants.

The relative importance of these sources is not known. The single largest source of surfactants is thought to be production by autochthonous marine organisms, principally phytoplankton, which exude natural surfactants as metabolic byproducts (Zutic et al., 1981). Excretion products of many types of marine phytoplankton include complex β-glucans and heteropolysaccharides of high molecular weight (Allan et al., 1972; Ramus, 1972; Smestad et al., 1975; Percival et al., 1980; Mykelstad, 1974; Mykelstad et al., 1982) and are frequently found in surface waters during blooms (Sukagawa and Handa, 1985a, 1985b). Most macromolecular materials exhibit some degree of surface activity (Leenheer, 1985). Although quite soluble, some of these polysaccharides are likely to be conjugated to hydrophobic moieties sufficient to make them at least weakly surface active. Proteins and lipids are also present in phytoplankton exudates but are generally less abundant than carbohydrates (Hellebust, 1974). However, their contribution to the surface physical properties of microlayer films may be disproportionately large, despite their low concentration levels (Van Vleet and Williams, 1983).

In addition, surface-active materials are contributed by the breakdown of dead organisms. The intermediate and end products of subsequent chemical and microbiological transformations are likely to include a variety of compounds whose molecular structures contain hydrophobic and hydrophilic moieties. Zutic et al. (1981) suggested that a large proportion of the surfactants produced in plankton cultures are secondary products of excretion rather than high molecular weight metabolic end products. These materials may result from rapid degradation by bacteria and extracellular enzymes. Another possible production pathway is condensation of relatively low molecular weight exudates to surface-active macromolecular structures (Nissenbaum, 1974). Phytoplankton exudates are thought to be components of humic materials (Rashid, 1985; Gillam and Wilson, 1985) that are known to be surface active.

Surfactants are concentrated at the air-sea interface over broad areas of the ocean by a number of physical processes including diffusion, turbulent mixing, scavenging and transport by bubbles and buoyant particles. Direct atmospheric deposition is also likely to contribute to films over broad areas and will be relatively more important at long distances from terrestrial sources. Convergent circulations driven by wind, tidal forces, current shear, upwelling and internal waves lead to localized concentrations of surface-active materials on various spatial scales, ranging from features a few meters (i.e., internal waves, current shear zones) to kilometers (i.e., large-scale eddies) in size.

Organized surfactant films, representing high surface concentrations of organic material, are prevalent on only a small fraction of the global oceans. Based on measurements of surface tension reduction (surface pressure) in the open ocean, surface concentrations of surfactants are quite low. This may not be an accurate reflection of their importance in modulating wave spectra or gas transfer since natural surfactants have been shown in the laboratory to exhibit substantial dynamic elasticities. It is this quantity that is relevant in controlling dynamical processes related to surface tangential straining of the ocean surface. Recent laboratory studies have demonstrated that natural surfactants reduce gas transfer at low surface pressures and surface concentrations (Goldman et al., 1988; Frew et al., 1990).

The composition and concentration of the surfactant films at the surface of the ocean are subject to dynamic changes. Various biological, chemical and physical processes lead to alteration of film chemical composition, surface physical properties, surface concentration and spatial distributions. The chemical composition of microlayer films is believed to be controlled mainly by source contributions, but may also be modified by physical processes (Bock and Frew, 1993).

Due to the complex mix of components, the composition and molecular arrangement of microlayer films can vary in response to physical forcing. Such films are capable of undergoing relaxation processes on a variety of timescales that lead to a surface physical response that is not purely elastic (van den Tempel and Lucassen-Reynders, 1983; Lucassen-Reynders, 1986). Instead, the film-influenced water surface will exhibit a complex stress-strain relation in response to compression and dilation (Bock and Frew, 1993). This response is quantified by the dilational viscoelastic modulus, a complex number that is useful in deriving dynamical relations at the air-sea interface (Levich, 1962; Hansen and Mann, 1964; Lucassen-Reynders and Lucassen, 1969; Bock and Mann, 1989; Fernandez et al., 1992). This modulus is determined by chemical composition and concentration, and by relaxation processes. These relaxations take place as the result of shift of the local surface composition away from equilibrium, and include adsorption, desorption, micelle and solid phase formation, and molecular reorientation. In the case of surfactants with appreciable solubility in the bulk phase, the surfactant is capable of diffusional exchange between the interface and bulk phase. For these molecules, the dilational viscosity may be appreciable. Surfactant films comprising many different molecular species, when subject to long-time compression, relax differentially by the desorption of the more soluble species. The remaining film materials (the more hydrophobic ones) dominate viscoelastic response and generally exhibit enhanced damping capabilities (Bock and Frew, 1993).

As with the source terms, only general statements can be made concerning the sink terms leading to dissipation of surface films. Sink terms that represent loss of material at the surface include microbial degradation, photooxidation, micellization, or loss due to adsorption onto particulates. Some estimates of microbial turnover rates for amino acids have been reported (Williams et al., 1986). Photooxidation effects can be estimated for coloured organic matter in the microlayer and are discussed in section 4 of this report. However, overall residence times of material in the surface microlayer are still poorly understood because of the lack of knowledge about the magnitude of the source and sink terms.

Surface films and gas exchange

Surfactant films are effective in reducing the amplitude of short (capillary, ~1cm wavelength) waves. Wind waves, the result of wind stress, are thought to be generated in a rather limited range of frequencies (Hasselmann, 1960, 1962, 1963a, 1963b; Hasselmann and Hasselmann, 1985), and nonlinear interactions and dissipative mechanisms redistribute wave energy into the resultant wave spectrum. The interaction between surfactants at the ocean surface and the wind stress results in the existence of a critical wind speed, below which waves either do not form or grow at a small rate. In the absence of surfactants, in carefully controlled laboratory conditions, waves have been observed to grow at wind speeds as low as 0.5 m s^{-1}. When surfactants are introduced into these clean systems, a critical wind speed is established. Figure 2.1 shows the mean square slope (a measure of waviness) as a function of wind speed. In the response of the surface to the onset of waves for the systems containing 0.03 ppm and 1.0 ppm concentrations of a water soluble surfactant, an abrupt knee demonstrates the existence of a critical wind speed. For wind speeds below this critical value, waves increase at a very low rate in response to wind. Above this speed, waves increase more rapidly, but do not attain the same level as they did in the case of a clean surface (at least not in the range of these experiments). Measurements of the transfer velocity (the term which quantifies the kinetics of air-sea gas transfer) indicate that it too is lower than for the clean water case. It appears that the presence of surfactant produces an energy barrier to the formation of a robust wind-wave field.

On the ocean, variability in the wind field makes assessment of the situation more difficult. However, qualitative observations have been made that are consistent with the laboratory results. At low wind speeds, slicked areas are prevalent, particularly in coastal areas where biological productivity is high. As winds increase, these slicks rapidly become developing waves, often at wind speeds of ~3-4 m s^{-1}. It is suspected that this speed represents the critical wind speed. In this respect, the natural ocean appears to behave similarly to samples tested in tank studies. As the wind continues to increase, wave breaking begins and whitecaps form. It is unclear what is happening to the surfactant material at the surface under these conditions, since mechanical continuity of the surface is broken in areas of plunging waves. More insoluble components may interact to produce micelles that are transported away from the surface, but very soluble components (already in solution and capable of readsorption) may rapidly reestablish the surface enrichment and a finite viscoelasticity. The bubble plumes generated by breaking waves may act as scavengers for the more soluble surfactants and help to promote their transport to the surface. Owing to these mechanisms of film renewal, it is likely that the more soluble components continue to influence gas exchange rates at wind speeds above the critical wind speed, as in the laboratory studies.

Surface films and bulk material

The material found in the sea-surface microlayer has properties which indicate that it contains only a small percentage of highly surface active material, such as straight chain lipids. The majority appears to be less surface active, with the molecules having both water soluble and surface-active groups arranged on convoluted polymeric chains. In this it is structurally similar to much of the organic material found in bulk seawater. There is certain to be continuous interchange of this material between the microlayer and bulk, under the action of turbulent mixing processes induced by wind, waves, currents, bubbles and tides. Support for this concept comes from the finding that if the surface material is removed, then the microlayer is reformed by material coming to the surface from the bulk. The speed of the renewal process is dependent on the degree of mixing in the water; the timescale being a few hours for stagnant conditions but a matter of minutes when the water is bubbled. In view of the existence in the bulk of material similar to that found near the surface, care needs to be exercised in interpreting results obtained from microlayer samplers which come into contact with subsurface water as well as microlayer material.

Extent and viscoelastic properties of surface films

The extent of surface films on the ocean is difficult to quantify. Observations from space, in the form of the now well known Sculley-Power photographs (Scully-Power, 1986), have shown the wide-spread occurrence of filamentous and eddy-like structures representing differences in roughness of the ocean surface. These structures are believed to be slicked zones that result from local convergence areas that pack surfactants to concentrations large enough to suppress waves, making areas of the ocean reflect light specularly (i.e., as if they were perfectly smooth). This effect was once considered to be restricted to areas in which oil production is high, and a direct result of seepage and production losses. The observation of these phenomena in areas like the New York Bight renewed interest in natural slicks and revitalized research in the surface chemistry of the world's oceans (e.g., Sea Surface Microlayer issue of J. Geophys. Res. 97:C4, (1992)). No evidence exists that organized structures are common in open ocean environments, but the conclusions reached above, that soluble surfactants quickly reestablish at the air-sea interface, suggest this possibility.

The probable range of the viscoelastic moduli on the ocean surface is between zero (for a clean, surfactant-free surface) and 50 mN m^{-1} (milliNewtons per meter). In visible slicks, spreading pressures can range from a few mN m^{-1} to tens of mN m^{-1}. In these cases, moduli can reach their highest values, but because of the relation between spreading pressure and viscoelastic modulus, higher pressure does not necessarily cause higher viscoelasticity. Large moduli (based on laboratory measurements and estimates obtained by Lombardini et al. (1989)) have values not exceeding 50 mN m^{-1}. To contrast this, areas not visibly slicked can have spreading pressures of the order of a few tenths of a mN m^{-1}, yet the viscoelasticity may be large enough to significantly reduce waves and gas transfer. The probability that regions of the ocean can actually have zero viscoelasticity is extremely low. It can be argued that the observed values measured globally for dissolved organic carbon imply that sufficient source material is generally available to obtain a surfactant-influenced surface.

Presently, it is not known how long-term environmental changes will affect the concentration and composition of the global ocean surface. It is reasonable to assume that the prevalence of oceanic films will closely track biological productivity, since this is a large source term. It may prove that the extent of film coverage on the ocean is a sensitive measure of productivity, including global mass flux. Because of this, it may be beneficial to develop the remote sensing capabilities described later which use multiple band backscatter, along with ground truthing methodologies, to create an ocean surfactant monitoring capability. This should be a realistic long-term goal.

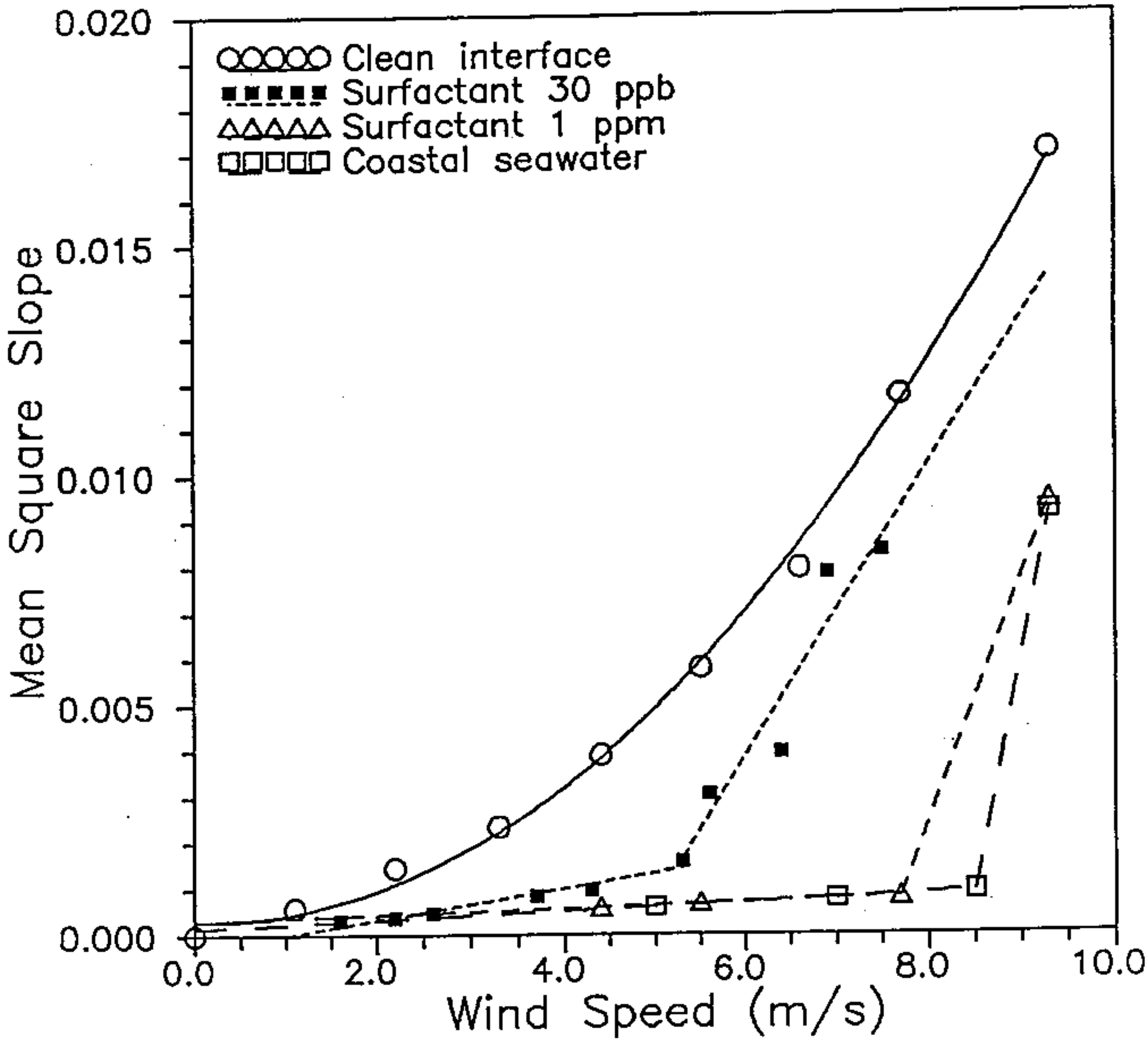

Figure 2.1 - Mean-square wave slope as a function of wind speed for clean and surfactant-influenced water surfaces (Frew, personal communication).

2.2 Physical Processes in the Microlayer

Comparison of surface renewal and boundary layer models of near-surface transfer

As the sea surface interface is approached, turbulence is damped. Within the diffusion sublayer, molecular transport dominates, while in the bulk of the water turbulence largely controls the transport. The concept of the viscous boundary layer explicitly describes the cooperation of molecular and turbulent transport in the transition between the two regimes, based on continuity arguments and observations. The surface renewal model assumes that at regular or irregular intervals parts of the surface layer is removed and replaced by water from the bulk. The significance of surface renewal can be seen by the exponent, n, of the Schmidt number (Sc, the ratio of viscosity to molecular diffusivity) in the equation for the transfer velocity (k). The value of n is -1/2 in the surface renewal model and -2/3 in the boundary layer model.

In wind/wave facilities, a clear correlation between the Schmidt number exponent and the mean square slope of the waves has been established (Jähne, 1985). With increasing mean square wave slope, the exponent gradually decreases from -2/3 to -1/2. However, no direct determination of the Schmidt number exponent from oceanic field experiments is available. For lakes Watson et al. (1991) showed that n = -1/2. For practical purposes, it has been widely assumed that n is -1/2 for moderate and higher wind speeds and -2/3 for low wind speeds. As the laboratory measurements indicate, this simple assumption might be wrong in the case of a surfactant-influenced surface, since n seems to be closely related to the presence of waves that are suppressed by surfactants. The uncertainty in n is most critical - up to a factor of about 2 (see later) for typical gases - if gas transfer rates are determined from measurements of heat transfer.

To eliminate this uncertainty, it is necessary to estimate the amount of surface renewal occurring in the oceanic surface microlayer. By dyeing the sea surface, Gemmrich and Hasse (1992) were able to identify certain types of surface streaming under natural conditions that would induce surface renewal. The uncertainty in n would also be eliminated if a satisfactory theory of gas exchange were available

Short capillary waves

One of the most striking phenomena observed in wind-wave facilities is the large enhancement of gas exchange with the onset of waves (Broecker et. al., 1978; Jähne et al., 1979; McCready and Hanratty, 1984; Jähne et al., 1984). Based on simple scale considerations, this effect was first attributed to short waves (Hasse and Liss, 1980; Coantic, 1986; Back and McCready, 1988). However, the experimental data from different wind/wave facilities taken by Jähne et al. (1987), do not support this hypothesis, but rather suggest that the gas exchange rate is better correlated to the mean square slope of the waves. Laboratory experiments from Frew (1996) show that this correlation still holds when various surfactants are present at the surface.

The strong correlation between mean square slope and the gas exchange rate is due to the fact that the mean square slope is a general measure of the nonlinearity, and thus instability, of the wave field. The detailed mechanisms are still not understood and require further detailed laboratory investigations, including simultaneous gas exchange, wave and turbulence measurements. Although there is no direct proof of the influence of waves on the air-sea gas exchange rate from direct field measurements, the effect manifests itself in the data indirectly. First, the field transfer velocities reach similar values at the same friction velocities as in wind-wave facilities. Such high transfer rates can only be brought into agreement with theoretical models if a higher turbulence level than for flow at a rough or smooth solid wall is assumed (Jähne, 1985). Second, the large variability of gas transfer rates found in the field is a clear indication that parameters other than the direct effect of waves are of importance. Variability of the wave field, which depends significantly on surface films and other parameters, is one possible explanation.

The relation between heat and mass transfer

Transfer of a gas such as CO_2 through the air-sea interface is affected by heat transfer in two distinct ways. First, the driving force for gas flux across the air layer adjacent to the surface contains a factor $\{(Q^*/RT)T'/T+P'/P\}$, where R is the ideal gas constant, T′ and P′ are the gradients of temperature and pressure across this air layer and Q* is the heat of transport of the gas. The need for the term involving Q* has been demonstrated for the wind-tunnel measurements of oxygen exchange by Liss et al. (1981). (In these calculations, the oxygen flux in the liquid was scaled to the total heat flux through the ratio of molecular and thermal diffusivities — another link between heat and matter transfer.) At a temperature of 290K, the factor Q*/RT varies from -2.2 for helium, through 4.0 for CO_2, to 14.2 for water vapour. The term involving Q* becomes important when Q*/RT is large and there is a significant temperature gradient at the interface. However, because over the majority of the oceans the difference between the bulk air and sea temperatures is generally small, this effect is invariably neglected by oceanographers.

The second way that mass transfer is affected by heat transfer is through the combined effect of the sensible, latent, and radiative heat fluxes on the surface temperature of the liquid. Matter transfer through the liquid layer immediately below the surface is controlled by the difference between the surface and bulk concentrations and by the liquid-phase diffusion coefficient, whose temperature dependence is small. The surface concentration is given by the product of the gas partial pressure adjacent to the surface and the gas solubility at the surface temperature. Further, correction of the air-sea flux of $CO_2$for change in its solubility caused by this skin temperature deviation appears large enough to be globally significant.

In common with almost all gases, CO_2 has a solubility which decreases with increasing temperature. For CO_2 at 20°C the solubility decreases by about 2.8% per degree. Typically, the surface p_{CO2} is about 35 Pa and the deviation of the skin temperature from the bulk temperature is of the order of -0.3°C, so surface p_{CO2} values have to be adjusted by $35 \times 0.028 \times -0.3 = -0.3$ Pa. If applied to the ocean p_{CO2} field globally, such a shift would be sufficient to increase the global air-to-sea flux by around 0.6 Gt (10^{15}g) C yr^{-1}, which is quite significant given that the global net flux is of the order of 2.0 Gt C yr^{-1}.

A recognition of this correction does not contribute directly to solving the 'missing carbon' problem: the accepted figure for ocean uptake of 2 Gt C is based on ocean model uptake and is not sensitive to measured values of air-sea CO_2 fluxes. However, it does help to explain why attempts to directly calculate the air-sea flux over the globe by integrating the gas transfer flux always give numbers which are low compared to these models (Tans et al., 1990). It is also important for identifying the distribution of sources and sinks of CO_2 in the ocean, which in turn is necessary in order to interpret correctly the distribution of atmospheric CO_2 measurements in terms of sources and sinks. This is currently the primary method for placing limits on the "missing carbon" problem and in particular for deducing the size of the enigmatic "land sink".

The importance of the skin temperature deviation for the global CO_2 budget has been pointed out by Robertson and Watson (1992), who made a more detailed spatial calculation of the effect using the parameterization of Hasse (1971) combined with monthly mean data on global heat fluxes and wind speeds. The largest changes to the air-sea flux were found at high latitudes in the winter season and in regions of especially high sea-to-air heat flux, such as the Gulf Stream and Kuroshio Current. Globally the effect integrated to 0.7 Gt C per year. Refinement of this calculation using a more accurate representation of skin temperature deviation, in particular at high wind speeds, needs to be attempted.

2.3 Wave Breaking and Bubbles

The role of bubbles in heat flux

A latent heat flux between the atmosphere and ocean is associated with marine aerosol droplets. Most atmospheric seawater droplets are film drops or jet drops produced by bubbles bursting at the sea surface (Blanchard, 1963 and 1983; Monahan, 1986; Woolf et al., 1987). Large jet drops and large drops torn directly from the sea surface are most effective in humidity transfer. The influence of droplets has been estimated to be very large by some investigators (Ling and Kao, 1976). Participants in HEXOS, a comprehensive experimental programme directed at answering this question, concluded however that the net influence on humidity and latent heat transfer was very small. There remains considerable interest in this issue and some still argue that spray is significant (e.g., Ocampo-Torres and Donelan, 1994).

The role of bubbles in gas exchange

The entrainment of bubbles by breaking waves contributes to gas exchange at high wind speeds in wind-wave tunnels (Memery and Merlivat, 1983; Broecker and Siems, 1984). Asher et al. (1992a) have shown in the laboratory that breaking waves greatly enhance gas transfer. It is well-established that deep bubble clouds are capable of significantly supersaturating very poorly soluble gases such as oxygen (Thorpe, 1982 and 1986; Woolf and Thorpe, 1991; Wallace and Wirick, 1992). Farmer et al. (1993) have found very high rates of gas transfer associated with bubble clouds. Two numerical models (Keeling, 1993; Woolf, 1993) predict a considerable contribution of large, near-surface bubbles to the air-sea transfer velocity of gases, but uncertainties in the value for any gas are still large. Measurements of the distribution of bubbles very near the sea surface and of the mass transfer coefficients of individual bubbles in nature are necessary to improve the models. In addition to transfer via bubbles (bubble-mediated exchange) the generation of turbulence by surfacing bubbles may also enhance exchange directly across the sea surface (Monahan and Spillane, 1984).

The effect of surfactants on bubble-mediated gas exchange

A bubble may carry surfactant from the sea surface on formation, and it will scavenge material from the bulk as it rises (Scott, 1975). A bubble may be covered with material after rising only a few centimeters (Blanchard, 1983). A coating of material (changing the bubble from hydrodynamically "clean" to "dirty") has a very great effect on the transfer rate of gas between the bubble and the surrounding water, particularly for large bubbles. Woolf and Thorpe (1991) assumed that small bubbles would usually be dirty. On the other hand, Keeling (1993) and Woolf (1993) have argued that formulae for clean bubbles are more appropriate for large near-surface bubbles. This assumption is quite uncertain. Woolf (1993) estimated a contribution of 8.5 cm h^{-1} to the mean global transfer velocity of carbon dioxide from bubbles if they were clean, but only 2.6 cm h^{-1} if the bubbles were dirty. Thus, the contribution of bubbles to air-sea gas exchange is sensitive to surfactants, and might respond significantly to changes in the concentration of these materials.

The effects of wave breaking on microlayer composition

The composition of the surface microlayer must be partly determined by the efficiency with which physical processes remove various materials from the sea surface and likewise supply new materials (MacIntyre, 1974). Simple turbulence cannot remove buoyant or bound material from the surface. Removal must depend on surface renewal (which is related to microscale breaking) and the especially vigorous overturning associated with wave breaking. The most highly surface-active materials will be the most difficult to remove. The production of bubbles involves the folding of part of the sea surface into the surface of bubbles and is presumably an irresistible removal process. Most of the larger bubbles will eventually return to the sea surface and burst (Woolf and Monahan, 1988). While below the surface, a bubble will scavenge material from the surrounding water (Blanchard, 1975; Wallace and Duce, 1978). The transfer of particulate material between a bubble and the surrounding water depends on the hydrodynamic flow around the bubble, the size of the particle and its adsorption properties. A bubble may become saturated with material, in which case globules of material will fall from the bottom of the bubble. This should be a fractionating process, with the most surface-active materials remaining on the bubble. When a bubble bursts, material originally on the bubble or on the sea surface may be ejected on the aerosol droplets generated (see below). Some of the aerosol droplets will quickly fall back to the sea surface. The paradigm of the effect of wave breaking on microlayer composition should be one of renewal rather than simply destruction. In addition to vertical movement of material, wave breaking will also affect the surface dispersion of materials in the microlayer. The compaction of materials associated with strong surface convergences will be superimposed on that associated with Langmuir cells (Sutcliffe et al., 1963) and small-scale surface streaming.

Bubble floatation and aerosol formation processes

When bubbles break at the surface of the ocean they skim off part of the surface microlayer to produce atmospheric film and jet droplets. In addition to providing an important mechanism for charge separation and electrification of the atmosphere (Blanchard, 1963), this process results in the injection of material enriched in both the sea surface microlayer before the bubble arrives at the surface and the composition of the bubble skin itself. Thus, aerosol particles often have concentrations significantly higher than the bulk composition of the seawater from which they were generated. This process enables materials, including pollutants, in one region of the ocean to be effectively transported horizontally via the atmosphere far from their marine source region. For example, a number of studies have shown that microorganisms such as bacteria and viruses can be enriched on aerosol particles produced by bursting bubbles, with subsequent atmospheric transport significant distances from the source area (Baylor et al., 1977; Blanchard and Syzdek, 1974, 1982; Aubert, 1974; Gruft et al., 1981). Similar results have been found for radionuclides (Walker et al., 1986), many organic substances, trace metals (Weisel et al., 1984), and irritants derived from dinoflagellate (red tide) blooms (Woodcock, 1948).

2.4 The Effect of Rain on Exchange Processes

Rain spectra show an exponential form, with an abundance of small droplets and a few large drops. Most of the mass flux is with the typical rain drops of 1 mm to 3 mm diameter - depending on the type of rain. Typical rain drops penetrate the microlayer. The formation of a stable layer of reduced salinity in the uppermost few meters of the ocean mixed layer has been reported. Rain is also known to calm the seas. It has been observed that primarily the smaller waves are damped by rain, producing a smoother appearance at the surface. It is also well known in hydrodynamics that rain drops striking the water surface at rest produce circular waves propagating outwards, as well as splash drops. Rain drops are expected to have a temperature equal to the wet bulb temperature of the air in the atmospheric boundary layer. Rain is known to be an important pathway for material transport from the atmosphere to the oceans (wet deposition, GESAMP, 1980), but this process is not dealt with in this report.

Since we lack direct measurements of the effect of rain on the microlayer, we must work from known features. The slowly falling fraction of small rain droplets below ~ 1 mm could form a thin film of lower density on top of the microlayer that is slowly mixed with the saline water below. Because of the usually cooler skin present on the ocean surface, the cooling effect of raindrops being added to the surface layer would not drastically change the temperature. The influence of salinity change on the properties of surfactants in the microlayer is deemed less important, but needs experimental verification. For the transport of chemicals from the atmosphere to the ocean it is probably less important whether these materials are deposited directly with the small droplet fraction of rain on top of the microlayer or with the primary mass flux by rain in the upper part of the mixed layer.

The primary dynamic effect of rain on the microlayer is the production of turbulence or secondary motions. The passage of rain drops through the microlayer disturbs the mean flow and leads to secondary motions that may well be a local source of turbulence in the microlayer. However, the mechanism of turbulence formation has not yet been identified. Whether secondary motion or turbulence, both effects would lead to localized surface renewal and similarly enhanced gas transfer. Rain drops cover only a small fraction of the surface area at a given time during rain, and at any single location it is raining only a small fraction of the time. Thus, the net effect of rain on gas exchange is usually believed to be negligible, but this requires confirmation.

Damping of small waves by heavy rain has been known for centuries. This effect need not influence gas exchange directly. However, it is likely to reduce the rate of wave dissipation through wave breaking. This implies less secondary motion, less surface renewal and therefore less effective gas exchange. Again, the direct effect on gas exchange will probably not be important. There is an indirect effect of small-scale wave damping by heavy rain implied by the parameterization of gas exchange in terms of mean square wave slope (see earlier). The error in global estimates again is likely to be small, and satellite microwave remote sensing during heavy rain is doubtful anyway. There are other physical effects of rain at the sea surface (e.g., momentum transfer) but they are not expected to have noticeable influence on gas transfer.

2.5 Horizontal Transport and Deposition of Surface Slicks in Coastal Zones

Surface slicks containing enhanced levels of organic and inorganic substances and biota can be moved by currents and winds such that they become grounded on tidal flats and other shallow water areas. This route is clearly one by which such areas could receive additional amounts of a variety of substances. The relative importance of this route will depend on what other sources (e.g., from adjacent rivers and the atmosphere) of the substances exist, and this is likely to be site specific. Thus, it is difficult to make other than very general statements relative to the possible importance of this transport. Nonetheless, the scums and foams formed by wind effects on microlayer films are very conspicuous in littoral areas and are often identified as "pollution" by the general public.

2.6 Review of Experimental Data on Gas Transfer

Gas Transfer Velocities

Gas transfer velocities at the surface of the ocean are derived from the application of three methods:

i) inventories of natural and bomb-produced $^{14}CO_2$ in the ocean,
ii) radon deficiencies in the surface layer,
iii) the dual-tracer technique.

Figure 2.2 shows all oceanic gas exchange data published before mid-1993. It includes two values utilizing $^{14}CO_2$, twenty utilizing radon, and four utilizing the dual-tracer method. Arguably, the ^{14}C data points should not be compared directly to the radon or SF_6-^3He data as they correspond to processes which take place on much longer time scales (order of several years), whereas the radon and SF_6-^3He results are adapted to time scales of the same order (i.e., several days). Line 1 represents the Liss and Merlivat (1986) relationship which, initially normalized for lake studies, appears to fit the oceanic measurements made with radon and SF_6-^3He. Line 2 represents the same relationship after normalization to ^{14}C and accounting for the nonlinear nature of the transfer velocity/wind speed relationship. There is a clear discrepancy between the two curves. A scaling factor of 1.6 must be introduced if the two curves are to be reconciled (Merlivat et al., 1993).

Line 3 represents the equation proposed by Wanninkhof (1992) for steady winds (i.e., valid for ^{14}C data points). Lines 2 and 3 necessarily coincide for $u = 7.6\ m\ s^{-1}$, as they go through the same ^{14}C data point. Wanninkhof has preferred for the sake of simplicity to use a quadratic relationship for transfer velocity-wind speed. This artificially introduces an increase in the transfer velocities at high wind speeds.

Nightingale et al. (1995) have shown eleven new results from experiments made using the dual-tracer technique in the North Sea. They confirm their previous data and fit the Liss and Merlivat relationship. Wanninkhof et al. (1993) have reported four results measured by the dual tracer technique on Georges Bank. In their analysis the results are above line 3. However, reanalysis of their raw data brings the results closer to the Liss and Merlivat relationship. This point is described in more detail in section 2.7.

Boutin and Etcheto (1994, 1995) have recently made detailed comparisons of colocated Special Sensor Microwave/Imager (SSM/I) wind speeds and those measured on board ship. They identified large biases (underestimations) for the SSM/I under high winds. After applying a correction to suppress this bias, they have recalculated the mean global exchange coefficient using the Liss and Merlivat relationship. Using their new value, the ratio with the ^{14}C data is now 1.4 instead of 1.6.

Discrepancy between ^{14}C-based and inert gas exchange rates

The entire set of experimental results reported in the literature since 1991 allows us to conclude that there is a discrepancy between exchange rates based on ^{14}C and measured using inert gases of the order of 40%. This should not be confused with scatter in the experimental data; there appears to be a systematic difference between the results for ^{14}C and other gases. However, it should be noted that the discrepancy may not be as large as 40% since a recent report (Hesshaimer et al., 1994) suggests that the previous estimates of the ocean uptake of ^{14}C may have to be revised downwards.

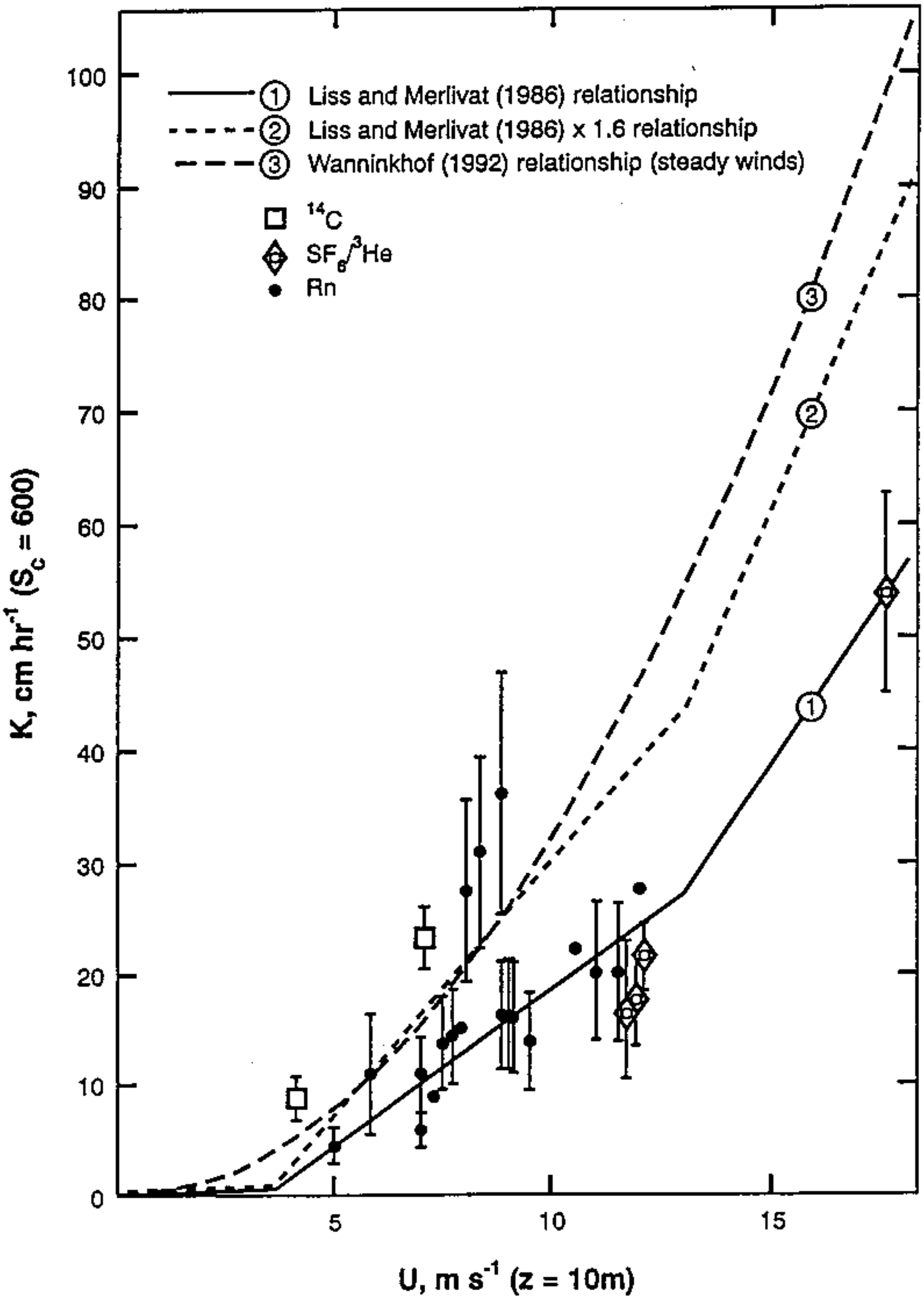

Figure 2.2 - Gas exchange measurements in the ocean and transfer velocity/wind speed relations (Merlivat, personal communication).

Taking into consideration all the knowledge that has been acquired in making the measurements at sea, there is a high priority to design experiments dedicated to understanding the behaviour of these different gases. These experiments could involve either laboratory measurements using natural sea water or field experiments. We have not discussed the possible effect of the surfactant-influenced sea surface; for example could it affect CO_2, SF_6, ^{3}He and radon differently? This effect, if important, must be identified in the existing data sets.

Do catalysts exist in the microlayer which may enhance CO_2 gas exchange?

A possibility not yet considered here is that the above discrepancy between CO_2 and inert gases is due to specific reactions of CO_2 occurring in the microlayer. Carbon dioxide reacts with water molecules on a timescale of the order of 1 minute in seawater to form H_2CO_3, which in turn very rapidly dissociates into bicarbonate. Because of the rather slow hydration of CO_2, it is normally possible to treat dissolved CO_2 as an inert gas for the process of gas exchange, and to ignore the presence of the bicarbonate in the microlayer. However, the enzyme carbonic anhydrase catalyses the hydration of CO_2; if this were present in sufficient quantities in the microlayer, the effect would be to increase the effective rate of gas exchange by making some of the bicarbonate available to transport CO_2 across the diffusion sublayer.

This idea was first suggested by Berger and Libby (1969). Subsequent studies (Goldman and Dennett, 1983) found no evidence for the presence of sufficient quantities of carbonic anhydrase in bulk sea water, but to our knowledge there have been no studies which have looked for this substance specifically in the microlayer. Given the large enrichments of biological activity sometimes observed there, it remains a possibility that warrants investigation.

2.7 Review of Experimental Techniques

'New' techniques for measuring air-sea gas exchange rates

Until quite recently methods used at sea for measuring gas exchange rates have been very crude. For example, the enclosure of a small area of sea surface by a cover and measurement of changes in gas concentration in it over a period of time suffers from the major problem that air and water motions are severely disrupted. More satisfactory methods have been tried recently, and further developments of them are on the horizon.

Dual tracer technique

One group of techniques uses micrometeorological methods, such as eddy correlation (which was developed for the measurement of terrestrial fluxes) and applies them to the generally smaller fluxes found over the sea. To date the results have been disappointing in the sense that the fluxes appear at least an order of magnitude larger than are expected or explicable given present understanding. The primary problem is that the flux being measured (generally CO_2) is at the sensitivity limit of the equipment, because a large correction has to be applied for the interfering effects of water vapour. Current developments of the technique involving conditional sampling and eddy accumulation approaches hold promise for an improvement in this situation.

Another technique for measuring gas exchange rates is a recently introduced experimental procedure in which two inert gas tracers are released into a region of the sea (Watson et al., 1991). Measurements of the ratio of the two tracers are then used to deduce the gas exchange rate as a function of time. The advantage of the technique is that measurements can be made at sea over times which are comparatively short (hours to days) so that it is unnecessary to average over widely different environmental conditions.

Ideally, one of the tracers should be completely non-volatile, in which case the measurements would enable the direct calculation of the gas exchange rate of the other one. In practice, there presently is no adequate non-volatile tracer (but a purposefully added strain of bacteria may be a possible candidate - Nightingale et al., 1995) so the two tracers used have been ^{3}He and sulphur hexafluoride, both of which are volatile though with very different diffusivities. When using two volatile tracers, the derivation of absolute values for gas transfer rates requires that the ratio of the transfer rates of the two gases be known. In the unbroken clean surface regime there is general agreement that this ratio can be calculated using a Sc^n where $n = -0.5$.

However, when spray and bubbles are present there is reason to expect that the component of the gas transfer carried by bubbles will not follow the same rule, but as yet there is no general agreement on what relationship they will follow. For example, Watson et al. reduced their data using a fixed ratio between the transfer velocities of the two tracers corresponding to Sc^n with $n = -0.5$, whereas Wanninkhof et al. (1993) used a variable-n formulation based on measurements made by Asher et al. (1992a) in a whitecap simulation tank.

If the $n = -0.5$ relationship breaks down due to the effect of bubbles, two types of error are potentially introduced into the procedure (Woolf, 1993). First, the reduction to a Schmidt number of 600 (corresponding to CO_2 at 20°C), commonly used to display and compare results, would be incorrect. If the effect of bubbles is to reduce n, the effect would be to make the results too low if the $n = -0.5$ relationship is used. However, the application of the results to more soluble gases such as CO_2 would additionally be incorrect because the contribution of bubbles to gas exchange is greater for less soluble gases, so the effect of bubbles would be overestimated. The net effect of these two errors appears to be that CO_2 exchange rates tend to be overestimated by the method (Merlivat et al., 1993). In fact these difficulties are not exclusive to the dual tracer method. They apply to the derivation of CO_2 exchange rates from those of other gases regardless of the experimental method, and are equally relevant to the results from the radon deficit technique, for example.

Asher et al. (unpublished results) have made observations of the effect of solubility on gas exchange in the presence of foam, using the same tank apparatus mentioned above. The experimental effect of solubility appears to be considerably less than the model of Memery and Merlivat (1983) predicts. Clearly, gas exchange measurements made using inert gases must for the present be interpreted with caution, particularly if they are to be used to predict CO_2 exchange. Further investigation of the effect of whitecapping on gas exchange, both in laboratory and field situations, is required. However, in the absence of a reliable method for directly measuring the exchange of CO_2, the dual tracer technique remains one of the few ways of obtaining field data with which to constrain models of gas exchange at high wind speeds.

How can we deal with the large spatial variability of p_{CO2}?

The gas flux through the interface is given as the product of the transfer velocity and the pressure difference. The values of the air-sea p_{CO2}concentration difference, Δp_{CO2}, at the surface of the ocean show a very high spatial and temporal variability. This is documented either from ship results sailing across the oceans or a few time series such as those at station P or the North Atlantic JGOFS site (Wong, 1991; Robertson et al. 1993).

The problem is to know how to average instantaneous values of the transfer velocity and Δp_{CO2} to obtain their corresponding mean values. This is important as the product of the means is not equal to the mean of the products. All existing studies have shown that at a given site, the most variable term is the wind speed-driven transfer velocity. For this reason, the time to consider is imposed by the temporal variability of the concentration difference. However, it must be remembered that the exchange coefficient must be computed from non-averaged wind speed data due to the non-linear character of the transfer velocity/wind speed relationship.

Recently, Etcheto et al. (1995) have studied a statistical method to determine the air-sea CO_2 flux using *in situ* CO_2 partial pressure measurements and satellite wind speeds, since meteorological measurements are not always available on the platforms on which the CO_2 data are obtained. They have demonstrated the validity of their method.

Controlled flux technique

Another very promising technique uses heat as a proxy tracer and is based on an entirely new concept. While conventional mass balance methods derive the flux density from a temporal change of the concentration of dissolved gases, this new technique forces a controlled flux density across the interface and infers the transfer velocity by simply measuring the surface concentration difference related to a certain change in the heat flux density. This techniques has been successfully used in wind-wave facilities (Jähne et al., 1989) using a mechanically chopped IR radiator to force a heat flux density across the interface and an IR radiometer to measure the skin temperature variations. In the field, this technique will be used for the first time on the West Coast of the United States during the U.S. Marine Boundary Layer Project in spring, 1995, when a CO_2 laser will be used as a heat source with an IR camera to image and track the heated spots.

This new technique has the tremendous advantage that it gives a local measurement with a high temporal resolution of only several minutes. Thus, it is possible to yield wide coverage with the technique, e.g., to traverse slicks; and to perform a direct parameterization with friction velocity, wave parameters, and properties of the surfactant-influenced surface such as the viscoelastic modulus. It would be especially valuable to use the technique together with the dual-tracer technique. While the latter appears to overestimate the CO_2 gas exchange rate (Merlivat et al., 1993), the controlled flux technique underestimates it by not including bubble-mediated transfer.

Are direct measurements of the heat flux possible?

Turbulent and longwave radiative heat fluxes have to be taken over by molecular and turbulent heat conduction through the oceanic thermal boundary layer. Thus, a temperature gradient across the thermal sublayer is established. Right at the surface, the gradient is given by molecular conduction only. Thus, the heat flux can be estimated from the temperature gradient at the surface. McAlister and McLeish (1969) proposed a method utilizing multispectral infrared measurements that retrieve information from different depths of the thermal sublayer. The penetration depths of radiation at wavelengths of 3.7, 4.0, 8.3, 10, and 20 micrometers amount to 80, 65, 20, 15, and 4 micrometers, respectively (e-folding depths).

Together with an accurate calibration that accounts for the non-blackness of the sea surface (Graßl and Hinzpeter, 1975; Schlüssel et al., 1990), it appears to be feasible to measure temperature gradients and thus the heat flux through the thermal sublayer. Given the significant progress in infrared technology, utilization of this technique appears worthwhile. Mammen and von Bosse (1990) utilized a buoyant pop-up profiler carrying a fast thermometer that measures the temperature profile just beneath the sea surface. While resolving parts of the entire depth of the microlayer, their technique could be used to elucidate heat transfer processes in the thermal sublayer in greater detail.

Novel ocean-surface sampling techniques

State-of-the-art microlayer sampling is defined by the rotating drum sampler (Hardy et al., 1988; Carlson et al., 1988). Microlayer samples are lifted from the ocean surface as an aqueous layer adhering to the surface of a rotating, partially submerged drum. Samples are then removed for *ex situ* study and analysis. Current understanding of microlayer chemical structure is largely based on samples obtained with this system. Questions exist, however, about the method. Does bulk water adhering to the drum dilute the microlayer sample and are there bulk material contributions? In addition, rotating drum samplers may not exhibit the real-time concentration sensitivity necessary to chemically characterize the complete range of surfactant-influenced surfaces. (Surfactant-influenced surfaces range from heavily slicked areas of ocean where surfactants can be highly compacted surface films to surfaces on which surfactants might be compared to highly expanded monolayers.) Based on existing knowledge of microlayer composition (Frew and Nelson, 1992a,b), some *ex situ* separation and analysis may always be necessary in surfactant characterization.

A solution is the application of nonintrusive *in situ* measurement methods which could be used in conjunction with existing sampling techniques. One group of possible techniques are optical sampling methods including nonlinear laser spectroscopy. Surface selective methods such as reflected second harmonic generation and reflected sum frequency generation have gained acceptance as laboratory surface probes (Shen, 1989). These interfacial spectroscopic probes have also been demonstrated to function as *in situ* probes for studying surfactant-influenced ocean surfaces (Korenowski et al. 1989; Frysinger et al., 1992; Korenowski et al., 1993). Korenowski et al. (1989) and Frysinger et al. (1992) demonstrated that it may be possible to use second harmonic generation as a true remote sensing probe of sea surface chemistry. Other laser-based methods such as reflected four-wave mixing spectroscopy are yet to be explored as *in situ* sea surface probes. Development and research into these methods could result in a host of *in situ* surface spectroscopic measurement techniques which are nonintrusive and sensitive to chemical composition (through functional groups) and physical structure.

2.8 Parameterization of Air-Sea Exchange Processes

Best parameterization for momentum, heat, and material fluxes

In the air-sea interaction community, parameterizations for momentum, heat and material fluxes are commonly formulated in terms of surface layer variables using the so-called bulk aerodynamic method and bulk transfer coefficients (drag coefficients, Stanton and Dalton numbers). Different formulations of the variation of the neutral drag coefficient with wind speed are available from different experiments but, for practical purposes, the parameterization for the drag coefficient by Large and Pond (1981) is recommended. Parameterization for water vapour flux is more difficult. The best known parameterization is given by DeCosmo et al. (1995). The parameterization for sensible heat is less well established. It is reasonable to use the bulk transfer coefficients for water vapour for heat too, or a slightly smaller coefficient (say by 8%).

The effect of surfactants on the transfer of momentum, sensible heat and water vapour is not explicitly formulated in these parameterizations. However, it is understood that the recommended parametrizations are obtained from measurements in the oceans under natural conditions. Hence, they should contain a possible influence of surfactants in the natural mix found in the sea. Part of the experimental scatter in the determination of bulk transfer coefficients could be from the varying influence of surfactants. At present, the accuracy of direct flux measurements is not good enough to determine such an influence.

Parameterizations including viscoelasticity of the air-sea interface

Capillary and capillary-gravity wave spectra are attenuated by the presence of surfactants at the air-sea interface (Lombardini et al., 1989; Bock and Frew, 1993). The mechanism by which surfactants damp waves is quantified through a description of the surface response function. Included in this description is the modulus of dilational viscoelasticity, which is a complex quantity that relates the stress and strain exhibited at air-liquid interfaces for small expansions and compressions of surface area. While experimental measurements can be obtained from wave propagation characteristics, quantification of the viscoelastic modulus is more difficult from *in situ* observation. An explanation of the equilibrium wave fields that exist as a result of wind stress has been put forward (Hasselmann, 1960, 1962, 1963a, 1963b; Hasselmann and Hasselmann, 1985). In this formulation, the resulting equilibrium wave spectrum is the result of three competing mechanisms, namely energy input into waves from wind, energy distribution between wavenumbers by nonlinear interactions, and dissipation of energy by linear wave damping and other dissipative processes. Hühnerfuß et al. (1987) have argued that the influence of surface films is limited to the damping enhancements described above. They suggested that an estimate of the viscoelastic modulus can be obtained from *in situ* measurements of wave spectra made in the presence and absence of surfactants under the same wind forcing. The ratio of these spectra is supposed to represent the damping ratio (the computed damping coefficient for a surfactant-influenced sea surface divided by the computed damping coefficient for a clean sea surface). By performing a fit of experimental spectra ratios to computed damping ratios, an appropriate estimate of viscoelastic modulus can be attained. Lombardini et al. (1989) report experimental results obtained with a microwave height gauge for wave height spectra. Their findings indicate moduli representative of both soluble and insoluble surfaces, but the scatter in their data is wide. Some of this scatter is probably a result of environmental variability, but some of it is undoubtedly due to the lack of rigour in the underlying assumption.

Recent experiments (Bock et al., 1995) have demonstrated that the ratio of slope spectra of wind driven waves with and without the presence of surfactants is not the same as the damping ratio, obtained from mechanically generated waves. This finding confirms that the effects of surface films influence not only the dissipation mechanisms of the Hasselman balance, but contribute to the other terms as well. This result indicates that no simple technique exists to derive the viscoelastic modulus from spectral data. Despite this, a parameterization that interrelates remotely sensed radar backscatter, transfer velocity, spectral levels, and viscoelastic modulus would be helpful for inclusion into global geochemical models. Such a parameterization would be facilitated by direct *in situ* measurements of capillary and capillary-gravity wave spectra and transfer velocity, along with images of radar backscatter obtained simultaneously. These data, compared with wave spectra obtained under controlled conditions, with coincident measurement of the viscoelastic modulus from mechanical wave experiments, may allow the formulation of an empirical descriptor of short wave spectra. This formulation would result in a functional relation of spectral variance to both wind stress and viscoelastic modulus. Since Bragg scattering theory has been shown to work well for intermediate angles of incidence, remote sensing from space-borne satellites can be used to infer spectral levels of short waves. Using multiple wavelength radar, it may be possible to infer the shape of the spectrum. If this turns out to be the case, intercomparison of spectra obtained in the field with spectra on surfaces that have been characterized under controlled conditions (as described above) and with remotely sensed spectra estimates will allow parameterization of a functional model of transfer velocity as a function of viscoelasticity. Laboratory wind-wave tank results have indicated a strong linear correlation between mean square slope and transfer velocity (Jähne et al., 1987; Bock and Frew, 1993). If this correlation applies to *in situ* wave fields, a direct estimate of transfer velocity using remotely sensed backscatter should be possible, owing to (among other validations obtained in wind wave tanks) the recent *in situ* validation of Bragg scattering by direct wave spectrum measurements (Bock and Hara, 1995; Hara et al., 1994).

A correlation between backscatter and transfer velocity using data collected in a wind-wave tunnel has been developed by Wanninkhof and Bliven (1991). This demonstrates, in principle, for one surface condition that the backscatter/transfer velocity correlation proposed here is possible.

A method for measuring transfer velocities at high wind speeds from a satellite-measurable parameter may be possible through passive microwave radiometry. It has been shown that there is a correlation between microwave brightness temperature and fractional area whitecap coverage (Asher et al., 1992b). Because the data of Asher et al. (1995) suggest that the transfer velocity is correlated with whitecap coverage, a direct relation between brightness temperature and transfer velocity may exist. This would provide a method for estimating transfer velocities at high wind speeds.

Estimating the effect of surfactant-influenced sea surfaces on air-sea gas fluxes

The impact of surfactant-influenced (SI) air-sea interfaces on the net global air-sea flux of a gas can be estimated using a direct regional flux model. For a liquid-phase, rate-controlled gas such as CO_2, this requires knowledge of the fractional area coverage of the SI sea surface, parameterizations of the air-sea transfer velocity for clean and SI surfaces in terms of a globally mapped environmental forcing function, and relations describing the effect of surfactants on the thermodynamic driving potential for gas exchange (air-sea concentration difference). Unfortunately, field data describing these variables are unavailable or, at best, poorly known on global scales. Therefore, estimation of the net global flux of CO_2 requires extrapolation of laboratory data to oceanic conditions and SI sea surface coverage estimated from primary productivity. The results of this exercise show that naturally occurring surfactants could possibly have a substantial effect on air-sea gas fluxes.

Figure 2.3 shows the results from a direct flux model of CO_2 uptake by the ocean for different fractional area coverages of SI sea surface, X (Asher, 199). When X = 0, the net global flux of CO_2, F_{CO2}, is equal to -1.9 Gt C yr^{-1}, where the minus sign denotes flux into the ocean. This is in excellent agreement with current estimates of the yearly oceanic CO_2 uptake (Sarmiento and Sundquist, 1992) and indicates that the model and its input parameters, Δp_{CO2} and transfer velocity values, are consistent with other estimates. (It must be stressed that this result should not be interpreted as a new "best-estimate" of the yearly global ocean CO_2 uptake. It is to be used solely for comparison purposes in this study, and as a rough check on the model's input data.) For X = 1.0, F_{CO2} = -0.32 Gt C yr^{-1}, which illustrates the maximum estimated impact of naturally occurring surfactants on the net flux of CO_2. A decrease of 1.58 Gt C yr^{-1} is very significant and suggests that SI sea surfaces have the potential for causing large changes in F_{CO2}.

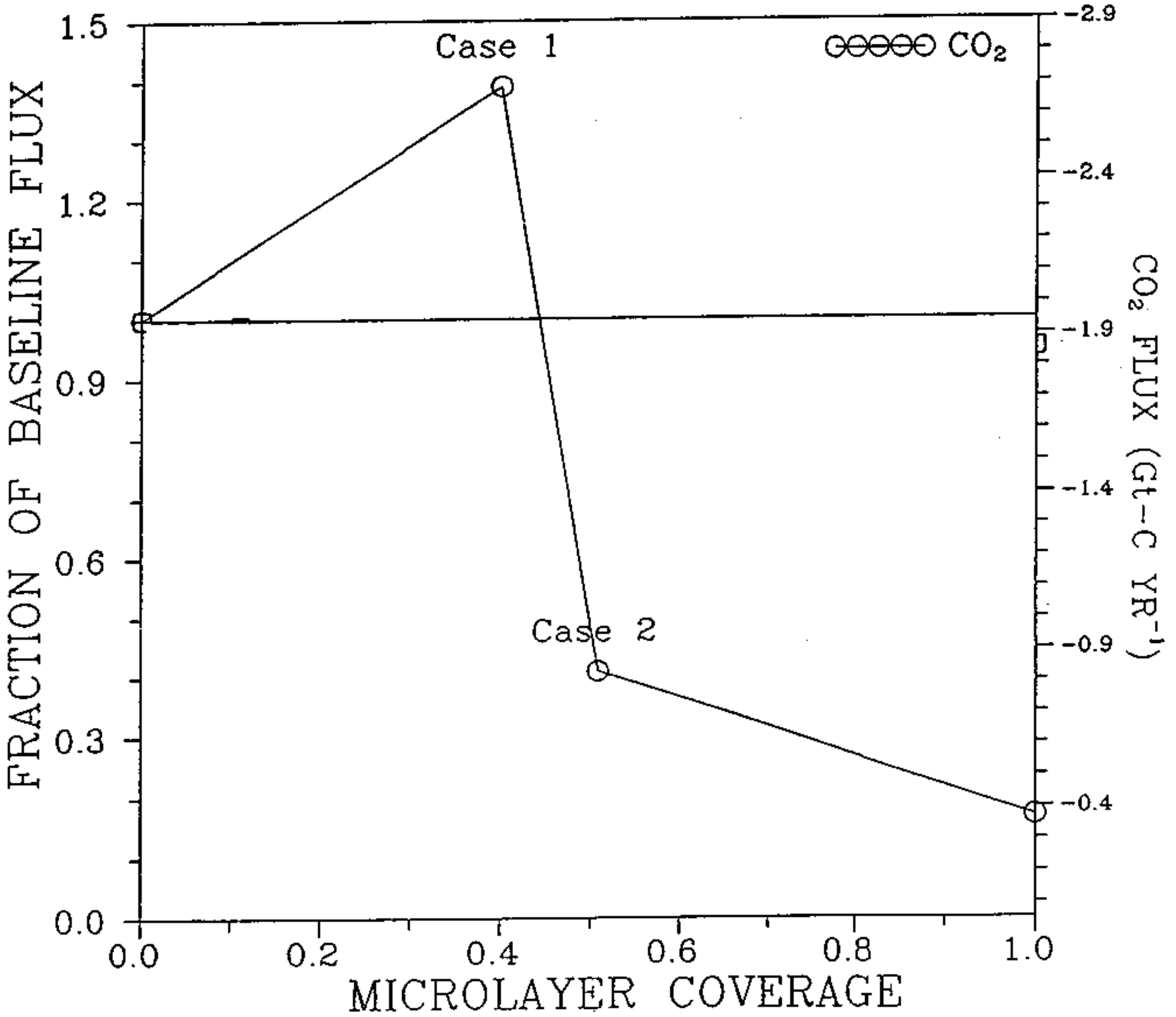

Figure 2.3 - Fractional reduction/increase in net flux of carbon dioxide as a function of fractional area coverage of SI sea surface. SI sea surface coverage has been estimated from synthetic primary productivity using the data of Berger and Herguera (1992) (From Asher, 1995).

In Figure 2.3, X = 0.4 (Case 1) corresponds to F_{CO2} = -2.6 Gt C yr^{-1}. This increase results from suppression of CO_2 evasion from the Equatorial Pacific and Equatorial Atlantic. When X = 0.5, (Case 2) F_{CO2} decreases to -0.78 Gt C yr^{-1}. This decrease is due primarily to suppression of CO_2 invasion in the North Atlantic. Comparison of the X = 0.4 and X = 0.5 fluxes show that a slight change in the presence of surfactants can cause a change of nearly 2 Gt C yr^{-1} in the net CO_2 flux, which is a very large difference. Furthermore, this decrease in F_{CO2} is caused by a 10% increase in global SI surface coverage, showing that fluxes are very sensitive to the regional presence of naturally-occurring surfactants.

There are obvious limitations to the modelling approach used here in light of the patchiness of ocean slicks and the largely unknown effect of the microlayer on transfer velocity. It is possible that the transfer velocity in the ocean at a particular wind speed may depend on surfactant concentration in the surface microlayer. In this case, the simple threshold model used to estimate X would not be correct and a range of transfer velocity/wind speed parameterizations would be necessary. However, the results presented here do illustrate that using the best available transfer velocity/wind speed parameterizations for clean and SI sea surfaces, the microlayer may have a significant effect on global or regional air-sea gas fluxes. Accurate estimation of this effect remains problematic because of a lack of field data on gas fluxes in the presence of SI sea surfaces.

2.9 Conclusions and Recommendations

There is increasing evidence for the importance of surface films in the transfer of mass, heat and momentum across the air-sea interface. However, in order to aid interpretation of the results of field experiments and to allow extrapolation of laboratory data to describe real ocean phenomena, we need to have a better understanding of the physics of near-surface transport mechanisms and the effect of films on them. The viscoelastic modulus appears to be the most relevant parameter to characterize the films' ability to modulate these transport processes.

The present global distribution of surfactants capable of affecting exchange processes is largely unknown, as are the factors controlling future distributions. Further, it is important to ascertain what fraction of the materials are of anthropogenic versus biogenic origin, both with respect to coastal and open ocean areas. For relatively unpolluted areas, it is reasonable to assume that marine biological productivity will give a good first order estimate of the extent of films, since it is clearly a large source term. If this is so, then remote sensing techniques, such as multiple band backscatter, may be useful in establishing a monitoring capability for ocean surfactants

With respect to air-sea gas exchange, effort needs to be devoted to several important uncertainties related to the microlayer. These include the importance of the cool skin effect particularly for CO_2 exchange, the role of bubbles as gas exchangers and more specifically differences between the exchange properties of clean versus dirty bubbles, and the possible role of carbonic anhydrase in enhancing uptake of CO_2. Direct methods, adapted from existing micrometerological or other techniques, capable of measuring air-sea gas fluxes in situ are urgently needed. Due to lack of knowledge concerning surfactant distributions, attempts at estimating the effect of films on current global gas fluxes across the sea surface are subject to great uncertainty (Asher, 1996).

The research in the above directions should be pursued via both field and laboratory experiments. Future field experiments need to be performed that include integrated measurements of, inter alia, wind stress, heat flux, bubble concentrations, wave spectra and breaking wave statistics, viscoelasticity of films and their biological properties, multi-tracer gas transfer, and a variety of remote sensing approaches. Laboratory experiments are necessary to elucidate fundamental physical and chemical phenomena, and they are necessary for interpretation of results obtained in the field.

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3. BIOLOGICAL EFFECTS OF CHEMICAL AND RADIATIVE CHANGE IN THE SEA SURFACE

3.1 Introduction

The physics, chemistry and biology of the sea surface are closely inter-related. Plankton in the water column produce an abundance of particulate and dissolved organic material, some of which is transported to the surface either passively by floatation or actively by bubble transport. Atmospheric deposition also enriches the sea surface with natural and anthropogenic compounds which often accumulate there in relatively high concentrations compared to the water column. The abundance of organic matter at the sea surface provides a substrate for the growth of organisms that inhabit the sea surface microlayer: the neuston. Most studies suggest that the sea surface represents a highly productive, metabolically active interface. Organisms from most major divisions of the plant and animal kingdoms either live, reproduce or feed in the surface layers. Of particular interest are the microneuston which may be involved in biogeochemical cycling and neustonic eggs and larvae of commercially-important fish and shellfish.

The quantities and types of anthropogenic chemicals entering the earth's atmosphere continues to grow. Many of these chemicals, some of which are highly toxic, are now globally distributed in the atmosphere and deposit to the sea surface even in remote areas. Due to stratospheric ozone depletion, ultraviolet-b (UV-B) radiation reaching the sea surface is increasing annually. These global changes represent a potential threat to the marine environment. Neuston, living in the sea surface, will experience the greatest increases in chemical and radiative change. The potential impact of global changes on this unique community should be assessed.

The condition of the neuston community could possibly be used as a "sentinel" or early indicator of changes in the marine environment occurring on a regional and global scale. For example, evidence suggests that in the Black Sea over the past 30 years eutrophication and other pollution has produced major alterations in the plankton and neuston communities (Zaitsev, 1992).

Chemicals and radionuclides that partition and concentrate at the surface may represent relatively recent inputs from both the water column and atmosphere and, thus, may be useful for source identification and "fingerprinting". For example, ratios of certain specific hydrocarbons in microlayer samples can suggest different types of sources such as fossil fuel combustion, petroleum spills, etc. (Hardy et al., 1990).

3.2 Samplers and Sampling Techniques

A variety of distinct methods have been used to sample the sea surface for chemical and biological analysis. These are distinguished from each other both by the physical manner in which they collect surface material and by the thickness of the sample collected.

The prism-dipping technique

The prism-dipping technique, devised by Baier (1972), samples monomolecular films of organic material adsorbed at the air-sea interface by adsorption onto a small germanium prism. This method is based on the technique first described by Blodgett (1934) for recovering fatty acid monolayers from a water surface. The recovered organic films may subsequently be examined by several techniques, including internal reflection infra-red (IR) spectroscopy to determine major functional groups, ellipsometry for measurement of film thickness and refractive index, surface potential and contact angle. Since these properties relate to general physical and chemical properties of the film, the results are difficult to compare with specific chemical analyses conducted on surface samples collected by other methods.

The screen sampler

With the screen sampler (Garrett, 1965), small rectangular cells of water from a layer of the sea surface are captured in the interstitial spaces of a wire or plastic mesh by means of surface tension forces. The physical thickness of the microlayer sample collected by the screen is calculated from the void area of the screen and the volume of seawater collected and is typically the upper 200-400 μm. This thickness is determined primarily by the diameter of the screen filaments.

Plate and drum samplers

These sampling devices collect a discrete slice of the water surface, including the air-water interface, by means of viscous adhesion to a solid surface, and superficially they resemble the screen sampler. The simplest type is the plate sampler in which a viscous film of water from the sea surface adheres to a glass plate that is submerged below the water surface and then withdrawn vertically at a velocity of about 20 cm s^{-1} (Harvey and Burzell, 1972; Hardy et al., 1985). The film is removed by using a wiper blade. More sophisticated variants use a rotating drum of ceramic, glass or Teflon that is pushed slowly forward while mounted on a catamaran (Harvey, 1966; Hardy et al., 1988; Carlson et al., 1988). The film adhering to the drum is automatically wiped off into a sample container.

The physical thickness of the sample obtained with these devices is calculated from the area of surface sampled and the volume of seawater collected, and varies from 20 to 100 μm for both plate and drum samplers. The thickness depends on a number of factors including water temperature, the presence and density of surface slicks and, in the case of drums, speed of rotation.

Techniques for Sampling neuston

Microneuston may be sampled using a membrane filter (Hardy and Apts, 1984), glass plate (Hardy et al., 1985), or rotating drum (Hardy et al., 1988). Macroneuston can be sampled using a variety of nets (e.g., Zaitsev, 1971; Brown and Cheng, 1981; Shenker, 1988). Care must be used to select the appropriate mesh size and net mouth size for different target species and life stages. Comparisons among sampling programmes must, therefore, consider the types of gear used to collect the samples.

3.3 Characteristics of the Surface Microlayer

Enrichment factors

The degree to which microlayer samples collected by screen, plate and drum samples are enriched in chemical or biological species is usually assessed by calculating the enrichment factor, EF, defined as the ratio of the concentration found in the microlayer to that of a sub-surface water sample (usually collected 10-20 cm below the surface):

$$EF = [X]_\mu/[X]_b \qquad (3.1)$$

where $[X]_\mu$ is the microlayer concentration of a species X, and $[X]_b$ is the concentration of X in bulk (sub-surface) water. EF values greater than unity indicate enrichment in the microlayer, while EF values less than 1 indicate depletion. Since the screen, plate and drum samplers collect mostly water along with materials adsorbed at the air-water interface, the possibility exists that some, or even most, of the sample collected may be sub-surface water not enriched in surface-active species. As discussed below, this can lead to dilution of actual surface concentrations and underestimation of EFs.

Surface excess concentrations

Because the sample thicknesses of the various sampling methods are different, the results of chemical or biological analysis cannot be directly compared in terms of either microlayer concentrations or enrichment factors. However, it is possible to compare results for different sampler thicknesses by calculating the *surface excess concentration* defined as:

$$SE = ([X]_\mu - [X]_b) \bullet d \qquad (3.2)$$

where d is the sample thickness (Hunter and Liss, 1981a). This relationship may be used to calculate total excess concentration through a cross-section of the surface. The results of such comparisons show only fair agreement between screen and plate samplers, consistent with their different modes of action (Carlson, 1982c). However, plate and drum samplers seem to operate similarly when results are corrected for sample thickness using the surface excess concentration.

Variability of organisms and contaminants

Distributions of sea-surface chemical contaminants and organisms are patchy, but both tend to become concentrated in the same areas. One of the unusual features of the surface microlayer, compared to subsurface waters, is the coincident concentration of contaminants and biota. Processes such as particle adsorption, organic complexation, and bubble scavenging concentrate natural organics and nutrients in the microlayer creating conditions for enhanced biological activity. Contaminants tend to concentrate in the microlayer due to the same processes that concentrate the organic materials and organisms. Therefore, the exposure hazard for neuston, i.e., occurrence of organisms in areas of contamination, may be higher than in the water column. This situation parallels that in the sediments.

The development of new chemical sensors for nutrients, trace elements and other chemical components in the near future, coupled with drum samplers, should provide much more detailed information on microlayer variability. More detailed, larger-scale information on microlayer spatial and temporal variability relevant to the issue of capillary wave damping effects on gas exchange is likely to arise from future applications of remote sensing techniques now being developed, e.g., the infrared radiometer, microwave radar, laser scattering and SHG (single harmonic generation) techniques. These methods will need "ground truthing" using more systematic chemical measurements of the microlayer, particularly of organic enrichments and film pressures.

Thickness of sea surface films

Because the sea surface microlayer is a complex phenomenon involving physical, chemical and biological processes operating over widely different physical dimensions, the question of its thickness has no simple answer. It is important, however, to consider how the methods used for sampling the microlayer for chemical or biological analysis are related to dimensions of the physical regions within which chemical and biological materials are accumulated. In particular, if the microlayer, seen as a region of concentrated contaminants, is significantly smaller in thickness than that sampled for chemical analysis, then microlayer organisms may be exposed to much higher concentrations of contaminants than are indicated by chemical studies. On the other hand, a much thinner region of enriched contaminants may mean that many neustonic organisms are not actually in contact with the enriched region and thus not exposed to the toxicant, particularly if they are not attached to the air-water interface.

Conventional wisdom from surface chemistry would suggest that the natural organic matter in the microlayer consists of material adsorbed at the air-water interface, making up a film of molecular thickness. This view is certainly supported by the visual appearance of surface slicks. However, visible surface slicks are relatively rare on the open oceans, although in coastal seas they are more prevalent. For example, Garebetian et al. (1993) report that in the Mediterranean slicks were present 30% of the time and covered >50% of the photographed area. General measures of organic concentration, such as dissolved organic carbon (DOC), show microlayer enrichment even when slicks are absent. EF values usually do not increase markedly even when slicks are present, suggesting that the appearance of surface films and enrichment of natural organic material in the microlayer may not be related to each other in a simple, linear fashion. However, in contaminated areas, EF values for contaminants are generally greater in slicks than outside (Hardy et al., 1988).

The compiled results for DOC enrichments (Carlson, 1982b) and other quantities often show depletion in microlayer samples ($E < 1$). Examples for UV absorbance and chlorophyll fluorescence are shown in Figure 3.1. If the region of enrichment is very near to the air-water interface, e.g., within 1 nm, then the much thicker plate, drum or screen microlayer samples would comprise mostly sub-surface water. In this case, it is very difficult to see how microlayer depletion can arise. On the other hand, if most of the enriched organic material in the microlayer region consists of very expanded, hydrated material extending over a thickness comparable to those of sampling devices (i.e., 50-200 μm), more hydrophillic fractions of the dissolved organic matter (DOM) could be volume-excluded from the microlayer region, thus giving rise to microlayer depletion.

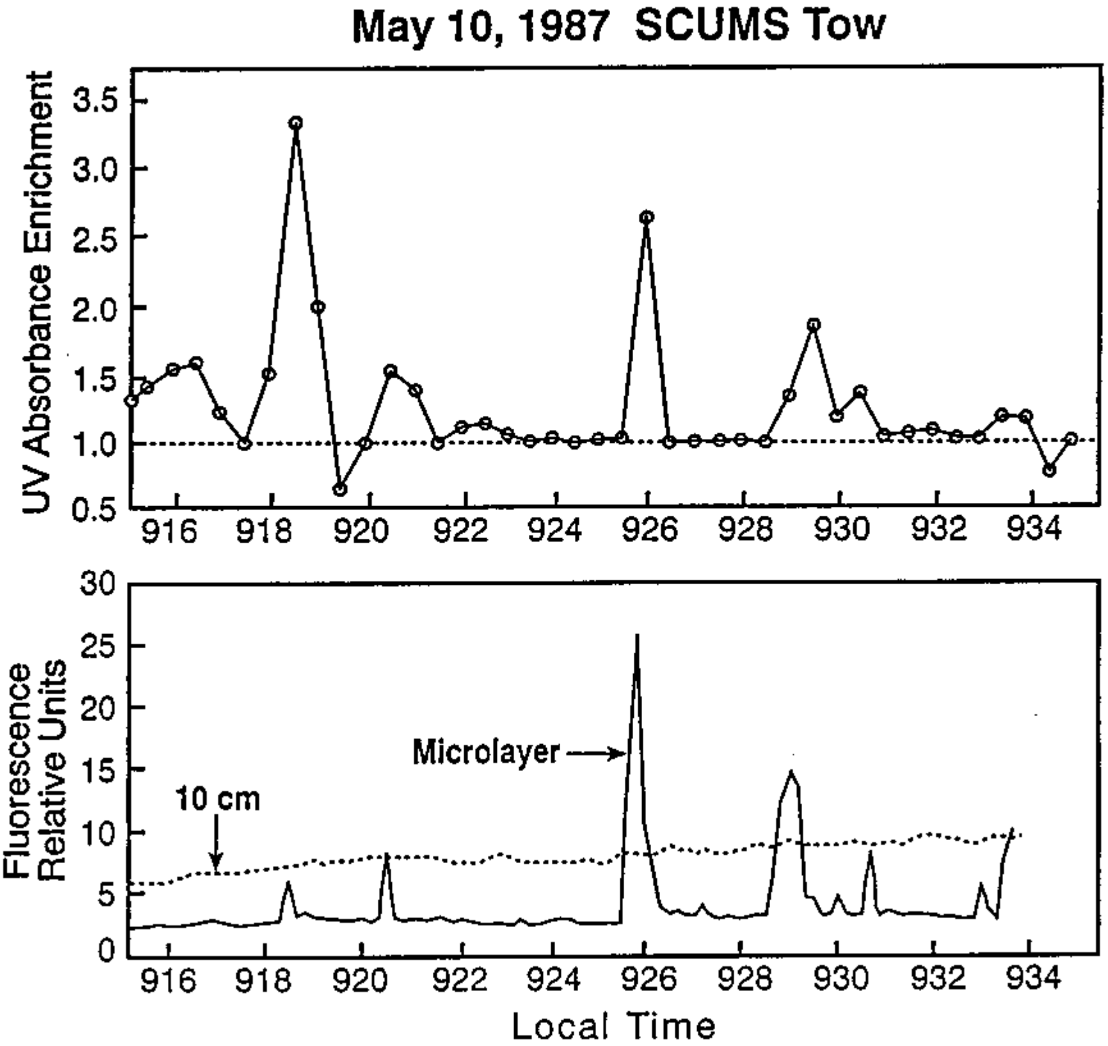

Figure 3.1 - Results from a SCUMS (Self-Contained Underway Microlayer Sampler) tow in Damariscotta Estuary, Maine. Upper panel shows microlayer UV absorbance enrichment. Lower panel shows surface microlayer and subsurface chlorophyll fluorescence, in relative fluorescence units (Carlson et al., 1988).

Other evidence points to the fact that microlayer film materials can be much thicker. Ellipsometric measurements of the thickness of organic layers collected using the prism-dipping technique shows that the dried material can be as thick as 1 μm (Baier et al., 1974). This suggests that once re-hydrated, the organic material is likely to occupy a much larger thickness. When the drum sampler is used to collect from slick-covered waters, the volume of sample obtained per unit time increases over that obtained in clean areas. This implies that the adsorbed film material is able to influence the viscous properties of the water film (thickness 20-100 μm) collected by the drum. The thickness of microlayer samples collected with the glass plate increases exponentially from 30 to 55 μm as the surface pressure (an indicator of the amount of organic film present) increases from 0 to $>$ 20 dyne cm^{-1} (Hardy et al., 1985).

The only evidence that the microlayer might be significantly thinner than that sampled conventionally comes from the use of "bubble microtome" samplers that are based on air bubbles bursting at the air-water interface (e.g., Fasching et al., 1974). However, the greater enrichments observed with this type of sampler compared to conventional methods most likely result from scavenging of surface-active material in sub-surface waters by air bubbles rather than a simple, very thin sample taken only from the air-water interface itself. This view is supported by studies on the scavenging of bacteria by rising bubbles (Blanchard, 1975) and by the considerable body of scientific knowledge concerned with mineral floatation processes.

The above considerations suggest that a simple monomolecular film, e.g., of a simple surfactant like oleic acid, is a poor analogue of natural microlayers. A more accurate picture is that of a gel-like structure occupying a significant thickness comparable to that sampled by screen, plate and drum samplers (50-200 μm).

3.4 Biology in the Sea Surface

The neustonic realm is a vast habitat covering 70% of the earth's surface. The unique physical and chemical characteristics of the sea surface have contributed to the evolution of a highly diverse and abundant assemblage of species, including many that are of commercial and ecological importance (Zaitsev, 1971)(Figure 3.2). Permanent inhabitants of the surface layer, such as bacterioneuston, phytoneuston, zooneuston and ichthyoneuston, often reach much higher densities than similar organisms found in subsurface waters. Temporary inhabitants of the neuston, particularly the eggs and larvae of a great number of fish and invertebrate species, utilize the surface during a portion of their embryonic and larval development. Temperature may be increased and permanent neustonic organisms may be concentrated by meteorological and oceanographic processes that result in convergences within the surface layer. Some neuston can remain in the upper milli- or centi- layer until turbulence created by winds exceeding 10-15 m s^{-1} disperse them (Zaitsev, 1971). Many organisms become strongly attached to the air/water interface because of surface tension forces, and for some this results in cell rupture.

Neuston, like plankton and nekton, may be classified for purposes of study according to their size.

Piconeuston

Piconeuston ($<$2 μm), like picoplankton (Sieburth et al., 1976), are being increasingly recognized as important links in the recycling of organic matter in aquatic ecosystems. High densities of metabolically active bacterioneuston are found in the surface microlayer (Sieburth, 1971; Bezdek and Carlucci, 1972; Sieburth et al., 1976; Carlucci et al., 1985). For example, bacterioneuston off the coast of Baja California accounted for 1.4 to 5.9% of the total microbial carbon biomass and a similar percentage (1.9 to 5.1%) of the microbial carbon production in the surface microlayer. The enrichment of bacteria in the surface microlayer results, at least in part, from the greater degree of hydrophobicity of bacterioneuston compared to bacterioplankton and, thus, their adhesion to organically-enriched surface microlayers (Dahlback, et al., 1981). Bacteria also adhere to the air-water interface of bubbles and may be injected into the atmosphere as part of sea-salt aerosol (Blanchard, 1983). Bacterioneuston likely play an important role in degrading not only natural organics, but also anthropogenic chemicals collected at the sea surface.

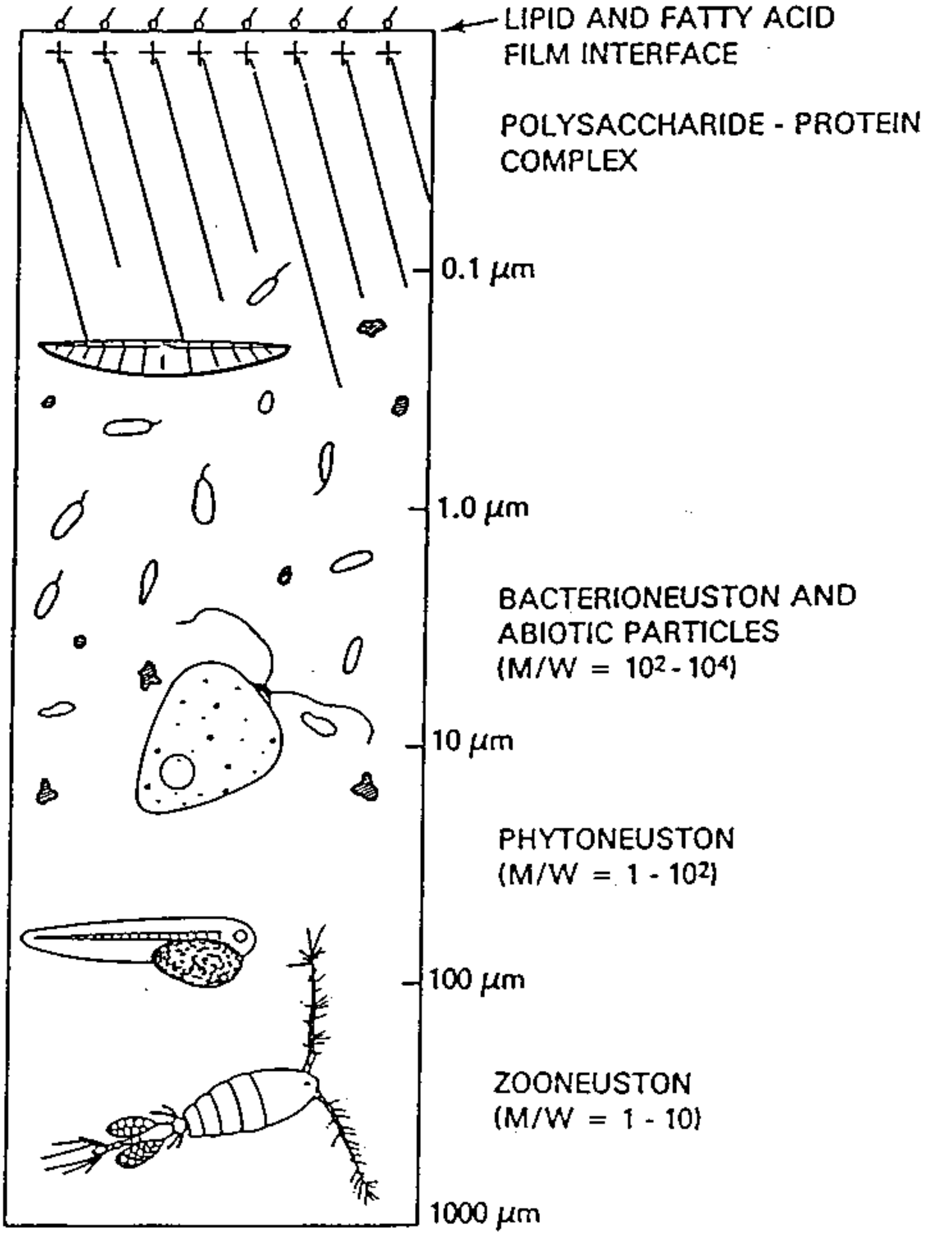

Figure 3.2 - Conceptual model of the sea-surface microlayer ecosystem. M/W = typical microlayer to water concentration ratios based on a number of studies.

The importance of autotrophic picoplankton is also being increasingly recognized (Johnson et al., 1982). In the water column in the subarctic Pacific, 28% of the biomass (as carbon) was in the $< 2\mu m$ size fraction and was almost exclusively the blue-green autotroph *Synechococcus spp.* (Booth et al., 1988).

Some early data for the enrichments of bacteria in microlayer samples may have given anomalously high enrichment factors because many allochthanous species grow readily on culture plates and may become over-represented in the final counts made by this method. Direct counting, e.g., using epifluorescence spectroscopy, autoradiography or adenosine triphosphate (ATP) biomass determination, is preferred for measurement of bacterioneuston. With direct counts of membrane-collected samples, bacterioneuston/bacterioplankton enrichments in Puget Sound are 10^2 to 10^6 (Hardy and Apts, 1984). However, few studies of open ocean samples have been made and the global distribution of bacterioneuston are poorly known.

Nano- and microneuston

Nano- and microneuston (2 to 200 μm in size), including dozens of species of microalgae (phytoneuston) occur in great abundance in the microlayer (Hardy and Apts, 1984; Hattori et al., 1983; De Souza-Lima and Chretiennot-Dinet, 1984; Hardy 1973; Hardy and Valett, 1981). Enrichment ratios (number of individuals per volume in the surface microlayer/ numbers per volume in the sub-surface water) are generally 10 to 1000.

The blue-green alga (cyanobacterium) *Trichodesmium* is a common phytoneustonic organism in tropical open ocean waters. In the tropical North Atlantic Ocean it is the most important primary producer (165 mg C $m^{-2} d^{-1}$) and is also responsible, through nitrogen fixation, for the largest fraction of new nitrogen to the euphotic zone (30 mg $m^{-2} d^{-1}$)(Carpenter and Romans, 1991). Although maximum densities of *Trichodesmium sp.* occurred at near-surface (15 m) depths (Carpenter and Romans, 1991), this may simply reflect the absence of microlayer sample collection, which might otherwise show the buoyant filaments even more concentrated in the microlayer. For example, in the Atlantic Ocean 150 km off the Florida coast, a surface microlayer enrichment ratio for total phytoneuston (dominated by *Trichodesmium sp.* and microflagellates) of 400 was found as well as a phytoneuston species composition very different from that of the subsurface phytoplankton community (Hardy et al., 1988).

Certain dinoflagellate species are often found in the surface microlayer. For example, in the North Sea, near the island of Sylt, a bloom of the dinoflagellate *Prorocentrum micans*, and several other phytoneuston species, contributed to the formation of visible surface slicks. Microlayer enrichment ratios for *P. micans* were > 1000 (Brockmann et al., 1976). The phytoneuston community off Baja California is dominated by dinoflagellates and differs greatly from the phytoplankton in species composition (Williams et al., 1986). Also, in the Black Sea continuing eutrophication has led to frequent algal blooms (including dinoflagellates) and screen-collected microlayer phytoneuston/phytoplankton enrichment ratios of 100 to 10000 (Nestrova, 1980).

There have been only a few measurements of photosynthetic carbon reduction in the surface microlayer. Most have focused on nearshore, productive environments: an enclosed lagoon (Hardy, 1973), a salt marsh (Gallagher, 1975), a river estuary (Albright, 1980) and the Mediterranean Sea near Marseilles (De Souza-Lima and Chretiennot-Dinet, 1984). One offshore study was conducted near Baja California (Williams et al., 1986). All these investigators enclosed collected microlayers and their communities (microneuston) in bottles, thus disrupting the natural surface-film habitat.

Hardy and Apts (1989) determined microalgal standing stocks and activities in the surface microlayer and sub-surface waters in areas with (S) and without (NS) visible natural surface slicks. Phytoneuston photosynthesis was measured without enclosing samples in bottles. Microlayer and subsurface water were enclosed in open top microcosms and incubated *in situ*. Enrichment ratios (surface microlayer/sub-surface water concentration) were: phytoneuston population abundance, 37 (NS) to 154 (S); total chlorophyll, 1.3 (NS) to 18 (S); particulate carbon fixation, 2 (NS) to 52 (S) and dissolved carbon excretion by autotrophs, 17 (NS) to 63 (S). As in other studies, the species composition of the phytoneuston was distinctly different from that of the phytoplankton.

Winter and spring carbon reduction rates at one coastal marine site were 20 to 150 times greater in the surface microlayer than in the sub-surface water (Hardy and Apts, 1984). However, in high summer light intensities, photoinhibition of 36 to 89% occurred in phytoneuston. Williams et al. (1986) also found evidence for photoinhibition in phytoneuston; i.e., photosynthesis increased 179% in neuston incubated at 1 m depth compared to incubation at the surface.

Microzooplankton (the heterogenous group of organisms between 2 and 200 μm) form a vital link in the planktonic food web between small bacteria, flagellates, and larger metazoans including fish. They include protozoa and the developmental stages of many pelagic and benthic animals, but few adult metazoans. Their feeding modes include particle filtration, phagotrophy, and pinocytosis (Conover, 1982). From 4 to greater than 70 percent of primary production is consumed by microzooplankton (Conover, 1982). Small ($<20\,\mu$m) ciliates at times make up 4 to 57% of the total biomass of heterotrophic (apochlorotic) nanoplankton in diverse marine systems (Sherr et al., 1986). Nano- and microheterotrophs release dissolved organics that form substrates (along with organics from phototrophs) for the growth of bacteria on which they feed. They can be thought of as "microbial gardeners" (Davis and Sieburth, 1982). Despite their probable importance, few quantitative data are available on their abundance or trophic relationships. "To be able to attach reliable rates and biomass to just one of the pathways would be a major achievement" (Conover, 1982).

Compared to the microzooplankton, even less is known about the species composition, abundance or dynamics of microzooneuston. Based on a limited number of investigations, heterotrophic microneuston inhabiting the surface microlayer include small ciliates (Zaitsev, 1971), protozoa (Norris 1965) and yeasts and molds (Kjelleberg and Hakansson, 1977). Tintinnids often form an important component of the marine neuston, probably feeding on the high densities of bacterioneuston (Hardy, 1971; Zaitsev, 1971). Also, the heterotrophic dinoflagellates *Noctiluca scintillans* and *Oxyrrhis marina* are often abundant in neuston samples (Hardy, 1971; Zaitsev, 1971).

Mesozooneuston

Some mesozooneuston (0.2 to 20 mm in size) feed on the high densities of microneuston (Zaitsev, 1971). Samples from many areas of the world's oceans indicate that copepods, often dominated by pontellid species, are abundant components of the surface microlayer (Zaitsev, 1971; Hardy, 1982). In Galway Bay (Tully and O'Ceidigh, 1986) and many other locations (Zaitsev, 1971), neustonic isopods and amphipods are abundant, often associated with floating driftweed and debris. Numerous species of fish, including cod, sole, flounder, hake, menhaden, anchovy, mullet, flying fish, greenling, saury, rockfish, halibut, and many others have surface-dwelling egg and/or larval stages (Ahlstrom and Stevens, 1975; Brewer, 1981; Kendall and Clark, 1982; Safronov, 1981; Shenker, 1988; Zaitsev, 1971). Some crab and lobster larvae in estuarine, coastal, and shelf areas concentrate in the surface film during midday as a result of positive phototaxis (Tully and O'Ceidigh, 1986; Jacoby, 1982; Provenzano et al., 1983; Smyth, 1980).

In Puget Sound, English sole (*Parophrys vetulus*) and sand sole (*Psettichthys melanostictus*) spawn between January and April, releasing trillions of eggs that collect on the water surface. The embryos float until hatching occurs, generally 6 to 7 days after fertilization. Because of the buoyancy of their large yolk sacks, newly hatched larvae of both species often float upside-down at the surface of the water (Budd, 1940).

Although the micro-vertical distribution of zooneuston in the upper 0 to 50 cm can be disturbed by wind mixing, the effect seems to disappear quickly once the wind subsides (Champalbert, 1977). As Zaitsev (1971) noted, "..most of the eggs must rise to the surface film and remain suspended there. Although the specific weight of the egg increases during development, it remains low enough to hold the egg close to the surface film... and surface enrichments of organisms were found to be stable even at sea states of 5 to 6 Beaufort." Fish eggs, concentrated at the sea surface, are dispersed at wave heights exceeding 1 to 2 m, while larvae and fry remain there even when waves reach heights of 3 to 4 m (Zaitsev, 1971).

Neuston net tows from widely dispersed areas of the global ocean indicate that floating tar and plastic debris is important as a habitat colonized by dozens of species of marine invertebrates. The distributional abundance of many neuston, including attached eggs, is positively correlated with the distribution of pelagic tar. While the tar acts as a habitat for some species, it may exert a detrimental effect on the majority of neuston (Holdway and Maddock, 1983).

Macroneuston

The larger (> 2cm) neuston organisms have been referred to as "pleuston", although a more consistent term might be "macroneuston". These organisms, of which there are perhaps 100 species, inhabit the surface layer (upper meter) generally by floatation or by association with floatable seaweed (Cheng, 1975). Coelenterates include the jellyfish *Physalia spp.* that feed on small fish, and *Velella spp.* that feed on copepods and fish and invertebrate eggs. Common gastropods in the open ocean surface layer are species of prosobranchiata and nudibranchiata. Oceanic crabs and many other organisms are found associated with the floating pelagic seaweed *Sargassum spp.* These macroneuston undoubtedly form part of the food web linking the sea surface and subsurface layer, but the details of this food web remain unclear.

Freshwater neuston

Neustonic populations in freshwaters, although represented by different species, fill analogous niches to their marine counterparts. Freshwater eutrophication (artificial and natural) often leads to increasing formation of surface materials and "scums" - thick organically-enriched films. One important difference in freshwaters is the absence of fish and benthic invertebrate species with neustonic eggs or larvae. In many high-latitude lakes, winter ice cover certainly alters the lake surface and would affect chemical and radiative exposures. Ice could trap surface materials and nutrients and release them again during the spring thaw rapidly enriching the surface layer. Algal blooms on the underside of ice form a unique surface community.

3.5 Chemistry in the Sea Surface

Organic components of natural origin

Organic compounds of natural (non-anthropogenic) origin are the principal film-forming components in aquatic systems and generally influence the presence of other microlayer constituents, including trace elements, radionuclides and particulate matter. The infrared spectra of marine films obtained using the prism-dipping technique show a functional group chemistry dominated by glycoprotein, with lipid components important only in samples collected from grossly polluted waters (Baier et al., 1974).

This analysis is confirmed by extensive measurements of general organic chemical quantities such as dissolved organic carbon (DOC) and nitrogen (DON), or specific organic compound classes such as protein, polysaccharide, lipid and hydrocarbons. Williams et al. (1986) have reported a very comprehensive study of microlayer samples from the Gulf of California and Baja California, the results of which are typical of most studies. Mean enrichment factors (screen sampler) were 1.1-2.4 for DOC, DON, urea, lipids, inorganic nutrients; 1.3-2.0 for ATP, chlorophyll-a, microplankton and bacteria and 1.1-3.7 for POC, PON, and protein. The authors report that systematic correlations between the measured variables were few. The results demonstrate that the bulk of microlayer organic material is a complex mixture of biologically-derived compounds dominated by polymeric proteins, carbohydrates and their condensation/degradation products, much like the dissolved organic matter (DOM) in bulk seawater from which microlayer materials are derived.

Fatty acids and other lipid components of natural origin have also been widely studied. Although they comprise only a few percent of the DOM in microlayer samples (Hunter and Liss, 1977; Hardy, 1982), these compound types are valuable as specific markers of biological and other sources. Marty et al. (1988) used lipids as specific markers for atmospheric input, floatation from sub-surface algae and input within the surface layer from neuston. Lipids are generally enriched in the microlayer to a similar extent as the major organic compound classes.

Indirect measures of the overall organic content of microlayer samples, for example UV absorbance, fluorescence and surfactant activities based on electrochemical methods (Cosovic and Vojvodic, 1982; 1989; Hunter and Liss, 1981b) have been widely applied to microlayer samples. The results obtained with these methods differ from each other since each measures, or responds to, a different fraction of the DOM that is enriched in microlayers. Carlson and Mayer (1982) consider that UV absorbance (280 nm), which is almost consistently higher in microlayer samples than sub-surface water, is therefore more representative of the presence of surface slicks than either fluorescence or DOC measurements. They also argue that UV absorbance results largely from phenolic materials rather than microalgal exudates. However, these conclusions are restricted to coastal waters in which terrestrial phenolic materials are present. The situation for the open ocean is not well understood.

The surfactant activity method based on suppression of polarographic streaming is well correlated with DOC and gives very similar microlayer enrichments to those of DOC (Hunter and Liss, 1981b). However, the techniques based on the capacity of the mercury electrode double layer are more closely related to surface film enrichments and UV absorbance (Marty et al., 1988).

Spatial and temporal variability in general microlayer properties with a resolution on the scale of meters and seconds can be attained by coupling continuous sensors of UV absorbance or fluorescence to drum-type microlayer samplers (e.g., Carlson et al., 1988). Results of this approach show that enrichments of UV absorbance or fluorescence vary significantly over short time and distance scales. Data from Carlson et al. (1988) show that UV absorbance is consistently higher in the microlayer relative to subsurface water, with absorbance peaks corresponding to areas covered with obvious surface slicks. By contrast, chlorophyll fluorescence is consistently lower in the microlayer than in subsurface water in unslicked areas, but much higher in the slick-affected areas. The results shown in Figure 3.1 emphasize the natural variability of the sea surface and the consequent need for adequate sample coverage to obtain an accurate picture of the surface state on a regional or global scale.

Microlayer enrichment factors for DOC rarely exceed 1.5 (50 μm plate sampler) (Carlson et al., 1982b; Savenko, 1990). This implies that most of the DOM pool is hydrophillic in nature with a relatively low affinity for the air-water interface, a conclusion supported by studies using electrochemical surfactant activity measurements (Hunter and Liss, 1981b; Marty et ai., 1988).

Organic components of anthropogenic origin

Trace organic compounds, primarily of anthropogenic origin, including polychlorinated biphenyls (PCBs), chlorinated pesticides, and hydrocarbons have been commonly measured in nearshore microlayer samples, but there is a paucity of open ocean data. Recent improvements in methodology include much better control of sample blanks and contamination, improved detection limits and improved ability to identify individual compounds through the use of GC-MS identification.

Early studies indicated microlayer/bulkwater enrichments for PCBs, pesticides, and PAHs of 10^1 to 10^4 or more (Hardy, 1982). In Puget Sound, microlayer samples frequently contain relatively high concentrations of pesticides, PCBs, and aromatic hydrocarbons, while these compounds are generally undetectable in bulk water samples from the same sites (Hardy et al. 1987b). Very few samples have been analyzed from open ocean microlayers. A recent study (Sauer et al., 1989) found few detectable PCBs and chlorinated insecticides in either microlayer or sub-surface waters samples collected in open ocean waters off the eastern US. coast and in the Gulf of Mexico.

Trace elements

Hunter (1980) reviewed the mechanisms through which particulate species are enriched in the microlayer. Both atmospheric deposition and floatation by rising bubbles have been demonstrated as important sources of particulate material for the microlayer. The residence times of particles at the surface depend on interfacial tension forces and can range from a few seconds for wettable, high-energy particles to tens of minutes for small hydrophobic, non-wettable particles (Hunter, 1980). Experimental data, using natural urban air particles deposited on the surface of seawater microcosms, suggest microlayer residence times for six different metals between 1.5 and 15 hours (Hardy et al. 1985).

For dissolved trace elements (particularly Pb, Zn and Fe) measurements of offshore samples prior to the early 1980s must be regarded with considerable caution, and it is likely that few, if any, uncontaminated microlayer samples have ever been collected from remote waters. Since the pioneering work of Patterson and others (e.g., Patterson and Settle, 1976; Bruland, 1980), it is now clear that extensive precautions must be taken to avoid spurious contamination artifacts during the collection, handling and analysis of environmental samples for trace elements. Thus, although enrichment of dissolved trace metals in microlayer samples in the remote ocean has not been reliably demonstrated, it almost certainly occurs to some extent. For particulate trace elements, problems of contamination artifacts are much less severe, and reliable particulate trace metal enrichments have been reported by a number of workers (e.g., Hoffman et al., 1974; Hardy et al., 1988). In coastal waters, especially those with elevated trace metal concentrations as a result of human activities, results are probably more reliable. In contaminated coastal waters, enrichment factors of 10 or more have been reported (e.g., Hardy, 1982; Hardy et al., 1985). The enrichment of dissolved trace metals in microlayers is considered to be mediated by association with the primary surface-active organic components of the sea surface (Hunter and Liss, 1981c).

The physical nature of microlayer sampling devices involves the large surface area of the collector making contact with the microlayer water sample. This aspect in particular makes it very difficult to ensure freedom from contamination artifacts. One method to ensure greater confidence in trace element data is to use several different microlayer sampler types in parallel collections. It is not likely that contamination effects will be identical for quite different samplers, such as the screen and the rotating drum. However, this approach cannot replace properly conducted inter-laboratory calibration exercises as a means for validating sample handling techniques. Few, if any, such exercises have been conducted for microlayer samples.

Organotin compounds

Organotin compounds are in widespread use as biocides in anti-fouling paints, fungicides in agriculture and miticides in fruit crop culture. Tributyltin compounds (TBT) are used primarily as anti-fouling agents in paints used on boats, ships, locks, buoys, etc., and they are among the most toxic anthropogenic pollutants introduced to marine and fresh waters (Goldberg, 1986). TBT concentrations as low as 2 ng l^{-1} can have serious effects on marine biota and can cause shell chambering and gel formation in *Crassostrea gigas* (Alzieu et al., 1989) and also initiate imposex in *Nucella lapillus* and *Ilyanassa obsoleta* (Bryan et al., 1989).

Because of their hydrophobic nature and high octanol-water partition coefficient (K_{ow}) ranging from 5500 to 7000 (Laughlin et al., 1986), organotins favour partition into the lipid phase and should therefore readily accumulate in the surface microlayer. Data from the United Kingdom, Canada, and the United States not only confirm the ubiquitous distribution of organotins in both freshwater and marine environments, but also the common occurrence of such surface microlayer enrichment. Studies of Canadian freshwater regions by Maguire and Tkacz (1987) found that microlayer EF values for TBT ranged from 41 to 47,300. In marine waters enhancement was generally lower, with maximum EF values of 35 in Chesapeake Bay (Hall et al., 1987) and 27 in coastal waters of southwest England (Cleary and Stebbing, 1987). Other studies have measured EF values of 135 in the Great Bay estuary in the United States (Donard et al., 1986) and 34 in Hamilton Harbor, Bermuda (Stebbing et al., 1990). The only reported offshore data are from the North Sea, where TBT and total organotin concentrations were significantly correlated with clam larval mortality using cryopreserved Manila clam (*Tapes philippinarum*) bioassay (Cleary et al., 1993), and EF values ranged from 2.0 to 16.5 (Hardy and Cleary, 1992).

Radionuclides

The distributions of natural and anthropogenic radionuclides in various marine compartments, including the surface microlayer, have been the subject of extensive research. Natural radionuclides such as ^{210}Po, ^{210}Pb and ^{14}C have been used as tracers of marine processes or differential time markers. Artificial radionuclides such as ^{137}Cs and isotopes of Pu, considered as anthropogenic contaminants of the marine environment, have been studied to assess potential impacts through their vertical and horizontal distributions. The results of these studies show a predominant downward vertical flux of radionuclides from the surface waters to deep water masses and the sediment. However, few field studies have explored the potentially significant accumulation of radionuclides in the surface microlayer. Although bomb-derived Pu isotopes are widely distributed through the upper water column in the global ocean, the open-sea distribution in the microlayer is not known.

Indirect indications of artificial radionuclide accumulation in the surface microlayer were proposed in studies of aerosol deposition on land along the coastal areas of the Irish Sea subjected to direct low-level radioactive liquid effluent discharges from the reprocessing plant of Sellafield (Eakins and Lally, 1984). Studies, based on radionuclide measurements of top soil and aerosols, have shown that Pu and Am isotopes (primarily adsorbed on particles) had higher concentrations in marine aerosols collected on land than in the bulk seawater of the same area. The observed enrichment factors were at least 5 for these radionuclides. However, these studies do not indicate the origin of the aerosols, e.g., surface film, foam, etc.

Two other studies performed in the Western Mediterranean Sea (Marseilles) used a rotating drum microlayer sampler to collect the surface microlayer (Badie et al., 1987; Calmet and Fernandez, 1990). Samples between 18 to 37 litres were collected whereas 100 litres were sampled for the surface water (0.5 m). The samples were collected on a 0.45 μm membrane filter. ^{137}Cs microlayer enrichment factors ranged between 4 and 15. The fraction greater than 0.45 μm gave the highest enrichment factors for both ^{137}Cs and ^{106}Ru. These differences can be explained by the presence of phytoplankton cells that are characterized with concentration factors of 20 (IAEA, 1985).

Systematic studies of natural radionuclides in the sea surface microlayer should be very valuable as a benchmark for elucidating trace element uptake mechanisms. Unlike stable elements, the measurement of natural radionuclides is usually free from contamination artifacts. To date, natural radionuclide concentrations in the surface microlayer are only known for ^{210}Pb and ^{210}Po. Bacon and Elzermann (1980) reported enrichment factors for these nuclides up to a factor of 7 in screen microlayer samples, with much greater enrichments observed in a surface foam sample from a coastal pond. From a consideration of possible source terms for the radionuclide pair, they concluded that in offshore areas a significant fraction of ^{210}Po and ^{210}Pb in the microlayer was derived from sub-surface waters, whereas in coastal waters this source was relatively less important than deposition of the nuclides from the atmosphere. Heyraud and Cherry (1985) demonstrated that ^{210}Po can accumulate in neuston.

Freshwater chemistry

The general chemical and physical features of the freshwater surface layer are similar to those of the marine surface layer (Gladyshev, 1986). Most studies have focused on freshwaters near pollution sources. In the Great Lakes, for example, metal, pesticide and PCB contamination has historically been great (Rapaport and Eisenreich, 1988). However, studies suggest that the freshwater surfaces in even remote areas are contaminated by chlorinated organics which may originate from long range atmospheric transport and deposition (Ofstad et al., 1979).

3.6 Effects of Ultraviolet Radiation

Anthropogenic release of chlorofluorocarbons is leading to global decreases in stratospheric ozone (Stolarski et al., 1992) and increases in ultraviolet-B radiation (UV-B) (Blumthaler and Ambach, 1990; Lubin et al., 1989). What are the likely implications of this trend for sea surface biota? Depletion of stratospheric ozone results in a proportionately larger increase in short UV-B radiation wavelengths compared to longer UV-B radiation wavelengths (Green et al., 1980). Because biological damage generally increases exponentially with decreasing wavelengths within the UV-B radiation band, small decreases in stratospheric ozone translate into rather large increases in biologically-damaging radiation. Thus, biologists apply an action spectra which weights the wavelength-specific damage (Behrenfeld et al., 1993).

Based on a time linear extrapolation of the ozone trend data (Storlarski et al., 1992) and spatial and temporal differences in the atmospheric attenuation of UV-B radiation (Green et al., 1980), it appears that noontime UV-B irradiance at the sea surface at mid-latitudes in the Southern Hemisphere could increase about 17% between the years 1979 and 2009. As shown in Figure 3.3, this increase in incident UV-B radiation would translate into a significant change in the biologically effective wavelength region below 310 nm. The sea surface is the region of maximum UV-B radiation exposure hazard, particularly since UV-B radiation may be disproportionately high in this layer because of photon backscatter from neuston and particulates as well as multiple reflections caused by wave action (Regan, 1992).

Considerable evidence indicates that relatively small increases in UV-B radiation can inhibit photosynthesis, growth or reproduction in a variety of marine species (Hardy and Gucinski, 1989). However, neuston occur at the sea surface where the intensity of UV-B radiation is greater than in the water column. Therefore, they should be adapted to high levels of UV-B radiation. Anecdotal evidence suggests that this may be the case. Many neustonic species are highly pigmented and this is thought to be protective in screening out UV-B radiation, while others are transparent at least to visible light. DNA radiation repair mechanisms exist in many organisms to different degrees, but the relative efficiency of repair in neustonic organisms has not been measured. Microsporine-like amino acids occur in some plankton and invertebrates and appear to be effective filters of UV-B radiation, but their presence in neuston has not been investigated (Hardy and Gucinski, 1989).

Many neustonic animals and plants exist near the upper levels of their demonstrated tolerance to UV-B radiation (Hardy and Gucinski, 1989). For example, phytoplankton primary production in temperate to tropical oceans, at least in summer, is already inhibited by UV-B radiation (Behrenfeld, et al., 1993a and b). Many marine fish and benthic organisms, including commercial species, have neustonic eggs and/or larvae that may be threatened by increases in microlayer chemical contamination and UV-B radiation. However, estimating the long-term effects of UV-B radiation on deeper water column organisms (plankton) is extremely difficult and complicated by such factors as vertical mixing, photo-repair, and photoadaptation (Behrenfeld et al., 1993a and b).

3.7 Effects of Chemical Contamination

The toxic effects of contaminants in the marine environment are affected by the exposure of organisms to contaminants, by the bioavailability of particular contaminants and by the sensitivity and response of different organisms. Any toxic effects of the microlayer that are different from sub-surface waters are likely to result from changes in exposure or bioavailability provided by the unusual conditions of the microlayer.

There is no evidence that microlayer organisms have significantly different sensitivities towards contaminants than the same life stages of the same taxa in sub-surface waters. However, changes in neuston photosynthesis or respiratory quotient could be important for CO_2 transport through the microlayer.

The fact that toxic materials such as trace metals or organics are enriched in the microlayer does not, by itself, imply a significant increase in exposure. Some microlayer organisms spend a significant fraction of time attached to, or floating in contact with, the air-water interface because of surface tension forces. However, some neuston remain free of the interface and enter the microlayer region on an irregular basis, e.g., for opportunistic reasons such as grazing or diurnal changes. For the purposes of a hazard assessment, a "worst-case" scenario can be developed by considering that neustonic organisms spend long enough in the microlayer that their exposure to contaminants is the same as if the organism were immersed in bulk seawater having the same composition as the microlayer. In this simplified scenario, exposure is proportional to the enrichment factor of the contaminant.

Usually the microlayer enrichment of toxic materials is less than an order of magnitude. In this case, parallel toxic effects in both the microlayer and sub-surface waters can often be expected, and the toxicities of microlayer and sub-surface waters at the same location should be correlated with each other (Thain, 1992). The greatest exposure for many organisms will be from the sub-surface water. Enhanced microlayer effects would only be expected for organisms that experience some degree of contact with the air-sea interface, including indirect effects due to feeding on organisms or particulate matter located there.

However, in some situations microlayer enrichment of contaminants can be very large, in which case toxic concentrations can occur in the microlayer when the sub-surface water at the same site is non-toxic (Hardy and Cleary, 1992; Hardy et al., 1987a).

Only general principles can be stated concerning the factors affecting bioavailability of contaminants to microlayer organisms. Many are common to bioavailability issues in the water column and/or sediments, e.g., the effects of physical form (particulate, colloidal, dissolved), chemical speciation (aquo ion vs metal-ligand complex), and the specific nature of different organisms (e.g., filter-feeders). Other factors will be specific to the microlayer. As already mentioned, dissolved trace metals are considered to be enriched in the microlayer because of their association with surface-active ligands or colloids. This association may reduce their toxicity toward many organisms. Similarly, the attachment of particles to the air-sea interface involves very strong surface tension forces (Hunter, 1980). Whether this affects their availability to filter-feeders is not known.

One of the most likely cases in which microlayer toxic effects would be expected is that of tributyl tin (TBT) because of its very high toxicity and lipophilic nature. In the absence of biological water quality measurements on samples where microlayer contaminant concentration is known, some interpretation of toxicity may be made from toxicity threshold data and water quality standard criteria. For example, this approach was used to interpret UK organotin microlayer data in relation to toxicity threshold values for neustonic and littoral organisms. Toxicity threshold levels for mussels were shown to range from 100-230 ng TBT l^{-1}, while lower concentrations of TBT resulted in other toxic effects in oysters at concentrations from 2.5-10 ng TBT l^{-1} (Cleary, 1992). Concentrations of 2.5 ng TBT l^{-1} have been demonstrated to induce imposex in gastropods. Microlayer TBT concentrations for Canadian freshwaters at all locations studied exceeded the 12-d LC-100 value of 4.5 μg TBT l^{-1} for rainbow trout yolk sac fry, and in the most contaminated microlayer the TBT concentration was 262 times this value (Maguire and Tkacz, 1987). Such relationships, while not defining microlayer toxicity, do give cause for concern with regard to chronic toxicity and effects on sensitive organisms.

These toxicity threshold concentrations are similar to, or exceeded by, TBT concentrations reported for marine sub-surface waters, e.g. 20-1000 ng TBT l^{-1} in coastal U.K. waters (Cleary and Stebbing, 1987) and 10-80 ng TBT l^{-1} in the North Sea (Cleary et al., 1993) and the German Bight (Hardy and Cleary, 1992). Since TBT can be enriched in the microlayer by an order of magnitude over these bulk water concentrations, it seems likely that significant toxic effects on microlayer organisms should result. Measurements of TBT from open ocean waters are not presently available. The overall ecological importance of any potential effects of TBT on microlayer organisms in coastal waters must be viewed in the context of the distribution of TBT. For example, in coastal environments the present state of ecological knowledge does not allow one to state, *a priori*, that the ecological impact of TBT contamination necessarily will be greater in the microlayer than in the sediment. The use of TBT on small boats in enclosed coastal waters is being phased out in many regions.

This situation is even less clear-cut for other microlayer contaminants. As discussed in Section 3.4, few reliable microlayer measurements exist for most trace metals, particularly for the open oceans, and much of the data that have been used to argue for the enhanced toxicity of the microlayer with respect to these components is unreliable. However, since enrichment of trace metals in the microlayer is almost certainly mediated by complexing with surface-active organic matter and association with particulate matter (Hunter and Liss, 1981c), trace metal enrichments in the microlayer are unlikely to exceed those of the primary dissolved and particulate organic

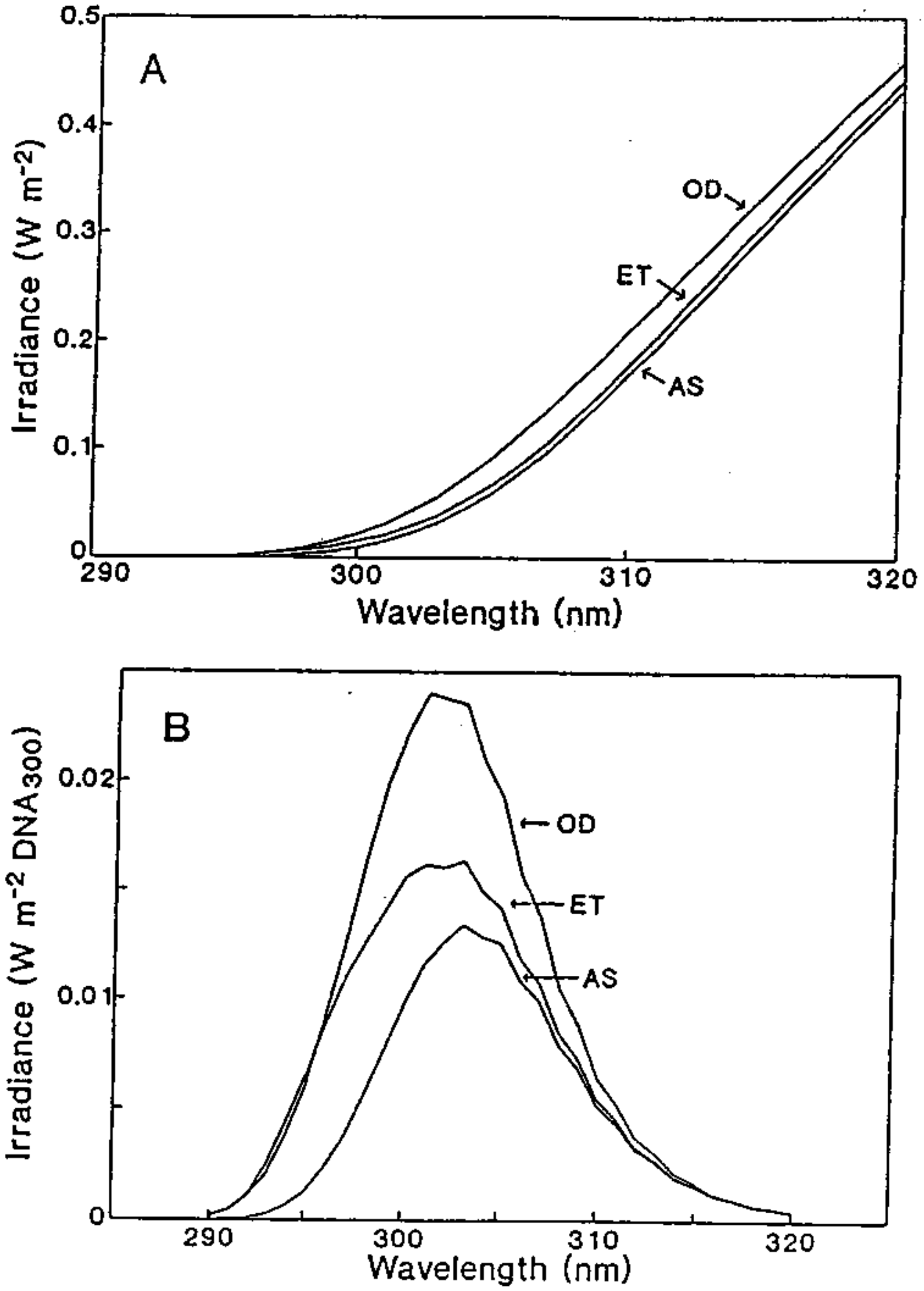

Figure 3.3 - UV-B radiation irradiance at noon at 45°S in March. AS = ambient solar for 1979; ET = UV-B radiation in enhanced experimental treatment; OD = UV-B radiation estimated for stratospheric ozone depletion by 2009. Panel A = unweighted UV-B radiation, panel B = biologically effective UV-B radiation weighted by the DNA$_{300}$ action spectrum. From Behrenfeld et al. (1993b).

components. On this basis, microlayer concentrations of dissolved trace metals are likely to be only 2-3 times greater than in sub-surface waters. This is not a large increase in potential exposure of microlayer organisms compared to that experienced in sub-surface waters. Furthermore, the complexing of metal ions necessary to produce enrichment is expected to reduce the toxicity of most metal ions compared to that of the free aquo ion in sub-surface waters.

For example, the lowest observable effect concentration (LOEC) for Cd in marine organisms is 5000 ng l^{-1}, and a range of 100-1000 ng l^{-1} is recommended as one above which toxic effects are likely (OSPAR, 1993). Cd concentrations in uncontaminated surface waters rarely exceed 40 ng l^{-1}, although levels above this have been reported for contaminated waters. Hardy et al (1990) reported microlayer dissolved Cd concentrations of 41-93 ng l^{-1} for Chesapeake Bay, which are just below the above threshold for toxic effects.

In contrast, some authors have argued that in contaminated inshore areas toxic effects may occur. For example, microlayer concentrations of PAHs, pesticides and metals such as Pb and Cu many times greater than known toxic levels or EPA water quality standards have been found in water off southern California (Cross et al., 1987), Puget Sound (Hardy et al., 1987a and b) and the North Sea (Hardy and Cleary, 1992). Further, microlayer PCB concentrations at many sites in Puget Sound exceeded water quality criteria by 130 times. Concentrations of metals and aromatic hydrocarbons at about half the stations in Chesapeake Bay were equal to or greater than concentrations proven toxic to developing fish embryos (and EFs for Cu and Pb were 8.5 and 43.3, respectively (Hardy, et al., 1990)). At most stations sampled in Puget Sound and Chesapeake Bay microlayer concentrations of Cu and Pb greatly exceeded the EPA Chronic Water Quality Criteria (2.9 $\mu g\ l^{-1}$ for Cu and 5.6 $\mu g\ l^{-1}$ for Pb).

Little is known about the quantitative importance of biological effects caused by particulate trace metals in the microlayer. Metals in particulate phases can attach readily to the air-sea interface (Hunter, 1980). However, the bioavailability of particulate metals varies greatly depending on their chemical and physical state. Metals bound in mineral phases are unlikely to be available, whereas those associated with organic particles and algae will be more readily available to filter feeders or grazers located at the air-water interface, or to organisms feeding on material deposited in intertidal habitats by surface films (Gardiner, 1992). The overall impact will depend on the ecological importance of organisms affected by these sources.

The chemical properties relevant to the microlayer and bioavailability of many toxic organic compounds (organochlorine insecticides, PCBs, PAHs) are considered similar to those of TBT. Many individual compounds in this group exhibit similarly high toxicity towards marine organisms and have the same high lipophilicity as TBT. For example, provisional ecotoxicological reference values at which toxic effects are expected in seawater solution are 50-500 ng l^{-1} for fluoranthene and 10-100 ng l^{-1} for benz[a]pyrene (OSPAR, 1993). For comparison, microlayer samples from Chesapeake Bay contain up to 928 ng l^{-1} of fluoranthrene (median 67 ng l^{-1}) and up to 440 ng l^{-1} of benz[a]pyrene (median 35 ng l^{-1}) (Hardy et al., 1990). In this case, sub-surface concentrations of both PAHs were extremely low (0.008, < 0.002 ng l^{-1} respectively).

Toxicity tests have been conducted using microlayer samples after collection by standard screen or drum methods (e.g., Williams, 1992). These experiments generally show toxic effects of different types, e.g., growth inhibition, increased mortality, chromosomal and developmental abnormalities in neustonic fish eggs and larvae (Dethelfson et al., 1985; Cross et al., 1987; Hardy et al., 1987a; Gardiner, 1992). However, as stated above, such results must be treated with caution because they may not properly reproduce the *in situ* exposure of the organism to the contaminants. On the other hand, the laboratory toxicity studies are supported by some limited in situ data. Fertilised floating fish eggs incubated in situ displayed marked reduction in hatching success at contaminated compared with uncontaminated field sites (Hardy et al. 1987a), and increased incidences of morphological and chromosomal abnormalities are associated with neustonic fish embryos collected from contaminated areas (Longwell and Hughes, 1980; Cameron and Berg, 1992).

Selection of the test organisms for bioassays is also important. There is a need for more detailed investigations on the exposure to, and bioavailability of, contaminants in the microlayer to resident organisms under realistic conditions. This will allow the development and interpretation of better bioassays. Other possibilities include the enzymatic-level Microtox® test (luciferin-luciferase) or algal growth tests. It would be valuable to develop tests that can be conducted at sea as part of multidisciplinary studies of the microlayer. Cryo-preserved embryos may be useful as model test organisms for overcoming seasonal availability of microlayer species (Karbe, 1992).

Study of the microlayer can be valuable in ascertaining chemical and biological conditions in the water column as a whole. For example, free fatty acids produced in the water column may indicate the diversity and physiological state of underlying bacterio-, phyto- and zooplankton (Gladyshev et al., 1993).

In summary, it appears that the concentrations of some highly toxic, particle-reactive contaminants with lipophilic properties, notably TBT, are high enough in some contaminated coastal waters, particularly semi-enclosed basins and harbours, to probably cause measurable toxic effects on some microlayer organisms. These predicted effects remain to be demonstrated by *in situ* studies. Moreover, their environmental significance is largely unknown and should be assessed in the context of concomitant ecological hazards associated with the same contaminants occurring in the underlying water column and sedimentary environments. A special issue of Marine Environmental Research, 23, No. 4, 1987, provides a comprehensive account of studies to that date on the effects of microlayer contamination on resident biota. Whether or not toxic effects on neuston occur in offshore oceanic microlayers remains unknown due to the lack of any study of such areas.

3.8 Effects of Greenhouse Warming

The increasing concentration of atmospheric greenhouse gases is believed to be one of the most important global environmental problems. Models predict that the relative temperature increase will be greatest at high latitude and that the ocean surface may experience a decrease in salinity toward the poles (Wright et al., 1986). One could expect the neustonic communities to expand toward the poles from the tropical and subtropical areas. However, changing wind and current patterns could have a significant influence on the distribution and survival of neuston through their influence on larval retention and transport. Application of general circulation global climate models predict a severe restriction in the distribution of some commercial fish species. For example, in response to a doubling of atmospheric CO_2 the neustonic larval reproductive stages of some species currently ranging from California to Alaska might be restricted only to the very northern part of their current range (Sibley and Strickland, 1985).

3.9 Global Change and the Microlayer

Particulate organic matter, as well as a variety of biogenic chemicals and gases, are produced by plankton in the water column and rise to the surface where they enter the microlayer with varying (mostly unknown) residence times. Such biologically-mediated processes as dimethylsulphide (DMS) production and CO_2 transport can certainly be inhibited if UV-B radiation reaches sufficiently high levels.

In the absence of sufficient experimental or *in situ* measurements, scientists currently differ in their assessment of the potential influence of microneuston on air-sea exchange of CO_2. One view holds that the rate of respiratory breakdown of particulate organic carbon in the microlayer would not be great enough compared to air-sea gas exchange rates to affect the concentration of CO_2 within the microlayer.

On the other hand, although the microlayer represents about 1 part in 10^6 of the total euphotic zone, it may account for a greater fraction of organic matter respiration because of the affinity of surface-active materials for the sea-surface interface. Significant respiratory CO_2 production can occur in the surface microlayer with the potential for enhanced CO_2 diffusion into the atmosphere (Garabetian et al., 1990). Measurements of the vertical upward flux of particulate carbon are lacking, but such fluxes could be substantial. For example, assuming a significant proportion (e.g., 1%) of the particulate carbon produced in the water column reaches the surface and undergoes respiratory breakdown in the microlayer itself, CO_2 partial pressure in the diffusion sub-layer may increase sufficiently to retard CO_2 input from the atmosphere. This "flux capping" hypothesis warrants further investigation.

3.10 Conclusions and Recommendations

The sea surface is a unique chemical and biological environment. The quantities and types of anthropogenic chemicals entering the earth's atmosphere and depositing on the ocean surface continue to grow. In addition, global changes in UV-B and global warming have the potential for negative impacts on the neustonic organisms living in the sea surface. However, at the present time it is not possible to predict local, let alone global, effects of these changes with any accuracy, given our current state of knowledge.

An important characteristic of the sea-surface microlayer is the patchiness, but also the coincidence, of high concentrations of both organisms and contaminants, resulting in potential exposures and subsequent hazards for neustonic organisms. To better characterize the temporal and spatial distribution of both organisms and contaminants, improved sea surface sampling programs, including remote sensing instrumentation, need to be developed that enable real-time chemical and biological measurements to be made.

Virtually all the studies to date of the chemical and biological characteristics of the sea-surface microlayer have been undertaken in coastal environments, where concentrations of contaminants in both the water column and the microlayer are expected to be particularly high. It appears that highly toxic, particle-reactive contaminants with lipophilic properties, notably TBT and some toxic organics, probably do cause measurable toxic effects on microlayer organisms in some contaminated coastal waters, particularly semi-enclosed basins and harbours. The environmental significance of these microlayer effects (which remain to be demonstrated by *in situ* studies) is largely unknown and should be assessed in the context of concomitant ecological hazards associated with the same contaminants occurring in the underlying water column and sediment environments.

Whether or not toxic effects on neuston occur in offshore oceanic microlayers remains unknown due to the lack of studies in such areas. To evaluate the global impact of microlayer enrichment, reliable measurements and process-oriented studies of the bioavailability of, and exposure to, contaminants in the microlayer in the open ocean would be needed, including the southern hemisphere. Chemical studies would require state-of-the art contamination-free sampling and analytical capabilities that are presently only available to a few groups. As part of any study in open ocean regions, rigorous inter-laboratory calibration exercises on sampling and on surface chemical and biological analyses must be conducted. This type of effort should also be undertaken for coastal studies.

Studies of the occurrence of natural radionuclides such as $^{210}Po/^{210}Pb$ in the sea surface microlayer can help in understanding the fluxes of metals and other substances to and in the microlayer. Radionuclides are particularly useful as tracers because contamination problems during collection and analysis of samples are much less severe. Studies using stable isotopes would also be useful in understanding processes in the sea surface.

In the absence of sufficient experimental or *in situ* measurements, scientists currently differ in their assessment of the potential influence of microneuston on air-sea exchange of CO_2. However, the possibility of "flux capping", i.e., a significant proportion of the particulate water-column carbon reaching the surface, undergoing respiratory breakdown in the microlayer, leading to increased CO_2 partial pressure, and thus retarding CO_2 input from the atmosphere, warrants further investigation.

To assess the chemical and radiation hazard to neuston, the establishment of a "neuston watch" might be considered. This could comprise a series of selected geographic sites which would be monitored on a continuing basis at least annually. Information from these stations would represent a database for assessing long-term status and trends of the sea surface.

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4. PHOTOCHEMISTRY IN THE SEA-SURFACE MICROLAYER

4.1 Introduction

Due to the enrichment of chemicals and biota within the sea-surface microlayer, there is the widely held presumption that the surface microlayer could act as a highly efficient and selective microreactor, effectively concentrating and transforming materials brought to the interface from the atmosphere and oceans by physical processes. Rapid photochemical, chemical, and biological reactions within the microlayer could produce a variety of interesting feedbacks. For example, photochemical reactions might destroy (or produce) surface-active species, thereby altering surface wave damping and gas exchange rates. Elevated levels of highly reactive intermediates produced within this zone could present a "reaction barrier" to the transport of some chemicals and trace gases across the air-sea interface, thus affecting their flux to the atmosphere or ocean. Further, reactions occurring within the microlayer potentially could enhance (or deplete) the surface concentrations of certain gases relative to those of bulk seawater, chemically modify compounds during their transport across the interface, alter the redox state, speciation and biological availability of trace metals deposited by the atmosphere to the interface, as well as influence the types and distributions of microlayer materials introduced to the atmosphere by bubble injection and to the deep ocean by particle settling.

Although very intriguing and potentially of great importance, in many instances evidence supporting the existence of these processes is lacking. Possible increases in ground-level UV-B radiation resulting from the depletion of stratospheric ozone may have important consequences for the microlayer and the processes it mediates, but the current absence of information does not allow a straightforward assessment of these possibilities.

One case where the presence of surface layer photochemistry has been demonstrated is the oxidation of hydrocarbons associated with petroleum contamination. While hydrocarbons usually are minor components of natural surface films, in spill situations they may easily exceed their solubilities in water (in the low 10^{-6} g l^{-1} range for low molecular weight aromatic hydrocarbons, decreasing with increasing molecular weight). In this case they form a separate phase on the sea surface and mix with components of the natural surface microlayer. Fossil hydrocarbons may become principal constituents of surface films, not only in an actual oil spill, but also in marine areas exposed to chronic low level petroleum contamination.

Recent advances in bulk-water photochemistry combined with new work on the composition and physical properties of the microlayer can provide fresh insights to the photochemical processes that may occur within this regime. To this end, this section will first review the photochemical properties of the major bulk-water chromophores and, where possible, will include pertinent information from studies of the microlayer. Data presented within this review will then be employed to acquire rough estimates of the rates of photochemical reactions within the microlayer. These estimates will be used to explore the possible impacts of microlayer photochemical reactions on a variety of processes occurring at the air-sea boundary.

4.2 Photochemistry in the Upper Ocean

A fundamental tenet of photochemistry is that light must first be absorbed for a photochemical reaction to be initiated. Thus, knowledge of the absorption spectra of chromophores residing within the microlayer is essential. Unfortunately, almost nothing is known about the optical absorption (and emission) properties of these species. Carlson and Mayer (1980) and Carlson (1982a, 1983) have shown that material absorbing at 280 nm is consistently enriched in the microlayer relative to bulk waters, and they concluded that dissolved phenolic material was the predominant light absorbing species. This material, referred to here as coloured or chromophoric dissolved organic matter (CDOM), is a chemically complex and ill-defined mixture of anionic organic oligoelectrolytes known to contain phenolic moieties (Aiken et al., 1985) and to exhibit surface active properties (Hayase and Tsubota, 1986). In addition to chromophores associated with organic matter, a variety of other light-absorbing substances may concentrate in the sea surface layer. These include nitrate, nitrite, transition metal complexes, keto acids, riboflavin, pteridines, algal pigments, cyanocobalamine, thiamin, biotin, and aromatic ketones. Unfortunately, not nearly enough is known about the identity and concentrations of these substances in the surface layer to perform a rigorous assessment of their photochemistry. Furthermore, until this information is acquired, possible differences between the optical properties of the microlayer and the underlying waters cannot be defined. Differences of this sort could arise from the selective partitioning of the more hydrophobic components of bulkwater CDOM into the microlayer, potentially leading to photochemical reactions within the microlayer that differ both qualitatively and quantitatively from those of bulkwaters.

Major photochemical reactions

The pathways by which photochemical processes occur in solution are of two types. First, if the absorption spectrum of the substrate overlaps with the spectrum of incoming radiation, the substrate may undergo photoreaction directly. Second, solar energy may be absorbed by other substances in the solution--known as sensitizers--that then react with the substrate of primary concern, resulting in an indirect phototransformation. These reactions are mediated by transient species that are rapidly consumed by subsequent reactions. For these mechanisms, the rate of reaction is determined by the quantity and type of substrate, sensitizer, and incoming radiation. Surface gradients involving any of these factors will lead to altered rates of photoprocesses near the air-sea interface.

The penetration of solar radiation into the upper water column depends strongly on the wavelength and degree of water colour. As shown in Table 4.1, UV-B radiation is attenuated much more rapidly than visible radiation, although in clear open ocean water UV-B still penetrates to below 10m (Smith and Baker, 1979). Most of the light-absorbing substances listed above only absorb light in the UV ($\lambda < 400$ nm). However, some of the unidentified chromophores in CDOM absorb light throughout the visible ($\lambda < 700$ nm); even though the absorption is weak, this can generate significant photochemistry below 10m in clear water (Plane et al., 1987). Another point to note in Table 4.1 is that there is effectively no attenuation of light passing through the microlayer itself.

Major photochemical intermediates in the sea include singlet oxygen, $^1O_2$; superoxide/hydroperoxide, O^-_2/HO_2; hydrogen peroxide, H_2O_2; and peroxy radicals, RO_2. $^1O_2$ is formed primarily through energy transfer from the excited triplet states of CDOM to ground state dioxygen, $^3O_2$, and wavelengths in the UV-A (315-400 nm) and UV-B (280-315 nm) are most effective in its formation (Zepp et al., 1985). Quantum yields (the fraction or percentage of absorbed photons which give rise to products) range from 1 to 3% and generally decrease with increasing wavelength (Haag et al., 1984). Because the decay of $^1O_2$ by solvent relaxation is very rapid, its loss is dominated by this pathway; the levels of $^1O_2$-reactive constituents in natural waters are generally too low to affect its steady-state concentration significantly.

The primary source of O^-_2) is believed to be CDOM, although the precise reactions producing this species remain unclear. Some workers have suggested that O^-_2 is formed by direct electron transfer from the excited triplet states of CDOM to O_2. However, reduction of O_2 by radicals or radical ions produced by intramolecular electron transfer reactions, H-atom abstractions and/or homolytic bond cleavages, is equally, if not more plausible (Blough and Zepp, 1994). In the absence of O^-_2-reactive compounds, the loss of O^-_2 is dominated by dismutation to form H_2O_2. However, transition metal complexes having one-electron reduction potentials falling between the O_2/O^-_2 and O^-_2/H_2O_2 couples can catalyze dismutation. Other potentially important sinks include reaction with NO, NO_2, phenoxy and peroxy radicals.

The primary source of H_2O_2 in the ocean is the dismutation of O^-_2 while bacteria or small phytoplankton provide the principal sink (Lean et al., 1992). Hydroxyl radical, OH, is produced primarily through other mechanisms such as the photolysis of nitrite or nitrate. OH reacts with Br^- to produce Br^-_2 (Zafiriou et al., 1987), which in turn reacts with carbonate (True and Zafiriou, 1987), producing carbonate radicals. The carbonate radical may self-terminate in competition with its oxidation of organic substrates. The fate of the other product of nitrite photolysis, NO, is likely to be dominated by reaction with O^-_2 (Blough and Zafiriou, 1985). This reaction yields peroxynitrite, which is also a strong oxidant and produces strong oxidants during its

Table 4.1

Penetration of UV-B and Visible Radiation in Seawater

Fraction of UV-B radiation ($\lambda = 310$ nm) that penetrates from the surface to a specified depth in the water column

Water Depth	1 cm	1m	10m	50m	100m
Clearest open ocean water	1.00	0.86	0.22	6×10^{-4}	--
Moderately productive water	0.99	0.40	1×10^{-4}	--	--

Fraction of visible radiation ($\lambda = 500$ nm) that penetrates from the surface to a specified depth in the water column

Water Depth	1 cm	1m	10m	50m	100m
Clearest open ocean water	1.00	0.98	0.78	0.29	0.08
Moderately productive water	1.00	0.90	0.33	4×10^{-3}	2×10^{-5}

decomposition. The photolysis of NO_3^- also generates OH as well as NO_2. Subsequent reactions of NO_2 can produce NO_2^- and NO_3^-, thereby coupling the dynamic cycles of NO_2^- and NO_3^- photolysis. Although the oxidation of reduced metals such Fe(II) and Cu(I) by H_2O_2 can also produce OH (Moffett and Zika, 1987; Millero and Sotolongo, 1989; Zepp et al., 1992), this process will be limited to those waters where significant levels of reduced metals are formed. The photolysis of H_2O_2 also is not a significant source of OH despite the high quantum yield for this reaction (0.98) due to the poor overlap between its absorption spectrum and the ground-level solar spectrum.

Peroxy radicals are thought to be formed by O_2 addition to primary (carbon-centered) radicals (R) produced photochemically from CDOM and other sensitizers via intramolecular H-atom abstractions, electron transfer reactions, and homolytic bond cleavages. These species can also be generated from secondary radicals produced by H-atom abstraction or addition reactions of RO_2 with DOM, or one-electron oxidations of DOM by CO^-_3 or Br^-_2). Earlier work by Mill et al. (1980) and Faust and Hoigne (1987) provided evidence for the photochemical production of this class of radicals, but could not supply information on the specific RO_2 species that were formed. Indirect evidence for the formation of specific RO_2 species has been acquired by employing stable nitroxide radicals to trap the carbon-centered radicals, the immediate precursors to the RO_2 (Blough, 1988; Kieber and Blough, 1990a,b). Using a highly-sensitive fluorescence detection scheme (Blough and Simpson, 1988) combined with high performance liquid chromatography, a number of low molecular weight radicals have been detected in seawater, principally the acetyl and methyl radicals. Evidence for the formation of radical centers on high molecular weight CDOM has also been obtained, although their yield appears to be significantly less than that of the low molecular weight species.

Quantum yields for the formation of the major species, the acetyl and methyl radicals, exhibit a different wavelength dependence and are 10- and 100-fold lower, respectively, than those for nitroxide reduction. These results imply that O^-_2production dominates RO_2 formation in surface seawaters and that different chromophores within the CDOM are responsible for the formation of these radicals. Estimated mid-day rates for formation of the acetylperoxy radical in natural waters range from 10^{-13}-10^{-11} M s^{-1} as compared with 10^{-11}-10^{-8} M s^{-1} for O^{-}_2 (Blough and Zepp, 1994).

While the acetylperoxy radical may react with superoxide to form peracetic acid, the fate of the methylperoxy radical as well as the high molecular weight radical centers is less clear. Possible pathways include termination reactions to form non-radical and non-peroxidic products, and H-atom abstractions or addition reactions to from organic peroxides and secondary radicals.

Photoalteration and photoproducts of CDOM

That aquatic dissolved organic carbon (DOC) is photoreactive has been established by several recent studies (Kouassi et al., 1990; Amador et al., 1989; Kieber et al., 1989; Mopper et al., 1991; Miller and Zepp, 1992; Valentine and Zepp, 1993). Evidence for such photoreactivity derives in part from observed changes in the electronic absorption spectrum of the organic matter as well as in the fluorescence intensity and spectrum. The sunlight-induced decrease in absorbance is not accompanied by a corresponding change in DOC, although conversion to various UV-transparent products does occur (see below). Other studies have shown that sunlight fades the fluorescence intensity of humic substances more rapidly than the absorbance (Kouassi et al., 1990).

Miller and Zepp (1992) have found that these spectral changes produce greater bleaching of the ultraviolet portion of the CDOM spectra. Thus, photodegradation of CDOM results in deeper penetration of solar UV (as compared with visible) radiation into the sea and freshwaters. This effect alone may have important effects on the carbon cycle by reducing photosynthesis and enhancing the photodegradation of CDOM.

The photoinduced fading of CDOM is accompanied by the formation of a variety of organic and inorganic compounds. The photoproducts of the biologically refractory CDOM in natural waters are low molecular weight compounds that are biologically labile, e.g., formaldehyde, acetaldehyde, and the α-keto acid, glyoxylate (Kieber et al., 1989). Photoproduction rates of these compounds are greatest for inland and coastal waters and smallest for open ocean waters. UV-B radiation is primarily responsible for the photodegradaton of marine DOC. Francko (1990) has reviewed the rather sparse literature on effects of solar radiation on the bioavailablity of CDOM.

Carbon cycling drives the flux of other elements through ecosystems so that any change in the former has significant effects on the latter. For example, the photodegradation of CDOM is likely to result in the release of inorganic nitrogen. Photoreactions involving CDOM also have been shown to increase the biological availability of phosphorus (Francko, 1990).

In addition, trace gases such as carbon dioxide, carbon monoxide and carbonyl sulphide are formed. Carbon dioxide is the major gaseous product (Miller and Zepp, 1992). Photooxidation of CDOM is believed to be an important source of carbon monoxide in seawater, while its loss has been ascribed primarily to microbial processes (Conrad et al., 1982). As a result of these two processes, carbon monoxide emissions from the sea follow a diurnal pattern, with maximum near-surface ocean concentrations greatly exceeding saturation during daylight. Although the sea is thought to be a net source of carbon monoxide, great uncertainty exists regarding the strength of this source. For example, a widely cited value for marine emissions is 10 to 40 Tg y^{-1} (Logan et al, 1981), but Conrad and co-workers (1982) have suggested that the oceanic source strength could range up to 180 Tg y^{-1} based on a study in the Atlantic Ocean.

Carbonyl sulphide is the most concentrated sulphur-containing gas in the troposphere (Bates et al., 1992; Khalil and Rasmussen, 1984). COS is considered to be the major source of sulphate aerosols in the stratosphere during periods of quiescent volcanic activity (Crutzen, 1976; Servant, 1986; Hofmann, 1990). As such, COS affects stratospheric temperature and chemistry, including chemical processes that affect the ozone layer. These studies indicate that COS is formed primarily by photooxidation processes in the upper layers of the ocean (Ferek and Andreae, 1984), with the highest fluxes in coastal/shelf waters. Studies by Zepp and Andreae (1990) indicate that the predominant pathway for photochemical formation of COS involves photosensitized oxidation of organosulphur compounds by the CDOM in sea water. Wavelength studies of COS formation in coastal seawater samples have confirmed that COS is predominantly formed by the action of UV-B radiation.

Hydrocarbon degradation

With the exception of condensed aromatics, most hydrocarbons occurring in seawater, whether fossil or recently biosynthesized, are transparent to solar UV radiation at sea level and should therefore be inactive photochemically. However, surface seawater contains a variety of substances which act as photosensitizers. They include components of the dissolved organic matter commonly referred to as marine humic material (Hoigne et al., 1989), and anthropogenic substances such as polycyclic aromatic ketones (Ehrhardt et al., 1982; Ehrhardt and Petrick, 1993). Their first excited singlet states are generated by absorption of solar UV light quanta, and these are then converted with high intersystem crossing yields to the first excited triplet states. These are sufficiently long-lived for energy transfer to, or reaction with, non-absorbing target molecules. In bulk seawater, the most important quencher of excited triplet states of sensitizers is dissolved molecular oxygen, which is converted to $^1O_2$. Analyses of photo-oxidation products both in field samples and in model experiments conducted under controlled conditions have shown that the generation of carbon-centered radicals by abstraction of a hydrogen atom is the first step in complex reaction sequences leading to the oxidation and decomposition of alkanes, phenylalkanes, and cycloalkanes (Ehrhardt and Petrick, 1984; 1985; 1986; Ehrhardt and Weber, 1991). $^1O_2$ is not energetic enough for hydrogen abstraction, although it is capable of adding to the double bonds of olefins, thereby mediating photo-oxidation reactions of this class of hydrocarbons (Kearns, 1971).

Elevated concentrations of triplet sensitizers and hydrocarbons in the sea surface microlayer apparently lead to reactions among these species which result in hydrogen abstraction. The carbon-centered radicals thus generated react with molecular oxygen to form peroxy radicals. By a variety of mechanisms the peroxy radicals can be reduced to oxyl radicals which experimental evidence strongly suggests are key intermediates in the photo-oxidation reactions of hydrocarbons. Abstraction of a hydrogen atom leads to the formation of alcohols; ketones are formed by reaction with molecular oxygen. It is still an open question whether cleavage of carbon-carbon bonds leading to lower molecular weight carbonyl compounds and terminal alkenes take place by the photo-decomposition of intermediate ketones, or whether oxyl radicals trigger the fragmentation reactions.

Alicyclic hydrocarbons form relatively stable hydroperoxides (Ehrhardt and Weber, 1995) which may account for the increased toxicity of sunlight-illuminated oil films (Pengerud et al., 1984). On the other hand, many photo-oxidation products of hydrocarbons are decomposed more rapidly by microorganisms than the parent compounds (Rontani et al., 1987). This effect is especially pronounced in the case of alicyclic hydrocarbons (Trudgill, 1979). There is reason to believe that more complex functionalized molecules are photo-decomposed following similar reaction pathways.

Hydrocarbons are also produced by near-surface photochemically mediated reactions. Alkenes are the most reactive of these compounds and are formed in the mixed layer via photosynthetic and photochemical processes. Isoprene is produced as a by-product of phytoplankton photosynthesis (Bonsang et al., 1992). Isoprene is highly reactive with ozone and various radical species in the atmosphere. It should exhibit similar reactivity in seawater, particularly in the vicinity of the microlayer where reactions with enriched levels of oxidants may limit its transport to the atmosphere. Recent evidence (Ratte et al., 1993) suggests that low molecular weight alkenes (i.e., C_2-C_4) are produced photochemically from CDOM in the surface ocean. Like isoprene these compounds are susceptible to oxidation in the near-surface layer, but because they are produced photochemically from DOM, they may also exhibit a production gradient from enriched CDOM in the microlayer. The hydrophobic nature of the alkenes, and particularly the higher molecular weight compounds like isoprene, may assist in their incorporation and oxidation within the microlayer.

4.3 Probable Photochemical Processes in the Microlayer

Assuming that microlayer CDOM exhibits absorption spectra and quantum yields similar to those of the underlying bulk waters, currently available data can be employed within a simple model to estimate photochemical formation rates and fluxes of species in the microlayer. In this model, the formation rates, $F_M(\lambda)$, and fluxes, $Y_M(\lambda)$, are given by

$$F_M(\lambda) = E_o(\lambda) \bullet \phi(\lambda) \bullet a(\lambda)_{i,M} \qquad (4.1)$$

$$Y_M(\lambda) = E_o(\lambda) \bullet \phi(\lambda) \bullet a(\lambda)_{i,M} \bullet z_M \qquad (4.2)$$

where $E_o(\lambda)$ is the downwelling irradiance at the surface, $\phi(\lambda)$ is the photochemical quantum yield, $a(\lambda)$ is the absorption coefficient of the species undergoing reaction and z_M is the microlayer depth. Integration over wavelength provides the total photochemical formation rate and flux in the microlayer:

$$F_M = \int E_o(\lambda) \bullet \phi(\lambda) \bullet a(\lambda)_{i,M}\, d\lambda \qquad (4.3)$$

$$Y_M = F_M \bullet z_M \qquad (4.4)$$

For CDOM photoreactions, Y_M can be compared to the total water column flux ($z \rightarrow \infty$),

$$Y = \int E_o(\lambda) \bullet \phi(\lambda)\, d\lambda \qquad (4.5)$$

assuming that light absorption by CDOM dominates, as it often does in coastal/shelf waters over the 300-400 nm wavelength range (Vodacek et al., 1994).

Equations 1-4 indicate that F_M and Y_M are directly proportional to the absorption coefficients of the material in the microlayer. Thus, for a 2-fold enrichment in absorption, F_M and Y_M will be twice as large as those obtained for an equivalent depth interval just beneath the microlayer. However, the dilution of material by sampling devices that collect over depths greater than that of the microlayer can produce significant underestimates of F_M and slight overestimates of Y_M. For example, if the true microlayer depth was 1 μm, the use of a 50 μm sampler would produce a 15-fold underestimate of F_M and a 3.3-fold overestimate of Y_M for an observed absorption enrichment of 1.4 relative to bulk-water. These dilution effects can be calculated from the relation

$$a(\lambda)_M = a(\lambda)_B \bullet [1 + z_s/z_M(E-1)] \qquad (4.6)$$

where $a(\lambda)_M$ and $a(\lambda)_B$ are the microlayer and bulk absorption coefficients, respectively, E is the apparent enrichment factor for samples collected from depth z_s, and z_M is the true microlayer depth.

In principle, the elevated levels of highly reactive species produced photochemically within the microlayer could act as a barrier to the exchange of certain compounds across the interface. However, ignoring atmospheric deposition, the 1.5- to 2-fold enrichments of light-absorbing material observed by Carlson (1982a) would produce, at most, a 1.5- to 2-fold increase in the steady-state levels of reactive species in the microlayer (Equation 1). Thus, the levels of trace constituents passing through the microlayer would be reduced by only two-fold over that for an equivalent depth interval just under the microlayer. If z_M is significantly smaller than z_s (Equation 6), this loss would be reduced even further; while a fifty-fold reduction in z_M for an observed enrichment of 1.4 yields a 15-fold increase in production rate, the residence time (t) for a species passing through this smaller layer is decreased 2500-fold due to the squared length dependence in the diffusion equation,

$$\tau = z_M^2/2D \qquad (4.7)$$

where D is the molecular diffusion coefficient. The significantly larger fluxes of reactive species generated in the near-surface bulk waters will act as the principal determinant of the surface concentrations of these compounds. This "barrier" will be important only if the material in the microlayer is significantly more photoreactive than that of the bulk, or if the microlayer material produces a different ensemble of reactive intermediates that exhibit selectivity for certain compounds.

In situ trace gas production

CO, CO_2, and COS (in coastal regions) will all be formed through the photochemical degradation of CDOM in the microlayer. However, given the low enrichments for CDOM, photoproduction rates are not likely to be more than two-fold over bulk, and thus will make a negligible contribution to the total water column flux.

Atmospheric inputs of trace species

As the microlayer forms the interface between the ocean and the atmosphere, it is instructive to compare the atmospheric deposition of reactive species such as H_2O_2 and peroxy radicals with their *in situ* photochemical production in the microlayer. The depositional fluxes of a number of atmospheric species have been modelled by Thompson and Zafiriou (1983). *In situ* production can be estimated by assuming a typical microlayer thickness of 50 μm, and a two-fold enrichment of organic chromophores in the microlayer over the bulk water column. This analysis indicates that atmospheric deposition of H_2O_2 and CH_3OO will far outweigh their *in situ* photochemical production within the microlayer (Table 4.2), unless the microlayer contains material substantially more photoreactive than the bulk-water CDOM on which these calculations are based. Wet deposition of H_2O_2 from fog and rain may constitute a significant input of this species to the microlayer over brief time periods, but water column production generally exceeds this input. As shown in Table 4.2, the photochemical flux of O_2^- within the microlayer is similar to the atmospheric flux of HO_2. O_2^- is likely to be important in the microlayer due to its efficient reaction with NO, phenoxy radicals, peroxy radicals, transition metal ions and possibly chlorinated hydrocarbons. Although the water column fluxes of O_2^- and H_2O_2 are usually far larger than the sum of their atmospheric and microlayer fluxes (Table 4.2), the effectively higher inputs of these very reactive species within this boundary due to atmospheric deposition and *in situ* photochemistry should lead to a more rapid oxidative turnover of materials within this "microreactor" and potentially to reactions not observed in bulk waters. The largest depositional flux of an atmospheric oxidant is that of ozone, a compound known to play a key role in the release of volatile iodine from the sea surface (Garland and Curtis, 1981; Thompson and Zafiriou, 1983).

The recent suggestion that a lack of available Fe limits primary production in certain open ocean waters (Martin and Fitzwater, 1988) has intensified interest in the transport and photochemical reactions of Fe species in both seawater (Wells et al., 1991; Wells and Mayer, 1991) and atmospheric aerosols (Duce, 1986; Behra and Sigg, 1990; Zhuang et al., 1990, 1992; Zhuang and Duce, 1992; Zuo and Hoigne, 1992; Zhu et al., 1993; Erel et al., 1993). At the oxygen concentrations and pH of surface sea waters, very little biologically-available Fe(III) is expected to exist due to the high thermodynamic stability of the colloidal iron (hydr)oxides. At lower pH where Fe(II) is more slowly oxidized by O_2 and H_2O_2 (Moffet and Zika, 1987; Millero and Sotolongo, 1989), evidence for the photoreductive dissolution of colloidal iron oxides by CDOM has been obtained by several groups (Waite and Morel, 1984; Sulzberger et al., 1989). While photoreduction still occurs at the higher pH of sea water, the Fe(II) that is produced appears to be oxidized more rapidly than its detachment from the oxide surface, so that little if any escapes to solution (see, however, O'Sullivan et al. (1991) and King et al. (1991)). Wells et al. (1991) have found that the chemical availability of iron as determined by chelation with 8-hydroxyquinoline (oxine) is strongly correlated with the growth rates of marine phytoplankton and that sunlight increases this availability. These workers have suggested that CDOM-driven cycles of light-induced reduction and rapid re-oxidation lead to the formation of amorphous Fe(III) precipitates that do serve as a source of available Fe (Wells and Mayer, 1991, Wells et al., 1991; Waite, 1990).

Clear evidence for the photochemical generation of significant levels of Fe(II) in atmospheric aqueous phases (at lower pH) has been acquired by a number of groups (Faust, 1994; Sulzberger et al., 1994; Waite and Szymczak, 1994). The fate of this Fe after deposition to the sea surface is not clear. However, higher levels of CDOM within the microlayer could act to maintain or increase the biological availability of this Fe through complexation and photochemical reduction at this interface.

Manganese oxides undergo light-induced reductive dissolution in seawaters (Sunda et al., 1983; Sunda and Huntsman, 1988). The product, Mn(II), is kinetically stable to oxidation in the absence of certain bacteria that are known to be photoinhibited in the upper ocean. These two effects of sunlight combine to produce a surface maximum in soluble Mn, unlike most transition metals which are depleted in surface waters due to biological removal processes. A more detailed discussion of transition metal photochemistry and its role in environmental processes is provided in Blough and Zepp (1994).

Table 4.2

Estimated Formation Rates and Fluxes for Species Generated Photochemically Within the Microlayer, Within the Water Column, and Through Dry Deposition from the Atmosphere[a]

Species	F_M ($cm^{-3}s^{-1}$)	Y_M ($cm^{-2}s^{-1}$)[b]	Y ($cm^{-2}s^{-1}$)	**Air-Sea Flux**[c] ($cm^{-2}s^{-1}$)
O^-_2/HO_2	7.6×10^{10}	3.8×10^{8}	3.8×10^{12}	1.0×10^{8}
H_2O_2	1.8×10^{10}	8.9×10^{7}	7.6×10^{11}	1.4×10^{10}
$CH_3\bullet(CH_3OO\bullet)$	1.3×10^{8}	6.6×10^{5}	5.1×10^{9}	1.1×10^{8}
$CH_3C(O)\bullet(CH_3C(O)OO\bullet)$	6.3×10^{8}	3.2×10^{6}	1.9×10^{10}	--
CO	2.0×10^{9}	9.8×10^{6}	9.2×10^{10}	--

[a] 24 hour averages
[b] Assumes a 50 μm microlayer
[c] From Thompson and Zafiriou (1983)

In situ halogen chemistry

The steady-state concentrations of reactive halogen species in the surface microlayer should be high relative to their concentrations in the bulk water, being maintained by atmospheric deposition of oxidants and photoreactions generating OH. The principal source of these species is through the deposition of O_3, which will react with I^- to such intermediates as I_2, HOI and possibly I^-_2 (Garland and Curtis, 1981). Another photochemical source of reactive iodine species is homolytic fission of iodo-organic compounds. Br^-_2 is another reactive halogen species that is formed through photoreactions in the microlayer.

The primary reactions of these halogen species should be oxidation of organic substrates, but substitution reactions of aromatic and unsaturated compounds are also possible (Waite et al., 1988). Halogenation of organic compounds can also take place via chloro- and bromo-peroxidases which employ hydrogen peroxide as the oxidant (Zepp and Ritmiller, 1995 and references therein).

Conversion of DOC

The characteristics of the sea surface microlayer combine to produce an environment that is unique with respect to transformation of dissolved (DOM) and particulate organic matter (POM). Hence, DOM within the interface may be converted to POM by aggregation or polymerization, or by compression associated with wave motions or bubble collapse, or by adsorption to other oceanic or atmospherically derived particles in the interface (Carlson, 1993). Collected microlayer samples can be strongly UV-absorbing relative to the bulk water (Carlson, 1982a,b), implying that photochemical processes may be important in transformations between and within the DOM and

POM fraction. Harvey et al. (1983) for example, showed that lipids could undergo photoinduced oxidation and cross-linking to produce polymers having properties similar to marine humus. The air-sea interface forces the aggregation of photosensitizers and redox species. Reactive substrates and the rapid replenishment of these species should make the microlayer a dynamic photochemically active boundary layer between the ocean and atmosphere. This should lead not only to particle formation, but also fragmentation, solubilization, mineralization and structural modification of the POM and DOM fractions that reside in this layer.

The consequences of the photochemically active boundary layer on the DOM and POM are numerous. One of the important consequences involves particulate formation and subsequent sinking. The process could potentially remove deleterious anthropogenic compounds or toxic metals to the sediments. Processes of molecular fragmentation or mineralization could process toxic and refractory materials into more readily biodegradable components. Modification of hydrophobic compounds (e.g., hydrocarbons and pigments) into surfactants via introduction of polar functional groups could be important in terms of producing, maintaining and modifying the nature of the organic sea surface layer.

Hydrocarbon degradation

There is some evidence to indicate that sunlight illumination increases the toxicity of surface films of petroleum (Pengerud et al., 1984). The enhanced toxicity has been attributed to stable hydroperoxides (Larson et al., 1992) which cycloalkanes form quite readily (Erhardt and Weber, 1994). Preliminary tests using luminescent marine bacteria as indicator organisms suggest that the photooxidation of phenyl alkanes results in somewhat lower toxicity, although the LC_{50} doses remained in the same order of magnitude (Burns and Ehrhardt, unpublished). Effects of enhanced toxicity may be offset by easier microbial degradability of other hydrocarbon photooxidation products, such as alcohols and ketones.

4.4 Global Change Issues

Changes in ultra-violet radiation

The depletion of stratospheric ozone is causing an increase in the levels of UV-B radiation reaching the surface, particularly at high latitudes. This change will affect photochemical processes with action spectra that are significant in the UV-B spectral region, relative to longer wavelengths (Figure 4.1). Such processes include the photolysis of ketones, halogenated hydrocarbons, phenols, and nitrate ions. A further consideration is that some processes will probably show a non-linear rate enhancement with increasing UV-B. For instance, the $O^{\cdot}_2$ radical is produced photochemically but also undergoes significant removal by reaction with other species mediated by photochemistry, such as NO, NO_2 and transition metals.

Increased UV-B can enhance or reduce the production of atmospherically-important trace gases in the sea through changes in biological and photochemical processes at the sea surface (SCOPE, 1993). These changes may trigger significant feedback mechanisms. For example, the increased evasion of CO reduces the hydroxyl radical concentration in the troposphere. This permits greater levels of CH_4 to reach the stratosphere, leading to increased stratospheric H_2O concentrations and a higher likelihood of stratospheric ice cloud formation and chlorine-catalysed O_3 depletion. Marine emissions of CH_3Cl and CH_3Br also affect stratospheric O_3, whereas bromoform and other brominated gases have been implicated in tropospheric O_3 removal in polar regions. Increased evasion rates of isoprene and other non methane hydrocarbons increase tropospheric O_3 in regions with elevated concentrations of nitrogen oxides. COS provides a major source of sulphate aerosols in the lower stratosphere (see section 4.2). These aerosols provide nuclei for polar stratospheric clouds and may also be involved directly in heterogeneous chemistry at low temperatures, enhancing stratospheric ozone depletion.

Dimethyl sulphide (DMS) is a sulphur-containing substance that is produced in the ocean and is known to be oxidised in the troposphere to species such as methane sulphonic acid and sulphate. This oxidation process could increase the condensation nuclei available for cloud formation in the marine troposphere (Bates et al., 1992). An increase in cloud cover would decrease the UV-B levels reaching the sea surface and also affect the tropospheric heat budget.

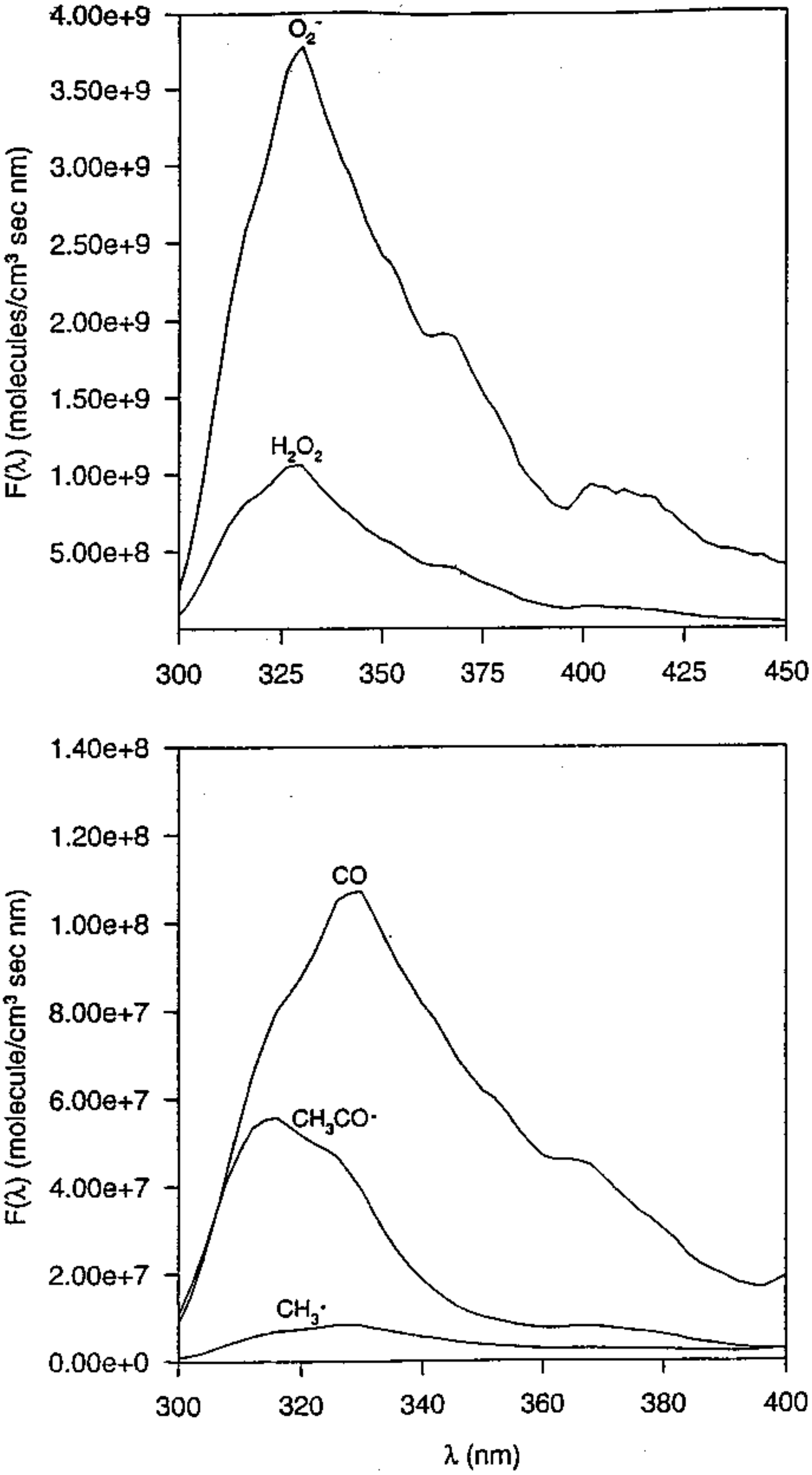

Figure 4.1 - Calculated spectral dependence of the midday photochemical production rates for O_2^- (hydroxyamine formation), H_2O_2, CO, $CH_3CO\bullet$ and $CH_3\bullet$ within the microlayer (see text) (Blough, 1996).

UV-B radiation potentially can affect fluxes of DMS through effects on phytoplankton that produce its precursor, dimethylsulphonium propionate, on bacteria that consume DMS (Kiene and Bates, 1990), and on the photooxidation of DMS (Brimblecombe and Shooter, 1986). Interactions of these processes have major effects on the sea-to-air flux of DMS: presently, only about 3% of the DMS that is produced in the upper ocean actually is transferred to the atmosphere (Kiene and Bates, 1990). Thus, future changes in solar UV-B potentially could have major effects on release of this gas from the sea surface.

Radiation balance

The ocean provides a large heat reservoir. Changes in the heat content of the ocean have the potential for global changes in climate. Therefore, microlayer processes could affect the transmission of radiation between the ocean and the atmosphere. The ocean, like any other medium, will heat or cool until the input energy matches the output energy. For the ocean the input energy includes the short-wave (solar) radiation from 0.3 to 4.0 μm, and the output energy includes the longwave blackbody radiation peaked near 10 μm. The longwave emission is controlled by the emissivity of the medium and the temperature. The short-wave input energy is controlled by many factors, including the reflectivity of the surface. This is determined by the real part of the index of refraction and the incident angle of the radiation.

The longwave radiation could be affected by the microlayer if this has a different emissivity than water in the spectral region near 10 μm. While it is likely that the emissivity of an organic film is different from that of water, the microlayer is not thick enough to absorb enough of the longwave blackbody radiation originating within the water to have any significant effect on the total longwave emission.

The index of refraction of an organic microlayer is likely to be higher than that of water in the short-wave region of the spectrum. This would increase the reflectance and cause a decrease in the heat transport into the ocean. Note that the organic film must be sufficiently thick, on the order of the wavelength of interest, for Fresnel's equations of reflectance to apply. If we assume an index of refraction for an organic microfilm of 1.5 (water = 1.34) and examine the reflectance for the case of a normally incident solar beam, the reflectance could increase from 2.1% to 4.0% in the presence of the organic film. For heat budget calculations, this could represent a significant decrease in short wave energy input. The actual loss of radiation will be a function of the solar zenith angle and the capillary wave spectrum which is itself governed by the nature of the microlayer.

4.5 Conclusions and Recommendations

Available evidence suggests that photochemical processes in the microlayer may not differ substantially from those of the near-surface bulk waters. Assuming the presence of a 50 μm thick microlayer that is enriched in organic chromophores by 2-fold over the bulk, it is concluded that the fluxes of reactive intermediates appear to be too small to affect significantly the transfer of reactive species across the air-sea interface. Further, the flux resulting from photochemical production of gases from within the microlayer is insignificant with respect to the total flux from the water column. It should be noted, moreover, that these processes do not appear to be limited by the transfer of photoreactive material from the underlying bulk waters.

There are several contexts in which microlayer photochemical processes may prove to be important. These are likely to include: 1) photochemical reactions within hydrocarbon slicks, 2) the fate of certain atmospheric species following deposition, and 3) changes in physical properties of the microlayer due to phototransformation of its constituents.

It should be noted that most of our conclusions are not based on direct experimental evidence. This situation has arisen in part through the lack of suitable techniques for studying photochemical processes within the microlayer on the required spatial and temporal scales. These limitations may be redressed by the application of new chemical and spectroscopic techniques.

Recommendations for further work in this area include i.) determination of the spectral characteristics of the microlayer in a range of environments; ii.) acquisition of action spectra for photochemical reactions of individual compounds that are enriched in the microlayer; iii.) determination of the effects of the photochemical alteration of the microlayer on the air-sea exchange of atmospherically-important trace gases; iv.) evaluation of the impact of the deposition of O_3 and other tropospheric oxidants on the microlayer; v.) determination of the influence of the microlayer on the sea-surface albedo and its susceptibility to photochemical alteration; and vi.) evaluation of the rates of photoinduced particle formation and removal and the role of these processes in the scavenging of toxic compounds from the upper ocean.

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GESAMP REPORTS AND STUDIES

The following reports and studies have been published so far. They are available from any of the organizations sponsoring GESAMP.

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