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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**

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## **GESAMP REPORTS AND STUDIES No.59**

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of Marine Environmental Protection (GESAMP)**

## **THE SEA-SURFACE MICROLAYER AND ITS ROLE IN GLOBAL CHANGE**



**WMO  
Geneva, 1995**

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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.

## 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 ( $< \sim 1 \mu\text{m}$ ) enriched in surface-active compounds; the surface microlayer ( $< \sim 1000 \mu\text{m}$ ) containing high densities of particles and microorganisms; and the surface millilayer ( $< \sim 10 \text{ mm}$ ) 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  $\sim 1000 \mu\text{m}$  (1 mm) of the ocean surface. It, together with an overlying atmospheric layer of thickness 50-500  $\mu\text{m}$ , 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  $\mu\text{m}$  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  $\text{CO}_2$  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  $\text{CO}_2$  uptake at the ocean surface.

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## TABLE OF CONTENTS

<b>Executive Summary</b>	<b>vii</b>
<b>1. Introduction</b>	<b>1</b>
<b>2. Physical Processes in the Microlayer and the Air-Sea Exchange of Trace Gases</b>	<b>2</b>
2.1 Surface Films	2
2.2 Physical Processes in the Microlayer	7
2.3 Wave Breaking and Bubbles	8
2.4 The Effect of Rain on Exchange Processes	10
2.5 Horizontal Transport and Deposition of Surface Slicks in Coastal Zones	10
2.6 Review of Experimental Data on Gas Transfer	11
2.7 Review of Experimental Techniques	13
2.8 Parameterization of Air-Sea Exchange Processes	16
2.9 Conclusions and Recommendations	19
References	20
<b>3. Biological Effects of Chemical and Radiative Change in the Sea Surface</b>	<b>27</b>
3.1 Introduction	27
3.2 Samplers and Sampling Techniques	27
3.3 Characteristics of the Surface Microlayer	28
3.4 Biology in the Sea Surface	31
3.5 Chemistry in the Sea Surface	35
3.6 Effects of Ultraviolet Radiation	38
3.7 Effects of Chemical Contamination	39
3.8 Effects of Greenhouse Warming	43
3.9 Global Change and the Microlayer	43
3.10 Conclusions and Recommendations	44
References	45
<b>4. Photochemistry in the Sea-Surface Microlayer</b>	<b>52</b>
4.1 Introduction	52
4.2 Photochemistry in the Upper Ocean	52
4.3 Probable Photochemical Processes in the Microlayer	57
4.4 Global Change Issues	60
4.5 Conclusions and Recommendations	62
References	64
<b>Annex I - Participants in the Preparation of the Report</b>	<b>69</b>

## 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  $\mu\text{m}$ , 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 ( $< \sim 1 \mu\text{m}$ ), enriched in surface-active compounds; the surface microlayer ( $< \sim 1000 \mu\text{m}$ ), with high densities of particles and microorganisms; and the surface millilayer ( $< \sim 10 \text{ mm}$ ), 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  $\mu\text{m}$  of the water surface. The thermal sub-layer is approximately the top 300  $\mu\text{m}$  of the water surface, while the diffusion sub-layer refers to the top 50  $\mu\text{m}$ .

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  $\beta$ -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,  $\sim 1$  cm 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  $0.5 \text{ m s}^{-1}$ . 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  $\sim 3\text{--}4 \text{ m s}^{-1}$ . 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  $50 \text{ mN m}^{-1}$  (milliNewtons per meter). In visible slicks, spreading pressures can range from a few  $\text{mN m}^{-1}$  to tens of  $\text{mN m}^{-1}$ . 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  $50 \text{ mN m}^{-1}$ . To contrast this, areas not visibly slicked can have spreading pressures of the order of a few tenths of a  $\text{mN m}^{-1}$ , 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.



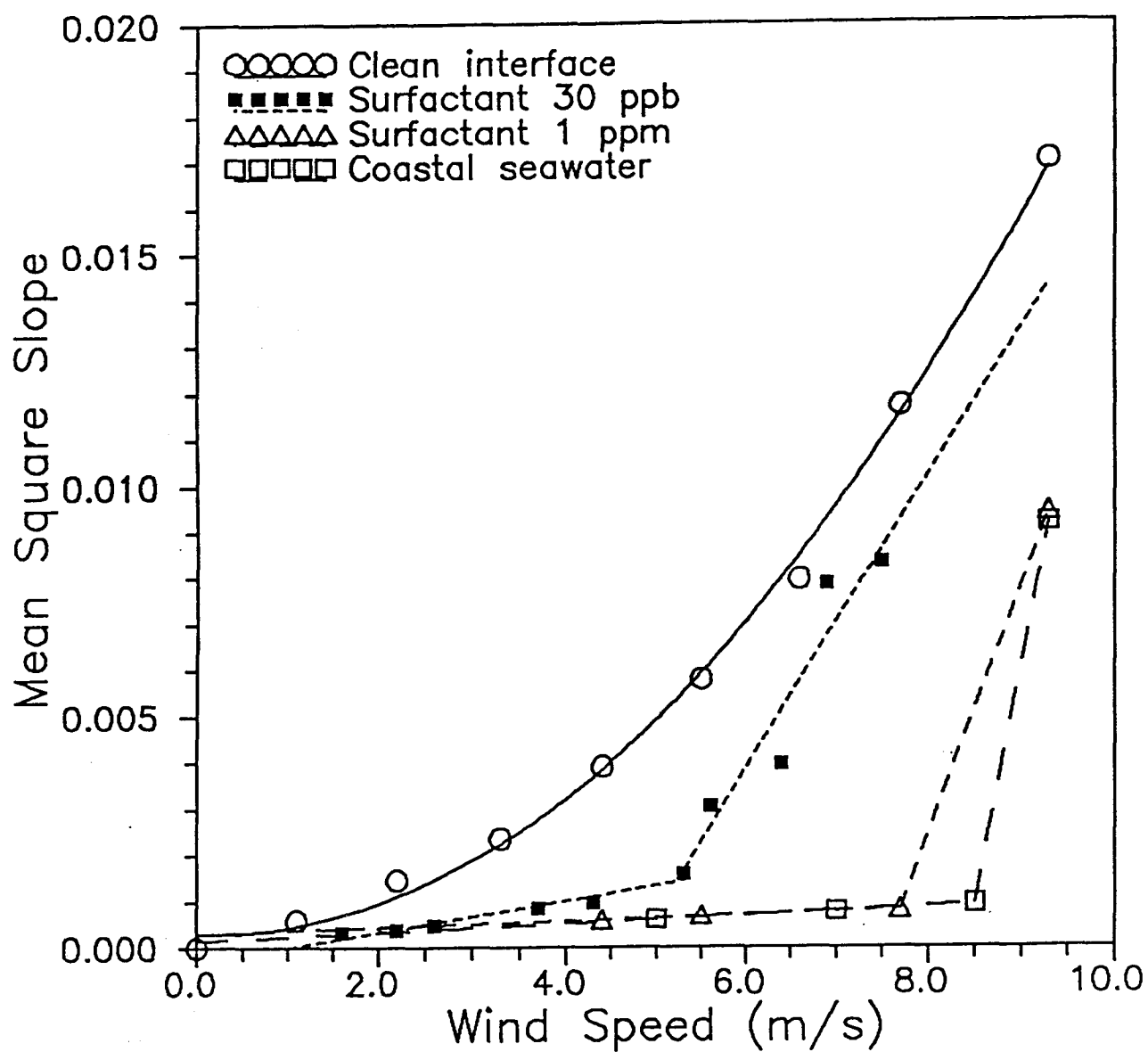


Figure 2.1 - Mean-square wave slope as a function of wind speed for clean and surfactant-influenced water surfaces (Frew, personal communication).