

Chapter 2

Sea Surface Microlayer

Abstract The top few millimeters of the ocean surface, where properties are most altered relative to deeper water, are often referred to as the sea surface microlayer. Physics, chemistry, and biology of the sea surface microlayer are the subject of this chapter. Very close to the air–sea interface, turbulent mixing is suppressed and molecular diffusion appears to dominate the vertical property transport. The viscous, thermal, and diffusive sublayers close to the ocean surface that exist as characteristic features of the air–sea momentum, heat, and mass transport are considered. Their dynamics are quite complex due to the presence of surface waves, capillary effects, penetrating solar radiation, rainfall, and surface films due to the presence of surfactants. The existing theories of the sea surface microlayer, numerical model parameterizations, available observations and new approaches, including computational fluid dynamics modeling and DNA analysis of the bacterial content of the sea surface microlayer, are critically analyzed in this chapter.

Keywords Sea surface microlayer • Viscous sublayer • Thermal sublayer • Diffusion sublayer • Neuston • Surfactant • Surface • Film • Slick • DNA analysis • SAR • Microscale wave breaking • Whitecapping • Coherent structures • Streaks • SST • Dimensional analysis • Renewal model • Renewal time • Cool skin • Solar radiation • Rain • Freshwater skin • Diurnal mixed layer • Diurnal thermocline • Gravity-capillary waves

2.1 Introduction

The microlayer is involved in the heat and momentum transfer between the ocean and atmosphere and plays a vital role in the uptake of greenhouse gases by the ocean. A striking variety of physical, biological, chemical, and photochemical interactions and feedbacks occur in the ocean surface microlayer. There is a widely held presumption that the microlayer is a highly efficient and selective micro-reactor, effectively concentrating and transforming materials brought to the interface from the atmosphere and oceans by physical processes (Liss and Duce 1997). These processes are very intriguing and potentially of great importance for remote sensing of sea surface temperature (SST) and salinity, climate change, and many other practical applications still waiting for their time to come.

Direct measurement of the sea surface microlayer is still a challenge. As a result, surprisingly little experimental information exists on the structure of the sea surface microlayer. The majority of microlayer results have been obtained from laboratory studies.

The physics of the sea surface microlayer is related to fundamental properties of turbulent boundary layers, such as intermittency (Kline et al. 1967) and quasi-periodic repeating patterns of coherent motion (Robinson 1991). While in the bulk of the water, turbulence largely controls the transport, molecular diffusion takes over the transfer of momentum, heat, and mass from the upper ocean to the sea surface because the vertical component of turbulent velocity is suppressed close to the surface. Surface organic and inorganic films formed as a result of complex interplay between biological, chemical, and physical processes can interfere with air–sea interaction (for instance, by modifying properties of capillary-gravity waves) and affect the properties of molecular sublayers.

Under very high wind-speed conditions, the sea surface can be defined only in the topological sense; as a result, the viscous sublayers is replaced with a two-phase transition layer, which consists of air bubbles, spray droplets, and the overhang of plunging waves (Chap. 6)

As a first approximation, the thickness of the viscous, thermal, and diffusion molecular sublayers at the ocean surface, outside of whitecaps and white outs, can be linked to the Kolmogorov's (1942) internal length scale of turbulence,

$$\eta_\nu = (\nu^3 / \varepsilon)^{1/4}, \quad (2.1)$$

where ν is the molecular kinematic viscosity and ε is the dissipation rate of the turbulent kinetic energy. Similar length scales also exist for thermal and diffusive turbulent processes,

$$\eta_T = \text{Pr}^{-1/2} (\nu^3 / \varepsilon)^{1/4} \quad (2.2)$$

and

$$\eta_D = \text{Sc}^{-1/2} (\nu^3 / \varepsilon)^{1/4} \quad (2.3)$$

where $\text{Pr} = \nu / \kappa_T$ is the Prandtl number ($\text{Pr} = 7.1$ for water at 20 °C), $\text{Sc} = \nu / \mu$ is the Schmidt number ($\text{Sc} \sim 10^3$), κ_T is the molecular coefficient of kinematic thermal diffusivity, and μ is the molecular coefficient of kinematic molecular diffusivity. The latter equation is applicable to tracer gases, passive contaminants, or sea salts.

An instructive schematic diagram is shown in Fig. 2.1. The logarithmic scale ranges from the diameter of a molecule to the maximum depth of the world ocean emphasizing the top millimeter of the ocean. Molecular sublayers extend from the surface to typical depths of about 1,500 μm (viscous sublayer), 500 μm (thermal sublayer), and 50 μm (diffusion sublayer). There are also organic films on the sea surface, of natural or anthropogenic origin, starting from a few nanometers thickness.

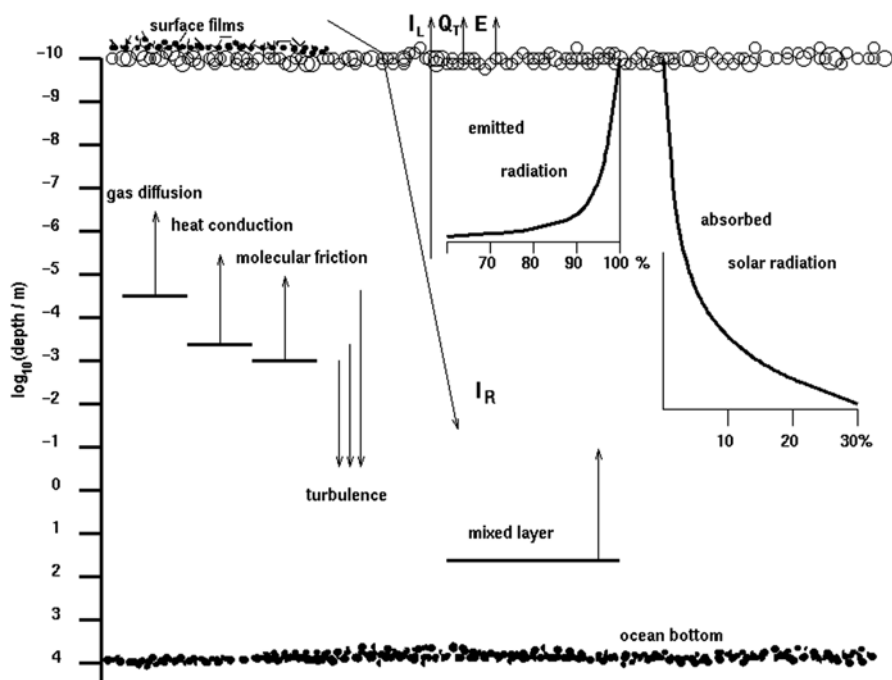


Fig. 2.1 Schematic representation of the vertical structure of physical processes related to the sea surface microlayer. (courtesy of Peter Schlüssel)

These are of course only nominal values. The thickness of molecular sublayers depends substantially on the air–sea interaction regime. In fact, the structure of the molecular sublayers are quite complex. It depends on wind stress acting on the sea surface, on turbulence and coherent motions, on shortwave radiation absorbed in the upper millimeters of the ocean, on heat, salt, freshwater, and gas fluxes crossing these sublayers, and on gravity and capillary waves and surface films. We will consider many of these factors in detail throughout this chapter.

Section 2.2 describes the phenomenology of the viscous, thermal, and diffusion sublayers at the waterside of the air–sea interface. Intimately linked to the physical processes are the complex chemical, photochemical, and biological metamorphoses that take place in the ocean microlayer. The physics of the microlayer, and even the regime of air–sea exchanges, depend on the organics and chemical composition of surface films, and, to some extent, on the sea surface microlayer ecosystem.

The physics of the microlayer are discussed in detail in Sect. 2.3. Renewal and boundary-layer models of the aqueous molecular sublayers are introduced in Sect. 2.4. The renewal model results in a coupled set of parameterizations describing the surface wind-drift current, cool skin, and interfacial gas-transfer velocity. In Sect. 2.5, we discuss the effect of solar radiation absorption on molecular sublayers. Section 2.6 is devoted to the effect of precipitation on the microlayer.

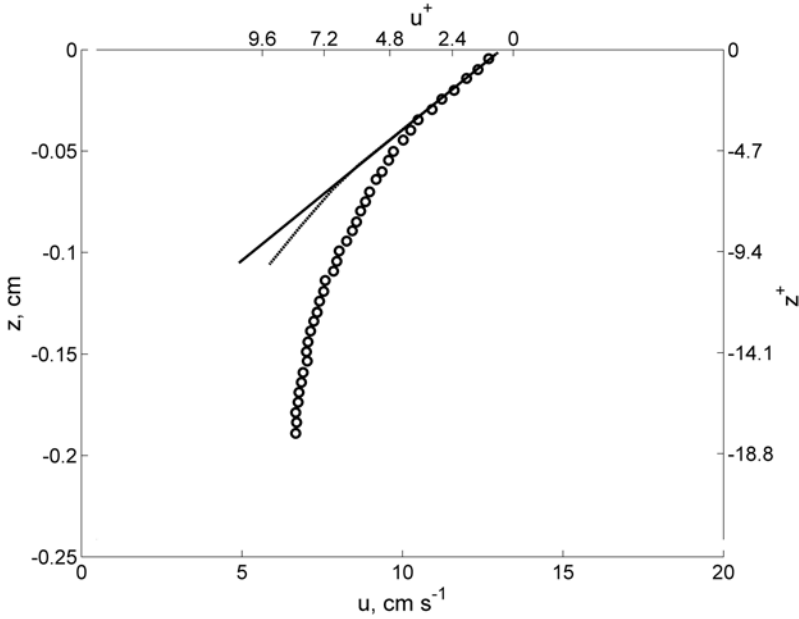


Fig. 2.2 Velocity profile below the free water surface measured in a laboratory tank (circles). The straight line fits the near-surface slope, and the curved line follows the mean profile at a solid boundary. The solid boundary dependence is derived from nondimensional values by Kline et al. (1967). The nondimensional coordinates are as follows: $z^+ = zu_* / \nu$ and $u^+ = (u_0 - u) / u_*$, u_* is the friction velocity in water, ν is the molecular kinematic viscosity of water, u is the downwind water velocity, and u_0 is the downwind water velocity at the surface. (After McLeish and Putland 1975)

2.2 Phenomenology

2.2.1 Viscous Sublayer

Viscous sublayers develop on both sides of the air–sea interface. To our knowledge, direct measurements of the viscous sublayer either from the oceanic or atmospheric side of the air–sea interface have never been made in real oceanic conditions. Information about the aqueous viscous sublayer of the ocean has been mainly obtained from theoretical considerations (for instance, Csanady 1978) or laboratory studies (McLeish and Putland 1975; Wu 1975; and others).

Figure 2.2 shows the velocity profile below the water surface measured at a 0.07 N m^{-2} wind stress in the laboratory experiment of McLeish and Putland (1975). The slope of the near-surface velocity profile is fit with a straight line. The linear vertical profile of velocity is a distinctive feature of the viscous sublayer. The departure of the velocity profile from its linear fit can therefore serve as an indicator of the viscous sublayer depth. It is remarkable that in dimensionless coordinates, the thickness of the viscous sublayer near the free surface is approximately half of

what it would be near a rigid wall. This is explained by the fact that only the vertical component of turbulent fluctuation is effectively suppressed near the free surface; as a result, turbulent eddies can penetrate closer to a free boundary than to a wall. However, this is not the only possible explanation. Another plausible explanation is that microscale wave breaking (see Banner and Phillips 1974; Csanady 1990) increases turbulent mixing near the surface, which reduces the thickness of aqueous viscous sublayer.

2.2.2 Thermal Sublayer

The SST may differ from the temperature of the underlying mixed layer due to the presence of the aqueous thermal molecular sublayer. This sublayer is also referred to as the *cool skin* of the ocean (Saunders 1967b). During daytime, the temperature difference across this aqueous sublayer due to absorption of solar radiation may change sign, turning into the *warm skin* (Soloviev and Schlüssel 1996).

Above the interface, there is a millimeter-thick atmospheric boundary layer, where the vertical transport is also dominated by the molecular diffusion. The largest temperature difference across the air–sea interface is observed in the air rather than water (Volkov and Soloviev 1986).

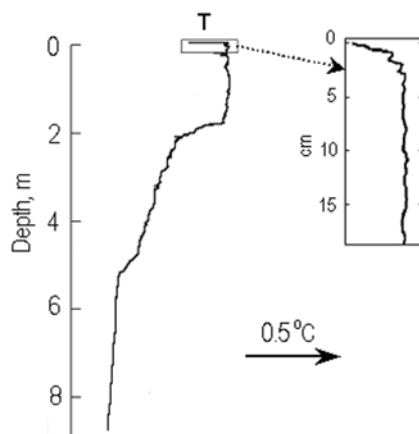
Figure 2.3 gives an example of the temperature profile in the upper 10 m of the ocean obtained with a *free-rising profiler* (Soloviev 1992). For this measurement, the profiler was equipped with a high-resolution temperature probe (5 μm diameter wire sensing element). The shunting of the micro-wire probe by seawater was small due to the fact that its internal resistance was only 7 Ω , while the surface area of the micro-wire was extremely small (Azizjan et al. 1984).

The vertical temperature profile shown in Fig. 2.3 was taken during night time. The upper part of the profile reveals an abrupt temperature change in the upper few millimeters due to the cool skin. The temperature difference across the cool skin in the example shown in Fig. 2.3 is $\Delta T = T_0 - T_b \approx -0.3^\circ\text{C}$, where T_0 is the SST and T_b is the temperature of the bulk (diurnal mixed layer) water. The temperature gradient below 2 m represents the remnants of the diurnal thermocline formed during the previous daylight hours.

The temperature difference across the cool skin depends on the local regime of air–sea interaction and thus varies in space and time. Historically, much effort has been devoted to the cool-skin parameterization. Saunders (1967b) initially parameterized the average temperature difference across the cool skin ΔT by ascribing a constant value to the nondimensional coefficient, $\lambda_s = c_p \rho u_* \Delta T / (\text{Pr} Q_0)$. Grassl (1976) found that λ_s varied with wind speed. The parameter λ_s increased from zero for calm weather conditions to approximately five at moderate wind speeds. Kudryavtsev and Soloviev (1985) explained this dependence of λ_s on wind speed by the transition from convection to a wind–wave regime.

The typical temperature difference across the cool skin is from -0.2 to -0.3°C increasing approximately two times under calm weather conditions (Horrocks et al.

Fig. 2.3 An “instantaneous” vertical profile of temperature in the upper ocean taken under low wind speed conditions. (After Soloviev 1992)



2003). Under strong insolation and/or air temperature exceeding water temperature, the interfacial layer can become slightly warmer than the underlying water.

Collecting high-quality measurements of the cool skin in the open ocean is still a challenge, requiring very specialized techniques. In the oceanographic literature, there are only a few reports of direct profile measurements in the cool skin in the open ocean (Mammen and von Bosse 1990; Soloviev 1992; Ward and Minnett 2001). At the same time, infrared measurement techniques have been under intensive development (Saunders 1967b; McAlister and McLeish 1969; Hasse 1971; Grassl 1976; Paulson and Simpson 1981; Schlüessel et al. 1990; Minnett 2003; and others). As a result, most of the open-ocean data on the cool skin come from infrared SST measurements. A problem of interpretation of the infrared SST measurements is that the longwave radiation reflected from clouds produces strong disturbance of the SST measurement. In order to address this problem, Grassl (1976) constructed an infrared radiometer moving the beam between the sea surface and a seawater bath, which substantially reduced the error due to the signal reflected from clouds. The Tropical Ocean Global-Atmosphere Coupled Ocean-Atmosphere Response Experiment (TOGA COARE) exploited an advanced version of Grassl's method: From 30 January to 24 February 1993, measurements were taken from the R/V *Vickers* in the western equatorial Pacific Ocean (156°E, 2°S). The skin temperature measured with this setup was accurate to 0.05 °C.

Fiedler and Bakan (1997) and Minnett et al. (2001) have developed a multichannel infrared interferometer, which does not require a reference seawater bath. This approach has provided large high-quality data sets of SST of the ocean.

For calculating the temperature difference across the cool skin from the infrared SST measurement, it is also necessary to know the bulk-water temperature below the cool skin. Unfortunately, measurements with sensors towed behind or near the ship are disturbed by the ship's wake, which may introduce substantial errors. The alternative approach is to derive the bulk-water temperature from a ship's thermosalinograph, which takes in water from 3 to 5 m depth, although, a shallow diurnal or rain-formed thermocline may result in a vertical temperature gradient between the

depth of the thermosalinograph intake and the cool-skin layer. An appropriate temperature correction can be calculated with a diurnal mixed layer model forced with the air–sea momentum, heat, and precipitation fluxes, assuming these are available. This correction, however, may introduce outliers by itself due to errors of the model and atmospheric forcing data.

2.2.3 Diffusion Sublayer

The near-surface molecular diffusion sublayer is a crucial element in air–sea gas exchange. The resistance to air–sea gas transfer is mainly due to the diffusion sublayer in water, which is of the order of 50 μm thick (Bolin 1960).

The diffusion sublayer associated with salinity transport has approximately the same thickness as the gas diffusion sublayer (Fedorov et al. 1979). Under evaporative conditions, the sea surface salinity is higher than in the bulk of water, while during rainy conditions, a *freshwater skin* of the ocean is formed (Schluessel et al. 1997).

There are no direct observations of the diffusion molecular sublayer in the open ocean because of the complexity of the microscale measurements near the moving air–sea interface. Some parameters of the aqueous diffusion sublayer can be evaluated from data on the gas-transfer velocity because practically all gas concentration difference is in the ocean rather than the atmospheric diffusion sublayer. In particular, the thickness of the diffusion sublayer is defined as follows:

$$\delta_\mu = \mu \Delta C / G_0 \quad (2.4)$$

where μ is the kinematic molecular diffusion coefficient of gas, G_0 is the flux of property C at the air–sea interface, $\Delta C = C_w - C_0$ is the ensemble averaged air–sea gas concentration difference in property C across the diffusion sublayer, and C_0 and C_b are the averaged concentrations of property C at the water surface and in the bulk (mixed layer) water, respectively. Taking into account (1.50), we obtain the following relationship connecting the gas exchange coefficient and the thickness of the diffusion sublayer:

$$\delta_\mu = \mu / K_\mu. \quad (2.5)$$

2.2.4 Sea Surface Microlayer Ecosystem

The sea surface is a highly productive, metabolically active interface (Hardy et al. 1997). Due to extreme conditions at the air–sea interface, the sea surface is believed to be the place where life on the Planet originated (a competing theory is that of extraterrestrial origin for life on the Earth).

Phytoplankton in the water column produces an abundance of particulate and dissolved organic material, some of which is transported to the surface either passively by buoyancy or actively by upwelling, turbulence, and bubble transport. The natural and anthropogenic compounds deposited from the atmosphere often accumulate on the ocean surface in relatively high concentrations compared to those in the water column. The abundance of organic matter at the sea surface provides a substrate for the growth of the surface-dwelling organisms, the marine *neuston*, which inhabits the sea surface microlayer (Zaitsev 1997).

Neuston realm is a vast habitat. The distinctive physical and chemical characteristics of the sea surface can explain a highly diverse and abundant assemblage of species in the microlayer. Organisms from most major divisions of the plant and animal kingdoms either live or reproduce or feed in the surface layers (Zaitsev 1971). Many of these species are of commercial and ecological importance. The *microneuston*, which may be involved in biogeochemical cycling, and neustonic eggs and larvae of commercially important fish and shellfish, are of particular interest.

Figure 2.4 shows Hardy's (1982) conceptual model of the sea surface microlayer ecosystem. Permanent inhabitants of the surface layer often reach much higher densities than similar organisms found in subsurface waters. The communities of bacteria, phytoplankton, and zooplankton present within this neuston layer are named the bacterioneuston, phytoneuston, and zooneuston, respectively.

There are also numerous temporary inhabitants of the neuston. These are particularly the eggs and larvae of a great number of fish and invertebrate species. The latter utilize the surface during a portion of their embryonic and larval development. Some neuston can remain in the microlayer until turbulence created by breaking waves at winds exceeding $10\text{--}15\text{ m s}^{-1}$ disperses them (Zaitsev 1971).

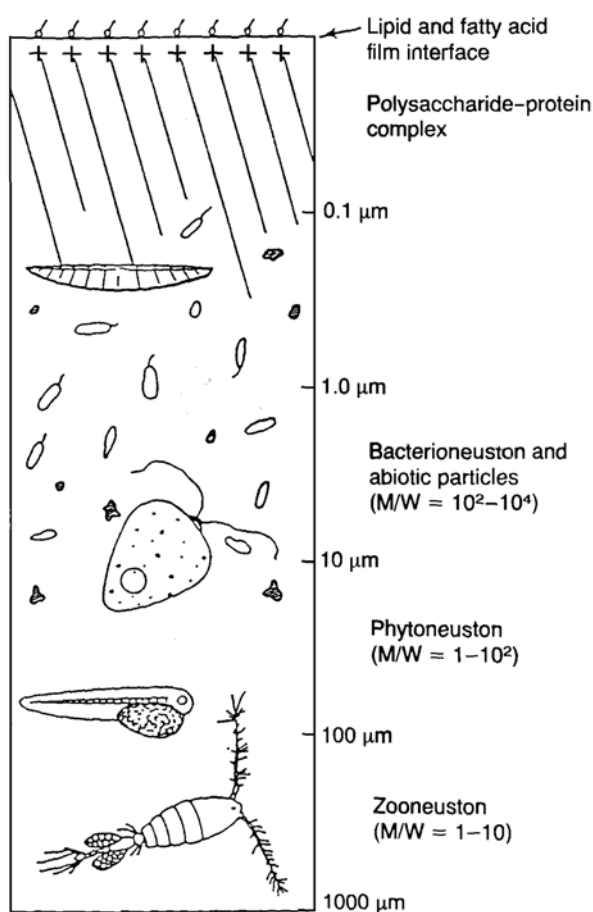
An alternative conceptual model of the sea surface microlayer is schematically shown in Fig. 2.5. In this model, the sea surface microlayer is a gelatinous biofilm, which is formed by transparent exopolymer particles (TEPs). This model is based on the Wurl and Holmes (2008) experimental result suggesting that some TEPs float up to the surface microlayer, forming a gelatinous film. TEPs are a result of the coagulation of biogenic polysaccharides, particularly those produced by phytoplankton. TEPs are critical in the formation of marine aggregates, acting as the binding matrix or "glue" that holds the aggregate together (Verdugo et al. 2004).

TEPs are also readily colonized by microorganisms, including surfactant-producing bacterium. The presence of surfactants may have important impact on dynamics of the sea surface (see Sect. 2.3).

2.2.5 Surfactants and Surface Films

Following Liss and Duce (1997), here we use the following terminology: A film refers to surfactant-influenced surface and a *slick* refers to a visibly surfactant-influenced surface.

Fig. 2.4 Conceptual model of the sea surface microlayer ecosystem. M/W = typical microlayer to water concentration ratios based on a number of studies. (Reproduced from Hardy (1982) by permission of Elsevier)



Sea surface films are derived from multiple, sea- and land-based sources, including bulk seawater dissolved organic matter, terrestrial sources (natural and anthropogenic), and petroleum seeps and spills (Liss et al. 1997). Surface films dissipate due to loss of material at the surface, including microbial degradation, chemical and photochemical processes, and loss due to absorption and adsorption onto particulates.

Under favorable physical conditions, the concentration of dissolved organic matter is sufficient to produce surface enrichments of organic matter even in oligotrophic waters, where biological productivity is low. Lifecycles of neuston organisms and phytoplankton blooms also lead to the production of the surface-active substances.

The source contribution primarily controls the chemical composition of surface films. A variety of biological, chemical, and physical processes may, nevertheless, change composition, concentration, and spatial structure of the surface films and thus modify physical properties of the air-sea interface. Turbulence and diffusion,

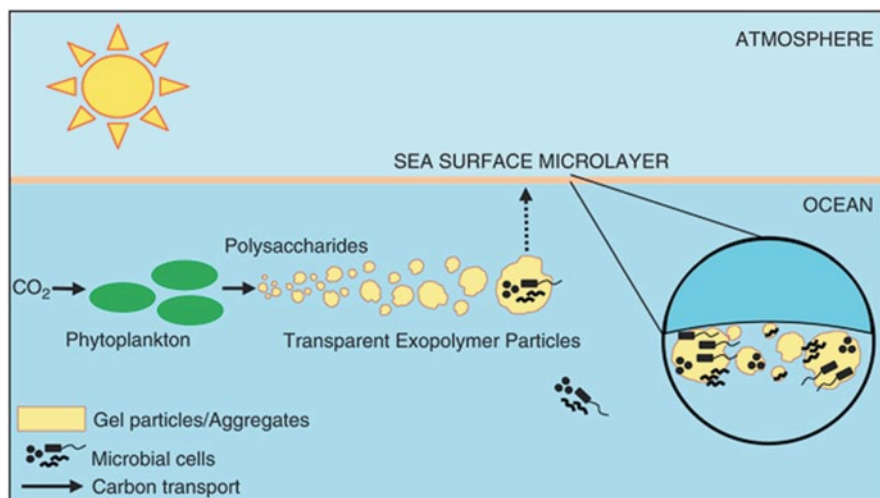


Fig. 2.5 Conceptual model of the sea surface microlayer based on the Wurl and Holmes (2008) study. The formation of transparent exopolymer particles (TEPs) in the near-surface layer of the ocean is a pervasive process, which is also a significant component of the global carbon cycle. Some TEPs float up to the surface microlayer, forming a gelatinous film. TEPs are readily colonized by microbial cells. (Reproduced from Cunliffe et al. (2009) by permission of John Wiley & Sons Ltd)

scavenging, and transport by bubbles and buoyant particles effectively spread surfactants over broad areas of the ocean surface. At the same time, flow convergences associated with organized structures, upwelling events, and internal waves have tendency to localize surface-active materials on various spatial scales, ranging from a few meters to kilometers (Bock and Frew 1993; Liss and Duce 1997).

Sampling of the sea surface microlayer is a challenge. A number of methods have been developed for surface microlayer sampling, including mesh screens (Garrett 1965), glass plates (Harvey and Burzell 1972), and membranes (Kjelleberg et al. 1979). All of these sampling methods, however, result in some degree of contamination, from either the research vessel or underlying water column.

Franklin et al. (2005) implemented DNA analysis of the sea surface microlayer. For this purpose, they used the 47-mm diameter, 2- μm pore polycarbonate membrane. The membrane was placed on the sea surface and attached to the surface by surface tension forces. Water samples were also collected from below the surface. Using this method, Franklin et al. (2005) showed that the bacterioneuston was distinctly different compared with subsurface water 0.4 m below the surface. The weakness of this method is that it is difficult to avoid distortions of the sea surface microlayer from the boat due to proximity of the sampling area to the boat hull.

Kurata (2012) and Kurata et al. (2013) improved this method by attaching the polycarbonate membrane filter to a fishing line and by using the fishing rod to deploy this filter away from the boat wake and then bringing it to the boat. They also used an advanced DNA analysis, which was able to identify surfactant-producing bacteria as well

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