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Review

Sea surface microlayers: A unified physicochemical and biological perspective of the air-ocean interface

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ABSTRACT

The sea surface microlayer (SML) covers more than 70% of the Earth's surface and is the boundary layer interface between the ocean and the atmosphere. This important biogeochemical and ecological system is critical to a diverse range of Earth system processes, including the synthesis, transformation and cycling of organic material, and the air-sea exchange of gases, particles and aerosols. In this review we discuss the SML paradigm, taking into account physicochemical and biological characteristics that define SML structure and function. These include enrichments in biogenic molecules such as carbohydrates, lipids and proteinaceous material that contribute to organic carbon cycling, distinct microbial assemblages that participate in air-sea gas exchange, the generation of climate-active aerosols and the accumulation of anthropogenic pollutants with potentially serious implications for the health of the ocean. Characteristically large physical, chemical and biological gradients thus separate the SML from the underlying water and the available evidence implies that the SML retains its integrity over wide ranging environmental conditions. In support of this we present previously unpublished time series data on bacterioneuston composition and SML surfactant activity immediately following physical SML disruption; these imply timescales of the order of minutes for the reestablishment of the SML following disruption. A progressive approach to understanding the SML and hence its role in global biogeochemistry can only be achieved by considering as an integrated whole, all the key components of this complex environment.

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1. Introduction

The sea surface microlaver (SML) constitutes the uppermost tens to hundreds of um of the surface of the ocean which is in direct contact with the atmosphere, and has physicochemical and biological properties that are measurably distinct from underlying waters (Liss and Duce, 2005; Zhang et al., 2003). Evidence for the existence of the SML has a long history. Natural slicks on the sea surface in areas of high biological activity, such as in coastal waters, are well documented. Work in the Sargasso Sea established an early link between visible slicks and phytoplankton blooms, and showed that slicks can have fundamental affects on the physical properties of the sea surface. Evidence for a biological origin and activity was revealed in carbohydrate enrichments in slicks relative to underlying waters (Sieburth and Conover, 1965). What is perhaps less well known, however, is that the SML is almost ubiguitous, pervading most of the ocean surface, even under conditions of high surface turbulence, although it is largely indiscernible with the naked eye. The unique position of the SML at the air-sea interface, thus linking the hydrosphere with the atmosphere, means that the SML is central to a range of global biogeochemical and climate-related processes. Consequently, an improved understanding of the SML is a key objective of the International SOLAS (Surface Ocean-Lower Atmosphere Study) Project (www.solas-int.org) and realising this objective requires integrating several scientific disciplines with interests both in SML structure and function.

Key early SML observations (e.g. Sieburth and Conover, 1965) were subsequently refined by researchers employing diverse scientific approaches operating in parallel, yet largely independent of each other. Important new findings include the enrichment of microgels in the SML and compelling molecular evidence for complex SML microbial communities.

Understanding important marine ecosystem processes and their interactions with the wider Earth system requires a holistic view of the ocean–atmosphere interface (Fig. 1). What is clear is that SML structure and functions are intimately bound together, and that a unified physicochemical and biological perspective must be embraced and developed. In this paper we integrate key scientific disciplines to review and discuss the current status of SML research. In particular we highlight recent important discoveries that have improved current understanding, present previously unpublished data on the rate of SML reestablishment following disruption and identify current knowledge gaps in this fundamentally important ecosystem that demand future scrutiny. We initially discuss the thickness of the SML and outline the critical importance of sampling in understanding the SML. The physiochemical structure of the SML is then discussed as visible slicks and as complex films. The stability and persistence of the SML are then examined, particularly in the context of physiochemical properties. We discuss the central role of microorganisms in sustaining SML physiochemical properties and maintaining key biogeochemical processes. The final sections focus on three specific processes, air–sea gas transfer, aerosol production and pollution.

2. Sea surface microlayer thickness, sampling and the need for scientific best practice

Notwithstanding recent advances that have broadened our overall understanding of the SML, there remains a need to develop and adopt agreed scientific best practice for SML research and data reporting, following the examples set in other areas of marine research, such as ocean CO_2 measurement (Dickson et al., 2007) and ocean acidification (Riebesell et al., 2010).

One fundamentally important area where agreed best practice is essential is SML sampling and how this relates to true SML thickness. Using a combination of laboratory and field measurements, Zhang et al. (2003, 1998) revealed a 'layer of sudden change' at a depth of $50 \pm 10 \,\mu\text{m}$ relating to physicochemical parameters including surface tension, pH, chlorophyll-a, organic matter, dissolved nutrients, trace metals, chemical and biological oxygen demand (Zhang et al., 2003, 1998). Even so, due to variability in sampling approaches and diverse analytical requirements the true SML thickness remains to be established unequivocally (Cunliffe et al., 2011). The SML sampling devices currently in use tend to sample distinctly different microlayer depths (Fig. 2). Some early samplers, including a floating tray (Hatcher and Parker, 1974), a



Fig. 1. Schematic diagram showing the properties and interconnections of the sea surface microlayer (SML) discussed in this review.



Fig. 2. Three examples of sea surface microlayer sampling devices in use, including typical sampling depths of each method. Membrane filter images reproduced from; Cunliffe et al. (2011). Glass plate and mesh screen images reproduced from; Wurl, O., 2009. Sampling and sample treatments. In: Wurl, O. (Ed.), Practical Guidelines for the Analysis of Seawater. CRC Press, Boca Raton, FL, USA.

freezing probe (Hamilton and Clifton, 1979) and a surface pumping device (Ignatiades, 1987) all had rather coarse sampling resolution >1000 µm. The original mesh screen (Garrett, 1965) and glass plate (Harvey, 1966; Harvey and Burzell, 1972) samplers still in common use today may typically sample $150\text{--}400\,\mu\text{m}$ and $20\text{--}150\,\mu\text{m}$ respectively and improved versions of the original rotating drum sampler or "surface skimmer" (Harvey, 1966) may sample the upper 50 µm (Brooks et al., 2009). The bubble microtome, designed to collect chemical and microbiological aerosols in air just above the SML (MacIntyre, 1968), is claimed to sample the upper 20 µm, while polycarbonate and polytetrafluoroethylene (PTFE) membrane filters used in microbiological sampling collect 35-42 μm and ${\sim}6\,\mu m$ respectively (Cunliffe et al., 2009a). Clearly, the SML is most commonly defined operationally by the selected sampling protocol, with wide ranging implications for data analyses and interpretation (Agogue et al., 2004; Cunliffe et al., 2009a; Hühnerfuss, 1981a.b).

A widely agreed standardisation of SML sampling clearly is highly desirable as it would legitimise the intercomparison of data between researchers from different scientific disciplines studying the SML under varying oceanographic regimes. Linked to this is a need to improve and standardise analytical methods, and to agree and implement the routine measurement of standard SML variables (e.g. dissolved organic carbon) that could aid inter-study comparisons. Such examples of scientific best practice would increase our understanding still further and ultimately broaden the global perspective of the SML.

3. Sea surface microlayers as visible slicks

It is important to differentiate between visible and invisible surface films, based on differences in their physiochemical properties and compositions. Visible films, hereinafter referred to as "slicks", are monomolecular films (monolayers) with a typical thickness of 2–3 nm (Hühnerfuss, 2006a), and are thus beyond the sampling resolution of the various SML samplers discussed in Section 2. Slicks spontaneously form when the concentration of insoluble surfactants exceeds some unknown threshold value and will be closely connected to the SML composition. The slick becomes visible due to capillary wave-damping, which importantly acts to reduce the air–sea exchange of material, gas, heat and momentum (Salter et al., 2011). We discuss the role of the SML in gas exchange in more detail in Section 7.

Slick conditions can be observed as patches during increased supply of organic material to the SML, for example in periods of high precipitation (Wurl and Obbard, 2005) or during bloom events (Lee and Williams, 1974; Sieburth and Conover, 1965; Wurl et al., 2011b). Slicks contain both hydrophobic and hydrophilic components. The amphiphilic structure forces the surface-active molecules to assemble in such a way that the hydrophobic components are directed into the air, while the hydrophilic components remain in the interfacial water layer. The density of molecules in monolayers changes with the surface pressure, typically measured in the laboratory with a Langmuir balance as pressure-area-isotherms (Fig. 3). Pressure-area isotherms provide very useful information on the physicochemical properties of the SML (Gladyshev, 2002), including measurements of the surface activity of different SML components, types of monolayers (Fig. 3) and the ability to relax after compression.

The most prominent property of slicks is their modulation of wave-damping of centrimetric-scaled waves through dissipation of wave energy due to changes in the visco-elasticity of the interfacial surface layer (Cini et al., 1983; Lucassen-Reynders and Lucassen, 1969). Such phenomena are often referred to as the Marangoni effect, and are a fundamental part of modern scientific discussions dealing with wave-damping effects on the ocean's surface and consequently air-sea transfer processes (Botte and Mansutti, 2005; Hühnerfuss, 2006a; Kozarac et al., 2003; McKenna and Bock,



Fig. 3. Typical surface pressure–area (π –A) isotherms and molecular arrangements during compression of sea surface microlayers (SMLs).

2006). The intensity of the Marangoni effect depends on the quantity and composition of surface-active compounds in slicks. During wind-wave tunnel experiments with artificial monomolecular lavers of single compounds, Hühnerfuss et al. (1984) reported that insoluble surface active compounds with long-chain saturated alkyl groups exhibited strong wave-damping effects, whereas hydrophobized amino acids and carbohydrates showed some effects, but not proteins and triglycerides (Hühnerfuss et al., 1984). Coastal and oligotrophic slicks are typically rich in lipids (including fatty acids, sterols, cyclic lipids and beta-carotene), polymers and humic materials, and the relative proportion of these compounds influences surface film elasticity (Frew et al., 2006). Lipid contents were also higher inside slicks than outside slicks (i.e. invisible SML) in coastal waters of the Mediterranean Sea (Garabetian et al., 1993). Conversely, the chemical composition of North Sea slicks did not differ from those of microlavers outside slicks (Kattner and Brockmann, 1978). Higher enrichments of particulate matter, surface-active substances (SASs) and coloured dissolved organic matter absorption have also been observed in slicks compared to non-slick samples (Stolle et al., 2010; Wurl et al., 2009).

New techniques continue to provide molecular scale information about the air-sea interface. For example, Frew et al. (2006) reported correlations between the molecular structures obtained by mass spectrometry and static elasticity, thereby revealing further insight into slick physiochemical properties (Frew et al., 2006). Hühnerfuss (2006b) used Brewster Angle Microscopy (BAM) and Infrared Reflection-Absorption Spectroscopy (IRAS) to study morphology and molecular structures respectively, of both artificial and biogenic slicks (Hühnerfuss, 2006b). The observed area coverage of slicks in coastal and open ocean waters was up to 22% and 10% respectively using a photographic system (Romano, 1996). Slicks typically start to disrupt at wind speeds above 4–5 m s⁻¹ (Romano, 1996), but they may still play some role in air-sea interactions in a global context (see Section 7). Remote sensing techniques are increasingly applied to monitor slick distribution on the ocean surface (Gade et al., 2006).

4. Sea surface microlayers as physicochemically complex gelatinous films

Historically, lipids were thought to comprise a significant fraction of SML material, forming a continuous layer above a protein–polysaccharide layer; this was the basis of an early "wet– dry" stratified model of the SML (Hardy, 1982; Hermansson, 1990; Norkrans, 1980). It is now evident that although lipid material is less abundant in the SML than previously thought, it may still be important in affecting SML physicochemical properties (Frka et al., 2009; Mazurek et al., 2008).

Lipids are composed of a variety of different classes; storage and membrane forms, and partially degraded (Parrish, 1988), and are important biochemical indicators for chemical and physical processes associated with biological activities in the sea (Parrish, 1988; Parrish et al., 2005). Concentrations of both dissolved and particulate SML lipids (6–265 μ g l⁻¹) vary depending on location, season, trophic state and prevailing meteorological conditions, contributing 3–7% and 10–15% (occasionally more than 30%) to the dissolved and particulate organic matter pools respectively (Gašparović et al., 1998; Penezić et al., 2010; Saliot et al., 1991).

The role of lipids in SML formation and stability is still not clear, but it is likely that lipids influence the viscoelastic properties of microlayers (Frew and Nelson, 1992). Laboratory model studies indicate that lipid monolayers efficiently accumulate bulk carbohydrates by hydrogen bonding, nonpolar and electrostatic interactions (Kozarac et al., 2000a). The hydrophobic character of lipids influences their self-assembly within the SML, forming vesicles, plate-like and elongated structures, depending on their chemical properties (Kozaraca et al., 2005; Risović et al., 2011). BAM has proven a useful approach in the visualisation of organic matter in the SML and has shown that during early stages of SML formation and development, films contain liquid-condensed domains that are most probably dominated by lipids embedded in a liquid-expanded phase (Kozaraca et al., 2005). As carbohydrates (discussed further below) in general do not form condensed films (Gaines, 1966), especially not at natural concentrations, it is probable that lipids could have important roles in the early stages of SML formation. Classical monolayer techniques that determine surface pressure-area $(\pi - A)$ have, however, established that gaseous and liquid-expanded film types are the most common form of microlavers in natural marine systems (Barger and Means, 1985; Frew and Nelson, 1992; Kozarac et al., 2000b), implying uniformity of the material affecting the shape of π -A isotherms that occur naturally at the air-water interface. Further research is needed to establish the role of lipids in film formation and stability, including determination of the extent to which natural SML lipids act as nucleation sites for other SML components.

Some researchers had long considered carbohydrates to be important in the SML. Sieburth (1983) proposed that the SML is a "highly hydrated loose gel of tangled macromolecules and colloids". Recent research findings have refined Sieburth's original ideas by identifying microgels as a dominant carbohydrate component of microlayers (Cunliffe et al., 2009b; Wurl and Holmes, 2008; Wurl et al., 2009, 2011a,b). Similarly, recent SML samples collected from open leads within the Arctic pack ice were found to be enriched in polysaccharides (Gao et al., 2012). Microgel aggregation rates in the SML have been shown to be five-fold higher than in underlying water just a few tens of cm below the SML (Wurl et al., 2011a). Compression and dilation due to capillary waves may also enhance polymer collision and further facilitate rapid gel formation within the SML.

Microgel particles, such as TEP, form from dissolved polysaccharides released during microbial production and decomposition processes (Alldredge et al., 1993). Reactive components of microbial polysaccharides such as uronic acids facilitate bonding and subsequent micro- and macro-gel aggregation (Verdugo et al., 2004). Microgels have been shown to form spontaneously in seawater (Chin et al., 1998), and their rate of formation is higher when more dissolved polysaccharides are brought into contact (Engel et al., 2004). Due to the sticky properties of microgels, they can aggregate both live and dead plankton, as well as mineral particles and consequently they are hotspots of microbial activity in the water column (Simon et al., 2002).

Amino acids and proteins in the SML have received less attention than lipids or carbohydrates. Accumulation of amino acids and proteins in the SML may be anticipated from the hydrophobic, and therefore surface-active nature of some amino acids having aliphatic and aromatic side chains. Protein chain length, amino acid sequence, and molecular shape may also contribute to the surfactant activity of proteins. It has been shown that different SML sampling devices may influence amino acids sampling efficiency, in particular hydrophobic glass plates collect amino acids more efficiently than metal screens (Momzikoff et al., 2004).

Underlying water is the main source of proteinaceous matter concentrating in the SML (Kuznetsova and Lee, 2001; Matrai et al., 2008). Momzikoff et al. (2004) reported dissolved total amino acid concentrations in the ranges of 0.6–9.2 µM in coastal north western Mediterranean waters (Momzikoff et al., 2004). Kuznetsova and Lee (2001) found total hydrolysable amino acids (THAAs) concentrations ranged from 4.6 to 115.0 µM in Stony Brook Harbor, New York (Kuznetsova and Lee, 2001). Dissolved free amino acid (DFAA) concentrations were in the range from 0.16 to 20.7 µM and dissolved combined amino acids (DCAAs) in the range

0.06–39.2 μ M in coastal areas of Long Island, New York, and the Caribbean Sea (Kuznetsova and Lee, 2002). DFAA, DCAA, and particulate amino acids (PAAs) were 0–1.7 μ M, 0.4–2.6 μ M and 0.1–8.0 μ M, respectively, along a transect from coastal Massachusetts to open ocean waters of the Sargasso Sea (Kuznetsova et al., 2004). Kuznetsova and Lee (2001, 2002, 2004) found enrichment factors of DFAA, DCAA and PAA of 0.4–201, 0.4–20 and 0.3–41.5, respectively. Enrichments of protein fractions in the SML are inversely related to trophic status, i.e. higher enrichments are observed in oligotrophic open ocean areas than in productive coastal waters (Kuznetsova et al., 2004). Difference in seasonal distribution of DFAA and DCAA have been observed, with greater concentrations measured in autumn than in spring (Carlucci et al., 1991).

SML organisms no doubt fulfil important roles as producers, consumers and modifiers of proteins in natural films. Turnover rates of proteinaceous material in the SML can be high. Protein hydrolysis experiments have shown that concentrations of amino acids are reduced significantly in SML samples, often reaching lower values than those found in the underlying water (Kuznetsova and Lee, 2001). Contrasting studies in the Atlantic Ocean and Mediterranean Sea have, however, indicated that SML amino acids are not always readily available for bacterial remineralisation (Reinthaler et al., 2008). Potentially high utilisation rates of amino acids are major carbon and energy sources for marine microbes (Keil and Kirchman, 1992).

Modelling protein structuring effects on surface films shows that proteins do not adsorb at the air–water interface to form films with any particularly noticeable lateral structure, but the introduction of particles did enable protein structuring at the surface (Murray et al., 2009). Furthermore, the immiscibility of proteins and lipids at the air–water interface can cause protein displacement by lipids at high surface concentrations (Patino et al., 2007). Future directions in the SML protein research should incorporate multiple physicochemical approaches that include major other biochemical and biological components to establish possible synergistic and antagonistic microlayer processes.

5. Stability of the sea surface microlayer

Wurl et al. (2011b) showed that the SML is stable enough to exist above the global average wind speed of 6.6 m s⁻¹, with no observed depletion of organic matter in the SML above a wind speed of 5 m s⁻¹. Other studies support this conclusion, with organic matter enrichments observed at wind speeds up to ~10 m s⁻¹ (Carlson, 1983; Kuznetsova et al., 2004; Reinthaler et al., 2008). Such stability fundamentally distinguishes the invisible SML from visible slicks in the open ocean, the latter typically starting to be disrupted at wind speeds above 4–5 m s⁻¹ (Romano, 1996). In contrast, during experiments in a linear wind–wave tunnel, an artificial surface film began to tear at a wind speed of 13 m s⁻¹, suggesting that artificial films may behave differently than natural slicks (Broecker et al., 1978).

Following temporary SML disruption by breaking waves that disperse SML material into the subsurface water, the dispersed material rapidly adsorbs to the surface of rising bubble plumes produced by the breaking waves (Wurl et al., 2011b), and these rising bubbles have been shown to also facilitate gel aggregation (Wallace and Duce, 1978; Zhou et al., 1998). This mechanism may well be the most important means of transferring surfaceactive material to the SML following wave breaking (Wurl et al., 2011b). Although each bubble is buoyant, the high energy of the upper ocean leads to the dispersion of bubbles to depths of several metres (Thorpe, 1982; Thorpe and Hall, 1983). Material is transferred between bubbles and the surrounding water as a result of

water flowing around them (generally due to the buoyant rise of bubbles relative to their surroundings) and during the lifetime of a bubble, both dissolved material and small particles will accumulate on its surface. Frequently termed "bubble scavenging", this process is key to the cycling of surface active material in the upper ocean. As well as being a major process in the organic enrichment of the SML, these bubbles will eventually burst upon reaching the ocean surface, ejecting their enriched contents to the atmosphere as aerosols. In bubble experiments using Arctic seawater, Gao et al. (2012) showed that bubble scavenging facilitated the formation of new aggregate particles from the coagulation of low molecular weight nanometre-sized gels, and that the aerosols that formed during the experiment were subsequently enriched with polysaccharides (Gao et al., 2012). The chemical composition of the surface-active organic matter that accumulates as standing sea surface foam during intense wind events includes polysaccharides, acetate, and aliphatic organic matter (Gogou and Repeta, 2010). We discuss the role of the SML in aerosol formation further in Section 8.

The chemical composition of the SML may also influence its stability. Enrichments of sulphate half-ester groups in the SML (Wurl and Holmes, 2008) can increase stability because these groups can influence the intrinsic viscosity of marine polymers (Nichols et al., 2005) and sulphur-containing algal carbohydrates are less soluble and hydrolysable (e.g. more recalcitrant) (Kok et al., 2000).

Direct estimates of SML reformation rates following disruption are few but the published data imply that they are rapid (Dragčević and Pravdić, 1981; Kozaraca et al., 2005; Kuznetsova and Lee, 2001; Van-Vleet and Williams, 1983; Williams et al., 1986). Van-Vleet and Williams (1983) investigated SML reformation in a laboratory tank in which the SML was removed at intervals using a slider. SML reformation estimated from measured film pressures was extremely rapid during the 20 s immediately following removal, and is believed to reflect rapid formation of a monolayer by diffusion. In subsurface coastal waters vigorously mixed and left to settle, Kuznetsova and Lee (2001) observed rapid establishment of a SML based on measuring enzyme activity, although this was lower than the initial enzyme activity in SML samples simultaneously collected from the same locations.

In previously unpublished laboratory tank experiments using \sim 100 l of coastal seawater (North Sea; salinity 34.6), SML reformation rates were investigated by monitoring bacterioneuson composition using denaturing gradient gel electrophoresis (DGGE) analysis of bacterial populations and surfactant activity (SA) was assessed by AC voltammetry (Salter, 2010). Following initial filling, the tank water was left undisturbed for 36 h before vigorous mixing of the uppermost 20 cm (total water depth 50 cm). Samples for SML DGGE analysis were collected on polycarbonate membranes and a glass plate was used to sample for SML surfactant activity. Subsurface waters for both analyses were obtained via a sampling port 10 cm below the surface. For DGGE analysis, SML and subsurface water were sub-sampled 18, 24 and 36 h following initial filling, initially and at 1 min intervals following stirring, and thereafter more infrequently (Fig. 4). Samples for SA analysis were collected less frequently (Fig. 5). There was a distinct difference between SML and subsurface bacterial populations (Fig. 4). Pearson similarities for the bacterioneuston, prior to and following stirring, were 93.4-98.9%, consistent with reestablishment of the bacterioneuston community being almost complete less than 1 min after disturbance. Further minor differences in the composition of the bacterioneuston subsequently developed, indicating the community was dynamic and not static.

The surfactant results (Fig. 5) were less clear, due to large excursions in SA in the SML and to a lesser extent in subsurface waters. Evidently the surfactant pool in North Sea coastal waters is highly chemically reactive, with both surfactant formation and removal



Fig. 4. Denaturing gradient gel electrophoresis (DGGE) analysis of bacterioneuston and bacterioplankton community profiles in the surface microlayer (SML) and subsurface (SS) water during a SML reformation experiment. Coastal water collected from the North Sea was added to the tank and allowed to settle for 36 h before the surface water was mixed. The SML and SS was regular sampled from <0.5 min after mixing to 68 h later. The arrows highlight a dominant DGGE band in the SML profiles, indicating a dominant bacterioneuston population.



Fig. 5. Surfactant concentrations determined by AC voltammetry in the surface microlayer (SML) and subsurface (SS) water during the same SML reformation experiment described in Fig. 4. Figure is reproduced from Salter (2010).

processes taking place. Following stirring, although the SA of the SML initially decreased linearly and stabilised after ~ 10 min, total SA remained substantially higher than in the subsurface waters, again consistent with a rapid SML recovery, as for the bacterioneuston. The several lines of evidence presented above are all consistent with a rapid timescale for SML reformation, typically <1 min. Nevertheless, it should be recognised that the nature of the problem has to date effectively precluded estimating SML reformation rates *in situ*.

6. Sea surface microlayers as active biofilms

The study of microbial life in aquatic surface films is not new. The Swedish botanist Einar Naumann in 1917 introduced the term neuston to identify organisms associated with the air–water interface that were ecologically distinct from plankton in underlying water (Naumann, 1917). Subsequently studies have now shown that the diversity of microorganisms in the SML can differ significantly from that in the underlying water, even a few centimetres below the SML, with bacterial diversity having received most attention through the utilisation of molecular ecology tools (recently reviewed by Cunliffe et al., 2011). Microlayer bacteria (bacterioneuston) assemblages are formed from underlying water recruitment (Agogue et al., 2005; Cunliffe et al., 2009a,c; Joux et al., 2006; Lindroos et al., 2011; Obernosterer et al., 2008; Stolle et al., 2011), often include differences in the relative abundance of cognate underlying taxa and microlayer-specific taxa (Cunliffe et al., 2009a,c, 2008; Franklin et al., 2005; Lindroos et al., 2011; Stolle et al., 2011), show evidence of synchronicity between different sites (Cunliffe et al., 2009a,c), and are affected by prevailing meteorological conditions (Stolle et al., 2011, 2010). Similar features have been reported for bacterial assemblages in estuarine surface microlayers, including differences in the relative abundance of microlayer taxa compared to those in underlying water (Azevedo et al., 2012; Cunliffe et al., 2008).

Phytoneuston are also important components of SML ecosystems and are often found to be enriched in the SML (Hardy and Apts, 1984, 1989; Joux et al., 2006). As with the bacterioneuston, phytoneuston assemblages can have different structures from those in underlying water (De Souza Limaa and Chretiennot-Dinet, 1984; Hardy and Apts, 1984, 1989; Hardy and Valett, 1981; Montes-Hugo and Alvarez-Borrego, 2007).

Phytoneuston may have important biogeochemical roles, especially in inshore waters (Montes-Hugo and Alvarez-Borrego, 2007; Yang et al., 2009). Autotrophic phytoneuston, in combination with SML heterotrophs, determine the net metabolic status of the airsea interface and can subsequently control O_2 (Ploug, 2008) and CO_2 (Calleja et al., 2005) exchange. Hardy and Apts (1989) have shown that because phytoneuston have a greater density in the SML, their total carbon fixation rate can be significantly higher than that of phytoplankton in underlying water. Neuston control on air-sea gas exchange is discussed in detail in Section 7.

SML-specific microbial diversity is not limited to bacteria and autotrophs (Hardy, 1982; Sieburth, 1983) as there is now molecular biology-based evidence that microlayer protist diversity is also distinct from pelagic assemblages. Components of a possible SML microbial loop have been identified, suggesting that the cycling of elements and energy through microbial trophic interactions could occur via different taxa in the SML compared to underlying water (Cunliffe and Murrell, 2010).

Early attempts to understand how microbes are adapted for living in the SML considered that individual cells must have specific cell-surface properties, such as hydrophobic surfaces, which



Fig. 6. Sea surface microlayer microgel particle collected using a mesh screen in the western English channel. The particle is dual-stained with the TEP alcian blue stain (a) and the DNA specific 4',6-diamidino-2-phenylindole (DAPI) fluorescent stain (b) showing attached bacterioneuston. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

facilitate attachment to hydrophobic moieties enriched in the SML (Norkrans, 1980). It is now believed, however, that many microorganisms within the SML are probably associated with the buoyant particles (e.g. microgels) that form the SML itself (Fig. 6) (Cunliffe and Murrell, 2009). Supporting this, recent studies in the southern Baltic Sea showed a strong dependence of bacterioneuston dynamics on particulate organic carbon content in the SML (Stolle et al., 2010), and that most of the distinctive bacterial taxa in the SML compared to the underlying water were particle-attached (Stolle et al., 2011). Similarly, a significantly higher proportion of bacterial cells in an estuarine SML were observed to be attached to particles than those in underlying water (Santos et al., 2011).

The proximity of the SML to the atmosphere means that resident microbial life could be potentially exposed to high levels of ultraviolet radiation (UV). There is some evidence that SML microorganisms employ specific adaptations to minimise UV damage, such as increased production of UV absorbing mycosporine-like pigments (Tilstone et al., 2010). It is still not clear, however, what effects increased exposure to UV has on bacterioneuston assemblages. Microbial responses to UV in the SML are discussed in more detail elsewhere (Cunliffe et al., 2011).

Microbial life in the SML significantly influences important biogeochemical processes (Cunliffe et al., 2011). The degradation of particulate organic matter (POM) to dissolved organic matter (DOM) in the water column by microbial extracellular enzymes and its substantial role in the global carbon cycle are well established (Azam, 1998). Not only are POM and microgels enriched, and likely to be formed in the SML, but they are probably also broken down there by microbial activity. The SML has already been shown to have elevated extracellular hydrolytic activity, leading to higher organic carbon turnover rates than in underlying waters (Kuznetsova and Lee, 2001). There is evidence that certain members of the bacterioneuston, e.g. Bacteroidetes, have a higher contribution to DOM turnover in the SML than in the underlying water (Obernosterer et al., 2008), most likely due to their ability to degrade complex polymers (Kirchman, 2002). In a study of various sites in the North West Mediterranean Sea, community respiration was enhanced in the SML and exceeded SML community production, therefore indicating that the neuston food web is supported by organic matter transported from the lower water column (Obernosterer et al., 2005). Future studies should examine the relative importance of microbial POM and DOM cycling in the SML and try to better elucidate the importance of the bacterioneuston in global carbon cycling.

7. Sea surface microlayers and air-sea gas exchange

Air-sea gas exchange has a fundamental role in global biogeochemistry and is driven by molecular and turbulent diffusion. Turbulent diffusion is defined by the length and velocity scales of turbulent eddies in bulk water and in air close to the air-water interface, while molecular diffusion operates at the scale of the SML where these eddies are suppressed (Upstill-Goddard, 2006). A "resistance" to gas exchange is thus manifested in gas concentration gradients either side of the interface, in so-called "diffusive sub-layers" through which gas transport rates constrain air-water gas exchange (Liss, 1983). Gas transfer velocities k_a and k_w , in air and water respectively, define these transport rates, being functions of gas diffusivity and the inverse of the diffusive sub-layer depth. For most biogenic gases of interest, however, only k_w is relevant. Modification of k_w occurs by various mechanisms including sea state and bubble bursting (Ho et al., 2000; Woolf, 2005a,b), and of particular relevance here, the physicochemical and biological composition of the SML (Frew, 2005; Upstill-Goddard et al., 2003).

The surface active (surfactant) components of the SML described earlier (Sections 3 and 4), including biogenic polysaccharides, lipids and proteins, influence air-sea gas exchange in two principal ways: as a physicochemical barrier and through modification of sea surface hydrodynamics and hence turbulent energy transfer (McKenna and McGillis, 2004; Tsai, 1996, 1998). Seawater contains both soluble and insoluble surfactants. Although the presence of either in the SML leads to k_w suppression, only the former are thought to be effective in suppressing k_w across a wide range of environmental wind speeds. This is because of a tendency for insoluble surfactants to be less persistent at high surface turbulence (Salter et al., 2011). Where slicks of insoluble surfactant form under calm conditions, they have been reported to dissipate at lower wind speeds than soluble surfactants (Bock et al., 1999; Frew et al., 1990; Goldman et al., 1988). As a consequence of k_w suppression, k_w parameterisations based on bulk turbulence measurements alone may be erroneous when applied to regions of high surfactant concentration. Although laboratory experiments show k_w suppression in the range 5-50% for natural phytoplankton exudates (Frew et al., 1990; Goldman et al., 1988) and 60-90% for synthetic soluble surfactants (Bock et al., 1999; Frew, 2005) added to seawater, quantifying the suppression of k_w by natural surfactants in situ remains a challenge. For example, a recent attempt to evaluate the effect of surfactant on k_w , in the open ocean utilised a deliberate release of a man-made surfactant (Salter et al., 2011). The results showed k_w suppression by the surfactant (oleyl alcohol) ~5%–55% for wind speeds in the range 7.2–10.8 m s⁻¹ relative to surfactantfree waters. A similar study in the North Sea showed that the release of an artificial oleyl alcohol surface film significantly reduced CO₂ exchange (Brockmann et al., 1982). Although these results clearly demonstrated the potential of surfactants to substantially suppress air–sea gas exchange, even at high wind speeds when wave breaking is frequent (Salter et al., 2011), experiments of this nature cannot resolve the effects of *in situ* biogenic surfactant. The extent to which variations in natural surfactants affect air–sea gas exchange at ocean basin scales from coastal waters to oligotrophic gyres remains unknown (Salter et al., 2011).

The direct involvement of the bacterioneuston in air-sea gas exchange has been examined experimentally in situ using free-floating gas exchange boxes (Conrad and Seiler, 1988; Frost, 1999) and with a laboratory gas exchange tank (Upstill-Goddard et al., 2003). Early in situ work revealed significant mismatches between the invasive and evasive exchange of carbon monoxide, methane, nitrous oxide and hydrogen in the open ocean, consistent with microbial gas consumption by the bacterioneuston as the only plausible gas sink (Conrad and Seiler, 1988). This was later corroborated by Frost (1999), who found around 8% invasion-evasion mismatch for methane in coastal seawater. Subsequent laboratory studies carried out with the addition of methane oxidising bacteria (methanotrophs) (Upstill-Goddard et al., 2003) confirmed the potential for active bacterioneuston control of air-sea methane exchange. Fig. 7 (Upstill-Goddard et al., 2003) illustrates apparent gas transfer velocities of methane corrected to constant diffusivity and normalised to corresponding estimates for inert sulphur hexafluoride (SF₆) derived simultaneously during invasive and evasive gas exchange experiments in a sealed laboratory tank in which surface turbulence was generated by a motor-driven baffle. For a situation where methane behaves as an inert gas during waterair gas exchange (all gas transfer under physical control, i.e. turbulence), the ratio of the two transfer velocities would equal unity. Clearly, this is not the case for methane exchange measured evasively in bacterial enrichment experiments, where the ratios all exceed unity (Fig. 7). This was interpreted as being due to modification of the methane concentration gradient at the air-water interface by the activity of methanotrophs in the microlayer. Consistent with this, for invasive experiments the additional methane flux due to microbial consumption was not measureable due to its consumption in the microlayer; hence the ratio of the



Fig. 7. Ratios of the apparent transfer velocities of methane and sulphur hexafluoride (SF₆) normalised to a constant diffusivity, as derived from laboratory gas exchange experiments: 9232, marine *Methylococcus*; KO and YO, marine *Methylomicrobium*; Community, marine methanotrophs; OB3B freshwater *Methylosinus trichosporium*. Figure reproduced by permission of American Geophysical Union from Global Biogeochemical Cycles, 2003, 17, 1108, doi: 10.1029/2003GB002043, 2003.

two transfer velocities measured invasively was always one (Upstill-Goddard et al., 2003).

Molecular ecology studies of the bacterioneuston have shown using functional gene probes that the metabolic capability for trace gas cycling is widespread in the SML (Cunliffe et al., 2008, 2011). The conclusion from these studies is that the bacterioneuston is closely involved in the cycling of at least some climatically active trace gases and that the bacterioneuston may potentially be both a small gas source and a small gas sink, contingent upon the prevailing microbial and biogeochemical regimes. This should be taken account of in future studies.

8. The sea surface microlayer and sea spray aerosol

Sea spray aerosol (SSA) are defined as a suspension in air of particles produced directly at the sea surface due to the bursting of bubbles generated by breaking waves or rainfall. Due to the size spectrum and hygroscopic nature of its component particles SSA is a medium for the uptake and reaction of trace gases and is suggested to be a major source of cloud condensation nuclei (CCN). As well as affecting the microphysical and radiative properties of marine clouds, SSA is a major source of uncertainty in evaluating indirect climate forcing by anthropogenic aerosol particles. Much of this uncertainty stems from a current lack of understanding of the sea-to-air exchange flux of SSA as a function of particle size (or particle size distribution), as well as the size dependant composition of newly produced particles. SSA production has been reviewed in detail elsewhere (Bigg and Leck, 2008; de Leeuw et al., 2011; Leck and Bigg, 2010; Lewis and Schwartz, 2004; Massel, 2007). Early work on SSA by Blanchard and Woodcock (1957) and Blanchard (1963) highlighted two distinct methods of particle formation. The first is formation from fragments of the bubble membrane (film) which is ejected into air when the bubble bursts, known as "film drops", and the second is from drops of water that become detached from the upward-moving water jet that follows the bubble burst, known as "iet drops" (Blanchard, 1963: Blanchard and Woodcock, 1957). The particles range in size from ~ 10 nm to at least several millimetres and have atmospheric residence times of seconds to days that are inversely related to particle size.

A major recent advance in understanding comes from recognition of the contribution of organic compounds to SSA. Laboratory and field measurements have shown that the submicron aerosolphase ratios of organic carbon to sodium range from 10^{-1} to 1 compared to 10^{-4} – 10^{-3} in subsurface ocean waters (Blanchard, 1964; Facchini et al., 2008; Keene et al., 2007; Oppo et al., 1999; Russell et al., 2010). Recent improvements in instrumentation have highlighted the enrichment of organics, specifically for particles with equilibrium radii at a relative humidity of 80% or $r_{80} < 1 \ \mu\text{m}$; contributions of organics have been shown to range from ~20% with $r_{80} < 1.3 \ \mu\text{m}$ (Putaud et al., 2000) to more than half of all marine particles with dry diameters greater than 0.16 μm (Middlebrook et al., 1998).

It is therefore most likely that the production of highly organically enriched particles results from fragmentation of the film cap formed from the SML, from which much of the seawater drains prior to bursting, leaving behind a film that is highly surfactant enriched (de Leeuw et al., 2011). Given the process of bubble scavenging (discussed in Section 5) and the possible interaction of bubbles with the SML, it is perhaps not surprising that several studies of the composition of airborne marine organic particles have found evidence of carbohydrates (Crahan et al., 2004; Facchini et al., 2008; Hawkins and Russell, 2010; Kuznetsova et al., 2005; Leck and Bigg, 2005a,b; Russell et al., 2010), marine gels (Bigg and Leck, 2008; Leck and Bigg, 2005a,b; Orellana et al., 2011), amino acids (Kuznetsova et al., 2005; Leck and Bigg, 1999), alcohols, fatty acid, esters (Gagosian et al., 1982; Schmitt-Kopplin et al., 2012), and marine microorganisms (Aller et al., 2005; Leck and Bigg, 2005a). Evidently most of organic components found in the SML are transferred to the marine atmosphere during aerosol formation.

Some recent experimental studies of SSA production involved generating aerosols by bubbling air through natural and artificial seawater, or by focusing water jets on surface water, thereby minimising atmospheric variability that can compromise controlled observations in situ (Hultin et al., 2010). Such investigations have allowed systematic examination of SSA as functions of variables such as seawater surfactant content and organic composition. Sellegri et al. (2006) amended artificial seawater with sodium dodecyl sulphate (SDS) and found that the resulting aerosol particle size distribution was similar to that for natural seawater but with a shift towards lower values of r_{80} for SDS concentrations exceeding 3 mg l^{-1} . Tyree et al. (2007) used natural seawater of varying organic composition dependent upon season (winter DOC 2300 μ g l⁻¹ C; winter chlorophyll 0.1 μ g l⁻¹; summer DOC = 3100 μ g l⁻¹ C, summer chlorophyll 1.8 μ g l⁻¹) but although they found little dependence of the size distribution on the organic components 20–40% more SSA particles were generated in winter (Tyree et al., 2007). Fuentes et al. (2010) added diatom exudate to filtered seawater to a concentration of 512 μ M and reported that although hygroscopic growth was suppressed, the influence of this added organic material on CCN production showed little size dependence (Fuentes et al., 2010), which is consistent with the presence of non-water soluble microgels (Leck and Bigg, 2005a). Using oligotrophic seawater to determine the size-dependant mass fraction of organic material in SSA particles, Keene et al. (2007) found calcium enrichment with respect to surface water. These findings imply complex interactions between organic compounds and the SML during SSA production. It is now generally accepted that for particles with r_{80} < 0.25 µm organics account for a substantial fraction of SSA, especially during periods of high biological activity (Facchini et al., 2008: Leck and Bigg, 2005a: O'Dowd et al., 2004). This is supported by correlations between satellite derived estimates of chlorophyll and the seasonality of SSA emissions and composition (Sellegri et al., 2006).

As mentioned above there is strong evidence that those aerosol particles produced by bubble bursting over the ocean with dry radii < 0.1 μ m consist almost entirely of organic matter (Bigg and Leck, 2008). Studies using transmission electron microscopy have reported high concentrations of solid, water-insoluble marine gel particles with dry radii < 0.025 μ m accompanied by larger particles with dry radii > 0.5 μ m (derived from marine bacteria and diatoms) and have concluded following comparison with SML samples that these particles have an SML origin (Bigg and Leck, 2001; Leck and Bigg, 1999; Leck and Bigg, 2005a,b; Orellana et al., 2011).

To date, the role of marine gels in SSA production is in general not well understood over the remote oceans, and much of the existing knowledge is from Arctic pack ice, which may present a special case. Recent work has raised the possibility of two potentially conflicting effects of marine gels on CCN which might occur simultaneously. Study of marine microgels originating from surface water organics in cloud fog and airborne aerosols suggests that microgels are themselves CCN, dominating total CCN numbers in the high Arctic (Orellana et al., 2011) and possibly elsewhere given the ubiquitous nature of marine microgels (Verdugo, 2012). Marine gels can also potentially compromise the ability of sea salt aerosols to act as CCN through reduction of their hygroscopicity (Fuentes et al., 2011; Wex et al., 2010). Fuentes et al. (2011) did not consider the fact that marine gels are likely to be predominantly hydrophobic in nature (with growth factors above 1), and therefore potentially have higher CCN activation efficiency than more soluble, inorganic aerosol (Ovadnevaite et al., 2011). When surface tension counteracts water activity the net effect may well be an enhancement of particle CCN activity. Notwithstanding the inherent complexities, there remains clear evidence for a biogenic, organic, wind-driven source of SSA-derived CCN that provides a direct link between SML biology and global-scale climate processes (Leck and Bigg, 2007; Quinn and Bates, 2011).

9. Sea surface microlayers and marine pollution

A range of chemical pollutants are found in the SML, including hydrocarbons, organochlorine compounds and trace metals, which may typically be ten to one hundred times more concentrated than in underlying waters. SML pollutants therefore have a range of potential environmental and ecotoxicological concerns for the functioning of the SML ecosystem (Wurl and Obbard, 2004). Notably, higher accumulations are found in the SML of coastal water close to anthropogenic sources of pollution (Cincinelli et al., 2001; Guitart et al., 2007). Both anthropogenic and natural processes, including direct inputs (e.g. oil spills and natural seepage), coastal discharges and both dry and wet atmospheric deposition, are the main contributors to increased concentrations of pollutants in the SML, all of which occur at inherently different temporal and spatial scales. Once at the SML, pollutant distribution, transport and fate depends on air-sea interface hydrodynamics and SML biogeochemical transformations (e.g. photoreaction and biodegradation) (Fig. 1) in accordance with their varied physicochemical properties.

SML pollutants participate in processes from the molecular scale (e.g. biochemical transformation) to the ecosystem scale (e.g. air-sea exchange). To investigate the major phase distribution processes of pollutants in the water column, a range of experimentally estimated phase distribution coefficients are used such as, the octanol-water (K_{OW}) and various particle-water (K_X) coefficients for sorption processes, which are applicable to the SML studies. Hydrophobic organic contaminants and metals are involved in sorption processes within the SML biogenic matrix (García-Flor et al., 2005). There is also evidence that microbial metabolism of organic pollutants such as polycyclic aromatics is important in the SML (Coelho et al., 2011; Guerin, 1989).

Compared to air-sea exchange of biogenic gases passing rapidly through the SML, the majority of the accumulated organic contaminants inhibit gaseous transport in favour of more complex diffusive, rain driven and aerosol-particle transport across the air-sea interface (i.e. dual mode) (Guitart et al., 2010; Lim et al., 2007; Marcomini et al., 2001; Saint-Louis and Pelletier, 2004). Furthermore, marine pollution episodes, such as oil spills, surface slicks and sheens of chemicals (i.e. high hydrophobic chemical concentrations), constitute another area of research within the SML pollution studies (Burns et al., 2010; Guitart et al., 2008; Romano and Garabetian, 1996).

Multiple processes are likely to occur simultaneously due to the complex nature of the SML (Fig. 1) yet few studies have addressed this. Many questions remain unsolved, including the potential ecotoxicological effects of pollutants in the SML and the transport of pollutants between the ocean and atmosphere. It remains unclear how the physicochemical structure of the SML, outlined in Section 4, affects pollutants. The occurrence and behaviour of less hydrophobic 'emerging pollutants', such as pharmaceutical chemical residues, in the SML remain unknown. Recent evidence has shown that microplastics are enriched in the SML of the North Western Mediterranean Sea (Collignon et al., 2012). The impacts of plastics on the wider marine environment are now established (Azzarello and Van Vleet, 1987; Derraik, 2002; Teuten et al., 2007), however, the potential impacts on SML ecosystems are unidentified. Large sampling variability and the lack of sampling standardisation (as discussed in Section 2), remains a significant challenge to fully understanding the effects of pollutants in the SML, specifically in linking SML biological and physicochemical properties with pollutant processes (Falkowska, 1999a,b; Guitart et al., 2004). From a marine pollution perspective, only scattered studies have been undertaken to investigate contaminant cycling in the SML. New approaches and standardised field studies are required for a better understanding of the cycling and fate of pollutants in the SML in terms of the oceans' health.

10. Future research direction and perspectives

To date, studies on the SML have been largely dominated by opportunistic sampling programmes that do not make multiple return visits to sample the same location. Greater understanding of the SML could be achieved by establishing a network of time-series study sites. Time-series observations of both pelagic and coastal systems, such as the Bermuda Atlantic Time Series (www.bats. bios.edu), the Hawaiian Ocean Time Series (www.hahana.soest. hawaii.edu/hot) and the Western Channel Observatory (www. westernchannelobservatory.org.uk) are extremely effective in understanding the complex and dynamic temporal interactions of marine biogeochemical and physical variables. Such an approach for the SML would help clarify the impact of seasonal events, such as phytoplankton blooms, on SML structure and function across broad regional scales.

Understanding the SML in its wider Earth system context must be a priority. Other processes such as the atmospheric deposition of terrestrial dust need to be studied alongside the SML by way of parallel sampling initiatives. Future research should also consider the effects of freshwater, estuarine, coastal and sea ice processes on the SML (Fig. 1).

Multidisciplinary scientific development is a fundamental challenge for SML research that requires progressive thinking from funding agencies. Key to this is the expansion of genuine and practicable multidisciplinary SML programmes. A holistic systems approach which details the obligate connectivity between biological diversity and ecosystem function, as outlined in Fig. 1, is essential to fully understand the SML. The application of contemporary biological oceanography techniques, such as metagenomics and metatranscriptomics, in combination with chemical and physical oceanography will help achieve such aims. Global-scale processes, such as the role of microbes in air–sea exchange, carbon cycling and marine pollution, cannot be fully evaluated in the absence of such endeavours.

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