



The Ocean's Vital Skin: Toward an Integrated Understanding of the Sea Surface Microlayer

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Despite the huge extent of the ocean's surface, until now relatively little attention has been paid to the sea surface microlayer (SML) as the ultimate interface where heat, momentum and mass exchange between the ocean and the atmosphere takes place. Via the SML, large-scale environmental changes in the ocean such as warming, acidification, deoxygenation, and eutrophication potentially influence cloud formation, precipitation, and the global radiation balance. Due to the deep connectivity between biological, chemical, and physical processes, studies of the SML may reveal multiple sensitivities to global and regional changes. Understanding the processes at the ocean's surface, in particular involving the SML as an important and determinant interface, could therefore provide an essential contribution to the reduction of uncertainties regarding ocean-climate feedbacks. This review identifies gaps in our current knowledge of the SML and highlights a need to develop a holistic and mechanistic understanding of the diverse biological, chemical, and physical processes occurring at the ocean-atmosphere interface. We advocate the development of strong interdisciplinary expertise and collaboration in order to bridge between ocean and atmospheric sciences. Although this will pose significant methodological challenges, such an initiative would represent a new role model for interdisciplinary research in Earth System sciences.

Keywords: sea surface microlayer, air-sea exchange, neuston, aerosols, surface films, gas exchange, review

INTRODUCTION

Surfaces and interfaces are critical zones where major physical, chemical, and biological exchanges occur. As the ocean covers 362 million km² (~71%) of the Earth's surface, the ocean-atmosphere interface is arguably one of the largest and most important interfaces on the planet. Every substance entering or leaving the ocean from or to the atmosphere passes through this interface, which on the

water-side -and to a lesser extent on the air-side- shows distinct physical, chemical, and biological properties. On the water side the uppermost 1–1,000 μm of this interface are referred to as the sea surface microlayer (SML) (Hunter, 1980) (**Figure 1**). Like a skin, the SML is expected to control the rates of exchange of energy and matter between air and sea, thereby potentially exerting both short-term and long-term impacts on various Earth system processes, including biogeochemical cycling and climate regulation (Cunliffe et al., 2013). Yet, processes occurring within the SML, as well as the associated rates of material exchange through the SML, are still poorly understood. Consequently, they are rarely represented in marine and atmospheric numerical models.

An improved understanding of the biological, chemical, and physical processes at the ocean's upper surface could provide an essential contribution to the reduction of uncertainties regarding ocean-climate feedbacks. Due to its positioning between atmosphere and ocean, the SML is the first to be exposed to climate changes including temperature, climate relevant trace gases, wind speed, and precipitation as well as to pollution by human waste, including nutrients, toxins, nanomaterials, and plastic debris.

During the past two decades the number of publications addressing the SML has more than tripled, from 15 year⁻¹ at the beginning of this century to ~ 50 year⁻¹ in 2016 (Web of Science, Thomson Reuters 2016). These studies shed new light on the organic and organismal constituents of the SML and emphasized its roles in air-sea gas-exchange and in the production of primary organic aerosols. Recent in-depth reviews summarize current knowledge of the SML, including aspects of its composition, key processes and overall role in the Earth system (Liss and Duce,

2005; Cunliffe et al., 2013; Law et al., 2013; Garbe et al., 2014; Carpenter and Nightingale, 2015). Conceptions of the structure of the SML and its dynamics are diverse, placing emphasis on a range of processes and spatial and temporal scales (**Figure 1**). The purpose of this critical review is to identify the main open questions, controversies, and challenges that inhibit our current understanding of the SML and to identify how SML studies can be better integrated into marine and climate research.

WHAT IS LIFE AT THE AIR-SEA INTERFACE?

As with other marine ecosystems, life in the SML is dominated by microorganisms, which are collectively referred to as the “neuston,” whereas “plankton” describes the microscopic organisms that inhabit the underlying water column. So far, most recent studies have focused on the diversity and abundance of bacterioneuston assemblages, principally through the application of molecular ecology tools (for a review see Cunliffe et al., 2011). The consensus view is that bacterioneuston assemblages form by recruitment from the underlying bacterioplankton; however, the species composition and activity of bacterioneuston assemblages can be very different compared to those in the underlying water column (Agogue et al., 2005; Franklin et al., 2005; Obernosterer et al., 2008; Stolle et al., 2011; Taylor et al., 2014). What exactly controls bacterioneuston species diversity is at present not fully understood, but evidence from both field observations (Cunliffe et al., 2009a) and large-scale mesocosm experiments (Cunliffe et al., 2009c) suggests that the development of bacterioneuston assemblages is ecologically regulated and not random (Cunliffe et al., 2011). Possible controls

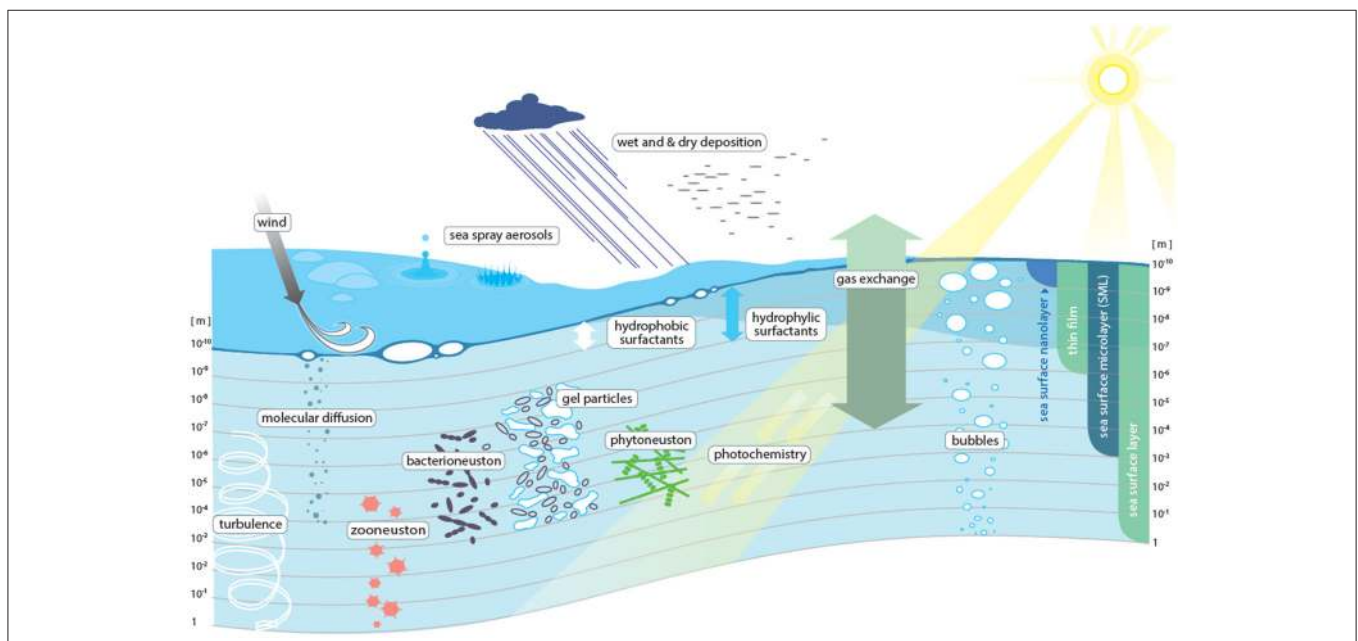


FIGURE 1 | Conceptual view of the processes determining transport across the sea surface microlayer (SML).

of bacterioneuston diversity and activity include the prevailing meteorological conditions, incident UV light, organic matter availability and aerosol deposition (Carlucci et al., 1985; Agogue et al., 2005; Stolle et al., 2010, 2011; Nakajima et al., 2013; Astrahan et al., 2016). It is, however, not clear whether solar and UV irradiance promote or inhibit neuston activity (Bailey et al., 1983; Carlucci et al., 1985; Santos et al., 2012).

The bacterioneuston has been shown to directly influence air-sea gas exchange by consuming and producing trace gases (e.g., CO, H₂, CH₄, N₂O) (Conrad and Seiler, 1988; Frost, 1999; Upstill-Goddard et al., 2003; Nakajima et al., 2013). The addition of methanotrophs in a laboratory gas exchange tank led to an enhancement of the apparent transfer velocity of CH₄ by 12 ± 10% (Upstill-Goddard et al., 2003). Later work reported bacterial growth efficiency in the SML and underlying water to be similar, but also showed higher respiration in the SML that pointed to some potential control of the air-sea exchange of CO₂ and O₂ by the bacterioneuston (Reinthal et al., 2008). Through the application of functional gene probes to a range of SML environments, the metabolic potential for trace gas cycling in the SML has since been established as being widespread (Cunliffe et al., 2008, 2011). It can therefore be concluded that for some trace gases such as CH₄ and CO₂, the bacterioneuston is intimately involved in their cycling and that it may potentially act as either a small gas source or sink in response to the prevailing microbial and biogeochemical conditions. The bacterioneuston may also modulate the enrichment of surfactants in the SML and thus indirectly influence air-sea gas exchange, as indicated by a recent study relating SML surfactant enrichment and the occurrence of specific bacterial taxa (Kurata et al., 2016).

The second major biological component of SML ecosystems is phytoneuston, historically studied using microscopes (Hardy and Valett, 1981; Hardy, 1982), and more recently through high-throughput sequencing (Taylor and Cunliffe, 2014). High-throughput sequencing of phytoneuston assemblages in the coastal SML of the English Channel showed that biodiversity at the interface was very different to that in the underlying water (Taylor and Cunliffe, 2014). Two major algal groups, the chrysophytes and the diatoms, were significantly enriched in the neuston, with diatom diversity in particular being distinctly different to that of planktonic diatoms. While the functional impacts of the differences between phytoneuston and phytoplankton abundance and diversity are not yet fully understood, it is believed that specific processes such as the maintenance of air-sea CO₂ disequilibria could be controlled, at least in part, by the phytoneuston (Calleja et al., 2005).

Other components of SML ecosystems such as heterotrophic protists and zooneuston have also been studied, but to a lesser extent. Looking forward, the application of contemporary tools, such as high-throughput sequencing, hold great promise in revealing new insights into the biology of the SML. The recent English Channel study discussed above also showed that the diversity of neustonic fungi (myconeuston) is also distinctly different from mycoplankton diversity (Taylor and Cunliffe, 2014). Relative to other marine microbial groups, the marine fungi remain poorly understood. A recent study of the coastal mycoplankton implicated marine fungi in a range of ecosystem

functions, including nutrient recycling and parasitism (Taylor and Cunliffe, 2016). Exactly what functional roles myconeuston may play at the ocean-atmosphere interface still remain to be revealed.

Marine aerosols that are formed from the SML via bubble bursting are a vector for the transfer of microbial life from the lower water column and SML into the atmosphere. Measurements of bacteria and viruses in sea spray aerosols (SSA) show large enrichments relative to both the SML (~5) and subsurface waters (~10) (Aller et al., 2005). A key factor in this process appears to be the embedding of microorganisms within the organic gel matrix that forms in the SML (discussed further below) (Aller et al., 2005). The global-scale implications for ocean-atmosphere exchange of microorganisms are profound because this process may have a major impact on the long-distance dispersal of marine microbial life. For example, phytoplankton viruses that are transported into the atmosphere from the SML can remain highly infective under prevailing meteorological conditions and can be spread across hundreds of kilometers to subsequently infect distal phytoplankton (Sharoni et al., 2015).

Organisms in the SML interact with the surface accumulation of organic matter produced by biological processes in the underlying water column (Galgani et al., 2014). Some dissolved compounds have surface active (surfactant) properties or adsorb onto floating compounds and selectively become enriched in the SML (Hunter and Liss, 1977). The accumulation of surfactants in the SML was found to be related to the occurrence of certain bacterioneuston taxa, indicating microbial contribution to surfactant production and decomposition (Kurata et al., 2016). In addition to soluble surfactants, the SML also accumulates a variety of colloidal and particulate organic matter that may serve as substrates for the bacterioneuston. Sieburth (1983) proposed the SML to be a complex hydrated “gel” of macromolecules and colloidal material.

The “gel” material has now been identified and studied in greater detail. Included in the gelatinous matrix are transparent exopolymer particles (TEP), i.e., polysaccharide-rich microgels that are produced primarily by the abiotic coagulation of phytoplankton exudates (Passow, 2002), and Coomassie stainable particles (CSP) containing proteinaceous polymers released during cell lysis and decomposition (Long and Azam, 1996). The aggregation of TEP precursors in the SML is enhanced due to the constant compression and dilation of the air-sea interface (Wurl et al., 2011), which may explain, at least in part, the gelatinous nature of the SML. Gel particles may serve as grazing protection for the phytoneuston and bacterioneuston, as has been shown for their planktonic counterparts (Passow and Alldredge, 1999; Dutz et al., 2005). In addition, TEP have been suggested to protect neuston from high irradiance (Ortega-Retuerta et al., 2009), possibly helping the neuston withstand periods of high irradiation of the SML.

Currently there is no consensus about which biogenic substances become selectively enriched in the SML, or why, and when. Many studies reported that particulate organic matter is more extensively enriched in the SML than is dissolved organic matter. Most studies report higher enrichment factors (the ratio

between SML and subsurface concentrations) for proteinaceous compounds than for others (Henrichs and Williams, 1985; Carlucci et al., 1992; Kuznetsova and Lee, 2001, 2002; Kuznetsova et al., 2004; Reinthaler et al., 2008). Several recent studies also showed that the SML can be highly enriched in gel particles, with enrichment factors >10 , in particular under calm wind conditions (Cunliffe et al., 2009b; Wurl et al., 2011, 2016; Galgani et al., 2014; Engel and Galgani, 2016; Thornton et al., 2016). However, in many of these studies enrichment was highly variable, with depletion of organic matter in the SML, including gels, also being observed. Clearly, understanding organic compound enrichment and microbial uptake and cycling in the SML requires an improved knowledge of: (i) the chemical nature of organic molecules; (ii) the functioning of the ecosystem below and within the SML; and (iii) the mechanisms that transport organic matter into and out of the SML.

DO WE NEED TO BETTER RESOLVE THE AIR-SEA INTERFACE TO ENABLE MORE ACCURATE DESCRIPTIONS OF AIR-SEA GAS EXCHANGE?

A classical view of the ocean's surface is that encapsulated in the surface film model, where two stagnant films (or viscous boundary layers), one at the air side and one at the water side, control the exchange of heat, momentum and gases between the ocean and the atmosphere (e.g., Liss and Slater, 1974).

More recent physical theories mechanistically connect the transfer of heat and momentum to mass flux, in particular gas flux, and distinguish between a skin or mass boundary layer of molecular diffusion about $10\ \mu\text{m}$ in thickness, and sub-layers, about $10^2\text{--}10^3\ \mu\text{m}$ thick, in which strong viscous dissipation of turbulence occurs (e.g., Soloviev and Schlüssel, 1994; Jähne and Haußecker, 1998; Turney et al., 2005). Two basic dynamical model approaches are currently applied.

The first is based on a stochastic description of the instantaneous near-surface renewal of small volume elements of the fluid (Danckwerts, 1951); this is referred to as the surface renewal model. It requires estimates of the mean surface renewal time, a parameter that expresses the duration between events when surface gas/mass concentrations are homogenized to those of the underlying bulk water. Infrared thermal imaging of the sea surface can be well-explained by the renewal model (e.g., Schimpf et al., 2004), which additionally supports it as a meaningful description of air-sea gas exchange. The major challenge to its application is its ability to allow reliable estimates for the timescale of renewal events and to link these timescales to the underlying physical processes.

The second dynamical model approach is via the surface divergence model. This considers the root mean square of surface divergence of those velocity components that are tangential to the air-sea interface (McCready et al., 1986). One advantage of the divergence model is that it does not require a renewal time to be specified (Banerjee et al., 2004). Another is that mass transfer velocities can be inferred from small-scale surface images that resolve small spatial-temporal variations in horizontal velocity

gradients (Turney et al., 2005). The ability of either model to simulate gas transfer strongly depends on wind conditions, the surface divergence model performing best under calm wind conditions. The successful combination of elements of surface renewal and surface divergence into a single model should improve future model predictions of air-sea gas exchange (Turney and Banerjee, 2013).

Many descriptions of air-sea gas exchange adopt the surface film model that treats the interface as a boundary for which a bulk gas transfer velocity for the water side (k_w) can be derived from wind speed, the solubility and molecular diffusivity of the gas in question, and the kinematic viscosity of seawater (e.g., Liss and Merlivat, 1986; Wanninkhof, 1992; Nightingale et al., 2000). Indeed, estimates of k_w derived from seawater salinity, temperature and wind speed data can explain between 50 and 80% of the variability observed during tracer studies (Ho et al., 2011). However, considerable uncertainties and biases remain in these estimates, particularly under both calm and stormy wind conditions, either because the underlying mechanisms remain unresolved or, as in the case of stormy conditions, they are technically difficult to investigate (see e.g., Wanninkhof et al., 2009; Garbe et al., 2014).

As alluded to above, air-sea gas transfer is influenced by molecular diffusion (Garbe et al., 2014). Therefore, the effective value of the gas diffusivity applied in gas transfer models is an important quantity. It is well-documented from measurements of gas permeability that the gas diffusivity in various dense surface films can be quite low (Blank, 1962). Even so, the extent to which the presence of a SML including particles, gels, and high molecular weight compounds modulates diffusion effects under ambient conditions remains unclear.

Another poorly characterized descriptor of air-sea gas exchange is the importance of surfactants accumulating at the air-sea interface. Recent work in the Atlantic Ocean implies that surfactant enrichment of the SML could be a ubiquitous feature of the open ocean up to wind speeds of $\sim 13\ \text{m s}^{-1}$ and possibly even higher (Sabbaghzadeh et al., 2017). This is important because surfactants have the ability to alter the hydrodynamic properties of the interface and suppress gas exchange by forming a physico-chemical barrier or by modifying aspects of sea surface hydrodynamics such as turbulent energy transfer, micro-scale wave breaking and surface renewal, and by damping small capillary waves (Frew et al., 1990; Tsai, 1996, 1998; McKenna and McGillis, 2004; Garbe et al., 2014; Pereira et al., 2016). In the SML, both insoluble (hydrophobic; dry) surfactants (e.g., fatty acids) that tend to form monolayers directly at the interface and soluble (hydrophilic, wet) surfactants (e.g., lipopolysaccharides) that dominate the surfactant pool in the bulk water phase accumulate. In contrast to dense monolayers formed by the insoluble surfactants that act as a potential static barrier for mass exchange, soluble surfactants establish concentration-dependent interfacial adsorption equilibria, which do not show static barrier effects (Springer and Pigford, 1970). For natural environments, where a complex mixture of surfactants is present, the overall effect on gas-exchange resulting from a subtle interplay of insoluble and soluble surfactants at the interface is difficult to predict.

Experimental studies have revealed substantial suppression of the k_w values of various gases by surfactants in the laboratory (see e.g., Mesarchaki et al., 2015) and in the field (see e.g., Salter et al., 2011). During the UK SOLAS Deep Ocean Gas Exchange Experiment in the NE Atlantic Ocean, addition of (i) SF₆/³He and (ii) SF₆/³He plus artificial surfactant showed that addition of the surfactant caused up to 55% suppression of k_w at wind speeds up to 11 m s⁻¹ (Salter et al., 2011). Due to the practical difficulties of estimating k_w for “naturally surfactant-enriched” vs. “surfactant-free” waters both *in situ* and in the laboratory, such experiments are conditioned by the addition of soluble or insoluble synthetic surfactants.

As of now the role of natural surfactants in modifying gas transfer velocities in the ocean is largely uncertain. Natural slicks of insoluble surfactants that may form under calm conditions tend to dissipate rapidly at high turbulence (Frew et al., 1990; Bock et al., 1999). The issue is further compounded by a high degree of spatial and temporal variability in total surfactant amount and in the chemical composition of the surfactant pool, both in the short-term and seasonally (Gašparović et al., 2011; Schmidt and Schneider, 2011; Wurl et al., 2011; Laß et al., 2013; Schneider-Zapp et al., 2014; Pereira et al., 2016). Compounds that contribute little to organic matter by mass, such as lipids, may have a strong influence on the physicochemical, and structural properties of the SML (Frka et al., 2012). Compositional variations in SML biosurfactants deriving from organic matter dynamics in natural waters and their specific impact on k_w still needs to be assessed (Pogorzelski et al., 2006). For example, in Baltic Sea coastal waters a factor ~2 variability in seasonal CO₂ uptake was related to productivity- (i.e., surfactant-) related variability in k_w of only 20% (Schmidt and Schneider, 2011). Modeling studies suggested that surfactants in the SML can reduce net oceanic CO₂ uptake by 15–50% (Asher, 1997; Tsai and Liu, 2003; Wurl et al., 2016). A recent study of N₂O air-sea and diapycnal fluxes in the eastern tropical North Atlantic (including the upwelling off Mauritania, NW Africa) revealed that the mean air-sea flux, calculated with a common gas exchange approach, is about four times larger than the mean diapycnal flux into the mixed layer (Kock et al., 2012). Neither vertical advection nor biological production could explain this discrepancy. Instead, flux calculations using an air-sea exchange parameterization that took account of the effect of surfactants in the SML were in good agreement with the N₂O diapycnal fluxes. This indicates that surfactants, especially in areas of high biological productivity, may exert a large dampening effect on the air-sea exchange of N₂O (Kock et al., 2012).

Very strong accumulation of organic matter in the SML can lead to the formation of surface slicks, which can be distinguished from non-slick surfaces by their different reflectance properties that result from increased wave damping (Figure 2). Slicks are frequently observed in the oceans, but it remains unclear whether they are specific cases of surfactant enrichment or whether they should be regarded as an exaggerated SML including chemical and biological constituents. It has recently been proposed that the accumulation of organic gels in the SML may directly suppress gas exchange by virtue of their inherently high surface to volume ratio, acting as a diffusional barrier (Engel and Galgani, 2016;



FIGURE 2 | Surface slicks attenuate small and capillary waves in the upper cm of the ocean, which causes a significant reduction of the glittering effect of sun beams. Photo by: Angela Stippkugel.

Wurl et al., 2016). So far, it has not been demonstrated how the coverage by a “gelatinous surface layer” could significantly affect the exchange of gas, heat, and momentum between the ocean and atmosphere. Moreover, spatial and temporal accumulation of gel particles in the SML may be highly variable, probably affecting instantaneous transfer velocities rather than time-integrated gas exchange fluxes. Clearly, further research is needed to understand the formation, composition and stability of surfactants/surface slicks as well as to evaluate their importance for gas fluxes across the air-sea interface.

Heterogeneous oxidation processes occurring directly at the air-sea interface are another example of a potential specific surface film effect. For example, the reaction between gaseous ozone and aqueous iodide or bromide is hypothesized to contribute to the formation of volatile halogenated species (Carpenter and Nightingale, 2015), which, when transferred to the atmosphere, can affect its oxidation capacity and potentially be important for secondary particle formation. Similarly, the products of photosensitized reactions depend on the molecular environment; a high concentration of surfactants may increase the probability of molecular contact between reactive species involved in the photochemistry. Such conditions could influence the reaction rate and result in additional products other than those originating from the corresponding bulk reaction. Recently Fu et al. (2015) demonstrated that the irradiation of an organic monolayer in the presence of

photosensitizers at the water surface leads to the release of unexpected unsaturated volatile organic compounds to the gas phase. Previously, unsaturated compounds were thought to be generated from biological activity alone. Further, Ciuraru et al. (2015a,b) showed that photosensitized reactions involving the SML produce a series of unsaturated volatile organic compounds and significant amounts of isoprene. It is well-known that in seawater unsaturated compounds including isoprene are produced by various biological processes. However, these recent studies suggest that interfacial photosensitized chemistry is an important source of unsaturated compounds even in the absence of any biological sources in the marine boundary layer (Tinel et al., 2016), clearly implying a global impact of reactions at the air-sea interface. There is huge potential for hitherto undiscovered chemical conversions that might take place under the special conditions of the SML. These could include the aforementioned photosensitization processes, but there is also potential for complex photochemistry, the generation of novel radicals and their involvement in a range of reactions in the special environment of the oceanic SML. Further experimental work, both in the laboratory and in the field, as well as the development of numerical models is necessary to untangle the complex kinetics of SML mediated chemistry and photochemistry and to better constrain their roles in ocean-atmosphere coupling.

DO WE NEED TO CONSIDER THE AIR-SEA INTERFACE WHEN ESTIMATING THE MARINE SOURCE OF ORGANIC ATMOSPHERIC AEROSOLS?

Marine aerosol particles are predominantly produced directly at the sea surface due to the interaction between wind and waves (“bubble bursting”) or indirectly by gas-to-particle conversion following the release of oceanic trace gases to the atmosphere. Air-sea-gas exchange produces secondary organic aerosol (SOA) precursors during calm and windy conditions. In contrast, the formation of sea spray aerosol (SSA) is triggered mainly in white caps under windy conditions and therefore is conceptually rather different. An as yet relatively unknown aspect is the role of bubbles ascending in the water-column as a transport vector for organic matter into and out of the SML via aerosol formation. In the water column the upward transport of organic matter is most likely associated with its adsorption onto floating bubbles that eventually approach the SML (Hunter, 1980). The formation and buoyancy of bubbles depends on wave characteristics and turbulence (e.g., Garrett et al., 2000; Deane and Stokes, 2002) and they are known to modulate air-sea gas exchange (e.g., Keeling, 1993; Liang et al., 2013). Bubble dynamics is also of primary concern when quantifying the formation of jet and film drops at the SML that facilitate the emission of primary aerosols into the atmosphere (e.g., Blanchard, 1964; Resch, 1986; Woolf et al., 1987). There is evidence to suggest that surfactants may modify the characteristics of the bubble plume and may increase the stability of bubble films, thus leading to enhanced thinning of the bubbles prior to bursting (Modini et al., 2013).

Organic matter transferred from the SML into the atmosphere by wave breaking and bubble bursting has been linked to the formation of cloud condensation nuclei (CCN) (Russell et al., 2010; Quinn and Bates, 2011). Consequently, the quantification of primary organic aerosol formation and emission is of particular relevance for climate modeling (Navakov and Penner, 1993; O’Dowd et al., 2004; McCoy et al., 2015; Wilson et al., 2015). So far, a detailed understanding of how the physical characteristics and chemical composition of marine aerosol particles may affect solar radiation transfer and cloud processes is lacking (de Leeuw et al., 2011; Gantt and Meskhidze, 2013). The numerous measurements of the atmospheric aerosol burden over pristine marine regions available today indicate that organic matter, including bacteria and viruses (Aller et al., 2005), is one constituent that is highly enriched in marine aerosols with respect to seawater (Quinn et al., 2015 and references therein). Thereby, the smaller the particles the higher the organic matter enrichment (O’Dowd et al., 2004).

Although much effort has been directed toward analyzing the organic matter from aerosols in general, the role of the SML in determining the mixing state of sea-salt and organics, the chemical fractionation of the organic matter, and the relative atmospheric enrichment remain unclear (Facchini et al., 2008; Collins et al., 2013; Gantt and Meskhidze, 2013; Quinn et al., 2015; Ceburnis et al., 2016).

Recently much attention has been paid to the gel-like compounds that are found to be accumulated in the SML and which have also been detected in cloud water and in aerosol particles over the Arctic Ocean (Orellana et al., 2011; Galgani et al., 2016). It was concluded that this gel-like organic matter originating in the SML of open leads between the ice masses of the central Arctic Ocean can account for a substantial fraction of the Arctic summer aerosol (Leck and Bigg, 2005a,b). Such gel-like phytoplankton exudates in SML-derived submicron aerosol particles are hypothesized to eventually become Ice Nucleating Particles (INPs) in the atmosphere and to affect the lifetime, precipitation, and radiation potential of clouds (Wilson et al., 2015). This marine biogenic source of atmospheric ice-nucleating particles is probably most relevant in remote regions, such as at the poles or in the Southern Ocean. A direct coupling between polar ocean biology and cloud formation could have important feed-back implications given that biological processes are sensitive to climate change.

The precise and selective mechanisms by which organic components transfer from the ocean to the atmosphere via the SML are however still poorly understood. Surface activity of the organic constituents is thought to play a key role in the transfer process, by driving strong partitioning of surface-active molecular components to the SML and to the surface of bubble films. The latter of these is an important source of film drop aerosol (Burrows et al., 2014). Schmitt-Kopplin et al. (2012) pointed out that not all compounds are transported to the same extent; rather there is a chemo-selective transfer of natural organic compounds (typically surfactants) from seawater to the atmosphere via bubble bursting. Cochran et al. (2016) recently demonstrated in a laboratory-based study that theoretically-predicted relative coverages of the air-water

interface by surface-active organic molecules predicted their relative contributions to artificially-generated sea spray aerosol. It remains unclear whether organic matter already enriched within the SML or adsorbed to rising bubbles contributes most to primary organic aerosol emissions.

Moreover, it is still unknown whether the organic composition of aerosols reflects short term biological dynamics, such as phytoplankton blooms and viral demise (O'Dowd et al., 2004, 2015), or rather the composition of the bulk dissolved organic matter pool that is rather invariant in time and space (Quinn et al., 2014).

Of particular relevance for climate, due to the potential impacts on cloud formation and properties, is the quantification of primary organic aerosol formation and emission (Navakov and Penner, 1993; O'Dowd et al., 2004; McCoy et al., 2015; Wilson et al., 2015). Methods of SSA parameterization are often based on wind speed normalized to a height of 10 m (u_{10}). However, it has been suggested that more fundamental quantities related to seawater, such as wind stress at the sea surface, seawater temperature, and whitecap fraction might help to improve the parameterization of SSA fluxes (Lewis and Schwartz, 2004; de Leeuw et al., 2011). In this direction, Ovadnevaite et al. (2014) developed a source function including the Reynolds number instead of the wind speed. This approach combines the effects of wind history and wave state along with sea surface temperature and salinity in one parameter. Salter et al. (2015) derived a temperature-dependent sea spray source function and employed it in large-scale models. Recent work indicates that the SML covers the ocean to a significant extent and is relevant over a range of oceanic conditions (Sabbaghzadeh et al., 2017). Following wave breaking, the SML reforms within seconds (Wurl et al., 2011). Furthermore, breaking waves promote the formation of the SML through ascending air bubble plumes and bring molecules and particles back to the surface. However, adequate knowledge of the production mechanisms of SSA and the role of processes in seawater especially in the SML, is lacking. In an artificial bubbling experiment, Frossard et al. (2014) observed that the presence of a thick stable SML might change SSA composition. They speculated that high surfactant concentrations enhance the persistence of bubbles at the sea surface and cause the drainage of more soluble compounds to leave the less soluble compounds enriched on the bubbles. The result is a larger fraction of non-soluble compounds on SSA. While this hypothesis warrants further examination, the inclusion of the SML in SSA parameterizations could be important for devising realistic model parameterizations.

Gantt et al. (2011) proposed a conceptual relationship between the organic mass fraction of SSA and wind speed, which imposes the presence of an air-sea enriched interface such as the SML. Their parameterization highlights the influence of the SML on the oceanic export of organic matter in the direction of a high organic enrichment in SSA at low wind speeds, when the sea surface is strongly enriched in organic material. Under stronger winds, sea spray production is increased but the organic content of SSA is reduced because the enhanced mixing of the SML with bulk water results in a lower enrichment of organic

material in the SML. However, the suitability of chlorophyll-*a* as proxy for biological activity—currently used in modeling the organic aerosol matter—is under debate, as it may not ideally reflect the surface ocean's organic carbon pool, and may therefore not represent the portion relevant for microlayer exchange processes (Sabbaghzadeh et al., 2017). Other studies have found high enrichments in organic aerosol to be connected with concentrations of dimethyl sulfide (DMS) (Bates et al., 2012) or heterotrophic bacteria (Prather et al., 2013). DMS is an indicator of oxidative stress and phytoplankton cell lysis (Wolfe and Steinke, 1996). The correlation between DMS and SSA organics suggests that the organics derive from cell exudate related to phytoplankton cell lysis (Bates et al., 2012). First attempts to introduce a novel framework for parameterizing the organic fraction in sea-spray aerosol were based on a competitive Langmuir adsorption equilibrium at bubble surfaces rather than chlorophyll-*a* abundance (Burrows et al., 2014, 2016). This new modeling approach links a global marine biogeochemistry model with aerosol chemical composition, incorporating the SML as an enriching interface. There remain even more basic questions about how the physical characteristics and chemical composition of marine aerosol particles may affect solar radiation transfer and cloud processes (de Leeuw et al., 2011; Gantt and Meskhidze, 2013; McCoy et al., 2015).

An improved comprehension of biogeochemical processes at the ocean surface, in particular those involving the SML as an important and determining interface, will make a crucial contribution to the reduction of uncertainties inherent in predicting aerosol-climate feedbacks. Ultimately, a greater understanding of SML processes and the relevance of marine aerosols for the climate system will greatly improve our understanding of the wider Earth system.

WHAT IS NEEDED TO STUDY THE AIR-SEA INTERFACE?

The several open questions addressed in this review demonstrate the strong interdependence of diverse biological (e.g., production, alteration, and decomposition of organic matter), chemical (e.g., photochemistry), and physical (e.g., coagulation, transport efficiencies) processes in the SML. A better understanding of the interactions and feedbacks between these processes is a necessary first step toward a more comprehensive understanding of the ocean/atmosphere interface. This also must implicate a better understanding of the temporal (from diurnal to seasonal) and spatial (from local heterogeneity to different oceanic regions) variability affecting the rates and composition of primary aerosols as well as the air-sea exchange of gases. To establish consistent links between biological diversity, the production and fate of organic matter, wave dynamics, bubble intrusion, the generation and dissipation of turbulence, gas exchange, and the emission of primary aerosols demands a truly interdisciplinary research approach. This in turn imposes new challenges in terms of comprehending the interdependencies between physical, chemical, and biological processes on the nano- and microscale.

Representatively sampling the air-sea interface is still one of the largest practical challenges to SML-related studies (Figure 3). For example, it is currently not possible to routinely resolve layering within the SML under ambient conditions and to separate the thin film effects of a surface nanolayer (i.e., the uppermost molecular layer directly at the air-water interface) from overall SML effects (Figure 1). The nano- and underlying sublayers concentrate organic and inorganic compounds as well as microorganisms beyond their average concentrations commonly found in surface ocean waters, but during sampling the “true” SML concentrations inevitably become diluted by mixing with underlying seawater.

Whereas measurements of the surface tension and surface-pressure isotherms can be taken as a physical measure of static and dynamic thin film characteristics (Bock and Frew, 1993), the underlying chemical composition derived from the analysis of samples collected by standard SML sampling techniques (screen, glass plate, etc., see Cunliffe and Wurl, 2014) is not representative of the uppermost layers. Recently, in an effort to close this critical knowledge gap, non-linear vibrational sum-frequency generation spectroscopy (SFG) was introduced as a surface-selective analytical technique. SFG provides new molecular insights into the structure, chemical composition, and seasonality of surface films (Laß et al., 2010), which will likely help to resolve possible mechanisms of organic enrichment

at the surface (Burrows et al., 2016). Consistent with the current view of a carbohydrate rich SML and the importance of bacterial degradation for surfactant enrichment (Cunliffe et al., 2013; Kurata et al., 2016), first SFG measurements revealed dense natural surfactant nanolayers with lipid-like compounds predominantly stemming from the soluble surfactant pool (Laß and Friedrichs, 2011) and a seasonal trend that was not directly related to phytoplankton abundance (Laß et al., 2013). Yet another SFG study supported the need for additional chemical interaction terms in process models developed for understanding the organic content of SSA. These extra terms are needed to account for the interaction between soluble monosaccharides and insoluble lipid surfactant monolayers (Burrows et al., 2016).

Current sampling methods, e.g., with screens or glass plates (Cunliffe and Wurl, 2014) do not permit any meaningful sampling of gases from the SML. A variety of climate relevant gases such as CO₂, NO, and halocarbons are produced or consumed in the SML (Bakker et al., 2014; Liss et al., 2014; Carpenter and Nightingale, 2015). Determining gas fluxes under *in situ* conditions therefore requires new sampling approaches.

Furthermore, physical, chemical and biological processes in the SML show strong mutual dependency, extensive dynamics and a strong selectivity with respect to other bulk ocean characteristics. The intimate contact of organic and inorganic compounds facilitates unusual chemical reactions, in particular

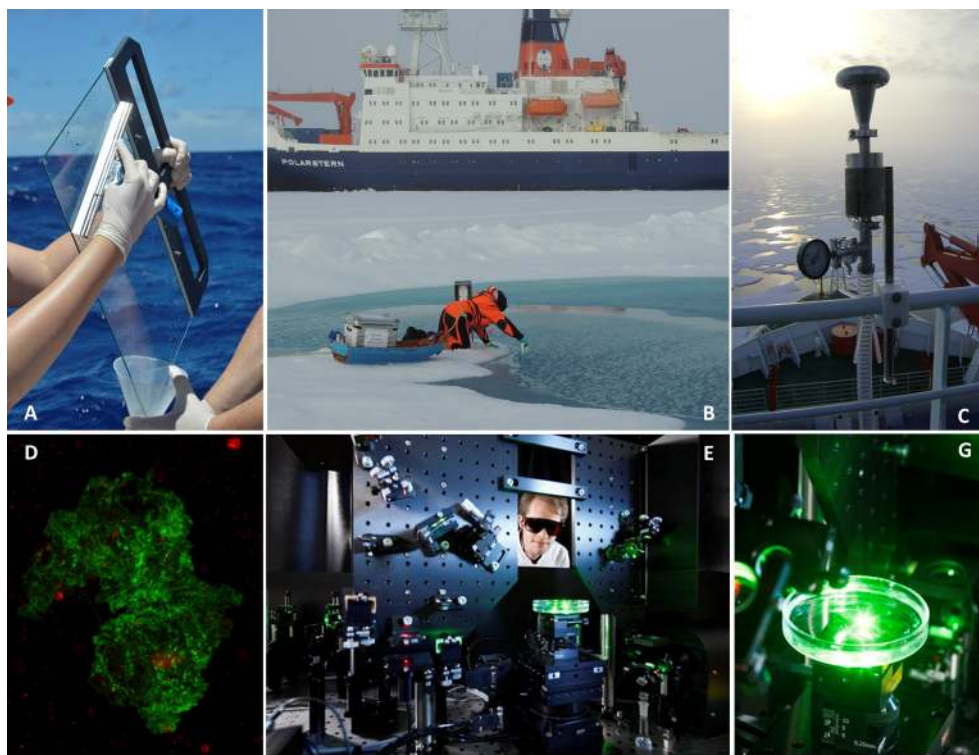


FIGURE 3 | Material accumulating in the SML can be sampled with a glass plate from the ocean (A) and melt ponds (B), or by using an aerosol collector (C). Advanced analysis of organic components in the SML, such as gel particles colonized by bacteria (D), reveal structural properties of the gelatinous SML matrix and nanolayer, which has been studied by new methods such as sum frequency generation spectroscopy (SFG) (E,G). Photos by: M. van Pinxteren, A. Stecher, L. Galgani, B. Zäncker, R. Frommann/Future Ocean. Written, informed consent has been obtained for the publication of images showing individuals.

under conditions of sunlight exposure (Blough, 1997). Here, metal-catalyzed redox reactions and photochemistry prevail. Again, this implies the need for improved sampling strategies as well as thorough characterization, for both *in vitro* and *in situ* observation.

Another major challenge is the intrinsic chemical and biological complexity of the SML. To date, a large fraction of the organic matter in the SML and in derived aerosol particles remains unidentified at the molecular level. The presence of e.g., organic amino compounds and carbonyl compounds in marine aerosol particles and in the SML clearly demonstrates the link between the ocean and the atmosphere, but individual compound analysis can only explain a minor part of the total organic matter pool (van Pinxteren et al., 2012; van Pinxteren and Herrmann, 2013). Revealing the molecular complexity of marine organic matter, as well as explaining how organisms, chemical reactions and physical processes affect organic matter composition and size distribution, may be the key to better describe processes in the SML, and to improve computations of the sources and sinks of organic aerosols in ocean-atmosphere models.

Extrapolating the variability in SML properties across ocean basins from coastal waters to oligotrophic gyres is another substantial challenge and may still be some way off. While satellite-based estimates of global gas transfer velocities in water (k_w) using the distributions of surfactant proxies such as chlorophyll-*a* have been developed (e.g., Liu et al., 2000; Lin et al., 2002; Tsai and Liu, 2003), a universal relationship linking chlorophyll-*a*, total surfactant, and k_w remains both unproven and unlikely (Upstill-Goddard, 2006; Sabbaghzadeh et al., 2017). New observational approaches and new experimental techniques to study gas-exchange in natural, un-amended seawater (e.g., Schneider-Zapp et al., 2014; Pereira et al., 2016) will be required to further resolve this issue. Such approaches will need to address contrasting biogeochemical, seasonal and turbulence regimes.

Models can be applied as tools for assessing those uncertainties that relate to effects of the SML on air-sea exchange processes. The exchange of gases between phases depends on both the solubility-corrected concentration difference between the ocean and atmosphere and on k_w , which controls the kinetics of gas exchange (Liss and Slater, 1974; Johnson, 2010). A microlayer, whether it be a surface monolayer or a slick, can affect both of these properties: (i) through modifying dissolved gas concentrations (e.g., by enrichment of SML related production); (ii) by modifying solubility via differences in temperature, salinity or the organic matrix between surface and bulk waters; and (iii) by modifying k_w as described above (Johnson et al., 2011). Furthermore, the chemical and/or biological alteration of concentration gradients through the mass boundary layer at a rate sufficient to modify the apparent value of k_w is likely to be enhanced by a biologically and chemically enriched, irradiated surface layer (e.g., Beale et al., 2014; Yang et al., 2014).

To date only a few modeling studies have explicitly resolved the interfacial transfer of mass (including gas) through the SML. Cen-Lin and Tzung-May (2013) proposed a dynamic three-layer model of gas transfer that considers a SML in which microbial activity and photochemical reactions can modify concentrations. Their model was applied to determine the

exchange of acetone in the Pacific, which demonstrated that the characteristics of the SML can explain significant discrepancies between observed fluxes and those predicted by a simple gas exchange model without any SML effect. Similarly, Yang et al. (2014) applied a simple chemical enhancement model to account for discrepancies between the predicted and observed fluxes of acetaldehyde in the Atlantic (although they did not explicitly consider the effect of a discontinuous microlayer). Such models currently have severe limitations in predictive skill, mainly due to uncertainties with respect to the underlying complexity of parameterisations and the associated quantification of credible parameter values. Nevertheless, by providing insight into the micro- and nano-scale processes that are unresolved by current measurement approaches, they are likely to prove an essential tool in the interpretation and integration of field, mesocosm, and laboratory measurements of air-sea gas exchange in the presence of surface films.

NEW RESEARCH PRIORITIES AND STRATEGIES FOR THEIR IMPLEMENTATION

It is clear from this review that the fundamental role of the SML in the interactions of the surface ocean with the lower atmosphere requires a critical reassessment. The exchange of momentum, energy (heat), and mass (gases and particles) across the ocean/atmosphere interface interacts with the physical structure, chemical composition and reactivity, and the biology of both the surface ocean and the lower atmosphere. Processes within the SML and exchange across its upper and lower boundaries impact the Earth's climate. Conversely, global environmental change, (warming, acidification, eutrophication, pollution) modifies SML processes and thereby alters the conditions of the upper ocean and lower atmosphere, with largely unknown consequences for the Earth system. It is important to note that these surface ocean/lower atmosphere feedback processes operate across a wide range of spatial and temporal scales, from molecular to global and from millisecond to decadal. Thus, an overarching goal of future SML research should be to develop a standard model of the SML that includes all relevant physical, chemical, and biological processes necessary to understand the role of the SML in the Earth system.

Priority research tasks in this context include:

- (1) To identify and quantify the physical processes driving the dynamics of the SML and across the ocean/atmosphere interface;
- (2) To characterize and quantify the chemical and biological composition of the SML, including organic compounds, microorganisms, gases, metals, and anthropogenic pollutants;
- (3) To identify and quantify the biological (e.g., microbial) and chemical processes that transform the chemical and biological composition of the SML;
- (4) To understand the role of organisms in the SML in influencing SML characteristics as well as exchange processes;

- (5) To significantly improve model approaches for computing gas exchange across the ocean/atmosphere interface;
- (6) To investigate the role of physical processes and SML composition for atmospheric aerosol formation;
- (7) To develop remote sensors and remote sensing algorithms to facilitate the measurement of (natural and anthropogenic) global-scale surfactant distributions and exchange processes with high temporal resolution;
- (8) To identify, quantify, and predict SML/global change feedbacks.

Investigation of the SML remains especially challenging because of its limited accessibility and the patchiness of the processes that take place within it. Its future study will require representative and standardized sampling (see e.g., Cunliffe and Wurl, 2014), the development of new analytical methods (e.g., *in-situ* SML measurements), and new observational and experimental frameworks (e.g., SML tracer studies). The objective of these should be to facilitate fully representative parameterizations of SML processes in numerical models. Moreover, micro-meteorological/oceanographic modelers should strive toward developing a model of the SML that is able to predict the water depth at which key SML properties change. This will allow us to begin to move away from the current (and mostly inadequate) techniques for SML sampling.

To this end it is evident that only multidisciplinary research initiatives, at both national and international levels, can effectively address the several open questions identified in this review. Joint projects should link laboratory, field, model and remote sensing approaches to better understand the complex interplay of the various physical, biological, and chemical processes operating in the SML and across the ocean/atmosphere interface. Furthermore, we should make use of expertise across transdisciplinary sectors, such as commercial detergents industries and chemical companies.

Following the proposal of Cunliffe et al. (2013), we advocate the establishment of a network of time-series measurements designed to help us better understand both regional variability and long-term trends in the physical structure, chemical composition, and biogeochemical processes of the SML. This could be achieved by augmenting ongoing time-series programmes in the open ocean (e.g., HOT, BATS, CVOO/CVAO, Line P, LTER HAUSGARTEN, and others) and in coastal shelf seas (e.g., Boknis Eck, Helgoland Roads, Saanich Inlet, Western Channel Observatory, Time Series site off Conception, CaTS, and others) with the appropriate instrumentation for SML study. Such an approach is critical for understanding the effects on the SML of seasonal events such as phytoplankton blooms, dry/wet deposition and storms in a range of ocean regions. In addition, time-series measurements in remote ocean regions

where minimal anthropogenic influence might reasonably be expected, such as in the Arctic and Southern Oceans, should be established as reference measurements.

Complementary to (ship-borne) field measurements, remote sensing and modeling efforts, joint wind/wave tank studies simulating the role of the SML in air/sea gas exchange and aerosol formation under controlled (including extreme, e.g., high wind speed) conditions should be conducted. The use of unmanned drones operated from research vessels or land stations also represents an exciting opportunity for future SML research.

National and international collaboration will be an integral aspect of the envisioned multidisciplinary SML studies. An improved understanding of the SML will contribute to our appreciation of the crucial role of the ocean/atmosphere interface in societal-relevant issues such as climate change, ocean acidification, air quality (pollution), and the overall health of the ocean. SML research should be a continuing long-term focus of international research initiatives such as SOLAS (Surface Ocean—Lower Atmosphere Study: www.solas-int.org) and Future Earth (www.futureearth.org).

AUTHOR CONTRIBUTIONS

All authors listed, have made substantial, direct and intellectual contribution to the work, and approved it for publication.

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