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Atmospheric Implications of Ocean-Atmosphere Physicochemical Interactions

Yiqun Wang[1]*, Sasho Gligorovski[2]*

[1]State Key Laboratory of Advanced Environmental Technology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[2]Department of Environmental Science and Engineering, Guangdong Technion - Israel Institute of Technology, 241 Daxue Road, Shantou, 515063, China

Correspondence to:
wangyiqun@gig.ac.cn
gligorovski@gig.ac.cn

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ABSTRACT.

The atmosphere is the fast component of the climate which determines the meteorology i.e. every day's whether. Ocean, on the other hand, is the slow component which regulates the climate on the long term. A detailed knowledge of the interactions between these two components is crucial in order to understand the global climate phenomena. The ocean-atmosphere interface is the largest one on our planet occupying about 70% of the Earth's surface. Hence, the physicochemical processes occurring at the interface can largely affect the chemical content of the Ocean waters and the composition of the atmosphere.

Here, we briefly discuss the chemical composition of the sea surface microlayer (SML), emphasizing the role of surface-active compounds concentrated in the SML that influence gas exchange and modulate the production of the largest natural primary aerosols (e.g., sea spray aerosols, SSA) across the ocean-atmosphere interface. We summarize recent research focused on multiphase and heterogeneous chemical processes, including photochemical reactions within the SML, and their impact on the formation of volatile organic compounds (VOCs), as well as subsequent effects on secondary organic aerosol (SOA) production.

Comprehensive understanding of the ocean-atmosphere physicochemical interactions is of paramount importance in order to properly address air quality and climate issues.

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INTRODUCTION.

Oceans cover approximately 71% (3.62×10^8 km^2) of Earth's total surface area. Lakes account for about 3% of the land surface(Messager et al., 2016), while rivers and streams make up roughly 0.58 ± 0.06% ($77.3 \pm 7.9 \times 10^4$ km^2) of the nonglacial land surface(Allen and Pavelsky, 2018). During interactions between the air and water systems, substances (gases, particulate matter, precipitation) and energy (light, heat) must cross the air-water interface for transfer and exchange. Consequently, the physicochemical properties of this interface significantly influence the interactions, composition, and processes occurring between the two phases.

Since the 18th century, oceans has absorbed 20-40% of anthropogenic carbon dioxide (CO_2) emissions (Pereira et al., 2018) and contributed about 50% of global oxygen (O_2) production. From an atmospheric perspective, oceans regulates the budget of greenhouse gases (CO_2, N_2O, CH_4, CH_3SCH_3)(Schneider-Zapp et al., 2014), while also serving as a source of many atmospheric trace species, such as aromatic hydrocarbons (Wohl et al., 2023; Rocco et al., 2021), non-methane hydrocarbons, aldehydes and ketones(Phillips et al., 2021), and other important compounds(Yang et al., 2014a; Yang et al., 2014b). Thus, the physical, chemical and biological processes at the ocean surface significantly influence the Earth's carbon cycle and atmospheric climate dynamics.

The CLAW hypothesis, proposed in 1987(Charlson et al., 1987), suggests that dimethyl sulfide (DMS) emissions from marine phytoplankton promote the formation of atmospheric aerosol particles and cloud condensation nuclei. This process increases cloud albedo, which in turn alters temperature and radiation, creating a feedback loop that affects DMS emissions from phytoplankton and ultimately forms a closed bioclimatic system(Charlson et al., 1987). Although this hypothesis is not entirely valid(Quinn and Bates, 2011; Woodhouse et al., 2008), it highlights the significant impact of ocean-atmosphere interactions on climate. Understanding energy and material transfer fluxes between atmospheric and aquatic systems, as well as key control processes such as biogeochemical and physical interactions and feedback mechanisms, is essential for comprehending how these coupled systems influence Earth's climate. Recent attention has focused on the physicochemical processes occurring at the atmosphere-ocean interface(Donaldson and George, 2012; Carpenter and Nightingale, 2015; Brooks and Thornton, 2018; Novak and Bertram, 2020). This area includes a thin layer of water, ranging from tens to hundreds of micrometers, known as the surface microlayer (SML).

SML is widely distributed at the ocean surface(Knulst et al., 2003), and other water bodies (e.g. lake, river and stream). It can be subdivided into slick and non-slick SML(Wurl et al., 2016), or even thinner layers, referred to as the surface nanolayer(Laβ et al., 2010). Owing to the inherent heterogeneity, a large variety of surface-active organic and inorganic substances accumulated in SML due to their interface affinities. Surface-active organics (surfactants) can also attract other more soluble organic compounds (e.g. saccharides) to the surface, leading to so-called "co-adsorption" effect (Burrows et al., 2016; Carter-Fenk et al., 2021). The elevated concentration of these active substances establishes a unique biological, physical, and chemical milieu in contrast to the underlying water layers.

This distinctive environment facilitates the formation of peptide bonds(Griffith and Vaida, 2012), substantially reducing the physical volatility of the SML, thereby promoting dominant molecular diffusion and resulting in pronounced gradients in heat, pH, and gas concentration. Additionally, it facilitates the breakdown of energy barriers associated with chemical reactions and accelerates substance transformations. As a result, the SML forms the largest active interface on the Earth(Donaldson, 2006).

The SML is globally distributed and can remain stable at wind speeds up to 13m s^{-1}(Sabbaghzadeh et al., 2017), and if disrupted, it regenerates quickly. Despite its thinness compared to the underlying water layer, its dynamic changes have a significant impact on global biogeochemical processes, including momentum and heat transfer, air-sea exchange, and aerosol production. SML is continually consumed and replenished by biogeochemical and physical processes, maintaining a dynamic equilibrium. Supply mechanisms include atmospheric deposition and physical transport from the subsurface water column. Wind-driven convergence circulation, tidal forces, ocean shear, upwelling, and internal waves lead to localized concentrations of surface-active substances across various spatial scales(Frka et al., 2012). Removal processes involve direct injection of enriched substances into the atmosphere following the bubble bursting, and the chemical transformation of dissolved organic matter (DOM) upon light irradiation, or by the interface oxidation processes, resulting in production of aerosols into the atmosphere. Hence, the SML holds substantial atmospheric significance. Its composition and biogeochemical transformation processes not only influence the input flux of non-biological source volatile organic compounds (VOCs) and aerosol particles (i.e. Sea Spray Aerosol, SSA) to the atmosphere, but also regulate the deposition rate of trace gases on ocean surface. Studies on the SML are crucial for understanding interactions between ocean aerosols and clouds, representing a significant area of focus in marine atmospheric chemistry. The ultimate goal is to uncover the driving forces and mechanisms behind climate change.

Currently, there is a foundational understanding of the role of SML in ocean aerosol-cloud interactions. This review aims to revisit scientific progress concerning environmental and climate issues associated with the SML from an atmospheric chemistry perspective. Specifically, it addresses advances in research on how physical and chemical processes at the ocean surface impact the atmosphere.

1. AIR-WATER INTERFACE.

The attention to the air-water interface began in the early 20th century with a series of studies on the surface tension of electrolyte solutions. At the time, a major obstacle was the absence of direct interfacial detection techniques, which restricted characterization of the interface to macroscopic experimental approaches, such as surface tension and electrostatic potential measurements(Petersen and Saykally, 2006). Consequently, theoretical models were employed to interpret experimental data and indirectly infer the behavior of inorganic ions at the interface. However, without calculations based on the atomic level, theoretical issues at the molecular level are difficult to address accurately(Jungwirth and Tobias, 2006).

Recent advances in computational capabilities and research methodologies have enabled the use of advanced surface-resolving techniques such as sum-frequency generation(Gordon et al., 2019; Seki et al., 2023), second harmonic generation, X-ray photoelectron spectroscopy(Kong et al., 2021), and molecular dynamics simulations(Petersen and Saykally, 2006). These advancements enable a more in-depth and direct exploration of the structure of the air-water interface and the specific behavior of ions at this interface in both theoretical and experimental domains. This progress has led to a paradigm shift, challenging traditional beliefs about ion behavior: certain ions are now understood to accumulate at the air-water interface(Jungwirth and Tobias, 2006). This propensity is associated with ion valence, polarity, and interactions with water molecules. Moreover, advances in technology have challenged some traditional viewpoints. For instance, recent studies using stimulated Raman three-dimensional imaging techniques have revealed the enrichment of HSO_4^{2-} ions on the surface of aerosol liquid films(Gong et al., 2023). These findings indicate a gradient change in the pH of deliquescent aerosol liquid films, suggesting that the method of using uniform aqueous solutions to simulate homogenous chemical processes in real aerosol liquid films may not replicate the actual chemical environment accurately. In addition to inorganic salt ions, organic molecules also exhibit a tendency to accumulate at the air-water interface(Rossignol et al., 2016) and interact with water molecules upon contact (polarization, solvation), storing at high concentrations at the air-water interface, lowering the activation energy of reactions; thus, altering the reactivity of chemical reactions, including changes in reaction rates and product yields, and even reaction pathways. This propensity of substances to accumulate at the air-water interface is one of the key reasons why this boundary has garnered significant scientific attention.

In addition to the substance propensity at the air-water interface, the structure, composition, and behavior of water molecules at the air-water interface differ from those in the bulk phase. Petersen et al. (2004) used the Multistate Empirical Valence Bond (MS-EVB) method to predict the presence of excess protons (H_3O^+) at the air-water interface(Petersen et al., 2004). However, it has been shown that the presence of excess charged water molecules with an odd number of hydrogen bonds at the water interface, indicating an excess negative charge on the surface(Ben-Amotz, 2022). Measurements of the electrophoretic mobility of oil droplets and bubbles in water also indicate a negatively charged interface. The simplest explanation for this phenomenon is the enrichment of hydroxide ions (OH^-) at the interface and the electrostatic repulsion of hydrated hydronium ions (H_3O^+). However, this explanation is inconsistent with some experimental results, such as second harmonic generation and sum-frequency generation techniques, which indicate the presence of excess H_3O^+ at the gas-liquid interface(Petersen and Saykally, 2005). Molecular dynamics models and continuous solvent models have also shown that H_3O^+ is more inclined to the gas-liquid interface compared to OH^-. The pH of the liquid surface may differ from that of the bulk phase, not only because of the sign of the liquid surface's electric field, but also due to the preference of OH^- or H_3O^+ for the gas-liquid interface. Therefore, there is controversy regarding the acidity of water interface(Saykally, 2013), as some research results indicate that the water surface is acidic (pH < 4.8)(Buch et al., 2007; Mamatkulov et al., 2017), while others indicate it is alkaline(Beattie et al., 2009; Mishra et al., 2012). These differences in research results may be caused by differences in experimental methods used. Although many research results are contradictory at present, there is undoubtedly a close relationship between hydrogen bonds, charge transfer, and the formation of the air-water interface charge layer, which objectively leads to an imbalance of positive and negative ions at the water interface(Hao et al., 2022; Ben-Amotz, 2022), thereby affecting the pH of the near-surface region, and consequently affecting the chemical processes at the air-water interface. It has been reported that not only that some chemical reactions occurring at the air-water interface are accelerated

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(see section 1.2), but also that spontaneous chemical processes occur at the air-water interface (section 1.3)(Lee et al., 2019b; Li et al., 2023), suggesting that the electric field existing at the air-water interface is the driving force behind spontaneous chemical processes. Some studies have observed a strong electric field at the oil-water interface of microdroplets using Raman-excited fluorescence microscopy, suggesting that this strong electric field may be caused by charge separation due to adsorbed negative ions on the surface(Xiong et al., 2020). Recently, Liu et al. (2024) detected a strong electric field at the gas-liquid interface of deliquescent nitrate aerosol microdroplets using surface-enhanced micro-Raman spectroscopy and molecular dynamics simulations (Liu et al., 2024), but the driving force behind this electric field remains to be answered.

1.1 Enrichment and depletion behavior of ions and their impact on chemical processes at the air-water interface.

Interest in the air-water interface was rekindled with advancements in studying halogen transformations in sea salt aerosols. Researchers realized that ion behavior at this interface may deviate from prior assumptions, particularly as some inorganic ions tend to concentrate there. Surface-exposed ions can boost gas reactivity at the interface, influencing key processes like gas absorption, halogen chemistry, and ozone (O_3) depletion (George et al., 2015).

Hu et al. (1995) examined $Cl_{2(g)}$ and $Br_{2(g)}$ uptake by sodium chloride (NaCl) and iodine chloride (ICl) aerosols (120-250 μm in diameter). Their findings showed that bulk-phase reactions alone could not account for the observed absorption levels or its dependence on ion concentrations. They thus concluded that reactions at the air-water interface played a crucial role in the uptake process(Hu et al., 1995). Knipping et al. (2000) investigated the photochemical formation of $Cl_{2(g)}$ on deliquescent NaCl aerosols under UV light (λ=254 nm) and O_3 conditions, using experiments, molecular dynamics, and kinetic models(Knipping et al., 2000). They concluded that air-water interfacial reactions were essential to explain their observations. Additionally, molecular dynamics simulations revealed that Cl^- enrichment at the surface of NaCl aerosols enhanced interfacial chemical processes(Knipping et al., 2000). Field observation data indicate that detected halogen molecules ($Cl_{2(g)}$, $Br_{2(g)}$, $BrCl_{(g)}$) in the marine atmosphere are correlated with O_3 depletion(Spicer et al., 1998; Spicer et al., 2002; Foster et al., 2001). Behnke et al. (1995) discovered that in the presence of O_3, simulated sunlight irradiation of sea salt aerosols produces an unidentified chlorine atom precursor(Behnke et al., 1995). Subsequent laboratory studies demonstrated that in the presence of O_3 and under light irradiation (λ=254 nm), deliquescent sea salt particles produce gaseous chlorine molecules, a process that may also occur on the ocean surface(Oum et al., 1998). Laboratory research by Laskin et al. (2003) showed that $OH_{(g)}$ radicals react with Cl^- on the surface of deliquescent NaCl aerosols to form sodium hydroxide (NaOH), increasing the alkalinity of sea salt particles and thereby enhancing the uptake of sulfur dioxide (SO_2) and the formation of sulfates(Laskin et al., 2003). These studies indicate that inorganic ions enriched at the air-water interface of sea salt aerosols can profoundly impact the composition and oxidation capacity of the marine atmosphere. Since inorganic salt ions are key components of atmospheric aerosols and ocean surfaces, many studies have shown that, in addition to halogen ions directly participating in atmospheric chemical processes, the surface propensity of inorganic salt ions causes ionic strength effects that profoundly modulate multiphase reactions at the air-water interface. These processes include sulfate formation(Yu et al., 2023), O_3 uptakes(Mekic et al., 2018b; Mekic et al., 2020a; Mekic and Gligorovski, 2021), generation and transformation of atmospheric pollutants including secondary organic aerosol (SOA)(Mekic et al., 2018a; Zhou et al., 2019; Mekic et al., 2020c; Mekic et al., 2020a; Wang et al., 2021; Gwendal Loisel, 2021; Pratap et al., 2021; Li et al., 2022). Although many studies have made efforts and achieved some results on this topic, most of the studies have focused on single-salt systems. A recent study investigated the interaction between ions for air-water interface propensity(Seki et al., 2023). Considering the complexity of the real atmospheric environment, extrapolating laboratory data to the atmospheric environment for evaluating environmental and climatic impacts still requires substantial effort.

1.2 Accelerated chemistry at air-water interface.

Many experimental and theoretical studies indicate that, compared to homogeneous environments, water interface can significantly accelerate the reaction rates of certain chemical processes(Kusaka et al., 2021; Narayan et al., 2005; Klijn and Engberts, 2005;

Kong and Evanseck, 2000), such as photochemistry(Kusaka et al., 2021; Gong et al., 2022), photodecomposition(Rao et al., 2023b), photosensitized reactions(Wang et al., 2024), spontaneous redox reactions(Lee et al., 2019a; Kong et al., 2021), and gas-gas reactions at the air-water interface(Liu and Abbatt, 2021).

Research into faster chemical reactions at the air-water interface draws inspiration from organic chemistry studies. Organic chemists typically avoid using water as a solvent because it can react with organic compounds, and its polarity makes it unsuitable for dissolving most nonpolar organics. As a result, aqueous solvents are generally seen as ineffective for organic reactions(Klijn and Engberts, 2005). Early studies found that some pericyclic reactions of hydrophobic organic compounds, such as the Diels-Alder cycloaddition(Breslow, 1991) and Claisen rearrangement(Gajewski, 1997), proceed faster in dilute aqueous solutions than in organic solvents or pure substances. Their acceleration may be due to the hydrophobic effect(Tian et al., 2024), which polarizes the transition state structure formed between the reactants, thus lowering the activation energy. Other factors include enhanced hydrogen bonding in the transition state, increased water cohesive energy density, and a stronger hydrophobic effect(Jung and Marcus, 2007; Kong and Evanseck, 2000; Breslow, 1991). In 2005, Barry Sharpless's group reported that the reaction rates of hydrophobic organic reactants dramatically increased under emulsion conditions (formed by rapidly stirring water-insoluble organics with water) compared to homogeneous or pure solute conditions. They concluded both the heterogeneity and the presence of the water interface played key roles in reaction acceleration(Narayan et al., 2005; Klijn and Engberts, 2005). Despite these findings, the exact mechanism for this acceleration remains elusive. One theory suggests that about one-quarter of the OH groups of water molecules at the interface are free (unbound by hydrogen bonds). These free OH groups "extend" into the organic phase at the interface, forming hydrogen bonds with reactants in the organic phase. The transition state between the reactants is stabilized by these stronger hydrogen bonds with free OH groups, thus dramatically speeding up reactions at the "oil-water interface"(Jung and Marcus, 2007). Recent research demonstrated that photochemical reactions at the oil-water interface can be accelerated through melting point depression(Tian et al., 2024). Further, Lixue et al. (2025) combined Raman spectroscopy and multivariate curve resolution to suggest that water structural disorder and enhanced electric fields at mesoscale interfaces in oil-water emulsions may contribute to accelerated chemical reactivity(Shi et al., 2025). Similar to the "oil-water interface", some gas molecules also exhibit faster reaction rates at the air-water interface. Typically, reactions of neutral closed-shell molecules in the gas phase, while thermodynamically feasible, are slow due to high reaction barriers. In contrast, the reaction rates of the same reactants (or appropriately modified forms in the condensed phase) in multiphase environments can exceed those in the gas phase. This acceleration stems from either reduced activation energy or higher reactant concentration in the condensed phase. The formation of acid rain is a key example. The reaction between $SO_{2(g)}$ and hydrogen peroxide ($H_2O_{2(g)}$) is inefficient in the gas phase but efficient in the liquid phase. This is because the concentration of H_2O_2 in the atmospheric waters ($H_2O_{2(aq)}$) is relatively high compared to $H_2O_{2(g)}$. Moreover, once $SO_{2(g)}$ dissolves in water and hydrolyzes to form HSO_3^-, the reaction between $H_2O_{2(aq)}$ and HSO_3^- is highly efficient.

While previous studies have documented reaction acceleration at water interfaces and proposed mechanisms like OH group interactions with organics, other factors may also play a role. These potential contributors include reactant confinement, partial solvation, preferential orientation, droplet curvature, and surface pH variations. Despite these insights, the exact reasons for the acceleration of reactions at the water surface remain inconclusive(Ruiz-Lopez et al., 2020).

1.3 Spontaneous chemistry at air-water interface.

The thermodynamics and kinetics of many chemical reactions at interfaces differ from those in the bulk phase due to the heterogeneity of the medium at or near the interface(Zhong et al., 2019; Ruiz-Lopez et al., 2020; Kusaka et al., 2021; Wei et al., 2020). At the air-water interface, the surrounding water exerts asymmetric molecular interactions on the observed water molecules and solutes. The density of interfacial water is lower than that of bulk water, and its density fluctuations generate macroscopic capillary waves, surface roughness, and tension. These factors result in differences in surface molecular dynamics, orientation, hydrogen-bond networks, and dielectric properties compared to the bulk phase(Deal et al., 2021). When ions or surfactants adsorb at the air-water interface, they alter surface tension and surface potential, ultimately changing interfacial chemical processes(Jungwirth and Tobias, 2006; Otten et al., 2012). Recent studies report that tiny droplets (diameter 1-20 μm) spontaneously produce hydrogen peroxide on their surface, with production inversely correlated to droplet diameter. It is suggested that H_2O_2 forms from the combination of OH radicals generated from OH^- at the droplet surface under the influence of an electric field(Lee et al., 2019b; Lee et al., 2020). This study has garnered significant attention because, thermodynamically, a pure water environment is unfavorable for H_2O_2 formation. Therefore, the study faces skepticism due to issues of reproducibility, potential contamination, and lack of a reasonable mechanistic explanation(Nguyen et al., 2023). Nevertheless, because the air-water interface is ubiquitous in the atmosphere, this spontaneous chemical process has attracted considerable attention from researchers. Following this study, a series of investigations into spontaneous chemical processes at the air-water interface have emerged. Examples include the spontaneous generation of OH radicals at the air-water interface in dark conditions(Li et al., 2023), the spontaneous conversion of I^- to I and I_2 at the air-water interface(Guo et al., 2023), mechanistic and quantitative studies of different inorganic salt ions on the spontaneous generation of H_2O_2 at the air-water interface(Angelaki et al., 2024), and the spontaneous oxidation of thiols and thioethers at the air-water interface of sea spray droplets(Rao et al., 2023a).

1.4 Molecular dynamics simulation of chemical processes at the air-water interface and their influence on the atmosphere.

Due to the rapid reactions of some atmospheric species at the air-water interface, such as Criegee intermediates and SO_3, it is difficult for existing experimental methods to capture their chemical reaction processes. Therefore, complementing experimental techniques, molecular dynamics simulations (such as Born-Oppenheimer molecular dynamics simulations) provide strong support for studying the fast reaction processes (picosecond scale) occurring at the air-water interface, effectively aiding in a deeper understanding of how the air-water interface influences reaction pathways, rates, and mechanisms at the molecular level(Zhong et al., 2018). For example, Born-Oppenheimer molecular dynamics simulations have shown that the rapid heterogeneous process of iodine oxidation on sea salt aerosol surfaces (picosecond scale) promotes aerosol growth(Ning et al., 2023).

In recent years, Francisco's research group(Anglada et al., 2014; Martins-Costa et al., 2019, 2018; Martins-Costa et al., 2012b; Anglada et al., 2020a) has used quantum mechanics/molecular mechanics molecular dynamics (QM/MM-MD) simulations to propose that many important atmospheric species such as O_3, H_2O_2, methylhydroperoxide, nitrogen dioxide (NO_2), and HO_2 radicals exhibit specific behaviors at the air-water interface, accelerating photodissociation rates, which may consequently impact the physicochemical characteristics of aerosols and the atmospheric environment. These species tend to accumulate at the air-water interface, leading to an increase in interface concentration, thus influencing interfacial chemical processes(Anglada et al., 2020b; Martins-Costa et al., 2012b). Simulation studies have found that the absorption band of O_3 accumulated at the air-water interface undergoes a red shift and broadening compared to that in the gas phase, leading to an order of magnitude faster photodissociation rate of O_3 at the interface than in the gas phase, resulting in a four-order-of-magnitude increase in the rate of OH radical generation at the interface(Anglada et al., 2014). Additionally, methylhydroperoxide in the air-water interface exhibits a blue shift and broadening in its UV-visible absorption spectrum, which is attributed to hydrogen bonding between methylhydroperoxide and water molecules(Martins-Costa et al., 2017). Similarly, NO_2 also exhibits accumulation behavior at the air-water interface, with broadening of its absorption band, leading to an increase in its photodissociation rate at the interface(Murdachaew et al., 2013; Martins-Costa et al., 2019). Intriguingly, the excited triplet state of SO_2 ($^3SO_2$*) produced under sunlight irradiation can react with water molecules leading to the formation of OH radicals and hydroxysulfinyl radical (HOSO) which is further converted to SO_2^- and then by oxidation-reduction process to sulfate (SO_4^{2-}) (Figure 1)(Ruiz-López et al., 2019).

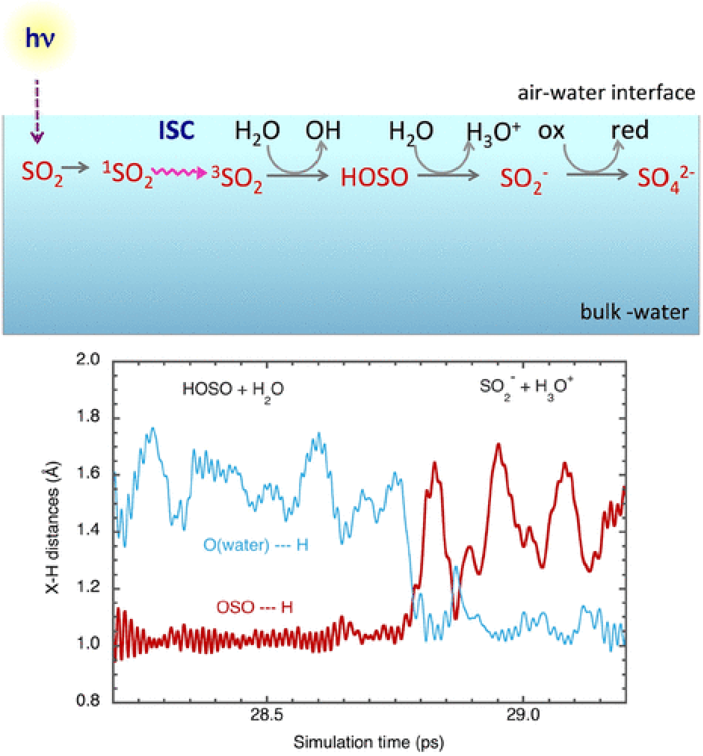

Figure 1. Light-induced oxidation of SO_2 is transformed to its excited triplet state ($^3SO_2$*) which further promotes photosensitized chemistry leading to the production of OH and HOSO radicals and sulfate(Anglada et al., 2020b).

The importance of the formed HOSO arises from the fact that is very acidic (pKa = −1) and undergoes fast ionic dissociation at the air-water interface. In addition, the formed SO_2^- ions can be further oxidized by H_2O_2, O_3, OH, or HO_2 to generate sulfuric acid(Ruiz-López et al., 2019; Anglada et al., 2020a). Furthermore, molecular dynamics simulations have revealed that important atmospheric gases such as N_2, O_2, O_3, OH, H_2O, HO_2, and H_2O_2 tend to accumulate at the water surface with the lowest free energy when located at the air-water interface(Vácha et al., 2004). These findings are significant not only for chemical processes occurring at aerosol surfaces but also for processes occurring at the atmosphere-ocean interface.

Although molecular dynamics theoretical studies have provided insights into how the air-water interface alters the reaction mechanisms of certain atmospheric chemical processes at the molecular level, there are still some unresolved issues. For instance, it is necessary to estimate the concentration scale of chemical processes occurring at the air-water interface to assess the significance of these specific chemical processes. Estimating the energy barriers of reaction pathways occurring at this interface is essential to determine the impact of these processes on atmospheric chemistry. Furthermore, it is essential to assess the influence of more complex compositional conditions, such as different pH values, ionic strengths, gas-liquid contact areas, and the morphology and size of hydrated aerosol particles, on the reactions at this interface.

2. OCEAN-ATMOSPHERE INTERFACE.

The ocean-atmosphere interface represents the largest air-water interface on earth. In recent years, the physicochemical processes at the ocean-atmosphere interface have received widespread attention(Donaldson and George, 2012; Carpenter and Nightingale, 2015; Brooks and Thornton, 2018; Novak and Bertram, 2020). As mentioned in the "Introduction" this region encompasses a thin layer of ocean surface, termed SML. The definition of the SML commonly refers to the uppermost layer of the sea surface, typically spanning 1-1000 µm, as defined by Liss & Duce(Liss and Duce, 1997). Sampling thickness varies with methodologies and research objectives(Cunliffe and Wurl, 2015). Zhang et al. (2003) observed a "sharp change in physicochemical characteristics" at a depth of 50 µm below the ocean-atmosphere interface, proposing a refined SML thickness of 50 ± 10 µm(Zhang et al., 2003b; Zhang et al., 2003a). Despite the thinness, its heterogeneity coupled with the enrichment of surface-active substances, making it pivotal in ocean-atmosphere interactions and playing a crucial role in the exchange of matter and energy between the two phases. Hence, comprehensive knowledge of the SML's characteristics is extremely important to understand the ocean-atmosphere interactions which in turn represents one of the biggest unknowns related to air quality and climate change issues.

The composition, concentration, and enrichment of the SML are variable spatiotemporally. The components mainly come from in situ biological activities, land (river) inputs(Jaffé et al., 2013; Wagner et al., 2015; Park et al., 2019), migration from underlying water column(Gašparović et al., 2007), atmospheric dry and wet deposition(Milinković et al., 2022; Hunter and Liss, 1977), sediments, etc. In general, the SML is enriched with substances such as sugars, amino acids, proteins, lipids, colloids, etc.(Liss and Duce, 1997; Laß et al., 2013; Laß and Friedrichs, 2011). Enrichment Factor (EF) is generally used to represent the degree of enrichment of substances in SML, as follows:

$$EF_{SML} = \frac{C_{SML}}{C_{SSL}} \qquad (Eq-1)$$

In the above equation, C_{SML} represents the concentration of a substance in the surface microlayer, and C_{SSL} represents the concentration of a substance in the corresponding lower layer of water in the surface microlayer. Some EFs of SML relevant for the ocean-atmosphere interactions and implications are shown in Table 1.

Table 1. Enrichment factors of various substances in SML

EF.	Species/property	Ref.
0.9–1.6	Surfactant activity	(Rickard et al., 2022)
1.0–2.3	CDOM	
1.6	DOC	(Ciuraru et al., 2015b)
2	POC	
2.2 ± 1.6	Surface-active substances	(Wurl et al., 2009)
1.5 ± 1.1	Total dissolved carbohydrates	
1.6 ± 0.6	CDOM	
1.7 ± 0.8	TEPs	
1.2-21	Low-molecular-weight carbonyls	(Zhou and Mopper, 1997)
1.9-9.2	Nitrogen containing organic compounds	(Van Pinxteren et al., 2012)
0.7-1.2	Dissolved carbohydrates	
1.2–2.8	Surface active organic substances	(Gašparović et al., 2007)
1.2–2.8	DOC	
1.3-5.1	Copper complexing ligands	
1.65±0.3	DOC	(Reinthaler et al., 2008)
3.7±1.5	DON	
10.5	Dissolved total hydrolysable amino acids	
32.3	Dissolved free amino acids	
6.42	Dissolved combined amino acids	
1.31±0.52	Gel-like transparent exopolymer particles	(Wurl and Holmes, 2008)
1.0±0.3	Total dissolved carbohydrates	
1.4±0.6	DOC	
1.45±0.41	TOC	(Gao et al., 2012)
1.7-7.0	Particulate polysaccharides	
3.5-12.1	HMWDOM polysaccharides	
2.08±0.86	Total dissolved carbohydrates	(Sieburth et al., 1976)

1.42±0.46	Total dissolved carbohydrates	(Henrichs and Williams, 1985)
1.4-7.6	PAHs	(Sakellari et al., 2021)
2-5	Fatty acid lipids, n-alkane and total hydrocarbons	(Marty et al., 1979)
1.0-1.9	Surfactant activity	(Pereira et al., 2016)
Up to~4.5	Surfactant activity	(Sabbaghzadeh et al., 2017)
1.1-6.1	Biological parameters	(Fabien et al., 2006)
0.9-2.3 4.3-8.1	DOC Surface pressure	(Tinel et al., 2020)
5.84 ± 8.97 9.10 ± 9.48	Organophosphate Esters	(Trilla-Prieto et al., 2024)
1.2 ± 0.4	CDOM	(Ribas-Ribas et al., 2017)
1.04 ± 0.04 (June) 1.09 ± 0.05 (Sept)	DOC	(Barthelmeß and Engel, 2022)
1.06 ± 0.12	Dissolved amino acid	
1.12 ± 0.28 (June) 0.93 ± 0.23 (Sept)	Particulate amino acids	
1.90 ± 1.76 (June) 0.86 ± 0.47 (Sept)	Particulate carbohydrate	
1.15 ± 0.08 (June) 1.08 ± 0.10 (Sept)	Surfactants	
1.7-6.4	Saccharides	(Jayarathne et al., 2022)
1.4-2.4	Coomassie staining particles	(Thornton et al., 2016)
1.2-2.8	Monosaccharides	

Note: TEPs: transparent exopolymer particles; CDOM: chromophoric dissolved organic matter; POC: particulate organic carbon; DOC: dissolved organic carbon; TOC: total organic carbon; DON: dissolved organic nitrogen; HMWDOM: high molecular weight DOM.

Most of the substances listed in Table 1 are typically enriched in SML through rising bubbles or diffusion. These compounds which constitute the primary organic components of the SML, not only confers biochemical activity to SML, but also modifies its physical properties such as dampening ocean surface waves. Current research indicates that SML significantly suppresses gas exchange between ocean and atmosphere. Furthermore, the physicochemical processes within the SML are closely linked to the budget of marine atmospheric VOCs, primary and secondary organic aerosols. Consequently, accounting for SML-specific processes is imperative when estimating the transfer rate of greenhouse gases(Pereira et al., 2018) and marine aerosol budget.

Surfactant activity (SA) is one of the most important physicochemical parameters of the SML, determined by the surface adsorption behavior of its surfactant compounds. Surfactants, also known as surface-active substances, are compounds that can significantly reduce surface tension or interfacial tension between two liquids, liquid-gas, and liquid-solid. The surface tension of pure seawater (devoid of organic matter and particulate material) slightly varies with temperature and salinity, typically ranging from 73 to 75 mN m^{-1}(Nayar et al., 2014). In comparison to pure seawater, the surface tension of coastal sea surface decreases by 10-15 mN m^{-1}, while that of remote ocean surfaces generally decreases by 0.5-1 mN m^{-1}(Frew and Nelson, 1992). Studies have reported that the SA of the SML is 0.1-1.57 mg L^{-1} T-X-100(Wurl et al., 2011; Sabbaghzadeh et al., 2017). Surfactant enrichment in the SML is greater in oligotrophic regions of the ocean than in more productive waters(Wurl et al., 2011). For instance, the SA of the SML in the Northern Hemisphere is significantly higher than that in the Southern Hemisphere, with higher enrichment of surfactants in the Southern Hemisphere Oceans(Sabbaghzadeh et al., 2017). This enrichment persists even at wind speeds reaching 13 m s^{-1}(Sabbaghzadeh et al., 2017), which suggests that the SML is stable enough to exist even at the global average wind speed of 6.6 m s^{-1}.

Temperature is an important parameter influencing surface adsorption behavior(Pereira et al., 2018). Results from a two-year continuous observation experiments show that SA of the SML varies seasonally, displaying a quasi-sinusoidal pattern from early to late in the year. This variation corresponds to changes in phytoplankton productivity, suggesting that variations in temperature, sunlight radiation, and nutrient input (from rivers) influencing primary productivity and salinity changes may be the driving forces behind SA variations(GašParović and Ćosović, 2001). This conclusion aligns well with findings from other studies, showing that sunlight radiation-induced degradation of large-molecule CDOM leads to an increase in SA(Rickard et al., 2022). Therefore, a deeper understanding of the photochemical processes in the SML is crucial for comprehending the transfer rates of important trace gases such as CO_2, CH_4, N_2O and DMS at the ocean-atmosphere interface, with significant implications for environmental climate studies(Rickard et al., 2022).

3. IMPACT OF SML ON GAS TRANSFER.

Early research on the SML primarily focused on the physical barrier effect of surfactants, suggesting that the organic film composed of surfactants would simultaneously hinder the evaporation of seawater and the transfer of atmospheric gases to the ocean(Liss and Duce, 1997; Donaldson, 2006; Rudich, 2003). Surfactants in SML are divided into water-soluble and water-insoluble categories, among which water-soluble surfactants (such as TEPs, lipids, polysaccharides, amino acids, etc.) play a significant role in inhibiting the gas transfer rate between the ocean and the atmosphere(Bock et al., 1999; Frew et al., 1990). For instance, Tsai and Liu (2003) estimated a reduction of 20-50% of the global annual net flux of CO_2 by correlating surfactant abundance and distribution with local primary productivity, assuming surfactant enrichment increases alongside productivity(Tsai and Liu, 2003). However, field measurements by Wurl et al. (2011) contradicted this assumption, demonstrating that surfactant enrichment decreases with primary productivity(Wurl et al., 2011). Their study also generated the first global maps of surfactant concentrations in the SML and their EFs by integrating experimental data on primary productivity and wind speed. These findings underscored the SML's potential global influence on air-sea gas exchange and biogeochemical cycles(Wurl et al., 2011). More recent study by Sabbaghzadeh et al. (2017) argued that SA enrichment in the SML should be essentially decoupled from ambient wind speed(Sabbaghzadeh et al., 2017). Instead, SA enrichment is more related to the SA in subsurface water(Sabbaghzadeh et al., 2017;

Pereira et al., 2016). Additionally, while chlorophyll α is widely used as a proxy for primary productivity(Pereira et al., 2016), field studies have shown it to be an unreliable indicator for parameterizing the inhibitory effect of surfactants in the SML(Sabbaghzadeh et al., 2017). Table 2 summarizes the impact of surfactants on the transfer rates of CO_2 at the air-water interface.

Table 2. Suppression effect of surfactants on the gas transfer velocity of CO_2.

Research Target	k_w^*	Ref.
Photo-derived surfactants	12.9% ~ 22.2%	(Rickard et al., 2022)
Surfactant activity	14% ~ 51%	(Pereira et al., 2016)
Biological surfactant	Up to 32%	(Pereira et al., 2018)
Artificial surfactant	5% ~ 55%	(Salter et al., 2011)
Slick-SML	Up to 15%	(Wurl et al., 2016)

*Suppression of the gas transfer velocity.

Currently, the variations in the mass fraction of surfactants in the DOM carbon pool in the SML are believed to be the reason for the large discrepancies in the estimated values of gas transfer velocity of CO_2 shown in Table 2(Pereira et al., 2016). In addition to CO_2, surfactants on water surface also impact gas-to-liquid phase transfer process of other gases, such as nitric acid (HNO_3), ammonia(NH_3), O_3 and nitrogen pentoxide (N_2O_5) through forming a well ordered, dense film(Clifford et al., 2007; Stemmler et al., 2008; Rouvière and Ammann, 2010; Thornton and Abbatt, 2005; Cosman and Bertram, 2008). Compared to branched-chain structures, straight-chain surfactant organic compounds exhibit the strongest inhibitory effect on gas absorption(Cosman and Bertram, 2008).

Surfactants in SML can also physically modulate interfacial chemical reactions. For instance, authentic SML has been shown to suppress significantly the chemical generation rate of gaseous $I_{2(g)}$ from O_3 + I_2 reaction at SML through enhancing solubility of I_2 in SML(Schneider et al., 2022). Additionally, surfactants accumulating at the water surface can form an organic phase, enabling otherwise water-insoluble substances to dissolve into the organic layer. This enrichment elevates the organic concentration at the interface, facilitating chemical reactions that are thermodynamically or kinetically constrained in bulk aqueous phases. A notable example is the role of organic films in promoting the enrichment of polycyclic aromatic hydrocarbons (PAHs)(Donaldson, 2006), which may subsequently undergo photochemical degradation upon solar irradiation(Jiang et al., 2021; Mekic et al., 2020c). Similarly, photosensitizers like 4-carboxybenzophenone (4-CB) and imidazole-2-carboxaldehyde (IC) are “attracted” to the surface when fatty acids or fatty alcohols coat the liquid surface, thereby initiating photochemical reactions(Tinel et al., 2016). Sum frequency generation experiments have revealed that soluble monosaccharides in solution can strongly adsorb to lipid monolayers covering the solution surface *via* coulombic interactions under appropriate conditions(Burrows et al., 2016). This “co-adsorption” phenomenon is critically important for interfacial photochemical processes in the SML, as it enhances the reactivity and compositional complexity of the organic layer.

4. IMPACT OF SML ON SSA PRODUCTION.

Sea spray aerosols (SSA), also known as primary marine aerosol particles, are directly generated by wind-wave interactions and represent the largest natural source of aerosols globally(Russell et al., 2023). SSA serves as one of the primary carriers for material and energy transfer between the atmosphere and the ocean. It influences atmosphere composition through physicochemical processes and under certain conditions, it may grow into warm and cold clouds (Figure 2), directly or indirectly impact surface radiative balance and profoundly affect climate change(Wang et al., 2019a; Jammoul et al., 2008; Brooks and Thornton, 2018; Demott et al., 2016; Wilson et al., 2015; Uetake et al., 2020). The current best estimate of SSA flux of 5000 Tg yr^{-1} can be used to calculate SSA-related carbon flux as 35 TgC yr^{-1}, by approximating <1 μm SSA particles as 10% of SSA flux with 7% organic carbon and > 1 μm particles as 90% of SSA flux with no organic carbon(Russell et al., 2023; Tsigaridis et al., 2013). However, significant uncertainty remains in our understanding of the cloud-forming role of SSA(Quinn et al., 2017; Xu et al., 2022). This is largely due to the ambiguous link connecting organic components in SML and the physicochemical properties of SSA and its cloud formation potentials(Russell et al., 2010), especially the prevalence and variability of SML's direct and indirect impact on SSA composition, size distribution and flux.

SSA forms when wind speeds exceed approximately 5 m s^{-1}(Quinn et al., 2015; Lewis, 2004), creating surface shear stress that breaks waves and entrains air bubbles transport organic matter (OM) to the surface(De Leeuw et al., 2011). Rising bubbles transport OM to the surface. At the air-sea interface, bubble bursting releases SSA through two mechanisms: "film jet" (submicron particles) from bubble film rupture and "drop jet" (supermicron particles) from cavity collapse(Brooks and Thornton, 2018; Quinn et al., 2014; Prather et al., 2013; Quinn et al., 2015). Therefore, wind speed, particularly on sea surface(Russell et al., 2010; Liu et al., 2021a; Parungo et al., 1986), and the physicochemical properties of surface seawater, such as sea surface temperature(Liu et al., 2021a; Christiansen et al., 2019; Sellegri et al., 2006; Mårtensson et al., 2003), salinity(Mårtensson et al., 2003; Tyree et al., 2007), and SA(Cochran et al., 2016a), are considered as crucial factors determining the mechanisms of SSA production.

As shown in Figure 2, the SML is believed to play a crucial role in SSA formation(O'dowd et al., 2004; Russell et al., 2010; Wang et al., 2015), as it is inherently involved in SSA production through bubble bursting and wave breaking(Schmitt-Kopplin et al., 2012), (i) linking its organic composition to SSA's chemical makeup(Lewis et al., 2022); (ii) modulating bubble lifetime and properties(Modini et al., 2013) and (iii) influencing SSA production mechanisms, all of which are primarily results of the presence of enriched surface-active organic materials (i.e., surfactant) such as lipids and fatty acids(Mochida et al., 2002; Cochran et al., 2016b; Cochran et al., 2016a; Cochran et al., 2017; Wang et al., 2015) and OM with positive buoyancy (e.g. EPSs) at SML(Keith Bigg et al., 2004). Such impact could further modulate the ice-nucleating particles (INPs) and cloud condensation nuclei (CCN) budget in marine

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atmosphere. Hence, bridging the link between SML and SSA organic composition is therefore important for understanding the physicochemical properties of SSA and their subsequent environmental and climatic effects(Russell et al., 2010).

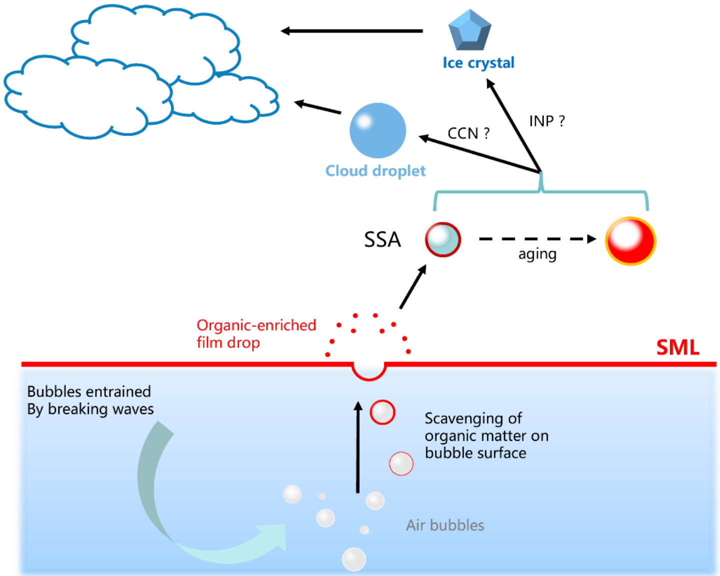

Figure 2: Illustration of the role of SML in regulating SSA production and properties which could further affect its ice nucleating and cloud condensation potentials and eventually cloud formation.

This is especially true for submicron SSA, given their dominant quantity, relatively high organic fraction and efficient light scattering compared to supermicron SSA(O'dowd et al., 2004; Quinn et al., 2015). It has been shown that the submicron SSA is predominately constituted by water insoluble organic matter with surfactant characteristics during high biological activity periods(Facchini et al., 2008; O'dowd et al., 2004). This is evidenced by aliphatic-rich organic species dominated submicron

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mode of SSA size distribution measured by aerosol mass spectrometry and Raman spectroscopy(Wang et al., 2015; Cochran et al., 2017) and by a relative increase in surface-active compounds in comparison with the surface water measured by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and nuclear magnetic resonance spectroscopy (NMR)(Schmitt-Kopplin et al., 2012), and other high resolution mass spectrometry(Cochran et al., 2016b). The ocean biology associated surfactants exhibited high SA, resulting in their enrichment in the SML; thus, provide efficient transfer such as long-chain fatty acids into film-drops during the bubble bursting process at SML(Cochran et al., 2017; Schmitt-Kopplin et al., 2012). The presence of biogenic surfactants can modulate bubble microphysics such as persistence time and bubble film cap thickness(Modini et al., 2013) and subsequent bursting process, resulting in the size distributions shift toward smaller sizes(Sellegri et al., 2006; Tyree et al., 2007; Fuentes et al., 2010a), particle flux enhancement in Aiken mode while suppression in other modes(Fuentes et al., 2010b; Sellegri et al., 2006), and suppression in the total number particles produced(Modini et al., 2013). This change has also been observed during a course of two-week phytoplankton growth in a mesocosm study(Alpert et al., 2015). However, the effect of surfactants is dependent on phytoplankton type(Fuentes et al., 2010a; Alpert et al., 2015), bubble generation method(Alpert et al., 2015), influenced by solubility(Modini et al., 2013) and could be offset by the sea surface temperature(Sellegri et al., 2006) as observed in the annual variation of marine aerosol particle size distribution modes(O'dowd et al., 2004). The mode shifts induced by surfactants could alter the cloud-forming potentials of SSA, as its particle size distribution and concentration of SSA are closely linked to its environmental effects(Cochran et al., 2016b; Fuentes et al., 2010b; Collins et al., 2014; Deane and Stokes, 2002; Laskina et al., 2015).

Understanding SML's impact on SSA composition requires widespread, simultaneous measurements of both SSA and SML organic composition(Lewis et al., 2022), along with further studies on mechanisms through which SML-enriched organics adsorb onto bubble films and eventually into SSA(Burrows et al., 2014; Burrows et al., 2016; Hasenecz et al., 2019; Carter-Fenk et al., 2021). Distinguishing 'fresh' from 'aged' marine aerosols using ambient measurements represents another challenge in this topic. Interferences may come from continental, anthropogenic influences and marine atmospheric aging. The recent developments of *in-situ* primary marine aerosol particle generator (Sea Sweep and MART)(Lewis et al., 2022; Bates et al., 2012; Quinn et al., 2014; Bates et al., 2020) and large-scale wave tunnels(Prather et al., 2013; Sauer et al., 2022; Cochran et al., 2016b; Demott et al., 2016; Collins et al., 2014; Ault et al., 2013; Quinn et al., 2015) enable investigation on SSA's physicochemical properties and the role of environmental factors under controlled conditions without external interferences. However, Sea Sweep and MART reproduced limited size-resolved number distributions that span the full range of that produced in ambient seawater(Bates et al., 2020; Lawler et al., 2024). However, the complex design of large-scale wave tunnel, along with the high requirements for operators and experimental equipment, limits its widespread application(Mayer et al., 2020), and the systematic change of original water system (e.g. filtration of zooplankton) may introduce unknown effects(Wang et al., 2015).

5. PHOTOCHEMISTRY AND MULTIPHASE CHEMISTRY AT SML.

The influence of the ocean on the atmosphere extends beyond heat transfer and water vapor transport. The ocean also serves as a source and sink for atmospheric aerosols and trace gases.

Over the past two decades, researchers in the field of atmospheric chemistry have conducted extensive research on chemical processes occurring at the air-water interface(George et al., 2015). Many studies have found that when certain molecules are at the gas-liquid interface, their free energy is minimized(Martins-Costa et al., 2012a; Martins-Costa et al., 2015; Mozgawa et al., 2014; Vácha et al., 2004). This characteristic greatly facilitates the migration, accumulation, and rapid occurrence of (photo)chemical processes at the interface. Therefore, it has been recognized that (photo)chemical processes occurring at the gas-liquid interface represent important sources and sinks for atmospheric trace gases(Rossignol et al., 2016). This chemical process is different from the previous understanding of chemistry occurring in homogeneous phase(Ravishankara, 1997).

Compared to the scientific knowledge of atmospheric chemical processes of terrestrial VOCs, there has been relatively limited understanding regarding the sources and sinks of marine-derived VOCs and the corresponding climate effects arising from the atmospheric physicochemical processes accompanying their lifecycle in the marine boundary layer (MBL). In addition, there is a limited quantity of field measurements data and limited number of observed species derived from marine environment across both temporal and spatial scales. Therefore, the current understanding of relevant scientific issues in this field mainly stems from field observational experiments and laboratory simulation studies.

Low molecular weight carbonyl compounds (methanol, formaldehyde, and acetone) observed in the SML were much higher than those in SSW(Dixon et al., 2013). Their concentrations exhibited diurnal variations peaking in the afternoon, indicating that the photolytic processes at the sea surface are the source of these carbonyl compounds(Dixon et al., 2013). Schlundt et al. (2017) simultaneously measured a series of oxygenated volatile organic compounds (OVOCs) in surface seawater and marine air, finding correlations among these OVOCs, suggesting similar sources and sinks in surface seawater(Schlundt et al., 2017). A five-year monitoring of acetone, methanol, and formaldehyde in the tropical oceanic boundary layer, revealed that the tropical Atlantic region acts as a net sink for acetone but a net source for methanol and formaldehyde(Read et al., 2012). A modeling study indicated that tropical and subtropical oceans are mainly net sources of acetone, while high-latitude oceans represent sources of acetone(Wang et al., 2020a). Another modeling study suggested that the Northern Hemisphere oceans act as sinks for acetone, while the Southern Hemisphere oceans is as source of acetone(Fischer et al., 2012). Wang et al. (2019) identified unknown sources of formaldehyde through aircraft observations, indicating that the ocean is an important source of formaldehyde in the MBL(Wang et al., 2019b).

These observational data indicated that chemical processes occurring in the SML may be significant sources of VOCs in the MBL(Mungall et al., 2017). Currently, known sources of VOCs in the MBL cannot explain the observed concentration levels of OVOCs in airborne and seaborne observational experiments(Sinreich et al., 2010), suggesting the presence of unknown sources of OVOCs in the MBL(Singh et al., 2001; Mungall et al., 2017). There are two conjectures regarding these sources: First, these OVOCs may originate from the oxidation of nonmethane hydrocarbons (NMHCs) in the atmospheric boundary layer. Due to their longer chemical lifetimes compared to NMHC precursors, they exhibit higher concentrations in the boundary layer atmosphere. Second, OVOCs may also originate from biological and chemical processes occurring in the SML, such as multiphase oxidation reactions between substances in the SML and atmospheric oxidants, or photodegradation processes of substances in the SML(Singh et al., 2001). These processes are likely driven by biological activities in the SML, although this biological driving relationship has not been fully established. This is mainly because the chemical processes occurring in the SML are currently understood primarily from results obtained by laboratory simulation experiments or theoretical model simulations(Carpenter and Nightingale, 2015). For instance, simulation study results suggested that photochemical processes occurring in the SML contribute to the formation of VOCs in the MBL at levels comparable to directly emitted VOCs from marine biological activities(Bruggemann et al., 2018). However, it remains uncertain whether these research findings can be representative of the mentioned chemical processes in the real world. On temporal and spatial scales, more extensive sampling and characterization of the SML are needed to clarify the main biogeochemical processes and influencing factors in this interface environment, especially the production, consumption mechanisms, and chemical compositions of surface-active substances. Only by deepening our understanding of this critical interface environment we may ultimately elucidate its effects on the climate.

In summary, current understanding suggests that marine VOCs primarily originate from three main processes: (*i*) direct emissions from marine biological activities such as DMS, isoprene, and monoterpenes released by the algae metabolism(Shaw et al., 2010; Novak et al., 2022; Halsey and Giovannoni, 2023), (*ii*) photochemical processes releasing OM from the SML of seawater(Carpenter and Nightingale, 2015; Novak and Bertram, 2020; Zhu and Kieber, 2018), and (*iii*) emissions of atmospheric trace gases from the interface oxidation processes at the ocean surface(Zhou et al., 2014; Schneider et al., 2019; Wang et al., 2023; Wang et al., 2022b). Compared to (*i*) and (*ii*), research on (*iii*) is relatively limited, and this aspect will be further elaborated in the following sections.

5.1 Photosensitized processes at SML as a source of VOCs and SOA in the MBL.

The photochemical processes occurring in the SML are one of the most significant drivers of biogeochemical processes, including the generation, degradation, and transformation of DOM. In recent years, many researchers have conducted extensive and in-depth research focusing on the scientific question: “How do the photochemical processes transform DOM into VOCs, and how does this impact the formation of SOA in the MBL?”

The organic compounds that exhibit photochemical activity in the SML are referred to as chromophoric dissolved organic matter (CDOM). Upon absorption of UV-light, CDOM gets electronically excited and goes to an excited singlet state (^{1}CDOM*) which then by intersystem crossing becomes an excited triplet state (^{3}CDOM*). Both, ^{1}CDOM* and ^{3}CDOM* can induce formation of hydroxyl radical (OH), singlet oxygen ($^1O_2$), superoxide (O_2^-), H_2O_2, aqueous electron (e^-_{aq}), and organic radicals(Sharpless and Blough, 2014; Mcneill and Canonica, 2016). In addition, an energy transfer occurs between CDOM and surrounding DOM molecules, manifesting as a series of important photochemical reactions such as photolysis, photosensitization, and photooxidation(George et al., 2015). The SML, as the top layer of the ocean surface is directly exposed to the most intense solar radiation, experiencing intensified SA under high-intensity UV radiation, although there is still ~10% of the surface UVA radiation (at 360 nm) presenting at a depth of 50–70 m in most oligotrophic waters (Lee et al., 2013; Smyth, 2011). This SA, also known as surfactant activity, is positively correlated with CDOM concentration but negatively correlated with salinity(Rickard et al., 2022; Sabbaghzadeh et al., 2017; Penezić et al., 2023). The photochemical processes occurring in the SML not only serve as significant sources of VOCs in the MBL but also act as important transformation sites for key atmospheric trace gases such as O_3, NO_2, and SO_2.

Nonanoic acid (NA) is the representative compound of lipid and saturated fatty acids, which are the most important biogenic DOM in the SML. When NA is present in the air or dissolved in water, its main absorption band peaks around 212 nm, while the absorption band around 272 nm is extremely weak resulting in minimal light absorption. However, the intensity of the absorption band at 272 nm increases and extends towards 340 nm as the concentration of NA enriched in the SML rises. When reaching the monolayer concentration (~0.6 mM), the light absorption extending to around 290-350 nm can induce electronic excitation to the excited triplet state of NA ($^3NA^*$), which can subsequently either undergo cleavage to form OH radicals and C_9 acyl radicals or capture hydrogen ions from other NA molecules to generate C_9 alcohol radicals and C_9 carboxylic acid radicals(Rossignol et al., 2016). Figure 3 shows the NA chemistry at the air-water interface and in the bulk water.

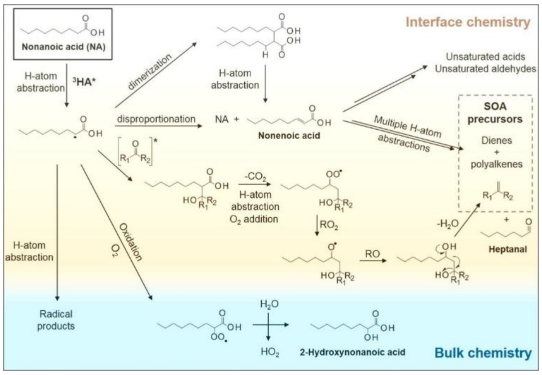

Figure 3. Reaction pathways of Nonanoic acid at the air-water interface and in the bulk water(Bernard et al., 2016).

These processes initiate subsequent radical chemistry, ultimately leading to the formation of a variety of VOCs containing multiple functional groups(Rossignol et al., 2016). Although recent study suggested impurity contribution to UV absorption of saturated fatty acids(Saito et al., 2023), the results nevertheless support the idea that photosensitized chemistry at the ocean surface can be a source of VOCs(Schneider et al., 2024).

Currently, few proxy compounds representing CDOM species such as 4-carboxy benzophenone (4-CB)(Gomez Alvarez et al., 2012, De Laurentiis et al., 2013), imidazole-2-carboxaldehyde (IC)(Tsui et al., 2017, Felber et al., 2020, Martins-Costa et al., 2022), and humic acid (HA) are widely used in exploring the impact of photochemical processes occurring in the sea SML on the marine atmosphere(Tinel et al., 2016; Fu et al., 2015; Ciuraru et al., 2015b). Experimental findings indicated that 4-CB and IC are attracted to the liquid surface by the fatty acids or fatty alcohols (e.g. nonanoic acid and 1-octanol) that are enriched at the sea surface(Fu et al., 2015). Moreover, saccharides and polysaccharides are also attracted to the sea surface by lipids (Burrows et al., 2016). This “co-adsorption” phenomenon suggests the presence of highly active photosensitized chemical processes at the SML. The excited triplet states of the photosensitizers (e.g. 4-CB, IC) can initiate radical chemical reactions by abstracting hydrogen (H) atoms from other organic substances present at the SML, such as NA and octanol(Fu et al., 2015). After losing an H atom the NA radical can undergo reactions such as addition with oxygen molecules or radical-radical reactions, ultimately leading to the formation of VOCs with different volatilities(Tinel et al., 2016). This reaction pathway occurring at the sea surface is similar and competitive to the H-abstraction mechanism initiated by OH radicals. Laboratory observations have shown that the photosensitized processes initiated by CDOM* can convert DOC present in the SML into VOCs containing double bonds and carbonyl groups, such as C_2-C_4 olefins(Riemer et al., 2000) and isoprene(Bruggemann et al., 2018). Furthermore, the oxidation of triplet-state phenol by halide anions in SML is considered as a source of marine atmospheric halogen radicals(Jammoul et al., 2009).

Humic substances (HS) enriched at the SML can also induce similar photosensitized processes(Ciuraru et al., 2015b). The photodegradation processes of triglycerides released by phytoplankton and unsaturated fatty acids such as oleic acid and linoleic acid are considered as *in situ* sources of HS in the ocean(Kieber et al., 1997). The photo-generation of humic-like compounds has also been observed in lake water(Carena et al., 2023). The excited-state of humic-like compounds play a crucial role in the oxidative degradation of DOM and the generation of VOCs such as isoprene(Ciuraru et al., 2015b; Ciuraru et al., 2015a), small molecular carbonyl compounds like formaldehyde, acetaldehyde, α-keto acids, etc(Mopper et al., 1991; Kieber et al., 1990; Kieber and Mopper, 1987). Additionally, processes including the formation of low molecular weight carbonyl compounds (acetaldehyde, glyoxal, and methylglyoxal)(Zhou and Mopper, 1997; Zhu and Kieber, 2019) are significant. Trueblood et al. (2019) compared the photochemical reactions between NA liquid films and 4-CB, humic acid, and DOM extracted from algal bloom seawater samples as photosensitizers(Trueblood et al., 2019). Although the photosensitization effect of DOM from seawater was found to be relatively low, this study provided evidence that photosensitized reactions can indeed occur in real environments(Trueblood et al., 2019).

It has been shown that pyruvic acid (PA) as a representative compound of α-dicarbonyl compounds can initiate photosensitized chemistry at the sea surface(Gomez Alvarez et al., 2012; Anglada et al., 2020a). Upon sunlight irradiation, the ketone form of PA is first excited to the singlet state and then by intersystem crossing goes to the excited triplet state (^{3}PA*). The excited triplet state of PA can react with another PA molecule in its ground electronic state either by the abstraction of the acidic hydrogen atom *via* proton coupled electron transfer(Guzmán et al., 2006) or a concerted hydrogen atom abstraction (Griffith et al., 2013) which can further initiate a chain of reactions that induce decarboxylation, and the formation of oligomers(Guzmán et al., 2006; Griffith et al., 2013; Eugene and Guzman, 2019; Reed Harris et al., 2017; Kappes et al., 2021).The formed oligomers at the air-water interface can further affect the VOCs fluxes between the ocean and the atmosphere.

Pyruvic acid absorbs UV fraction of sunlight with its n →π* transition band (λ_{max} = 318 nm) at the surface water(Gordon et al., 2019). More interestingly, the absorption spectrum of PA is red shifted by 13 nm when going from dilute aqueous solution (λ_{max}

= 318 nm) to a solution with ionic strength (NaCl), (I) = 2.7 M (λ_{max} = 331nm)(Mekic et al., 2019).

Considering that pH of seawater is around 8, PA will be present as pyruvate which is the conjugate base of pyruvic acid, arising from deprotonation of the carboxy group. Analysis by 1H NMR photolysis experiments of PA has shown that the presence of Ca^{2+} and Na^{+} in the sea water can further deprotonate PA(Luo et al., 2020).

It has been shown that charged species at the air-water interface, such as deprotonated PA, would enhance the intensity of vibrational sum frequency in the coordinated-OH stretching region (~3000−3400 cm^{-1}). The examination of OH stretching band provides a means to qualitatively evaluate the presence of charged species without needing to know the actual percentage of deprotonated species(Gordon et al., 2019).

Multiphase chemistry of PA indicated that the air-water interface plays a significant role in promoting chemistry not possible in either the gas or bulk aqueous phase(Kappes et al., 2021). Interestingly, PA acting as a photosensitizer, may initiate cross reactions with other organics such as glyoxal(Mekic et al., 2019) and glyoxylic acid(Xia et al., 2018), leading to formation of highly oxygenated multifunctional compounds which remain in the water or partition to the gas phase according to their physical and chemical properties (molecular mass, boiling point, etc).

PAHs are ubiquitous compounds at the ocean surface. Although many efforts have been made to reduce the emission of PAHs, their concentrations in the aquatic environment remains high(Ravindra et al., 2008; Keyte et al., 2013). The primary emitted PAHs are deposited into the surface waters *via* atmospheric deposition(Ma et al., 2013). It has been shown that PAHs play an important role in the photochemical processes of SML. Fluorene (FL), for example, can act as a photosensitizer at the sea surface while irradiated by sunlight and initiate photochemical formation of toxic compounds and a wide variety of functionalized and unsaturated organic compounds in both the aqueous phase and gas phase(Mekic et al., 2020b). The photosensitized reaction between triplet states of PAHs (pyrene, fluoranthene, and phenanthrene) and dimethyl sulfoxide (DMSO) in the sea surface layer has recently been identified as a source of organic sulfur compounds such as ethylsulfonylmethane, ethyl methanesulfonate, methanesulfonic acid, methanesulfinic acid, hydroxymethanesulfonic acid, and 2-hydroxyethanesulfonic acid in the marine atmosphere(Mekic et al., 2020c; Mekic et al., 2020b).

Although significant efforts have been made to explore the photochemical processes occurring in SML, the research framework mentioned above remains relatively simplistic, primarily focusing on the photochemical characteristics of various organic surfactants, with many environmental factors impacting the reactions not thoroughly investigated. Although studies have shown a positive correlation between light intensity and VOCs production rates(Alpert et al., 2017), the influence of other factors on the overall rate of photochemical reactions remains to be investigated. In order to better simulate the marine environment, researchers have attempted to increase the complexity of the research system, by enhancing the complexity of photosensitizers(Trueblood et al., 2019) or introducing inorganic salt components to explore the photochemical processes in complex systems(Mekic et al., 2018a). It has been shown that the photochemical processes occurring in the SML of marine and freshwater bodies differ(Stirchak et al., 2021), and the chemical processes of organic and inorganic substances in the SML are strongly coupled and complex. For example, the ionic strength effect can quench ^{1}[DOM], increase the generation of steady-state ^{3}[DOM] and $^1O_2$(Abdel-Shafi et al., 2001; Glover and Rosario-Ortiz, 2013), and the increase in the concentration of steady-state ^{3}[DOM]* may be due to the ionic strength effect suppressing the consumption of ^{3}[DOM]* through the electron transfer reaction pathway(Parker et al., 2013). Decreasing the ^{3}[DOM]* indirectly affects the photodegradation rate of other organic substances(Grebel et al., 2012). However, this effect is selective for different types of ^{3}[DOM]*, such as halogens affecting the photodegradation kinetics of anthracene, while having little effect on phenanthrene (Grossman et al., 2019). Additionally, the ionic strength effect has been reported to influence the photochemical generation of volatile organic sulfur compounds (Figure 4) (Mekic et al., 2020c).

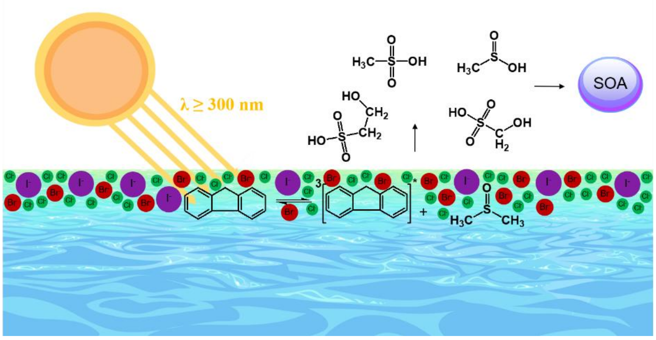

Figure 4: Simplified illustration of ionic strength effect on photosensitized reaction between excited triplet state of fluorene and DMSO at the air-water interface.

Figure 4 illustrates the formation of gas-phase methanesulfonic acid (CH_3SO_3H), methanesulfinic acid (CH_3SO_2H), hydroxymethanesulfonic acid (CH_4O_4S), and 2-hydroxyethenesulfonicacid ($C_2H_5O_4SH$). These compounds are typical precursors of aerosol particles, and they are commonly detected in ambient particles(Hopkins et al., 2008; Gaston et al., 2010).

Conversely, studies have reported that DOM can promote the photodegradation of nitrates to produce reactive oxygen species(Wang et al., 2020b). Therefore, investigating the behavior of photochemical processes in different salt gradients is crucial for extrapolating laboratory data to real environments.

While significant progress has been made in related studies, these research systems still diverge considerably from real SML environments. This is manifested not only in the much higher concentrations of simulated samples in the laboratory compared to real environments(Rossignol et al., 2016) but also in the significantly lower photochemical activity of real samples compared to experimental ones(Trueblood et al., 2019). For instance, recent field measurements do not confirm a photochemical production of isoprene at SML(Kilgour et al., 2024; Kim et al., 2017) as it has been shown in the laboratory measurements(Ciuraru et al., 2015a). Therefore, many efforts have to be taken to demonstrate that the chemical processes elucidated in the laboratory occur in real environments. Additionally, the complexity of the environment, such as the presence of inorganic salts, metal ions(Li et al., 2024a), etc., may greatly influence the progress of chemical reactions, either promoting or quenching them, to the extent that the chemical processes elucidated in the laboratory may not occur in real environments, thus lacking practical significance. In order to investigate the chemical processes occurring in real SML environments, it is imperative to continuously make more complex the research system to better approximate the real environment.

5.2 Multiphase chemistry of atmospheric oxidants at SML.

In addition to being exposed to solar radiation, the SML is in direct contact with the atmosphere, this thus drives a series of complex multiphase chemical processes at the ocean-atmosphere interface (i.e. SML) where atmospheric oxidants are deposited. Research estimates that approximately one-third of global O_3 deposition occurs at the ocean surface, accounting for 600-1000 Tg O_3 yr^{-1}(Martino et al., 2012). Another important and highly water-soluble acidic gas is SO_2, which exhibits significantly higher deposition rates at the marine surface ($pH \approx 8$). Observational studies indicate that approximately 27% of atmospheric SO_2 is absorbed by the ocean(Faloona et al., 2009). Furthermore, two-layer model estimates suggest that the annual flux of SO_2 deposited into the ocean is 150 Tg yr^{-1}(Liss and Slater, 1974), which is comparable to the global anthropogenic emissions of SO_2 (95.8-119.8 Tg yr^{-1}(Zhong et al., 2020)). This highlights the critical role of the ocean in regulating atmospheric oxidants concentration. In addition to physical factors such as wind speed, surface turbulence, and molecular diffusion, multiphase photochemical reactions at the SML play a significant role in controlling the deposition rates of O_3 and SO_2(Chang et al., 2004; Liss and Slater, 1974). These processes are also major sources of VOCs and other active species in the marine atmosphere. For example, The multiphase chemical reaction between ozone ($O_{3(g)}$) and iodide ions ($I^-_{(aq)}$) in the SML is a primary source of gaseous iodine in the atmosphere (R-1)(Schneider et al., 2023). This reaction not only accelerates the dry deposition rate of atmospheric O_3 directly(Garland et al., 1980; Chang et al., 2004), but also indirectly drives atmospheric iodine chemistry, leading to new particle formation(He et al., 2023). These processes have significant implications for the atmospheric environment.

$$I^-_{(aq)} + O_{3(g)} + O_2 + H^+ \rightarrow I_{2(g)} + HOI_{(g)} \qquad (R-1)$$

$$OM_{(aq)} + O_{3(g)} \rightarrow Product_{(aq)} + Product_{(g)} \qquad (R-2)$$

In addition to its reaction with $I^-_{(aq)}$, recent studies have demonstrated that the multiphase chemical reaction between O_3 and OM (R-2) in the SML exhibits reactivity comparable to R-1(Kilgour et al., 2024). Current research primarily focuses on the universality of this reaction and its VOC products. For example, Zhou et al. (2014) investigated multiphase chemical reactions between O_3 and oleic acid films, along the western coast of Canada, and in the SML of the northeast Pacific, observing the formation of carbonyl-containing VOCs(Zhou et al., 2014). Schneider et al. (2019) explored O_3 multiphase chemistry with model SML samples (obtained by culturing *Thalassiosira pseudonana* under sterile conditions) and detected the generation of C_7-C_9 carbonyl-containing VOCs(Schneider et al., 2019). Recently, our group employed liquid chromatography and mass spectrometry to identify the molecular structures of primary VOC products from O_3 multiphase chemical reactions with 10 SML samples collected in the South China Sea (e.g., acetaldehyde, acetone, propionaldehyde, and C_6–C_9 saturated aldehydes)(Wang et al., 2023), providing a robust scientific foundation for assessing the atmospheric environmental impacts of this reaction. Figure 5 shows the formation profiles of four compounds, *m/z* 59, 69, 83, 101, observed in real time during the reaction of O_3 (100 ppb) with ten SML samples collected from coastal areas and open sea in South China Sea.

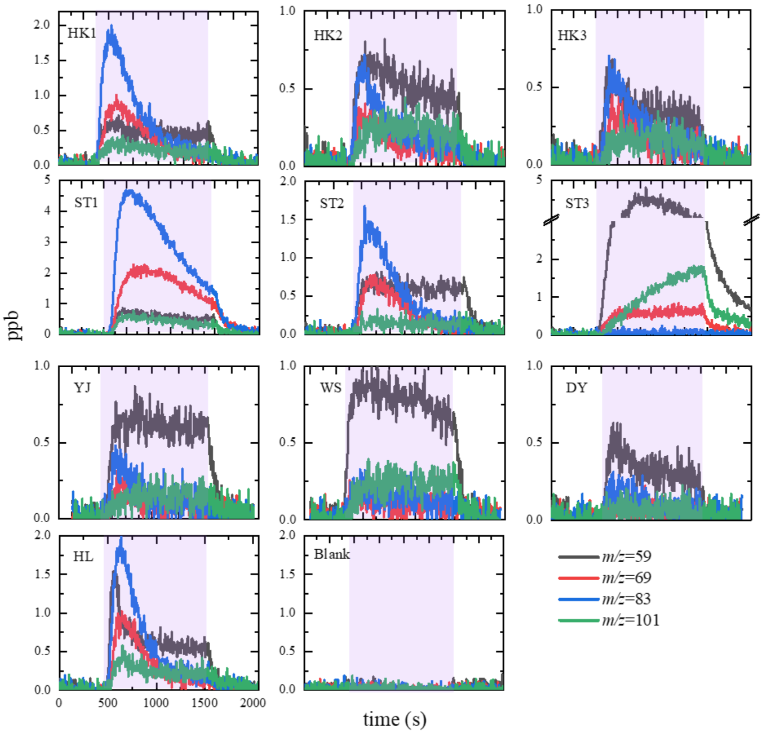

Figure 5: Formation profiles of *m/z* 59, 69, 83, 101 as a function of relative time measured by PTR-ToF-MS with H_3O^+ as reagent ion. The sensitivities used for converting the signals (ncps) into concentration (ppb) are acetone-based. To reduce the noise, the data have been treated with a moving average smoothing with a period of 5s. Pink background represents the period of ozone (100ppb) exposure on SML samples

This study aligns well with two following studies, one examined O_3 multiphase chemistry in SML from coastal waters near California, observing the formation of C_5-C_{11} aldehyde VOCs(Kilgour et al., 2024), and another investigated O_3 reactions in the Arctic Ocean SML, detecting acetaldehyde, acetone/propionaldehyde, and other aldehyde VOCs(Schneider et al., 2024). While there are minor differences among the observed VOCs product, they collectively indicate that the multiphase chemical reaction between atmospheric O_3 and OM in the SML is a significant driver of O_3 dry deposition. Furthermore, this reaction represents an important source of carbonyl-containing VOCs in the marine atmosphere. It is worth emphasizing that our group and Schneider et al. (2024) independently observed similar nitrogen-containing VOCs (e.g., amines and nitriles) in the studies of SML from the South China Sea and the Arctic Ocean, respectively(Schneider et al., 2024; Wang et al., 2023; Wang et al., 2022b). These findings suggest that this reaction may also serve as a source of reactive nitrogen in the marine atmosphere. Taking one of the primary reaction products, nonanal (C_9 saturated aldehyde), as an example, its reaction rate with atmospheric hydroxyl radicals (OH) is approximately an order of magnitude faster than that of DMS. Specifically, the rate constants for DMS + OH and nonanal + OH are 4.80×10^{-12} and 3.60×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively(Atkinson et al., 2004). Recent studies have further revealed that saturated aldehyde VOCs play a significant role in the regeneration of OH radicals(Yang et al., 2024). These findings suggest that O_3 multiphase chemical reactions in the SML may significantly alter the oxidation capacity of marine atmospheres and subsequently influence aerosol formation and the evolution of atmospheric composition. However, while current research has preliminarily identified the universality of this reaction and characterized its primary VOC species and molecular structures, uncertainties remain regarding the kinetic features of VOC emissions. Consequently, there is significant uncertainty in estimating the emission fluxes of VOCs from this reaction at present.

Based on three independent studies, the annual flux of VOCs emitted into the atmosphere from the multiphase chemical reaction between O_3 and OM in the SML has been estimated as follows: 45-450 Tg yr^{-1} (Schneider et al., 2024), 17.5-87.3 Tg yr^{-1} (Novak and Bertram, 2020), and 10.7-167 Tg yr^{-1}(Kilgour et al., 2024). While these estimates exhibit significant uncertainty, it is notable that the lower bounds of all three datasets are comparable to the annual emission flux of DMS (20.3 Tg yr^{-1})(Hulswar et

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al., 2022). This further underscores the potential for substantial impacts of this reaction on marine atmospheric chemistry. In summary, to elucidate the atmospheric chemical fate and environmental-climatic effects of these reactive VOCs, investigating the kinetic characteristics of VOCs generation from this multiphase chemical reaction under different environmental conditions is essential. Such research will help better estimate the yields and production rates of VOCs products, making this one of the key focuses for the future study.

In addition to O_3, SO_2 can also undergo multiphase chemical reactions with active substances in the SML, such as fatty acids(Passananti et al., 2016; Shang et al., 2016). In marine atmospheres, SO_2 primarily originates from terrestrial transport, shipping emissions, and in situ biological releases, with concentrations typically ranging from tens of parts per trillion to a few parts per billion(Nguyen et al., 1983; Kim et al., 2001; Li et al., 2024b). Among these sources, DMS and methanethiol (MeSH), released by marine phytoplankton metabolism, are the primary natural contributors of SO_2 in the marine atmosphere(Novak et al., 2022).

Over the past decade, research on SO_2 has predominantly focused on the formation processes and mechanisms of sulfate aerosols(Liu and Abbatt, 2021; Liu et al., 2021b). However, studies on the multiphase chemical reactions of SO_2 at the ocean surface and their associated environmental effects have only recently begun to receive attention. Unlike O_3, SO_2 exhibits photochemical activity, adding another layer of complexity to its atmospheric chemistry.

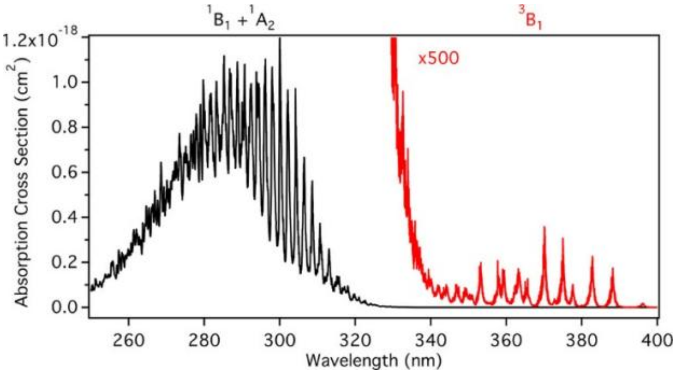

Figure 6: Spectrum of SO_2 showing the mixed $^1B_1$ and $^1A_2$ state from 250 to 340 nm and the forbidden $^3B_1$ state from 240 to 400 nm(Kroll et al., 2018b).

As shown in Figure 6, SO_2 absorbs radiation in the range of $250\ nm < \lambda < 340\ nm$, causing the molecule to enter an excited singlet state ($^1B_1 + ^1A_2$) (R-3). Subsequently, through intersystem crossing or collisional relaxation, it rapidly transforms into the excited triplet state ($^3B_1$). Additionally, absorption in the range of $340\ nm < \lambda < 400\ nm$ induces a forbidden spin transition, directly exciting SO_2 to the triplet state ($^3B_1$) (R-4). The triplet-state SO_2 ($^3B_1$) has a relatively long lifetime ($7.97 \pm 1.7 \times 10^{-4}$ s; (Collier et al., 1970)) and exhibits high reactivity, making it an active participant in the photochemical reactions of SO_2(Sidebottom et al., 1972).

$$SO_2 + hv(250nm < \lambda < 340nm) \rightarrow SO_2(\,^1B_1 + \,^1A_2) \qquad (R-3)$$

$$SO_2 + hv(340nm < \lambda < 400nm) \rightarrow SO_2(\,^3B_1) \qquad (R-4)$$

$$SO_2(\,^3B_1) + H_2O \rightarrow OH + HOSO \qquad (R-5)$$

SO_2 in its triplet state ($^3B_1$) has been demonstrated to react with various substances, including alkanes, alkenes, and carboxylic acids (Anglada et al., 2024; Kroll et al., 2018b). Furthermore, recent theoretical calculations and experimental studies have shown that SO_2 (3B_1) reacts rapidly with water molecules at water surfaces to generate OH and HOSO radicals (R-5)(Martins-Costa et al., 2018; Kroll et al., 2018a). These radicals can initiate further radical chemistry, leading to the oxidation of OM in the liquid phase and subsequent VOCs formation. However, only a limited number of studies have explored the multiphase photochemical reactions of SO_2 at air-sea interface, highlighting the need for further research in this area.

Passananti et al. (2016) and Shang et al. (2016) investigated the multiphase photochemical reactions of SO_2 on unsaturated fatty acids and long-chain olefins, which are typical active organic compounds in the SML. Their studies detected the formation of organosulfates in the liquid phase(Passananti et al., 2016; Shang et al., 2016). Liang et al. (2024) explored the multiphase photochemical reactions of SO_2 on biomass burning organic aerosols (BBOA), finding that the reaction between excited-state $^3BBOA^*$ and SO_2 is a major source of sulfate aerosols, rather than the reaction involving SO_2 in its triplet state (R-5)(Liang et al., 2024). However, these studies did not further investigate the contribution of SO_2 multiphase photochemical reactions to atmospheric VOCs.

Recently, our group studied the multiphase photochemical reactions of SO_2 on PAHs and PAH/dimethyl sulfoxide (DMSO) films, detecting the formation of sulfur-containing VOCs(Jiang et al., 2021). Subsequently, Deng et al. (2022) examined the multiphase photochemical reactions of SO_2 on urban building surfaces and found that photolytic conversion significantly enhances VOCs production. Notably, these VOC products are like those generated by O_3 reactions under simulated sunlight irradiation (Deng et al., 2022). This critical finding suggests not only that O_3 and SO_2 may share common precursor compounds in VOC formation but also implies similarities in their reaction mechanisms. For example, in the dark, both O_3 and SO_2 exhibit competitive effects on reactive functional groups such as the C=C bonds in unsaturated fatty acids(Passananti et al., 2016; Shang et al., 2016; Criegee, 1975). Under sunlight irradiation, SO_2 in its triplet state ($^3B_1$) and its derived radicals (R-5) could compete with O_3 for the same reactive functional groups. Therefore, it is crucial to study and analyze O_3 and SO_2 as a unified system to fully understand their roles in atmospheric chemistry and VOCs production.

Although the concentration of O_3 in marine atmospheres is typically one order of magnitude higher than that of SO_2(Li et al., 2024b), and SO_2 may be oxidized to sulfate by O_3 in the aerosol phase(Yu et al., 2023), studies have shown that the chemical uptake reactivity of SO_2 at environmental interfaces (10^{-6}) is generally one order of magnitude higher than that of O_3 (10^{-7})(Shang et al., 2016; Wang et al., 2022a; Deng et al., 2022) (Shang et al., 2016; Wang et al., 2022a; Deng et al., 2022). Additionally, Passananti et al. (2016) observed chemical uptake of SO_2 and the formation of organosulfates in their studies of multiphase photochemical reactions on unsaturated fatty acids and long-chain olefins, even in the presence of O_3(Passananti et al., 2016). Similarly, Ye et al. (2018) demonstrated that when SO_2 coexists with O_3, it can react with Criegee intermediates derived from ozonolysis to form organosulfates and promote the generation of SOA(Ye et al., 2018). These findings suggest that the multiphase photochemical reactions of O_3 and SO_2 in the SML are not simply competitive but may involve complex synergistic or interactive mechanisms, thereby influencing the species, yields, and production rates of VOCs. Therefore, investigating the multiphase photochemical reactions of O_3 and SO_2 in the presence of one another, particularly focusing on the kinetic characteristics and key reaction mechanisms of VOC formation, holds significant practical importance for quantitatively describing the multiphase photochemical reactions occurring at marine-atmospheric interfaces and their associated environmental impacts.

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CONCLUSION AND OUTLOOKS.

This review demonstrates that the ocean-atmosphere physicochemical interactions is an important scientific issue that remains to be further evaluated to better understand their influence on air quality and climate.

Recent research has revealed that multiphase and heterogeneous chemistry occurring at ocean-atmosphere interface leads to the formation of numerous organic compounds which in function of their physical and chemical properties remain in the ocean waters or partition to the atmosphere and ultimately participate in the formation of SOA. The chemical composition of the ocean SML plays, yet unexplored, an important role with respect to the multiphase and heterogeneous chemical processes. The SML consists plethora of organic and inorganic compounds, with concentrations reaching one or more orders of magnitude higher relative to the underneath water. Surfactants which mostly emerged from phytoplankton bloom are enriched at the ocean surface by physical processes such as diffusion, turbulent mixing, scavenging and transport by bubbles influencing the exchange of gasses between the ocean and atmosphere. For example, it is still an enigma if the ocean is a source or a sink of some important carbonyl compounds (e.g. acetone, acetaldehyde).

The importance of acetone in the atmosphere arises from the fact that sunlight induced photodissociation of acetone produces peroxyacetyl radicals which can be transformed to peroxyacetylnitrates (PAN) influencing the budget of nitrogen oxides (NO_x) which in turn affects the ozone concentration in the atmosphere(Singh and Hanst, 1981; Singh et al., 1994). In the upper troposphere photolysis of acetone leads to the production (30 to 40% of the total) of OH radicals (Wang et al., 2020a). Acetaldehyde exhibits a fast rate constant with OH ($k = 1.62 \times 10^{-11}$ cm^3 $molecules^{-1}$ s^{-1}) and therefore it plays an important role in the atmospheric OH budget(Atkinson et al., 1997).

Another important organic compounds enriched at the ocean surface are light absorbing molecules which are acting as photosensitizers and are capable of indirect phototransformation of the substrates of primary concern leading to the formation of VOCs that are released in the atmosphere.

However, majority of the studies are performed under controlled laboratory conditions by using proxy compounds of photosensitizers. Therefore, it is uncertain to which degree photosensitized reactions occurring at the ocean surface can transform the organic compounds and ultimately lead to the VOCs formation. It is essential to increase the complexity of the studied samples and use authentic ocean SML to better understand the reaction mechanisms and ultimately the impact of the oceanic chemical processes on the VOCs and SOA formation processes. For example, recent study has shown the excited triplet states of authentic biomass burning organic aerosols can induce multiphase reactions such as SO_2 oxidation and formation of sulfate(Liang et al., 2024).

The deposition of trace gases such as O_3 and SO_2 on the ocean surface and consequent chemical reactions can lead to the formation of VOCs in the atmosphere. Both oxidants react by addition to the C=C double bonds of unsaturated organic compounds enriched at the ocean surface. Intriguingly, O_3 reacts by addition to the C=C during nighttime (under dark conditions) and under sunlight irradiation, as well(Wang et al., 2023; Wang et al., 2022b), while this is not the case for SO_2. The formation of charge transfer complexes may occur between SO_2 and the alkenes present in the SML. As a result, the absorption spectrum of the formed charge transfer complexes may be altered extending from 315nm to 390 nm(Kroll et al., 2018b). During daytime under sunlight irradiation the formation of excited triplet state of SO_2 ($^3SO_2^*$) may occur and consequently initiate photosensitized chemistry at the ocean-atmosphere interface(Kroll et al., 2018a). However, scientific knowledge of the reaction mechanisms of O_3 and SO_2 and their impact on VOCs is far from to be understood. Laboratory and field studies are recommended by using authentic ocean SML samples and combination of trace gases in dark and under sunlight irradiation supported by molecular dynamic simulation. Only by increasing the complexity of the research studies we can obtain relevant data to properly run the models and predict the impact of ocean-atmosphere interactions on the topical issues of 21st century such as air quality and climate change.

The suggestions for future studies emerge from our own research plan commenting on issues that might be an important and interesting topic.

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