Atmospheric Implications of Ocean-Atmosphere Physicochemical Interactions

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36 **ABSTRACT.**

37 The atmosphere is the fast component of the climate which determines the meteorology

38 i.e. every day's whether. Ocean, on the other hand, is the slow component which

39 regulates the climate on the long term. A detailed knowledge of the interactions between

40 these two components is crucial in order to understand the global climate phenomena.

41 The ocean-atmosphere interface is the largest one on our planet occupying about 70%

42 of the Earth's surface. Hence, the physicochemical processes occurring at the interface

43 can largely affect the chemical content of the Ocean waters and the composition of the

44 atmosphere.

45 Here, we briefly discuss the chemical composition of the sea surface microlayer (SML),

46 emphasizing the role of surface-active compounds concentrated in the SML that

47 influence gas exchange and modulate the production of the largest natural primary

48 aerosols (e.g., sea spray aerosols, SSA) across the ocean-atmosphere interface. We

49 summarize recent research focused on multiphase and heterogeneous chemical

50 processes, including photochemical reactions within the SML, and their impact on the

51 formation of volatile organic compounds (VOCs), as well as subsequent effects on

52 secondary organic aerosol (SOA) production.

53 Comprehensive understanding of the ocean-atmosphere physicochemical interactions

54 is of paramount importance in order to properly address air quality and climate issues.

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 $0.58 \pm 0.06\%$ ($77.3 \pm 7.9 \times 10^4$ 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~~ an acronym derived from the initials of its four authors, was proposed by Charlson et al. (1987), suggests that dimethyl sulfide

77   (DMS) emissions from marine phytoplankton promote the formation of atmospheric

78   aerosol particles and cloud condensation nuclei. This process increases cloud albedo,

79   which in turn alters temperature and radiation, creating a feedback loop that affects

80   DMS emissions from phytoplankton and ultimately forms a closed bioclimatic

81   system(Charlson et al., 1987). Although this hypothesis is not entirely valid(Quinn and

82   Bates, 2011; Woodhouse et al., 2008), it highlights the significant impact of ocean-

83   atmosphere interactions on climate. Understanding energy and material transfer fluxes

84   between atmospheric and aquatic systems, as well as key control processes such as

85   biogeochemical and physical interactions and feedback mechanisms, is essential for

86   comprehending how these coupled systems influence Earth's climate. Recent attention

87   has focused on the physicochemical processes occurring at the atmosphere-ocean

88   interface(Donaldson and George, 2012; Carpenter and Nightingale, 2015; Brooks and

89   Thornton, 2018; Novak and Bertram, 2020). This area includes a thin layer of water,

90   ranging from tens to hundreds of micrometers, known as the surface microlayer (SML).

91   SML is widely distributed at the ocean surface(Knulst et al., 2003), and other water

92   bodies (e.g. lake, river and stream). It can be subdivided into slick and non-slick

93   SML(Wurl et al., 2016), or even thinner layers, referred to as the surface nanolayer(Laβ

94   et al., 2010). Owing to the inherent heterogeneity, a large variety of surface-active

95   organic (surfactants) and inorganic substances accumulated in SML due to their

96   interface affinities. Surface-active organics can also attract other more soluble organic

97   compounds (e.g. saccharides) to the surface, leading to so-called "co-adsorption"

98   effect(Burrows et al., 2016; Carter-Fenk et al., 2021). The elevated concentration of

99   these active substances establishes a unique biological, physical, and chemical milieu

100   in contrast to the underlying water layers.

101   This distinctive environment facilitates the formation of peptide bonds(Griffith and

102   Vaida, 2012), substantially reducing the physical volatility of the SML, thereby

103   promoting dominant molecular diffusion and resulting in pronounced gradients in heat,

104   pH, and gas concentration. Additionally, it facilitates the breakdown of energy barriers

105   associated with chemical reactions and accelerates substance transformations. As a

106   result, the SML forms the largest active interface on the Earth(Donaldson, 2006).

107   The SML is globally distributed and can remain stable at wind speeds up to 13m s^{-}

108   ^{1}(Sabbaghzadeh et al., 2017), and if disrupted, it regenerates quickly. Despite its

109   thinness compared to the underlying water layers, its dynamic changes have a

110   significant impact on global biogeochemical processes, including momentum and heat

111   transfer, air-sea exchange, and aerosol production. SML is continually consumed and

112   replenished by biogeochemical and physical processes, maintaining a dynamic

113   equilibrium. Supply mechanisms include atmospheric deposition and physical transport

114   from the subsurface water column. Wind-driven convergence circulation, tidal forces,

115   ocean shear, upwelling, and internal waves lead to localized concentrations of surface-

116   active substances across various spatial scales(Frka et al., 2012). Removal processes

117   involve direct injection of enriched substances into the atmosphere following the

118   bubble bursting, and the chemical transformation of dissolved organic matter (DOM)

119 upon light irradiation, or by the interface oxidation processes, resulting in production

120 of aerosols into the atmosphere. Hence, the SML holds substantial atmospheric

121 significance. Its composition and biogeochemical transformation processes not only

122 influence the input flux of non-biological source volatile organic compounds (VOCs)

123 and aerosol particles (i.e. Sea Spray Aerosol, SSA) to the atmosphere, but also regulate

124 the deposition rate of trace gases on ocean surface. Studies on the SML are crucial for

125 understanding interactions between ocean aerosols and clouds, representing a

126 significant area of focus in marine atmospheric chemistry. The ultimate goal is to

127 uncover the driving forces and mechanisms behind climate change.

128 Currently, there is a foundational understanding of the role of SML in ocean aerosol-

129 cloud interactions. This review aims to revisit scientific progress concerning

130 environmental and climate issues associated with the SML from an atmospheric

131 chemistry perspective. Specifically, it addresses advances in research on how physical

132 and chemical processes at the ocean surface impact the atmosphere.

133

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

155 traditional viewpoints. For instance, recent studies using stimulated Raman three-

156 dimensional imaging techniques have revealed the enrichment of HSO_4^{2-} ions on the

157 surface of aerosol liquid films(Gong et al., 2023). These findings indicate a gradient

158 change in the pH of deliquescent aerosol liquid films, suggesting that the method of

159 using uniform aqueous solutions to simulate homogenous chemical processes in real

160 aerosol liquid films may not replicate the actual chemical environment accurately. In

161 addition to inorganic salt ions, organic molecules also exhibit a tendency to accumulate

162 at the air-water interface(Rossignol et al., 2016) and interact with water molecules upon

163 contact (polarization, solvation), storing at high concentrations at the air-water interface,

164 lowering the activation energy of reactions; thus, altering the reactivity of chemical

165 reactions, including changes in reaction rates and product yields, and even reaction

166 pathways. This propensity of substances to accumulate at the air-water interface is one

167 of the key reasons why this boundary has garnered significant scientific attention.

168 In addition to the substance propensity at the air-water interface, the structure,

169 composition, and behavior of water molecules at the air-water interface differ from

170 those in the bulk phase. Petersen et al. (2004) used the Multistate Empirical Valence

171 Bond (MS-EVB) method to predict the presence of excess protons (H_3O^+) at the air-

172 water interface. However, it has been shown that the presence of excess charged water

173 molecules with an odd number of hydrogen bonds at the water interface, indicating an

174 excess negative charge on the surface(Ben-Amotz, 2022). Measurements of the

175 electrophoretic mobility of oil droplets and bubbles in water also indicate a negatively

176 charged interface. The simplest explanation for this phenomenon is the enrichment of

177 hydroxide ions (OH^-) at the interface and the electrostatic repulsion of hydrated

178 hydronium ions (H_3O^+). However, this explanation is inconsistent with some

179 experimental results, such as second harmonic generation and sum-frequency

180 generation techniques, which indicate the presence of excess H_3O^+ at the gas-liquid

181 interface(Petersen and Saykally, 2005). Molecular dynamics models and continuous

182 solvent models have also shown that H_3O^+ is more inclined to the gas-liquid interface

183 compared to OH^-. The pH of the liquid surface may differ from that of the bulk phase,

184 not only because of the sign of the liquid surface's electric field, but also due to the

185 preference of OH^- or H_3O^+ for the gas-liquid interface. Therefore, there is controversy

186 regarding the acidity of water interface(Saykally, 2013), as some research results

187 indicate that the water surface is acidic (pH < 4.8)(Buch et al., 2007; Mamatkulov et

188 al., 2017), while others indicate it is alkaline(Beattie et al., 2009; Mishra et al., 2012).

189 These differences in research results may be caused by differences in experimental

190 methods used. Although many research results are contradictory at present, there is

191 undoubtedly a close relationship between hydrogen bonds, charge transfer, and the

192 formation of the air-water interface charge layer, which objectively leads to an

193 imbalance of positive and negative ions at the water interface(Hao et al., 2022; Ben-

194 Amotz, 2022), thereby affecting the pH of the near-surface region, and consequently

195 affecting the chemical processes at the air-water interface. It has been reported that not

196 only that some chemical reactions occurring at the air-water interface are accelerated

197   (see section 1.2), but also that spontaneous chemical processes occur at the air-water

198   interface (section 1.3)(Lee et al., 2019b; Li et al., 2023), suggesting that the electric

199   field existing at the air-water interface is the driving force behind spontaneous chemical

200   processes. Some studies have observed a strong electric field at the oil-water interface

201   of microdroplets using Raman-excited fluorescence microscopy, suggesting that this

202   strong electric field may be caused by charge separation due to adsorbed negative ions

203   on the surface(Xiong et al., 2020). Recently, Liu et al. (2024) detected a strong electric

204   field at the gas-liquid interface of deliquescent nitrate aerosol microdroplets using

205   surface-enhanced micro-Raman spectroscopy and molecular dynamics simulations, but

206   the driving force behind this electric field remains to be answered.

207

1.1 Enrichment and depletion behavior of ions and their impact on chemical

209   ***processes at the air-water interface.***

210   Interest in the air-water interface was rekindled with advancements in studying halogen

211   transformations in sea salt aerosols. Researchers realized that ion behavior at this

212   interface may deviate from prior assumptions, particularly as some inorganic ions tend

213   to concentrate there. Surface-exposed ions can boost gas reactivity at the interface,

214   influencing key processes like gas absorption, halogen chemistry, and ozone (O_3)

215   depletion(George et al., 2015).

216   Hu et al. (1995) examined $Cl_{2(g)}$ and $Br_{2(g)}$ uptake by sodium chloride (NaCl) and iodine

217   chloride (ICl) aerosols (120-250 μm in diameter). Their findings showed that bulk-

218 phase reactions alone could not account for the observed absorption levels or its

219 dependence on ion concentrations. They thus concluded that reactions at the air-water

220 interface played a crucial role in the uptake process(Hu et al., 1995). Oum et al. (1998)

221 and Knipping et al. (2000) investigated the reaction between hydroxyl radicals (OH)

222 and sea salt particles, the results indicated that air-water interfacial reactions were

223 essential to explain the observations, a process that may also occur on the ocean surface.

224 Knipping et al. (2000) investigated the photochemical formation of $Cl_{2(g)}$ on

225 deliquescent NaCl aerosols under UV light (λ=254 nm) and O_3 conditions, using

226 experiments, molecular dynamics, and kinetic models. They concluded that air-water

227 interfacial reactions were essential to explain their observations. Additionally,

228 molecular dynamics simulations revealed that Cl^- enrichment at the surface of NaCl

229 aerosols enhanced interfacial chemical processes(Knipping et al., 2000). Field

230 observation data indicate that detected halogen molecules ($Cl_{2(g)}$, $Br_{2(g)}$, $BrCl_{(g)}$) in the

231 marine atmosphere are correlated with O_3 depletion(Spicer et al., 1998; Spicer et al.,

232 2002; Foster et al., 2001). Behnke et al. (1995) discovered that in the presence of O_3,

233 simulated sunlight irradiation of sea salt aerosols produces an unidentified chlorine

234 atom precursor. Subsequent laboratory studies demonstrated that in the presence of O_3

235 and under light irradiation (λ=254 nm), deliquescent sea salt particles produce gaseous

236 chlorine molecules, a process that may also occur on the ocean surface(Oum et al.,

237 1998). Laboratory research by Laskin et al. (2003) showed that $OH_{(g)}$ react with Cl^- on

238 the surface of deliquescent NaCl aerosols to form sodium hydroxide (NaOH),

239 increasing the alkalinity of sea salt particles and thereby enhancing the uptake of sulfur

240 dioxide (SO_2) and the formation of sulfates(Laskin et al., 2003). These studies indicate

241 that inorganic ions enriched at the air-water interface of sea salt aerosols can profoundly

242 impact the composition and oxidation capacity of the marine atmosphere. Since

243 inorganic salt ions are key components of atmospheric aerosols and ocean surfaces,

244 many studies have shown that, in addition to halogen ions directly participating in

245 atmospheric chemical processes, the surface propensity of inorganic salt ions causes

246 ionic strength effects that profoundly modulate multiphase reactions at the air-water

247 interface. These processes include sulfate formation(Yu et al., 2023), O_3 uptakes(Mekic

248 et al., 2018b; Mekic et al., 2020a; Mekic and Gligorovski, 2021), generation and

249 transformation of atmospheric pollutants including secondary organic aerosol

250 (SOA)(Mekic et al., 2018a; Zhou et al., 2019; Mekic et al., 2020c; Mekic et al., 2020a;

251 Wang et al., 2021; Gwendal Loisel, 2021; Pratap et al., 2021; Li et al., 2022). Although

252 many studies have made efforts and achieved some results on this topic, most of the

253 studies have focused on single-salt systems. A recent study investigated the interaction

254 between ions for air-water interface propensity(Seki et al., 2023). Considering the

255 complexity of the real atmospheric environment, extrapolating laboratory data to the

256 atmospheric environment for evaluating environmental and climatic impacts still

257 requires substantial effort.

258

259 *1.2 Accelerated chemistry at air-water interface.*

260   Many experimental and theoretical studies indicate that, compared to homogeneous

261   environments, water interface can significantly accelerate the reaction rates of certain

262   chemical processes(Kusaka et al., 2021; Narayan et al., 2005; Klijn and Engberts, 2005;

263   Kong and Evanseck, 2000), such as photochemistry(Kusaka et al., 2021; Gong et al.,

264   2022), photodecomposition(Rao et al., 2023b), photosensitized reactions(Wang et al.,

265   2024), spontaneous redox reactions(Lee et al., 2019a; Kong et al., 2021), and gas-gas

266   reactions at the air-water interface(Liu and Abbatt, 2021).

267   Research into faster chemical reactions at the air-water interface draws inspiration from

268   organic chemistry studies. Organic chemists typically avoid using water as a solvent

269   because it can react with organic compounds, and its polarity makes it unsuitable for

270   dissolving most nonpolar organics. As a result, aqueous solvents are generally seen as

271   ineffective for organic reactions(Klijn and Engberts, 2005). Early studies found that

272   some pericyclic reactions of hydrophobic organic compounds, such as the Diels-Alder

273   cycloaddition(Breslow, 1991) and Claisen rearrangement(Gajewski, 1997), proceed

274   faster in dilute aqueous solutions than in organic solvents or pure substances. Their

275   acceleration may be due to the hydrophobic effect(Tian et al., 2024), which polarizes

276   the transition state structure formed between the reactants, thus lowering the activation

277   energy. Other factors include enhanced hydrogen bonding in the transition state,

278   increased water cohesive energy density, and a stronger hydrophobic effect(Jung and

279   Marcus, 2007; Kong and Evanseck, 2000; Breslow, 1991). In 2005, Barry Sharpless's

280   group reported that the reaction rates of hydrophobic organic reactants dramatically

281   increased under emulsion conditions (formed by rapidly stirring water-insoluble

282   organics with water) compared to homogeneous or pure solute conditions. They

283   concluded both the heterogeneity and the presence of the water interface played key

284   roles in reaction acceleration(Narayan et al., 2005; Klijn and Engberts, 2005). Despite

285   these findings, the exact mechanism for this acceleration remains elusive. One theory

286   suggests that about one-quarter of the OH groups of water molecules at the interface

287   are free (unbound by hydrogen bonds). These free OH groups "extend" into the organic

288   phase at the interface, forming hydrogen bonds with reactants in the organic phase. The

289   transition state between the reactants is stabilized by these stronger hydrogen bonds

290   with free OH groups, thus dramatically speeding up reactions at the "oil-water

291   interface"(Jung and Marcus, 2007). Recent research demonstrated that photochemical

292   reactions at the oil-water interface can be accelerated through melting point

293   depression(Tian et al., 2024). Further, Lixue et al. (2025) combined Raman

294   spectroscopy and multivariate curve resolution to suggest that water structural disorder

295   and enhanced electric fields at mesoscale interfaces in oil-water emulsions may

296   contribute to accelerated chemical reactivity(Shi et al., 2025). Similar to the "oil-water

297   interface", some gas molecules also exhibit faster reaction rates at the air-water

298   interface. Typically, reactions of neutral closed-shell molecules in the gas phase, while

299   thermodynamically feasible, are slow due to high reaction barriers. In contrast, the

300   reaction rates of the same reactants (or appropriately modified forms in the condensed

301   phase) in multiphase environments can exceed those in the gas phase. This acceleration

302 stems from either reduced activation energy or higher reactant concentration in the

303 condensed phase. The formation of acid rain is a key example. The reaction between

304 $SO_{2(g)}$ and hydrogen peroxide ($H_2O_{2(g)}$) is inefficient in the gas phase but efficient in the

305 liquid phase. This is because the concentration of H_2O_2 in the atmospheric waters

306 ($H_2O_{2(aq)}$) is relatively high compared to $H_2O_{2(g)}$. Moreover, once $SO_{2(g)}$ dissolves in

307 water and hydrolyzes to form HSO_3^-, the reaction between $H_2O_{2(aq)}$ and HSO_3^- is highly

308 efficient.

309 While previous studies have documented reaction acceleration at water interfaces and

310 proposed mechanisms like OH group interactions with organics, other factors may also

311 play a role. These potential contributors include reactant confinement, partial solvation,

312 preferential orientation, droplet curvature, and surface pH variations. Despite these

313 insights, the exact reasons for the acceleration of reactions at the water surface remain

314 inconclusive(Ruiz-Lopez et al., 2020).

315

316 *1.3 Spontaneous chemistry at air-water interface.*

317 The thermodynamics and kinetics of many chemical reactions at interfaces differ from

318 those in the bulk phase due to the heterogeneity of the medium at or near the

319 interface(Zhong et al., 2019; Ruiz-Lopez et al., 2020; Kusaka et al., 2021; Wei et al.,

320 2020). At the air-water interface, the surrounding water exerts asymmetric molecular

321 interactions on the observed water molecules and solutes. The density of interfacial

322 water is lower than that of bulk water, and its density fluctuations generate macroscopic

323 capillary waves, surface roughness, and tension. These factors result in differences in

324 surface molecular dynamics, orientation, hydrogen-bond networks, and dielectric

325 properties compared to the bulk phase(Deal et al., 2021). When ions or surfactants

326 adsorb at the air-water interface, they alter surface tension and surface potential,

327 ultimately changing interfacial chemical processes(Jungwirth and Tobias, 2006; Otten

328 et al., 2012). Recent studies report that tiny droplets (diameter 1-20 μm) spontaneously

329 produce hydrogen peroxide on their surface, with production inversely correlated to

330 droplet diameter. It is suggested that H_2O_2 forms from the combination of OH radicals

331 generated from OH^- at the droplet surface under the influence of an electric field(Lee

332 et al., 2019b; Lee et al., 2020). This study has garnered significant attention because,

333 thermodynamically, a pure water environment is unfavorable for H_2O_2 formation.

334 Therefore, the study faces skepticism due to issues of reproducibility, potential

335 contamination, and lack of a reasonable mechanistic explanation(Nguyen et al., 2023).

336 Nevertheless, because the air-water interface is ubiquitous in the atmosphere, this

337 spontaneous chemical process has attracted considerable attention from researchers.

338 Following this study, a series of investigations into spontaneous chemical processes at

339 the air-water interface have emerged. Examples include the spontaneous generation of

340 OH radicals at the air-water interface in dark conditions(Li et al., 2023), the

341 spontaneous conversion of I^- to I and I_2 at the air-water interface(Guo et al., 2023),

342 mechanistic and quantitative studies of different inorganic salt ions on the spontaneous

343 generation of H_2O_2 at the air-water interface(Angelaki et al., 2024), and the spontaneous

344 oxidation of thiols and thioethers at the air-water interface of sea spray droplets(Rao et

345 al., 2023a).

346

347 ***1.4 Molecular dynamics simulation of chemical processes at the air-water interface***

348 ***and their influence on the atmosphere.***

349 Due to the rapid reactions of some atmospheric species at the air-water interface, such

350 as Criegee intermediates and SO_3, it is difficult for existing experimental methods to

351 capture their chemical reaction processes. Therefore, complementing experimental

352 techniques, molecular dynamics simulations (such as Born-Oppenheimer molecular

353 dynamics simulations) provide strong support for studying the fast reaction processes

354 (picosecond scale) occurring at the air-water interface, effectively aiding in a deeper

355 understanding of how the air-water interface influences reaction pathways, rates, and

356 mechanisms at the molecular level(Zhong et al., 2018). For example, Born-

357 Oppenheimer molecular dynamics simulations have shown that the rapid

358 heterogeneous process of iodine oxidation on sea salt aerosol surfaces (picosecond scale)

359 promotes aerosol growth(Ning et al., 2023).

360 In recent years, Francisco's research group(Anglada et al., 2014; Martins-Costa et al.,

361 2019, 2018; Martins-Costa et al., 2012b; Anglada et al., 2020a) has used quantum

362 mechanics/molecular mechanics molecular dynamics (QM/MM-MD) simulations to

363 propose that many important atmospheric species such as O_3, H_2O_2,

364 methylhydroperoxide, nitrogen dioxide (NO_2), and HO_2 radicals exhibit specific

365 behaviors at the air-water interface, accelerating photodissociation rates, which may

366 consequently impact the physicochemical characteristics of aerosols and the

367 atmospheric environment. These species tend to accumulate at the air-water interface,

368 leading to an increase in interface concentration, thus influencing interfacial chemical

369 processes(Anglada et al., 2020b; Martins-Costa et al., 2012b). Simulation studies have

370 found that the absorption band of O_3 accumulated at the air-water interface undergoes

371 a red shift and broadening compared to that in the gas phase, leading to an order of

372 magnitude faster photodissociation rate of O_3 at the interface than in the gas phase,

373 resulting in a four-order-of-magnitude increase in the rate of OH radical generation at

374 the interface(Anglada et al., 2014). Additionally, methylhydroperoxide in the air-water

375 interface exhibits a blue shift and broadening in its UV-visible absorption spectrum,

376 which is attributed to hydrogen bonding between methylhydroperoxide and water

377 molecules(Martins-Costa et al., 2017). Similarly, NO_2 also exhibits accumulation

378 behavior at the air-water interface, with broadening of its absorption band, leading to

379 an increase in its photodissociation rate at the interface(Murdachaew et al., 2013;

380 Martins-Costa et al., 2019). Intriguingly, the excited triplet state of SO_2 ($^3SO_2^*$)

381 produced under sunlight irradiation can react with water molecules leading to the

382 formation of OH radicals and hydroxysulfinyl radical (HOSO) which is further

383 converted to SO_2^- and then by oxidation-reduction process to sulfate (SO_4^{2-}) (Figure

384 1)(Ruiz-López et al., 2019).

385
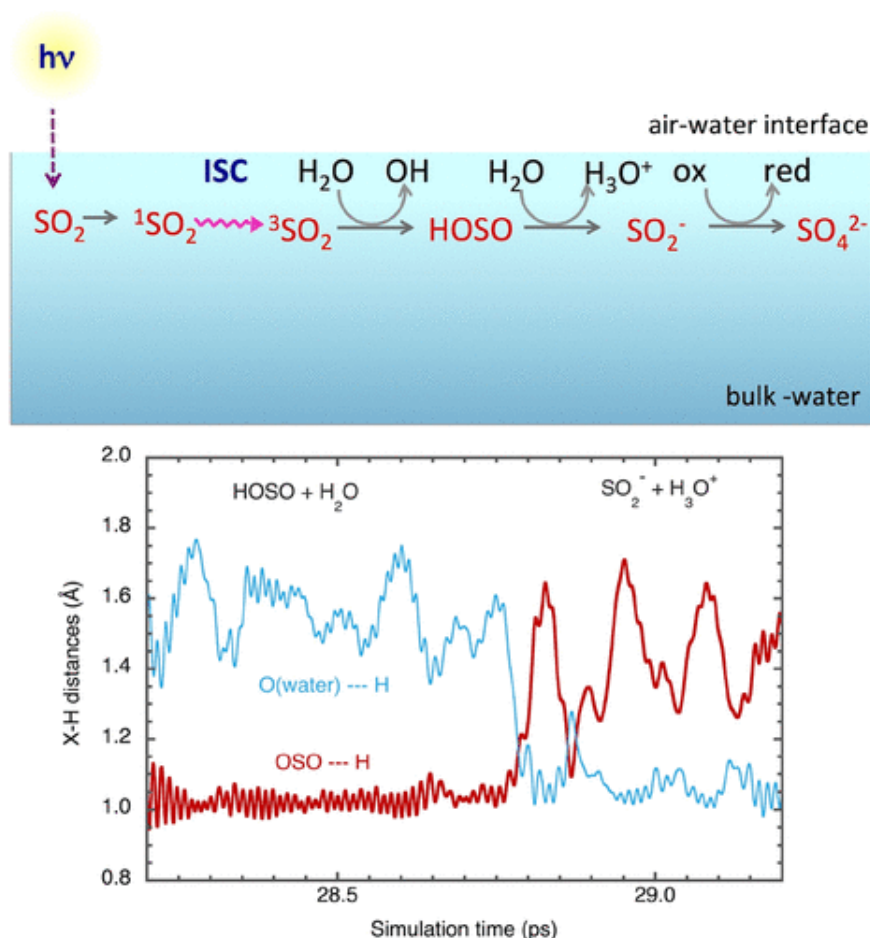
Figure 1. Light-induced oxidation of SO_2 is transformed to its excited triplet state ($^3SO_2^*$) which further promotes photosensitized chemistry leading to the production of OH and HOSO radicals and sulfate(Anglada et al., 2020b).

389

390 The importance of the formed HOSO arises from the fact that is very acidic ($pKa = -1$)

391 and undergoes fast ionic dissociation at the air-water interface. In addition, the formed

392 SO_2^- ions can be further oxidized by H_2O_2, O_3, OH, or HO_2 to generate sulfuric

393 acid(Ruiz-López et al., 2019; Anglada et al., 2020a).

394 Furthermore, molecular dynamics simulations have revealed that important

395 atmospheric gases such as N_2, O_2, O_3, OH, H_2O, HO_2, and H_2O_2 tend to accumulate at

396 the water surface with the lowest free energy when located at the air-water

397 interface(Vácha et al., 2004). These findings are significant not only for chemical

398   processes occurring at aerosol surfaces but also for processes occurring at the

399   atmosphere-ocean interface.

400   Although molecular dynamics theoretical studies have provided insights into how the

401   air-water interface alters the reaction mechanisms of certain atmospheric chemical

402   processes at the molecular level, there are still some unresolved issues. For instance, it

403   is necessary to estimate the concentration scale of chemical processes occurring at the

404   air-water interface to assess the significance of these specific chemical processes.

405   Estimating the energy barriers of reaction pathways occurring at this interface is

406   essential to determine the impact of these processes on atmospheric chemistry.

407   Furthermore, it is essential to assess the influence of more complex compositional

408   conditions, such as different pH values, ionic strengths, gas-liquid contact areas, and

409   the morphology and size of hydrated aerosol particles, on the reactions at this interface.

410

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. 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

432 underlying water column(Gašparović et al., 2007), atmospheric dry and wet

433 deposition(Milinković et al., 2022; Hunter and Liss, 1977), sediments, etc. In general,

434 the SML is enriched with substances such as sugars, amino acids, proteins, lipids,

435 colloids, etc.(Liss and Duce, 1997; Laß et al., 2013; Laß and Friedrichs, 2011).

436 Enrichment Factor (EF) is generally used to represent the degree of enrichment of

437 substances in SML, as follows:

438
$$EF_{SML} = \frac{C_{SML}}{C_{SSL}} \qquad (Eq-1)$$

439 In the above equation, C_{SML} represents the concentration of a substance in the surface

440 microlayer, and C_{SSL} represents the concentration of a substance in the corresponding

441 lower layer of water in the surface microlayer. Some EFs of SML relevant for the ocean-

442 atmosphere interactions and implications are shown in Table 1.

443

444 **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 DOC 4.3-8.1 Surface pressure	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	

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

449 Most of the substances listed in Table 1 are typically enriched in SML through rising

450 bubbles or diffusion. These compounds which constitute the primary organic

451 components of the SML, not only confers biochemical activity to SML, but also

452 modifies its physical properties such as dampening ocean surface waves. Current

453 research indicates that SML significantly suppresses gas exchange between ocean and

454 atmosphere. Furthermore, the physicochemical processes within the SML are closely

455 linked to the budget of marine atmospheric VOCs, primary and secondary organic

456 aerosols. Consequently, accounting for SML-specific processes is imperative when

457 estimating the transfer rate of greenhouse gases(Pereira et al., 2018) and marine aerosol

458 budget.

459   Surfactant activity (SA) is one of the most important physicochemical parameters of

460   the SML, determined by the surface adsorption behavior of its surfactant compounds.

461   Surfactants, also known as surface-active substances, are compounds that can

462   significantly reduce surface tension or interfacial tension between two liquids, liquid-

463   gas, and liquid-solid. The surface tension of pure seawater (devoid of organic matter

464   and particulate material) slightly varies with temperature and salinity, typically ranging

465   from 73 to 75 mN m^{-1}(Nayar et al., 2014). In comparison to pure seawater, the surface

466   tension of coastal sea surface decreases by 10-15 mN m^{-1}, while that of remote ocean

467   surfaces generally decreases by 0.5-1 mN m^{-1}(Frew and Nelson, 1992). Studies have

468   reported that the SA of the SML is 0.1-1.57 mg L^{-1} T-X-100(Wurl et al., 2011;

469   Sabbaghzadeh et al., 2017). Surfactant enrichment in the SML is greater in oligotrophic

470   regions of the ocean than in more productive waters(Wurl et al., 2011). For instance,

471   the SA of the SML in the Northern Hemisphere is significantly higher than that in the

472   Southern Hemisphere, with higher enrichment of surfactants in the Southern

473   Hemisphere Oceans(Sabbaghzadeh et al., 2017). This enrichment persists even at wind

474   speeds reaching 13 m s^{-1}(Sabbaghzadeh et al., 2017), which suggests that the SML is

475   stable enough to exist even at the global average wind speed of 6.6 m s^{-1}.

476   Temperature is an important parameter influencing surface adsorption behavior(Pereira

477   et al., 2018). Results from a two-year continuous observation experiments show that

478   SA of the SML varies seasonally, displaying a quasi-sinusoidal pattern from early to

479   late in the year. This variation corresponds to changes in phytoplankton productivity,

480   suggesting that variations in temperature, sunlight radiation, and nutrient input (from

481   rivers) influencing primary productivity and salinity changes may be the driving forces

482   behind SA variations(GašParović and Ćosović, 2001). This conclusion aligns well with

483   findings from other studies, showing that sunlight radiation-induced degradation of

484   large-molecule CDOM leads to an increase in SA(Rickard et al., 2022). Therefore, a

485   deeper understanding of the photochemical processes in the SML is crucial for

486   comprehending the transfer rates of important trace gases such as CO_2, CH_4, N_2O and

487   DMS at the ocean-atmosphere interface, with significant implications for

488   environmental climate studies(Rickard et al., 2022).

489

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. 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. Instead, SA enrichment is more related to the SA in subsurface water(Sabbaghzadeh et al., 2017; Pereira et al., 2016). Additionally, while chlorophyll

511 α is widely used as a proxy for primary productivity(Pereira et al., 2016), field studies

512 have shown it to be an unreliable indicator for parameterizing the inhibitory effect of

513 surfactants in the SML(Sabbaghzadeh et al., 2017). Table 2 summarizes the impact of

514 surfactants on the transfer rates of CO_2 at the air-water interface.

515

516 **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)

517 *Suppression of the gas transfer velocity.
518

519 Currently, the variations in the mass fraction of surfactants in the DOM carbon pool in

520 the SML are believed to be the reason for the large discrepancies in the estimated values

521 of gas transfer velocity of CO_2 shown in Table 2(Pereira et al., 2016). In addition to

522 CO_2, surfactants on water surface also impact gas-to-liquid phase transfer process of

523 other gases, such as nitric acid (HNO_3), ammonia(NH_3), O_3 and nitrogen pentoxide

524 (N_2O_5) through forming a well ordered, dense film(Clifford et al., 2007; Stemmler et

525 al., 2008; Rouvière and Ammann, 2010; Thornton and Abbatt, 2005; Cosman and

526 Bertram, 2008). Compared to branched-chain structures, straight-chain surfactant

527 organic compounds exhibit the strongest inhibitory effect on gas absorption(Cosman

528 and Bertram, 2008).

529 Surfactants in SML can also physically modulate interfacial chemical reactions. For

530 instance, authentic SML has been shown to suppress significantly the chemical

531 generation rate of gaseous $I_{2(g)}$ from O_3 + I_2 reaction at SML through enhancing

532   solubility of I_2 in SML(Schneider et al., 2022). Additionally, surfactants accumulating

533   at the water surface can form an organic phase, enabling otherwise water-insoluble

534   substances to dissolve into the organic layer. This enrichment elevates the organic

535   concentration at the interface, facilitating chemical reactions that are

536   thermodynamically or kinetically constrained in bulk aqueous phases. A notable

537   example is the role of organic films in promoting the enrichment of polycyclic aromatic

538   hydrocarbons (PAHs)(Donaldson, 2006), which may subsequently undergo

539   photochemical degradation upon solar irradiation(Jiang et al., 2021; Mekic et al.,

540   2020c). Similarly, photosensitizers like 4-carboxybenzophenone (4-CB) and imidazole-

541   2-carboxaldehyde (IC) are "attracted" to the surface when fatty acids or fatty alcohols

542   coat the liquid surface, thereby initiating photochemical reactions(Tinel et al., 2016).

543   Sum frequency generation experiments have revealed that soluble monosaccharides in

544   solution can strongly adsorb to lipid monolayers covering the solution surface *via*

545   coulombic interactions under appropriate conditions(Burrows et al., 2016). This "co-

546   adsorption" phenomenon is critically important for interfacial photochemical processes

547   in the SML, as it enhances the reactivity and compositional complexity of the organic

548   layer.

549

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

571 organic matter (OM) to the surface(De Leeuw et al., 2011). Rising bubbles transport

572 OM to the surface. At the air-sea interface, bubble bursting releases SSA through two

573 mechanisms: "film jet" (submicron particles) from bubble film rupture and "drop jet"

574 (supermicron particles) from cavity collapse(Brooks and Thornton, 2018; Quinn et al.,

575 2014; Prather et al., 2013; Quinn et al., 2015). Therefore, wind speed, particularly on

576 sea surface(Russell et al., 2010; Liu et al., 2021a; Parungo et al., 1986), and the

577 physicochemical properties of surface seawater, such as sea surface temperature(Liu et

578 al., 2021a; Christiansen et al., 2019; Sellegri et al., 2006; Mårtensson et al., 2003),

579 salinity(Mårtensson et al., 2003; Tyree et al., 2007), and SA(Cochran et al., 2016a), are

580 considered as crucial factors determining the mechanisms of SSA production.

581 As shown in Figure 2, the SML is believed to play a crucial role in SSA

582 formation(O'dowd et al., 2004; Russell et al., 2010; Wang et al., 2015), as it is inherently

583 involved in SSA production through bubble bursting and wave breaking(Schmitt-

584 Kopplin et al., 2012), (i) linking its organic composition to SSA's chemical

585 makeup(Lewis et al., 2022); (ii) modulating bubble lifetime and properties(Modini et

586 al., 2013) and (iii) influencing SSA production mechanisms, all of which are primarily

587 results of the presence of enriched surface-active organic materials (i.e., surfactant)

588 such as lipids and fatty acids(Mochida et al., 2002; Cochran et al., 2016b; Cochran et

589 al., 2016a; Cochran et al., 2017; Wang et al., 2015) and OM with positive buoyancy

590 (e.g. EPSs) at SML(Keith Bigg et al., 2004). Such impact could further modulate the

591 ice-nucleating particles (INPs) and cloud condensation nuclei (CCN) budget in marine

592   atmosphere. Hence, bridging the link between SML and SSA organic composition is

593   therefore important for understanding the physicochemical properties of SSA and their

594   subsequent environmental and climatic effects(Russell et al., 2010).

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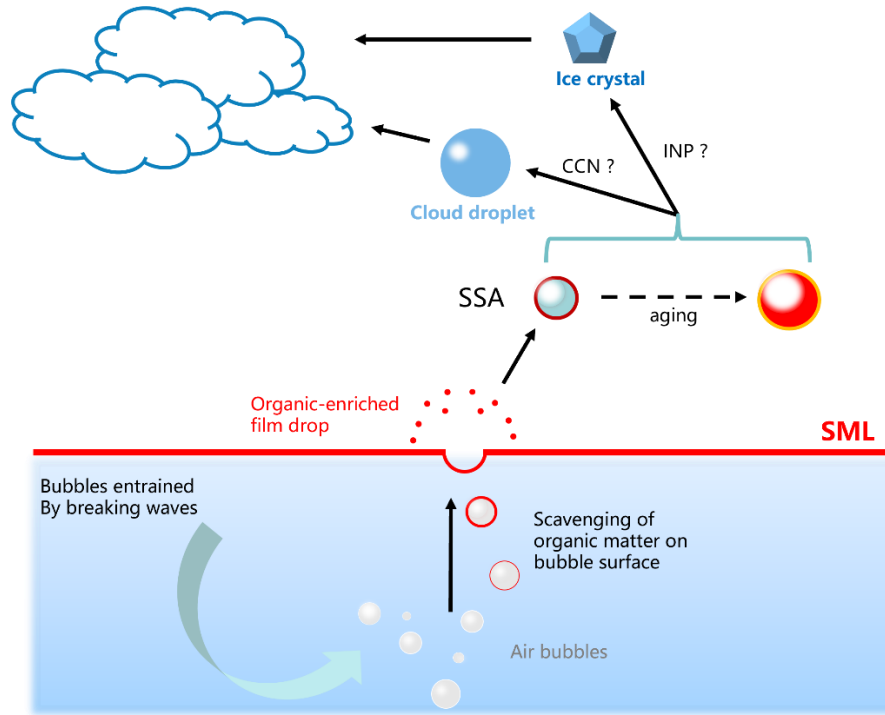
596
597 **Figure 2:** Illustration of the role of SML in regulating SSA production and properties
598 which could further affect its ice nucleating and cloud condensation potentials and
599 eventually cloud formation.

600

601   This is especially true for submicron SSA, given their dominant quantity, relatively high

602   organic fraction and efficient light scattering compared to supermicron SSA(O'dowd et

603   al., 2004; Quinn et al., 2015). It has been shown that the submicron SSA is

604   predominately constituted by water insoluble organic matter with surfactant

605   characteristics during high biological activity periods(Facchini et al., 2008; O'dowd et

606   al., 2004). This is evidenced by aliphatic-rich organic species dominated submicron

607 mode of SSA size distribution measured by aerosol mass spectrometry and Raman

608 spectroscopy(Wang et al., 2015; Cochran et al., 2017) and by a relative increase in

609 surface-active compounds in comparison with the surface water measured by Fourier

610 transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and nuclear

611 magnetic resonance spectroscopy (NMR)(Schmitt-Kopplin et al., 2012), and other high

612 resolution mass spectrometry(Cochran et al., 2016b). The ocean biology associated

613 surfactants exhibited high SA, resulting in their enrichment in the SML; thus, provide

614 efficient transfer such as long-chain fatty acids into film-drops during the bubble

615 bursting process at SML(Cochran et al., 2017; Schmitt-Kopplin et al., 2012). The

616 presence of biogenic surfactants can modulate bubble microphysics such as persistence

617 time and bubble film cap thickness(Modini et al., 2013) and subsequent bursting

618 process, resulting in the size distributions shift toward smaller sizes(Sellegri et al., 2006;

619 Tyree et al., 2007; Fuentes et al., 2010a), particle flux enhancement in Aiken mode

620 while suppression in other modes(Fuentes et al., 2010b; Sellegri et al., 2006), and

621 suppression in the total number particles produced(Modini et al., 2013). This change

622 has also been observed during a course of two-week phytoplankton growth in a

623 mesocosm study(Alpert et al., 2015). However, the effect of surfactants is dependent

624 on phytoplankton type(Fuentes et al., 2010a; Alpert et al., 2015), bubble generation

625 method(Alpert et al., 2015), influenced by solubility(Modini et al., 2013) and could be

626 offset by the sea surface temperature(Sellegri et al., 2006) as observed in the annual

627 variation of marine aerosol particle size distribution modes(O'dowd et al., 2004). The

628   mode shifts induced by surfactants could alter the cloud-forming potentials of SSA, as

629   its particle size distribution and concentration of SSA are closely linked to its

630   environmental effects(Cochran et al., 2016b; Fuentes et al., 2010b; Collins et al., 2014;

631   Deane and Stokes, 2002; Laskina et al., 2015).

632   Understanding SML's impact on SSA composition requires widespread, simultaneous

633   measurements of both SSA and SML organic composition(Lewis et al., 2022), along

634   with further studies on mechanisms through which SML-enriched organics adsorb onto

635   bubble films and eventually into SSA(Burrows et al., 2014; Burrows et al., 2016;

636   Hasenecz et al., 2019; Carter-Fenk et al., 2021). Distinguishing 'fresh' from 'aged'

637   marine aerosols using ambient measurements represents another challenge in this topic.

638   Interferences may come from continental, anthropogenic influences and marine

639   atmospheric aging. The recent developments of *in-situ* primary marine aerosol particle

640   generator (Sea Sweep and MART)(Lewis et al., 2022; Bates et al., 2012; Quinn et al.,

641   2014; Bates et al., 2020) and large-scale wave tunnels(Prather et al., 2013; Sauer et al.,

642   2022; Cochran et al., 2016b; Demott et al., 2016; Collins et al., 2014; Ault et al., 2013;

643   Quinn et al., 2015) enable investigation on SSA's physicochemical properties and the

644   role of environmental factors under controlled conditions without external interferences.

645   However, Sea Sweep and MART reproduced limited size-resolved number distributions

646   that span the full range of that produced in ambient seawater(Bates et al., 2020; Lawler

647   et al., 2024). However, the complex design of large-scale wave tunnel, along with the

648   high requirements for operators and experimental equipment, limits its widespread

649   application(Mayer et al., 2020), and the systematic change of original water system (e.g.

650   filtration of zooplankton) may introduce unknown effects(Wang et al., 2015).

651

652

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654

655

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

677   both temporal and spatial scales. Therefore, the current understanding of relevant

678   scientific issues in this field mainly stems from field observational experiments and

679   laboratory simulation studies.

680   Low molecular weight carbonyl compounds (methanol, formaldehyde, and acetone)

681   observed in the SML were much higher than those in SSW(Dixon et al., 2013). Their

682   concentrations exhibited diurnal variations peaking in the afternoon, indicating that the

683   photolytic processes at the sea surface are the source of these carbonyl

684   compounds(Dixon et al., 2013). Schlundt et al. (2017) simultaneously measured a series

685   of oxygenated volatile organic compounds (OVOCs) in surface seawater and marine

686   air, finding correlations among these OVOCs, suggesting similar sources and sinks in

687   surface seawater. A five-year monitoring of acetone, methanol, and formaldehyde in the

688   tropical oceanic boundary layer, revealed that the tropical Atlantic region acts as a net

689   sink for acetone but a net source for methanol and formaldehyde(Read et al., 2012). A

690   modeling study indicated that tropical and subtropical oceans are mainly net sources of

691   acetone, while high-latitude oceans represent sources of acetone(Wang et al., 2020a).

692   Another modeling study suggested that the Northern Hemisphere oceans act as sinks

693   for acetone, while the Southern Hemisphere oceans is as source of acetone(Fischer et

694   al., 2012). Wang et al. (2019b) identified unknown sources of formaldehyde through

695   aircraft observations, indicating that the ocean is an important source of formaldehyde

696   in the MBL.

697   These observational data indicated that chemical processes occurring in the SML may

698   be significant sources of VOCs in the MBL(Mungall et al., 2017). Currently, known

699   sources of VOCs in the MBL cannot explain the observed concentration levels of

700   OVOCs in airborne and seaborne observational experiments(Sinreich et al., 2010),

701   suggesting the presence of unknown sources of OVOCs in the MBL(Singh et al., 2001;

702   Mungall et al., 2017). There are two conjectures regarding these sources: First, these

703   OVOCs may originate from the oxidation of nonmethane hydrocarbons (NMHCs) in

704   the atmospheric boundary layer. Due to their longer chemical lifetimes compared to

705   NMHC precursors, they exhibit higher concentrations in the boundary layer atmosphere.

706   Second, OVOCs may also originate from biological and chemical processes occurring

707   in the SML, such as multiphase oxidation reactions between substances in the SML and

708   atmospheric oxidants, or photodegradation processes of substances in the SML(Singh

709   et al., 2001). These processes are likely driven by biological activities in the SML,

710   although this biological driving relationship has not been fully established. This is

711   mainly because the chemical processes occurring in the SML are currently understood

712   primarily from results obtained by laboratory simulation experiments or theoretical

713   model simulations(Carpenter and Nightingale, 2015). For instance, simulation study

714   results suggested that photochemical processes occurring in the SML contribute to the

715   formation of VOCs in the MBL at levels comparable to directly emitted VOCs from

716   marine biological activities(Bruggemann et al., 2018). However, it remains uncertain

717   whether these research findings can be representative of the mentioned chemical

718   processes in the real world. On temporal and spatial scales, more extensive sampling

719   and characterization of the SML are needed to clarify the main biogeochemical

720   processes and influencing factors in this interface environment, especially the

721   production, consumption mechanisms, and chemical compositions of surface-active

722   substances. Only by deepening our understanding of this critical interface environment

723   we may ultimately elucidate its effects on the climate.

724   In summary, current understanding suggests that marine VOCs primarily originate from

725   three main processes: (*i*) direct emissions from marine biological activities such as

726   DMS, isoprene, and monoterpenes released by the algae metabolism(Shaw et al., 2010;

727   Novak et al., 2022; Halsey and Giovannoni, 2023), (*ii*) photochemical processes

728   releasing OM from the SML of seawater(Carpenter and Nightingale, 2015; Novak and

729   Bertram, 2020; Zhu and Kieber, 2018), and (*iii*) emissions of atmospheric trace gases

730   from the interface oxidation processes at the ocean surface(Zhou et al., 2014; Schneider

731   et al., 2019; Wang et al., 2023; Wang et al., 2022b). Compared to (*i*) and (*ii*), research

732   on (*iii*) is relatively limited, and this aspect will be further elaborated in the following

733   sections.

734

735   *5.1 Photosensitized processes at SML as a source of VOCs and SOA in the MBL.*

736   The photochemical processes occurring in the SML are one of the most significant

737   drivers of biogeochemical processes, including the generation, degradation, and

738   transformation of DOM. In recent years, many researchers have conducted extensive

739 and in-depth research focusing on the scientific question: "How do the photochemical

740 processes transform DOM into VOCs, and how does this impact the formation of SOA

741 in the MBL?"

742 The organic compounds that exhibit photochemical activity in the SML are referred to

743 as chromophoric dissolved organic matter (CDOM). Upon absorption of ~~UV~~ light with

744 sufficient energy, a given CDOM molecule gets electronically excited (electrons

745 undergo excitation from their ground state to higher-energy unoccupied or singly

746 occupied molecular orbitals) and goes to an excited singlet state (^{1}CDOM*) which then

747 react immediately or quickly relax to the lower vibrational levels. The remaining excess

748 energy is subsequently released via mechanisms including photochemical reactions and

749 nonreactive processes such as fluorescence, internal conversion and~~by~~ intersystem

750 crossing (ISC) where the singlet state decays to~~becomes an~~ the lower-energy excited

751 triplet state (^{3}CDOM*). Both, ^{1}CDOM* and ^{3}CDOM* can induce formation of

752 hydroxyl radical (OH), singlet oxygen ($^1O_2$), superoxide (O_2^-), H_2O_2, aqueous electron

753 (e^-_{aq}), and organic radicals through various mechanisms(Sharpless and Blough, 2014;

754 Mcneill and Canonica, 2016). Photosensitized reaction represents a special subset of

755 photochemical reactions. In this process, CDOM acts as a sensitizer, its absorption of

756 light initiates chemical reactions involving a second species, resulting reforming

757 CDOM and/or generating excited or ionized states of the second species and other

758 species.~~In addition, an energy transfer occurs between CDOM and surrounding DOM~~

759 ~~molecules, manifesting as a series of important photochemical reactions such as~~

760 ~~photolysis, photosensitization, and photooxidation~~ This represents a key characteristic

761 of photosensitized processes: they enable photoreactions at wavelengths where the

762 "target" molecule itself does not absorb light(George et al., 2015; Gomez Alvarez et al.,

763 2012). The SML, as the top layer of the ocean surface is directly exposed to the most

764 intense solar radiation, experiencing intensified SA under high-intensity UV radiation,

765 although there is still ~10% of the surface UVA radiation (at 360 nm) presenting at a

766 depth of 50–70 m in most oligotrophic waters (Lee et al., 2013; Smyth, 2011). This SA,

767 also known as surfactant activity, is positively correlated with CDOM concentration but

768 negatively correlated with salinity(Rickard et al., 2022; Sabbaghzadeh et al., 2017;

769 Penezić et al., 2023). The photochemical processes occurring in the SML not only serve

770 as significant sources of VOCs in the MBL but also act as important transformation

771 sites for key atmospheric trace gases such as O_3, NO_2, and SO_2.

772 Nonanoic acid (NA) is the representative compound of lipid and saturated fatty acids,

773 which are the most important biogenic DOM in the SML. When NA is present in the

774 air or dissolved in water, its main absorption band peaks around 212 nm, while the

775 absorption band around 272 nm is extremely weak resulting in minimal light absorption.

776 However, the intensity of the absorption band at 272 nm increases and extends towards

777 340 nm as the concentration of NA enriched in the SML rises. When reaching the

778 monolayer concentration (~0.6 mM), the light absorption extending to around 290-350

779 nm can induce electronic excitation to the excited triplet state of NA (^{3}NA*), which can

780 subsequently either undergo cleavage to form OH radicals and C_9 acyl radicals or

781 capture hydrogen ions from other NA molecules to generate C_9 alcohol radicals and C_9

782 carboxylic acid radicals(Rossignol et al., 2016). Figure 3 shows the NA chemistry at

783 the air-water interface and in the bulk water.

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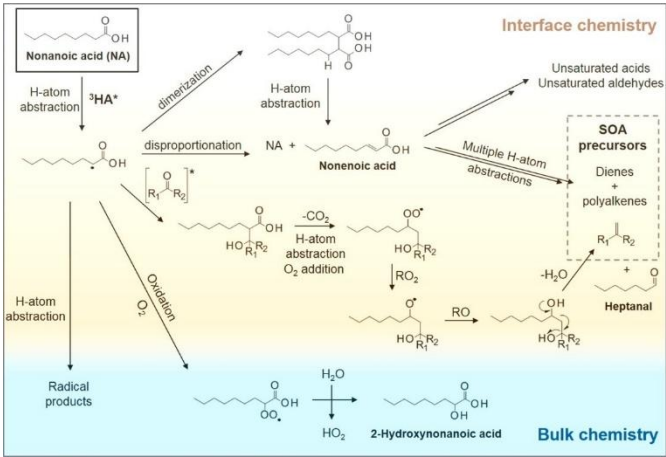

785
786 **Figure 3.** Reaction pathways of Nonanoic acid at the air-water interface and in the bulk
787 water(Bernard et al., 2016).

788

789 These processes initiate subsequent radical chemistry, ultimately leading to the

790 formation of a variety of VOCs containing multiple functional groups(Rossignol et al.,

791 2016). Although recent study suggested impurity contribution to UV absorption of

792 saturated fatty acids(Saito et al., 2023), the results nevertheless support the idea that

793 photosensitized chemistry at the ocean surface can be a source of VOCs(Schneider et

794 al., 2024).

795 Currently, few proxy compounds representing CDOM species such as 4-carboxy

796 benzophenone (4-CB)(Gomez Alvarez et al., 2012; De Laurentiis et al., 2013),

797 imidazole-2-carboxaldehyde (IC)(Felber et al., 2020; Martins-Costa et al., 2022; Tsui

798 et al., 2017), and humic acid (HA) are widely used in exploring the impact of

799   photochemical processes occurring in the sea SML on the marine atmosphere(Tinel et

800   al., 2016; Fu et al., 2015; Ciuraru et al., 2015b). Experimental findings indicated that

801   4-CB and IC are attracted to the liquid surface by the fatty acids or fatty alcohols (e.g.

802   nonanoic acid and 1-octanol) that are enriched at the sea surface(Fu et al., 2015).

803   Moreover, saccharides and polysaccharides are also attracted to the sea surface by lipids

804   (Burrows et al., 2016). This "co-adsorption" phenomenon suggests the presence of

805   highly active photosensitized chemical processes at the SML. The excited triplet states

806   of the photosensitizers (e.g. 4-CB, IC) can initiate radical chemical reactions by

807   abstracting hydrogen (H) atoms from other organic substances present at the SML, such

808   as NA and octanol(Fu et al., 2015). After losing an H atom the NA radical can undergo

809   reactions such as addition with oxygen molecules or radical-radical reactions,

810   ultimately leading to the formation of VOCs with different volatilities(Tinel et al.,

811   2016). This reaction pathway occurring at the sea surface is similar and competitive to

812   the H-abstraction mechanism initiated by OH radicals. Laboratory observations have

813   shown that the photosensitized processes initiated by CDOM* can convert DOC

814   present in the SML into VOCs containing double bonds and carbonyl groups, such as

815   C_2-C_4 olefins(Riemer et al., 2000) and isoprene(Bruggemann et al., 2018). Furthermore,

816   the oxidation of triplet-state phenol by halide anions in SML is considered as a source

817   of marine atmospheric halogen radicals(Jammoul et al., 2009).

818   Humic substances (HS) enriched at the SML can also induce similar photosensitized

819   processes(Ciuraru et al., 2015b). The photodegradation processes of triglycerides

820 released by phytoplankton and unsaturated fatty acids such as oleic acid and linoleic

821 acid are considered as *in situ* sources of HS in the ocean(Kieber et al., 1997). The photo-

822 generation of humic-like compounds has also been observed in lake water(Carena et al.,

823 2023). The excited-state of humic-like compounds play a crucial role in the oxidative

824 degradation of DOM and the generation of VOCs such as isoprene(Ciuraru et al., 2015b;

825 Ciuraru et al., 2015a), small molecular carbonyl compounds like formaldehyde,

826 acetaldehyde, α-keto acids, etc(Mopper et al., 1991; Kieber et al., 1990; Kieber and

827 Mopper, 1987). Additionally, processes including the formation of low molecular

828 weight carbonyl compounds (acetaldehyde, glyoxal, and methylglyoxal)(Zhou and

829 Mopper, 1997; Zhu and Kieber, 2019) are significant. Trueblood et al. (2019) compared

830 the photochemical reactions between NA liquid films and 4-CB, humic acid, and DOM

831 extracted from algal bloom seawater samples as photosensitizers(Trueblood et al.,

832 2019). Although the photosensitization effect of DOM from seawater was found to be

833 relatively low, this study provided evidence that photosensitized reactions can indeed

834 occur in real environments(Trueblood et al., 2019).

835 It has been shown that pyruvic acid (PA) as a representative compound of α-dicarbonyl

836 compounds can initiate photosensitized chemistry at the sea surface(Gomez Alvarez et

837 al., 2012; Anglada et al., 2020a). Upon sunlight irradiation, the ketone form of PA is

838 first excited to the singlet state and then by intersystem crossing goes to the excited

839 triplet state (^{3}PA*). The excited triplet state of PA can react with another PA molecule

840 in its ground electronic state either by the abstraction of the acidic hydrogen atom *via*

841 proton coupled electron transfer(Guzmán et al., 2006) or a concerted hydrogen atom

842 abstraction(Griffith et al., 2013) which can further initiate a chain of reactions that

843 induce decarboxylation, and the formation of oligomers(Guzmán et al., 2006; Griffith

844 et al., 2013; Eugene and Guzman, 2019; Reed Harris et al., 2017; Kappes et al.,

845 2021).The formed oligomers at the air-water interface can further affect the VOCs

846 fluxes between the ocean and the atmosphere.

847 Pyruvic acid absorbs UV fraction of sunlight with its n→π* transition band (λ_{max} = 318

848 nm) at the surface water(Gordon et al., 2019). More interestingly, the absorption

849 spectrum of PA is red shifted by 13 nm when going from dilute aqueous solution (λ_{max}

850 = 318 nm) to a solution with ionic strength (NaCl), (I) = 2.7 M (λ_{max} = 331nm)(Mekic

851 et al., 2019).

852 Considering that pH of seawater is around 8, PA will be present as pyruvate which is

853 the conjugate base of pyruvic acid, arising from deprotonation of the carboxy group.

854 Analysis by 1H NMR photolysis experiments of PA has shown that the presence of Ca^{2+}

855 and Na^+ in the sea water can further deprotonate PA(Luo et al., 2020).

856 It has been shown that charged species at the air-water interface, such as deprotonated

857 PA, would enhance the intensity of vibrational sum frequency in the coordinated-OH

858 stretching region (~3000−3400 cm^{-1}). The examination of OH stretching band provides

859 a means to qualitatively evaluate the presence of charged species without needing to

860 know the actual percentage of deprotonated species(Gordon et al., 2019).

861   Multiphase chemistry of PA indicated that the air-water interface plays a significant role

862   in promoting chemistry not possible in either the gas or bulk aqueous phase(Kappes et

863   al., 2021). Interestingly, PA acting as a photosensitizer, may initiate cross reactions with

864   other organics such as glyoxal(Mekic et al., 2019) and glyoxylic acid(Xia et al., 2018),

865   leading to formation of highly oxygenated multifunctional compounds which remain in

866   the water or partition to the gas phase according to their physical and chemical

867   properties (molecular mass, boiling point, etc).

868   PAHs are ubiquitous compounds at the ocean surface. Although many efforts have been

869   made to reduce the emission of PAHs, their concentrations in the aquatic environment

870   remains high(Ravindra et al., 2008; Keyte et al., 2013). The primary emitted PAHs are

871   deposited into the surface waters *via* atmospheric deposition(Ma et al., 2013). It has

872   been shown that PAHs play an important role in the photochemical processes of SML.

873   Fluorene (FL), for example, can act as a photosensitizer at the sea surface while

874   irradiated by sunlight and initiate photochemical formation of toxic compounds and a

875   wide variety of functionalized and unsaturated organic compounds in both the aqueous

876   phase and gas phase(Mekic et al., 2020b). The photosensitized reaction between triplet

877   states of PAHs (pyrene, fluoranthene, and phenanthrene) and dimethyl sulfoxide

878   (DMSO) in the sea surface layer has recently been identified as a source of organic

879   sulfur compounds such as ethylsulfonylmethane, ethyl methanesulfonate,

880   methanesulfonic acid, methanesulfinic acid, hydroxymethanesulfonic acid, and 2-

881   hydroxyethanesulfonic acid in the marine atmosphere(Mekic et al., 2020c; Mekic et al.,

882   2020b).

883   Although significant efforts have been made to explore the photochemical processes

884   occurring in SML, the research framework mentioned above remains relatively

885   simplistic, primarily focusing on the photochemical characteristics of various organic

886   surfactants, with many environmental factors impacting the reactions not thoroughly

887   investigated. Although studies have shown a positive correlation between light intensity

888   and VOCs production rates(Alpert et al., 2017), the influence of other factors on the

889   overall rate of photochemical reactions remains to be investigated. In order to better

890   simulate the marine environment, researchers have attempted to increase the

891   complexity of the research system, by enhancing the complexity of

892   photosensitizers(Trueblood et al., 2019) or introducing inorganic salt components to

893   explore the photochemical processes in complex systems(Mekic et al., 2018a). It has

894   been shown that the photochemical processes occurring in the SML of marine and

895   freshwater bodies differ(Stirchak et al., 2021), and the chemical processes of organic

896   and inorganic substances in the SML are strongly coupled and complex. For example,

897   the ionic strength effect can quench ^{1}[DOM], increase the generation of steady-state

898   ^{3}[DOM] and $^1O_2$(Abdel-Shafi et al., 2001; Glover and Rosario-Ortiz, 2013), and the

899   increase in the concentration of steady-state ^{3}[DOM]* may be due to the ionic strength

900   effect suppressing the consumption of ^{3}[DOM]* through the electron transfer reaction

901   pathway(Parker et al., 2013). Decreasing the ^{3}[DOM]* indirectly affects the

902 photodegradation rate of other organic substances(Grebel et al., 2012). However, this

903 effect is selective for different types of ^{3}[DOM]*, such as halogens affecting the

904 photodegradation kinetics of anthracene, while having little effect on

905 phenanthrene(Grossman et al., 2019). Additionally, the ionic strength effect has been

906 reported to influence the photochemical generation of volatile organic sulfur

907 compounds (Figure 4)(Mekic et al., 2020c).

908

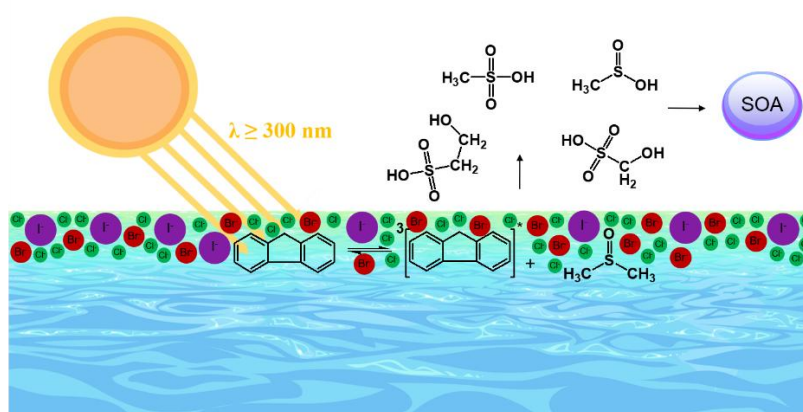



Figure 4: Simplified illustration of ionic strength effect on photosensitized reaction
between excited triplet state of fluorene and DMSO at the air-water interface.

911

912 Figure 4 illustrates the photosensitized reaction initiated by sunlight-activated fluorene

913 and dimethylsulfoxide (DMSO) in the presence of halide ions Cl$^-$, Br$^-$ and I$^-$. The

914 prompt formation of gas-phase methanesulfonic acid (CH$_3$SO$_3$H), methanesulfinic acid

915 (CH$_3$SO$_2$H), hydroxymethanesulfonic acid (CH$_4$O$_4$S), and 2-

916 hydroxyethenesulfonicacid (C$_2$H$_5$O$_4$SH) was observed. These compounds are typical

917 precursors of aerosol particles, and they are commonly detected in ambient

918 particles(Hopkins et al., 2008; Gaston et al., 2010).

919 Conversely, studies have reported that DOM can promote the photodegradation of

920 nitrates to produce reactive oxygen species(Wang et al., 2020b). Therefore,

921 investigating the behavior of photochemical processes in different salt gradients is

922 crucial for extrapolating laboratory data to real environments.

923 While significant progress has been made in related studies, these research systems still

924 diverge considerably from real SML environments. This is manifested not only in the

925 much higher concentrations of simulated samples in the laboratory compared to real

926 environments(Rossignol et al., 2016) but also in the significantly lower photochemical

927 activity of real samples compared to experimental ones(Trueblood et al., 2019). For

928 instance, recent field measurements do not confirm a photochemical production of

929 isoprene at SML(Kilgour et al., 2024; Kim et al., 2017) as it has been shown in the

930 laboratory measurements(Ciuraru et al., 2015a). Therefore, many efforts have to be

931 taken to demonstrate that the chemical processes elucidated in the laboratory occur in

932 real environments. Additionally, the complexity of the environment, such as the

933 presence of inorganic salts, metal ions(Li et al., 2024a), etc., may greatly influence the

934 progress of chemical reactions, either promoting or quenching them, to the extent that

935 the chemical processes elucidated in the laboratory may not occur in real environments,

936 thus lacking practical significance. In order to investigate the chemical processes

937 occurring in real SML environments, it is imperative to continuously make more

938 complex the research system to better approximate the real environment.

939

940 *5.2 Multiphase chemistry of atmospheric oxidants at SML.*

941 In addition to being exposed to solar radiation, the SML is in direct contact with the

942 atmosphere, this thus drives a series of complex multiphase chemical processes at the

943 ocean-atmosphere interface (i.e. SML) where atmospheric oxidants are deposited.

944 Research estimates that approximately one-third of global O_3 deposition occurs at the

945 ocean surface, accounting for 600-1000 Tg O_3 yr^{-1}(Martino et al., 2012). Another

946 important and highly water-soluble acidic gas is SO_2, which exhibits significantly

947 higher deposition rates at the marine surface (pH ≈ 8). Observational studies indicate

948 that approximately 27% of atmospheric SO_2 is absorbed by the ocean(Faloona et al.,

949 2009). Furthermore, two-layer model estimates suggest that the annual flux of SO_2

950 deposited into the ocean is 150 Tg yr^{-1}(Liss and Slater, 1974), which is comparable to

951 the global anthropogenic emissions of SO_2 (95.8-119.8 Tg yr^{-1}(Zhong et al., 2020)).

952 This highlights the critical role of the ocean in regulating atmospheric oxidants

953 concentration. In addition to physical factors such as wind speed, surface turbulence,

954 and molecular diffusion, multiphase photochemical reactions at the SML play a

955 significant role in controlling the deposition rates of O_3 and SO_2(Chang et al., 2004;

956 Liss and Slater, 1974). These processes are also major sources of VOCs and other active

957 species in the marine atmosphere. For example, The multiphase chemical reaction

958 between ozone ($O_{3(g)}$) and iodide ions ($I^-_{(aq)}$) in the SML is a primary source of gaseous

959 iodine in the atmosphere (R-1)(Schneider et al., 2023). This reaction not only

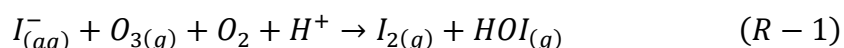
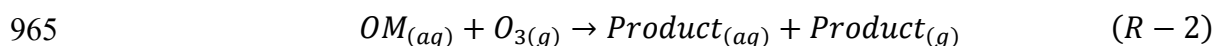
960 accelerates the dry deposition rate of atmospheric O_3 directly(Garland et al., 1980;

961 Chang et al., 2004), but also indirectly drives atmospheric iodine chemistry, leading to

962 new particle formation(He et al., 2023). These processes have significant implications

963 for the atmospheric environment.

964
$$I^-_{(aq)} + O_{3(g)} + O_2 + H^+ \rightarrow I_{2(g)} + HOI_{(g)} \qquad (R-1)$$

$$965 \qquad OM_{(aq)} + O_{3(g)} \rightarrow Product_{(aq)} + Product_{(g)} \qquad (R-2)$$

966   In addition to its reaction with $I^-_{(aq)}$, recent studies have demonstrated that the

967   multiphase chemical reaction between O_3 and OM (R-2) in the SML exhibits reactivity

968   comparable to R-1(Kilgour et al., 2024). Current research primarily focuses on the

969   universality of this reaction and its VOC products. For example, Zhou et al. (2014)

970   investigated multiphase chemical reactions between O_3 and oleic acid films, along the

971   western coast of Canada, and in the SML of the northeast Pacific, observing the

972   formation of carbonyl-containing VOCs. Schneider et al. (2019) explored O_3

973   multiphase chemistry with model SML samples (obtained by culturing *Thalassiosira*

974   *pseudonana* under sterile conditions) and detected the generation of C_7-C_9 carbonyl-

975   containing VOCs. Recently, our group employed liquid chromatography and mass

976   spectrometry to identify the molecular structures of primary VOC products from O_3

977   multiphase chemical reactions with 10 SML samples collected in the South China Sea

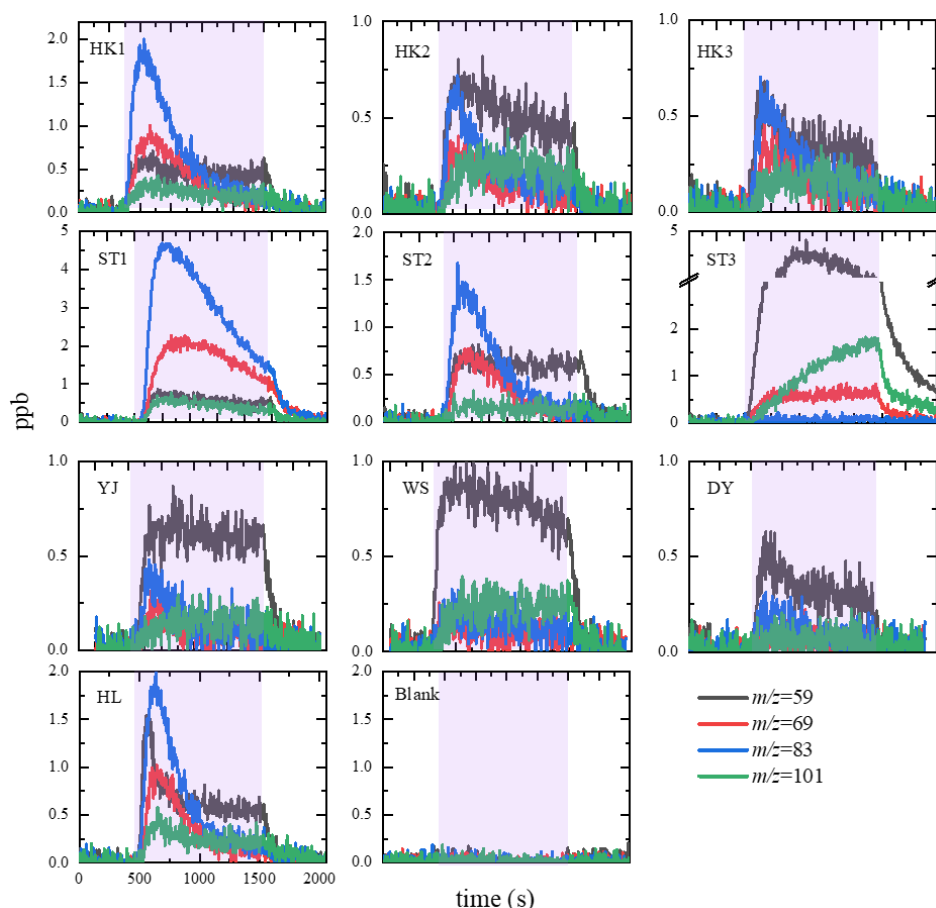
978   (e.g., acetaldehyde, acetone, propionaldehyde, and C_6–C_9 saturated aldehydes)(Wang

979   et al., 2023), providing a robust scientific foundation for assessing the atmospheric

980   environmental impacts of this reaction. Figure 5 shows the formation profiles of four

981   compounds, *m/z* 59, 69, 83, 101, observed in real time during the reaction of O_3 (100

982   ppb) with ten SML samples collected from coastal areas and open sea in South China

983   Sea.

984
985 **Figure 5:** Formation profiles of *m/z* 59, 69, 83, 101 as a function of relative time
986 measured by PTR-ToF-MS with H_3O^+ as reagent ion. The sensitivities used for
987 converting the signals (ncps) into concentration (ppb) are acetone-based. To reduce the
988 noise, the data have been treated with a moving average smoothing with a period of 5s.
989 Pink background represents the period of ozone (100ppb) exposure on SML samples
990
991 This study aligns well with two following studies, one examined O_3 multiphase

992 chemistry in SML from coastal waters near California, observing the formation of C_5-

993 C_{11} aldehyde VOCs(Kilgour et al., 2024), and another investigated O_3 reactions in the

994 Arctic Ocean SML, detecting acetaldehyde, acetone/propionaldehyde, and other

995 aldehyde VOCs(Schneider et al., 2024). While there are minor differences among the

996 observed VOCs product, they collectively indicate that the multiphase chemical

997 reaction between atmospheric O_3 and OM in the SML is a significant driver of O_3 dry

998 deposition. Furthermore, this reaction represents an important source of carbonyl-

999 containing VOCs in the marine atmosphere. It is worth emphasizing that our group and

1000 Schneider et al. (2024) independently observed similar nitrogen-containing VOCs (e.g.,

1001 amines and nitriles) in the studies of SML from the South China Sea and the Arctic

1002 Ocean, respectively(Schneider et al., 2024; Wang et al., 2023; Wang et al., 2022b).

1003 These findings suggest that this reaction may also serve as a source of reactive nitrogen

1004 in the marine atmosphere. Taking one of the primary reaction products, nonanal (C_9

1005 saturated aldehyde), as an example, its reaction rate with atmospheric hydroxyl radicals

1006 (OH) is approximately an order of magnitude faster than that of DMS. Specifically, the

1007 rate constants for DMS + OH and nonanal + OH are 4.80×10^{-12} and 3.60×10^{-11} cm^3

1008 $molecule^{-1}$ s^{-1}, respectively(Atkinson et al., 2004). Recent studies have further revealed

1009 that saturated aldehyde VOCs play a significant role in the regeneration of OH

1010 radicals(Yang et al., 2024). These findings suggest that O_3 multiphase chemical

1011 reactions in the SML may significantly alter the oxidation capacity of marine

1012 atmospheres and subsequently influence aerosol formation and the evolution of

1013 atmospheric composition. However, while current research has preliminarily identified

1014 the universality of this reaction and characterized its primary VOC species and

1015 molecular structures, uncertainties remain regarding the kinetic features of VOC

1016 emissions. Consequently, there is significant uncertainty in estimating the emission

1017 fluxes of VOCs from this reaction at present.

1018 Based on three independent studies, the annual flux of VOCs emitted into the

1019 atmosphere from the multiphase chemical reaction between O_3 and OM in the SML has

1020 been estimated as follows: 45-450 Tg yr^{-1} (Schneider et al., 2024), 17.5-87.3 Tg yr^{-1}

1021 (Novak and Bertram, 2020), and 10.7-167 Tg yr^{-1}(Kilgour et al., 2024). While these

1022 estimates exhibit significant uncertainty, it is notable that the lower bounds of all three

1023 datasets are comparable to the annual emission flux of DMS (20.3 Tg yr^{-1})(Hulswar et

1024 al., 2022). This further underscores the potential for substantial impacts of this reaction

1025 on marine atmospheric chemistry. In summary, to elucidate the atmospheric chemical

1026 fate and environmental-climatic effects of these reactive VOCs, investigating the

1027 kinetic characteristics of VOCs generation from this multiphase chemical reaction

1028 under different environmental conditions is essential. Such research will help better

1029 estimate the yields and production rates of VOCs products, making this one of the key

1030 focuses for the future study.

1031 In addition to O_3, SO_2 can also undergo multiphase chemical reactions with active

1032 substances in the SML, such as fatty acids(Passananti et al., 2016; Shang et al., 2016).

1033 In marine atmospheres, SO_2 primarily originates from terrestrial transport, shipping

1034 emissions, and in situ biological releases, with concentrations typically ranging from

1035 tens of parts per trillion to a few parts per billion(Nguyen et al., 1983; Kim et al., 2001;

1036 Li et al., 2024b). Among these sources, DMS and methanethiol (MeSH), released by

1037 marine phytoplankton metabolism, are the primary natural contributors of SO_2 in the

1038 marine atmosphere(Novak et al., 2022).

1039 Over the past decade, research on SO_2 has predominantly focused on the formation

1040 processes and mechanisms of sulfate aerosols(Liu and Abbatt, 2021; Liu et al., 2021b).

1041 However, studies on the multiphase chemical reactions of SO_2 at the ocean surface and

1042 their associated environmental effects have only recently begun to receive attention.

1043 Unlike O_3, SO_2 exhibits photochemical activity, adding another layer of complexity to

1044 its atmospheric chemistry.

1045

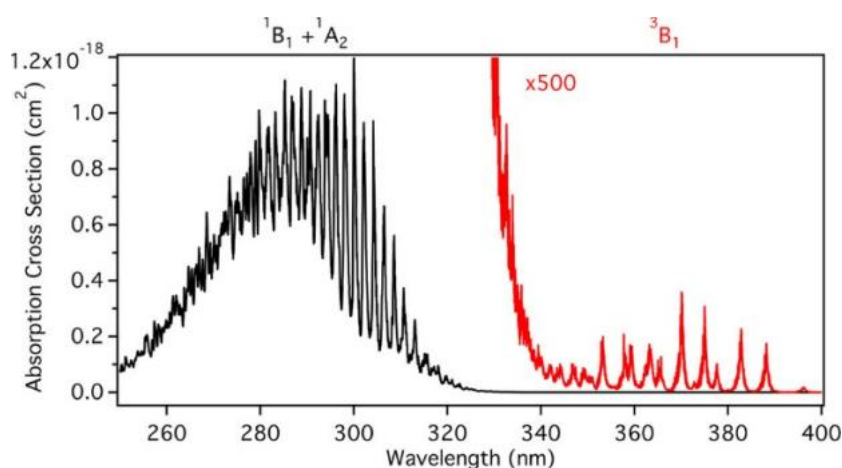
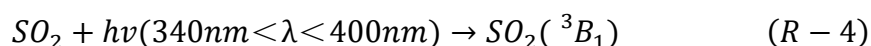
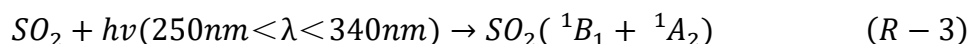



Figure 6: Spectrum of SO_2 showing the mixed $^1B_1$ and $^1A_2$ state from 250 to 340 nm and the forbidden $^3B_1$ state from 240 to 400 nm(Kroll et al., 2018b).

As shown in Figure 6, SO_2 absorbs radiation in the range of 250 nm < λ < 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 < λ < 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).

$$SO_2 + h\nu(250nm{<}\lambda{<}340nm) \rightarrow SO_2(\,^1B_1 + \,^1A_2) \qquad (R-3)$$
$$SO_2 + h\nu(340nm{<}\lambda{<}400nm) \rightarrow SO_2(\,^3B_1) \qquad (R-4)$$
$$SO_2(\,^3B_1) + H_2O \rightarrow OH + HOSO \qquad (R-5)$$

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 (3B1) 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. Liang et al. (2024) explored the multiphase photochemical reactions of SO_2 on biomass burning organic aerosols

1074   (BBOA), finding that the reaction between excited-state $^3BBOA^*$ and SO_2 is a major

1075   source of sulfate aerosols, rather than the reaction involving SO_2 in its triplet state (R-

1076   5). However, these studies did not further investigate the contribution of SO_2 multiphase

1077   photochemical reactions to atmospheric VOCs.

1078   Recently, our group studied the multiphase photochemical reactions of SO_2 on PAHs

1079   and PAH/dimethyl sulfoxide (DMSO) films, detecting the formation of sulfur-

1080   containing VOCs(Jiang et al., 2021). Subsequently, Deng et al. (2022) examined the

1081   multiphase photochemical reactions of SO_2 on urban building surfaces and found that

1082   photolytic conversion significantly enhances VOCs production. Notably, these VOC

1083   products are like those generated by O_3 reactions under simulated sunlight irradiation.

1084   This critical finding suggests not only that O_3 and SO_2 may share common precursor

1085   compounds in VOC formation but also implies similarities in their reaction mechanisms.

1086   For example, in the dark, both O_3 and SO_2 exhibit competitive effects on reactive

1087   functional groups such as the C=C bonds in unsaturated fatty acids(Passananti et al.,

1088   2016; Shang et al., 2016; Criegee, 1975). Under sunlight irradiation, SO_2 in its triplet

1089   state ($^3B_1$) and its derived radicals (R-5) could compete with O_3 for the same reactive

1090   functional groups. Therefore, it is crucial to study and analyze O_3 and SO_2 as a unified

1091   system to fully understand their roles in atmospheric chemistry and VOCs production.

1092   Although the concentration of O_3 in marine atmospheres is typically one order of

1093   magnitude higher than that of SO_2(Li et al., 2024b), and SO_2 may be oxidized to sulfate

1094   by O_3 in the aerosol phase(Yu et al., 2023), studies have shown that the chemical uptake

1095   reactivity of SO_2 at environmental interfaces (10^{-6}) is generally one order of magnitude

1096   higher than that of O_3 (10^{-7})(Shang et al., 2016; Wang et al., 2022a; Deng et al., 2022).

1097   Additionally, Passananti et al. (2016) observed chemical uptake of SO_2 and the

1098   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. 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. 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.

Phytoplankton communities in seawater have long been considered the primary source of reactive surfactants, such as fatty acids. Atmospheric deposition, in contrast, is typically viewed as a minor contributor, providing only supplementary nutrients. However, recent research reveals that wildfire smoke can directly deposit substantial quantities of microbes into the SML. This microbial input can be comparable to the estimated supply from seawater and may significantly diversify the SML's microbial community(Yue et al., 2025). Critically, biomass burning also transports biologically important trace metals particularly soluble iron (SFe), a well-established growth-limiting nutrient that can alter the growth rate and composition of the phytoplankton community(Bergas-Masso et al., 2025; Guieu et al., 2005; Mahowald et al., 2018). Model estimates indicate that rising SFe deposition, driven by increasing socio-economic activity, could boost phytoplankton productivity in the iron-limited North Atlantic by up to 20% annually(Bergas-Masso et al., 2025). Consequently, key

1124   questions arise: How does aerosol-induced modification of SML phytoplankton

1125   communities alter the production and abundance of reactive surfactants? Furthermore,

1126   how might these changes affect multiphase chemical reactions involving surfactants

1127   and atmospheric oxidants, with implications for atmospheric chemistry?

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CONCLUSION AND OUTLOOKS.

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1134 This review demonstrates that the ocean-atmosphere physicochemical interactions is an

1135 important scientific issue that remains to be further evaluated to better understand their

1136 influence on air quality and climate.

1137 Recent research has revealed that multiphase and heterogeneous chemistry occurring at

1138 ocean-atmosphere interface leads to the formation of numerous organic compounds

1139 which in function of their physical and chemical properties remain in the ocean waters

1140 or partition to the atmosphere and ultimately participate in the formation of SOA. The

1141 chemical composition of the ocean SML plays, yet unexplored, an important role with

1142 respect to the multiphase and heterogeneous chemical processes. The SML consists

1143 plethora of organic and inorganic compounds, with concentrations reaching one or more

1144 orders of magnitude higher relative to the underneath water. Surfactants which mostly

1145 emerged from phytoplankton bloom are enriched at the ocean surface by physical

1146 processes such as diffusion, turbulent mixing, scavenging and transport by bubbles

1147 influencing the exchange of gasses between the ocean and atmosphere. For example, it

1148 is still an enigma if the ocean is a source or a sink of some important carbonyl

1149 compounds (e.g. acetone, acetaldehyde).

1150 The importance of acetone in the atmosphere arises from the fact that sunlight induced

1151 photodissociation of acetone produces peroxyacetyl radicals which can be transformed

1152 to peroxyacetylnitrates (PAN) influencing the budget of nitrogen oxides (NO_x) which

1153 in turn affects the ozone concentration in the atmosphere(Singh and Hanst, 1981; Singh

1154   et al., 1994). In the upper troposphere photolysis of acetone leads to the production (30

1155   to 40% of the total) of OH radicals (Wang et al., 2020a). Acetaldehyde exhibits a fast

1156   rate constant with OH (k = 1.62×10^{-11} cm^3 $molecules^{-1}$ s^{-1}) and therefore it plays an

1157   important role in the atmospheric OH budget(Atkinson et al., 1997).

1158   Another important organic compounds enriched at the ocean surface are light absorbing

1159   molecules which are acting as photosensitizers and are capable of indirect

1160   phototransformation of the substrates of primary concern leading to the formation of

1161   VOCs that are released in the atmosphere.

1162   However, majority of the studies are performed under controlled laboratory conditions

1163   by using proxy compounds of photosensitizers. Therefore, it is uncertain to which

1164   degree photosensitized reactions occurring at the ocean surface can transform the

1165   organic compounds and ultimately lead to the VOCs formation. It is essential to

1166   increase the complexity of the studied samples and use authentic ocean SML to better

1167   understand the reaction mechanisms and ultimately the impact of the oceanic chemical

1168   processes on the VOCs and SOA formation processes. For example, recent study has

1169   shown the excited triplet states of authentic biomass burning organic aerosols can

1170   induce multiphase reactions such as SO_2 oxidation and formation of sulfate(Liang et al.,

1171   2024).

1172   The deposition of trace gases such as O_3 and SO_2 on the ocean surface and consequent

1173   chemical reactions can lead to the formation of VOCs in the atmosphere. Both oxidants

1174   react by addition to the C=C double bonds of unsaturated organic compounds enriched

1175   at the ocean surface. Intriguingly, O_3 reacts by addition to the C=C during nighttime

1176   (under dark conditions) and under sunlight irradiation, as well(Wang et al., 2023; Wang

1177   et al., 2022b), while this is not the case for SO_2. The formation of charge transfer

1178   complexes may occur between SO_2 and the alkenes present in the SML. As a result, the

1179   absorption spectrum of the formed charge transfer complexes may be altered extending

1180   from 315nm to 390 nm(Kroll et al., 2018b). During daytime under sunlight irradiation

1181   the formation of excited triplet state of SO_2 ($^3SO_2$*) may occur and consequently initiate

1182   photosensitized chemistry at the ocean-atmosphere interface(Kroll et al., 2018a).

1183   However, scientific knowledge of the reaction mechanisms of O_3 and SO_2 and their

1184   impact on VOCs is far from to be understood. Laboratory and field studies are

1185   recommended by using authentic ocean SML samples and combination of trace gases

1186   in dark and under sunlight irradiation supported by molecular dynamic simulation. Only

1187   by increasing the complexity of the research studies we can obtain relevant data to

1188   properly run the models and predict the impact of ocean-atmosphere interactions on the

1189   topical issues of 21st century such as air quality and climate change.

1190   The suggestions for future studies emerge from our own research plan commenting on

1191   issues that might be an important and interesting topic.

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