Impacts of marine organic emissions on low level stratiform clouds – a large eddy simulator study

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Abstract. The goal of this study is to investigate the role of organic aerosols emitted with sea spray or formed from marine gas phase emissions of volatile organic compounds (VOCs) in influencing the stability of stratiform marine clouds. We aim at pointing out the processes and drivers that could be relevant in larger scale and should thus be considered in global climate models.

We employ large eddy simulator that includes a detailed description of aerosols, cloud droplets and rain drops together with different model parameterizations for emission of sea salt, primary organic aerosol and VOCs from sea surface, and oxidation of the emitted VOCs and partitioning of the resulting semi-volatile organic species between vapor and aerosol phases. As a case study, we apply the model to simulate the conditions of the DYCOMS-II observational campaign characterized by low level stratocumulus clouds transitioning from closed cells to drizzling open cell structure.

We find that the inclusion of online sea spray emissions can both extend and shorten the lifetime of the cloud layer based on the parameterization employed. Fine sea spray provides extra cloud condensation nuclei (CCN) and delays the onset of drizzle as the collision-coalescence process is slowed down due to smaller cloud droplet mean size. From the same emissions, the coarse mode has an opposite effect due to giant CCN (GCCN) speeding up the drizzle formation through the enhanced collision-coalescence processes. The balance between two process depends on the model parameterization employed. Compared to differences between different sea spray parameterizations, the sensitivity of the clouds to the variations in organic fraction of sea spray and hygroscopicity of the emitted fine aerosols is relatively limited. However, our results show that it is important to account for the size dependence of the sea spray organic fraction as attributing organic emissions to coarse mode noticeably reduces the GCCN effect. In addition, including the secondary aerosol formation from VOCs can potentially have a noticeable impact, but only when emitting the highest observed fluxes of monoterpenes. This impact is also highly sensitive on the size distribution of the background aerosol population. SOA production from isoprene is visible only if aqueous phase SOA production pathways are included in the model, and even then, the effect is lower than from monoterpenes.

1   Introduction

The 5th Assessment Report of IPCC (2013) recognized aerosols and clouds as the dominant sources of uncertainty in climate projections and aerosol-cloud interactions remain challenging also for models in the 6th Assessment Report (Forster et al., 2021). They point out that in both Coupled Model Intercomparison Projects CMIP3 and CMIP5 aerosol-cloud interactions constituted the dominant source of inter-model differences and majority of this spread is attributable to differences in parameterizations for shallow clouds prevalent over oceans (Dufresne and Bony, 2008; Vial et al., 2013). Meehl et al (2020) and Zelinka et al (2020) show that the same still holds for the recent CMIP6 ensemble and call for more research into aerosol-cloud interactions.

In addition to available water vapour and updraft velocity that determines the cooling rate and thus the supersaturation, cloud droplet formation depends on the concentration of the available cloud condensation nuclei (CCN) (e.g. Rosenfeld et al 2019). The two major controlling factors of CCN concentration are aerosol number concentration and size distribution, while particle composition also can have an effect through the hygroscopicity (Bougiatioti et al., 2020). Thus, it is important to explicitly model the concentration, size distribution and composition of the CCN. Over the oceans the major source of CCN is sea spray (consisting of sea salt and organic species), and an additional noticeable contribution comes from secondary organic aerosols (SOA) formed from oxidation products of marine emitted volatile organic compounds (VOCs) (McCoy et al., 2015). It has been found challenging for models to reproduce the secondary and primary organic aerosols over remote ocean areas (Hodzic et al., 2020).

In the current modelling study, we investigate how marine emissions of sea spray and VOCs affect the low-level liquid clouds and how the emission related uncertainties transfer to the prediction of cloud properties. Large uncertainties still exist in the parameterizations of sea spray flux, size distribution and composition (Naik et al., 2021). These uncertainties are especially large during warm, biologically active periods, as both water temperature and organic content have been shown to impact the sea spray emission. Both of these factors are going to be impacted by the changing climate, but it is hard to distinguish these two effects when developing sea spray emission schemes for large scale models. Grythe et al (2014) compared a number of sea spray emission schemes and showed that the emitted mass fluxes can differ by more than an order of magnitude with strong disagreements in emitted size distributions and the wind speed and sea surface temperature (SST) dependence of the emission. Observations and model-measurement comparisons support the growth of sea salt mass flux with increasing SST (Jaeglé et al., 2011; Liu et al., 2021; Sofiev et al., 2011) and point out the importance of including it in model parameterizations. However, the case is not clear for the particle number flux that mostly consists of small particles. Forestieri et al (2018) show strong disagreements between laboratory experiments and large-scale model-measurement comparison based parameterizations – while the latter tend to extend the mass flux based monotonic temperature dependence also to the number flux, the laboratory experiments show a different dependence with increase of particle number flux for the low temperatures. For example, (Mårtensson et al., 2003) show different temperature dependence for fine and coarse sea spray, with the fine mode that dominates the number flux having opposite temperature dependence from the coarser

particles. However, as shown by (Barthel et al., 2019; Forestieri et al., 2018), large uncertainties exist in the magnitude of this dependence.

65 Cochran et al (2017) reported large diversity of molecules making up the organic fraction of sea spray, which varied depending on the prevalent phytoplankton and bacteria species in the surface water. Large fraction of these organic molecules are surface active and experiments conducted by Nielsen and Bilde, (2020) demonstrated a complex interdependence of the effects of temperature and organic surfactants to particulate emission from breaking bubbles. Considering these complexities, it is not surprising that disagreements exist related to the impact of the organic content of the

70 sea water. For instance, Modini et al (2013) show suppression of aerosol emission from bursting of a single bubble by organic surfactant, while Fuentes et al (2010) and Long et al (2014) report significant increase of particle number flux with increased dissolved organic carbon (DOC) content from diatomaceous exudates, and Bates et al (2020) and Mayer et al (2020) did not see any significant effect of plankton bloom on primary sea spray emission flux. According to Lv et al (2020) and Fuentes et al (2010), the effect depends on the type of surfactant or algal exudate, which might explain these

75 disagreements.

The organic content can also affect the particle hygroscopicity and thus its ability to act as CCN (Forestieri et al., 2016; Fuentes et al., 2011). Cochran et al (2017) showed that the hygroscopicity of the sea spray aerosol depended on the type of the organic molecules dominant in the sea spray, which varied between different sized particles. Size dependence of the composition has also been demonstrated by Ault et al. (2013), Facchini et al. (2008) and Kaluarachchi et al. (2022).

80 However, some other recent publications (Bates et al., 2020; Collins et al., 2016; Cravigan et al., 2020) have reported that the hygroscopicity of sea spray aerosol seems to stay largely invariable regardless the organic fraction, while Ovadnevaite et al (2011) reported a complex behaviour of low hygroscopic growth in aerosol phase combined with high CCN activation efficiency.

Marine emission of volatile VOCs plays an important role in controlling the size distributions of marine aerosol by

85 condensing on ultrafine particles and growing them to CCN size (Burkart et al., 2017; Croft et al., 2019, 2020; Yu and Li, 2021). In fact, the role of secondary marine aerosol has even been found to dominate over that of primary (Mayer et al., 2020). DMS is considered the most important source of CCN in the clean ocean areas, others include alkanes, alkenes, aromatics, terpenoids and amines, halogenated organics and oxygenated volatile organic compounds (OVOCs). Large amount of research already exists on DMS while, with the exception of the terpenoids, not enough is currently known about

90 the emission rates and chemistry of the other above-mentioned VOCs to include them in model simulations. Thus, in the current study we focus on isoprene and monoterpenes.

Isoprene has been detected in sea water and marine atmosphere (Kim et al., 2017; Rodríguez-Ros et al., 2020; Shaw et al., 2010; Yassaa et al., 2008). Its oxidation products have been observed in marine aerosol (Cui et al., 2019; Hu et al., 2013) and proposed to explain the observed variability in CCN concentration over Southern Ocean (Meskhidze and Nenes, 2006).

95 Little observational data exists of monoterpenes in ocean water (Button and Jüttner, 1989; Hackenberg et al., 2017), although its marine production has been confirmed (Yassaa et al., 2008) and relatively high air concentrations have been observed in

marine atmosphere (Kim et al., 2017; Shaw et al., 2010; Yu and Li, 2021) and its oxidation products have been detected in marine aerosol (Cui et al., 2019; Hu et al., 2013). While oceanic emission of monoterpenes is generally estimated to be smaller than that of isoprene (Meskhidze et al., 2015; Yassaa et al., 2008), it can have larger impact due to larger SOA yields 100 (Yu and Li, 2021).

However, the uncertainties in the terpenoid ocean to atmosphere fluxes are large and estimating their emissions either bottom-up from algal production or top-down from air concentrations leads to large discrepancy (Luo and Yu, 2010). Kim et al (2017) measured sea to air fluxes of both isoprene and monoterpenes. On average the fluxes were low while substantially higher peak values were observed over biologically active areas with recently elevated nutrient content due to increased 105 vertical mixing by wind or rising currents. This large variability can at least partly explain the challenges in estimating the emissions.

Clouds are influenced by covariations in air flows and aerosols in noticeably smaller spatial scale than the current resolution of climate models. Large eddy simulators (LES) can resolve these scales and have proved useful for understanding climate relevant cloud feedbacks (e.g. Bretherton, 2015). In the current study we use the UCLALES-SALSA large eddy simulator 110 with representation of aerosol-cloud-precipitation interactions (Tonttila et al., 2017), where we have included sea spray and gas phase emissions from sea surface. Our goal is to investigate the role of organic aerosols emitted with sea spray or formed from marine gas phase emissions of volatile organic compounds in stability of liquid phase clouds. In order to quantify the sensitivity of the lifetime of marine stratiform clouds to the above discussed processes and parameters we perform multiple model simulations with different published parameterizations of sea spray and terpenoid emissions. We aim to point out the 115 processes and drivers that can be relevant to climate in large scale and should thus be considered in climate models.

2   Methods

2.1 Model description

We use the UCLALES-SALSA model (Tonttila et al., 2017) that combines the large eddy simulator UCLALES (Stevens et al., 1999, 2005; Stevens and Seifert, 2008) with a detailed sectional model of aerosol microphysics SALSA (Kokkola et al., 120 2008, 2018) extended with cloud and precipitation processes. SALSA simulates microphysical processes such as coagulation, sedimentation, partitioning of water between vapour and liquid phases, activation of aerosols to cloud droplets and growth of droplets to form precipitation. Aerosol is described by two externally mixed modes, each consisting of a set of size bins with unique chemical composition. Separate tracers are used for the chemical species in aerosol and cloud phases and in precipitation. In the current study we used 15 bins ranging from 3 nm to 10 micrometres. Tracking the two externally 125 mixed modes allows us to separately follow the fate of the background aerosol and sea spray emitted during the simulation.

Several different sea spray emission parameterizations were included in the model. In various simulations in this study (Table 1) we make use of the emissions parameterizations by Mårtensson et al (2003), Gong (2003), Fuentes et al (2010) and Monahan et al (1986). In majority of the presented simulations (case names starting with F10 and G11 in Table 1) the

emission fluxes for submicron (dry) particles are modelled following Fuentes et al (2010) who parameterized the impact of
130   sea water dissolved organic content (DOC) on emitted aerosol number size distribution. As Fuentes et al (2010) do not
provide scaling from their experimental setup to emission from open ocean surface, we have scaled their flux to reproduce
the number flux of Mårtensson et al (2003) in the size range covered by both parameterizations (20-450 nm) at our base case
sea surface temperature of 10°C by multiplying it with 5500. The temperature dependence of submicron sea spray emission
for this parameterization is implemented following Forestieri et al. (2018), the smaller modes having no temperature
135   dependence and largest one increasing linearly. The flux of supermicron particles is computed following Monahan et al (
1986). To study the impact of the uncertainties in the sea spray emission parameterizations, extra simulations are made using
the temperature dependent scheme of Mårtensson et al (2003) extended with the Monahan et al (1986) scheme for sizes
coarser than 2.8 micron (M03 in Table 1) and Gong (2003) scheme (G03 in Table 1). Monahan et al (1986) and Gong (2003)
schemes are coupled with temperature dependence from Jaeglé et al (2011).

140   The selected sea spray flux size distributions are shown in Figure 1. As the Fuentes et al (2010) scheme (black) was scaled to
reproduce the flux of Mårtensson et al (2003) at 10° C (MO3, green line), the emissions by these schemes are relatively
similar. The parameterization by Gong (2003) (G03, blue line) was included in this study to cover the wide range of fluxes
predicted by various sea spray emission parameterizations, as it differs from the other used parameterizations by much lower
emission of small particles. As seen from comparing the black (F10) and brown (F10-DOC512) lines on Figure 1, the impact
145   of the largest concentration of dissolved organic carbon considered by Fuentes et al (2010) (512μM) on the emission flux of
the Aitken mode sea spray is comparable in size with the temperature effect shown for the Mårtensson et al (2003)
parameterization (light to dark green), while there is almost no effect on the rest of the size range.

The organic fraction of the emitted particles is computed following the wind, particle size and Chlorophyll alpha (Chl α)
dependent parameterization of Gantt et al (2011). Experiments with nonzero Chl α start with G11 in Table 1. As the relation
150   between Chl α and DOC in sea surface is complex (Fuentes et al., 2010; Van Pinxteren et al., 2017), this scheme is applied
independently of the DOC dependent sea spray flux parameterization. When using it, no changes are made to the total sea
spray flux or the emission size distribution, but for each size bin part of the sea spray is emitted as primary organic matter
instead of sea salt. Internal mixing of sea salt and organic matter is assumed. Hygroscopicity parameter of pure sea salt is set
to 1.0 (Christiansen et al., 2020) and 0.1 is used for organic matter, which is in the range reported by Kuang et al. (2020) for
155   SOA and by Fuentes et al. (2011) for algal exudate and only slightly lower than what was reported by Mayer et al. (2020) for
marine organic species. The effect of organic content on particle hygroscopicity is demonstrated by the yellow lines on
Figure 1. With high chlorophyll alpha concentration (2 μg/L) the small particles up to 0.3 microns in diameter consist almost
entirely of organic matter while the large ones stay almost free of organics, leading to large difference in their
hygroscopicities. Primary marine organics are treated as nonvolatile.

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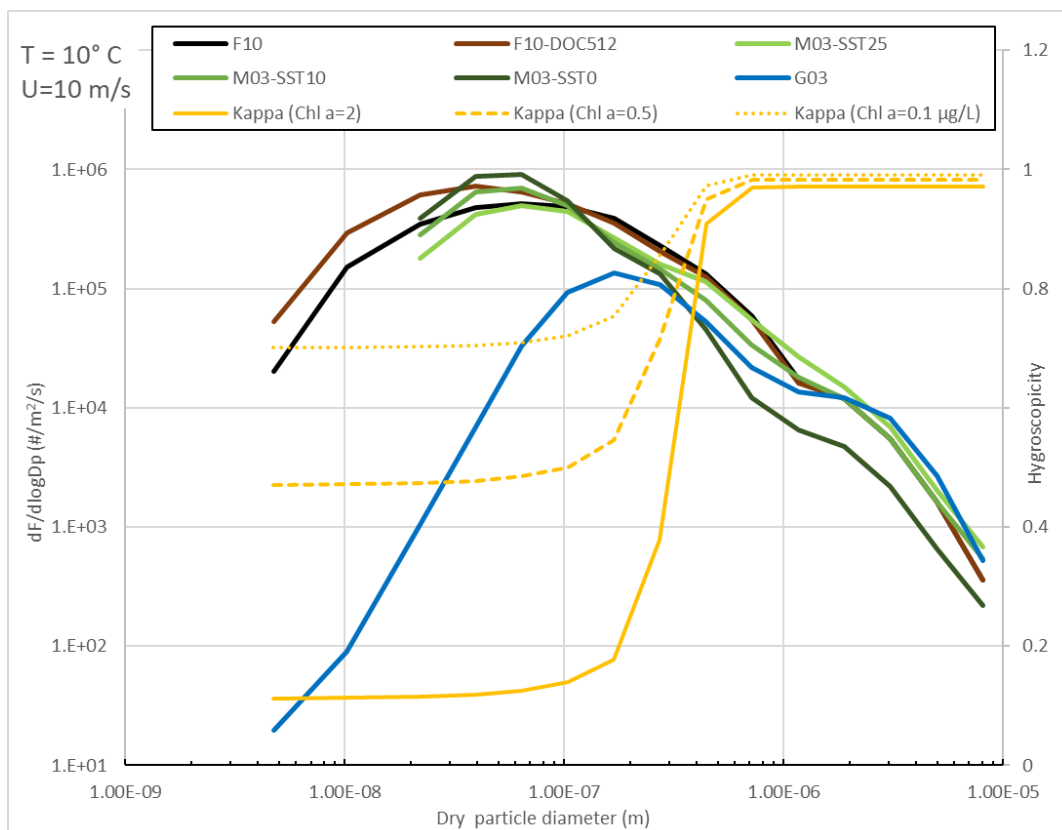
Figure 1. Sea spray flux from different parameterizations and hygroscopicity parameter kappa derived based on the size dependent organic fraction for different Chlorophyll alpha concentrations in sea water. Kappa values of 1 and 0.1 are assumed for the sea salt and the organics respectively.

165 Partitioning of semivolatile organic species between aerosol and gas phase has been implemented using the Volatility Basis Set approach (VBS, Donahue et al 2006, Robinson et al 2007) following Farina et al (2010). VBS is coupled to SALSA identically to what was used by Mielonen et al. (2018). We use three volatility bins with saturation concentrations 0, 1, and 10 µg/m³. As the study concentrates on clean marine areas, we focus on biogenic isoprene and monoterpenes as SOA precursors. In the model, their fluxes from marine surface can either be prescribed or computed from their concentrations in

170 sea water following Wanninkhof (2014). The concentrations of gas phase oxidants (OH and NO₃ radicals and ozone) are prescribed and stay constant over the simulation period of 12 hours. The stoichiometric coefficients give the yields of the different semivolatile organic species, which are described by the volatility bins, resulting in from precursor oxidation. The coefficients for monoterpenes originate from Kokkola et al. (2014) and for isoprene these are derived from the values used by Henze and Seinfeld (2006). The condensation of the semivolatiles to aerosol, cloud droplet and precipitation size bins is

175 computed based on the diffusion-limited condensation equation that accounts for particle size and composition. Aging of the semivolatile organic species is ignored in these relatively short simulations. Due to their low water solubility, the impact of liquid water on partitioning is ignored. The model also includes an additional aqueous phase SOA formation route through

the reactive partitioning of isoprene epoxydiols (IEPOX) and glyoxals to aqueous aerosol, cloud and precipitation. The chemistry of these species is simulated as specified by Mielonen et al (2018) with partitioning constants from Nguyen et al (2014) and Kampf et al (2013). To reduce the computational demands the aqueous processes were turned on only in a dedicated sensitivity simulation.

2.2 Model experiments

The parameters for the LES simulations are based on the second research flight of the DYCOMS II nocturnal aircraft campaign near Californian coast in July 2001 (Stevens et al., 2003), characterized by lightly drizzling deck of closed-cell stratocumulus transitioning to heavily drizzling open cells. Additional CCN can substantially weaken the precipitation and retain cloud water in weakly precipitating marine boundary layer making it more sensitive to changes in aerosol concentration than strongly precipitating or non-precipitating regimes (Wang et al., 2011). Ackerman et al (2009) adapted the DYCOMS II case for LES intercomparison and demonstrated its aerosol sensitivity. The case has been previously used by Tonttila et al. (2017) for evaluating the UCLALES-SALSA model, demonstrating good skill to capture the cloud properties. Apart from including the marine emissions, the model setup and inputs used for the current study are almost identical to those used by Tonttila et al. (2017), with only a couple of small differences. Firstly, the model domain has been enlarged from 6 to 10 km to better represent the scale of the open cell structures. Secondly, to reduce computational demands, the radiative transfer parameterization of Ackerman et al., (2009) is used instead of the 4-stream scheme. Thirdly, the original autoconversion parametrization used by Tonttila et al. (2017) is replaced by the double-moment scheme by Seifert and Beheng (2001). In UCLALES-SALSA, these schemes essentially move the cloud droplets that grow to drizzle-size from the dry-size based cloud bins to the wet-size based rain bins, allowing accurate modelling of precipitation formation via condensation and coalescence processes (Ahola et al., 2021). The parameterization is a computationally efficient alternative for explicitly simulating the initial rain formation step based on collisions between cloud droplets (Tonttila et al., 2021). Although the onset of precipitation is seen earlier with the time-independent autoconversion approach than with the collision-based rain formation, the schemes produce consistent precipitation rates.

The model domain covers 10 x 10 km with 60 m horizontal resolution. Vertically the domain consists of 97 layers reaching up to 1.5 km, layer thickness increasing from 5 m at the surface to 80 m at the model top. The 12 hours long simulations were run with 1 s timestep. For each grid cell, the background aerosol was initialized with a bimodal distribution of ammonium bisulfate aerosol defined by Ackerman et al (2009). The first hour of the simulations is used as a spin-up period to allow the turbulence to build up and boundary layer to settle. In addition to drizzle formation, also the marine emissions are inactive during spin-up to avoid build-up of emitted components in the lowest model layers while the turbulence is still developing. Horizontally averaged vertical profiles and domain average parameters are saved every 60 seconds; 3D fields are saved once per hour.

Affecting the cloud processes by changing CCN number and properties could lead to feedbacks to the sea spray emission through changing wind fields. This kind of feedback processes are out of the scope of the current study but could mask or

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230   In majority of cases the VOC concentrations in the model were initialized with steady state mass mixing ratios reached by
       the model at cloud level (1 ng/kg of monoterpenes and, 2 ng/kg of isoprene) by the end of a 5-day long preliminary
       simulation on reduced horizontal grid. VOC fluxes in this preliminary simulation where kept constant at the mean levels
       observed by Kim et al (2017) (0.83 pmol/m²/s of isoprene and 0.44 pmol/m²/s of monoterpenes) and oxidant concentrations
       representative of clean marine areas were applied (20 ppb of ozone, 0.1 ppt of OH and 0.01 ppt of NO3 radicals, marked as
235   "default" in Table 2). Boundary layer ozone concentrations close to this were measured during DYCOMS II campaign
       (UCAR/NCAR, 2006). Similar ozone and OH concentrations were also used by Kim et al (2017) in their calculations.
       Section 3.4 discusses the changes in the cloud layer due to the SOA formed from the measured mean and maximum VOC
       fluxes and concentrations. The sensitivity of the SOA cloud effects to the background aerosol is discussed in Section 3.5.

240   **Table 2. Model experiments for VOC emission**

Experiment	Aerosol initial condition	VOC initial condition (ng/kg)	VOC emission (pmol/m²/s)	Oxidants (ppb)	Section
NoEms	*A09*	0	0	-	
K17	*A09*	Isop: 2 Mtrp: 1	Isop: 0.83 Mtrp: 0.44	Default: O3 20 OH 10⁻⁴ NO3 10⁻⁵,	3.4 SOA formation from isoprene and monoterpenes
K17-iniMean	*A09*	Isop: 23.5 Mtrp: 85	Isop: 0.83 Mtrp: 0.44		
K17-iniMed	*A09*	Isop: 23.5 Mtrp: 15	Isop: 0.83 Mtrp: 0.44	hiOx: O3 40 OH 10⁻³ NO3 10⁻⁴	
K17-flxMax	*A09*	Isop: 2 Mtrp: 1	Isop: 18 Mtrp: 27		
K17-Isop	*A09*	Isop: 2 Mtrp: 0	Isop: 18 Mtrp: 0	hiOx	
K17-Mtrp	*A09*	Isop: 0 Mtrp: 1	Isop: 0 Mtrp: 27	hiOx	
K17-Isop - aqSOA	*A09*	Isop: 2 Mtrp: 0	Isop: 18 Mtrp: 0	hiOx	
K17Max-IC-coarse	*A09*, no fine mode	Isop: 2 Mtrp: 1	Isop: 18 Mtrp: 27	hiOx	3.5 Sensitivity to background aerosol size distribution
NoEms-IC-coarse	*A09*, no fine mode	0	0	-	
K17Max-IC-sslt	*F10* size distribution	Isop: 2 Mtrp: 1	Isop: 18 Mtrp: 27	hiOx	
NoEms-IC-sslt	*F10* size distribution	0	0	-	
A09 - (Ackerman et al., 2009), *F10* - (Fuentes et al., 2010), *K17* - (Kim et al., 2017).					

3   Results and discussion

3.1 Development of the cloud scene

Figure 2 illustrates the development of the cloud layer in the UCLALES-SALSA simulations. At the beginning of the
simulation (left column) the clouds consist of closed cells with 1-2 km diameter and very little drizzle is observed. As the
245   simulations progress (middle column), the size of these structures grows and light drizzle is formed. In the simulations
without sea spray emissions (upper row) the clouds start to break after about 6 hours while the amount of drizzle increases.
By the end of the run (right panel) the closed cells have turned into large open cells with heavy drizzle. The horizontal size
of the structures grows from couple of kilometres to more than ten, exceeding the size of the 10 km model domain
(Yamaguchi and Feingold, 2015). In the F10 case simulations that include sea spray (lower row) the changes are slower and
250   by the end of the run the clouds have not yet fully reorganized.

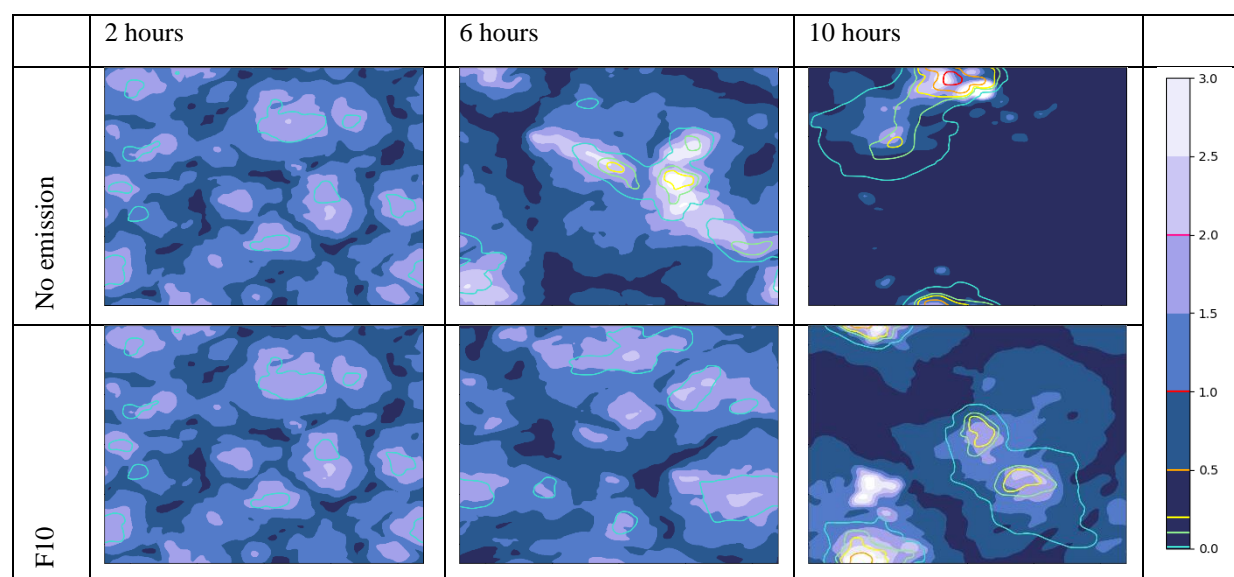



**Figure 2. Development of the cloud layer and drizzle 2, 6 and 10 hours after the simulation start in the no-sea-spray (upper row)
and F10 case (lower row) simulations. Contours – surface precipitation rate (mm/h), white shading –liquid water path (g/m²) *0.01
(scaled to fit on same scale as precipitation).**

3.2 Sea spray flux parameterization and its temperature dependence

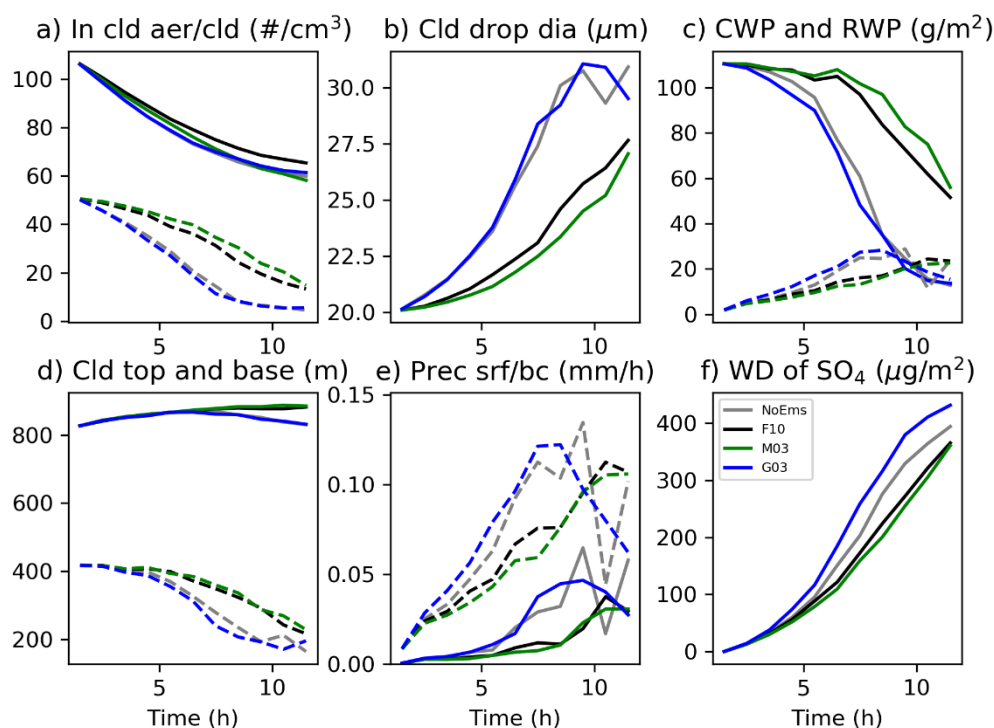
255   Comparing the no-sea-spray control run (grey) on Figure 3 with the base case (F10, black) shows that including the sea spray
emission to the simulations can substantially increase the number of cloud droplets (dashed lines on panel a) and thus lead to
smaller cloud droplets (panel b) delaying the drizzle (panel e) and slowing down the removal of the background aerosol
(panel f). This introduces a positive feedback to the system as the slower washout of the aerosol results in higher CCN
concentration. As seen from the cloud water path plotted on panel c, this can increase the cloud lifetime by several hours.

260   In order to evaluate the impact of uncertainties in sea spray emission, simulations were made with two alternative sea spray
parameterizations: i) G03 - Gong (2003) and ii) M03 - Mårtensson et al (2003) extended with Monahan et al (1986) scheme

for coarse sizes. While the emission flux for dry diameters below ~0.5 µm in the base case was scaled to match that of the M03 scheme (green) and supermicron flux in both cases is computed according to the same Monahan et al (1986) scheme, the different shapes of the size distributions (see Figure 1) still lead to somewhat different outcomes. The M03 scheme

265 produces more particles with diameters below 0.1 µm and fewer larger ones, which leads to activation of large number of smaller particles resulting in smaller average cloud droplet size.

As the parameterization of G03 (blue) was originally developed to reduce the overestimation that was evident when extending the Monahan et al (1986) formula towards smaller sizes (Gong, 2003), its fine particle flux is significantly lower than the other parameterizations give for the same SST (about 5 times lower for 0.1 µm particles and more than an order of

270 magnitude for smaller) while for the supermicron range it gives slightly higher flux (Figure 1). Compared with fine particles that extend the cloud lifetime, the effect of the coarse fraction is different - acting as giant CCN (GCCN) they speed up the collision-coalescence process that can lead to earlier drizzle formation (Houghton, 1938). For this reason, the cloud water path (panel c on Figure 3) reduces even faster with G03 emission (blue) than without any sea spray (grey).

275 **Figure 3. Impact of sea spray flux on the cloud layer for different emission parameterizations. Hourly averaged time series, mean over the model area. Panels: a – in-cloud cloud interstitial aerosol (solid) and cloud droplet (dashed) concentration, b – Cloud droplet size, c –Cloud liquid water path (solid) and rain water path (dashed), d – height of cloud top (solid) and base (dashed), e – precipitation rate at surface (solid) and below cloud (dashed), f – cumulative wet deposition of background aerosol (ammonium bisulfate). Simulations: grey – no-emission control, black –F10, Blue – G03, green – M03 setups. All schemes were run with SST**

280 **10°C and 10 m/s windspeed.**

The importance of temperature effects on sea spray emissions was tested by varying the SST only in the sea spray emission without affecting any other fluxes in the LES. Both the temperature dependency parameterization of Forestieri et al (2018) coupled with the Fuentes et al (2010) sea spray flux and Mårtensson et al (2003) temperature dependent parameterizations (F10 and M03 on Figure 4) were used. In addition to the 10°C base case, two alternative sea surface temperatures were

285   simulated, covering the range from 0°C to 25°C.

As seen from the dark red and blue lines on Figure 4, for the case of the temperature dependency parameterization of Forestieri et al (2018) used in the base case setup with the Fuentes et al (2010) emission scheme that keeps the emission of fine modes constant regardless of SST, the effects are not large. The substantial differences between the light blue, green and red lines on Figure 4 demonstrate that in the Mårtensson et al (2003) scheme the temperature effects are much larger, as

290   smaller number of fine particles and larger amount of coarse fraction is emitted with warmer SST (Figure 1), both working in the same direction of reducing cloud lifetime. In the cold conditions of 0°C SST (light blue on Figure 4) the clouds only start to reorganize at the very end of the simulation.

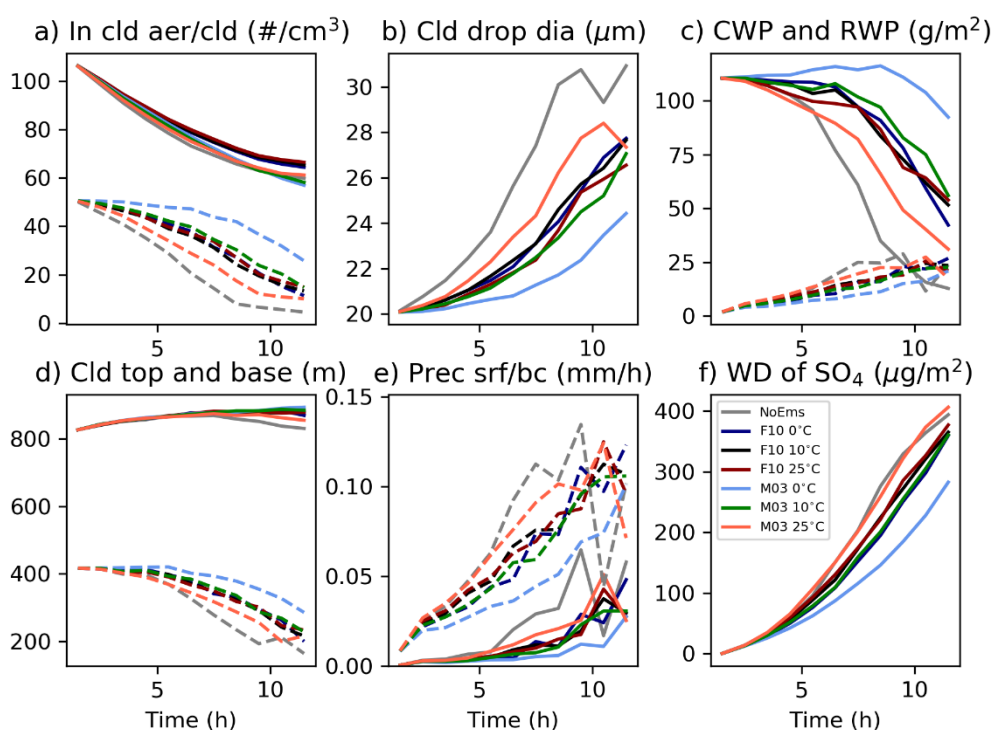



Figure 4. Impact of sea surface temperature based on Forestieri et al (2018) (dark colours) and Mårtensson et al (2003) (light
295   **colours). Panels are the same as Figure 3. Temperatures from cold to warm: blue: 0°C, green/black: 10°C, red: 25°C**

As demonstrated by Terai et al. (2012), the ability of aerosols to suppress precipitation is relatively weak for clouds thicker than ~200 m. In our case the clouds start out about 400 m thick and indeed the drizzle increases and the cloud liquid water path starts reducing by the end of the simulation even with the case with the highest sea spray emission (M03 at 0 °C SST,

light blue on Figure 4). In the base case about 1.5 million particles are emitted from a square meter of sea surface per second,

300 around 2/3 of those in the size range to activate as CCN. The loss rate of particle number due to coalescence processes in the cloud is about 2.5 times higher than the emission of potential CCN, leading to continuous decrease in cloud droplet number. In the highest emission case (M03 at 0°C) the emission of potential CCN is only ~10% higher than in the base case, indicating that the noticeably longer cloud lifetime than in the base case could be partly also due to lower number of GCCN emitted in colder conditions.

305 Grythe et al (2014) reports that the maximum annual sea spray production occurs with winds in the range of 7-16 m/s for the emission schemes they reviewed. We selected the midpoint of this range (10 m/s) to force the sea spray emission schemes in our simulations. However, the most frequent wind speeds over the ocean are somewhat lower, between 5 and 7 m/s (Grythe et al., 2014). In these conditions the sea spray effects would be substantially smaller as the fraction of sea surface covered with whitecaps where the bubble mediated sea spray production takes place depends strongly on the wind speed. For

310 example, 10-meter wind is in power 3.41 in the widely used whitecap parameterization of Monahan et al (1986). This also means that only about 30% higher windspeed would be needed to balance the loss of CCN due to in-cloud coalescence that in the base case exceeds the emission rate by ~2.5 times.

3.3 Impacts of marine organic carbon and assumptions about hygroscopicity

Organic content of surface sea water can impact the aerosol by either changing the emission size distribution or changing the

315 composition and thus the hygroscopicity of the emitted particles. The impact of changing the size distribution was tested via a simulation (F10-DOC512) otherwise identical to the base case but the dissolved organic carbon content in sea water was changed from zero to 512μM, the maximum value for the parameterization. This results in increased emission of sub 0.1 micron particles (Figure 1). In this simulation sea spray composition and resulting hygroscopicity was not changed. In order to evaluate the impact of changing hygroscopicity, another simulation (G11-Chlα2) was run with sea water Chlorophyll

320 alpha concentration set to 2 μg /L and the organic fraction of the particles was computed by the Gantt et al (2011) aerosol size dependent scheme. In this simulation DOC was set to zero. The results of these simulations are shown on Figure 5 (flux enhancement from dissolved organic carbon in sea water with brown line and hygroscopicity reduction due to high organic fraction of small particles with yellow line). Both effects are relatively small compared to the temperature impacts of the M03 parameterization (Figure 4) and in the expected direction. The larger fine mode emission flux due to DOC leads to

325 more cloud drops activating and a slight delay in sub-cloud precipitation (dashed lines on panel e) and thus slightly longer cloud lifetime. The reduction of fine particle hygroscopicity (yellow line) has somewhat more noticeable effect and expectedly in the opposite direction - reduced hygroscopicity of the fine aerosol leads to smaller number of particles activating, earlier drizzle and loss of clouds.

In order to evaluate the importance of the particle size dependence of the organic fraction, an extra sensitivity simulation

330 (G11-Chlα2-allSize) was performed where the maximum organic fraction was attributed to emitted sea spray of all sizes

(orange line on Figure 5). The difference between this simulation and the size-dependent scheme is noteworthy. Lower water uptake of the coarse sea spray due to its large organic fraction substantially reduces the GCCN effect keeping the cloud field stable noticeably longer. As observations do not support large organic fraction in coarse sea spray, caution is needed when using organic fraction parameterizations that do not include size dependence.

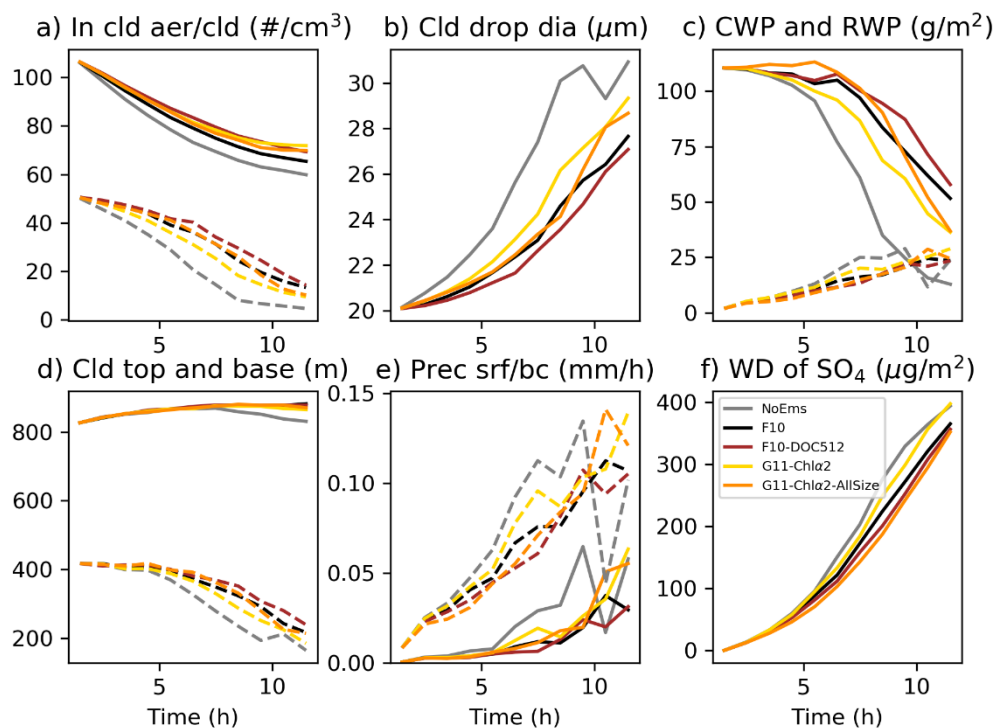



Figure 5. Impact of dissolved organic carbon dependent enhancement of emission flux (brown) and organic aerosol fraction impact through hygroscopicity change (yellow – size dependent scheme, orange – maximum organic fraction applied to all sizes). Panels are the same as Figure 3.

We concentrated on how the sea spray emissions affect the properties of lightly drizzling stratocumulus found to be sensitive for aerosol changes. As the aerosol sensitivity of marine stratocumulus depends for instance on background aerosol, cloud thickness and drizzle intensity (Terai et al., 2012; Wang et al., 2011), the results could differ for different meteorological conditions and for other cloud types even the aerosol relevant processes might differ. For example, as shown by Raatikainen et al. (2022), the marine primary organic emissions could be more important for mixed clouds by providing ice nuclei.

3.4 SOA formation from isoprene and monoterpenes

In this section we investigate the impact of secondary organic aerosol formed from marine isoprene and monoterpenes emissions on the cloud layer. The simulations are listed in Table 2.

The mean fluxes observed by Kim et al. (2017) during the HiWinGS measurement campaign over the Northern Atlantic (0.83 pmol/m²/s of isoprene and 0.44 pmol/m²/s of monoterpenes) were emitted in the K17 case. The model was initialized

350   with the steady state VOC in-cloud mixing ratios reached by UCLALES-SALSA with the mean fluxes - 1 ng/kg of monoterpenes and 2 ng/kg of isoprene. The mean VOC air mixing ratios measured during the HiWinGS cruise were substantially higher - 85 and 23.5 ng/kg of monoterpenes and isoprene respectively - than the ones reached by the model with the mean fluxes. Especially for monoterpenes, this imbalance between the marine fluxes and air concentrations was also noticed by Kim et al (2017). For monoterpenes the occasionally observed high peaks also caused the mean to be much

355   higher than the median (15 ng/kg). In order to investigate the impact of such background concentrations, we run additional simulations where the model was initialized with both of those mixing ratios (K17-iniMean and K17-iniMed).

As the VOC fluxes also exhibited high spatial and temporal variability and values much higher than the mean were regularly observed during the campaign, an extra simulation (K17-flxMax) was run with the reported maximum fluxes, which were more than an order of magnitude larger than the mean (18 pmol/m²/s of isoprene and 27 pmol/m²/s of monoterpenes). As

360   these high emissions are not expected to be long-lasting, the model was initialized with the steady state conditions of 1 and 2 ng/kg to see the impact of short-term emission peaks.

To study the impact of the selected oxidant concentrations, the simulations were repeated with doubled ozone concentration and OH and NO3 increased by an order of magnitude, representative of areas with higher anthropogenic impact, such as Northern Atlantic (indicated with -hiOx in Table 2 and case names).

365   As no sea spray was emitted in these simulations, we evaluate the effects of the emissions by comparing with the NoEms case. As seen from Figure 6 and Figure 7, SOA formed from marine monoterpenes and isoprene can have as strong impact on clouds as the direct sea spray emissions at 10 m/s windspeed. However, the K17 case (green line) with the mean fluxes and steady state background VOC concentrations does not differ from the case without VOC emission (grey) noticeably even with the higher oxidant levels. As the mean monoterpene air concentration observed by Kim et al. (2017) was

370   influenced by the rare but high peak values, we ran simulations initializing the model also with their median observed mixing ratio, which we considered more representative of an average day. The simulation with low oxidant concentrations representing clean marine atmosphere (light blue line on Figure 6) also does not differ from the NoEms case in a noticeable manner, while some impact can be observed in more polluted atmosphere (blue line on Figure 7). The mean initial concentration (yellow) has the largest effect, but the maximum fluxes (light and dark red on figures 6 and 7) can also

375   increase the cloud lifetime by hours even with low initial concentration. The impact is dependent on the rate of oxidation that is defined in the model by prescribed oxidant concentrations.

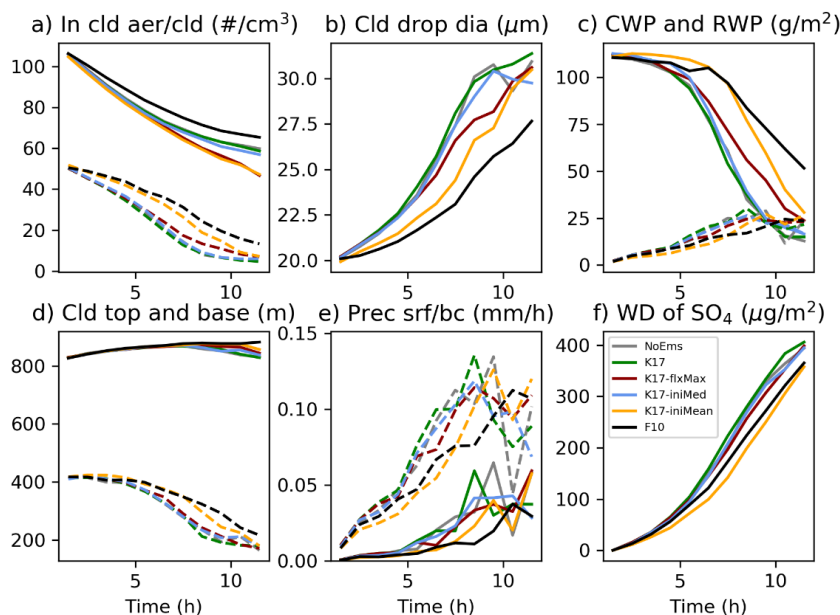



Figure 6. Impact of VOC emissions. Panels are the same as Figure 3. Gray – no emission,; green – mean fluxes of monoterpenes and isoprene from Kim et al (2017), dark red - maximum fluxes, blue – initialized with observed median concentrations, mean fluxes emitted, yellow – initialized with mean observed concentrations, mean fluxes emitted; black – base (F10 sea spray, no VOC) for comparison.

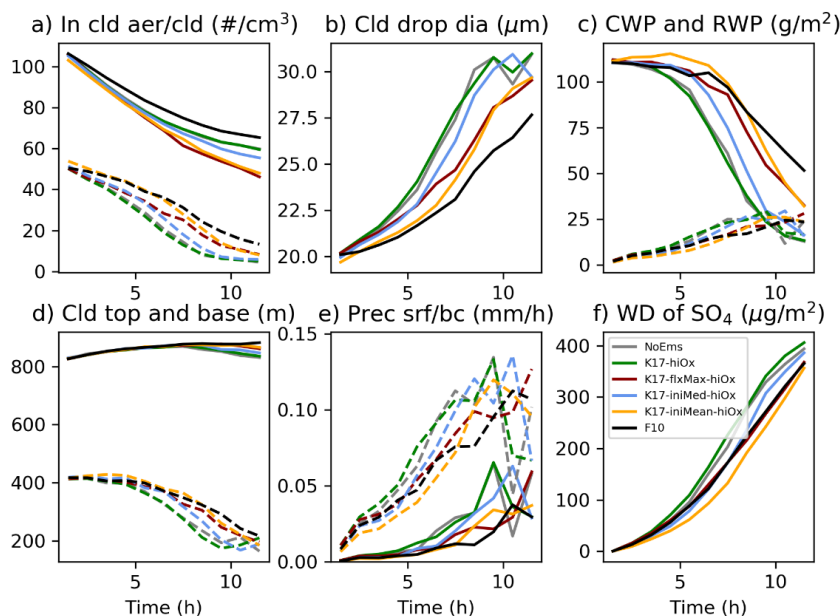



Figure 7. Impact of VOC emissions in high oxidant case. Panels are the same as Figure 3. Gray – no emission; green – mean fluxes of monoterpenes and isoprene from Kim et al (2017), dark red - maximum fluxes, blue – initialized with observed median concentrations, mean fluxes emitted, yellow – initialized with mean observed concentrations, mean fluxes emitted; black – base (F10 sea spray, no VOC) for comparison.

It is noteworthy that significant effects to cloud layer are seen only when emitting the largest reported VOC fluxes or initializing the model with the mean observed mixing ratios that were far higher than the steady state mixing ratios reached with the mean observed fluxes. Box model calculations by Kim et al. (2017) also show that the fluxes necessary to sustain
390   the atmospheric mean monoterpenes mixing ratios observed by them or by Yassaa et al. (2008) noticeably exceed their observed mean fluxes. Yassaa et al. (2008) presents compelling evidence for oceanic origin for their observations making it unlikely that this mismatch would be solely due to high contribution from non-oceanic sources. Kim et al. (2017) suggest higher contribution of lower reactivity monoterpenes as an alternative explanation for the imbalance. While this could be the case for their total monoterpenes measurements, the observations of Yassaa et al. (2008) identified α-pinene as the major
395   contributor to their measurements. Although large uncertainties are introduced by the simple treatment of the oxidants in our model, according to our results the equilibrium mixing ratio reached by the highest fluxes is not so far from the observations, especially when taking into account the vertical profiles of the surface emitted VOCs. As seen in Figure 8, depending on the oxidant level, the surface and cloud level concentrations can differ from a factor of two up to more than an order of magnitude. The observations of Kim et al (2017) (85 ng/kg mean and 15 ng/kg median for monoterpenes) were made at the
400   altitude of 17 meters. The high observed concentrations at this height could be at least partly explained if monoterpene fluxes comparable to the maximum observed ones would have been relatively common in the upwind areas during the measurement campaign.

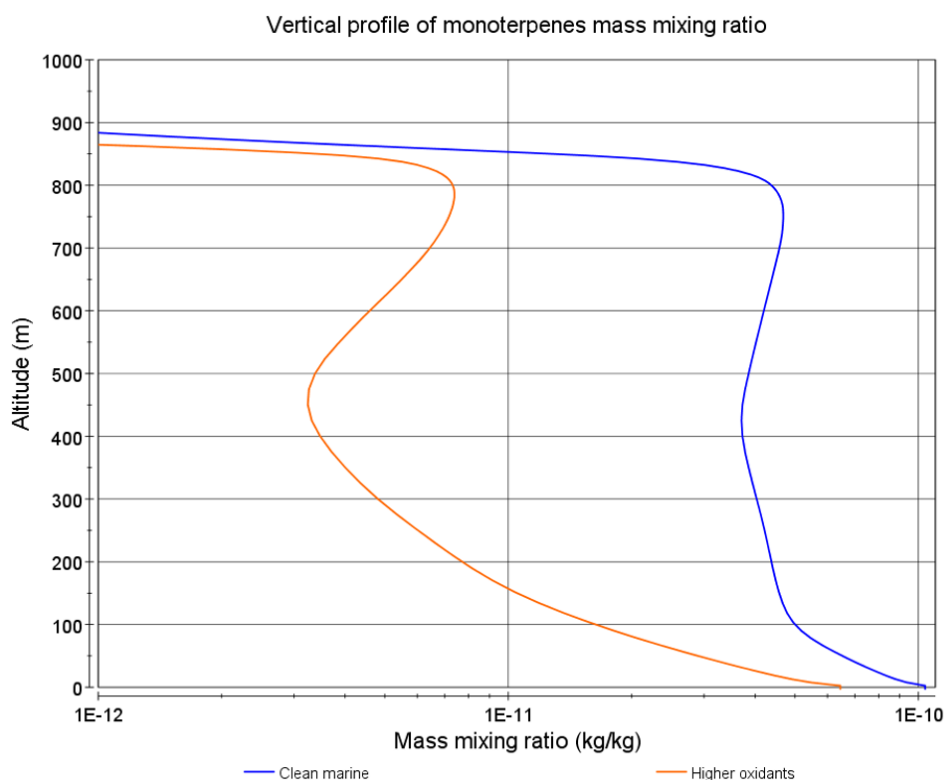



Figure 8. Vertical profiles of equilibrium monoterpene mass mixing ratios rising from the maximum flux observed by Kim et al., (2017) with higher and lower oxidant concentrations.

In order to elucidate the individual contributions from isoprene and monoterpenes, two simulations were made based on the K17-flxMax-hiOx simulation by zeroing either isoprene or monoterpene emission and emitting the maximum observed flux of the other VOC (K17-Isop and K17-Mtrp). As seen from the sensitivity studies where either isoprene or monoterpene emissions were zeroed (green and pink on Figure 9), the whole SOA production in the model and its effect to clouds was solely due to monoterpenes.

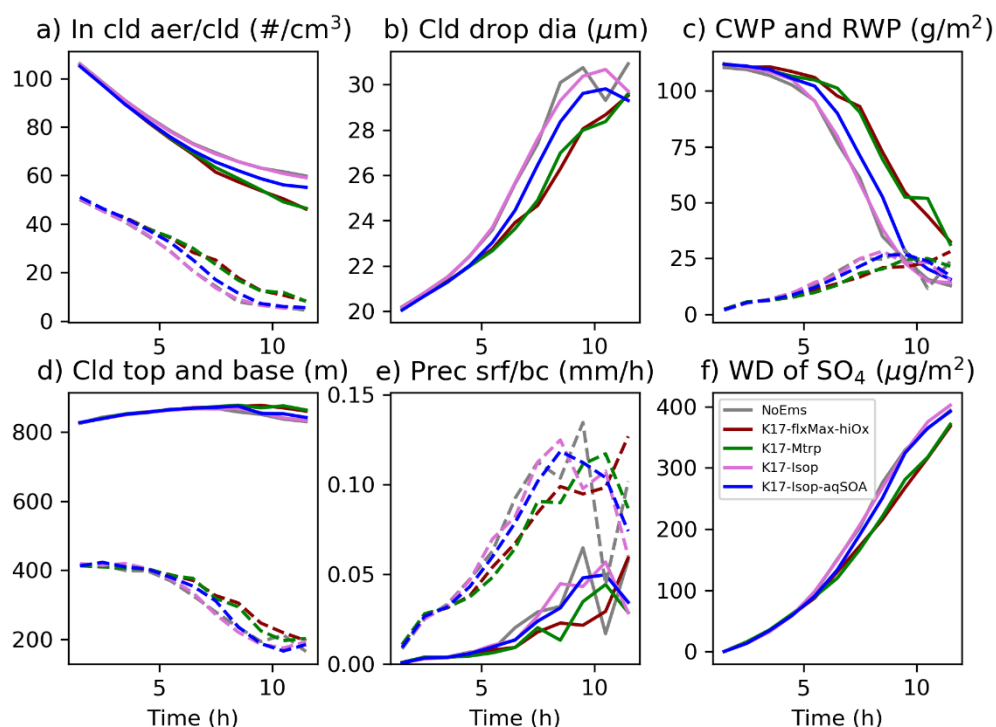



Figure 9. Contributions from monoterpenes and isoprene and impact of including aqueous SOA formation. Gray – no emission, dark red - maximum fluxes of monoterpenes and isoprene emitted, higher oxidant levels; green – only monoterpenes emitted, pink – only isoprene emitted, blue – same as pink but aqueous formation of SOA included.

The simulations of Gantt et al. (2009) with 3% aerosol yield from isoprene also showed only very minor impact of isoprene derived SOA to total marine organic aerosol as global annual average, but reported much higher short term contributions over the tropical regions when high isoprene emissions coincided with small primary organic fluxes due to their different dependencies on meteorological driver such as windspeed. Similar results were shown by Prank et al (2018) for the biogenic organic aerosol in Europe using a similar VBS scheme without aqueous phase processes – the majority of SOA in the model originated from vegetation emitted monoterpenes while the role of isoprene was modest. The isoprene SOA yields used in UCLALES-SALSA are on the higher end of what has been reported in the literature (0.0295 for the VBS bin with saturation concentration of 1 µg/m^3 and 0.0453 for 10 µg bin/m^3), suggesting that at least in the conditions and timescale of the study,

gas phase production of semivolatile organics from isoprene oxidation does not lead to enough low volatility products to have a noticeable impact.

However, significant amounts of isoprene oxidation products have been observed in remote marine aerosol by e.g. Hu et al., (2013). As pointed out by Yu and Li (2021), the role of isoprene in forming marine aerosol could be underestimated in current models as substantially larger SOA yields have been shown using more sophisticated chemistry schemes (e.g. Bates and Jacob 2019), especially when accounting for aqueous phase chemical processes involving isoprene epoxydiols (Nguyen et al., 2014). To save the computational resources, the aqueous phase SOA formation from isoprene had been turned off in all the previously discussed simulations. The impact of these processes was investigated with the K17-Isop-aqSOA setup which was otherwise identical to K17-Isop but accounted also for aqueous phase SOA formation through isoprene epoxydiols and glyoxals. Isoprene products indeed became visible when the aqueous phase production was turned on (blue line on Figure 9). However, their impact still stayed significantly lower than that of monoterpenes. Although we did not detect any immediate effect from the gas phase isoprene oxidation for the conditions of the DYCOMS II campaign, it is possible that it would become more noticeable in longer time scales or in different meteorological conditions than in the simulated case.

Use of a more comprehensive chemistry scheme could also leads to reduction of SOA, as chemical interactions between isoprene and monoterpene oxidation products can reduce the yield of low volatility compounds from monoterpenes (McFiggans et al., 2019). Unfortunately, a sophisticated gas phase chemistry scheme is currently not feasible in a LES model like UCLALES-SALSA due to prohibitively high computational requirements.

3.5 Sensitivity to background aerosol size distribution

In the high VOC emission case (K17-flxMax-hiOx, dark red on Figure 6) the lifetime of clouds is extended by ~3 hours. As the mass fraction of SOA stays very small (<2.5% within 1 km height from surface), its unexpectedly large impact requires further investigation. The background aerosol is defined by Ackerman et al (2009) as bimodal distribution of ammonium bisulfate with high number concentration of Aitken mode aerosol below the sizes that readily act as CCN (Figure 10). Comparing the simulations with and without marine VOC emissions (Figure 11, left panel) shows that the condensing organic vapours help these particles to grow to the next size bin, though even then they mostly stay too small to contribute much to the activated CCN (Figure 11, right panel). However, both the aerosol and the cloud droplet concentration of the coarser bins stay higher in the simulation with the SOA formation indicating that the large impact stems from positive feedback of the extra particles delaying the drizzle that would otherwise scavenge larger fraction of the particles from the whole size range.

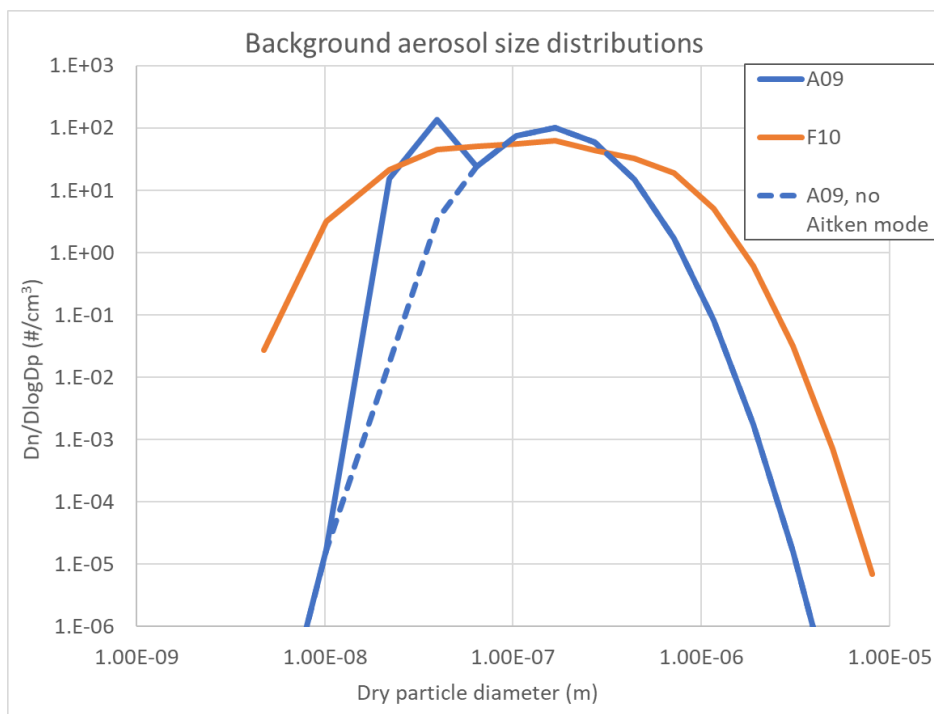



Figure 10. Model initial condition background aerosol size distributions. Solid blue – bimodal ammonium bisulfate size distribution defined by Ackerman et al (2009), dashed blue – same with fine mode removed, orange – sea salt emission distribution from Fuentes et al (2010).

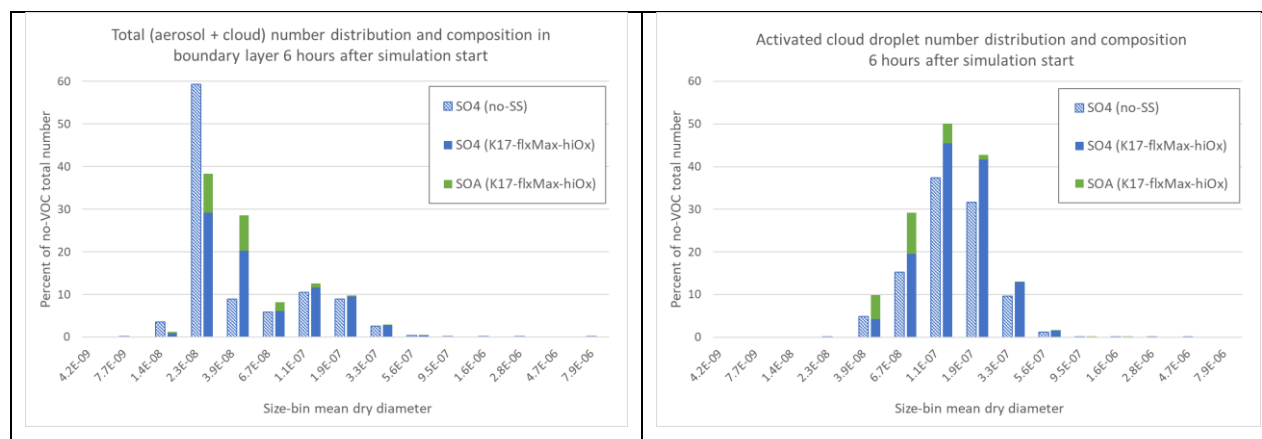



Figure 11. Boundary layer total particle (aerosol + cloud, left panel) and cloud droplet (right panel) number size distribution and composition for all size bins 6 hours after simulation start, simulations without (stippled bars) and with VOC emissions (solid bars). Normalized to the total number in the zero VOC case.

Considering this we performed two sensitivity studies – one with removing the fine size mode entirely (K17Max-IC-coarse) and another initializing the model with sea salt aerosol with size distribution defined by (Fuentes et al., 2010) emission scheme (K17Max-IC-sslt) as background (see Figure 10). In the latter case the concentration was normalized to reproduce the same number of cloud droplets as the noEms case immediately after the model spin-up. The setups were otherwise

identical to K17-flxMax-hiOx simulation. Corresponding no-emission control simulations without any VOCs were run for both of the alternative initial conditions (noEms-IC-coarse and noEms-IC-sslt). The results of these simulations are shown

465 on Figure 12.

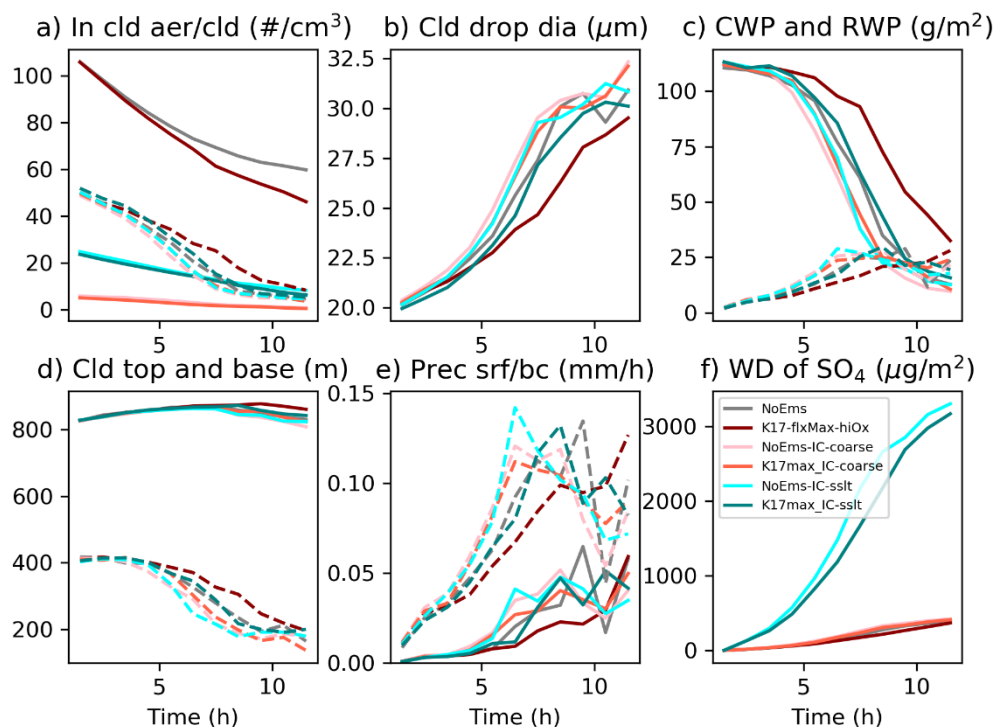



Figure 12. Impact of background aerosol on VOC effect. Dark red (K17-flxMax-hiOx) - maximum fluxes of monoterpenes and isoprene emitted, higher oxidant levels, background aerosol initialized with Ackerman et al (2009) size distribution, Gray – no-emission control case for K17-flxMax-hiOx,; red (K17max-IC-coarse) – VOCs same as K17-flxMax-hiOx, fine mode removed from
470 **the initial background aerosol, pink – no-emission control for K17max-IC-coarse, teal (K17max-IC-sslt) – VOCs same as K17-flxMax-hiOx, background aerosol initialized with sea salt size distribution from Fuentes et al (2010), cyan – no-emission control for K17max-IC-sslt**

Comparing the three emission free control simulations (grey, pink and cyan lines on Figure 12) shows that the reduced initial aerosol number concentration itself leads to slightly shorter cloud lifetime in both of the alternative background cases
475 although both of the alternative initial conditions reproduce the same cloud droplet number in the beginning of the simulations (dashed lines on panel a). Comparing the pink line with the red one shows that the effect of VOC emission disappears completely when the Aitken mode is removed from the background aerosol. Thus, we conclude that the large VOC effect critically depends on the underlying background aerosol distribution. Marine aerosol regularly exhibits a bimodal distribution (Hoppel and Frick, 1990; Hudson et al., 2015), where the dip between the modes is caused by activation
480 of large enough particles and their subsequent growth due to cloud processing or removal through wet deposition. Both in-cloud coalescence and wet deposition of activated particles lead to reduction of particles available to act as CCN. The small mode consists of primary and secondary particles that are too small for cloud activation in their current size but capable of

growing to CCN size by condensation of organic vapours. Larger number of small particles are likely to exist downwind marine areas with high biological activity as a result of DMS emission, oxidation and following aerosol nucleation (Sanchez et al., 2018). However, as seen from Figure 1, some of the sea spray parameterizations also produce noticeable number of particles in this size range, although they are not separated from the larger particles by a gap. Thus, it is interesting to consider the case where the background aerosol consists of freshly emitted sea spray. Comparing the simulations without and with VOC emission (cyan and teal lines on Figure 12) shows that condensation of the organic vapours on the wide fresh sea salt distribution from Fuentes et al (2010) also extends cloud lifetime, although in lesser extent. Thus, significant impact of marine VOCs on cloud lifetime is more likely in areas with high biological activity, as they can provide both larger amount of Aitken mode particles and the organic vapours to condense on them to grow them to CCN size.

3   Conclusions

In this study we used the UCLALES-SALSA large eddy simulator that includes a detailed description of aerosols, clouds and precipitation to model the conditions of the DYCOMS-II observational campaign characterized by low level stratocumulus clouds transitioning from closed cells to drizzling open cell structure. Our aim was to investigate the impacts of sea spray and marine VOCs on cloud stability. Our simulations were designed to cover the ranges of the driving parameters (SST, DOC, Chl α, and terpenoid fluxes) that would have the largest impact.

Including a sea spray emission scheme with high flux of Aitken and accumulation mode particles, such as parameterized by Mårtensson et al (2003) or Fuentes et al (2010) to our simulations had a noticeable impact, extending the cloud lifetime by several hours by delaying the onset of drizzle, as the extra CCN lead to activation of larger number of cloud droplets and slower growth of droplet size. Opposite effect was seen from coarse particles acting as giant CCN that speed up the coalescence of cloud droplets and drizzle formation.

While the importance of sea spray emission temperature dependence has been pointed out by several sources (Grythe et al., 2014; Liu et al., 2021; Mårtensson et al., 2003), its magnitude and even direction differs between different parameterizations. For our selected parameterizations the effects of SST varied from negligible in case of the Forestieri et al. (2018) parameterization to extension of cloud lifetime beyond the experiment timescale for the commonly used Mårtensson et al. (2003) scheme. Varying the sea water organic content from zero to the high limit of our considered parameterizations had smaller impact on the clouds than would be seen from changing SST between summer and winter conditions in the Mårtensson et al (2003) parameterization. However, it was important to account for the size dependence of the organic fraction of the emitted particles, as changing the hygroscopicity of the coarse fraction has opposite effect to that of fine. Previous studies have shown that while marine stratocumulus can be highly sensitive to giant CCN, the related uncertainties are large due to complex dependencies on the background CCN concentration (Feingold et al., 1999) and GCCN size distribution (Dror et al., 2020). Our results show that the effect of GCCN is also highly sensitive to the assumptions

regarding the water uptake of these coarse particles, making the size dependence of sea spray organic fraction relevant for
515   models with comprehensive autoconversion schemes that account for the GCCN effects.

According to our results, the secondary organic aerosol formation from terpenoids can have a large impact, delaying the drizzle and extending cloud lifetime up to several hours. The SOA effect critically depends on the background aerosol distribution – condensation of semivolatiles can affect the clouds when sufficient Aitken mode particles are present to grow into CCN size. Nucleation of oxidation products of DMS emitted by marine phytoplankton is considered as an important
520   source of new particles in clean marine atmosphere. As the emissions of DMS and other VOCs coincide in the biologically active areas, the terpenoid emissions could potentially play important role in growing the newly formed particles to CCN size.

In the considered conditions and timescale, gas phase production of semivolatile organics from isoprene oxidation did not lead to enough low volatility products to have a noticeable impact even with the highest isoprene levels. Simulating the
525   reactive partitioning IEPOX and glyoxals to aerosol water, on the other hand, had a noticeable impact, stressing the importance of including in models the aqueous phase SOA production processes.

Significant effects from monoterpenes were seen in some simulations, extending the cloud lifetime by hours. However, cloud stability was noticeably impacted only when emitting the largest VOC fluxes reported in literature or initializing the model with the mean observed mixing ratios that were far higher than the steady state reached with the mean observed
530   fluxes. More observations of monoterpenes in ocean water and air above it are needed to understand the frequency of such high fluxes and role of these species in marine atmosphere.

5   Code and data availability

The source code of UCLALES-SALSA version used in this work is available from https://github.com/UCLALES-SALSA/UCLALES-SALSA/tree/IceDevelOrg. Simulation results presented in this paper are available at https://a3s.fi/MOA-
535   LES_ppr/index.html.

6   Author contributions

MP and TR designed the study. MP performed and analysed the model simulations. All authors have contributed to developing the UCLALES-SALSA model. MP prepared the manuscript with contributions from all co-authors.

7   Competing interests

540   The authors declare that they have no conflict of interest.

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