



# 1 The potential role of organics in new particle formation and initial 2 growth in the remote tropical upper troposphere

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## 16 **Abstract.**

17 Global observations and model studies indicate that new particle formation (NPF) in the upper troposphere (UT) and  
18 subsequent particles supply 40-60 % of cloud condensation nuclei (CCN) in the lower troposphere, thus affecting the Earth's  
19 radiative budget. There are several plausible nucleation mechanisms and precursor species in this atmospheric region, which,  
20 in the absence of observational constraints, lead to uncertainties in modeled aerosols. In particular, the type of nucleation  
21 mechanism and concentrations of nucleation precursors, in part, determine the spatial distribution of new particles and resulting  
22 spatial distribution of CCN from this source. Although substantial advances in understanding NPF have been made in recent  
23 years, NPF processes in the UT in pristine marine regions are still poorly understood and are inadequately represented in global  
24 models.

25 Here, we evaluate commonly used and state-of-the-art NPF schemes in a Lagrangian box model to assess which  
26 schemes and precursor concentrations best reproduce detailed in situ observations. Using measurements of aerosol size  
27 distributions ( $0.003 < D_p < 4.8 \mu\text{m}$ ) in the remote marine troposphere between ~0.18 and 13 km altitude obtained during the  
28 NASA Atmospheric Tomography (ATom) mission, we show that high concentrations of newly formed particles in the tropical  
29 UT over both the Atlantic and Pacific oceans are associated with outflow regions of deep convective clouds. We focus analysis  
30 on observations over the remote Pacific Ocean, which is a region less perturbed by continental emissions than the Atlantic.  
31 Comparing aerosol size distribution measurements over the remote Pacific with box-model simulations for 32 cases shows  
32 that none of the NPF schemes most commonly used in global models, including binary nucleation of sulfuric acid and water



33 (neutral and ion-assisted) and ternary involving sulfuric acid, water, and ammonia, are consistent with observations, regardless  
34 of precursor concentrations. Through sensitivity studies, we find that the nucleation scheme among those tested that is able to  
35 explain most consistently (22 of 32 cases) the observed size distributions is that of Riccobono et al. (2014), which involves  
36 both organic species and sulfuric acid. The method of Dunne et al. (2016), involving charged sulfuric acid-water-ammonia  
37 nucleation, when coupled with organic growth of the nucleated particles, was most consistent with the observations for 5 of  
38 32 cases. Similarly, the neutral sulfuric acid-water-ammonia method of Napari (2002), when scaled with a tuning factor and  
39 with organic growth added was most consistent for 6 of 32 cases. We find that to best reproduce both nucleation and growth  
40 rates, the mixing ratios of gas-phase organic precursors generally need to be at least twice that of SO<sub>2</sub>, a proxy for dimethyl  
41 sulfide (DMS). Unfortunately, we have no information on the nature of oxidized organic species that participated in NPF in  
42 this region. Global models rarely include organic-driven nucleation and growth pathways in UT conditions where globally  
43 significant NPF takes place, which may result in poor estimates of NPF and CCN abundance and contribute to uncertainties  
44 in aerosol-cloud-radiation effects. Furthermore, our results indicate the organic aerosol precursor vapors may be important in  
45 the tropical UT above marine regions, a finding that should guide future observational efforts.

## 46 **1 Introduction**

47 The majority of particles found in the atmosphere are formed through gas-to-particle conversion (i.e. nucleation) from  
48 clustering of low-volatility vapors (Gordon et al., 2017; Pierce, 2017). While the formation of these molecular clusters appears  
49 to take place almost everywhere and at all times in the atmosphere (Kerminen et al., 2018), the formation of thermodynamically  
50 stable aerosol particles with diameters ( $D_p$ )  $\geq 1.5$  nm requires favorable conditions in terms of temperature, availability of  
51 condensable vapors, and the background of pre-existing bigger particles that compete for condensing vapors, and so may not  
52 occur in every atmospheric environment (Kulmala et al., 2014). Most of these newly formed particles are lost by coagulation  
53 with larger particles, and do not contribute to particle number (Westervelt et al., 2014). A subset of the nucleated particles  
54 grows by condensation to become larger particles with reduced Brownian motion, and hence lower coagulation loss rates  
55 (e.g., Pierce and Adams, 2007). Particles with  $D_p \geq 50$  nm can serve as CCN at supersaturations found in typical marine  
56 cumulus and stratocumulus clouds (Quinn et al., 2008), increasing droplet number concentrations and cloud albedo, and thus  
57 indirectly affecting the Earth's radiative budget (Twomey, 1974; IPCC, 2013).

58 The tropical UT is known to be a major source region of new particles (e.g. Clarke, 1993; Brock et al., 1995; Clarke  
59 and Kapustin, 2002; Weigel et al., 2011; Williamson et al., 2019). This strong aerosol production is believed to be linked with  
60 frequent deep convection in this region. The mechanism proposed by Clarke (1992) involves the formation of new particles in  
61 the UT from convectively lifted and cloud-processed boundary layer air. At the conditions of cold temperatures, high photolytic  
62 fluxes, and low concentrations of pre-existing aerosol particles found in the outflow of deep convection at altitudes  $>8$  km,  
63 aerosol precursor gases that may survive convective transport and scavenging can oxidize and nucleate new particles which  
64 then grow to CCN sizes as they descend in the gradually subsiding air that compensates for the upward convection. Raes



65 (1995) used a box model to determine that observed concentrations of CCN in the remote marine boundary layer (MBL), and  
66 their temporal stability, could not be explained without a source of particles being entrained from the free troposphere (FT).  
67 Clarke et al. (2006) estimated that entrainment from the FT provides 35-80 % of the CCN flux into the MBL over latitudes  
68 between 40° S and 40° N with the rest coming from sea salt aerosol. More recently, Quinn et al. (2017) found that at ~0.5 %  
69 supersaturation, the accumulation mode aerosol, composed primarily of sulfate compounds rather than sea-spray particles,  
70 provides ~70 % of the CCN population throughout the MBL of the tropics and midlatitudes, and suggested that these particles  
71 originate from the FT.

72 Despite the climatic importance of NPF in the tropical UT, the chemical mechanisms are poorly understood (e.g.,  
73 English et al., 2011). This lack of understanding is driven by the fundamental complexity and variability of the atmosphere,  
74 the range of potential chemical species and mechanisms that could lead to NPF and subsequent growth of the newly formed  
75 particles to CCN, and the difficulty in obtaining observations of processes occurring in remote areas, at high altitudes, and  
76 over time scales ranging from minutes (NPF) to weeks (condensational growth during gradual descent). Together, these issues  
77 have made it difficult to validate NPF schemes used in global models and have hindered our ability to reduce uncertainty in  
78 aerosol-cloud-radiation interactions.

79 Williamson et al. (2019) showed that three of four global models examined in their study underestimated the  
80 magnitude of NPF in the tropical Pacific UT and all failed to accurately simulate the abundance of CCN-sized particles in the  
81 lower troposphere of the same region (the fourth model significantly overestimated aerosol loadings throughout the  
82 troposphere). None of these models used a NPF scheme involving organics, and the three models may lack sufficient precursor  
83 vapors for growth, in addition to other deficiencies. Previous model studies (e.g., Kazil et al., 2010; Yu et al., 2010; Zhang et  
84 al., 2010; Zhu et al., 2019) show that the choice of NPF mechanism can drive substantial changes in the predicted abundance  
85 and spatial distribution of particles. While Westervelt et al. (2014) suggested that the global-mean boundary layer CCN are  
86 not very sensitive to the number of particles formed in the UT due to the dampening effects of coagulation (i.e., more nucleation  
87 leads to faster coagulation losses), different choices of NPF mechanisms in models might alter the spatial and temporal  
88 pattern of NPF, and thus affect the spatial distribution and magnitude of CCN abundance. It is clear that accurate simulation  
89 of NPF and growth processes is essential to adequately represent particle size distributions and their spatial distribution in  
90 global models and improve predictions of aerosol-cloud-radiation effects (Hodshire et al., 2018; Williamson et al., 2019).

91 Field measurements have shown that sulfuric acid is a key component in atmospheric NPF in the continental boundary  
92 layer (e.g., Weber et al., 1997; Riipinen et al., 2007; Sihto et al., 2006). Several nucleation schemes involving sulfuric acid  
93 have been used in global models as a consequence. These include activation nucleation scheme that depends on sulfuric acid  
94 only (Kulmala et al., 2006), binary schemes that involve sulfuric acid and water to form new particles (e.g., Vehkamäki et al.,  
95 2002), or ternary schemes in which sulfuric acid, water and ammonia condense to form new particles (e.g., Napari et al. 2002).  
96 The activation nucleation scheme, however, is an empirical formulation tuned to mid-latitude continental boundary layer  
97 observations so it is appropriate to use only there. Binary NPF has been suggested to be favored in the remote tropical UT due  
98 to cold temperatures, high relative humidity (RH), and the availability of supersaturated sulfuric acid (Clarke, 1992; Brock et



99 al., 1995; Clarke and Kapustin, 2002). Ion-assisted nucleation of sulfuric acid and water clusters has been identified as a  
100 potential pathway for binary NPF (Kirkby et al., 2011; Lovejoy et al., 2004; Kazil and Lovejoy, 2007; Raes et al., 1997; Yu  
101 2010). Ions stabilize the molecular clusters so that nucleation can occur at warmer temperatures and lower nucleating-vapor  
102 concentrations (Yu, 2010).

103 Recent observations of the composition of molecular clusters present during NPF have highlighted the role that  
104 organics may play (Kulmala et al., 2013; Smith et al., 2004). Murphy et al. (2006) and Froyd et al. (2009) found that larger  
105 particles ( $D_p > 0.15 \mu\text{m}$ ) in the UT contained significant organic matter that was likely secondary, which suggests that  
106 condensable gas-phase organic compounds are present in the UT. Andreae et al. (2018) postulated that biogenic volatile organic  
107 compounds carried from the boundary layer to the UT by deep convection and oxidized to form condensable species over the  
108 Amazon are responsible for NPF observed in this continental UT region. Weigel et al. (2011) also suggested that organics  
109 might contribute to NPF events observed in the UT. Other nucleation processes combining sulfuric acid with ammonia (Kürten  
110 et al., 2016; Merikanto et al., 2007), amines (Almeida et al., 2013), di-amines (Jen et al., 2016), or organics (Kulmala et al.,  
111 2006; Metzger et al., 2010; Riccobono et al., 2014), or organics alone (Kirkby et al., 2016; Bianchi et al., 2016), have been  
112 proposed to explain some field and laboratory observations of NPF, primarily at warmer temperatures and continental  
113 locations. In a modeling study, Zhu et al. (2019) found that pure organic nucleation from biogenic volatile organic compounds  
114 could be an important source of particles, especially in the UT of modern-day pristine, continental environments and during  
115 the pre-industrial period.

116 Because there have been no in situ observations of the composition of molecular clusters and nano-particles found in  
117 convective outflow in the UT, it is difficult to ascertain which of these varied mechanisms, if any, contribute to NPF in the  
118 remote FT. In this study, we use unique observations obtained during the Atmospheric Tomography Mission (ATom), a multi-  
119 year airborne program to measure gas and aerosol properties of the remote troposphere over both the Atlantic and Pacific  
120 oceans across four seasons. Recently formed particles observed in the tropical UT were linked to recent outflow from deep  
121 convection. We use box models constrained by trajectory calculations to evaluate how well different NPF formation  
122 mechanisms can simulate the observed particle size distributions. We perform extensive model sensitivity studies to determine  
123 which nucleation mechanisms and initial precursor mixing ratios allow for the model to match observed size distributions.

## 124 2. Methods

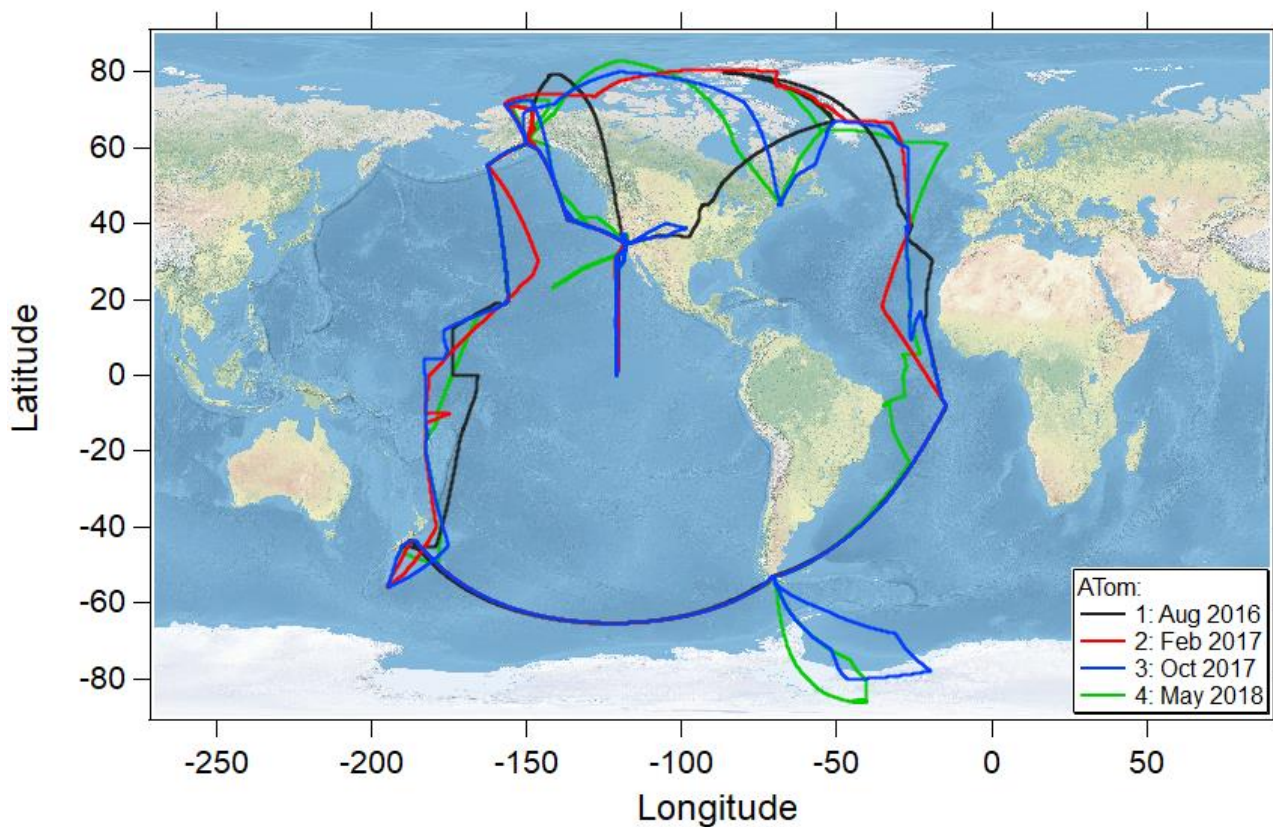
125 To establish a link between convection and NPF, and to explore the processes that govern NPF and initial growth in  
126 the tropical and subtropical free troposphere over the Pacific Ocean, we couple measured size distributions between 2.6 nm  
127 and 4.8  $\mu\text{m}$  in diameter from the four ATom missions with calculated air mass back trajectories and two box models. The back  
128 trajectories identify air masses potentially influenced by recent convection. We compare our simulations with in-situ ATom  
129 observations of aerosol size distributions. We examine which nucleation schemes best explain the observations, and evaluate  
130 whether observed sulfur precursors ( $\text{SO}_2$  and dimethyl sulfide (DMS)) can explain the NPF and the particles' initial growth.



131 In one model, we simulate particle formation by neutral and charged binary and ternary schemes, and a neutral organic scheme,  
132 and we also add organics for initial growth of the particles in all schemes. In an additional model, we form particles using both  
133 neutral and charged binary schemes.

## 134 2.1 The Atmospheric Tomography Mission

135 The NASA Atmospheric Tomography Mission (ATom) was an airborne global survey that used the NASA DC-8  
136 research aircraft to map for the first time the composition of the remote atmosphere over both the Pacific and Atlantic basins  
137 ( $\sim 82^\circ$  N to  $\sim 86^\circ$  S; Fig. 1) in nearly continuous ascents and descents between  $\sim 0.18$  and 13 km in all four seasons (July-August  
138 2016, January-February 2017, September-October 2017, and April-May 2018). The primary objectives of the mission were to  
139 examine the composition of the remote atmosphere to improve understanding of photochemical mechanisms for reactive and  
140 long-lived gas-phase species and to identify the abundance, distribution, sources of aerosol particles in the remote marine  
141 troposphere (Wofsy et al., 2018).



142  
143 **Figure 1: Flight tracks of the NASA DC-8 research aircraft during the ATom 1 (July-August 2016), ATom 2 (January-February**  
144 **2017), ATom 3 (September-October 2017) and ATom 4 (April-May 2018) missions covering the remote marine atmosphere of the**  
145 **Pacific and Atlantic Oceans between  $\sim 83^\circ$  N and  $\sim 86^\circ$  S.**

146



## 147 2.1 Measurements

148 A suite of fast time response (1 Hz) particle counters and optical particle size spectrometers were used to measure dry  
149 size distributions between 2.6 nm and 4.8  $\mu\text{m}$  in diameter (Brock et al., 2019). Two nucleation mode aerosol size spectrometers  
150 (NMAS; Williamson et al., 2018), each consisting of five continuous-flow condensation particle counters (CPCs) with  
151 different fixed cut-off diameters (i.e. diameters at which each CPC detects 50 % of the incoming particles) between 3.2 and  
152 59 nm, measured particle number concentration. Two optical aerosol counters, an ultra-high-resolution sensitivity aerosol  
153 spectrometer (UHSAS; Kupc et al., 2018) and a laser aerosol spectrometer (LAS; Froyd et al., 2019), measured particle size  
154 distributions from  $0.06 < D_p < 1 \mu\text{m}$  and  $0.12 < D_p < 4.8 \mu\text{m}$ , respectively. All concentrations reported here are corrected to standard  
155 temperature and pressure (STP), 1013 hPa and 273.15 K. The NOAA Particle Analysis by Laser Mass Spectrometry (PALMS)  
156 instrument measured the composition of individual aerosol particles (Froyd et al., 2009; 2019). For this study the PALMS size  
157 range is restricted to 0.125-1.5  $\mu\text{m}$ . Due to inlet sampling artifacts (Weber et al., 1998; Murphy et al., 2006), cloudy periods  
158 were removed from the analysis. Clouds were detected using a second-generation cloud, aerosol, and precipitation  
159 spectrometer (CAPS) mounted under the wing, which also measured coarse aerosols  $>0.5 \mu\text{m}$  (Dollner et al., in preparation)  
160 at ambient conditions.

161 Temperature, pressure, and wind speed with high time resolution (1 Hz) were measured with an accuracy of  $\pm 0.3 \text{ K}$ ,  
162  $\pm 0.3 \text{ hPa}$ , and  $\pm 1.0 \text{ m s}^{-1}$ , respectively (Scott et al., 1990). Highly sensitive sulfur dioxide ( $\text{SO}_2$ ) measurements were made  
163 during ATom 4 using laser-induced fluorescence (Rollins et al., 2016; Rollins et al., 2017) with a precision ( $1\sigma$ ) of 1-2 pptv at  
164 10 s and an overall uncertainty of  $\pm(9 \% + 2 \text{ pptv})$ . Laser-induced fluorescence was used to measure OH and  $\text{HO}_2$   
165 simultaneously (Faloona et al., 2004; Brune et al., 2020) with an accuracy of  $\pm 35 \%$ . Measurements of carbon monoxide (CO)  
166 were made using a Picarro G2401m (Chen et al., 2013) with a precision ( $1\sigma$ ) of 2-3 ppb at 10 s and an average uncertainty of  
167 4 ppb. All data used in this analysis can be found in Kupc et al. (2020).

## 168 2.2 Air mass back trajectories and convective influence

169 To identify air in the UT influenced by recent deep convection, we calculated 10-day air mass back-trajectories using  
170 the Bowman trajectory model (Bowman, 1993) driven with meteorological fields (3 hourly,  $0.25^\circ$  horizontal resolution) from  
171 the National Centers for Environmental Prediction (NCEP) Global Forecast System (GFS). Trajectories were also run with  
172 MERRA2 and ERA5 reanalysis meteorology and the results were similar. Meteorological products from NCEP interpolated  
173 to the aircraft flight track agreed best with quantities measured on the aircraft during ATom, so all analyses were done using  
174 the trajectories based on the NCEP data.

175 A cluster of 245 trajectories was initialized within a grid ( $0.3^\circ \times 0.3^\circ \times 20 \text{ hPa}$ ; Fig. S1) centered around the DC-8  
176 flight track location every minute of flight (Fig. 1). The back-trajectory time step was 3 hours, based on the reanalysis data,  
177 while a time step of 15 minutes interpolated from the 3 hours reanalysis data was used for box model simulations. Uncertainty  
178 in the back-trajectory locations is represented by the 3-D spread in the trajectory cluster. The vertical uncertainty is estimated



179 as the standard deviation in pressure (hPa) of the trajectory cluster at each time. The horizontal uncertainty is estimated using  
180 a probability grid based on the trajectory cluster in longitude and latitude at each time (Fig. S1), where probability grid refers  
181 to the number of trajectories at each time that are within each latitude-longitude grid box ( $2^\circ \times 2^\circ$ ). For instance, if 24 of the  
182 trajectories are within a certain grid box at a certain time then the probability for that grid box is  $\sim 10\%$  (24/245). The probability  
183 that air sampled by the aircraft was influenced by deep convection was calculated based on coincidences of the back-trajectory  
184 cluster with satellite derived cloud locations and characteristics such as cloud top and base pressure levels (NASA Langley).  
185 To isolate deep convection, only clouds with vertical extent  $>5$  km were considered in the convective influence (CI)  
186 calculation. The CI probability is the fraction of the trajectories in each cluster that intersected a convective system within a  
187 distance tolerance of  $0.15^\circ$  ( $\sim 10$ - $15$  km), and for which the RH with respect to liquid water ( $RH_w$ ) of the trajectory was  $>50$   
188 %. If the CI probability determined in this manner was  $>95\%$ , we assume that the aircraft was sampling air strongly influenced  
189 by deep convection.

### 190 **2.3 Description of models**

191 We use two independent aerosol nucleation and growth box models to test if different nucleation schemes are  
192 consistent with observations, following the trajectories from convective outflow to the location of the aircraft. These two  
193 models are conceptually similar, but differ in size resolution and their support for different nucleation mechanisms. Our  
194 primary model, the Two-Moment Aerosol Sectional (TOMAS; Adams and Seinfeld, 2002; Pierce and Adams, 2009; Pierce  
195 et al., 2011) includes both neutral and charged mechanisms. The neutral mechanisms include sulfuric acid and water (binary  
196 scheme; Vehkamäki et al. (2002)), sulfuric acid, water, and ammonia (ternary scheme; Napari et al. (2002)), and sulfuric acid  
197 with organics (organics scheme; Riccobono et al., 2014; Yu et al., 2017). The charged mechanism is Dunne et al. (2016),  
198 which quantifies NPF in terms of sulfuric acid, ammonia, and ion concentration (also including neutral pathways). In addition  
199 to testing the role of organics in nucleation and growth, we also test the influence of organics on aerosol initial growth when  
200 added as a condensing species following the nucleation of particles formed by each of the nucleation schemes in TOMAS, as  
201 described in Sect. 2.3.1.

202 We also use the Model of Aerosols and Ions in the Atmosphere (MAIA; Lovejoy et al., 2004; Kazil and Lovejoy,  
203 2007) to test ion-assisted nucleation of sulfuric acid and water. Since ion-assisted nucleation simulations using MAIA did not  
204 explain the observed size distributions in our work, we focus on TOMAS model description and results, and the details on the  
205 MAIA model are in the Supplemental Material (Section S1). Some features common to both models are described below.

206 The MAIA and TOMAS box models are constrained to follow the meteorological conditions along the trajectories.  
207 They are initialized at the point where the trajectories intersect deep convection, and proceed forward in time until reaching  
208 the aircraft sampling location and time. The temperature, pressure, and  $RH_w$  vary based on the trajectory. We vary the initial  
209  $SO_2$ ,  $NH_3$ , and organic aerosol precursors in TOMAS and  $SO_2$  in MAIA (Table 1 and Supplemental Material Table S1) to see  
210 which initial values of these species allow for the best matches to the observed size distribution. We note that neither model  
211 explicitly simulates DMS, which is likely to be an important aerosol precursor through its oxidation to form  $SO_2$  and



212 subsequently  $\text{H}_2\text{SO}_4$ , as well as through its oxidation to methanesulfonic acid (MSA; Hodshire et al., 2019), which is a  
213 condensing species that may also be able to participate in NPF (Bork et al., 2014; Chen et al., 2015; Chen and Finlayson-Pitts,  
214 2017). Previous analyses have shown that most of the observed reactive gas phase sulfur above the boundary layer is in the  
215 form of  $\text{SO}_2$  (Veres et al., 2019). In this work, both models are initialized with a measurement-based, pre-existing background  
216 aerosol population that acts as a sink for condensable vapors and small particles (see Section 2.4). Nucleation-mode particles  
217 are initialized at zero concentration. We calculate the OH diurnal cycle using a prescribed peak noontime value based on  
218 observations of OH on the DC-8 aircraft (Section 2.4 and Supplemental Material Fig. S3). The OH concentration along the  
219 trajectory and the resulting production rate of  $\text{H}_2\text{SO}_4$  from oxidation of  $\text{SO}_2$  are then calculated. We ignore possible enhanced  
220 OH due to cloud reflectivity in the vicinity of convective outflow and reduced OH from shading by higher clouds.

### 221 2.3.1 The TOMAS box model

222 The TOMAS model simulates particle nucleation, condensation, and coagulation in 43 logarithmically spaced particle  
223 size bins, which represent dry diameters from 0.7 nm-10  $\mu\text{m}$ . TOMAS tracks the total aerosol number and mass of each species  
224 for each size bin. The simulated aerosol species are sulfate, ammonia, a representative oxidation product of biogenic organics,  
225 and water. In these simulations, neutral sulfuric acid-water nucleation is based on Vehkamäki et al. (2002), neutral sulfuric  
226 acid-water-ammonia nucleation is from Napari et al. (2002), ion-induced and neutral sulfuric acid-water and sulfuric acid-  
227 water-ammonia nucleation is from Dunne et al. (2016), and neutral sulfuric acid-organic nucleation is from Riccobono et al.  
228 (2014).

229 Vehkamäki et al. (2002), referred to here as VEHK, describe a parametrization for neutral sulfuric acid-water particle  
230 formation based on a classical nucleation model. They use a model for the hydrate formation relying on *ab initio* calculations  
231 of small sulfuric acid clusters and on experimental data for vapor pressures and equilibrium constants for hydrate formation.  
232 The parameterized formulas are valid at temperatures between 230.15 K and 305.15 K,  $\text{RH}_w$  from 0.01%-100%, and sulfuric  
233 acid concentrations from  $10^4$ - $10^{11}$   $\text{cm}^{-3}$ . Temperatures along the trajectories ranged between 218 and 252 K and thus were  
234 below the applicable temperatures of this nucleation scheme in 18 out of 32 simulated cases. In these low-temperature cases,  
235 we assume the temperature to be 230.15 K (i.e., we do not extrapolate beyond the bounds of the parameterization). When  
236 sulfuric acid concentration was  $<10^4$  molecules  $\text{cm}^{-3}$ , the model assumes a nucleation rate of zero, and it limits the maximum  
237 concentration of gas phase sulfuric acid to  $10^{11}$  molecules  $\text{cm}^{-3}$ .

238 In the Napari et al. (2002) scheme, referred to here as NAPA, the nucleation rate is parameterized using four variables:  
239 temperature,  $\text{RH}_w$ ,  $\text{H}_2\text{SO}_4$  concentration, and  $\text{NH}_3$  mixing ratio. The parameterization is valid for temperatures from 240–300  
240 K,  $\text{RH}_w$  from 5–95%, sulfuric acid concentrations from  $10^4$ – $10^9$  molecules  $\text{cm}^{-3}$ , ammonia mixing ratios from 0.1–100 ppt,  
241 and nucleation rates from  $10^{-5}$ – $10^6$   $\text{cm}^{-3}\text{s}^{-1}$ . When temperature is  $<240$  K or  $>300$  K (25 out of 32 simulated cases), or  $\text{RH}_w$  is  
242 outside of the limits stated above, the model assumes the temperature to be 240 or 300 K, and  $\text{RH}_w$  to be 5 or 95 %, respectively.  
243 When the sulfuric acid concentration is  $<10^4$  molecules  $\text{cm}^{-3}$  the model assumes a nucleation rate of zero, and it limits the  
244 maximum concentration of gas phase sulfuric acid to  $10^9$  molecules  $\text{cm}^{-3}$ .





245 This parametrization accounts only for hydrate formation and neglects the formation of ammonium bisulfate and its  
246 effect on nucleation rate (Zhang et al., 2010). It overpredicts the effect of ammonia on nucleation when compared with  
247 laboratory measurements (Zhang et al., 2010). Merikanto et al. (2007) showed that nucleation rates based on the NAPA scheme  
248 were biased high, and Lucas and Akimoto (2006) indicated that this scheme in a global model predicted unrealistically high  
249 nucleation rates throughout the troposphere. To address these issues, Westervelt et al. (2013) and Jung et al. (2010) used a  
250 nucleation rate tuning factor of  $1 \times 10^{-5}$  in the boundary layer and found that the model produced a reasonable agreement with  
251 observations. In this study we performed simulations both with (NAPAt) and without (NAPA) this tuning factor.

252 In Dunne et al. (2016), referred to here as DUN, the inorganic nucleation rates determined experimentally in the  
253 CLOUD chamber are parametrized in four dimensions: sulfuric acid, ammonia, temperature (208-292 K) and ion formation  
254 rates ( $0-75 \text{ cm}^{-3} \text{ s}^{-1}$ ). Humidity is not included in this parametrization. The overall nucleation rate is given by the sum of the  
255 individual processes

$$256 J_{b,n} = k_{b,n}(T)[H_2SO_4]^{p_{b,n}} \quad (1)$$

$$257 J_{t,n} = k_{t,n}(T)f_n([NH_3], [H_2SO_4]) \quad (2)$$

$$258 J_{b,i} = k_{b,i}(T)n_-[H_2SO_4]^{p_{b,i}} \quad (3)$$

$$259 J_{t,i} = k_{t,i}(T)n_-f_i([NH_3], [H_2SO_4]), \quad (4)$$

260 where  $J_{b,n}$  is the binary neutral rate,  $J_{b,i}$  is the binary ion-induced rate,  $J_{t,n}$  is the ternary neutral rate,  $J_{t,i}$  is the ternary ion-  
261 induced rate,  $n_-$  is the steady state concentration of small negative ions and  $[H_2SO_4]$  and  $[NH_3]$  are gas concentrations ( $\text{cm}^{-3}$ ).  
262 In this paper, we investigated separately ion-induced binary (DUN with  $NH_3$  set to 0) scheme as well as the overall nucleation  
263 scheme (DUN) given by the sum of the above.

264 Sulfuric acid-organic nucleation was simulated using the scheme described in Riccobono et al. (2014), referred to  
265 here as RIC. While this scheme was developed to represent terrestrial organic species, we use it here as a surrogate for marine  
266 organic compounds because there are no specific mechanisms that have been developed for remote marine-sourced precursors.

267 The model includes a secondary organics aerosol precursor (SOAP;  $MW=200 \text{ g mol}^{-1}$ ) variable, which can oxidize  
268 to form a condensable aerosol species. This species can both participate in nucleation in the RIC scheme and condense onto  
269 particles in all schemes studied here. We assume a reaction rate constant for the oxidation of biogenic organic species against  
270 OH is  $\sim 3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ molec}^{-1}$ , which is roughly an average reaction rate of non-methane alkanes according to Table 1 of  
271 Atkinson and Arey (2003). This rate constant gives a SOAP lifetime of  $\sim 2$  days for a typical diurnally averaged UT OH  
272 concentration of  $2 \times 10^6 \text{ cm}^{-3}$ . The yield of SOAP to secondary organic aerosol (SOA) is set to 1, which allows us to use SOAP  
273 as a simple, tunable variable to determine how much SOA may be necessary to match observed aerosol formation and growth.  
274 We use the SOAP oxidation product (i.e. condensable organic) in the RIC scheme, but also use it to explore the effects of  
275 organics on new particle growth for each of the nucleation schemes (Riipinen et al., 2011).

276 In the RIC mechanism, nucleation occurs when only a fraction of the oxidation products of biogenic organic  
277 compounds (*BioOxOrg* in the terminology of the RIC mechanism), formed from SOAP oxidation, are able to form stabilized



278 clusters. The formation rate dependence on sulfuric acid and *BioOxOrg* concentration is given by a fit to experimental data in  
279 the form

$$280 \quad J_{ORG} = k_{NUC}[H_2SO_4]^p[BioOxOrg]^q, \quad (5)$$

281 where  $J_{ORG}$  is the formation rate ( $\text{cm}^{-3} \text{s}^{-1}$ ) of stable particles with diameters  $\sim 1.7 \text{ nm}$ ,  $k_{NUC}$  is the nucleation rate constant with  
282 a value of  $3.27 \times 10^{-21} \text{ cm}^6 \text{ s}^{-1}$  at 278 K and  $\text{RH}_w$  at 39 %, *BioOxOrg* represents concentration of later generation oxidation  
283 products of biogenic monoterpenes ( $\text{cm}^{-3}$ ), and the exponents  $p=2$  and  $q=1$  represent the power law dependence of  $J_{ORG}$  upon  
284 the concentrations of sulfuric acid and *BioOxOrg*.

285 Using the RIC scheme, we test the effect of different fractions of condensable organic formed from SOAP oxidation.  
286 This fraction,  $F_{orgnuc}$  represents the fraction of the condensable *BioOxOrg* that may participate in nucleation by stabilizing the  
287 cluster. The value of  $F_{orgnuc}$  does not affect the condensation of organics onto already-nucleated or pre-existing particles. Using  
288  $F_{orgnuc}$  allows us to decouple the possible role of organics in nucleation vs. their role in subsequent condensational growth.

289 Since RIC scheme does not consider the possible effect of temperature on the nucleation rate, we modify the  
290 nucleation rates predicted in equation (5) using the temperature dependence (270-310 K) for this nucleation rate from Yu et  
291 al. (2017)

$$292 \quad J_{ORG-T} = J_{ORG} f_T \quad (6)$$

$$293 \quad f_T = \exp \left[ \frac{\Delta H}{k} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (7)$$

294 where  $f_T$  is the nucleation rate scale factor accounting for the temperature dependence, and  $\Delta H$  is the change in enthalpy of -  
295 38.3  $\text{kcal mol}^{-1}$  associated with the critical cluster formation. We assume that  $\Delta H$  is constant throughout our full temperature  
296 range.

297 One of the limitations of our box modeling effort is that the temperatures along the trajectories ranged between 218  
298 and 252 K, often below the applicable temperatures of the three nucleation schemes: VEHK, NAPA and RIC (Supplemental  
299 material Table S2). We would expect faster nucleation rates at the lower trajectory temperatures than are simulated by these  
300 schemes (e.g. Yue and Hamill, 1979). Using VEHK and NAPA schemes below their lower temperature limit means forcing  
301 them to their lowest rated temperature 230.15 K and 240 K respectively. This in turn may result in underestimating particle  
302 concentration and size. This bias for cold cases means that VEHK and NAPA schemes may predict  $\text{SO}_2$  and organic precursors  
303 that would be anomalously high. In the RIC scheme the temperature dependence of Yu et al. (2017) is not experimentally  
304 verified down to the tropical UT temperatures. Thus, we tested the impact of changing the  $\Delta H$  by  $\pm 3 \text{ kcal mol}^{-1}$  (Supplemental  
305 material Fig. S2). We also have not explored the organic-only nucleation scheme by Kirkby et al. (2016).

## 306 2.4 TOMAS input data

307 Measured and estimated inputs needed to initialize the TOMAS box model (Adams and Seinfeld, 2002; Pierce and  
308 Adams, 2009; Pierce et al., 2011) are given in Table 1. TOMAS was configured to use measured size distributions ( $>12 \text{ nm}$ )  
309 in discrete bins. Each input in Table 1 represents the initial conditions present at the start of the simulation ( $t_0$ ). Hence,



310 condensing vapor in the gas phase can contribute both to the formation and growth of new particles and growth of the pre-  
311 existing background aerosol.

312 We expect the output of the TOMAS model to be sensitive to the temperature dependence of nucleation rates, the  
313 type and number of organic compounds, SO<sub>2</sub>, OH, NH<sub>3</sub> mixing ratios, and the pre-existing background aerosol into which the  
314 convective outflow is mixed. The variability of the simulated aerosol size distribution to various initial conditions was  
315 examined by conducting sensitivity simulations (Table 1) on SO<sub>2</sub>, NH<sub>3</sub>, OH, background aerosol size distribution, organics  
316 added for initial growth (e.g., SOAP), and on the RIC scheme scale factor  $F_{orgnuc}$  for organics involved in cluster formation.

317 The pre-existing aerosol is estimated based on the 1-minute averaged size distributions for  $D_p > 12$  nm as observed at  
318 the aircraft location. The concentration of particles with  $D_p < 12$  nm is set to zero under the assumption that these particles were  
319 produced by the new particle formation being modeled and were not present in the background air at the point of mixing with  
320 the air detrained from convection. The box model simulations do not explicitly account for the mixing of highly scavenged air  
321 detraining from convective outflow with surrounding UT air containing more aged aerosol (e.g., Weigel et al. 2011). We have  
322 undertaken sensitivity studies that vary the pre-existing background aerosol used as initial input parameter (Table 1).

323 The box model simulations were run forward in time from the moment the parcel exited the convection ( $t_0$ ) to the  
324 point of measurement by the aircraft ( $t_{fin}$ ), with temperature, pressure, and RH<sub>w</sub> varying as a function of time as determined  
325 from the back trajectory. The concentration of OH at solar zenith angle of 0° in the simulations was set to  $3 \times 10^6$  molecules  
326 cm<sup>-3</sup>; however, we also tested OH concentrations of  $1 \times 10^6$  and  $4.3 \times 10^6$  molecules cm<sup>-3</sup>. These estimates agree well with  
327 aircraft-measured concentrations (Supplemental Material Fig. S3) and with values given in Seinfeld and Pandis (2006). In  
328 TOMAS, OH is parameterized as a function of the cosine of the solar zenith angle, where the night-time OH is  $1 \times 10^5$  molecules  
329 cm<sup>-3</sup>. The solar zenith angle is calculated for the time, altitude, latitude, and longitude of the back trajectories.

330 The SO<sub>2</sub> and NH<sub>3</sub> mixing ratios were varied between 1 and 100 pptv to explore a large range of plausible conditions.  
331 The evaluated SO<sub>2</sub> range exceeds that measured on ATom 4 (Supplemental Material Figs. S4 and S5) and covers the <30 pptv  
332 mixing ratios previously reported in the UT over the central and western tropical Pacific (Thornton et al., 1997; Rollins et al.,  
333 2017; Rollins et al., 2018). Organic aerosol precursors are unknown in the UT and were not directly measured; thus we explored  
334 a range of probable mixing ratios between 1 and 100 pptv.

335

336 Table 1. Ranges of parameters used for sensitivity studies in the TOMAS box model. Values varied to match the observed size  
337 distribution in *italic*).

Parameter		Initial value used
Abbreviation	Unit	TOMAS
SO <sub>2</sub> *	pptv	<i>1-100</i>
NH <sub>3</sub>		<i>1-100</i>
Secondary organic aerosol precursors (SOAP)		<i>1-100</i>
$F_{orgnuc}$ **	%	<i>10, 50, 100</i>
OH at solar zenith angle of 0°	molecule cm <sup>-3</sup>	<i>1x10<sup>6</sup>, 3x10<sup>6</sup>, 4.3x10<sup>6</sup></i>



OH at night		1x10 <sup>5</sup>
Napari et al. (2002) scheme; nucleation rate tuning factor 1x10 <sup>-5</sup>		tuning factor on/off
Time since CI	hours	0.4-23.3
Ion concentration	cm <sup>-3</sup> s <sup>-1</sup>	15
Background pre-existing aerosol		
Size distribution (SD)		Varied measured initial input size distribution: ***SD>12nm, SD>12nm x2, SD>12nm /2, SD=0, SD>12nm-5nm, SD>8nm, SD as logarithmic fit

338 \* SO<sub>2</sub> measured on ATom 4 only  
 339 \*\* fraction of SOAP participating in nucleation when using Riccobono et al. (2014) in TOMAS.  
 340 \*\*\* initial background aerosol size distribution was varied: SD>12nm means background SD as described in the text was used to initiate the  
 341 model; SD>12nm x2 means background SD multiplied by 2; SD>12nm /2 means SD divided by 2; SD=0 means no background aerosol;  
 342 SD>12nm-5nm means SD was shifted by 5 nm to smaller diameters; SD>8nm means measured background SD >8nm was used as initial  
 343 SD.  
 344

## 345 2.5 Evaluating simulated size distributions

346 To determine which sets of parameters allow the models to reproduce the observed size distributions best, we evaluate  
 347 every simulation against observations using the normalized mean error (*NME*) statistic of the first four moments (0<sup>th</sup> through  
 348 3<sup>rd</sup>) of the size distribution for each model simulation as

$$349 \quad NME = \frac{\sum_{i=0}^3 \frac{|S_i - O_i|}{O_i}}{4}, \quad (8)$$

350 where  $S_i$  and  $O_i$  are  $i^{\text{th}}$  moments of the simulated and observed size distributions, respectively (Hodshire et al., 2018).

351 The  $i^{\text{th}}$  moment is defined as

$$352 \quad M_i = \int_{2.6}^{20} n_N D_p^i dD_p, \quad (9)$$

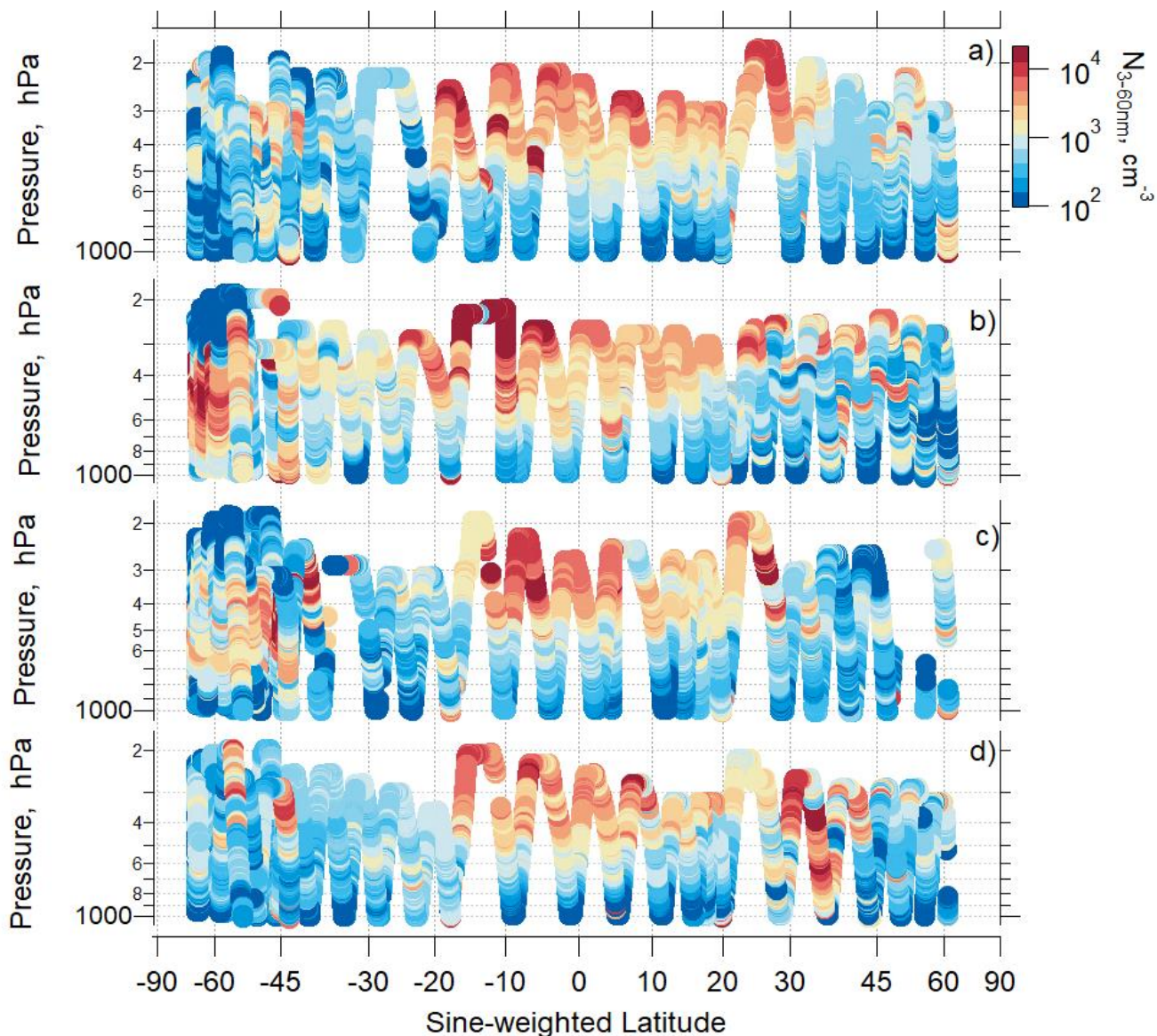
353 where  $n_N$  is the number of particles in size interval  $dD_p$  and  $D_p$  is the diameter. Equation (9) is integrated over the diameter  
 354 range from 2.6-20 nm, and  $M_i$  represents either  $S_i$  or  $O_i$ . The zeroth moment ( $i=0$ ) corresponds to the number of particles, the  
 355 first moment ( $i=1$ ) to the total diameter of particles (i.e. total aerosol length), the second moment ( $i=2$ ) is proportional to the  
 356 total surface area of particles, and the third moment ( $i=3$ ) is proportional to the total volume of particles. A *NME* of 0 is a  
 357 perfect fit between the simulation and observations; a *NME* of 1.0 indicates that the average bias of the 0<sup>th</sup> through 3<sup>rd</sup> moments  
 358 between the simulation and observations is 100%. As the *NME* is given as an absolute value, we do not discriminate between  
 359 cases in which the model is underpredicting or overpredicting the moments on average. Since these moments are equally  
 360 weighted, a low value of *NME* can be achieved only if the modeled size distribution accurately simulates both the shape and  
 361 magnitude of the observed size distribution over the full range of sizes evaluated.



362 **3. Results**

363 **3.1 Observations**

364 Our data show seasonally persistent high nanoparticle concentrations over the remote tropical UT (Fig. 2; Williamson  
365 et al., 2019). In this region, the highest concentrations of particles were in the nucleation mode (3-12 nm), which have a short  
366 lifetime and are the products of recent NPF. This tropical UT feature was observed in all ATom deployments over all four  
367 seasons, over both the Pacific and Atlantic basins. The concentrations of particles observed in the UT over the tropical Atlantic  
368 were lower in concentration than observed over the Pacific (Supplemental Material Fig. S6). In this study, we focus on  
369 observations over the remote Pacific, which is a region less perturbed by continental emissions than the Atlantic (Fig. 3 and  
370 Supplemental Material Fig. S7 and S8).



371

372 **Figure 2: Ambient pressure as a function of latitude colored by the measured number concentration of particles with  $D_p$  from 3 - 60**  
373 **nm over the Pacific Ocean for a) ATom 1, July-August 2016; b) ATom 2, January-February 2017; c) ATom 3, September-October**  
374 **2017; and d) ATom 4, April-May 2018). Periods of flight in clouds, over continents and near airports have been removed.**

375

376 Previous studies (e.g. Clarke, 1992, 1993; Clarke et al., 1998, 2006; Brock et al., 1995; Weber et al., 1995; Raes et  
377 al., 1997; Thornton et al., 1997; Weber et al., 1998; Clarke and Kapustin, 2002; Twohy et al., 2002; Froyd et al., 2009;  
378 Borrmann et al., 2010; Weigel et al., 2011) have provided strong evidence of NPF in the tropical UT and its link to convective  
379 activity. However, these earlier studies did not provide such extensive, representative, and global-scale coverage of the remote

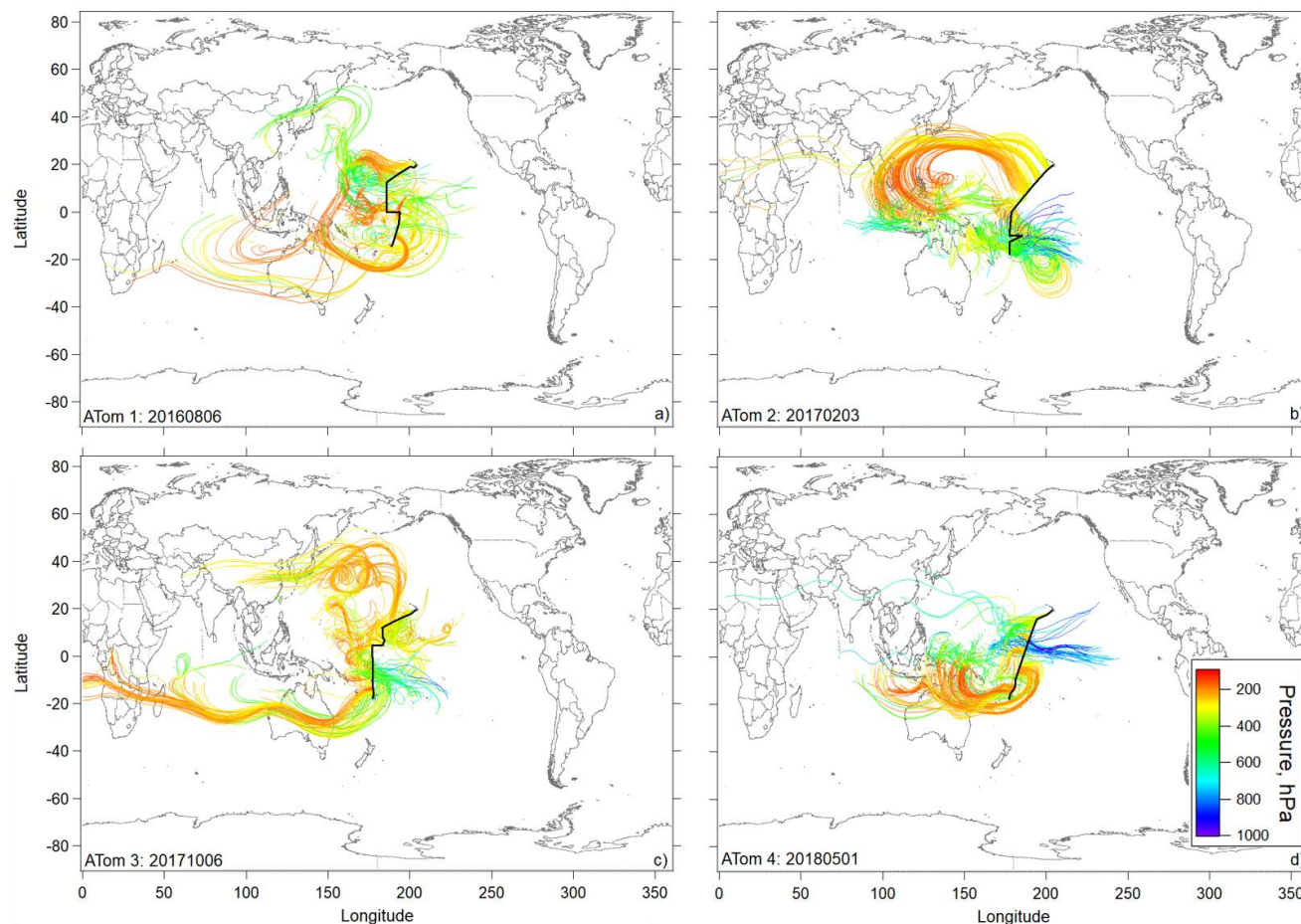


380 marine troposphere over a wide range of altitudes and latitudes (Williamson et al., 2019). The ATom observations also provide  
381 accurate and sensitive, state-of-the-science measurements of the chemical composition of the bulk aerosol and the abundance  
382 of hundreds of gas-phase species in all four seasons, making these observations the most comprehensive to date. However, no  
383 measurements were made during ATom of  $\text{NH}_3$ , the highly oxygenated organic molecules that are likely aerosol precursors,  
384 or molecular cluster composition, and measurements of  $\text{SO}_2$  took place only during the fourth ATom deployment.

385 Ten-day back trajectories in the region of NPF in the central Pacific showed transport primarily over the Pacific, with  
386 some possible terrestrial influence from the western Pacific region (Fig. 3). However, trajectories coming from the western  
387 Pacific generally stayed at high altitudes and did not show recent convective uplift from regions influenced by terrestrial  
388 sources. Further, CO and other continental tracers were at background levels over the Pacific, confirming little continental  
389 influence in the sampled air masses (Supplemental Material Fig. S7), as opposed to the Atlantic (Supplemental Material Fig.  
390 S6 and S7). Thus, the precursors of the recently formed particles are likely mostly marine in origin. The latter is also supported  
391 by the measurement of particle phase methanesulfonic acid (MSA) that can be considered as a tracer for maritime influence  
392 on the tropical UT (Fig. S9).

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**Figure 3: Flight track and selected 10-day back trajectories initiated for times in flight at pressures <400 hPa (<~260 K) sampled along the DC-8 flight track during ATom 1, 2 (a, b), 3 and 4 (c, d) during the most tropical flight in each deployment (Hawaii-Samoa on ATom 1 and Hawaii-Fiji on ATom 2-4). Trajectories are colored according to the pressure along their pathway.**

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The observations and trajectory modeling show that newly formed particles were often associated with deep convection. Using the CI probability criterion of 95% to identify when the aircraft was sampling air recently influenced by convection (Sect. 2.2), and considering the latitude range 30° S - 30° N and ambient temperatures <260 K, for ATom 1 and 2, the shorter the time since convection, the higher the number of small particles (Fig. 4a-d). Such strong trends were not evident for ATom 3 and 4 indicating that factors other than time since CI affect nucleation-mode concentrations. The more recent the convection, the smaller the diameter of the nucleation mode (Fig. 4e-h). These relationships are again strongest for ATom 1 and 2 and also 4. Our hypothesis for these relationships is that with increasing time since CI, particles with diameters <12 nm grew by condensation and coagulation and decreased in concentration by coagulation, leading to the decrease in nucleation-mode concentration and increase in diameter. A similar trend was observed over the Atlantic (Supplemental Material Fig.

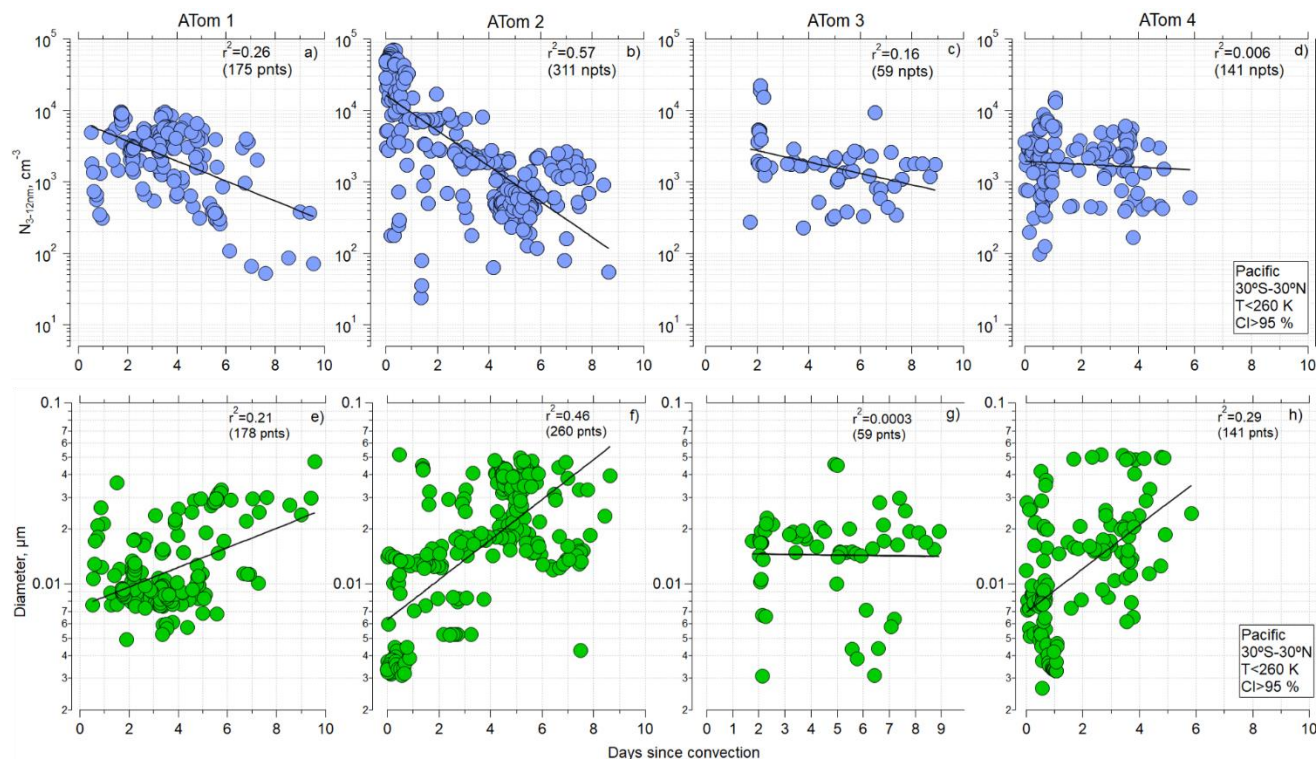




409 S10). The highest concentrations of nucleation-mode particles occurred during ATom 2 and were associated with the shortest  
410 times since CI.

411

412

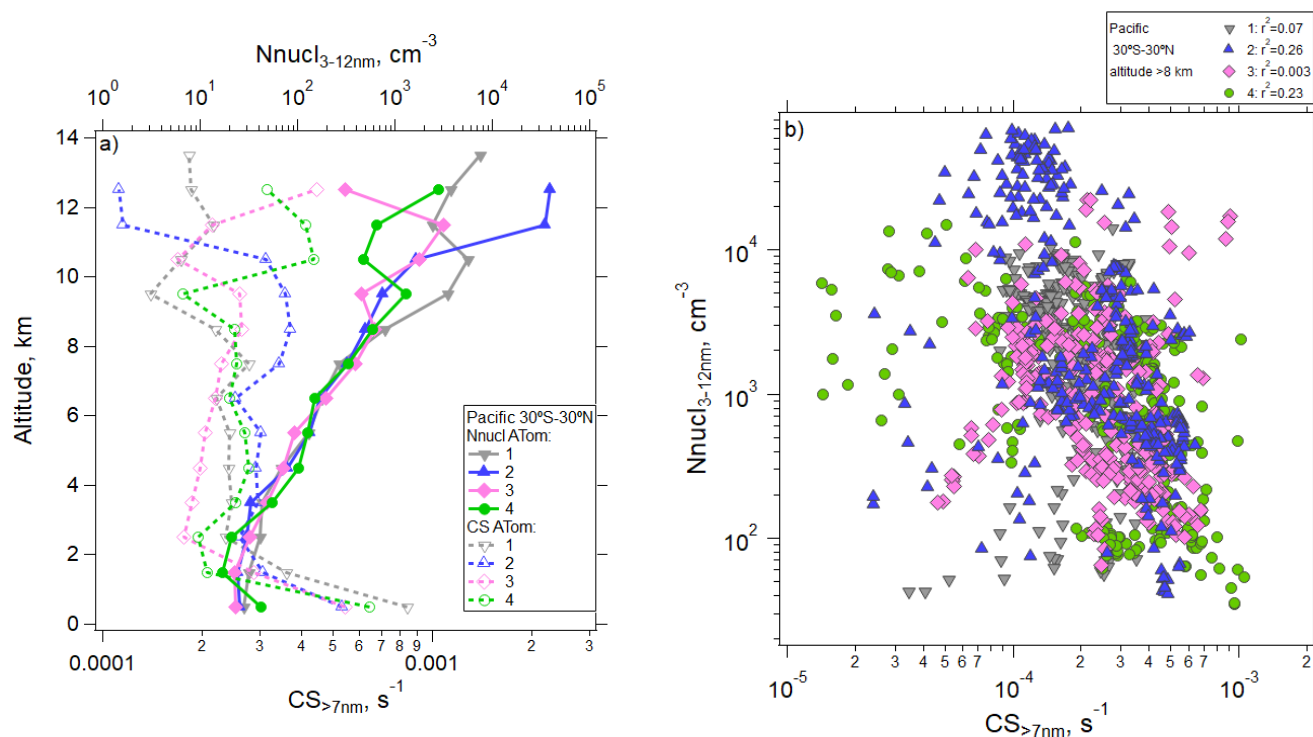


413

414 **Figure 4:** (a-d) Concentration of nucleation mode particles as a function of time since convective influence for ATom 1-4, over Pacific  
415 (30° S - 30° N), T<260 K and probability of convective influence >95 %, respectively. (e-h) Modal diameter of particles with  $D_p < 0.06$   
416  $\mu\text{m}$  as a function of time since convective influence (30° S - 30° N) for ATom 1-4, respectively. Black line, used to guide the eye,  
417 represents the linear regression fitted to log-y values. A corresponding Pearson correlation coefficient  $r^2$  is indicated.

418

419 Air detraining from deep convection is likely depleted in pre-existing particles due to in-cloud removal, leading to a  
420 reduced condensation sink (CS) that enhances the likelihood of NPF (e.g., Clarke, 1992; Williamson et al., 2019). Figure 5  
421 shows the concentration of measured nucleation-mode particles as a function of altitude for the Pacific basin over four ATom  
422 missions. The median concentration of nucleation mode particles averaged from 30° S to 30° N is highest at altitudes >10 km,  
423 reaching  $\sim 40,000 \text{ cm}^{-3}$  (Fig. 5a), coinciding with the lowest values of CS, which competes with NPF for condensing vapors.  
424 The CS term is calculated for particle diameters >7 nm following Williamson et al. (2019). Over the Atlantic, the maximum  
425 concentration of nucleation-mode particles >8 km in altitude averaged from 30° S to 30° N,  $\sim 3,000 \text{ cm}^{-3}$ , is considerably  
426 smaller than over the Pacific, but the shape of the profile is similar (Fig. S11).



427 **Figure 5. a)** Vertical profile of the median number concentration of nucleation mode particles (3-12 nm) and condensation sink (CS)  
 428 averaged between 30° S - 30° N as a function of altitude for the four ATom deployments. **b)** One minute average nucleation mode  
 429 particle concentrations at  $>8$  km in altitude as a function of CS between 30° S - 30° N over the Pacific Ocean. Pearson correlation  
 430 coefficient values ( $r^2$ ) are indicated in the legend.

431 Some variability in the strength of NPF and its dependence on CS can be observed. In general, CS is weakly negatively  
 432 correlated ( $r^2$  between 0.03 and 0.26 depending on the ATom mission with the concentration of nucleation mode particles (Fig.  
 433 5b), as would be expected if NPF were competing with CS for condensing vapors. Factors other than CS are also important in  
 434 controlling the concentrations of newly formed particles. These factors may include temperature and  $RH_w$ , actinic flux, and  
 435 OH that drive photochemical reactions that oxidize precursor species, the abundance of those precursor species in the air lifted  
 436 by convection and in the background air, and the time since the air parcel exited a convective cloud (Figs. S12-S13).

### 437 3.2 Box model simulations

438 Case studies were selected for box model simulations based on specific criteria such as temperature and CI  
 439 probability. We restrict the analysis to data taken nominally in the tropics and subtropics, between 30° S - 30° N latitude. We  
 440 consider the case for analysis by box modeling if the CI probability is  $>95\%$ , temperature at the point of measurement is  $<260$   
 441 K, and an aerosol number mode with a modal peak diameter  $<12$  nm is present (Table 2). We performed simulations for 32  
 442 cases randomly selected from the ATom 2 (20 out of 47 identified cases) and ATom 4 (12 out of 60 identified cases) datasets  
 443 over the remote tropical Pacific from the total number of 109 cases with time since convection  $<1$  day (Table 2). Data from



444 ATom 2 and ATom 4 were selected for simulations because these deployments had the most identified cases with time since  
445 CI <1 day. During ATom 2, we observed the highest numbers of nucleation mode particles, lowest condensation sink, and  
446 shortest time since convection (Fig. 5) among all missions. Measurements of SO<sub>2</sub> mixing ratio were made only during the  
447 ATom 4 deployment, providing an important constraint for the box model simulations. We did not perform simulations on  
448 ATom 1 and ATom 3 data as there were only 2 and 0 identified cases with time since CI <1 day, respectively (Table 2).

449 The correlation between nucleation-mode particles and time since CI was strongest in ATom 2 (Fig. 4), while CO  
450 levels, a proxy for continental influence, were the lowest for trajectory times <1 day (Supplemental Material Fig. S7). Although  
451 SO<sub>2</sub> was not measured during ATom 2, we expect SO<sub>2</sub> in this region in the UT to be <30 pptv based on SO<sub>2</sub> levels measured  
452 during ATom 4 and other missions in the Pacific (Supplemental Material Figs. S4, S5).

453

454 Table 2. Number of identified cases of recent NPF associated with CI for the Pacific (Atlantic in Table S4) between 30° N and  
455 30° S latitude that meet the following criteria: T<260 K, CI > 95%, and modal peak diameter < 12 nm.

ATom mission	Number of cases meeting selection criteria		
	Trajectory age <1 day	Trajectory age 1-2 days	Trajectory age 2-3 days
1	2	20	49
2	47	3	4
3	0	0	5
4	60	9	2
Total	109	32	60

456

457 The size distributions simulated by TOMAS were smoothed to avoid the artificial distortion of the distribution caused  
458 through size-bin emptying (Hodshire et al., 2019; Stevens et al., 1996). The latter and the smoothing technique are described  
459 in Supplemental Material Section S2.

460 We performed box model simulations on the 32 selected cases using the range of values listed in Table 1. The success  
461 of each model simulation was evaluated using the *NME* described by Eq. 8. As an example using a single case, Fig. 6a shows  
462 the observed and simulated aerosol size distribution with the best *NME* obtained for each of the various nucleation schemes  
463 tested, along with the corresponding mixing ratios of SO<sub>2</sub>, NH<sub>3</sub>, or organics. Organics here refer to the SOAP oxidation product  
464 (i.e. condensable organic) that participates in nucleation in the RIC scheme (as *BioOxOrg*), and in the particle condensational  
465 growth in all schemes. The value of *NME* as a function of the mixing ratios of SO<sub>2</sub>, NH<sub>3</sub>, and organics for each nucleation  
466 scheme is also shown (Fig. 6b-j). The summary of each of the 32 simulated cases is presented in Supplemental Material Table  
467 S4 and Figs. S15-S45. The simulations in Fig. 6 used the default OH scheme with a maximum concentration of 3x10<sup>6</sup> cm<sup>-3</sup> at  
468 a solar zenith angle of 0° (Supplemental Material Fig. S3). Sensitivity studies for maximum OH values of 1x10<sup>6</sup>, 3x10<sup>6</sup> and  
469 4.3x10<sup>6</sup> cm<sup>-3</sup> are presented in Supplemental Material Fig. S46-S50.



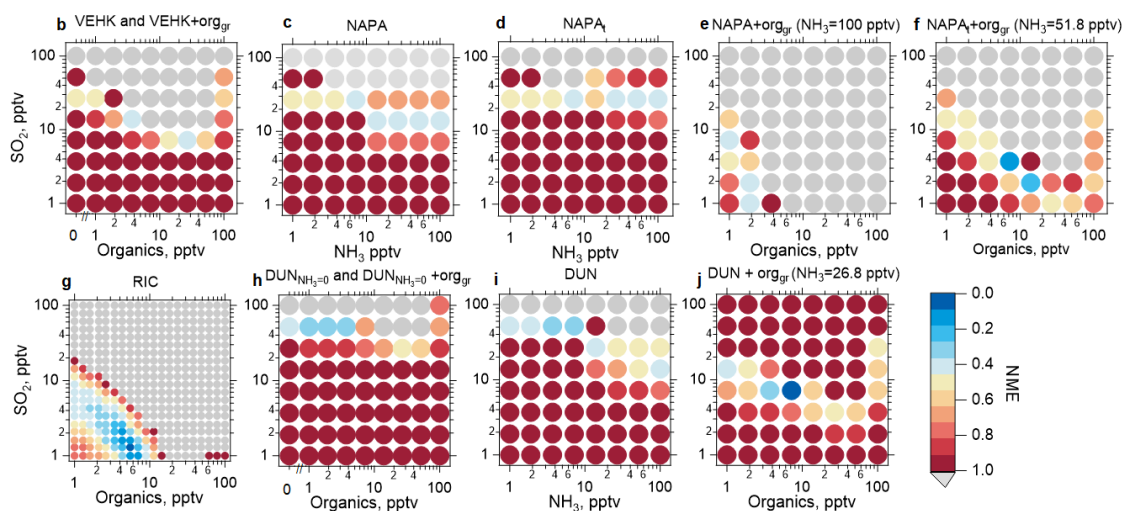
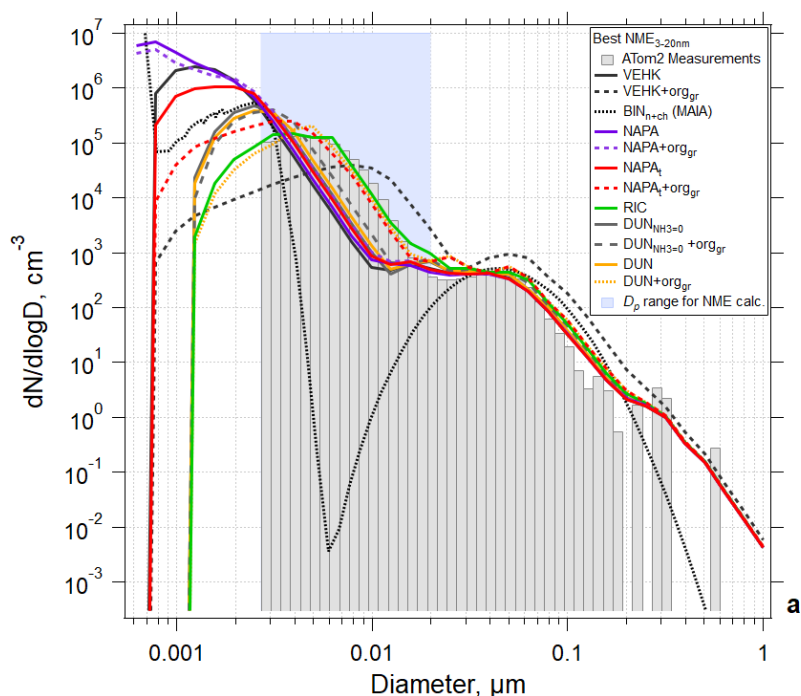
470 TOMAS simulations using VEHK scheme substantially underpredict the observed tropical nucleation-mode number  
471 concentration, with resulting poor values of *NME* (Fig. 6). Sensitivity tests that vary the pre-existing initial (background)  
472 aerosol or completely remove background particles do not change the results significantly (Supplemental Material Fig. S51-  
473 S53). Further, we find that changing initial input parameters such as SO<sub>2</sub> and OH as indicated in Table 1 do not improve the  
474 *NME* for VEHK scheme (Fig. 6b; Supplemental Material Fig. S46). Adding organics to grow particles nucleated by the VEHK  
475 scheme, while reducing *NME* slightly, does not provide adequate agreement with the observations. Similarly, the ion-assisted  
476 binary nucleation scheme of the MAIA box model does not provide good matches with observations (Supplemental Material  
477 Table S4).

478 The NAPA scheme, both with (NAPAt) and without (NAPA) the tuning factor, did not significantly reduce the *NME*  
479 values from the VEHK results for this case (Fig. 6c). However, when organics were added to condense on the particles  
480 nucleated by this mechanism, the *NME* was reduced to 0.17. The RIC nucleation scheme, updated by the temperature  
481 dependence of Yu et al. (2017), provides the best *NME* (*NME*=0.02) for all the schemes investigated (Fig. 6f) for the case  
482 shown in Fig. 6. We explored this mechanism with 6 more sensitivity simulations, including various combinations of initial  
483 SO<sub>2</sub> and organic mixing ratios, to see how sensitive *NME* is to small changes of initial precursor vapor mixing ratios. For the  
484 example case presented in Fig. 6a, organic mixing ratios <10 pptv and SO<sub>2</sub> mixing ratios <5 pptv were sufficient to produce  
485 size distributions that matched the observations with good fidelity (*NME* =0.02). Varying the scale factor of organics taking  
486 part in nucleation ( $F_{orgnuc}$ ) did not change the results significantly (Supplemental Material Fig. S48).

487 The most recently developed NPF mechanism, the ion-induced sulfuric acid-water, referred here as DUN with NH<sub>3</sub>  
488 set to 0, and the sulfuric acid-water-ammonia (DUN) nucleation scheme from Dunne et al. (2016), did not provide the lowest  
489 *NME* values among the schemes tested, although adding organics for initial growth of the nucleated particles improved the fits  
490 (*NME*=0.04) (Fig. 6i, Supplemental Material Table S4). The addition of organics resulted in best *NME* values for DUN in 5  
491 out of the 32 cases simulated.

492 Overall, a reduction in *NME* when organics are added for initial particle growth was also observed for other schemes  
493 (Supplemental Material Table S4). Out of 32 case studies, we found 6 cases when the NAPAt with organics for growth and  
494 the tuning factor applied gave lower *NME* values than all other schemes. However, 4 out of these 6 cases require SO<sub>2</sub> or NH<sub>3</sub>  
495 mixing ratios >50 pptv that exceed ATom 4 SO<sub>2</sub> observations and literature values in the tropical UT for SO<sub>2</sub> of <30 pptv (Fig.  
496 S4; (Rollins et al., 2018; Rollins et al., 2017; Thornton et al., 1997) and for NH<sub>3</sub> of <10 pptv (Höpfner et al., 2016; Feng and  
497 Penner, 2007; Adams et al., 1999).

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	VEHK*	VEHK*+org <sub>gr</sub>	BIN <sub>n+ch</sub> (MAIA)	RIC*	NAPA*	NAPA*+org <sub>gr</sub>	NAPA <sub>i</sub> *	NAPA <sub>i</sub> *+org <sub>gr</sub>	DUN <sub>NH<sub>3</sub>=0</sub>	DUN <sub>NH<sub>3</sub>=0</sub> +org <sub>gr</sub>	DUN	DUN+org <sub>gr</sub>
NME <sub>3-20nm</sub>	0.48	0.41	0.73	0.02	0.42	0.38	0.39	0.17	0.37	0.30	0.34	0.04
SO <sub>2</sub> , pptv	26.8	7	26.8	1.3	13.9	7.2	26.8	3.7	51.8	51.8	51.8	7.2
Organics, pptv		26.8		5.5		1		7.2		1		7.2
NH <sub>3</sub> , pptv					13.9	100	100	51.8			7.2	26.8

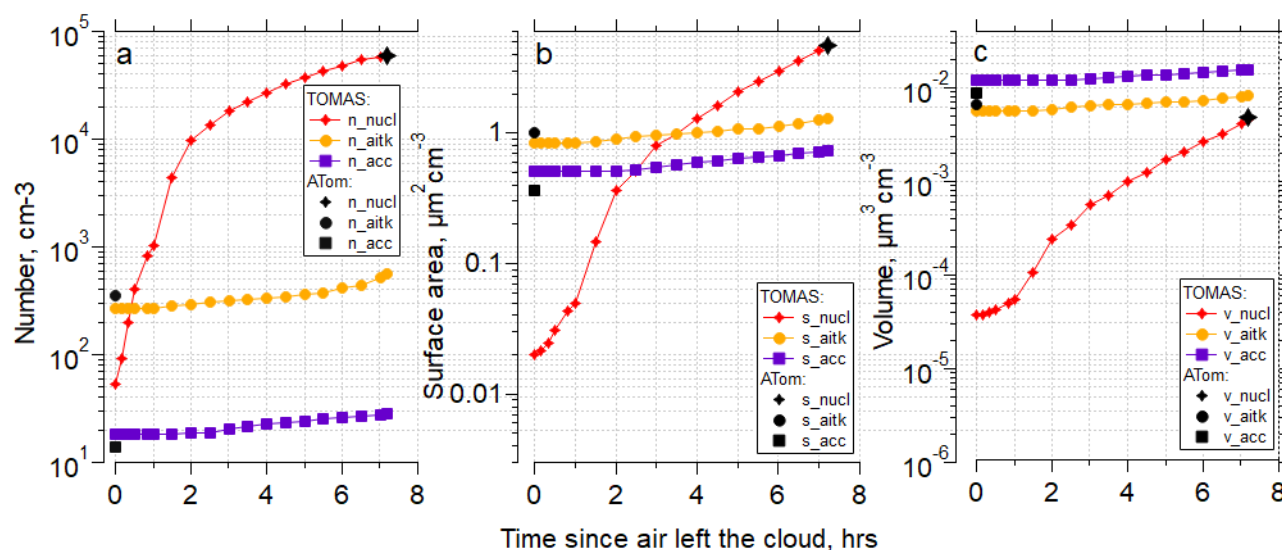
\*Temperature along the trajectory does not lie within the temperature range of the scheme

502 **Figure 6:** Results of simulations using the TOMAS box model for an example case (ATom 2, 2017-02-04, 03:05:31-03:06:30 UTC)  
 503 where measurements were made 7.3 hours following convective influence, and temperature along the trajectory varied between 218  
 504 and 226 K. (a) Observed (shaded bars) and simulated (lines) aerosol size distributions with best normalized mean error (NME)



505 calculated for  $D_p$  between 2.6 and 20 nm (blue shading) for each of the NPF and growth schemes investigated. Best results from the  
 506 MAIA box model ion-assisted + neutral binary nucleation scheme shown as a dotted black line. (b) *NME* between the modeled and  
 507 measured size distribution for the VEHK scheme with varying organics mixing ratios for condensational growth. The color of the  
 508 circle indicates the value of *NME* corresponding to a particular initial mixing ratio of  $\text{SO}_2$ ,  $\text{NH}_3$ , or organics that varied between 0  
 509 and 100 pptv. Blue represents the best agreement, red poorer agreement, and grey the worst ( $NME > 1$ ). There were 64 sensitivity  
 510 tests. (c) As in (b), but for the NAPA scheme. d) As in (c), but for the NAPAt scheme. (e) and (f) as in (c) and (d) respectively,  
 511 but with  $\text{NH}_3$  fixed and varying organics for condensational growth. (g) as in (b) but for the RIC scheme, which provides the lowest *NME*.  
 512 There were 400 sensitivity tests for this scheme. (h) as in (b) but for the DUN scheme with  $\text{NH}_3$  set to 0 ( $\text{DUN}_{\text{NH}_3=0}$ ). (i) as in (c) but  
 513 for the DUN scheme. (j) as in (i) but with varying organics for condensation growth. The table presents the *NME* results for the  
 514 corresponding size distributions in panel (a) and associated initial mixing ratios of gas-phase precursors.

515  
 516 Figure 7 shows the time evolution for particle number concentration, surface area, and volume for the nucleation,  
 517 Aitken, and accumulation modes using the Riccobono et al. (2014) scheme for the same case as shown in Fig. 6 for the  
 518 simulation with the lowest *NME* in Fig. 6g ( $\text{SO}_2=1.3$  pptv, organics=5.5 pptv). There is rapid evolution of the nucleation mode  
 519 and slower changes of the larger modes, and the model effectively matches the number, surface and volume of the measured  
 520 nucleation mode.  
 521



522  
 523 **Figure 7:** (a) TOMAS box model simulation of the case shown in Fig. 6 for the lowest (best) *NME* for the RIC scheme, showing  
 524 number concentration of the nucleation (3-12 nm), Aitken (12-60 nm) and accumulation (60-500 nm) modes as a function of time  
 525 since the air parcel exited the cloud to the time of measurement by the aircraft. Black symbols indicate values at the point of  
 526 measurement. The measured Aitken and accumulation mode values from the observations were used as approximate initial  
 527 conditions for the model simulation and are thus shown at time  $t=0$  (cloud outflow). (c) as in (a), but for surface area concentrations.  
 528 (c) as in (a), but for volume concentrations. Conditions for the simulations were diurnally varying OH concentrations with solar  
 529 zenith angle. Initial  $\text{SO}_2=1.3$  pptv, and initial organics=5.5 pptv.  
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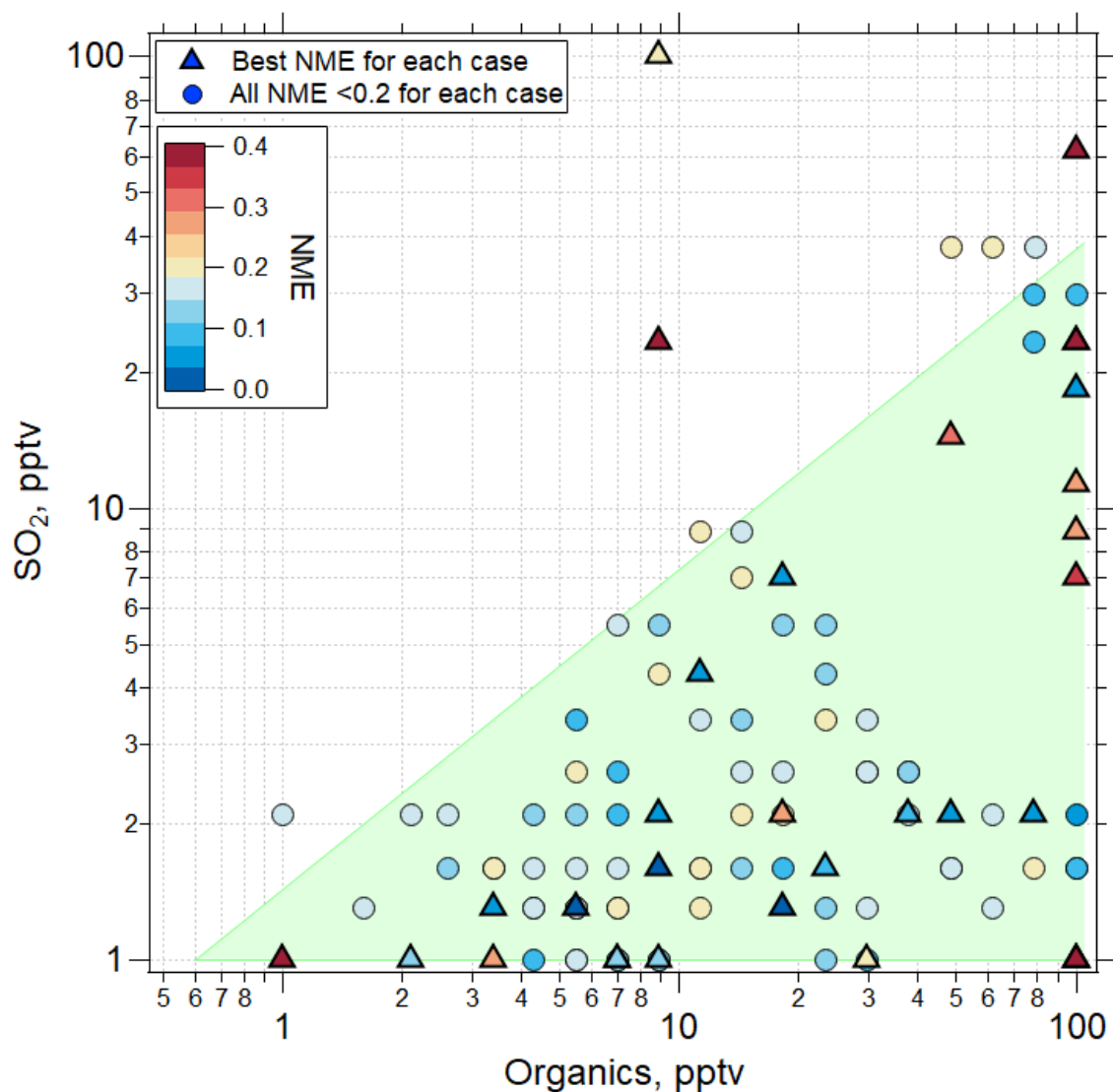


532 In 22 out of the 32 cases for which multiple box-model simulations were run, the sulfuric-acid-organic nucleation  
533 scheme of (Riccobono et al., 2014) produced lower (better) values of *NME* than the other parameterizations tested  
534 (Supplemental Material Table S4). Two of those 22 best *NME* cases for RIC were tied with NAPA and NAPAt, both with  
535 organics added for initial particle growth. The remaining 12 best *NME*s came from two different ternary nucleation schemes  
536 with added organics for growth of particles. These schemes were the NAPA or NAPAt, or the DUN with both charged and  
537 neutral channels. The majority of these ternary cases, however, required initial conditions of  $\text{NH}_3$  of 52 pptv or more, much  
538 greater than the mixing ratios expected at these locations in the UT (Höpfnér et al., 2016). Regardless of the available  $\text{NH}_3$ ,  
539 together these results strongly suggest that pure binary sulfuric acid-water nucleation, whether ion-assisted or neutral, and  
540 whether coupled with organic growth or not, generally cannot explain the ATom observations. While we are limited by the  
541 lack of direct observations of  $\text{NH}_3$ , amines, and condensable organic species, it is plausible that there are enough of these  
542 compounds—a few to tens of pptv—to participate in ternary nucleation and subsequent growth to be consistent with the ATom  
543 measurements.

544 The findings for the case of organic-mediated NPF are summarized in Fig. 8, where we show the  $\text{SO}_2$  and organic  
545 precursor mixing ratios for all sensitivity simulations with  $\text{NME} < 0.2$  for all the cases analyzed using the RIC scheme,  
546 highlighting the assumptions that yielded the lowest *NME* for each case. The results show that for all of the cases where  
547 sulfuric acid-organic nucleation most successfully simulated the observations (22 of 32 cases), initial  $\text{SO}_2$  mixing ratios  $< 30$   
548 pptv and organic precursors  $< 100$  pptv (with an assumed yield of 1) were needed. These  $\text{SO}_2$  mixing ratios are consistent with  
549 observations during ATom 4 (Figs. S4, S5, Table S5) and earlier results (Rollins et al., 2017; Rollins et al., 2018). Lacking  
550 measurements of condensable organic species, we can only speculate that a few to tens of pptv are reasonable for the marine  
551 tropical UT. Williamson et al. (2019; Extended Data Fig. 7) suggested that organics dominate the composition of smaller  
552 particles at pressure  $< 400$  hPa. We note that we performed no simulations with mixing ratios of  $\text{SO}_2$  or organics above 100  
553 pptv. While we cannot exclude that for some cases the mixing ratios of these precursors at levels above 100 pptv could improve  
554 fits, these levels are outside of prior observations so were not considered in this study.

555 In the case shown in Fig. 6, mixing ratios of  $\text{SO}_2$  and organics of  $\sim 1.3$  pptv and 5.5 pptv, respectively, were sufficient  
556 to nucleate particles and produce a size distribution that matched the observations with an *NME* of 0.02 using the RIC scheme.  
557 In a majority of the cases, the RIC scheme predicted  $\text{SO}_2 < 5$  pptv that are lower than typical UT  $\text{SO}_2$  concentrations, suggesting  
558 that our temperature extrapolation may overpredict nucleation rates at the typical  $\text{SO}_2$  mixing ratios of  $\sim 30$  pptv in the UT.  
559 Overall, the lowest *NME* values were obtained when initial  $\text{SO}_2$  values were low ( $< 30$  pptv), while organics varied over a  
560 range of mixing ratios as shown by triangles in Fig. 8. This suggests that organic matter will often contribute significantly to  
561 the composition of the nucleated and growing particles on a mole basis, and even more so on a mass basis because the assumed  
562 molecular weight of organic precursors and products is  $200 \text{ g mol}^{-1}$  compared  $96 \text{ g mole}^{-1}$  for  $\text{SO}_4$ .

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**Figure 8:** Values of *NME* (colored symbols) for best fits of the sensitivity studies. TOMAS model simulations were made using the RIC sulfuric acid-organic scheme. Among the sensitivity tests using this scheme, the one with the lowest *NME* case is shown with a triangle located at the initial conditions of SO<sub>2</sub> and organics for that case, while the next best *NME* case (provided *NME* < 0.2) is shown as a circle. The shaded region represents the approximate parameter space in which the best agreement between model and measurement is found for all the convective influence cases studied. Note a different *NME* color scale range (0 - 0.4) than the one presented in Fig. 6 (0 - 1).





### 573 3.3 Discussion

574 Comparing aerosol size distribution measurements with box-model simulations shows that none of the binary neutral  
575 or ion-assisted NPF schemes are consistent with observations, regardless of precursor concentrations and the presence or  
576 absence of condensing organics for further growth. These schemes predict significant nucleation but do not make enough  
577 particles in the 5-20 size range (Fig.6) to match observations. Adding organics for initial growth of particles shifts the size  
578 distribution to bigger sizes but only slightly improves the model-to-measurement fits (Table S4).

579 However, schemes that incorporate organic compounds or  $\text{NH}_3$  to nucleate particles, plus condensing organics as  
580 growth agents, can plausibly replicate the observed size distributions. These results suggest that organic precursor species are  
581 likely important in NPF and initial growth in the tropical upper troposphere, even above marine regions remote from  
582 continental sources. In general, the RIC scheme provided best model-to-measurement fits; however, the improvement in the  
583 fit values for DUN scheme when organics are added for initial growth of particles suggests that organics may be more important  
584 for growth than for nucleation (Table S4).

585 We find that to best reproduce both nucleation and growth rates by the RIC scheme, the mixing ratios of gas-phase  
586 organic precursors generally needs to be at least twice that of  $\text{SO}_2$  (Fig.8). While an example in Figure 6 shows that the source  
587 of condensable organics may be even  $\sim 5$  times the  $\text{SO}_2$  mixing ratio in the remote tropical UT (Fig. S66), we do not know  
588 whether or not there may be that much more organic precursor available in this region. Although, regions where the oceanic  
589 source of SOA may be higher than the DMS source have been reported previously (e.g. Croft et al., 2019).

590 Unfortunately, we have no information on the nature and mixing ratios of oxidized organic species that participated  
591 in NPF and initial growth in this environment. The mixing ratios used in this study do not seem out of the range of possibility.  
592 Potential precursors to these condensing species, such as isoprene or monoterpenes (e.g. alpha- or beta-pinene), were found to  
593 be below the limit of instrument detection (2 pptv for isoprene, 0.1 pptv for alpha-pinene, and 0.2 pptv for beta-pinene) in the  
594 tropical UT during the ATom deployments. The exact identification of these condensing organic species would require  
595 instrumentation such as an atmospheric-pressure-interface time-of-flight (API-TOF) mass spectrometer to measure the  
596 composition of molecular clusters, which was not a part of the suite of instrumentation during the ATom mission. Other studies  
597 also suggest that NPF and growth involving organic species may be common in the remote troposphere. Willis et al. (2016)  
598 showed that marine organics contribute to the growth of newly formed particles in the summertime Arctic at low altitude;  
599 however, it was unclear if marine organics were involved in nucleation. Burkart et al. (2017) found that particle growth in the  
600 remote Arctic was largely due to condensation of unidentified organic compounds, possibly of marine origin, associated with  
601 oxidation or photochemistry of the sea-surface micro-layer (Abbatt et al., 2019). Andreae et al. (2018) proposed that oxidized  
602 biogenic VOCs were the source of recently formed particles found in the outflows and anvils of convective storms over  
603 Amazonia.

604 Chemistry-climate models rarely include organic-driven nucleation pathways in the UT where globally significant  
605 NPF takes place. This may result in poor estimates of NPF and CCN abundance and contribute to uncertainties in aerosol-



606 cloud-radiation effects. Williamson et al. (2019) showed that the production of newly formed particles and their growth to  
607 cloud-active sizes during descent towards the surface is not adequately captured in the global chemical transport models, which  
608 tend to underestimate the magnitude of tropical UT NPF and subsequent growth. This underestimate might be related to  
609 missing organic precursors, missing chemical mechanisms, or structural errors associated with convective parameterizations.  
610 According to Williamson et al. (2019), the combined direct and indirect radiative effect of NPF in the tropical UT is  $\sim 0.1$  W  
611  $\text{m}^{-2}$ , globally.

612 The assumptions in our box model simulations point to the need for further observational and modeling studies. For  
613 example, we do not directly simulate in TOMAS the oxidation of DMS to  $\text{SO}_2$  and MSA. However, the  $\text{SO}_2$  mixing ratios  
614 estimated in this study may serve as a proxy for DMS in the modeling in our study, although the timescale for forming  $\text{H}_2\text{SO}_4$   
615 from  $\text{SO}_2$  will be incorrect. We had measurements of  $\text{SO}_2$  only during the fourth ATom deployment, and no measurements of  
616  $\text{NH}_3$  or highly oxygenated organic molecules that are likely aerosol precursors. Instead, we have constrained the box model  
617 simulations using reasonable lower and upper limits of their mixing ratios based on literature data and in case of  $\text{SO}_2$ , ATom  
618 4 data. Further, nucleation schemes themselves are simply imperfect parameterizations extrapolated from laboratory  
619 observations. One of the limitations of our box modeling effort is that the temperatures along the trajectories were often below  
620 the lower range limit of three (out of four) nucleation schemes evaluated (Table S5). In these cases (marked with a “\*” in  
621 Supplemental Material Figs. 15-45 and Table S5) the best-fit  $\text{SO}_2$  and organic concentrations are expected to be biased high.  
622 Although experimentally unverified, we incorporated temperature dependence into the Riccobono et al. (2014) scheme after  
623 Yu et al. (2017). We would expect faster nucleation rates at the lower trajectory temperatures than are simulated by these  
624 schemes (e.g. Yue and Hamill, 1979). Further, we have tested the Napari et al (2002) scheme both with and without a tuning  
625 factor of  $10^{-5}$  that was developed for continental regions (Jung et al., 2010; Westervelt et al., 2013), an obvious source of  
626 uncertainty when simulating NPF in the UT over the oceans. These are schemes that many models use and they do not appear  
627 to (often) work for this region, possibly due to their limited range of operating temperatures. We also have not explored the  
628 organic-only nucleation scheme described by Kirbky et al. (2016). Further, we did not account for mixing with surrounding  
629 air on the path between the cloud outflow and the point of measurement when running simulations.

630 The limitations described above are important and point out the need to undertake further in situ measurements and  
631 modeling studies to confirm the suspected role of organics in UT NPF and subsequent growth in the remote troposphere. Better  
632 understanding of NPF in the remote UT, and the growth of these particles to cloud-active sizes, could substantially improve  
633 model simulations of the preindustrial atmosphere, would allow better evaluations of the effect of current anthropogenic  
634 perturbations, and could allow more confident predictions of the evolution of the climate and its response to future emission  
635 scenarios. Modeling efforts should focus on developing new nucleation mechanisms based on chamber studies conducted at  
636 temperatures more representative of the UT. Further airborne research should focus on measuring the composition of molecular  
637 clusters, sulfuric acid, organics, and  $\text{NH}_3$  over the oceans and tropical continental areas. The planned Chemistry of the  
638 Atmosphere: Field Experiment in Brazil (CAFE-Brazil) study is the first expected to combine airborne measurements of



639 nucleation-mode particle size distributions with API-TOF mass spectrometer measurements of the composition of nucleating  
640 clusters.

#### 641 4. Summary

642 Airborne observations during the ATom mission show a globally significant source region of newly formed particles  
643 in the tropical and subtropical UT that persists over both the Atlantic and Pacific Ocean basins over all seasons. These particles  
644 are often associated with the outflow from deep convection. Averaged across the tropics and subtropics over the Pacific, the  
645 particle number concentrations were a maximum (reaching as high as  $\sim 40,000 \text{ cm}^{-3}$ ) at altitudes above 10 km where the  
646 condensation sink from pre-existing aerosol particles was a minimum. Using back-trajectories to identify convectively  
647 influenced air parcels, the highest concentrations of recently formed particles were generally found where the CI was most  
648 recent, particularly during the first and second ATom deployments. The number concentration of nucleation-mode particles  
649 decreased with time since CI due to the effects of coagulation and condensational growth. During ATom 1 and 2, particle size  
650 increased with time since CI, showing clear evidence for this growth.

651 We simulated particle nucleation and growth using two box models constrained to follow the calculated trajectories  
652 from the point of convective detrainment to the point of measurement by the aircraft, and we performed sensitivity tests varying  
653 the nucleation mechanisms and initial conditions such as precursor ( $\text{SO}_2$ ,  $\text{NH}_3$ , organics), OH, and pre-existing particle  
654 concentrations.

655 These simulations indicate that nucleation schemes commonly used in global models, such as binary homogeneous  
656  $\text{H}_2\text{SO}_4$  (both neutral by Vehkamäki et al. (2002) or ternary  $\text{H}_2\text{SO}_4 + \text{NH}_3$  (neutral with and without a tuning factor by Napari  
657 et al (2002) and Jung et al. (2010))), as well as the recently developed neutral and ion-induced binary and ternary nucleation  
658 scheme by Dunne et al. (2016), were all inconsistent with observed size distributions in all simulated cases when no organics  
659 were included for growth. This result also held for the binary nucleation mechanisms even when organics were added as a  
660 condensing, but not nucleating, species. Adding organics for initial growth of particles formed by either of tested ternary  
661 schemes (Napari et al. (2002) or Dunne et al. (2016)) provided the best fits in 12 out of 32 simulated cases (Table S4). However,  
662 the majority of these ternary inorganic simulations required initial conditions of  $\text{NH}_3 > 50 \text{ pptv}$ , which is substantially greater  
663 than expected at these locations in the UT (Höpfner et al., 2016).

664 In contrast, a scheme involving oxidation products of biogenic organics and  $\text{H}_2\text{SO}_4$  (Riccobono et al., 2014) gave  
665 results that were most consistent among the various models with observations in 22 out of 32 cases, while in 2 cases it was  
666 tied for the lowest NME with other schemes. These results strongly suggest that organics are involved in NPF and subsequent  
667 initial growth in the remote tropical UT. This supports the finding by Simon et al (2019) that organics, despite their lower  
668 oxidation level and yield at low temperatures, may be important for nucleation and growth in the UT. However, the predicted  
669  $\text{SO}_2$  concentrations were often anomalously low ( $< 5 \text{ pptv}$ ), suggesting that our temperature extrapolation may overestimate



670 the nucleation rates. While the Riccobono scheme was most consistent, the analysis suggests that multiple nucleation  
671 mechanisms may be plausible across the 32 cases.

672 We have assumed that the Riccobono et al. (2014) scheme, which was developed from laboratory measurements of  
673 nucleation from the oxidation products of terrestrial biogenic VOCs, represents processes in the remote marine UT of the  
674 tropical Pacific. In fact, there is virtually no information on the nature of oxidized organic species (or ammonia and amines)  
675 that may participate in NPF in this environment. Also, the Riccobono scheme required a large extrapolation in temperature to  
676 simulate UT conditions. Given that NPF in the tropical UT is a major source of CCN over a large portion of the globe  
677 (Williamson et al., 2019), we recommend that future work investigate the species contributing to NPF and growth explicitly,  
678 including direct measurements when possible. Additionally, we recommend studies that focus on potential tropical marine  
679 sources of aerosol precursor gases, the efficiency of their transport to the UT, the products of their oxidation, and the  
680 mechanisms of NPF at temperatures  $<230$  K.

#### 681 **Data availability**

682 The full ATom dataset is available as given in Wofsy et al. (2018), and may also be accessed at  
683 <https://espoarchive.nasa.gov/archive/browse/atom>. Data presented in this analysis are available at the Oak Ridge National  
684 Laboratory (ORNL) Distributed Active Archive Center, (DAAC) Kupc et al. (2020).

#### 685 **Author contributions**

686 AK, CW, CB, KF, MD, BW, TB, AR collected data. AK, JP, CB, and AH conceived and designed the study. AK performed  
687 the analysis and wrote the manuscript with help from CB and JP, with contributions from all co-authors. JP, AH, JK provided  
688 TOMAS and MAIA box models and helped with model upgrades. AK performed all model simulations. MD and BW analysed  
689 cloud properties. ER calculated the air parcel back-trajectories.

#### 690 **Competing interests**

691 The authors declare that they have no conflicts of interest.

#### 692 **Disclaimer**

693 The contents do not necessarily represent the official views of the University of Colorado, the University of Vienna, NOAA  
694 or of the respective granting agencies. The use or mention of commercial products or services does not represent an  
695 endorsement by the authors or by any agency.



## 696 Acknowledgements

697 We thank Ken Aikin for contributions to this analysis, and the ATom science team and NASA DC-8 flight crew for their  
698 contributions to the ATom data. We are grateful for the hard work of the ATom leadership and logistics teams. We thank the  
699 Whole Air Sampler (WAS; UCI) and the Trace Organic Gas Analyzer (TOGA; NCAR) teams for access to their data.

## 700 Financial Statement

701 This work was funded by NASA's Earth System Science Pathfinder Program under award NNH15AB12I and by NOAA's  
702 Health of the Atmosphere and Atmospheric Chemistry, Carbon Cycle, and Climate Programs. Agnieszka Kupc was supported  
703 by the Austrian Science Fund FWF's Erwin Schrodinger Fellowship J-3613. Bernadett Weinzierl and Maximilian Dollner  
704 were supported by European Research Council (ERC) under the European Union's Horizon 2020 research and innovation  
705 framework program under grant 640458 (A-LIFE) and by the University of Vienna. Jeffrey Pierce and Anna Hodshire were  
706 supported by the US Department of Energy's Atmospheric System Research, an Office of Science, Office of Biological and  
707 Environmental Research program, under grant DE-SC0019000; and the NOAA, Office of Science, Office of Atmospheric  
708 Chemistry, Carbon Cycle, and Climate Program, under cooperative agreement award NA17OAR430001.

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