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**Article:**

Gordon, H, Sengupta, K, Rap, A et al. (2016) Reduced anthropogenic aerosol radiative forcing caused by biogenic new particle formation. *Proceedings of the National Academy of Sciences*, 113 (43). pp. 12053-12058. ISSN: 0027-8424

<https://doi.org/10.1073/pnas.1602360113>

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10 chamber show that particle formation in atmospheric conditions can  
11 occur solely from biogenic vapours. Here we evaluate the potential  
12 effect of this new source of particles on pre-industrial cloud conden-  
13 sation nucleus (CCN) concentrations and on aerosol-cloud radiative  
14 forcing over the industrial period. Model simulations show that the  
15 pure biogenic particle formation mechanism has a much larger relative  
16 effect on CCN concentrations in the pre-industrial atmosphere than  
17 in the present atmosphere because of the lower aerosol concentrations.  
18 Consequently, pre-industrial cloud albedo is increased more than under  
19 present-day conditions, so the cooling forcing of anthropogenic  
20 aerosols is reduced. The new mechanism increases CCN concentra-  
21 tions by 20-100% over a large fraction of the pre-industrial lower at-  
22 mosphere and the magnitude of annual global mean radiative forcing  
23 caused by changes of cloud albedo since 1750 is reduced by  $0.22 \text{ Wm}^{-2}$   
24 (27%) to  $-0.60 \text{ Wm}^{-2}$ . Model uncertainties, relatively slow formation  
25 rates and limited available ambient measurements make it difficult to  
26 establish the significance of a mechanism that has its dominant effect  
27 under pre-industrial conditions. Our simulations predict more particle  
28 formation in the Amazon than is observed. On the other hand, the  
29 first observation of pure organic nucleation has now been reported for  
30 the free troposphere. Given the potentially significant effect on an-  
31 thropogenic forcing, effort should be made to better understand such  
32 naturally-driven aerosol processes.

## 33 1 Significance Text

34 A new mechanism for the formation of atmospheric aerosols via the gas-to-  
35 particle conversion of highly oxidised organic molecules is found to be the  
36 dominant aerosol formation process in the pre-industrial boundary layer over  
37 land. The inclusion of this process in a global aerosol model raises baseline  
38 pre-industrial aerosol concentrations, and could lead to a reduction of 27%  
39 in estimates of anthropogenic aerosol radiative forcing.

## 40 2 Article

41 Measurements in the CERN CLOUD chamber under atmospheric conditions  
42 show that new particles can form purely from the oxidation products of  $\alpha$ -  
43 pinene, a compound emitted by the biosphere [1]. Nucleation of new aerosol

44 particles via gas-to-particle conversion has been studied for fifty years [2] and  
45 is responsible for around half of global cloud condensation nuclei (CCN) [3],  
46 which affect Earth’s radiation balance via aerosol-cloud interactions. The  
47 involvement of oxidised organic molecules in the process, alongside sulphuric  
48 acid, was proposed in early studies, and has been well-established for some  
49 time [4, 5]. The new mechanism for organic particle formation without sul-  
50 phuric acid presented in Ref. [1] could be important for Earth’s climate be-  
51 cause it provides a way to form particles in the pristine pre-industrial atmo-  
52 sphere, when the concentrations of sulphuric acid and ammonia were much  
53 lower. The pre-industrial environment forms the baseline for calculations in  
54 global models of the radiative forcing caused by anthropogenic emissions [6],  
55 and uncertainties in this baseline are the largest component of the overall  
56 uncertainty on aerosol radiative forcing [7]. This is because an incremental  
57 increase in particle concentrations when they are low has a much stronger  
58 radiative effect than when they are high. Previous model uncertainty anal-  
59 yses suggested that the sensitivity of radiative forcing to particle formation  
60 rates is low compared to many other factors [7]. However, these studies var-  
61 ied the nucleation rate assuming that sulphuric acid is required for particle  
62 production. Here we show that the inclusion of a new nucleation mechanism  
63 that does not require sulphuric acid could have a more significant effect on  
64 radiative forcing than previously thought [8, 7].

65 Our modelling study is inspired by and based on measurements in which  
66  $\alpha$ -pinene, a volatile organic compound (VOC) emitted into the atmosphere  
67 by vegetation, was oxidised by ozone and hydroxyl radicals in the CLOUD  
68 chamber under ultra-clean conditions without sulphuric acid [1]. The mass  
69 spectra of the highly oxidised multifunctional organic molecules (HOMs) pro-  
70 duced from the VOCs closely resemble those observed in the atmosphere [9].  
71 Therefore, while the concentrations of some reactive gases in the chamber  
72 do not perfectly match those in the troposphere, we have confidence in our  
73 assumption that the chamber results can be generalised to the atmosphere.  
74 Particle counters show that typical atmospheric concentrations of the HOMs  
75 produce particles at significant rates, even when sulphuric acid is absent from  
76 nucleating clusters. We describe this process as pure biogenic nucleation.

77 In this paper, we examine the implications of pure biogenic nucleation  
78 for atmospheric aerosol and Earth’s radiation balance using the GLOMAP  
79 global model of aerosol microphysics [10]. A parametrisation of the pure  
80 biogenic nucleation rate that depends on the HOM concentration and the  
81 concentration of ions is provided in supplementary materials of Ref. [1]. We

82 assume for this study that this can be added linearly to parametrisations  
 83 of the nucleation rate involving sulphuric acid only [11] and sulphuric acid  
 84 with organics similar to HOMs [5]. Ref. [1] also provided the yields of HOMs  
 85 from the oxidation of  $\alpha$ -pinene by ozone (2.9%) and by the hydroxyl radical  
 86 (1.2%). The yield of HOM from endocyclic monoterpenes such as  $\alpha$ -pinene is  
 87 higher than that from exocyclic monoterpenes, so we separate these classes in  
 88 our model and use the yields from  $\beta$ -pinene in Ref. [12] to produce HOM from  
 89 exocyclic monoterpenes. The rate of formation of 1.7 nm diameter aerosols by  
 90 gas-to-particle conversion is therefore described by the sum of the following  
 91 parametrisations:

92 1. Binary homogeneous nucleation of sulphuric acid and water [11].

93 2. Nucleation of organics with sulphuric acid [5], also used in Ref. [13]:

$$J_{\text{sa-org}} = k_{\text{sa-org}}[\text{H}_2\text{SO}_4]^2[\text{BioOxOrg}] \quad (1)$$

94 where BioOxOrg refers to the oxidation products of monoterpenes with  
 95 OH and  $k_{\text{sa-org}} = 3.27 \times 10^{-21} \text{ cm}^6\text{s}^{-1}$  (see Methods).

96 3. Pure biogenic nucleation, a sum of neutral ( $J_n$ ) and ion-induced ( $J_{\text{iin}}$ )  
 97 components [1]:

$$J_{\text{org}} = J_n + J_{\text{iin}} \quad (2)$$

$$J_n = a_1[\text{HOM}]^{a_2+a_5/[\text{HOM}]} \quad (3)$$

$$J_{\text{iin}} = 2[n_{\pm}]a_3[\text{HOM}]^{a_4+a_5/[\text{HOM}]} \quad (4)$$

98 where HOMs are produced as described above but given here for con-  
 99 venience in units of  $10^7$  molecules per cubic centimetre,  $n_{\pm}$  is the ion  
 100 concentration and  $a$  are free parameters. Ions in the model are pro-  
 101 duced from radon and galactic cosmic rays (see SI Appendix).

102 Ammonia and amines can also contribute to nucleation by stabilising sul-  
 103 phuric acid clusters, but the binary homogeneous mechanism has been shown  
 104 to be a reasonable representation of free tropospheric nucleation [14], and nu-  
 105 cleation at low altitudes involving amines or ammonia is important only in  
 106 polluted regions where the changes in radiative forcing calculated here are  
 107 very insensitive to nucleation rates.

108 In our model, aerosols formed in this way, and those emitted directly from  
 109 Earth's surface, grow by condensation and coagulation, are transported in

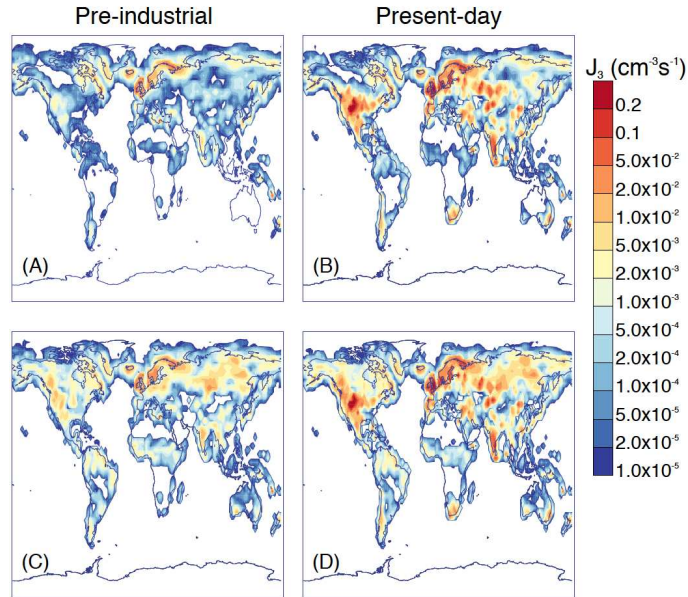


Figure 1: Nucleation rates at 3 nm diameter ( $J_3$ ,  $\text{cm}^{-3}\text{s}^{-1}$ ) within approximately 500 m of the surface averaged over June without pure biogenic nucleation in (A) pre-industrial and (B) present-day conditions, and with pure biogenic nucleation in (C) pre-industrial and (D) present-day conditions.

110 the atmosphere, and are ultimately removed by dry or wet deposition. We  
 111 consider the radiative forcing between 1750 and 2008 via the effect of these  
 112 aerosols on cloud albedo, which is evaluated at the top of the atmosphere  
 113 (0.03 Pa atmospheric pressure). To determine the effects of pure biogenic nu-  
 114 cleation, particle formation rates, aerosol concentrations and radiative forcing  
 115 from model runs with and without mechanism 3 are compared.

### 116 3 Biogenic nucleation rates and observational 117 evidence

118 Fig. 1 shows the effect of pure biogenic nucleation on the pre-industrial and  
 119 present-day atmospheres. When sulphuric acid is required for nucleation  
 120 to proceed, substantially less nucleation is expected for pre-industrial times  
 121 (Fig. 1A) compared with the present (Fig. 1B). However, when pure bio-  
 122 genic nucleation is included, the nucleation rates in pre-industrial (C) and  
 123 present-day times (D) become more similar. While pure biogenic nucleation

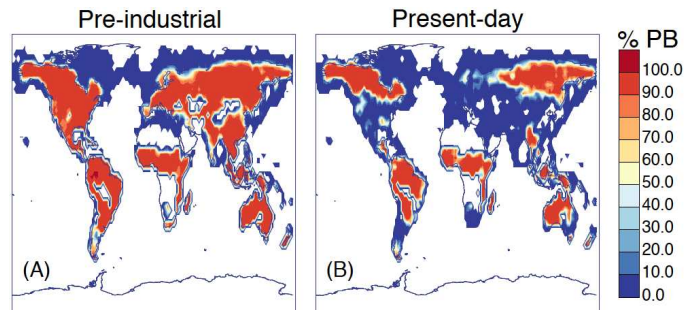


Figure 2: Percentage of particles produced via pure biogenic (PB) nucleation within approximately 500 m of the surface, averaged over June in (A) pre-industrial and (B) present-day conditions. We note that our model predicts large changes to particle formation at the surface and very little change above the boundary layer.

124 is much less important today (compare the change from B to D with that  
 125 from A to C), it is still expected to be significant in some continental regions  
 126 remote from pollution, for example boreal regions, Australia and, according  
 127 to our simulations (discussed later), the Amazon. Within around 500 m of  
 128 the surface pure biogenic nucleation increases total production of particles of  
 129 at least 3 nm in diameter via nucleation by 2.1% globally in the present-day  
 130 atmosphere, but by 90% in pre-industrial conditions.

131 Fig. 2 shows that pure biogenic nucleation is predicted to be the domi-  
 132 nant mechanism for particle formation over large parts of the land surface  
 133 above 50°N in summer even in the present-day. However, both pure biogenic  
 134 and sulphuric acid particle formation rates are often insufficient to produce  
 135 detectable nucleation events (see SI Appendix, Fig. S4). Pure biogenic nucle-  
 136 ation has more effect in June than in January because terpene emissions are  
 137 higher in June. The diurnal cycles of nucleation rates at Hyytiälä and Pal-  
 138 las in Finland, shown in SI Appendix Fig. S4, indicate that nucleation rates  
 139 in these areas are occasionally higher than around  $0.1 \text{ cm}^{-3} \text{ s}^{-1}$ . Experience  
 140 from these boreal forest sites [15] suggests that nucleation rates above this  
 141 value will result in detectable nucleation events. This is confirmed by the  
 142 modelled size distributions shown in SI Appendix Fig. S6. As is observed,  
 143 simulated nucleation rates are substantially higher during the day than at  
 144 night.

145 To our knowledge, Hyytiälä and Jungfraujoch are the only locations with  
 146 published measurements from the APi-TOF and CI-APi-TOF mass spec-

147 trometers needed to unambiguously detect pure biogenic nucleation [15]. There  
148 is strong evidence in Ref. [16] that pure organic nucleation proceeds alongside  
149 sulphuric acid-driven nucleation at Jungfraujoch. For example, their Fig. 2  
150 shows that, on the Nucleation Day 3, most organic clusters of masses of up  
151 to 400 amu contain no sulphuric acid, there is no inorganic nucleation, and  
152 the nucleation rate exceeds  $10 \text{ cm}^{-3} \text{ s}^{-1}$  when sulphuric acid concentrations  
153 are less than  $5 \times 10^5 \text{ cm}^{-3}$ .

154 There are no measurements of pure biogenic nucleation so far from Hyytiälä  
155 since almost all the nucleation rates measured in Ref. [15] are at  $[\text{H}_2\text{SO}_4] >$   
156  $1 \times 10^6 \text{ cm}^{-3}$ . Observations at Hyytiälä were, however, used alongside those  
157 from Melpitz and Hohenpeissenberg to derive parameterizations of particle  
158 formation rates in Ref. [17]. The authors found that nucleation could be  
159 described well by

$$J_2 = k_1[\text{H}_2\text{SO}_4]^2 + k_2[\text{H}_2\text{SO}_4][\text{org}] + k_3[\text{org}]^2, \quad (5)$$

160 for constant  $k_{1-3}$ , suggesting that pure biogenic nucleation is a statistically  
161 detectable component of nucleation in these environments.

162 In addition to the Jungfraujoch observations, there is extensive circum-  
163 stantial evidence for pure biogenic nucleation. The Amazon, where the lowest  
164  $\text{SO}_2$  concentrations over land are found, is an obvious place to look. While  
165 some nucleation mode particles are seen in pristine regions of the Amazon [18]  
166 (on 19% of days sampled in the study referenced), no clear nucleation events  
167 or conclusive evidence for biogenic nucleation have yet been published, and  
168 growth of nucleation mode particles to CCN size is rarely observed there.  
169 Our model does not produce Hyytiälä-like nucleation events (see SI Ap-  
170 pendix Figs. S5-S7) but it does predict non-zero particle formation rates.  
171 It slightly overestimates CCN concentrations compared to Ref. [19] in the  
172 Amazon even without pure biogenic nucleation, and pure biogenic nucle-  
173 ation further increases the discrepancy, by around a factor two. This may  
174 point to a chemical suppression of HOM yields by isoprene [20] or  $\text{NO}_x$  [21],  
175 but could also be due to other sources of model error, for example, under-  
176 estimation of particle size and therefore condensation sink. Overprediction  
177 of particle concentrations over the Amazon seems to be a common feature  
178 among models [22]. Comparing models with observations in this region is  
179 challenging due to large uncertainties in emissions of biogenic VOCs and a  
180 complex wet scavenging environment.

181 Pure biogenic nucleation is also predicted to be the dominant source of  
182 secondary particles in the cleanest high latitude boreal regions. Low  $\text{SO}_2$

183 concentrations, often below 100 ppt, and nocturnal nucleation were reported  
184 in a study at Värriö, Finland (67°N) at similar temperatures to the CLOUD  
185 chamber [23]. Similar observations of nocturnal nucleation were made at  
186 Abisko, Sweden [24] and Tumbarumba, Australia [25], although SO<sub>2</sub> concen-  
187 trations were not reported. At Pallas, Finland, H<sub>2</sub>SO<sub>4</sub> concentrations are  
188 reported below  $3 \times 10^5 \text{cm}^{-3}$  in a large number of new particle formation  
189 events [26]. The air masses in Pallas are usually of marine origin, which  
190 leads to low condensation sinks favourable to nucleation, but may also allow  
191 halogens of marine origin to locally influence nucleation. Three instances of  
192 new particle formation with  $[\text{H}_2\text{SO}_4] < 3 \times 10^5 \text{cm}^{-3}$  shown in Ref. [26] Fig.  
193 6 are unambiguously continental. This should also allow the contribution  
194 of halogens to be excluded, making it highly likely the nucleation was pure  
195 biogenic.

196 With only sparse or indirect observational evidence for pure biogenic nu-  
197 cleation, an alternative strategy is to compare modelled particle concentra-  
198 tions against observations. However, this is also inconclusive because there  
199 are many compensating causes of model error [7], making attribution of bi-  
200 ases ambiguous. Substantial changes in total particle number concentration  
201 are caused by pure biogenic nucleation (SI Appendix Fig. S2). However,  
202 when we compare the monthly mean model predictions to particle number  
203 concentrations at 37 surface sites [27, 28], and the daily mean concentrations  
204 to those measured during the ARCTAS aircraft campaign [29] in 2008 (SI Ap-  
205 pendix Figs. S8 and S9), we find that the effect of pure biogenic mechanism,  
206 increasing summertime particle concentrations by up to a factor 2, is also  
207 comparable to, or smaller than, existing discrepancies between observations  
208 and the model.

## 209 4 Impact on CCN and radiative forcing

210 Fig. 3 shows the effect of pure biogenic nucleation on present-day and pre-  
211 industrial CCN concentrations, calculated at 0.2% supersaturation. When  
212 pure biogenic nucleation is included, global annual average concentrations of  
213 these particles at cloud base level (approximately 600 m altitude) increase by  
214 4% in the present-day and 12% in the pre-industrial atmospheres. Although  
215 nucleation rates are affected mostly close to sources of biogenic gases, CCN  
216 are affected over much wider areas due to the slower removal rate of larger  
217 aerosol particles. This spread is important because it carries the particles to

218 cloudy marine regions where most of the anthropogenic aerosol-cloud radia-  
219 tive forcing occurs [30]. The change in CCN production across the pristine  
220 pre-industrial atmosphere is particularly important for global climate be-  
221 cause cloud droplet concentrations and albedo are both more sensitive to  
222 CCN changes in pristine environments.

223 The change in aerosol radiative forcing from 1750 to 2008 attributable  
224 to pure biogenic nucleation was calculated by comparing simulations with  
225 and without pure biogenic nucleation. We only consider changes in the cloud  
226 albedo effect. The aerosol direct forcing is unlikely to be substantially in-  
227 fluenced by the new nucleation mechanism as it is not strongly affected by  
228 the aerosol size distribution [31]. The change in radiative forcing when pure  
229 biogenic nucleation is included is presented in Fig. 4. We estimate that the  
230 global annual mean cloud albedo forcing since 1750, after including pure bio-  
231 genic nucleation, is  $-0.60 \text{ Wm}^{-2}$ . The *change* in calculated aerosol radiative  
232 forcing due to pure biogenic nucleation is  $+0.22 \text{ Wm}^{-2}$ , corresponding to a  
233 27% reduction in the negative forcing. This change is a result of the non-  
234 linear dependence of the forcing on the baseline CCN concentration [7]. We  
235 note that our simulations may underestimate the net effect since they do not  
236 account for possible increases in cloud fraction and thickness, which, in pris-  
237 tine regions (CCN below  $100 \text{ cm}^{-3}$ ), may be highly sensitive to small changes  
238 of CCN [32]. We also do not account for the possibility of pure biogenic nu-  
239 cleation involving sesquiterpenes. However, we also emphasise that including  
240 pure biogenic nucleation in our model leads to an over-prediction of CCN in  
241 the Amazon region, which may indicate that it is chemically suppressed. In-  
242 hibition of nucleation, if it happens, may be local to the tropical rainforest  
243 environment or more widespread. If we artificially set pure biogenic nucle-  
244 ation rates to zero within  $10^\circ$  latitude of the Equator, the effect on aerosol  
245 forcing when pure biogenic nucleation is included changes only slightly, to  
246  $+0.20 \text{ Wm}^{-2}$ .

247 The largest changes in radiative forcing occur over the NH, especially over  
248 oceans with high annual cloud cover (Fig. 4b) where CCN concentrations are  
249 most strongly perturbed by anthropogenic emissions. The NH is also where  
250 pure biogenic nucleation causes the largest reduction in contrast between  
251 pre-industrial and present day CCN concentrations driven by the large con-  
252 tinental source of biogenic gases. However, the relative change in forcing in  
253 the SH is greater than the NH: pure biogenic nucleation reduces the annual  
254 southern hemispheric mean from  $-0.25 \text{ Wm}^{-2}$  to  $-0.14 \text{ Wm}^{-2}$  (compared to  
255 a change in the NH of  $-1.39 \text{ Wm}^{-2}$  to  $-1.06 \text{ Wm}^{-2}$ ). In some tropical and

256 southern regions, there are higher CCN in pre-industrial times than today,  
257 and a positive radiative forcing. In these regions and nearby, pre-industrial  
258 OH· and HOMs were higher than today and particle condensation sinks were  
259 lower, while SO<sub>2</sub> levels (largely marine) were comparable.

260 We consider the principal uncertainties in our analysis to be associated  
261 with a) VOC, SO<sub>2</sub> and primary particle emissions as in Ref. [7], b) how  
262 representative  $\alpha$ -pinene and the pinanediol used in Ref. [5] are of VOCs in  
263 the atmosphere, c) yields of HOM from  $\alpha$ -pinene oxidation in the presence of  
264 other vapours such as NO<sub>x</sub>, and d) temperature dependence of the nucleation  
265 rates.

266 To investigate the effect of a plausible temperature dependence we re-  
267 ran the model multiplying all boundary-layer nucleation rates by  $\exp(-(T -$   
268  $278)/10)$ . The charged nucleation rate remained limited by the ion produc-  
269 tion rate and the overall rate by the kinetic limit. We find annually averaged  
270 changes to cloud albedo radiative forcing over the industrial period from pure  
271 biogenic nucleation are reduced to +0.14 Wm<sup>-2</sup> from +0.22 Wm<sup>-2</sup>.

272 The yields of HOM have an experimental uncertainty around a factor  
273 two (and were reported to be about a factor two higher in an earlier cham-  
274 ber study [33]). These uncertainties are comparable to uncertainties in the  
275 VOC emissions themselves [34]. The yields could be affected by nitrogen ox-  
276 ides [21], and were found to differ substantially between monoterpenes [12].  
277 To test the sensitivity to the uncertainty in yields, which is a proxy for the  
278 overall intrinsic uncertainty on the experimental measurements, we repeated  
279 our analysis with the yield of the HOMs that participate in pure biogenic  
280 nucleation perturbed by a factor 3. This gives an uncertainty range for the  
281 increase in CCN due to the pure biogenic mechanism of 4–19% in the pre-  
282 industrial and 1–6% in the present-day, as shown in Table S2. The lower  
283 limit still leads to a significant change to cloud albedo forcing of 0.10 Wm<sup>-2</sup>  
284 when the corresponding parametrisation is added to the model.

285 We have also investigated the sensitivity of our radiative forcing estimate  
286 to other sources of uncertainty. We perturb the pre-industrial volcanic SO<sub>2</sub>  
287 emissions and find this does not strongly affect our reported CCN changes.  
288 When we perturb the biomass burning and sea spray emissions (see SI Ap-  
289 pendix for details) we find larger changes both to CCN and forcing, especially  
290 when emissions are reduced. The model becomes slightly more sensitive to  
291 pure biogenic nucleation when different baseline nucleation mechanism from  
292 Ref. [17] instead of Ref. [5] is used. The percentage changes to CCN from  
293 including pure biogenic nucleation under these scenarios are given in SI Ap-

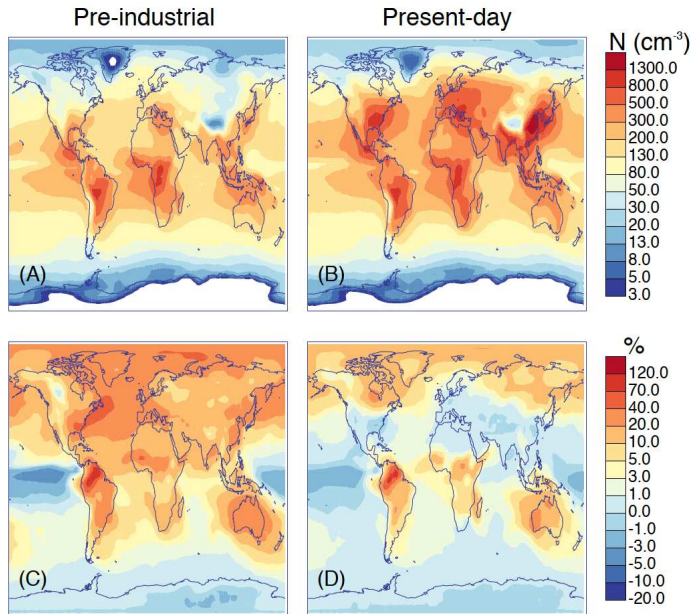


Figure 3: Concentrations of cloud condensation nuclei calculated at 0.2% supersaturation, in  $\text{cm}^{-3}$ , annually averaged at cloud base level in (A) pre-industrial and (B) present-day conditions, and (C, D) percentage changes to these concentrations when pure biogenic nucleation is introduced. In this Figure we assume HOM formation and pure biogenic nucleation proceed at the rates measured at the CLOUD chamber.

294 pendix Table S2, and the changes to forcing in Table S3.

## 295 5 Discussion and conclusions

296 Our global aerosol simulations indicate that pure biogenic nucleation [1] dom-  
 297 inates particle formation in the pre-industrial boundary layer, producing 59%  
 298 of new particles below approximately 500 m altitude and 36% below around  
 299 1.5 km. For the organic system, laboratory measurements are currently the  
 300 only route to a comprehensive understanding of the processes leading to  
 301 particle formation. This is particularly the case for a mechanism that is  
 302 difficult to decouple from sulphuric acid-driven nucleation pathways in the  
 303 polluted present-day atmosphere. This mechanistic understanding is required  
 304 to perform accurate extrapolations from present-day conditions back to the  
 305 pre-industrial. Improving such extrapolations is of critical importance as un-

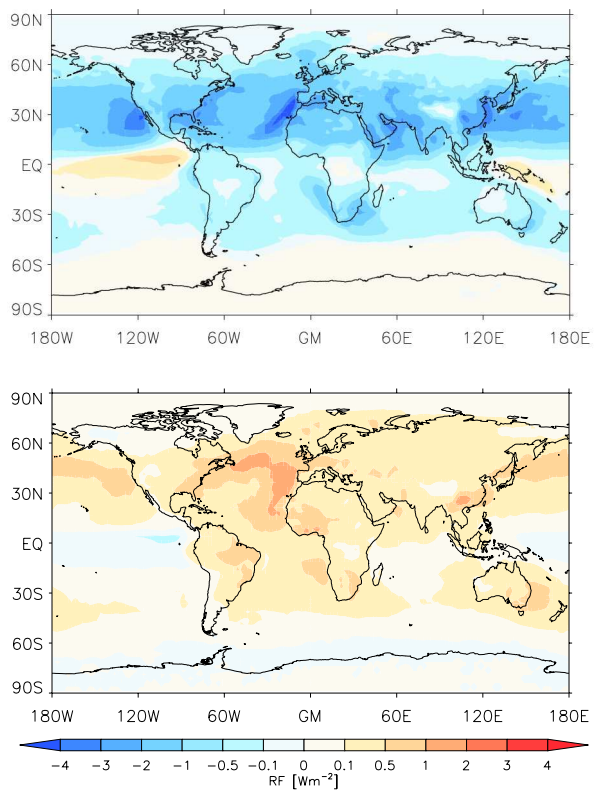


Figure 4: Distribution of (A) cloud albedo radiative forcing and (B) change to this distribution when pure biogenic nucleation is included in the model.

306 certainties in pre-industrial aerosol are a large component of the uncertainty  
307 in IPCC estimates of radiative forcing. While nucleation in tropical environ-  
308 ments is relatively unimportant for global mean cloud albedo radiative forc-  
309 ing in our model, discrepancies between modelled and observed nucleation  
310 in these regions suggest further investigation of Amazon aerosol chemistry  
311 could significantly improve our understanding of pristine aerosol processes.

312 Based on the nucleation rates reported by CLOUD [1], we show here  
313 that pure biogenic nucleation may reduce the magnitude of pre-industrial  
314 to present-day aerosol cloud albedo forcing by as much as  $0.22 \text{ Wm}^{-2}$ , or  
315 27%. This change in forcing is greater than the combined one standard  
316 deviation uncertainty of twenty-eight parameters related to emissions and  
317 aerosol processes in this model [7], which is 19%. Other forcing mechanisms  
318 or uncertainties in the results quoted here could still lead to stronger effects.  
319 Although the calculated change in forcing is comparable to the model para-  
320 metric uncertainty, it shifts the entire probability distribution of forcing,  
321 and therefore represents a significant downward revision in the likelihood  
322 of high negative aerosol-cloud forcings in this model. Similar revisions are  
323 likely to occur in other models [35] due to the same chain of processes: 1)  
324 proportionally greater increases in aerosol concentrations in the cleaner pre-  
325 industrial atmosphere than in the present day; 2) high sensitivity of cloud  
326 albedo and adjustments on the pre-industrial aerosol concentrations; 3) re-  
327 duction in the magnitude of anthropogenic aerosol radiative forcing by raising  
328 the pre-industrial baseline aerosol concentration. To remain consistent with  
329 the observed temperature rise over the industrial period, reduced aerosol  
330 forcing implies reduced climate sensitivity [30, 36].

## 331 **6 Materials**

332 The modal version of the global aerosol model GLOMAP [10] is used to de-  
333 termine the impact of the biogenic nucleation mechanism reported in Ref.  
334 [1]. The model resolution is  $2.8^\circ \times 2.8^\circ$  horizontally, and there are 31 vertical  
335 levels from ground level to 10 hPa. GLOMAP is embedded within a chemical  
336 transport model, TOMCAT [37], and simulates the formation or emission,  
337 growth, coagulation, advection, cloud processing and deposition of aerosol in  
338 seven log-normal size modes. Four modes (nucleation, Aitken, accumulation  
339 and coarse) are hydrophilic, and there are also hydrophobic Aitken, accu-  
340 mulation and coarse modes. The composition of each mode is determined

341 by the relative fractions of the sulfate, sea-salt, black carbon, and organic  
 342 carbon compounds. Dust is not included, as it was not found to contribute  
 343 significantly to CCN [38]. Meteorology is forced by fields from the Euro-  
 344 pean Centre for Medium-range Weather Forecasting. Total monoterpene  
 345 emissions are taken from Ref. [34] and the ratio of endocyclic to exocyclic  
 346 monoterpenes was calculated from a run of the MEGAN model with the set-  
 347 tings prescribed to follow Ref. [39]. Ref. [40] suggests that terpene emissions  
 348 are (within uncertainties) unchanged through the industrial period.

349 While sulphuric acid, ammonia, amines, halogens and HOMs can all partici-  
 350 pitate directly in nucleation, here we consider only sulphuric acid and  
 351 HOMs. The HOMs are formed via the oxidation of monoterpenes (MT)  
 352 by ozone ( $O_3$ ) and hydroxyl radicals ( $OH\cdot$ ). The concentrations of these ox-  
 353 idants are read in every six hours from a dedicated TOMCAT simulation.  
 354 Instead of modelling the full reaction mechanism, we represent the HOM  
 355 concentrations by

$$[HOM] = (Y_{AP.O_3}k_{AP.O_3}[AP][O_3] + Y_{BP.O_3}k_{BP.O_3}[BP][O_3] + Y_{AP.OH}k_{AP.OH}[AP][OH\cdot] + Y_{BP.OH}k_{BP.OH}[BP][OH\cdot]) / CS$$

356 where  $Y_{AP.O_3} = 2.9\%$  and  $Y_{AP.OH} = 1.2\%$  are the yields of HOM from  $\alpha$ -  
 357 pinene (AP) oxidation with ozone and hydroxyl radicals in the CLOUD cham-  
 358 ber, described below,  $Y_{BP.O_3} = 0.12\%$  and  $Y_{BP.OH} = 0.58\%$  are taken from  
 359 Ref. [12] and CS is the condensation sink ( $s^{-1}$ ), determined assuming the dif-  
 360 fusion characteristics of a typical  $\alpha$ -pinene oxidation product (see Appendix  
 361 A1 of Ref. [10]). The temperature-dependent reaction rate constants  $k$  for  
 362 oxidation of  $\alpha$  and  $\beta$ -pinene by ozone and hydroxyl radicals are taken from  
 363 IUPAC [41].

364 The ozonolysis yield is determined with chemical ionisation time-of-flight  
 365 mass spectrometers in the presence of a hydroxyl scavenger (0.1%  $H_2$ ), repli-  
 366 cating the effect of atmospheric  $OH\cdot$  sinks such as methane and carbon  
 367 monoxide. The HOM yield from reaction with hydroxyl radicals is deter-  
 368 mined from measurements in the absence of ozone, and where photolysed  
 369 HONO provides the  $OH\cdot$  source.

370 BioOxOrg in nucleation mechanism 2 and HOM in mechanism 3 play  
 371 equivalent roles but the former refers to the parametrised oxidation products  
 372 derived from pinanediol, a first-generation oxidation product of  $\alpha$ -pinene. Its  
 373 concentration, as described in Ref. [5], is

$$[\text{BioOxOrg}] = k_{\text{MT.OH}} \cdot [\text{MT}] \cdot [\text{OH}\cdot] / CS$$

374 where  $CS$  is the condensation sink. The BioOxOrg concentration was not  
 375 measured directly in a mass spectrometer, but calculated from the pinanediol  
 376 concentration assuming a yield of 100%. The nucleation rate in mechanism 2  
 377 is measured as a function of this BioOxOrg, so the yield is incorporated into  
 378 the rate constant for nucleation. In Ref. [5] monoterpenes are assumed to  
 379 be equivalent to  $\alpha$ -pinene, and so we assume only endocyclic monoterpenes  
 380 participate in this nucleation mechanism.

381 Particles are formed according to the mechanisms described in the main  
 382 text at a critical diameter usually around 1.7 nm. Ion concentrations are  
 383 determined by balancing production from radon and galactic cosmic rays  
 384 with losses to pre-existing particles and to ion-ion recombination (see SI  
 385 Appendix). The formation rates are then adjusted to account for losses  
 386 during the initial growth with the Kerminen-Kulmala equation [42] using  
 387 growth rates taken from the parametrisation of Ref. [43].

388 Particles subsequently grow by kinetic condensation of organic molecules  
 389 produced from oxidation of terpenes or isoprene by nitrate or hydroxyl rad-  
 390 icals, or ozone, with a 13% assumed yield for terpenes [10] and a 3% yield  
 391 for isoprene [44]. They also coagulate, and hence the overall particle number  
 392 is determined by solving the coagulation-nucleation equation [10]. Finally,  
 393 particles may be lost by dry or wet deposition.

394 Present-day simulations are run for 2008 and pre-industrial simulations  
 395 are run with 2008 meteorology and 1750 emissions. For the 1750 simulation,  
 396 anthropogenic sources of  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  were removed from the model,  
 397  $\text{OH}$ ,  $\text{NO}_3$  and ozone concentrations were adjusted to pre-industrial levels  
 398 determined from a dedicated TOMCAT simulation, and black and organic  
 399 carbon primary emissions were adjusted to a representation of pre-industrial  
 400 levels.

401 Cloud condensation nuclei (CCN) and cloud droplet number concentra-  
 402 tions (CDNC) are calculated for each simulation from the particle size dis-  
 403 tributions using the parametrisation of Ref. [45], assuming for the CDNCs  
 404 constant updraft velocities of  $0.15 \text{ ms}^{-1}$  over sea and  $0.30 \text{ ms}^{-1}$  over land.  
 405 The hygroscopicity parameters assigned to each chemical component follow  
 406 Ref. [44]: sulphate (0.61, assuming ammonium sulphate), sea salt (1.28),  
 407 black carbon (0.0), and organics (0.1). The change in cloud droplet effective

408 radii corresponding to the CDNC change is calculated in accordance with  
409 Ref. [31], while the cloud albedo is estimated using the radiative transfer  
410 model of Ref. [46].

## 411 **7 Acknowledgments**

412 We would like to thank CERN for supporting CLOUD with important techni-  
413 cal and financial resources, and for providing a particle beam from the CERN  
414 Proton Synchrotron. We also thank P. Carrie, L.-P. De Menezes, J. Dumol-  
415 lard, F. Josa, I. Krasin, R. Kristic, A. Laassiri, O.S. Maksumov, B. Marichy,  
416 H. Martinati, S.V. Mizin, R. Sitals, A. Wasem and M. Wilhelmsson for their  
417 important contributions to the experiment. We thank D. Veber from Envi-  
418 ronment and Climate Change Canada for maintenance and calibrations of in-  
419 struments at East Trout Lake and NOAA/ESRL for collaboration with data  
420 collection and QA/QC software. We thank A. D. Clarke and C. L. S. Red-  
421 dington for making available processed data from the ARCTAS campaign.  
422 The global modelling simulations were performed on ARC1 and ARC2, part  
423 of the High Performance Computing facilities at the University of Leeds,  
424 U.K. This research has received funding from the EC Seventh Framework and  
425 Horizon 2020 Programmes (Marie Curie Initial Training Network MC-ITN  
426 CLOUD-TRAIN no. 316662, Marie Sklodowska-Curie grant agreements Nos.  
427 656994 and 600377, ERC-Consolidator grant NANODYNAMITE no. 616075  
428 and ERC-Advanced grant ATMNUCLE no.227463), the German Federal  
429 Ministry of Education and Research (project no.01LK1222A), the Swiss  
430 National Science Foundation (project nos.200020\_135307, 200021\_140663,  
431 206021\_144947/1 and 20FI20\_149002/1), the Academy of Finland (Center  
432 of Excellence project no. 1118615), the Academy of Finland (135054, 133872,  
433 251427, 139656, 139995, 137749, 141217, 141451), the Finnish Funding Agency  
434 for Technology and Innovation, the Väisälä Foundation, the Nessling Foun-  
435 dation, the Austrian Science Fund (FWF; project no. L593), the Portuguese  
436 Foundation for Science and Technology (project no. CERN/FP/116387/2010),  
437 the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Pre-  
438 sidium of the Russian Academy of Sciences and Russian Foundation for  
439 Basic Research (grant 12-02-91522-CERN), the U.K. Natural Environment  
440 Research Council (grant NE/K015966/1), the Royal Society (Wolfson Merit  
441 Award), the U.S. National Science Foundation (grants AGS1136479, AGS1439551,  
442 AGS1447056 and CHE1012293), Caltech ESE Grant (Davidow Foundation),

443 Dreyfus Award EP-11-117, the French National Research Agency (ANR),  
444 the Nord-Pas de Calais, the European Funds for Regional Economic Devel-  
445 opment (FEDER, Labex-Cappa, ANR-11-LABX-0005-01), and the French  
446 Civil Aviation Office (MERMOSE).

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## 584 **8 Supplementary: Ion concentrations in the** 585 **GLOMAP aerosol model**

586 We consider two sources of ions in the atmosphere: radon and galactic cosmic  
587 rays. Radon is dominant at the land surface, where most biogenic nucleation  
588 is likely to happen. Ion production rates from radon are read in from look-  
589 up tables [1]. Above the surface and over the ocean, cosmic ray ionisation is  
590 more important. The ionization rates from cosmic rays are calculated from  
591 lookup tables [2] which are provided for several solar cycles, so the effect  
592 of the Sun’s magnetic field can be incorporated via the heliospheric modu-  
593 lation potential. The technique of Fraser-Smith [3] is used to calculate the  
594 geomagnetic cut-off rigidity from the International Geomagnetic Reference  
595 Field coefficients. These are available with five-yearly time resolution so are  
596 interpolated within the five-year periods, then the atmospheric depth (which  
597 determines the interaction probability of a cosmic ray) and the heliospheric  
598 modulation potential are spatially interpolated across the model grid-boxes.

The small-ion concentration of either sign,  $[n_{\pm}] = [n_+] = [n_-]$ , is calcu-  
lated from the steady state solution of the ion balance equation [4]

$$d[n_{\pm}]/dt = q - \alpha[n_{\pm}]^2 - k_i[n_{\pm}] \quad (6)$$

599 where  $q$  is the ion pair production rate from GCRs and  $\alpha$  is the ion-ion recom-  
600 bination coefficient ( $\text{cm}^3\text{s}^{-1}$ ). The factor 2 in Eq. 4 accounts for nucleation  
601 from both positive and negative ions. The ion loss rate,  $k_i$ , is due to the con-  
602 densation sink,  $CS$ , and ion-induced nucleation, so that  $k_i = CS + J_{iin}/2 [n_{\pm}]$   
603 where  $J_{iin}/2 [n_{\pm}]$  is given by Eq. 4 and the steady state concentration of small  
604 ions is  $[n_{\pm}] = [(k_i^2 + 4\alpha q)^{0.5} - k_i]/2\alpha$ . From Eq. 6,  $J_{iin}$  saturates at  $2q$  at high  
605 nucleation rates (see Ref. [5] Fig. 2).

## 606 **9 Supplementary: Simulating the pre-industrial** 607 **atmosphere**

608 The concentrations of key precursor gases for particle formation are compared  
609 between present-day and pre-industrial in Fig. S1. The percentage changes  
610 between pre-industrial and present-day are compared in Table S1 for sum-  
611 mer and winter in the two hemispheres. The sulphuric acid concentration  
612 is substantially higher in the present day atmosphere due to much higher

613 emissions, while the organic concentrations are higher in the pre-industrial  
614 atmosphere due to lower sinks.

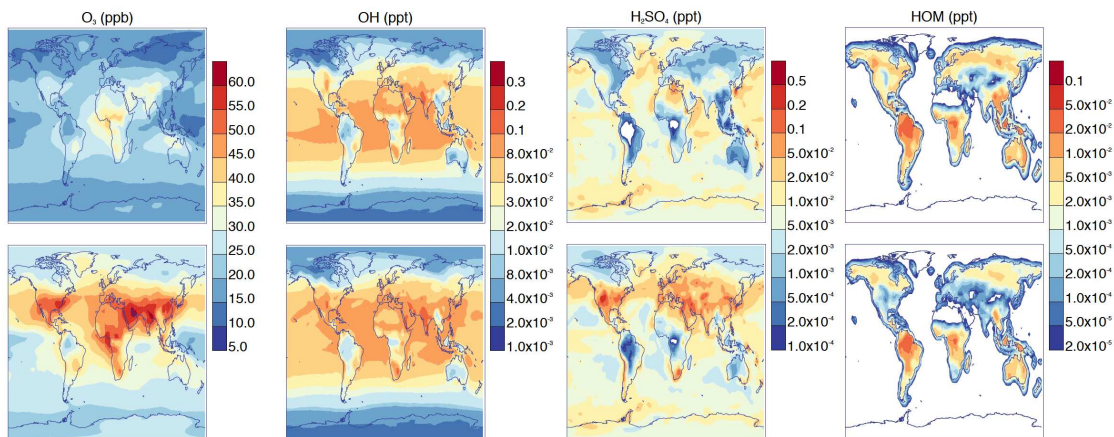


Figure S1: Concentrations of key gases: ozone, hydroxyl radicals, sulphuric acid and HOMs in pre-industrial (top row) and present-day atmospheres (bottom row) at cloud base level, annually averaged.

614

## 615 **10 Supplementary: modelled changes in par-** 616 **ticl e concentrations and further discussion** 617 **of particle numbers in the Amazon region**

618 In Fig. S2 we present the seasonal cycle in surface 3 nm particle concentra-  
619 tions with and without pure biogenic nucleation, and the change when pure  
620 biogenic nucleation is included. This figure shows that the strongest effects  
621 are in the present-day in summertime in boreal regions, Australia, southern  
622 Africa and the Amazon region. Fig. S3 shows the effect of pure biogenic  
623 nucleation on cloud-level CCN concentrations in months chosen to reflect  
624 the Amazon wet and dry seasons (February and August). In Sect. 12, we  
625 further show that the present-day concentrations are in good agreement with  
626 observations at a diverse range of surface sites.

627 As discussed in the main text, on average our model predicts greater  
628 numbers of particles in the Amazon than observations suggest. According  
629 to the review by Martin *et al* [6], the mean number concentration in the

Table S1: Relative changes between present-day and pre-industrial atmosphere at cloud level, averaged over the month for January and July, and averaged over the entire year in the “Annual” column. The value quoted is the percentage increase in the mean in the present-day compared to the pre-industrial atmosphere. Pure biogenic nucleation is included.

Quantity	Change w.r.t. pre-industrial (%)				
	Jan. NH	Jul. NH	Jan. SH	Jul. SH	Annual
O <sub>3</sub>	76.9	70.2	32.5	37.9	59.1
OH	41.7	21.3	-0.9	-0.1	14.6
H <sub>2</sub> SO <sub>4</sub>	361.4	84.4	0.8	42.3	79.3
HOM	-69.4	-36.1	-21.6	-26.4	-39.8
total J	1255.0	445.3	23.0	341.5	491.6
$J_R$	1264.5	164.3	24.5	343.2	484.0
$J_{org}$	-90.3	-47.5	-33.6	-65.3	-57.8
N <sub>3</sub>	136.4	36.8	3.0	10.6	42.9
N <sub>70</sub>	117.0	36.9	6.0	7.5	41.8
CCN 1%	122.2	42.2	4.6	7.3	44.4
CCN 0.2%	99.3	72.0	7.5	9.5	54.2

630 Aitken mode is  $239 \text{ cm}^{-3}$  and that in the accumulation mode is  $177 \text{ cm}^{-3}$ ,  
631 so the total concentration of particles of at least 70 nm in diameter (N70, a  
632 reasonable proxy for CCN, usually equivalent to a supersaturation between  
633 0.4% and 1%) is  $\sim 300 \text{ cm}^{-3}$  in the wet season. Our model predicts N70 of  
634  $\sim 500 - 800 \text{ cm}^{-3}$  in the wet season (higher near Manaus, lower near the  
635 coast, see Fig. S3) so it is still high, but within a factor 2 or 3, which may  
636 be larger than the measurement uncertainty but is certainly within our best  
637 estimate of the model parametric uncertainty [7]. In February in Manaus, we  
638 predict CCN concentrations at 0.2% supersaturation to be  $127 \text{ cm}^{-3}$  with-  
639 out pure biogenic nucleation, and pure biogenic nucleation increases this to  
640  $299 \text{ cm}^{-3}$ . Observations in the wet season in the pristine forest near Man-  
641 aus are considerably lower, at  $30 - 80 \text{ cm}^{-3}$ . However, our model averages  
642 over both the pristine forest and the Manaus pollution plume in this area  
643 so would be expected to yield higher concentrations than the pristine ob-  
644 servations. There is the additional challenge that Manaus is so close to the  
645 Equator that it is close to the boundary between the wet season and the  
646 dry season. The observed transition season concentrations of  $200 - 300 \text{ cm}^{-3}$   
647 may be more appropriate, which would agree with our model. In the dry

648 season, our model is in reasonably good agreement with observations, with  
649 on average  $400 - 800 \text{ cm}^{-3}$  CCN 0.2% (Fig. S3, Ref. [6]).

650 Overprediction of nucleation rates in the Amazon region suggests that  
651 pure biogenic nucleation may be suppressed there. The implications of the  
652 CLOUD results for the global atmosphere thus depend on whether a mecha-  
653 nism that suppresses pure biogenic nucleation exists, and if it does, whether  
654 or not it has a seasonal dependence, or is localised to regions with similar  
655 characteristics to the Amazon. For example, it could be associated with high  
656 humidity which increases the effective condensation sink [8, 9], high isoprene  
657 concentrations [10], high temperatures, or high levels of peroxy radicals, or  
658 it could be present globally all year round.

659 We note that overprediction of CCN (even without pure biogenic nucle-  
660 ation) is a feature of many global aerosol models. The AeroCom assessment  
661 of 15 global aerosol models [12] shows annual mean N100 concentrations in  
662 the Amazon of over  $500 \text{ cm}^{-3}$  and N30 concentrations of closer to  $1000 \text{ cm}^{-3}$ .  
663 This suggests that there are general model weaknesses in the Amazon which  
664 makes it difficult to say anything with confidence about the effects an addi-  
665 tional aerosol source would have on this region.

666 In Ref. [6], it is observed that particles in the nucleation and Aitken modes  
667 in the wet season rarely grow to larger sizes (although it is certainly the case  
668 that some condensational growth does occur). This is *a priori* surprising  
669 since the terpene and condensable organic concentrations are very high in this  
670 area. The most likely explanation must be very high losses: high precipitation  
671 frequency in the wet season and high condensation sink in the dry season,  
672 or very strong vertical mixing that prevents particle growth being observed  
673 adequately from a single surface location. Any losses are also likely to be  
674 inhomogenously distributed, and therefore their non-linear effects could be  
675 easily underestimated in a low-resolution model like ours.

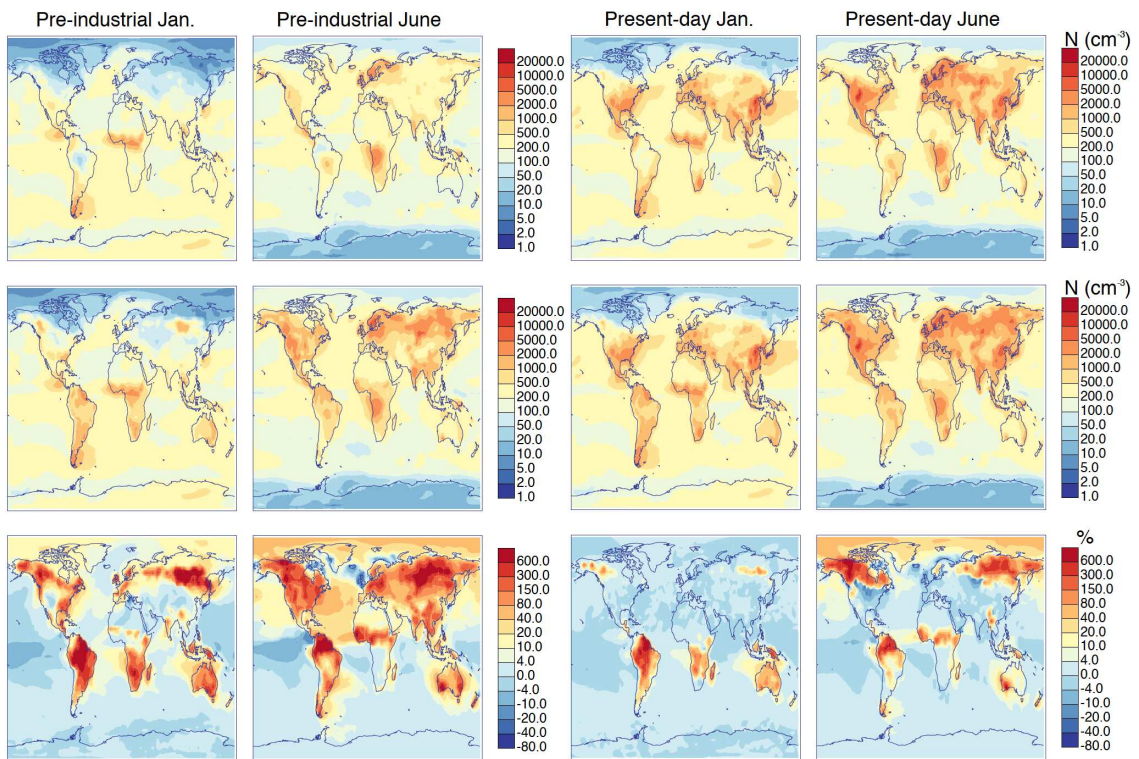


Figure S2: Monthly average surface level concentrations of particles larger than 3 nm in diameter, along each row pre-industrial January, pre-industrial June, present-day January and present-day June. Top: without pure biogenic nucleation. Middle: with pure biogenic nucleation. Bottom: percentage changes when pure biogenic nucleation is added.

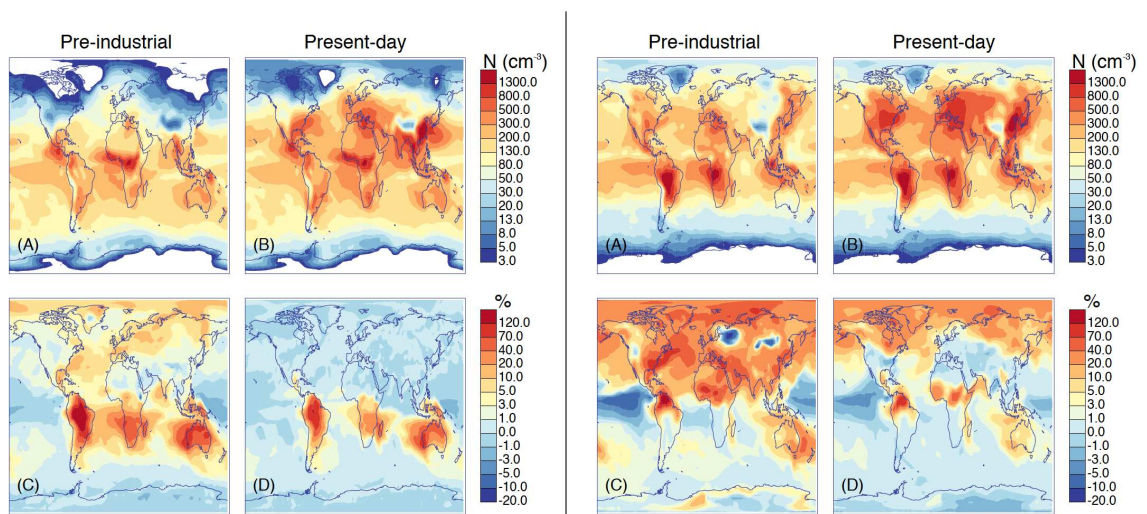


Figure S3: Concentrations of cloud condensation nuclei calculated at 0.2% supersaturation, in  $\text{cm}^{-3}$ , in February (left four panels) and August (right four panels). On either side of the line, average CCN concentrations at cloud base level over the month in (A) pre-industrial and (B) present-day conditions are shown, and, below these in subfigures (C, D), the percentage changes to these concentrations when pure biogenic nucleation is introduced.

## 676 **11 Supplementary: diurnal cycles of particle** 677 **formation rates**

678 In Fig. S4, we show model predictions of the diurnal cycle of particle for-  
679 mation in July at Pallas and at the most studied field site, Hyytiälä, also in  
680 Finland. We predict that pure biogenic nucleation contributes significantly  
681 to the nucleation rate at both sites in July. One would expect APi-TOF data  
682 at Hyytiälä in July to show clusters of HOMs both with and without sul-  
683 phuric acid. However, identifying the absence of sulphuric acid from clusters  
684 large enough to be equivalent to nucleated particles in mass spectra from  
685 field measurements at Hyytiälä has not been possible [13]. Furthermore, nu-  
686 cleation measurements at Hyytiälä are usually made in spring, when pure  
687 biogenic nucleation is predicted to make a much smaller contribution (see  
688 also Fig. S8, below). At Pallas, on the other hand, nucleation events will be  
689 rarer and signals are likely to be smaller, but the background particle con-  
690 centrations responsible for the condensation sink are lower. Therefore, the  
691 peaks in nucleation at 200 and 520 hours into the month in Fig. S4 might  
692 well lead to observable ‘banana’-type events, and our model suggests that  
693 all nucleation at this site should be dominated by pure biogenic processes.  
694 We note that while the pure biogenic nucleation mechanism can in principle  
695 operate both day and night, the model does not predict any nucleation at  
696 night, principally because terpene emissions are higher during daytime.

697 We also show the diurnal cycle in February (wet season) and August (dry  
698 season) at the most studied observation site in the Amazon, Manacapuru,  
699 in Fig. S5. Manacapuru is in the same model gridbox as the Amazon Tall  
700 Tower Observatory and as Manaus. At the surface level, approximately 0 to  
701 30 m above ground level, we predict quite a substantial amount of nucleation,  
702 but rarely, perhaps never, enough to produce observable banana-type events,  
703 especially in the dry season.

704 Further, we show the evolution of the size distributions at the surface  
705 level at Hyytiälä and Pallas in August in Fig. S6, and in Manacapuru for  
706 February and August in Fig. S7. Clear nucleation events are seen at both  
707 Finnish sites which are similar to the observations detailed in, for example,  
708 Refs. [14] or [15] for Hyytiälä and [16] or [17] for Pallas. The size distributions  
709 also show that in the dry season in the Amazon essentially no nucleation is  
710 predicted, while in the wet season very weak additions to the Aitken mode are  
711 predicted. We speculate that these signals would rarely, if ever, be observable

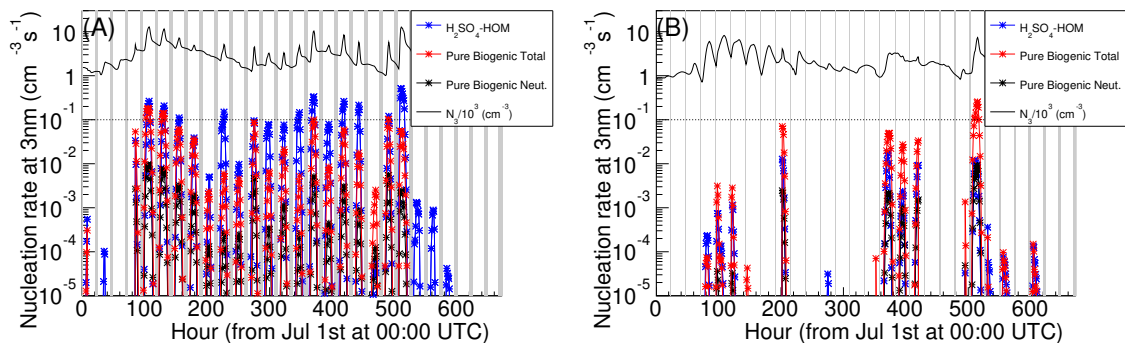


Figure S4: Modelled diurnal cycles of nucleation rates and particle concentrations at present-day (A) Hyytiälä (61.85°N, 24.28°E) and (B) Pallas (68.00°N, 24.23°E) in the first four weeks of July 2008. July is the month where the pure biogenic nucleation rate at Hyytiälä is strongest. Intervals between sunset and sunrise are marked in grey. The wind changes direction around 90 hours into the month. Observable nucleation events are likely when the nucleation rate is above around  $0.1 \text{ cm}^{-3} \text{ s}^{-1}$ , indicated by the dotted line. At Pallas, Aitken mode particles are transported from nucleation happening elsewhere, which explains the daytime peaks in particle number concentration even when nucleation rates at Pallas are very low.

712 as nucleation events due to the complicated and inhomogenous meteorology.

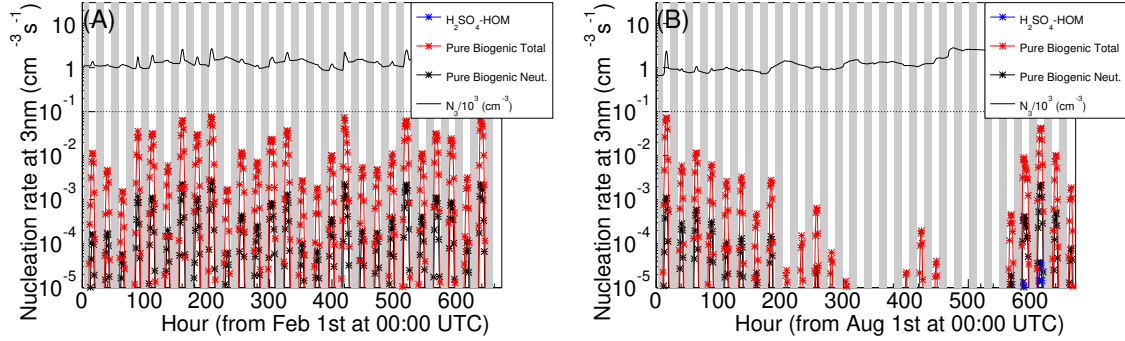


Figure S5: Modelled diurnal cycles of nucleation rates at present-day Manacapuru (3.30°S, 60.62°W) in (A) the wet season (February) and (B) the dry season (August), in 2008. The particle number concentration shows small spikes during nucleation events, often increasing from around  $1000\text{ cm}^{-3}$  to around  $2000\text{ cm}^{-3}$  due to nucleation. However, in these figures, our spatial model resolution smears out much larger, more local fluctuations in the particle concentrations (which can easily be a factor 10), and so in reality such small spikes would be difficult, and probably impossible, to discern in atmospheric observations.

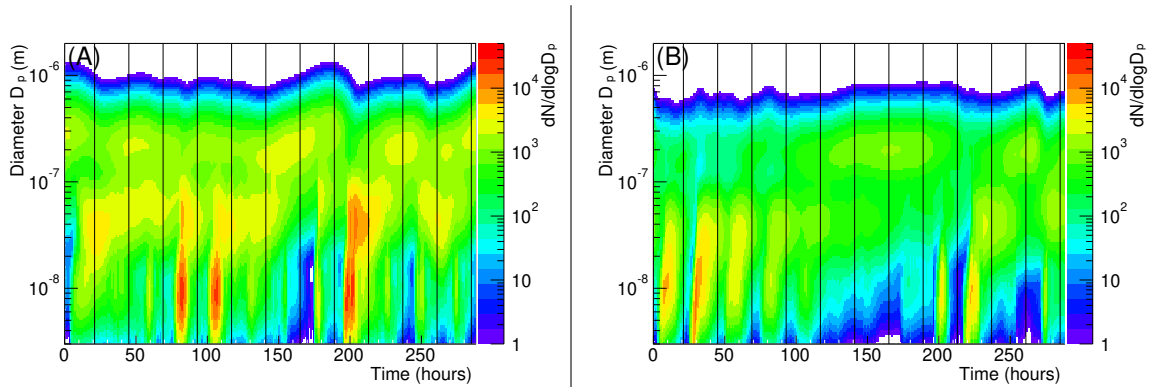


Figure S6: Modelled diurnal cycles of particle size distribution  $dN/d\log D_p$  at present-day (A) Hyytiälä and (B) Pallas, in the first twelve days of August (UTC time). The vertical lines mark midnight Finnish local time (UTC+3). In this figure  $d\log D_p = 0.02$ .

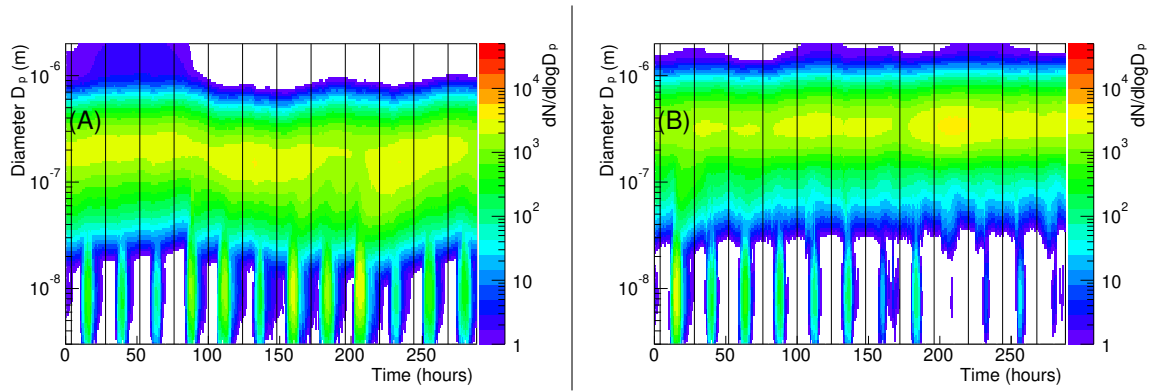


Figure S7: Modelled diurnal cycles of particle size distribution at present-day Manacapuru in (A) the wet season (the first twelve days of February, UTC time) and (B) the dry season (the first twelve days of August). Like the fluctuations in particle number concentration shown in Fig. S5, the small spikes in the nucleation mode would be difficult to see in observation data. The vertical lines mark midnight local time (UTC-4). In this figure  $d \log D_p = 0.02$ .

## 713 **12 Supplementary: Model evaluation against** 714 **measurements**

715 The model was evaluated by comparing the particle number concentrations  
716 it predicts to those measured at 37 surface sites (Fig. S8). The first thirty-  
717 six are those used in Ref. [18]. We also added previously unpublished data  
718 recorded in 2010, 2011 and 2013 from a condensation particle counter with  
719 a 4 nm cut-off diameter at the East Trout Lake Global Atmosphere Watch  
720 station (54.35° N 104.98° W) because our model predicts a significant contri-  
721 bution from pure biogenic nucleation in central Canada. When measurements  
722 from multiple years are available, the data from the months in each year were  
723 averaged. Averaging over all sites and over the whole year, we find including  
724 pure biogenic nucleation leads to a modest improvement in the model bias  
725 from -42% to -41%. In summer the bias changes from -36% to -34% when  
726 pure biogenic nucleation is included and in winter it is unchanged at -53%.  
727 The overall low bias, particularly in winter, is likely to be because we do not  
728 include the effects of ammonia or anthropogenic organic molecules on nu-  
729 cleation in our model. Fig. S8 shows that pure biogenic nucleation strongly  
730 affects particle concentrations only at East Trout Lake, Listvyanka and Point  
731 Barrow.

732 We also compared the daily mean particle number concentrations from the  
733 model to observations made during the ARCTAS campaign [19] in spring and  
734 summer 2008 (Fig. S9). We interpolate these modelled particle concentra-  
735 tions within model grid boxes to match the locations of one-minute-averaged  
736 condensation particle counter measurements from a NASA P3-B aircraft.  
737 We note that the campaign during summer, when pure biogenic nucleation  
738 has most effect, was designed to investigate the influence of boreal forest  
739 fires. Our low model resolution and averaged fire emissions inventory mean  
740 that close agreement between the model and the measurements is not ex-  
741 pected. However, we attempt the comparison anyway as the measurements  
742 are, unusually, in a particularly relevant region where pure biogenic nu-  
743 cleation is predicted to have a strong effect. Averaged over all altitudes, the  
744 model without pure biogenic nucleation is biased low (-57.9%); including  
745 pure biogenic nucleation leads to a smaller bias of -37.4%. Most of the pure  
746 biogenic contribution is in a band of latitudes from 51 to 62°N, correspond-  
747 ing to flights starting from Cold Lake between 26 June and 14 July 2008. While  
748 the relatively large underprediction of particle number without pure biogenic

749 nucleation suggests a particle formation pathway for pristine regions like ours  
750 may be needed, large local deviations of the model and measurements evi-  
751 dent in Fig. S9 preclude any firm conclusion being drawn. These deviations  
752 could be attributed to the fire emissions or low model resolution discussed  
753 earlier, temperature or chemistry effects on new particle formation that we  
754 did not account for, or uncertainties in the observation data.

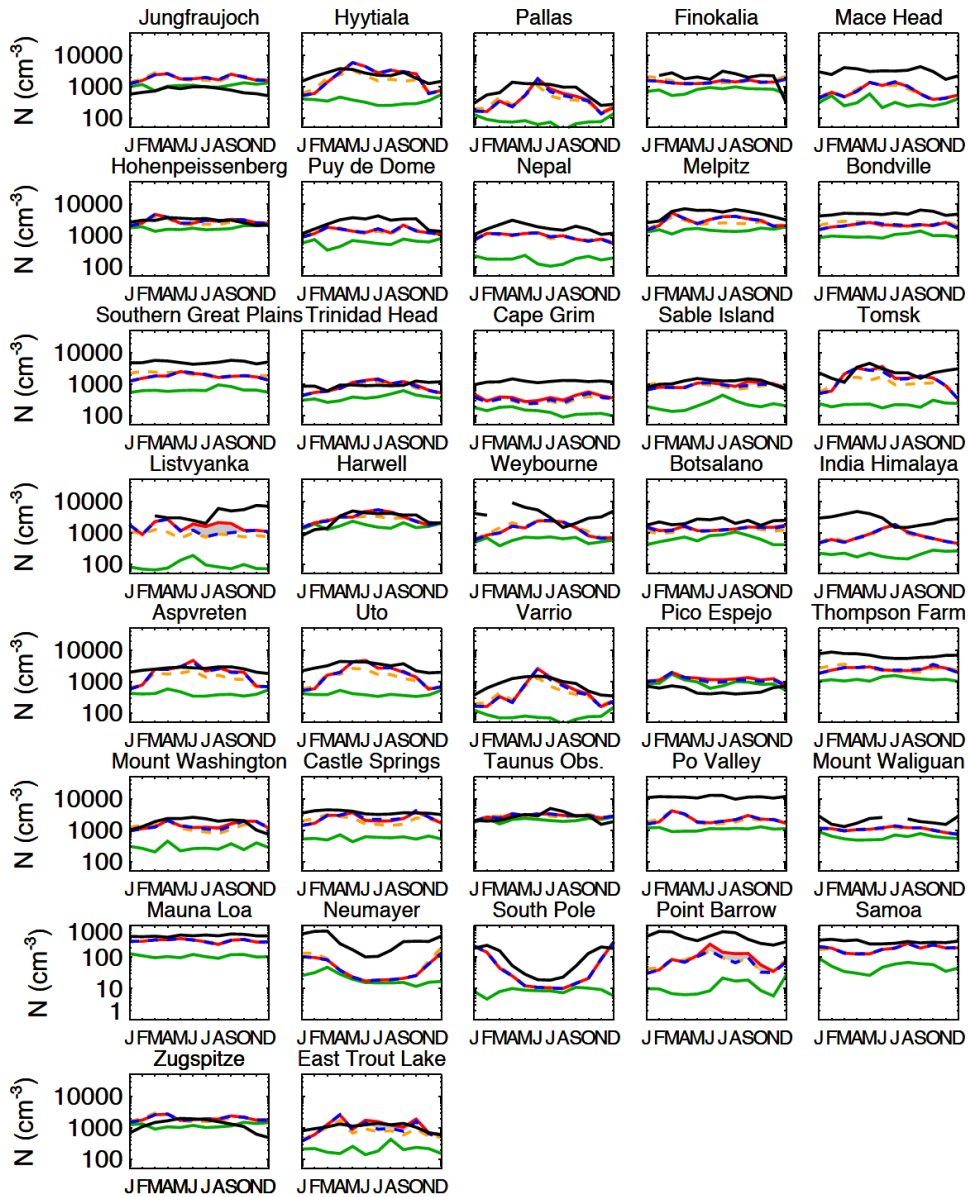


Figure S8: Particle concentrations at selected measurement sites [18, 20], in black, measured by counters with cut off sizes varying from 3 nm to 14 nm, compared to model predictions. The red curve shows the particle concentrations predicted by the baseline nucleation mechanisms, numbered 1-3 in the main text and including pure biogenic nucleation. The blue dotted curve shows the particle concentrations predicted without pure biogenic nucleation. A grey band is drawn between these two curves. The orange dotted curve shows particle concentrations predicted by the parametrisation of Paasonen et al [21], including a component of pure biogenic nucleation proportional to the square of the organic concentration. The dark green curve shows particles from primary emissions only.

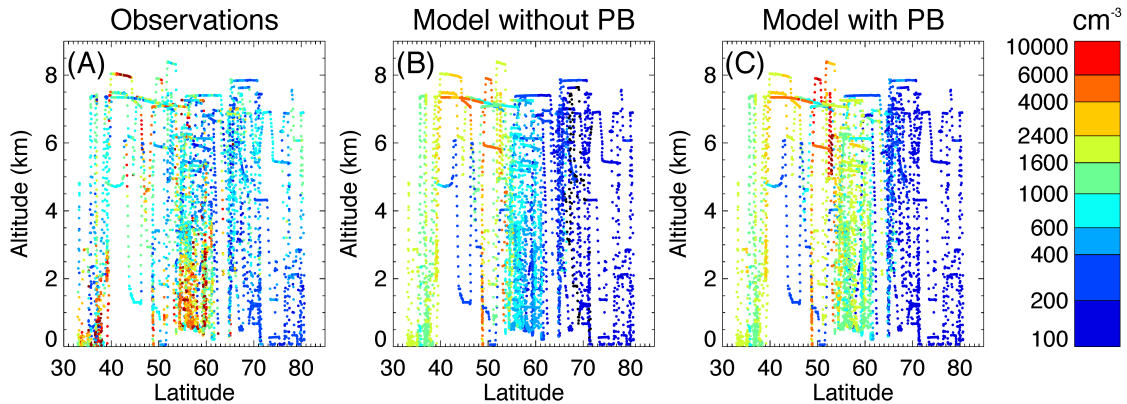


Figure S9: Vertical profiles of particle number concentrations calculated at S.T.P. (all particles of at least 3 nm in diameter), (A) measured during the ARCTAS campaign [19] in 2008, (B) modelled without pure biogenic nucleation (PB) and (C) modelled including pure biogenic nucleation.

755 **13 Supplementary: further discussion of un-**  
 756 **certainties and summary tables of sensi-**  
 757 **tivity studies**

758 Table S2 gives the changes to CCN concentrations due to pure biogenic  
 759 nucleation in different scenarios (e.g. if organic nucleation is temperature-  
 760 dependent, or if primary emissions are higher in our simulation than in re-  
 761 ality). Following Ref. [7], the high primary emissions scenario corresponds  
 762 to a doubling of biomass burning primary particulate emissions, a reduction  
 763 in the mode diameter of biomass burning primary emissions from 150 nm to  
 764 100 nm, and a factor 2.5 increase in the sea spray flux. The low emissions  
 765 scenario corresponds to a halving of biomass burning emissions, an increase  
 766 in the mode diameter to 175 nm and a reduction in the sea spray flux by  
 767 60%. Table S3 gives the corresponding changes to radiative forcing.

768 In the main text, we discussed various sources of uncertainty, such as  
 769 uncertainties in the CLOUD experimental measurements or HOM yields,  
 770 in the possible temperature dependence of pure biogenic nucleation, and in  
 771 primary emissions. The experiment in which we determine the sensitivity to

Table S2: Annual average global mean changes to the concentrations of particles larger than 70 nm in diameter, a proxy for CCN, when pure biogenic nucleation is introduced. The differences between the contents of the first row and the subsequent rows give an indication of the sensitivity of the analysis to different perturbations. The temperature dependence is added for both the baseline organic and the pure biogenic nucleation mechanisms, so changes both the control and perturbed simulations.

Variation	Change to CCN 0.2% (PI) (%)	Change to CCN 0.2% (PD) (%)
Add pure biogenic nucleation (PBN)	12	4
Add PBN with trebled yield	19	6
Add PBN with one-third yield	4	1
Add T dependence	7	2
Double pre-industrial volcanic SO <sub>2</sub>	11	-
Halve pre-industrial volcanic SO <sub>2</sub>	13	-
High primary emissions	7	2
Low primary emissions	14	5
Use baseline $J$ from Ref. [21]	14	5

Table S3: Annual average global mean radiative forcings (including pure biogenic nucleation) and absolute changes to forcing when pure biogenic nucleation is introduced.

Variation	Forcing (PD-PI) Wm <sup>-2</sup>	Change to forcing with pure biogenic nucleation (Wm <sup>-2</sup> )
Add pure biogenic nucleation (PBN)	-0.60	+0.22
Add PBN with trebled yield	-0.52	+0.30
Add PBN with one-third yield	-0.72	+0.10
Add T dependence	-0.64	+0.14
High primary emissions	-0.63	+0.17
Low primary emissions	-0.54	+0.33
Use baseline $J$ from Ref. [21]	-0.63	+0.24
Exclude area close to Equator	-0.62	+0.20

772 primary emissions also tests our sensitivity to uncertainty in the condensation  
773 sink.

774 In the particularly interesting Amazon region, this uncertainty will be  
775 strongly influenced by the quantity and mode diameter of biomass burning  
776 emissions [7]. The 150 nm diameter used, following Ref. [22], is already larger  
777 than that of fresh smoke particles (averaged over all vegetation types) of  
778 117 nm [23], and in theory condensation of secondary organic vapours in our  
779 model should increase this diameter to the aged diameter of 235 nm in a few  
780 days. However, the aged diameter in reality depends on cloud processing of  
781 organics as well as condensation, and this is not included in our model. To  
782 compensate for this, the larger fresh diameter of 150 nm is used by default in  
783 GLOMAP, but it has a large uncertainty [7]. We increase it to 175 nm in our  
784 sensitivity study with high primary emissions, which is still well within the  
785 uncertainty and the ranges for different phases of typical Amazon burning  
786 found in Ref. [24].

787 Another possible source of uncertainty in the Amazon region, which we  
788 are not able to quantify directly, is the condensation sink during periods of  
789 high humidity [8, 9] or aerosol-cloud interaction [25]. Clouds in the Amazon  
790 region are likely to be strongly affected by both of these. For the latter,  
791 impaction scavenging in GLOMAP is due to raindrops but the only loss  
792 mechanism to cloud droplets is nucleation scavenging. In a cloud, the coag-  
793 ulation sink should surely dramatically increase. This is not modelled. The  
794 effective condensation sink in a monodisperse cloud with 100 droplets  $\text{cm}^{-3}$   
795 of diameter  $15.6 \mu\text{m}$  (corresponds to LWC  $0.2 \text{ gm}^{-3}$ ) is  $0.16 \text{ s}^{-1}$ . We investi-  
796 gated this further by including a crude treatment of this effect in our model.  
797 The perturbation to the model results in this test was small, mostly because  
798 clouds rarely cover more than half a model gridbox in areas where pure bio-  
799 genic nucleation is important, and therefore the average effect is smeared out.  
800 With higher model resolution, however, the effect would likely be stronger  
801 due to the nonlinear nature of nucleation and survival probability.

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