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► To cite this version:

J. Kammer, P.-M. Flaud, A. Chazeaubeny, Raluca Ciuraru, K. Le Ménach, et al.. Biogenic volatile organic compounds (BVOCs) reactivity related to new particle formation (NPF) over the Landes forest. *Atmospheric Research*, 2020, 237, pp.1-11. 10.1016/j.atmosres.2020.104869 . hal-02553094

HAL Id: hal-02553094

<https://hal.inrae.fr/hal-02553094>

Submitted on 21 Jul 2022

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1 **Title: Biogenic Volatile Organic Compounds (BVOCs)**
2 **reactivity related to New Particle Formation (NPF) over the**
3 **Landes forest**

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24 **Abstract**

25 Atmospheric particles play a major role in both air quality and climate change. Formation of
26 secondary particles in the atmosphere has been observed over many different environments
27 and is believed to provide up to half of the atmospheric cloud condensation nuclei (CCN) at a
28 global scale. However, high uncertainties are still remaining in the description of mechanisms
29 involved in new particle formation (NPF). Especially, more evidences of the implication of
30 biogenic volatile organic compounds (BVOCs) in NPF from field studies are still needed. To
31 investigate this question, two field campaigns have been set up during July 2014 and July
32 2015, in the French Landes forest (south west of France). Summer 2015 was characterised
33 by a strong hydric stress, whereas summer 2014 was rainy. In 2015, frequent nocturnal NPF
34 was observed, reaching a frequency of occurrence of ~55% of the nights, while only one
35 event was observed in 2014. In July 2015, monoterpene mixing ratios (dominated by α - and
36 β -pinene) were higher, mostly due to high ambient temperatures and drought. A focus was
37 made on the 2015 field campaign, where NPF was mostly observed. The mean diurnal
38 variation of the ratio between α - and β -pinene mixing ratios highlighted in-canopy reactivity of
39 monoterpenes with ozone in the early night. This hypothesis was reinforced by the increasing
40 gas phase levels of pinonaldehyde and nopinone, the main first-generation products arising
41 from α - and β -pinene ozonolysis, at night, before NPF started. It strongly suggests that
42 monoterpene oxidation further generated very-low volatility gases involved in NPF. This
43 finding is also supported by the high concentrations of the SOA traditional biogenic tracers,
44 *e.g.* pinic and pinonic acids, quantified in the particulate phase. The role of BVOCs in NPF is
45 thus highlighted, as well as the importance of nighttime NPF.

46

47 **Keywords:** Monoterpenes, BVOCs, oxidation products, nighttime NPF, Landes forest

48 **Highlights**

- 49 • High monoterpene mixing ratios were related to high nighttime NPF frequency.
- 50 • In canopy α - and β -pinene ozonolysis was highlighted in the evening.
- 51 • Nopinone and pinonaldehyde levels increase before NPF started.
- 52 • Biogenic tracer (pinic and pinonic acids) concentration levels were high in the
- 53 particulate phase.
- 54 • BVOC oxidation was strongly involved in nighttime NPF in the Landes forest.

55

56 **1 Introduction**

57 Forest ecosystems are key components of our environment, representing around 30% of the
58 Earth land surface (United Nations food and agricultural organization, 2015). Also, forests
59 represent a large source of Volatile Organic Compounds (VOCs). It is widely recognized that
60 90% of VOCs are emitted by biogenic sources, isoprene and monoterpenes being the most
61 emitted biogenic VOCs (BVOCs) in the atmosphere (Guenther et al., 1995; Sindelarova et
62 al., 2014). Once oxidized in the atmosphere, some of their products have sufficiently low
63 volatility to partition between the gas and the particle phases. Through this process, forests
64 act as a source of secondary organic aerosol (SOA), which play a crucial role in air quality
65 and climate change (Hallquist et al., 2009; IPCC, 2013; Kazil et al., 2010; Pope III and
66 Dockery, 2006).

67 New Particle Formation (NPF) is a process that consists of the secondary formation of
68 atmospheric particles (Dal Maso et al., 2005). Currently, NPF is estimated to contribute
69 around half of the global Cloud Condensation Nuclei (CCN) at a global scale (Merikanto et
70 al., 2009). NPF was observed in a large number of locations worldwide (Kulmala et al.,
71 2004). However, processes governing NPF remain quite uncertain (Andreae, 2013; Kulmala
72 et al., 2013; Nallathamby et al., 2014). Until recently, it was accepted that NPF could not
73 occur without the involvement of sulphuric acid in the first step, *i.e.* nucleation (Andreae,
74 2013; Kulmala, 2003; Kulmala et al., 2013; Nallathamby et al., 2014). In the atmosphere, gas
75 phase sulphuric acid is mainly generated from SO₂ reaction with OH radicals in the presence
76 of water. It may also be produced in the gas phase by oxidation of SO₂ with H₂O₂ or by
77 reaction with Criegee intermediates (Sipilä et al., 2014). Due to its very low vapour pressure,
78 sulphuric acid may easily form clusters with other molecules, *i.e.* water or oxygenated
79 molecules (Elm et al., 2014; Kulmala, 2003; Neitola et al., 2015; Praplan et al., 2015;
80 Riccobono et al., 2014). Then, if this cluster is stable, it can grow through the condensation
81 of extremely low volatility organic compounds (ELVOCs), produced from autoxidation (Ehn et
82 al., 2014; Kulmala et al., 2013; Praplan et al., 2015; Riccobono et al., 2014). Recently, it was

83 demonstrated from laboratory studies that NPF can be caused solely by α -pinene ozonolysis
84 (Kirkby et al., 2016; Tröstl et al., 2016). It was highlighted from the CLOUD chamber
85 experiments that highly oxidized molecules (like HOMs) can be rapidly formed, and induce
86 NPF, following autoxidation mechanisms (Ehn et al., 2014; Jokinen et al., 2014). Direct
87 evidence of such implication of HOMs in the real atmosphere was highlighted very recently in
88 the free troposphere, where one of the main driver of NPF could be anthropogenic VOCs
89 (Bianchi et al., 2016). More, Rose *et al.* (2018) observed that biogenic ions can induce stable
90 cluster formation. But identification of biogenic NPF still needs more investigations in real
91 atmosphere, especially at pristine locations. As a consequence, new measurements in
92 ecosystems poorly or not yet investigated are needed.

93 In this context, the goal of the present study was to reinforce our knowledge on the relation
94 between BVOCs and NPF. For that purpose, two field measurement campaigns took place in
95 the summers of 2014 and 2015 in the Landes forest, in the south west of France. A first
96 paper by our group recently evidenced frequent nocturnal NPF in 2015, together with high
97 monoterpene mixing ratios (Kammer et al., 2018). This new paper first presents a
98 comparison between 2014 and 2015 field campaigns. Then, the focus is made on the main
99 emitted BVOCs at the measurement site, their reactivity and their oxidation products both in
100 the gas and the particulate phases. Finally, considering the recent findings, the link between
101 in canopy BVOC reactivity and NPF is discussed.

102 **2 Methodology**

103 **2.1 Site description**

104 As part of the LANDEX-episode zero project, two intensive field campaigns were conducted,
105 in the French Landes forest. The first campaign started from the 5th of July until the 18th of
106 July 2014, and the second started from the 5th to the 23rd of July 2015. The measurement
107 site, located at Bilos (44°29'39.69"N, 0°57'21.75"W, and 37 m above sea level) in the
108 northern part of the Landes forest, is a measurement site of the European Integrated Carbon

109 Observation System (ICOS). The nearest urban area is Bordeaux and surroundings, at 40
110 km northeast, and the Atlantic Ocean is 23 km west of the site. The measurement area is a
111 maritime pine (*Pinus pinaster* Aiton) stand sowed in 2004, with an understorey mostly
112 composed of gorse (*Ulex europaeus* L.), grass (*Molinia caerulea* (L.) Moench) and heather
113 (*Calluna vulgaris* (L.) Hull). Tree height was around 7 m in 2014 and 8 m in 2015, over a
114 sandy hydromorphic podzol. A more complete description of Bilos site can be found
115 elsewhere (Moreaux *et al.*, 2011; Kammer *et al.*, 2018). Due to the proximity of the Atlantic
116 Ocean, the local climate is oceanic, and winds are consequently frequently originating from
117 west-north west.

118 **2.2 Field measurements**

119 Meteorological parameter measurements have been performed on a mast during each
120 campaign, at 15 m above ground level (a.g.l.). Air temperature and relative humidity (HMP
121 155, VAISALA HUMICAP), wind speed and direction (Windsonic 1, Campbell scientific),
122 global solar radiation (CMP22 and CNR4, Campbell scientific) and rainfall was continuously
123 measured at a half hourly scale. To complete these meteorological measurements, air mass
124 backward trajectories have been computed using the NOAA HYSPLIT model (Stein *et al.*,
125 2015). Daily backward trajectories were calculated for each day of the campaign using the
126 GDAS (Global Data Assimilation System) meteorological dataset, indicating the origin of the
127 analysed air mass at Bilos. Besides, eddy covariance fluxes of momentum, heat, water
128 vapour and CO₂ were measured at 15 m a.g.l., in order to evaluate the physiological state of
129 the ecosystem. The details of the eddy covariance methods have been fully described
130 elsewhere (Aubinet *et al.*, 2000; Burba and Anderson, 2010).

131 A mobile laboratory truck (the “Barracuda” facility), located in the centre of the area, was
132 used for physico-chemical measurements with air tubing devoted to aerosol and gas
133 sampling being located at 4 m a.g.l., corresponding to the canopy level. A 5 m Teflon tubing
134 (4.5 mm inner diameter) was used for the gas phase measurements, whereas a 4 m long

135 conductive silicone tubing (4.5 mm inner diameter) was used to sample particles. Both gas
136 and particle sampling inlets were located right next (about 20 cm) to ensure the collection of
137 the same air masses. Preliminary tests were performed by measuring the same air with and
138 without tubing. As no difference was observed, it is assumed that no significant wall losses of
139 terpenes occurred in tubing. During the campaign, ozone and nitrogen oxides ($\text{NO}_x = \text{NO} +$
140 NO_2) mixing ratios were monitored through a UV absorption analyzer (APOA 370, HORIBA,
141 detection limit (DL) = 0.5 ppb) and a chemiluminescence analyzer (APNA 370, HORIBA, DL
142 = 0.5 ppb), respectively. Sulphur dioxide (SO_2) measurements were performed only during
143 the 2015 field campaign using a UV fluorescence monitor (API 100 E, Teledyne, DL = 0.4
144 ppb). All the three monitors (O_3 , NO_x and SO_2) have been calibrated before the campaigns,
145 and leak checks were frequently performed using activated charcoal air filters. A scanning
146 mobility particle sizer (SMPS, TSI model 3080) was used to characterize particle number
147 size distribution every 10 minutes. It combines a differential mobility analyser (DMA, TSI
148 model 3081) and an optical counter (CPC, TSI model 3772). Aerosol flow and sheath flow
149 were set respectively to 0.5 L min^{-1} and 5 L min^{-1} to ensure a 1:10 ratio in the DMA. Under
150 these flow conditions, particle number size distribution and concentration were measured for
151 particles having an electric mobility diameter between 10.9 nm and 487 nm. Particle wall
152 losses were calculated following the methodology described in Baron and Willeke (2001).
153 The estimated particle loss rates were estimated to be 34.7% for the smallest particles (with
154 a 10.9 nm diameter) analysed. The particle number and size distribution data were corrected
155 to account for the calculated wall losses. Then, a proton transfer reaction - time of flight -
156 mass spectrometry (PTR-TOF-MS, Kore Technology) was used to study the composition of
157 the gaseous phase, especially the evolution of BVOCs and their related oxidation products.
158 This instrument is based on the proton transfer reaction from H_3O^+ to the analytes, a soft
159 ionisation which prevents from strong fragmentation. Basically, the air mass composition
160 could thus be analyzed by recording the temporal evolution of the MH^+ ions. During the
161 campaign, the PTR-TOF-MS was operated at 600 V drift voltage and 1.3 mbar reactor
162 pressure, ensuring an E/N ratio around 130 Td ($1 \text{ Townsend} = 10^{-17} \text{ V cm}^{-2}$), with E being the

163 electric field strength in the reactor and N the gas number density. The PTR-TOF-MS was
164 tuned to work at this E/N ratio as it is a good compromise to prevent from high fragmentation
165 in the mass spectrometer and ambient relative humidity effect (Pang, 2015; Tani et al.,
166 2003). PTR-TOF-MS blanks and calibrations were daily performed using the vapour pressure
167 (at 0°C and diluted in N_2 flow) of a pure α -pinene solution, regulated by a mass flow controller
168 (Millipore, Coastal Instruments). Typical day to day sensitivity variations were about 10 %.
169 The variation of the sensitivity may be sometimes larger, when the PTR-TOF-MS parameters
170 (for example, the voltage applied to extraction lenses) were optimized during the campaign.
171 For non-calibrated compounds (other than α -pinene), calibration coefficients determined for
172 α -pinene were used to consider the day-to-day sensitivity variations of the instrument. But as
173 we could not consider that these calibration coefficients provide a real estimation of the
174 concentration of these other compounds, then each signal was normalized by its maximum
175 count number.

176 As monoterpenes $C_{10}H_{16}$ present many isomers and as the PTR-TOF-MS was only able to
177 measure their total concentrations, an online gas chromatograph coupled to a flame
178 ionization detector (GC-FID, airmoVOC, Chromatotec) was used to discriminate their
179 speciation. The GC-FID sampled air at 0.11 L min^{-1} , and concentrated VOCs on a cold air
180 trap composed of adsorbent Tenax TA (20–35 mesh, Chrompack). The desorbed VOCs to
181 analyse were then separated using a Chrompack Sil 8CB low bleed capillary column, and
182 finally detected with the FID. A complete description of the GC-FID can be found elsewhere
183 (Staudt and Lhoutellier, 2011). In 2015, the GC-FID was only available during the last five
184 days of the campaign.

185 The chemical composition of particles collected during the 2015 field campaign was
186 investigated using high performance liquid chromatography coupled to mass spectrometry.
187 Briefly, a high volume sampler (DA-80, Digitel, with an air flow set to $30 \text{ m}^3 \text{ h}^{-1}$) was used to
188 collect $PM_{2.5}$ (particles with an aerodynamical diameter smaller than $2.5 \mu\text{m}$) onto quartz fiber
189 filters ($\varnothing = 150 \text{ mm}$). Different laboratory tests showed that ultrasonic extraction provides the

190 highest and more reproducible extraction yields. If there are still some uncertainties related to
191 this technique, it is widely used to measure pinic acid and pinonic acid in aerosol samples
192 (Anttila et al., 2005; Feltracco et al., 2018; Kourtchev et al., 2014; Nozière et al., 2015). As a
193 result, particles were extracted two times by placing a 47 mm diameter disc in 3 mL of a
194 mixed acetonitrile/water solution (70/30) under ultrasonication for 15 min. Then, each extract
195 was centrifugated and the supernatant was transferred in a 15 mL vial and concentrated to
196 about 400 μ L under a gentle pure nitrogen flow (99.995 % purity, Linde Gas SA) at 40 °C.
197 Samples were weighted using gravimetry (precision: 10^{-4} g), then stored at -18°C until
198 analysis. LC-HRMS analyses were carried out using an Agilent 1290 HPLC system coupled
199 to an Agilent 6540 QToF mass spectrometer equipped with an Agilent Jet Stream
200 electrospray ionization source (ESI) operating in the negative mode. The chromatographic
201 separation was performed on a Zorbax Eclipse XDB-C18 (2.1 \times 150 mm; 3.5 μ m) regulated at
202 30°C. Gradient LC elution was performed at a flow rate of 0.5 mL min⁻¹ using 0.2% formic
203 acid in purified water as mobile phase A and 0.2% formic acid in acetonitrile as mobile phase
204 B. Sample injection volume was set at 5 μ L. In this study, pinic acid and pinonic acid were
205 quantified using authentic standards of the two targeted compounds (pinic acid 98 % and cis-
206 pinonic acid 98 %, Sigma-Aldrich) as external standards. More details about LC-QTOF-MS
207 parameters can be found in the supplementary information (**Table S1**).

208 **3 Results and discussion**

209 **3.1 Meteorological conditions during 2014 and 2015 field campaigns**

210 Meteorological parameters are crucial as they may greatly influence BVOC emissions and
211 the oxidative capacity of the atmosphere. The Bilos site is for instance frequently subject to
212 periods of large hydric stress during summer. Detailed meteorological conditions during 2014
213 and 2015 field campaigns can be found in **Figures S1** and **S2**. For each campaign, the
214 conditions were very different. The 2015 field campaign was very hot, with few rain events
215 (see **Figures S1.a, d** and **Figures S2.a, d**). During this last campaign, the air temperature

216 frequently exceeded 30°C during the day and was hardly ever below 15°C at night, which
217 was not the case in July 2014. Such high temperature values were already reported to
218 induce a thermic stress on trees (Laothawornkitkul et al., 2009). One particularity of the site
219 was that relative humidity increased to reach its maxima (*i.e.* 100%) almost every night, in
220 both July 2014 and 2015.

221 No rainfall was observed from the middle of June 2015 (meteorological parameters outside
222 the campaign range are available from the ICOS network) and only few mm of rain was
223 recorded between the 5th and the 22nd July in 2015. As a result, a very weak water vapour
224 flux was observed in July 2015, whereas the sensible heat flux was very high (**Figure S2.b**),
225 especially comparing to 2014 fluxes (**Figure S1.b**). The Bowen ratio (between sensible heat
226 fluxes and water vapour fluxes) is a powerful tool to evaluate the hydric stress level. During
227 drought, the water vapour fluxes decrease whereas the heat fluxes increase (by
228 compensation to conserve the energy balance), making the Bowen ratio particularly
229 elevated. Indeed, the 2015 campaign was characterized by Bowen ratio values about 10,
230 which is very high for a forest stand (Gu et al., 2006). Such high Bowen ratios were not
231 observed during the 2014 field campaign, with values only around 0.5 (Kammer et al., 2019).
232 Thus, a thermic stress (due to temperatures over 30°C) coupled to a hydric stress occurred
233 during the 2015 campaign. The presence of such a stress situation may increase BVOC
234 emissions (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009; Loreto et al., 1998;
235 Peñuelas and Staudt, 2010). Wind directions indicated that air masses were mostly coming
236 from west-northwest direction in 2014 as well as in 2015 (**Figures S1.e** and **S2.e**), which was
237 confirmed by backward air mass trajectories calculations. Air masses were thus mostly
238 influenced by the Atlantic Ocean in both campaigns.

239 **3.2 General conditions of the campaigns**

240 A previous study reported by our group (Kammer et al., 2018) showed that NPF has been
241 frequently observed during the 2015 field campaign, mostly during the night, although a few

242 events (only 2) were also recorded during daytime. NPF events were defined as an increase
243 of particle concentration in the nucleation mode followed by a subsequent growth during at
244 least 2 hours (Dal Maso et al., 2005). In 2014, only one NPF event was observed, occurring
245 during nighttime. This leads to a NPF frequency of occurrence (i.e. the number of nights
246 where NPF events were observed divided by the total number of nights during the field
247 campaign) of about 8% during the 2014 field campaign. In 2015, 12 NPF events were
248 reported, reaching a high frequency of occurrence of around 55% (Kammer et al., 2018).
249 NPF thus occurred more frequently in a summer influenced by a hydric stress (according to
250 the high Bowen ratio values measured during the 2015 campaign). This observation may
251 further suggest that the presence of a hydric stress is indirectly inducing more NPF events
252 because of stronger monoterpene emissions. Nevertheless, more studies about the effect of
253 hydric stress on NPF will be needed to confirm such hypothesis. All the observed NPF
254 events are listed in **Table S2**. A more complete analysis of NPF events (growth rates,
255 nucleation rates, etc.) can be found in Kammer et al. (2018).

256 Analyses of wind directions and air mass back trajectories have shown that air mass origin
257 did not affect NPF. During both campaigns, NPF were always recorded along (i) high relative
258 humidity (i.e. $RH \geq 75\%$), (ii) temperatures higher than 16°C and (iii) $1/u^*$ (where u^* is the
259 friction velocity) over 2.5 s m^{-1} , indicating vertical stratification (this parameter was usually
260 below 2 s m^{-1} during the day where turbulence occurred, see the meteorological parameters
261 in **Figures S1** and **S2** during NPF events). It shows that NPF started once the stable
262 nocturnal boundary layer was taking hold. As suggested by the air mass analysis, nocturnal
263 NPF were very likely influenced by local emissions, limiting the impact of transported
264 compounds.

265 NO , NO_2 , SO_2 (only for 2015 campaign) and ozone mixing ratios are represented on **Figures**
266 **S3** and **S4**. NO_x mixing ratios were very low during both campaigns, confirming the very rural
267 feature of the Bilos site. The mixing ratios of SO_2 , which is recognized as a key species for
268 daytime nucleation, was always around the DL value of the instrument (only available in

269 2015, **Figure S4.b**). As a consequence, and taking into account the nocturnal nature of NPF,
270 it is highly probable that sulphuric acid was not responsible for nocturnal NPF at Bilos,
271 conversely to classical daytime NPF. Ozone mixing ratios presented a typical diurnal cycle
272 with maximal values reached during the afternoon, and frequently dropped under the
273 analyser limit (*i.e.* 0.5 ppb) in the middle of the night. The nights of July 15th and 16th in 2014
274 and 12th to 15th, 17th, 18th and 20th in 2015 are perfect examples of this ozone drop (**Figures**
275 **S3.c** and **S4.c**). The meteorological conditions observed during these nights indicate that
276 these ozone drops occurred under stratified atmosphere conditions (low wind speed and high
277 $1/u^*$).

278 **3.3 Monoterpene mixing ratios**

279 The sum of monoterpene as well as ozone mixing ratios are represented in Figure 1 for both
280 field campaigns. A strong diurnal cycle was observed in July 2014 as well as in July 2015 for
281 both ozone and monoterpenes. A typical ozone diurnal cycle was observed, with higher
282 values in the afternoon (Figure 1). The ozone cycle was mirrored by the monoterpenes cycle,
283 with higher monoterpene mixing ratios values during the night, as previously reported in the
284 Landes forest (Simon et al., 1994). Monoterpenes were dominated from far by α - and β -
285 pinene, accounting for around 90% of total monoterpenes, in accordance with previous
286 studies (Riba et al., 1987; Simon et al., 1994). Maritime pines are well-known to be strong
287 temperature driven BVOC emitters (Kesselmeier and Staudt, 1999; Lathiere et al., 2006).
288 Although emissions are higher during the day, the larger dilution of emissions in the surface
289 layer and the higher oxidant levels conduct to lower BVOC mixing ratios during light hours.
290 More explanation about the diurnal cycle and the effect of the change in the boundary layer
291 height on monoterpene mixing ratios can be found in Kammer *et al.* (2018). In 2015,
292 monoterpene mixing ratios frequently (*i.e.* almost half of the nights) reached around 15 ppb,
293 whereas they were always lower than 10 ppb in 2014, except the night of July 16th to 17th
294 (**Figure 1**). The highest values were reached the 21st of July 2015, where the sum of
295 monoterpene mixing ratios exceeded 35 ppb (**Figure 1.b**). The very high mixing ratios of

296 monoterpenes observed in 2015 were assumed to be the result of the meteorological
297 conditions, and more specifically the thermic/hydric stress. The high frequency of occurrence
298 of NPF in 2015 occurred for the highest monoterpene mixing ratios, emphasizing the role of
299 monoterpenes at night at Bilos.

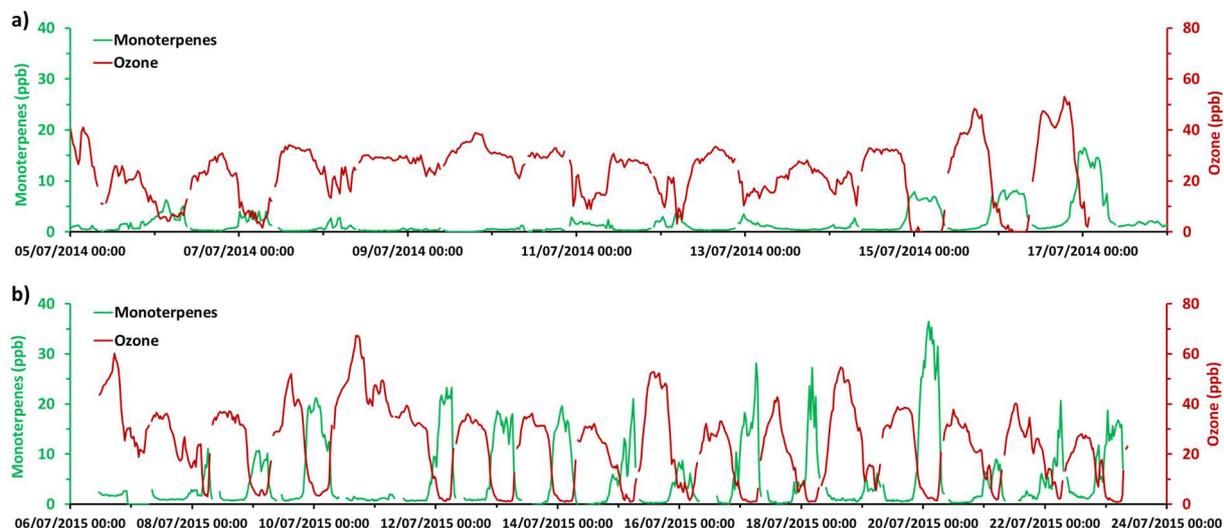


Figure 1: Time series of the sum of monoterpene mixing ratios (in ppb, green line) and ozone mixing ratios (in ppb, red line) for **a)** 2014 and **b)** 2015 field campaigns.

300 **3.4 Monoterpene/O₃ reactivity**

301 Time series of ozone and monoterpene mixing ratios (**Figure 1**) suggest that their respective
302 diurnal cycles were closely anti-correlated. The monoterpene mixing ratios increased every
303 night, as reported on **Figure 1**, when it is likely that no ozone was produced (because of its
304 dependence on solar radiation), nor ozone advection from higher layers of the atmosphere
305 (because of the nocturnal stratified boundary layer). The anti-correlation between ozone and
306 monoterpenes can be observed on **Figure 2.a**. Interestingly, when ozone was close to 0,
307 monoterpene mixing ratios values were at least of 5 ppb during the corresponding nights
308 (**Figure 2.a**). Reaction between ozone and monoterpenes in the early night could thus be
309 expected. Such reactions could only partially explain the ozone drop to levels close to zero,
310 as their kinetic rate constants are quite low (Atkinson and Arey, 2003). A rough estimation,
311 assuming pseudo-first order reactions between ozone and monoterpenes, led to a maximal

312 contribution to the ozone decrease being around 50 %. Thus, there is also a possibility for
313 other reactive BVOCs to be co-emitted with monoterpenes and react very fast with ozone
314 (like β -caryophyllene, for example). Further modelling of ozone deposition and chemical
315 reactions between ozone and BVOCs will be needed for a detailed estimation.

316 As monoterpene emissions come from the diffusion of resin stored in pools, the ratio
317 between α - and β -pinene in maritime pine emissions is assumed to be constant (Simon et al.,
318 1994). Hence, changes in the α/β -pinene ratio can mostly be assigned to differences in
319 oxidation processes, as the reactivity of α - and β -pinene with the main atmospheric oxidants
320 differs (see **Table 1**). The daily evolution of the α/β -pinene ratio may provide an interesting
321 tool to evaluate the importance of each oxidation processes. When the OH-initiated
322 monoterpene photooxidation is the dominant process, β -pinene mixing ratio should decrease
323 faster than that of α -pinene, because of its larger reactivity with OH (**Table 1**). In the morning,
324 the α/β -pinene ratio measured at Bilos was increasing, meaning that photooxidation was
325 increasingly dominated by OH radicals (**Figure 2-b**). In the afternoon, the α/β -pinene ratio
326 was found to drop, during both 2014 and 2015 field campaigns. Such decrease reflects that
327 the dominating oxidation process was changing, as the reaction rate constants of α -pinene
328 with ozone and NO_3 are known to be larger than for β -pinene (**Table 1**). It is recognized that
329 NO_3 reactivity is mostly significant during nighttime, as nitrate radicals are photolysed by
330 solar radiations (Seinfeld and Pandis, 2006). As a result, the drop of the α/β -pinene ratio
331 highlighted the dominant role of ozone oxidation processes in the afternoon.

Table 1: Chemical kinetic rate constants of reactions of α - and β -pinene with the main atmospheric oxidants (OH, O₃ and NO₃)

	Rate constant (at 298K, in cm ³ molecule ⁻¹ s ⁻¹)		
	OH	O ₃	NO ₃
α -pinene	$(5.3\pm 0.2) \times 10^{-11}$	$(9.0\pm 0.2) \times 10^{-17}$	$(6.2\pm 0.1) \times 10^{-12}$
β -pinene	$(7.6\pm 0.1) \times 10^{-11}$	$(1.9\pm 0.3) \times 10^{-17}$	$(2.5\pm 0.1) \times 10^{-12}$

IUPAC recommended values (Atkinson et al., 2006)

332 The **Figure 2.b** shows that the α/β -pinene ratio mean diurnal cycle was more pronounced in
333 2015. Solar radiation, taken as a simple proxy for OH concentration, and ozone mixing ratios,
334 were higher in 2015 than in 2014 (**Figures 2.c** and **2.d**). Higher OH concentration or ozone
335 mixing ratios led to a more pronounced increase or drop in the α/β -pinene ratio values,
336 respectively. The **Figure 2.b** illustrates that the mean diurnal cycle of the α/β -pinene ratio
337 logically followed the solar radiation and ozone diurnal profiles. The analysis of the mean
338 diurnal evolution of the α/β -pinene ratio also supports the hypothesis of the importance of
339 ozone reactions with monoterpenes in the afternoon/evening. To check this hypothesis, the
340 presence (or absence) of monoterpene oxidation products in the gas phase was
341 investigated.
342

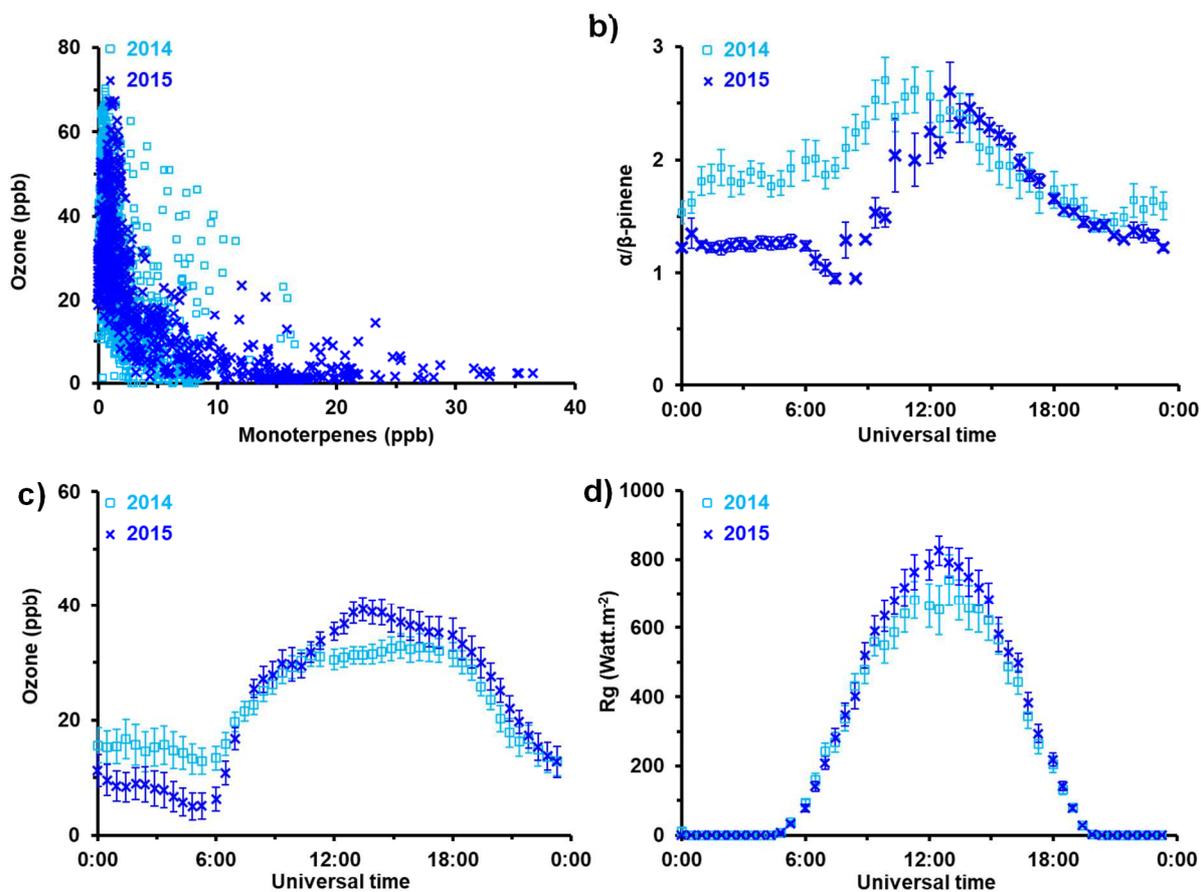


Figure 2: **a)** Anti-correlation between ozone and monoterpene mixing ratios **b)** mean diurnal profile of the α/β -pinene ratio **c)** mean diurnal profile of the ozone mixing ratios **d)** mean diurnal profile of global radiation, during each campaign. The error bars represent the standard errors of each variable. For each graphics, light blue squares represent 2014 dataset, and dark blue crosses represent 2015 dataset. (Universal time = local time – 2h)

343

344 3.5 BVOC oxidation products

345 As the PTR-TOF-MS has a good mass resolution, and considering the high mixing ratios of
 346 both α - and β -pinene at the Bilos site, several detected ions were able to be attributed to
 347 biogenic oxidation products. The identification of the following ions was proposed based on
 348 the proximity of the peak with the theoretical mass, and considering the characteristics of the
 349 Bilos site (very rural, high monoterpene mixing ratios, etc.). However, a contribution of a
 350 compound with a m/z very closed to the proposed compound could not be fully excluded.

351 First, m/z 139.11 was proposed to be attributed to nopinone (C₉H₁₄O) and m/z 169.12 to
352 pinonaldehyde (C₁₀H₁₆O₂), as both compounds were frequently reported at rural field sites
353 (Bourtsoukidis et al., 2014; de Gouw and Warneke, 2007; Park et al., 2014, 2013; Rantala et
354 al., 2014; Ruuskanen et al., 2011). Relevant signals were also observed at m/z 135.11, m/z
355 151.10 and m/z 155.13, but their attribution was more difficult. The m/z 135.11 protonated
356 ion corresponds to compounds of the molecular formula C₁₀H₁₄. Among several potential
357 hydrocarbons, the m/z 135.11 ion may correspond to *p*-cymene, which has already been
358 reported by Gratien *et al.* (2011) as a secondary product of α -pinene photo-oxidation. Even if
359 *p*-cymene has not yet been reported among monoterpene emissions from maritime pines,
360 some works have already pointed out its emission from different plant species (Bäck et al.,
361 2012). *P*-cymene could thus have been emitted by understorey species (for which BVOC
362 emissions remain unknown or poorly investigated), or result from α -pinene photo-oxidation.
363 *P*-cymene levels were found to be highly correlated with pinonaldehyde and nopinone ($R^2 =$
364 0.8), suggesting the secondary origin of this compound.

365 The molecular formula [C₁₀H₁₄O]H⁺ was proposed to be the major contributor of m/z 151.10
366 ion. This ion is recognized as a monoterpene oxidation product, and some studies attributed
367 this mass to a significant pinonaldehyde fragment (de Gouw and Warneke, 2007; Holzinger
368 et al., 2007; Park et al., 2014; Rantala et al., 2014). Note that *i*) other compounds such as
369 myrtenal or verbenone, that may have primary sources, could also be important contributors
370 to the m/z 151.10 signal (Kim et al., 2010) and *ii*) OH initiated oxidation of nopinone was also
371 reported to yield products with m/z 151.10. Finally, the PTR-TOF-MS signal recorded at
372 m/z 155.13 has been identified as C₁₀H₁₈O compounds. Several isomers can potentially
373 contribute to this signal. Notably, primary OVOCs such as linalool or 1,8-cineol have already
374 been reported at m/z 155.13 elsewhere (Bourtsoukidis et al., 2014; Park et al., 2013; Rantala
375 et al., 2014). However, a contribution of secondary oxygenated compounds cannot be
376 excluded. The presence of all such monoterpene oxidation products confirms that
377 monoterpenes were oxidized at the Bilos site. Especially, pinonaldehyde and nopinone are

378 known to be exclusively formed from the oxidation (by ozone or OH radical) of α - and β -
379 pinene, respectively, supporting the occurrence and the importance of the oxidation of
380 monoterpenes in the Landes forest. Indeed, OH can be formed as a secondary product of
381 the ozonolysis of monoterpenes. Any observed OH reactivity during nighttime would thus be
382 an indication of a primary monoterpene ozonolysis process. It was finally assumed that the
383 increase of nopinone and pinonaldehyde during the night was arising from monoterpene
384 ozonolysis.

385 The temporal evolution of the compounds of interest measured during the 2015 field
386 campaign is represented on **Figure 3**. In this section, we make the choice to focus on the
387 2015 data as *i*) oxidation product concentration values were frequently around the DL of the
388 instrument in 2014 and *ii*) there was only one NPF event in 2014. This is consistent with
389 lower monoterpene mixing ratios observed during this first campaign. As oxidation products
390 were not quantified in this study, their corresponding signals were normalized to their
391 maximum to allow the comparison of their temporal evolution profiles and diurnal dynamics.
392 Interestingly, all the oxidation products globally followed the same diurnal cycle, similar to
393 that observed for monoterpenes (**Figure 3**). Their levels started to increase with the sunset,
394 then decreased when the first rays of the sunlight appeared (**Figure 3**). The decrease of the
395 monoterpene oxidation product could be explained by *i*) a higher dilution due to the increase
396 of the surface layer height as soon as the first rays break the stable nocturnal boundary layer
397 and *ii*) potential photolysis, especially in the case of pinonaldehyde and nopinone, as both
398 are carbonyl compounds prone for photolysis. Although oxidation products are quite volatile
399 and thus are not expected to directly contribute significantly to NPF, they highlight a strong
400 reactivity between ozone and monoterpenes, also yielding (at night) to potential very low
401 volatile oxidation products that may contribute to nocturnal NPF at Bilos.

402

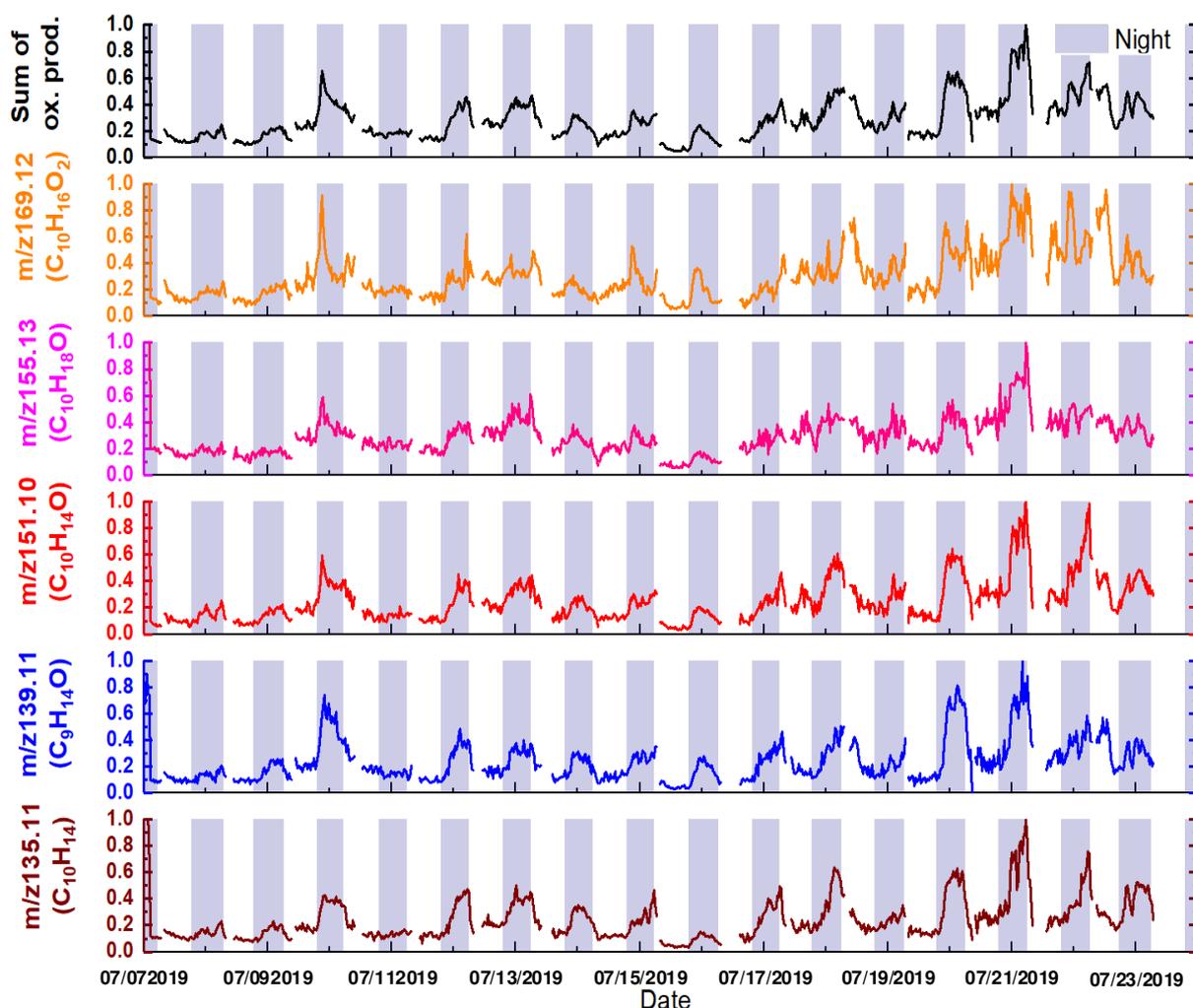


Figure 3: Half hourly evolution of m/z 135.11 ($C_{10}H_{14}$), m/z 139.11 ($C_9H_{14}O$, nopinone), m/z 151.10 ($C_{10}H_{14}O$), m/z 155.13 ($C_{10}H_{18}O$), m/z 169.12 ($C_{10}H_{16}O_2$, pinonaldehyde) and their sum. Y axes are unit less as signals (number of counts) have been normalized to their maximum. Missing data are due to calibrations and blanks of the instrument. The blue shaded areas denote the nighttime periods (defined as the time when global radiation was below 50 W m^{-2}).

403 **3.6 Nighttime reactivity of BVOC oxidation products**

404 In order to go further in the understanding of the role of oxidation products observed in the
 405 forest, it was decided to particularly focus on a short period, on m/z 139.11 and m/z 169.12
 406 signals, corresponding to nopinone and pinonaldehyde respectively (**Figure 4**). This is of
 407 particular interest as they are directly related to α -pinene (for pinonaldehyde) and β -pinene
 408 (for nopinone) oxidation. To the best of our knowledge, no direct comparison of diurnal

409 behaviours of both nopinone and pinonaldehyde from online field measurements has ever
410 been reported. The **Figure 4** presents the temporal evolution of nopinone, pinonaldehyde,
411 total monoterpenes and ozone mixing ratios during two nights (12/13 and 13/14 July 2015),
412 representative of the entire campaign. It can be observed that during both nights,
413 pinonaldehyde signal first increased faster than that of nopinone, reaching its maximum
414 within a few hours and then decreased throughout the night. At the end of the night, a new
415 increase was observed for pinonaldehyde mixing ratios, which finally returned to its daily
416 level in the morning. The nocturnal dynamics of nopinone was observed to be simpler.
417 Nopinone level started to increase at the sunset and decreased in the morning as turbulence
418 reappeared. Such a strong difference between the nocturnal profiles of these two
419 compounds probably results from their different physico-chemical properties and related
420 reactivity. The formation yields of pinonaldehyde and nopinone from ozonolysis of α - and β -
421 pinene have been reported to be highly dependent on the physico-chemical conditions (Lee
422 et al., 2006). More, the range of formation yields for both compounds are quite similar and
423 very large (**Table 2**). If formation yields did not directly allow elucidating the faster increase of
424 pinonaldehyde, the higher reaction rate constant of α -pinene ozonolysis (compared to β -
425 pinene) may at least partially explain such trend.

Table 2: Formation yields of nopinone and pinonaldehyde from β - and α -pinene ozonolysis, reaction rate constants with the main atmospheric oxidants OH, O₃ and NO₃ and saturation vapour pressures (P_s in Torr).

	Compounds	
	Nopinone	Pinonaldehyde
Formation yields (%)	16-40 ^a	6-53 ^a
k _{OH} (cm ³ molecule ⁻¹ s ⁻¹)	(1.7±0.2) × 10 ⁻¹¹ ^b	(3.9±0.2) × 10 ⁻¹¹ ^c
k _{O₃} (cm ³ molecule ⁻¹ s ⁻¹)	< 5 × 10 ⁻²¹ ^b	< 2 × 10 ⁻²⁰ ^c
k _{NO₃} (cm ³ molecule ⁻¹ s ⁻¹)	(1.1±0.3) × 10 ⁻¹⁵ ^b	(2.0±0.3) × 10 ⁻¹⁴ ^c
P _s at 298K (Torr)	0.4	0.038 ^d

^a Lee *et al.* (2006) and references therein ^b Calogirou *et al.* (1999) ^crecommended IUPAC values (Atkinson *et al.*, 2006) ^dHallquist *et al.* (2009)

426 The second difference between the two nighttime product time profiles was the decrease of
 427 pinonaldehyde during the night, not (or less) observable in the case of nopinone, highlighting
 428 a larger sink for pinonaldehyde than for nopinone (**Figure 4**), assumed to be due to its faster
 429 reactions with atmospheric oxidants (**Table 2**). The reaction of pinonaldehyde with ozone is
 430 known to be very slow, and may not be responsible of such a decrease. NO₃-initiated
 431 reaction might be an important removal process for pinonaldehyde but would have required
 432 larger concentrations of nitrate radicals that those expected at the very low NO_x levels
 433 measured during the campaign (**Figures S3.a** and **S4.a**). In addition, NO₃ reaction rate
 434 constants with α - and β -pinene are at least 100 times faster than nopinone and
 435 pinonaldehyde (**Table 1**). As a result, any NO₃ radicals present at Bilos would first react with
 436 monoterpenes, not allowing to explain the decrease of pinonaldehyde.

437 Many studies have reported the secondary formation of OH radicals following the
438 monoterpene ozonolysis, with yields up to 1 (Rickard *et al.*, 1999; Aschmann *et al.*, 2002;
439 Fick *et al.*, 2002; Atkinson and Arey, 2003; Forester and Wells, 2011). Moreover, Faloon *et al.*
440 *al.* (2001) reported unexpected high OH concentrations at a deciduous forest site during
441 nighttime. Therefore, it is reasonable to hypothesize that the nighttime pinonaldehyde
442 decrease was due to its reaction with OH (this reaction being 5 times faster than that of
443 nopinone) (**Table 2**). Obviously, future measurement of OH radicals at the Bilos site will be
444 required to deeply answer to this question.

445 Another hypothesis can be put forward to tentatively explain the different profiles of
446 pinonaldehyde and nopinone: their potential condensation on the particle phase. Indeed, the
447 saturation vapour pressures of the two compounds differ by one order of magnitude,
448 pinonaldehyde being 10 times less volatile than nopinone at ambient temperature (**Table 3**).
449 But Kavouras *et al.* (1999) have shown that both compounds are usually mostly present in
450 the gas phase. As a result, gas/particle partitioning might only weakly impact their
451 concentration in the gas phase. Lastly, heterogeneous reactions (as for example, reactions
452 with amines) could not be excluded from this discussion, and may play an important role in
453 the fate of both products (Duporté *et al.*, 2016), but the investigation of such reactions was
454 beyond the scope of the present study and might be considered in the further measurement
455 campaigns at Bilos.

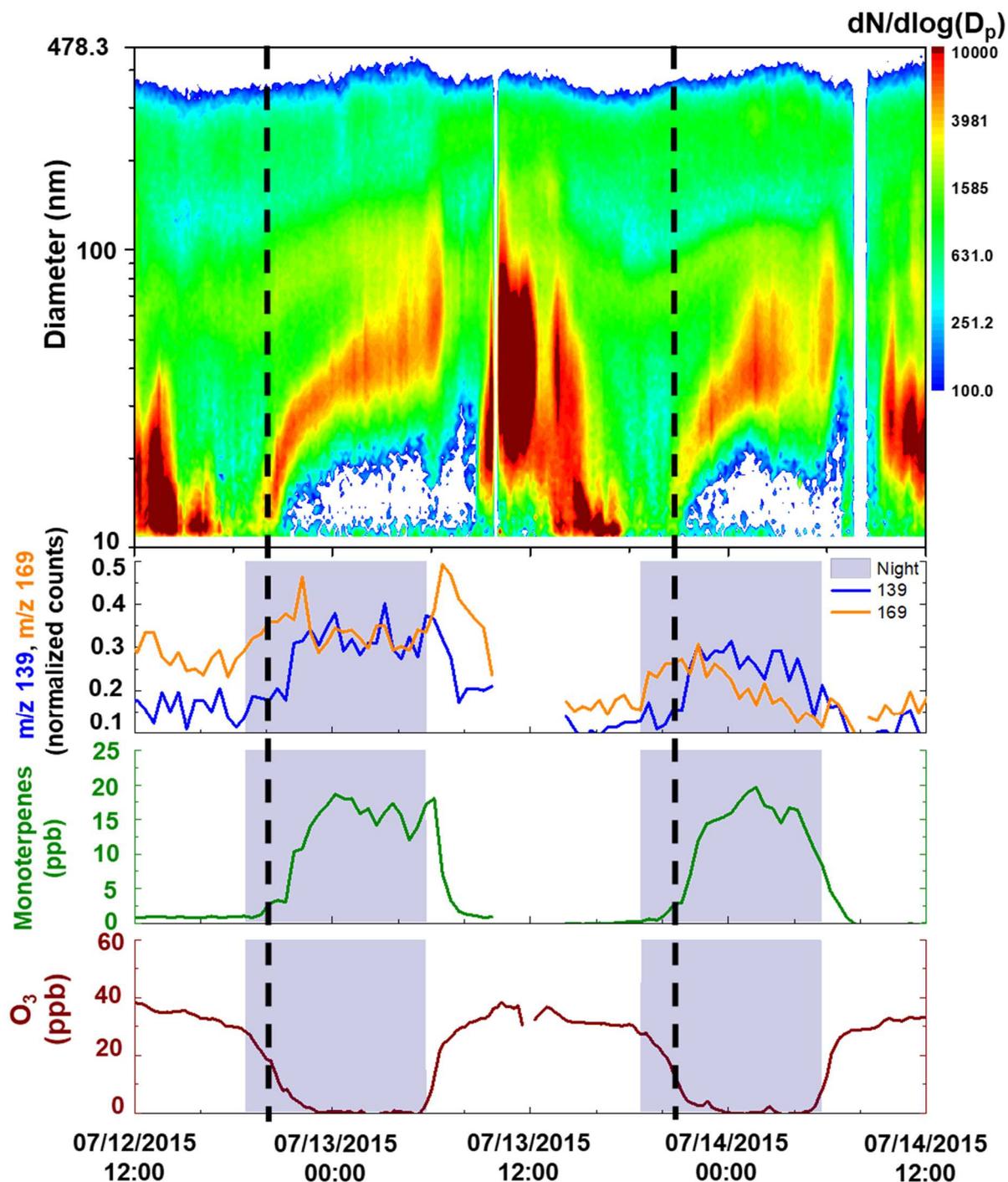


Figure 4: Size distribution of particles between 10 nm and 478.3 nm, during two typical NPF events observed at Bilos in July 2015. On lower panels: the half hourly evolution of m/z 139.21 ($C_9H_{14}O$, nopinone) and m/z 169.24 ($C_{10}H_{16}O_2$, pinonaldehyde) normalized signals, total monoterpene and ozone mixing ratios are represented. Intensities of oxidation product signals (number of counts) have been normalized to their maximum. Blue shaded areas denote the nighttime periods (defined as the time when global radiation was below $50 \text{ W}\cdot\text{m}^{-2}$).

457 **3.7 Contribution of BVOC oxidation products to NPF**

458 This work raises the question of the link between the in-canopy reactivity of monoterpenes
459 and the NPF events observed at night. In a recent paper (Kammer et al., 2018), we reported
460 that NPF always occurred *i)* when the condensation sink was low, *ii)* after the nocturnal
461 boundary layer was taking hold and *iii)* for the nights where monoterpene mixing ratios were
462 high, suggesting their contribution to nocturnal NPF. In the **section 3.5**, we relate that the
463 mixing ratios of monoterpene oxidation products increased at night. The **Figure 4** presents
464 two consecutive nights (12/13 and 13/14 July 2015) where NPF occurred, as a typical
465 example of what was observed during the campaign. At night, the sum of monoterpene
466 mixing ratios started to increase about 1-2 hours before NPF took place, at the same time as
467 nopinone and pinonaldehyde. This time might corresponded to a switch from condensation to
468 nucleation, resulting from the drop of the condensation sink and the higher abundance of low
469 volatile intermediates. To go further, a better knowledge of nanometer particle formation and
470 size-resolved chemical composition of aerosols will be necessary. **Figure 4** shows that
471 monoterpenes and their oxidation products levels increased simultaneously, which means
472 that the main drivers that are triggering NPF are probably physical. However, the time lag
473 between the simultaneous increase and the beginning of the NPF event may be due to *i)* the
474 inability of the SMPS to catch the first steps of NPF and *ii)* the required time for condensable
475 vapors to reach their saturation limit. This last hypothesis suggests a fast oxidation process,
476 able to generate very low volatile gases in a short time. Auto-oxidation process has been
477 shown to be able to produce highly oxidized multifunctional organic compounds (HOMs) very
478 fast, which can then promote particle nucleation and growth (Jokinen et al., 2014; Kirkby et
479 al., 2016; Tröstl et al., 2016). Hence, simultaneously to nopinone and pinonaldehyde
480 generations, HOMs may have been produced by fast auto-oxidation processes, participating
481 *in fine* to nocturnal NPF (Jokinen et al., 2014). In addition, OH radicals were very probably
482 produced from the ozonolysis of monoterpenes during the night. This is supported by the
483 time evolution of pinonaldehyde, which decreased in the middle of the night, probably due to

484 its reaction with OH. Thus, secondary reactions involving OVOCs might also be involved in
485 NPF. The lag time described above might also be the time required for these secondary
486 reactions to take place. But, even if the reactions between OH and OVOCs could be
487 important for NPF at Bilos, the main source of OH during nighttime was arising from the
488 primary ozonolysis of monoterpenes, highlighting the importance this process as an initial
489 step. To go further, the contribution of each oxidation pathways (*i.e.* ozone and OH) to NPF
490 will need more investigations. Considering that most of NPF events occurred during
491 nighttime and the very low SO₂ mixing ratios observed at Bilos, it was not expected that
492 sulfuric acid was involved, emphasizing again the role of BVOCs. The recent studies about
493 NPF from pure BVOC ozonolysis, and the high monoterpene mixing ratios at our site let us
494 hypothesise that ozonolysis of monoterpenes - and potentially other BVOCs - may be one of
495 the main drivers of nocturnal NPF at the Bilos site (Kirkby *et al.*, 2016; Tröstl *et al.*, 2016).

496 **3.8 Molecular tracers of BVOC oxidation in the particle phase**

497 To support our hypothesis about the contribution of BVOCs to the nocturnal NPF, SOA
498 tracers from α - and β -pinene oxidation were investigated in the PM_{2.5} particulate fraction
499 collected during the 2015 field campaign. Even if the chemical composition of PM_{2.5} and
500 newly formed particle could be different, it is well-recognized that pinic and pinonic acids are
501 good tracers for SOA formed from α - and β -pinene ozonolysis (Claeys *et al.*, 2009; Faiola *et al.*,
502 2014; Hallquist *et al.*, 2009; Jaoui *et al.*, 2005; Kristensen *et al.*, 2016; Nozière *et al.*,
503 2011; Yasmeen *et al.*, 2011). Thus, the presence of such markers in PM_{2.5} would support our
504 hypothesis. During July 2015, pinic and pinonic acids were detected and quantified in all
505 samples. Both products were found in large quantities in the particles collected at Bilos, in
506 every 24 hours filters. Mean concentration of pinic acid was 18.3 ng m⁻³, and reached the
507 maximum value of 33.8 ng m⁻³ (**Table 3**). These values are in the same order of magnitude
508 as those previously reported in studies conducted in other rural forested areas around the
509 world. For example, the concentration of pinic acid measured in a boreal forest (Hyytiälä,
510 Finland) during summertime was 7.2 ng m⁻³, and reached a maximal concentration of 31 ng

511 m⁻³. Pinic acid concentrations reported at other sites (**Table 3**) were reported to be between 4
512 and 8 ng m⁻³, slightly lower than those measured at Bilos. This is consistent with the high
513 monoterpene mixing ratios presented above. The mean concentrations of pinonic acid during
514 the campaign was 10.2 ng m⁻³, also close to the reported values in **Table 3**. The high
515 concentrations of these markers arising from α - and β -pinene oxidation measured in this
516 work support the high reactivity between monoterpenes and ozone, which is an important
517 oxidation pathway for monoterpenes during nighttime at the Bilos site. This result attests that
518 oxidation products of pinenes are well transferred to the particle phase, resulting from either
519 gas/particle transfer during NPF or condensation. Further measurements of the size-resolved
520 chemical composition of aerosols will be necessary to differentiate these processes.

521 In the present study, the concentrations of markers in the particle phase were in the same
522 range as the reported values (or around twice as high), whereas monoterpene mixing ratios
523 were at least one order of magnitude higher (**Table 3**). Such differences in the ratio between
524 particulate SOA tracers concentrations and gaseous monoterpene mixing ratios suggest that
525 different physico-chemical processes may occur at our site.

526 To further investigate the link between in-canopy monoterpene reactivity and nocturnal NPF,
527 night and day filter sampling should be performed. Mochizuki *et al.* (2014) observed strong
528 differences in the concentration of night and day particulate SOA tracers. In the case of
529 nocturnal NPF identified in this study, such information could help to unravell the detailed
530 processes. the This will be considered in a next field campaign implemented at Bilos. Note
531 that a large panel of other biogenic SOA tracers were detected in the particles collected. The
532 detailed chemical composition of atmospheric particles collected during the campaign will be
533 the subject of a future publication.

534

535

Table 3: Comparison of pinic and pinonic acid concentrations measured at the Bilos site in

July 2015 and those reported in the literature

Field site	Pinic acid		Pinonic acid		Monoterpenes	Ref.
	Mean	Min – Max	Mean	Min - Max	Mixing ratios (ppb)	
Concentrations (ng m⁻³)						
Landes forest (Bilos, France) July 2015	18.3	4.3 – 33.8	10.2	2.2 – 31.7	10 – 30	This work
Boreal forest (Hyytiälä, Finland) July/August 2010/2011	7.2	0.64 – 31	10.7	0.1 - 80	<1	(Vestenius et al., 2014)
Deciduous forest (Jülich, Germany) July 2003	4.2	0.9 – 9.9	-	-	-	(Kourtchev et al., 2014)
Pine plantation (California, USA) Sept 2007 July 2009	7.6 7.1	- -	6.1 11	- -	0.7 - 2.1	(Kristensen et al., 2013)
Larch forest (Fujiyoshida, Japan) July 2012	Day Night	0 – 18.2 0.8 – 14.5	12.7 3.1	1.7 – 28 0.9 – 6.8	0.5 - 4.4	(Mochizuki et al., 2014)

536 Conclusions

537 Two intensive field measurement campaigns were conducted in the French Landes forest, at
538 Bilos, in the summers of 2014 and 2015. Frequent nocturnal NPF events were observed
539 during periods of strong thermic and/or hydric stress (dry and hot summer). In parallel,
540 monoterpene mixing ratios (dominated by α - and β -pinene) reached very high levels almost
541 every night, frequently over 20 ppb in summer 2015. A strong anti-correlation between ozone
542 and monoterpene mixing ratios was highlighted, suggesting a high chemical reactivity. This
543 hypothesis was reinforced by the mean diurnal variation of the ratio between α - and β -pinene
544 mixing ratios. Products from the oxidation of α - and β -pinene, namely pinonaldehyde and
545 nopinone, were measured in the gas phase. The diurnal profiles of these two oxidation
546 products is consistent with the high reactivity between α - and β -pinene mostly with ozone in
547 the evening. Furthermore, pinonaldehyde and nopinone presented different nocturnal

548 profiles, suggesting a possible secondary source of OH radicals from monoterpene
549 ozonolysis during the night. Further work will be necessary to address this issue. The particle
550 phase analysis allowed to identify and quantify pinic and pinonic acids, confirming the
551 oxidation of monoterpenes observed at Bilos as well as the contribution of these precursors
552 to SOA. Considering the differences between 2014 and 2015 field campaigns in the
553 frequency of occurrence of NPF, the monoterpene mixing ratios, and the observed
554 monoterpene in-canopy reactivity, monoterpene ozonolysis is proposed to very likely
555 contribute to nocturnal NPF at our site. Measurements of size-resolved aerosol composition
556 will be required to determine more specifically to which extent monoterpene oxidation
557 products are involved in nucleation and/or aerosol growth in the Landes pine tree forest.

558 The high NPF frequency of occurrence observed in 2015 may be associated to the direct
559 consequence of the hydric/thermic stress, which promotes strong BVOC emissions.
560 Considering that the number of hydric stress periods will continue to increase due to the
561 global warming, it can be hypothesized that NPF events may be more and more important in
562 southwestern France. More studies will thus be required to confirm the effect of hydric stress
563 on NPF.

564

565 **Acknowledgements**

566 This work was supported by the French Environment and Energy Management Agency
567 (ADEME), the CNRS-INSU LEFE-CHAT research program, the NEEDS action, and the
568 PEPS IdEx Bordeaux. The authors want to acknowledge the Bilos ICOS team (Christophe
569 Chipeaux, Sébastien Lafont and Denis Loustau) for meteorological data and site availability
570 and Michael Staudt (CEFE-CNRS) for the loan of the GC-FID during the campaign. We also
571 thank Didier Garrigou (ISPA-INRA) for his precious help during the field campaigns,
572 especially in the installation and the maintenance of instruments.

573 **Competing interests:** The authors declare no competing of interest.

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