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1 **Isoprene contribution to ozone production in a context of climate change in French**
2 **Mediterranean area**

3

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26 **Abstract**

27 Tropospheric ozone is a strong oxidant which affects human health, agricultural yields, and
28 ecosystems functioning. Thus, it is very important to determine ozone formation in order to
29 control air pollution. It is well known that isoprene participates in ozone formation. In this
30 study, we assess the potential impact of climate change in the Mediterranean region on ozone
31 concentration, through drought-related increase or decrease in isoprene emissions after 1 (Short
32 Drought scenario – 1 year of 35% annual rain restriction) and 3 (Long Drought scenario – 3
33 repeated years of 35% annual restriction) years of drought stress.

34 Using an original experimental dataset of Downy oak isoprene emissions for several drought
35 conditions and idealized drought scenarios in a modeling framework, we showed that ozone
36 concentrations follow the same pattern than isoprene emissions. The Short Drought scenario
37 used an isoprene emission factor (which is the standardized emission rate at 30°C and
38 $1000\mu\text{mol.m}^{-2}.\text{s}^{-1}$ of photosynthetically active radiation (PAR)) 83% higher compared with
39 natural drought and, thus, ozone concentrations increased by 5-30 $\mu\text{g.m}^{-3}$ (3-17%). The Long
40 Drought scenario used an isoprene emissions factor 26% lower compared with natural drought,
41 and ozone concentrations accordingly decreased by 1-10 $\mu\text{g.m}^{-3}$ (0.6-6%). Our results showed
42 that ozone concentration is affected by drought intensity and duration through modification of
43 isoprene emissions indicating that drought stress should be implemented in models (predicting
44 the BVOC emissions).

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46 **Key words:** drought, climate change impact, isoprene emissions, ozone formation

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67 **Introduction**

68 Tropospheric ozone can be formed from the reaction between isoprene, globally the most
69 emitted Biogenic Volatile Organic Compound (BVOC) (Harrison *et al.* 2013) and nitrogen
70 oxides (NO_x), coming from anthropogenic emissions (Atkinson 2000). This reaction especially
71 occurs in the Mediterranean region where conditions (high NO_x concentrations, high solar
72 radiation, high temperatures and widely distributed high isoprene emitters) are very favourable
73 to ozone formation. For instance, in this region, it has been estimated that isoprene emissions,
74 the main BVOC emitted by plants, lead to the formation of 16-20% of tropospheric ozone
75 formation (Curci *et al.* 2009).

76 It is expected that extreme drought, such as that observed in summer 2003, can occur more
77 frequently in the future (Beniston *et al.* 2007) changing the global ozone budget. During August
78 2003, an extreme heat wave was recorded in Europe (above 40 °C as maximal temperature)
79 implying an increase of ozone levels. For instance, an hourly value of 417 µg.m⁻³ in terms of
80 ozone was recorded near the urban area in Marseille. Ozone levels were also very high in rural
81 areas and often above 180 µg.m⁻³, the EU hourly thresholds recommendation to initiate
82 population information (Council Directive 2008/50/EU). It has been shown that contribution of
83 BVOCs to ozone formation during this particular period was non-negligible (Vautard *et al.*
84 2005). Besides these punctual extreme events, ozone budget could change in the future with the
85 annual reduction of precipitations (~30%) expected with climate change and its impact on
86 BVOCs emissions, especially isoprene (Giorgi & Lionello 2008; IPCC 2013; Polade *et al.*
87 2014). Indeed, it has been shown that around 2% of assimilated carbon is released as isoprene
88 under optimal condition (Sharkey *et al.* 1991). This proportion increases up to 10% under
89 moderate drought (Kesselmeier *et al.* 2002). Isoprene could protect plants and the
90 photosynthetic apparatus by quenching the Reactive Oxygen Species (ROS) produced over a
91 stress period (Velikova 2008) and maintain the stability of thylakoids membranes (Velikova *et*
92 *al.* 2011). The link between isoprene emissions and drought is still unclear since isoprene
93 emissions can increase, decrease or remain unchanged related to stress intensity, the studied
94 species and the experiment length (Niinemets 2010; Peñuelas & Staudt 2010). Moreover, the
95 drought recurrence over time in the field are also important factors to take into account
96 (Brzostek *et al.* 2014) but such studies are still scarce.

97 In the Mediterranean area, Downy oak (*Quercus pubescens* Willd.) represents the major source
98 of isoprene emissions (Simon *et al.* 2005; Keenan *et al.* 2009) and is widespread in the Northern
99 part of the Mediterranean basin (Quézel & Médail 2003), occupying 2 million ha (personal

100 communication from T. Gauquelin). Hence, extrapolating results obtained in a Downy oak
101 forest, at the O₃HP (Observatoire de Haute Provence) site regarding the impact of short and
102 long-term drought on isoprene emissions (Saunier *et al.* 2017; Genard-Zielinski *et al.* 2018)
103 could give a key insight on the potential future evolution of isoprene emissions and,
104 consequently, on ozone concentrations in the Mediterranean region. At this site, a 33-35%
105 rainfall exclusion experiment has been installed in a natural forest to mimic the projected
106 decrease in rainfall according to the most severe scenario of climate change (RCP 8.5) in terms
107 of precipitation reduction in the Mediterranean region at the end of the century. Measurements
108 on isoprene emissions were performed after 1 and 3 years of amplified drought. An increase in
109 isoprene emission factor by 83% (Genard-Zielinski *et al.* 2018) and a 26 % decrease was
110 observed during the summer period compared with natural drought (Saunier *et al.* 2017), for 1
111 and 3 years of drought, respectively. These relative isoprene emission changes (increase and
112 decrease compared with natural drought) were, then, used to model ozone formation through
113 the regional chemistry-transport model CHIMERE to assess the effect of short and long-term
114 drought on this pollutant through isoprene emissions.

115 Based on these results, this study aims to evaluation the impact of short and recurrent drought
116 on ozone formation through the modifications of isoprene emissions from Downy oak at the
117 regional scale in the South of France using CHIMERE over an extreme temperature event
118 (summer 2003) since it has been shown that such events can occur more often in the future
119 (Beniston *et al.* 2007).

120

121 **Material and methods**

122 ***Model description***

123 The CHIMERE model (Schmidt *et al.* 2001; Menut *et al.* 2013) is a three-dimensional
124 chemistry-transport model (CTM), commonly used to study air pollution (Monteiro *et al.* 2005;
125 Menut *et al.* 2012). It is notably part of the French air pollution forecast system: Prev'air (Rouil
126 *et al.* 2009). Source code as well as documentation are available on the website
127 <http://www.lmd.polytechnique.fr/chimere/> (v2008 version). The CHIMERE model considers
128 the emission fluxes for 15 compounds (NO, NO₂, HONO, SO₂, CO, ethane, *n*-butane, ethene,
129 propene, isoprene, α -pinene, *o*-xylene, formaldehyde, acetaldehyde and methyl vinyl ketone).

130 The modeling set-up is applied on the Provence Alpes Cote d'Azur region (PACA-Regions
131 Sud) for the summer 2003 (between 1st June and 31st August), an exceptional heatwave period
132 whose frequency is expected to increase in the future (Vautard *et al.* 2005). Three imbricated

133 domains were used to perform the modelling experiment: the largest domain, called GFR27
134 afterward, has a resolution of 27 km. The intermediate domain, called FRSE9 afterward, has a
135 resolution of 9km and the smallest domain has a resolution of 3km (Fig. S1 in supplementary
136 files). The PACA region is composed by several departments whose surfaces of Downy oak
137 vary (Fig. S2 in supplementary files): Alpes de Haute-Provence (AHP, 70 000 ha, 31.9 %), Var
138 (VAR, 69 000 ha, 31.5 %), Vaucluse (VAU, 38 000 ha, 17.4 %), Alpes Maritimes (AM, 22 500
139 ha, 10.3 %), Hautes-Alpes (HA, 12 500 ha, 5.7 %) and Bouches-du-Rhône (BR, 7000 ha, 3.2
140 %). The emissions of anthropogenic compounds come from the EMEP database (2007) for the
141 first two domains (GFR27 and FRSE9) and from the official network in charge of pollution
142 survey and forecast in the PACA region: the AtmoSud database for the smallest domain
143 (PACA).

144 The forest characteristics and topography are fixed boundary conditions. The initial conditions
145 consist only in initial atmospheric concentrations and physical parameters describing the
146 composition of the atmosphere at the beginning of the experiment. Other boundary conditions
147 such as the concentrations of the atmosphere outside the considered domain or anthropogenic
148 emissions vary with time and location during the simulations and have been predetermined
149 before the simulation. BVOC emission variability of the first two domains (GFR27 and FRSE9)
150 was modelled according to MEGAN (Model of Emissions of Gases and Aerosols from Nature,
151 widely used throughout the community, Guenther *et al.* 2006) and the meteorological data.
152 CORINE Land Cover (2006) was used to determine the vegetation cover (e.g. needleleaf forest,
153 broadleaf forest, shrubland) on the modeling area. Then, the species repartition (e.g. *Q.*
154 *pubescens*) was added for each type of vegetation cover according to departments.

155 Hourly meteorological data were computed using the WRF model version 3.8 (Grell *et al.*
156 2013). The chemical mechanism used in this study is the reduced MELCHIOR scheme which
157 includes 44 molecular species and 120 reactions instead of 80 molecular species and 300
158 reactions in the full MELCHIOR scheme (Derognat *et al.* 2003). Secondary organic aerosols
159 were not considered in this work.

160

161 ***Experimental protocol***

162 In this study, CHIMERE model was used with modifications of the MEGAN model to integrate
163 the relative change of Downy oak isoprene emissions factors highlighted in two field studies at
164 O₃HP during short and long term drought simulations. Emissions factors are the emission rates

165 standardized at 30°C and 1000 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ of photosynthetic active radiation (PAR). These data
166 are generally used in modelling work (Guenther *et al.* 2006).

167 Relative changes were observed in summer 2012 (August) and summer 2014 (July) at the O₃HP
168 site (<https://o3hp.obs-hp.fr/index.php/en/>). This field site is equipped with an automated
169 monitored roof deployed during chosen rain events and set up over part of the O₃HP forest.
170 Thus, this device allowed to reduce natural rain of 33-35% which is very close to climatic model
171 expectations using the worst scenario of climate change (Giorgi & Lionello 2008; IPCC 2013)
172 to evaluate the effect of drought expected with climate change on isoprene emissions. Rain
173 exclusion started in May 2012 and was continuously applied every year, during the growth
174 period (from April to November). Data on cumulative precipitation showed that 35 % of rain
175 was excluded in 2012, 33 % in 2013 and 35.5 % in 2014 (Saunier *et al.* 2018). In 2012, the first
176 year of drought, an 83 % increase of the isoprene emission factors was observed (Genard-
177 Zielinski *et al.* 2018) under rain restriction compared with natural drought, whereas in 2014,
178 the third year of drought, a decrease by 26 % was observed (Saunier *et al.* 2017).

179

180 *Scenarios*

181 According to these experimental results, three idealised drought scenarios were considered in
182 this work. The REF scenario was the reference scenario which takes into account the current
183 isoprene emission factor of Downy oak equal to 67.78 $\mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ in MEGAN to estimate
184 isoprene emissions.

185 The Short Drought scenario corresponded to a 83% increase of the reference isoprene emission
186 factor, that is, an emission factor equal to 123.95 $\mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$. The Long Drought scenario
187 was associated to a 26% decrease of the reference isoprene emission factor, and thus, the
188 emission factor used in this scenario was 49.96 $\mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$.

189 The number of days exceeding a daily maximum of 180 $\mu\text{g}\cdot\text{m}^{-3}$ in terms of ozone concentration
190 according to the EU threshold recommendation for human health (Council Directive 2008/50/EU)
191 and 160 $\mu\text{g}\cdot\text{m}^{-3}$ as a threshold for plant health (Iriti & Faoro 2008) were taken into account to
192 estimate the air quality on two urban areas (Marseille and Aix-en-Provence city centers) and
193 two rural areas (Ste Beaume and Observatoire de Haute Provence). Those four sites were
194 chosen because they are well representative of the modelling area (Mediterranean France).

195

196 **Results**

197 The projection with the REF scenario showed that there are strong isoprene emissions during
198 all summer (Fig. 1A, B and C). Isoprene emissions reached 1155 g.day⁻¹ in June, 630 g.day⁻¹ in
199 July and, finally, 1230 g.day⁻¹ in August. The Short Drought scenario involved an increase of
200 isoprene emissions for all months (Fig. 1D, E and F). Isoprene emissions increased in some
201 departments by 850 g.day⁻¹ in June, 530 g.day⁻¹ in July and, finally, 910 g.day⁻¹ in August. By
202 contrast, the Long Drought scenario showed a decrease of isoprene emissions during all the
203 studied period (Fig. 1G, H and I). Isoprene emissions decreased by 270 g.day⁻¹ in June, by 170
204 g.day⁻¹ in July and, by 290 g.day⁻¹ in August. The areas most impacted by the Short and the
205 Long Drought scenarios are those where there are the strongest isoprene emissions, that is, the
206 VAR and VAU departments and, to a lesser extent, AHP, AM and BR in terms of absolute and
207 relative changes (Table S1 in supplementary files).

208 The maximum ozone concentrations modeled with the REF scenario show that there was a
209 strong ozone production throughout the studied period (June, July and August, Fig. 2A, B and
210 C, respectively). It must be noted that the ozone concentration increased through the summer
211 and was the strongest in August. The coastal VAR and AM departments were the most affected
212 areas in terms of ozone pollution in June with concentration around 180 µg.m⁻³. In the rest of
213 PACA region, ozone concentrations ranged between 108 and 144 µg.m⁻³. In July, the ozone
214 concentration was especially intense since together with the coastal areas of VAR and AM,
215 high ozone levels were also observed in the South of AHP as well as the whole VAU
216 department. In these areas, ozone concentrations ranged between 144 and 180 µg.m⁻³. In
217 August, the whole PACA region is affected by ozone pollution with a maximum concentration
218 higher than 180 µg.m⁻³. The Short Drought scenario led to a local increase of ozone
219 concentration in the range of 5.3 to 16 µg.m⁻³ in June (3-9%), 5.3 to 16.0 µg.m⁻³ in July (3-9%)
220 and 4.3 to 28.8 µg.m⁻³ in August (2.4-16%, Fig. 2D, E and F, respectively). By contrast, the
221 Long Drought scenarios involved a local decrease of ozone concentrations in a range of 1.4 to
222 4.3 µg.m⁻³ in June (0.8-2.4%), 1.4 to 4.3 µg.m⁻³ in July (0.8-2.4%) and 4.3 to 10.1 µg.m⁻³ in
223 August (2.4-5.6%, Fig. 2G, H and I, respectively).

224 Moreover, the number of days with an ozone level exceeding the threshold of 180 µg.m⁻³ is
225 equal to 9, 13 and 8 for the REF, the Short Drought and the Long Drought scenarios,
226 respectively (Table 1) in the rural areas such as OHP. For Ste Beaulieu site, 11, 13 and 10 days
227 were above this threshold the REF, the Short Drought and the Long Drought scenarios,
228 respectively. The same trend was observed for the urban sites, especially in Aix-en-Provence
229 city centre with 9, 13 and 7 for the REF, the Short Drought and the Long Drought, respectively.

230 To a lesser extent, the same phenomenon was observed in Marseille city center with 4 days of
231 high ozone levels for the REF and the Long scenarios whereas 5 days were detected for the
232 Short Drought scenario. Regarding the $160 \mu\text{g.m}^{-3}$ threshold, the Long Drought scenario did not
233 have such impact since the days exceeding this level remained unchanged or decreased by one
234 or two days both in urban and rural areas. The same results were found in urban areas with the
235 Short drought scenario. By contrast, an important increase of days exceeding $160 \mu\text{g.m}^{-3}$ was
236 observed in rural areas by 7 and 8 days, respectively at OHP and St Beaume.

237

238 **Discussion**

239 It is well known that increasing droughts, expected with climate change, can impact isoprene
240 emissions (Peñuelas & Staudt 2010) and that its recurrence over years has a strong effect as
241 well (Saunier *et al.* 2017; Genard-Zielinski *et al.* 2018). Our simulations considering this
242 recurrence showed that ozone concentrations were modified through changes in atmospheric
243 isoprene emissions (with increases with a range of 2.7 and $18 \mu\text{g.m}^{-3}$ in the Short Drought
244 scenario and decreases with a range of 1.4 and $10.1 \mu\text{g.m}^{-3}$ in the Long Drought scenario),
245 especially in June and July. Those changes could have an important effect on human health,
246 especially under the Short Drought scenario since our study showed an increase in the number
247 of days when the maxima ozone concentration exceeded the hourly threshold of $180 \mu\text{g.m}^{-3}$.
248 Moreover, the ozone maxima occurred more often in rural areas, indicated by the high ozone
249 concentrations in VAR and AM departments which is in agreement with previous findings (Coll
250 *et al.* 2005; Monks *et al.* 2015). In these rural areas closed to highly anthropized zones, all
251 conditions favoring the net ozone formation are filled, that is high light intensity and
252 temperatures, high BVOC emissions from plants and NO_x presence coming from urban areas
253 (in this study, Marseille-Aix en Provence areas). The Short Drought scenario could also be
254 harmful to plants as well with an increase of days exceeding the threshold of $160 \mu\text{g.m}^{-3}$, known
255 as an acute exposure. At this ozone concentration, plants show several damage such as necrotic
256 spots on leaves (Iriti & Faoro 2008) which often implies a decrease of photosynthesis (Wittig
257 *et al.* 2007). However, in this study, we only presented the daily maxima ozone concentrations.
258 Future research should also take into account the AOT40 (Accumulated Ozone exposure over
259 a Threshold of 40 ppb) which is the sum of hourly O_3 concentrations above a threshold of 40
260 ppb between 8 and 20h. The European objective is to remain below 3000 ppb during the
261 growing season since this is a critical value above which O_3 causes damage to sensitive
262 agriculture and natural plant species (Viaene *et al.* 2016). Besides, we modeled ozone

263 concentrations during the extreme summer period in 2003 and it could be also interesting to use
264 the Short and the Long Drought scenarios to simulate ozone concentrations using a less extreme
265 period in terms of climatic conditions. It has to be noted that the highest ozone concentrations
266 were detected in August whatever the drought scenarios considered, because the conditions
267 were very favorable to ozone formation (see above).

268 Our results also revealed that the duration of drought is an important factor to take into account
269 for isoprene and ozone modeling. However, the impact of a longer recurrent drought (e.g.10
270 years) on isoprene emissions is unknown. On the one hand, plants growth is strongly limited
271 by drought in temperate regions after long periods of stress *in situ* (over 7 years, Kröel-Dulay
272 *et al.* 2015) suggesting that above such period, BVOC emissions could be importantly
273 diminished at the ecosystem scale. On the other hand, recurrent drought could also have
274 progressive and cumulative effects over time, on forested ecosystems dominated by long-lived
275 species (Smith *et al.* 2009). Our previous experimental studies indicated that the response of
276 Downy oak in terms of isoprene emissions is modified by a short and long recurrent drought
277 (Saunier *et al.* 2017; Genard-Zielinski *et al.* 2018). If we assume that isoprene emissions still
278 decrease under longer recurrent drought periods, the ozone concentrations will decrease as well
279 based on our results. However, ozone concentrations can increase or decrease isoprene
280 emissions according to the species sensitivity to ozone and the concentration exposure (see
281 Peñuelas & Staudt 2010 for a review) as also shown by Velikova *et al.* (2005) for Downy oak.
282 Thus, it is highly speculative to assume that isoprene emissions will remain lower after 10 years
283 of recurrent amplified drought (compared to natural drought). Studies about isoprene emission
284 response to long-term recurrent drought could show different results to those considered herein
285 and this issue needs further investigations.

286 Seasonality has a strong impact on isoprene emissions (Goldstein *et al.* 1998). Then, taking into
287 account the seasonality of isoprene emissions could lead to larger changes in ozone
288 concentrations than demonstrated, especially in a context of climate change. In our modelling
289 experiment, only one isoprene emission factor (issued from relative emission changes measured
290 in August for the Short Drought scenario and in July for the Long Drought scenario) was taken
291 into account for the three months of the summer 2003 (June, July and August) to estimate the
292 global amount of isoprene in the atmosphere. After a short drought (1 year), although an overall
293 increase of isoprene emission factor was observed between natural and amplified drought, the
294 significant increases (a factor of 2) were reached only in August and September (Genard-
295 Zielinski *et al.* 2018). After recurrent drought (3 years), there were also seasonal variations.

296 During this 3rd year, decreases were observed in spring (measurement in May which can be
297 affiliated to June in our modelling) and summer (measurements in July) but in different
298 proportions (Saunier *et al.* 2017). These seasonal variations could play a non-negligible role in
299 the global budget of isoprene emitted by plants and, consequently, ozone concentration could
300 also change. This seasonal parametrization of isoprene emission factors could improve ozone
301 projections. Moreover, it has been shown that alternance of drought and rain events can also
302 affect the seasonality of isoprene emissions (Malik 2018; Nogues *et al.* 2018) adding an
303 additional layer of complexity to ozone modeling that should be considered in future works.
304 Surprisingly, isoprene maxima were detected in VAR and VAU areas whereas the highest *Q.*
305 *pubescens* surface is in the AHP department. This is due to the release of isoprene and/or other
306 terpenoids (e.g. monoterpenes) by a large variety of Mediterranean species (Owen *et al.* 2001).
307 For instance, it has been shown that emissions from *Quercus ilex*, one of the main
308 Mediterranean monoterpene-emitters, can also vary when recurrent drought is applied in the
309 field (Lavoit *et al.* 2009, 2011). Thus, in further investigations, it would be worth to include the
310 main emitting-species in the Mediterranean area, especially those emitting monoterpenes since
311 it has been demonstrated that those compounds tend to decrease the ozone formation in presence
312 of isoprene (Chatani *et al.* 2015; Bonn *et al.* 2017).

313

314 **Conclusion**

315 Drought, expected with climate change, can strongly impact isoprene emissions and,
316 consequently, ozone concentrations. Our results showed also that the duration of drought is an
317 important factor to take into account for some modeling exercises. It could be interesting to
318 evaluate the effect of a recurrent drought (e.g 10 years) on isoprene emissions in order to
319 estimate the eventual consequences on ozone levels reached in Mediterranean region after
320 several years of climate change. It could also be interesting to refine our modelling by taking
321 into account the seasonality of isoprene emissions.

322

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334

335 **Author contribution**

336 AS, EO, ACG and CF designed the experiments. AS, DP, AA and ACG conducted the research,
337 collected and analyzed the data. CG, JL and EO obtained the funding to perform the studies.
338 AS, EO, DP, AA, CB, JL, SS, ACG and CF wrote the manuscript.

339

340 **Conflict of interest**

341 AS, EO, DP, AA, CB, JL, SS, ACG and CF declare that they have no conflict of interest.

References

- Beniston, M., Stephenson, D.B., Christensen, O.B., Ferro, C.A.T., Frei, C., Goyette, S., *et al.* (2007). Future extreme events in European climate: an exploration of regional climate model projections. *Clim. Change*, 81, 71–95.
- Bonn, B., Kreuzwieser, J., Sander, F., Yousefpour, R., Baggio, T. & Adewale, O. (2017). The uncertain role of biogenic VOC for boundary-layer ozone concentration: Example investigation of emissions from two forest types with a box model. *Climate*, 5, 78.
- Brzostek, E.R., Dragoni, D., Schmid, H.P., Rahman, A.F., Sims, D., Wayson, C.A., *et al.* (2014). Chronic water stress reduces tree growth and the carbon sink of deciduous hardwood forests. *Glob. Chang. Biol.*, 20, 2531–2539.
- Chatani, S., Matsunaga, S.N. & Nakatsuka, S. (2015). Estimate of biogenic VOC emissions in Japan and their effects on photochemical formation of ambient ozone and secondary organic aerosol. *Atmos. Environ.*, 120, 38–50.
- Coll, I., Pinceloup, S., Perros, P.E., Laverdet, G. & Le Bras, G. (2005). 3D analysis of high ozone production rates observed during the ESCOMPTE campaign. *Atmos. Res.*, 74, 477–505.
- Genard-Zielinski, A.-C., Boissard, C., Ormeño, E., Lathièrre, J., Guenet, S.B., Gauquelin, T., *et al.* (2018). Simulating precipitation decline under a Mediterranean deciduous Oak forest: effects on isoprene seasonal emissions and predictions under climatic scenarios.
- Giorgi, F. & Lionello, P. (2008). Climate change projections for the Mediterranean region. *Glob. Planet. Change*, 63, 90–104.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I. & Geron, C. (2006). Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.*, 6, 3181–3210.
- IPCC. (2013). In: Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change. Cambridge University Press Cambridge, pp. 15–19.
- Iriti, M. & Faoro, F. (2008). Oxidative stress, the paradigm of ozone toxicity in plants and animals. *Water. Air. Soil Pollut.*, 187, 285–301.
- Kesselmeier, J., Ciccioli, P., Kuhn, U., Stefani, P., Biesenthal, T., Rottenberger, S., *et al.* (2002). Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget. *Global Biogeochem. Cycles*, 16, 71–73.
- Lavoit, A. V, Duffet, C., Mouillot, F., Rambal, S., Ratte, J.P., Schnitzler, J.P., *et al.* (2011). Scaling-up leaf monoterpene emissions from a water limited *Quercus ilex* woodland. *Atmos. Environ.*, 45, 2888–2897.
- Lavoit, A. V, Staudt, M., Schnitzler, J.P., Landais, D., Massol, F., Rocheteau, A., *et al.* (2009). Drought reduced monoterpene emissions from the evergreen Mediterranean oak *Quercus ilex*: results from a throughfall displacement experiment. *Biogeosciences*, 6, p-1167.
- Malik, T.G. (2018). Seasonality in emission patterns of isoprene from two dominant tree species of Central India: Implications on terrestrial carbon emission and climate change. *Proc. Int. Acad. Ecol. Environ. Sci.*, 8, 204.
- Monks, P.S., Archibald, A.T., Colette, A., Cooper, O., Coyle, M., Derwent, R., *et al.* (2015). Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer.
- Niinemets, Ü. (2010). Mild versus severe stress and BVOCs: thresholds, priming and consequences. *Trends Plant Sci.*, 15, 145–153.
- Nogues, I., Medori, M., Fortunati, A., Lellei-Kovács, E., Kröel-Dulay, G. & Calfapietra, C.

- (2018). Leaf gas exchange and isoprene emission in poplar in response to long-term experimental night-time warming and summer drought in a forest-steppe ecosystem. *Environ. Exp. Bot.*, 152, 60–67.
- Owen, S.M., Boissard, C. & Hewitt, C.N. (2001). Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species:: VOC speciation and extrapolation to habitat scale. *Atmos. Environ.*, 35, 5393–5409.
- Peñuelas, J. & Staudt, M. (2010). BVOCs and global change. *Trends Plant Sci.*, 15, 133–144.
- Polade, S.D., Pierce, D.W., Cayan, D.R., Gershunov, A. & Dettinger, M.D. (2014). The key role of dry days in changing regional climate and precipitation regimes. *Sci. Rep.*, 4, 4364.
- Saunier, A., Ormeño, E., Boissard, C., Wortham, H., Temime-Roussel, B., Lecareux, C., *et al.* (2017). Effect of mid-term drought on *Quercus pubescens* BVOCs' emission seasonality and their dependency on light and/or temperature. *Atmos. Chem. Phys.*, 17, 7555–7566.
- Saunier, A., Ormeño, E., Havaux, M., Wortham, H., Ksas, B., Temime-Roussel, B., *et al.* (2018). Resistance of native oak to recurrent drought conditions simulating predicted climatic changes in the Mediterranean region. *Plant. Cell Environ.*
- Sharkey, T.D., Loreto, F. & Delwiche, C.F. (1991). High carbon dioxide and sun/shade effects on isoprene emission from oak and aspen tree leaves. *Plant. Cell Environ.*, 14, 333–338.
- Vautard, R., Honore, C., Beekmann, M. & Rouil, L. (2005). Simulation of ozone during the August 2003 heat wave and emission control scenarios. *Atmos. Environ.*, 39, 2957–2967.
- Velikova, V., Várkonyi, Z., Szabó, M., Maslenkova, L., Nogues, I., Kovács, L., *et al.* (2011). Increased thermostability of thylakoid membranes in isoprene-emitting leaves probed with three biophysical techniques. *Plant Physiol.*, 157, 905–916.
- Velikova, V.B. (2008). Isoprene as a tool for plant protection against abiotic stresses. *J. Plant Interact.*, 3, 1–15.
- Viaene, P., Deutsch, F., Mensink, C., Vandermeiren, K., Vancraeynest, L., Vanpoucke, C., *et al.* (2016). Assessment of Damage to Vegetation in Belgium Based on an Ozone Flux Model Approach. In: *Air Pollution Modeling and its Application XXIV*. Springer, pp. 147–153.
- Wittig, V.E., Ainsworth, E.A. & Long, S.P. (2007). To what extent do current and projected increases in surface ozone affect photosynthesis and stomatal conductance of trees? A meta - analytic review of the last 3 decades of experiments. *Plant. Cell Environ.*, 30, 1150–1162.

Table 1: Number of days that showed a daily maximum of hourly averages in terms of ozone concentrations above **A)** the threshold of $180 \mu\text{g.m}^{-3}$ according to the EU recommendation and **B)** the threshold of $160 \mu\text{g.m}^{-3}$, an acute ozone exposure for plants throughout the modelling period (June, July and August) on two urban (Aix-en-Provence and Marseille city center) and two rural sites (Observatoire de Haute Provence or OHP and Ste Beaume) according to the short and long-drought scenarios.

A	Sampling sites	Numbers of days		
		REF	Short	Long
Urban sites	Marseille city center	4	5	4
	Aix-en-Provence city center	9	13	7
Rural sites	OHP	9	13	8
	Ste Beaume	11	13	10
B	Sampling sites	Numbers of days		
		REF	Short	Long
Urban sites	Marseille city center	10	11	10
	Aix-en-Provence city center	19	22	18
Rural sites	OHP	28	35	26
	Ste Beaume	22	30	20

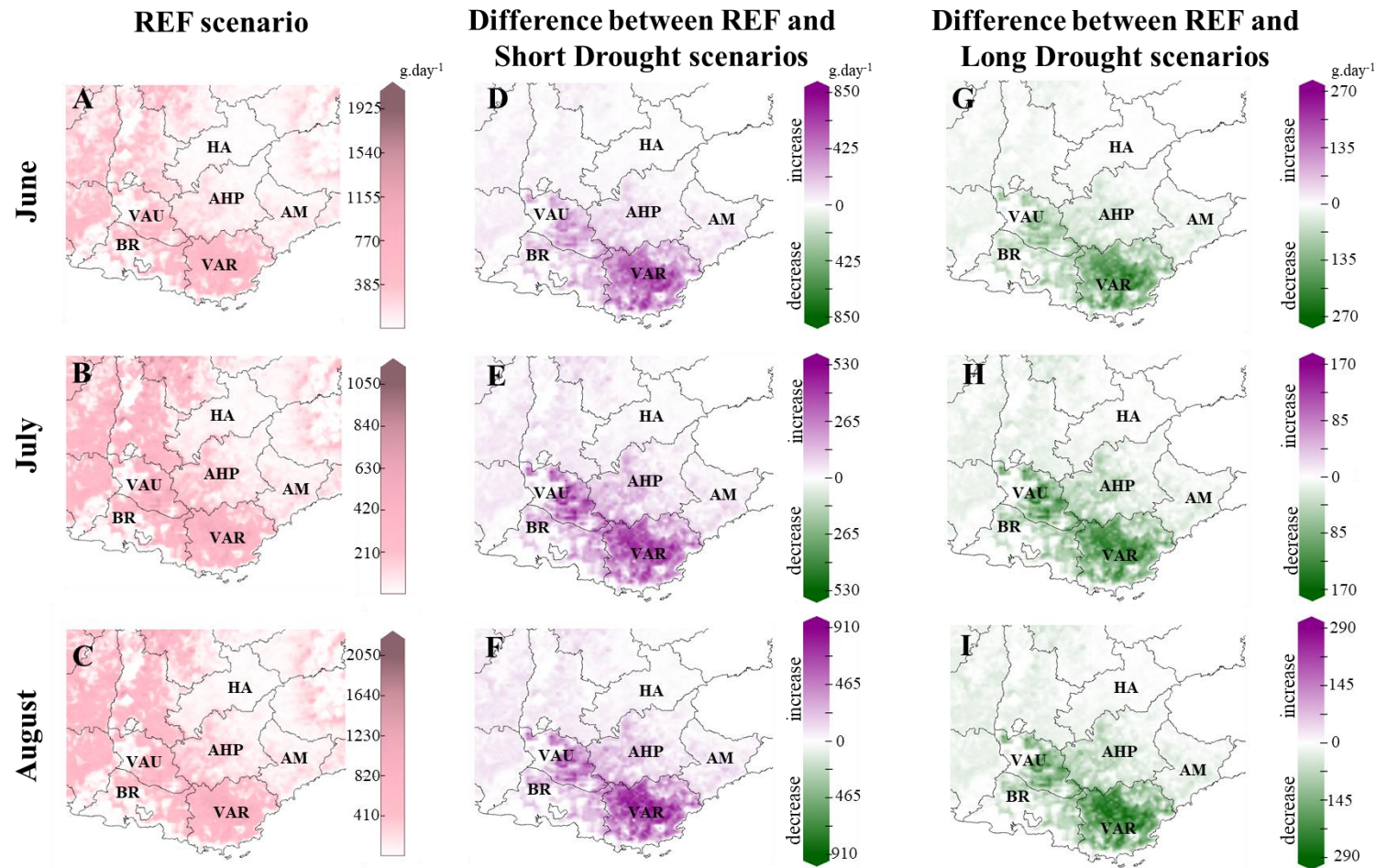


Figure 1: Daily maxima of hourly averages simulated for isoprene emissions ($\text{g}\cdot\text{day}^{-1}$, A - I) through MEGAN model (Model of Emissions of Gases and Aerosols from Nature) over the PACA region (Provence-Alpes-Côte d'Azur) according to climatic conditions over the PACA region model (June : 15th, July : 15th and August : 13th) with the REF scenario (A, B and C), differences between the Short Drought and the REF scenarios (D, E and F) and differences between the Long Drought and the REF scenarios (G, H and I).

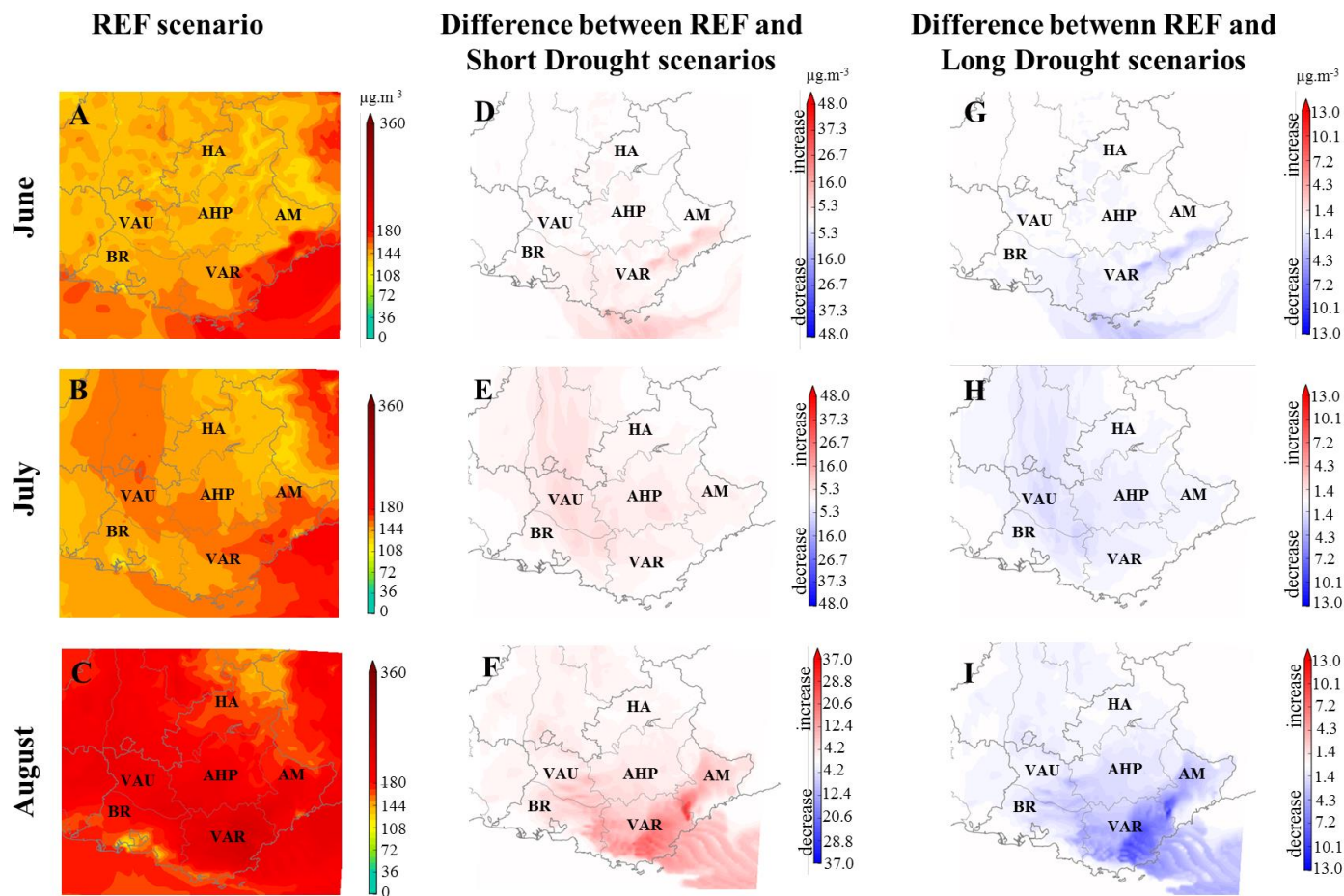


Figure 2: Daily maxima of hourly averages simulated for ozone levels ($\mu\text{g.m}^{-3}$, A - I) through CHIMERE model over the PACA region (Provence-Alpes-Côte d’Azur) according to climatic conditions over the region model (June : 15th, July : 15th and August : 13th) with the REF scenario (A, B and C), differences between the Short Drought and the REF scenarios (D, E and F) and differences between the Long Drought and the REF scenarios (G, H and I).

