Isoprene contribution to ozone production under climate change conditions in the French Mediterranean area

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

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Abstract

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

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

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

Length of the manuscript: 3374 words

Introduction

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

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

In the Mediterranean area, Downy oak (*Quercus pubescens* Willd.) represents the major source of isoprene emissions (Simon *et al.* 2005; Keenan *et al.* 2009) and is widespread in the Northern part of the Mediterranean basin (Quézel & Médail 2003), occupying 2 million ha (personal communication from T. Gauquelin). Hence, extrapolating results obtained in a Downy oak forest, at the O_3HP (Observatoire de Haute Provence) site regarding the impact of short and long-term drought on isoprene emissions (Saunier *et al.* 2017; Genard-Zielinski *et al.* 2018) could give a key insight on the potential future evolution of isoprene emissions and, consequently, on ozone concentrations in the Mediterranean region. At this site, a 33-35% rainfall exclusion experiment has been installed in a natural forest to mimic the projected decrease in rainfall according to the most severe scenario of climate change (RCP 8.5) in terms of precipitation reduction in the Mediterranean region at the end of the century. Measurements on isoprene emissions were performed after 1 and 3 years of amplified drought. An increase in isoprene emission factor by 83% (Genard-Zielinski *et al.* 2018) and a 26 % decrease was observed during the summer period compared with natural drought (Saunier *et al.* 2017), for 1 and 3 years of drought, respectively. These relative isoprene emission changes (increase and decrease compared with natural drought) were, then, used to model ozone formation through the regional chemistry-transport model CHIMERE to assess the effect of short and long-term drought on this pollutant through isoprene emissions.

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

Material and methods

Model description

The CHIMERE model (Schmidt *et al.* 2001; Menut *et al.* 2013) is a three-dimensional chemistry-transport model (CTM), commonly used to study air pollution (Monteiro *et al.* 2005; Menut *et al.* 2012). It is notably part of the French air pollution forecast system: Prev'air (Rouil *et al.* 2009). Source code as well as documentation are available on the website http://www.lmd.polytechnique.fr/chimere/ (v2008 version). The CHIMERE model considers the emission fluxes for 15 compounds (NO, NO_2, HONO, SO_2, CO, ethane, *n*-butane, ethene, propene, isoprene, α-pinene, *o*-xylene, formaldehyde,acetaldehyde and methyl vinyl ketone).

The modeling set-up is applied on the Provence Alpes Cote d'Azur region (PACA-Regions Sud) for the summer 2003 (between 1st June and 31st August), an exceptional heatwave period whose frequency is expected to increase in the future (Vautard *et al.* 2005). Three imbricated domains were used to perform the modelling experiment: the largest domain, called GFR27 afterward, has a resolution of 27 km. The intermediate domain, called FRSE9 afterward, has a resolution of 9km and the smallest domain has a resolution of 3km (Fig. S1 in supplementary files). The PACA region is composed by several departments whose surfaces of Downy oak vary (Fig. S2 in supplementary files): Alpes de Haute-Provence (AHP, 70 000 ha, 31.9 %), Var (VAR, 69 000 ha, 31.5 %), Vaucluse (VAU, 38 000 ha, 17.4 %), Alpes Maritimes (AM, 22 500 ha, 10.3 %), Hautes-Alpes (HA, 12 500 ha, 5.7 %) and Bouches-du-Rhône (BR, 7000 ha, 3.2 %). The emissions of anthropogenic compounds come from the EMEP database (2007) for the first two domains (GFR27 and FRSE9) and from the official network in charge of pollution survey and forecast in the PACA region: the AtmoSud database for the smallest domain (PACA).

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

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

Experimental protocol

In this study, CHIMERE model was used with modifications of the MEGAN model to integrate the relative change of Downy oak isoprene emissions factors highlighted in two field studies at O_3HP during short and long term drought simulations. Emissions factors are the emission rates standardized at 30°C and 1000µmol.m^{-2}.s^{-1} of photosynthetic active radiation (PAR). These data are generally used in modelling work (Guenther *et al.* 2006).

Relative changes were observed in summer 2012 (August) and summer 2014 (July) at the O_3HP site (https://o3hp.obs-hp.fr/index.php/en/). This field site is equipped with an automated monitored roof deployed during chosen rain events and set up over part of the O_3HP forest. Thus, this device allowed to reduce natural rain of 33-35% which is very close to climatic model expectations using the worst scenario of climate change (Giorgi & Lionello 2008; IPCC 2013) to evaluate the effect of drought expected with climate change on isoprene emissions. Rain exclusion started in May 2012 and was continuously applied every year, during the growth period (from April to November). Data on cumulative precipitation showed that 35 % of rain was excluded in 2012, 33 % in 2013 and 35.5 % in 2014 (Saunier *et al.* 2018). In 2012, the first year of drought, an 83 % increase of the isoprene emission factors was observed (Genard-Zielinski *et al.* 2018) under rain restriction compared with natural drought, whereas in 2014, the third year of drought, a decrease by 26 % was observed (Saunier *et al.* 2017).

Scenarios

According to these experimental results, three idealised drought scenarios were considered in this work. The REF scenario was the reference scenario which takes into account the current isoprene emission factor of Downy oak equal to 67.78 µgC.g_{DM}^{-1}.h^{-1} in MEGAN to estimate isoprene emissions.

The Short Drought scenario corresponded to a 83% increase of the reference isoprene emission factor, that is, an emission factor equal to 123.95 µgC.g_{DM}^{-1}.h^{-1}. The Long Drought scenario was associated to a 26% decrease of the reference isoprene emission factor, and thus, the emission factor used in this scenario was 49.96 µgC.g_{DM}^{-1}.h^{-1}.

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

Results

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

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

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

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

Discussion

It is well known that increasing droughts, expected with climate change, can impact isoprene emissions (Peñuelas & Staudt 2010) and that its recurrence over years has a strong effect as well (Saunier *et al.* 2017; Genard-Zielinski *et al.* 2018). Our simulations considering this recurrence showed that ozone concentrations were modified through changes in atmospheric isoprene emissions (with increases with a range of 2.7 and 18 µg.m^{-3} in the Short Drought scenario and decreases with a range of 1.4 and 10.1 µg.m^{-3} in the Long Drought scenario), especially in June and July. Those changes could have an important effect on human health, especially under the Short Drought scenario since our study showed an increase in the number of days when the maxima ozone concentration exceeded the hourly threshold of 180 µg.m^{-3}. Moreover, the ozone maxima occurred more often in rural areas, indicated by the high ozone concentrations in VAR and AM departments which is in agreement with previous findings (Coll *et al.* 2005; Monks *et al.* 2015). In these rural areas closed to highly anthropized zones, all conditions favoring the net ozone formation are filled, that is high light intensity and temperatures, high BVOC emissions from plants and NO_x presence coming from urban areas (in this study, Marseille-Aix en Provence areas). The Short Drought scenario could also be harmful to plants as well with an increase of days exceeding the threshold of 160 µg.m^{-3}, known as an acute exposure. At this ozone concentration, plants show several damage such as necrotic spots on leaves (Iriti & Faoro 2008) which often implies a decrease of photosynthesis (Wittig *et al.* 2007). However, in this study, we only presented the daily maxima ozone concentrations. Future research should also take into account the AOT40 (Accumulated Ozone exposure over a Threshold of 40 ppb) which is the sum of hourly O_3 concentrations above a threshold of 40 ppb between 8 and 20h. The European objective is to remain below 3000 ppb during the growing season since this is a critical value above which O_3 causes damage to sensitive agriculture and natural plant species (Viaene *et al.* 2016). Besides, we modeled ozone concentrations during the extreme summer period in 2003 and it could be also interesting to use the Short and the Long Drought scenarios to simulate ozone concentrations using a less extreme period in terms of climatic conditions. It has to be noted that the highest ozone concentrations were detected in August whatever the drought scenarios considered, because the conditions were very favorable to ozone formation (see above).

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

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

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

Conclusion

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

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Author contribution

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

Conflict of interest

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

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Table 1: Number of days that showed a daily maximum of hourly averages in terms of ozone concentrations above **A**) the threshold of 180 µg.m^{-3} according to the EU recommendation and **B**) the threshold of 160 µg.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

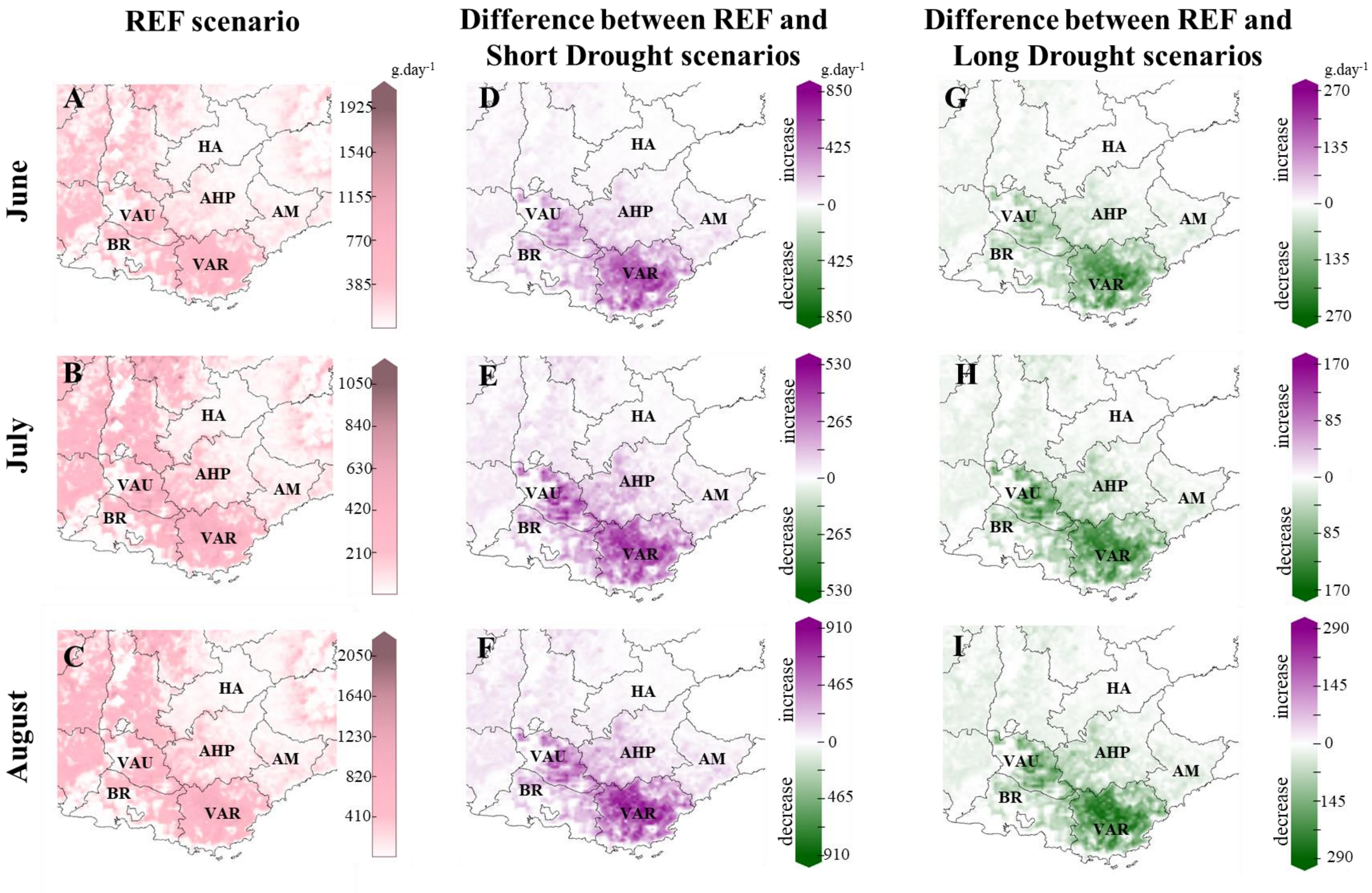

Figure 1: Daily maxima of hourly averages simulated for isoprene emissions (g.day^{-1}, **A - I**) through MEGAN model (Model of Emissions of Gases and Aerosols from Nature) over the PACA region (Provence-Alpes-Côte d'Azur) according to climatic conditions over the PACA region model (June : 15th, July : 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).

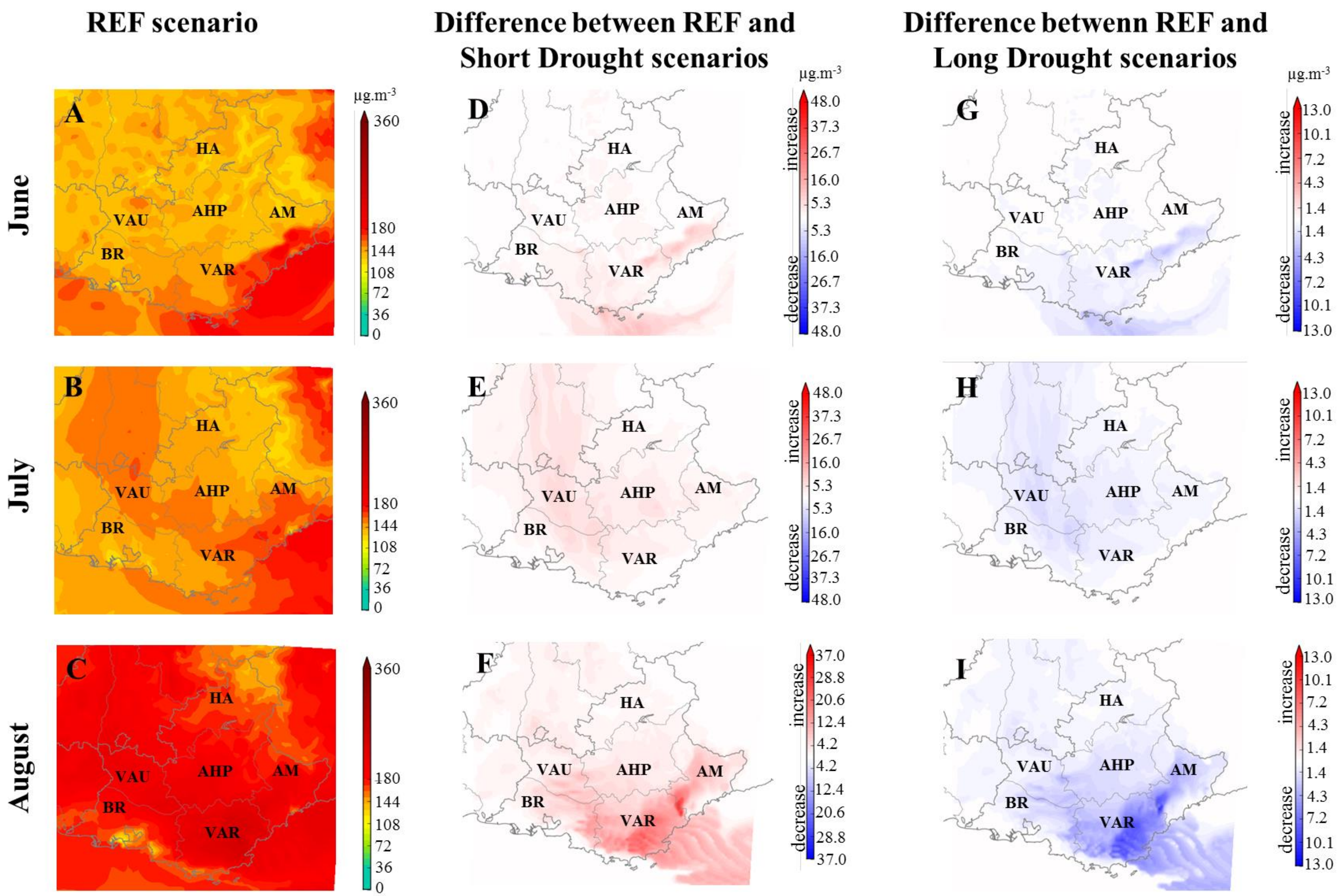

Figure 2: Daily maxima of hourly averages simulated for ozone levels (µg.m^{-3}, **A - I**) through CHIMERE model over the PACA region (Provence-Alpes-Côte d'Azur) according to climatic conditions over the region model (June : 15th, July : 15th and August : 13th) with the REF scenario (A, B and C), differences 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).