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Improvement of local ozone phytotoxicity modelling for autochthonous grape cultivars

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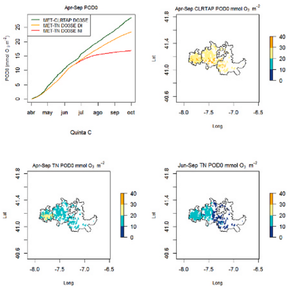
HIGHLIGHTS

- DO3SE parametrization for key autochthonous grape cultivars was developed.
- The grapevine stomatal flux gradient in the region was successfully replicated.
- Adjusted DO3SE PODs were lower and with different spatial extent than CLRTAP ones.
- Under irrigated conditions, POD values increase being closer to default CLRTAP PODs.
- Air quality management must also be considered for sustainable grape production.

GRAPHICAL ABSTRACT



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ABSTRACT

The grapevine is a key crop for Mediterranean environments and is both sensitive to climate warming and air pollutants, of which ozone is the most damaging to crop yield and quality. Ambient ozone effects on the grapevine have been noticed since the late fifties but risk assessments are still impaired by the lack of information concerning differences in cultivar sensitivity, and adaptation capacity to environmental factors including drought conditions. This study develops a specific parametrization for autochthonous grape cultivars within a leaf-level stomatal flux model, the DO3SE model, coupled with a meteorological and atmospheric chemical transport modelling system, the WRF-CHIMERE, by using a renowned wine producing area, the Douro wine region of Portugal, as case study. The DO3SE model parametrization introduced in this study included phenology, photosynthetic active radiation, air temperature, air vapour pressure deficit, and leaf water potential as a proxy of soil water content. The modelling experiments, which included simulations with the current default Convention on Long-Range Transboundary Air Pollution DO3SE parametrization and with the proposed parametrization, covered a reference grapevine growing season (from April to September 2017), during which a measuring campaign was carried out. Simulation results show that the proposed parametrization succeeded to replicate the observed grapevine leaf-level stomatal flux gradient in the region. Both field and modified DO3SE model values indicate that considerable areas in the Douro wine region of Portugal can exceed critical phytotoxic ozone dose (POD) values, although with a lower and different spatial extent when compared to the default DO3SE parametrization for the grapevine. However, under irrigated conditions, the POD values increase, and the

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values are close to those obtained with the default parametrization. Overall, the research results indicate that air quality management, in particular the reduction of ozone levels in the ambient air, must also be considered to define sustainable grape and wine production strategies in the context of climate and wine production management change.

1. Introduction

Surface ozone (O_3) is considered to be by far the most phytotoxic air pollutant worldwide at present (Krupa et al., 2000; Sicard et al., 2017; The Royal Society, 2008). Surface O_3 has its main entrance through plant stomata causing foliar and tissue injury, impairing photosynthesis, and reducing growth, yield and quality on many agronomic and horticultural crops (Booker et al., 2009; Cho et al., 2011; Hayes et al., 2007). It is produced by a series of chemical reactions involving primary pollutants such as nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOC) and is favoured by high light intensity and temperature conditions, such as those found in summer days (Marshall et al., 1997; Monks et al., 2015; The Royal Society, 2008). It is expected that background levels of surface O_3 will continue to increase globally in relation to the increasing industrialization of developing countries and intercontinental transport, despite the fact that emission reduction polices have caused a reduction of O_3 peak levels, levelling off or even declining long-term trends in Europe, North America and Japan (Oltmans et al., 2013; Paoletti et al., 2014; Sicard et al., 2013). Hence, it has been estimated that by 2050 global staple crop production of wheat, rice, maize and soybean could be reduced in more than 10% by global warming alone, but those losses could even reach 40% for sensitive crops in the more polluted areas (Burney and Ramanathan, 2014; Tai et al., 2014).

Perennial crops can also show a high vulnerability to ambient ozone. Based on historical records, Hong et al. (2020) estimated a reduction of yield from 2% (strawberries) to 22% (table grapes) and economic losses of approximately US $ 1 billion per year in areas with high ambient O_3 levels in California, indicating a large opportunity to improve crop yields through pollution mitigation. The grapevine is the crop where the phytotoxic effects of ambient O_3 were first noticed (Richards et al., 1959). Although it is not a food security crop, such as wheat, rice, soybean, maize or potato, it has immense cultural, economic and ecological importance for Mediterranean areas, besides being the fruit crop with the largest acreage and highest economic value globally (Ponti et al., 2018). Wide regions of the world between latitudes 30° and 50°N where the grapevine has been traditionally cultivated are exposed to ambient O_3 levels that can affect both yield and quality, with potential yield (i.e. grape fresh weight) reductions in the range of 20–31% and reductions in quality (i.e. polyphenols) in the range 15–23% (Blanco-Ward et al., 2021a).

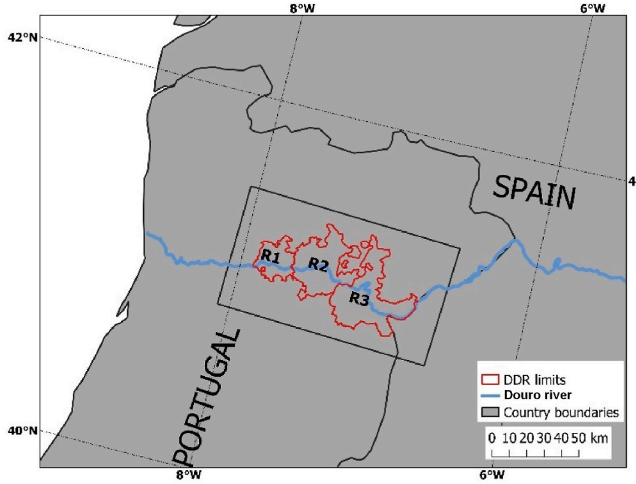


Fig. 1. The Douro Demarcated Region (DDR) with subregions “Baixo Corgo” (R1), “Cima Corgo” (R2) and “Douro Superior” (R3).

Risk assessment studies concerning ambient O_3 for a crop such as the grapevine face however important limitations. A first issue is that the cumulative exposure (level-I) approach has been extensively criticized, because it does not reflect the actual dose or flux of O_3 entering the plant (Massman, 2004; Mauzerall and Wang, 2001; Musselman et al., 2006; Paoletti and Manning, 2007). To overcome these limitations, a flux-based, or level-II approach, was developed under the Convention on Long-range Transboundary Air Pollution (CLRTAP) (Mills et al., 2011). This approach has a stronger biological basis since it considers a Phytotoxic Ozone Dose (POD) by taking into account the O_3 stomatal uptake, which can be understood as the amount of O_3 molecules that penetrate the leaf tissue through the stomata as a function of ambient O_3 concentration and several other critical environmental parameters, such as temperature, water vapour pressure, light, soil water potential and plant growth (phenological) stage (Emberson et al., 2000a, 2000b). Most commonly, the parametrization of those functions is performed by a semiempirical Jarvis type process model, the DO3SE model, as described and currently used by the CLRTAP (CLRTAP, 2017a). Even though the DO3SE model can be used to give broad estimates at the continental European scale (e.g. Anav et al., 2016), it does not account for the existing varietal and niche adaptation at the regional scale for a crop such as the grapevine. Furthermore, even though the standard CLRTAP DO3SE model also considers the inclusion of a leaf water or soil water potential factor, these are not frequently incorporated due to the lack of such measured data or reliable soil moisture models at the global scale (Anav et al., 2018; De Marco et al., 2016). Thus, although the use of stomatal flux process type models in combination with regional or downscaled results from climate or atmospheric chemical transport models is already reachable for phytotoxic O_3 risk assessment for the grapevine at the continental (CLRTAP, 2017b) or even at regional scale (Blanco-Ward et al., 2021b), there is still a lack of research concerning the specific parametrization for autochthonous cultivars also including the role of the water balance in the soil. The inclusion of a soil related factor is a key issue for Mediterranean crops such as the grapevine where there is also the need to define irrigation policies on a sustainable basis to maintain yield and quality in the context of climate change (Bernardo et al., 2018; Fraga et al., 2018).

The main purpose of this work is to develop a phytotoxic ozone risk assessment including specific parametrization for autochthonous grapevine cultivars and the soil water component, and to assess to what extent the results differ from those produced without refining the methodology. For this purpose, the leaf-level stomatal flux model, the DO3SE model, was coupled with a meteorological and atmospheric chemical transport modelling system, the WRF-CHIMERE, to simulate ozone phytotoxicity of grapevines from the Demarcated Douro Region using data from a specific field campaign. The simulation and the measuring campaign covered a reference grapevine growing season.

2. Study area

The Portuguese Douro Demarcated Region (DDR) is the oldest wine region in Portugal and is famous for its Port wine (Fraga et al., 2017). It integrates areas of both banks of the Douro River from the border with Spain until halfway of its course. The Douro valley stretches along 90 km in the west-east direction and along 50 km in the north-south direction (Fig. 1).

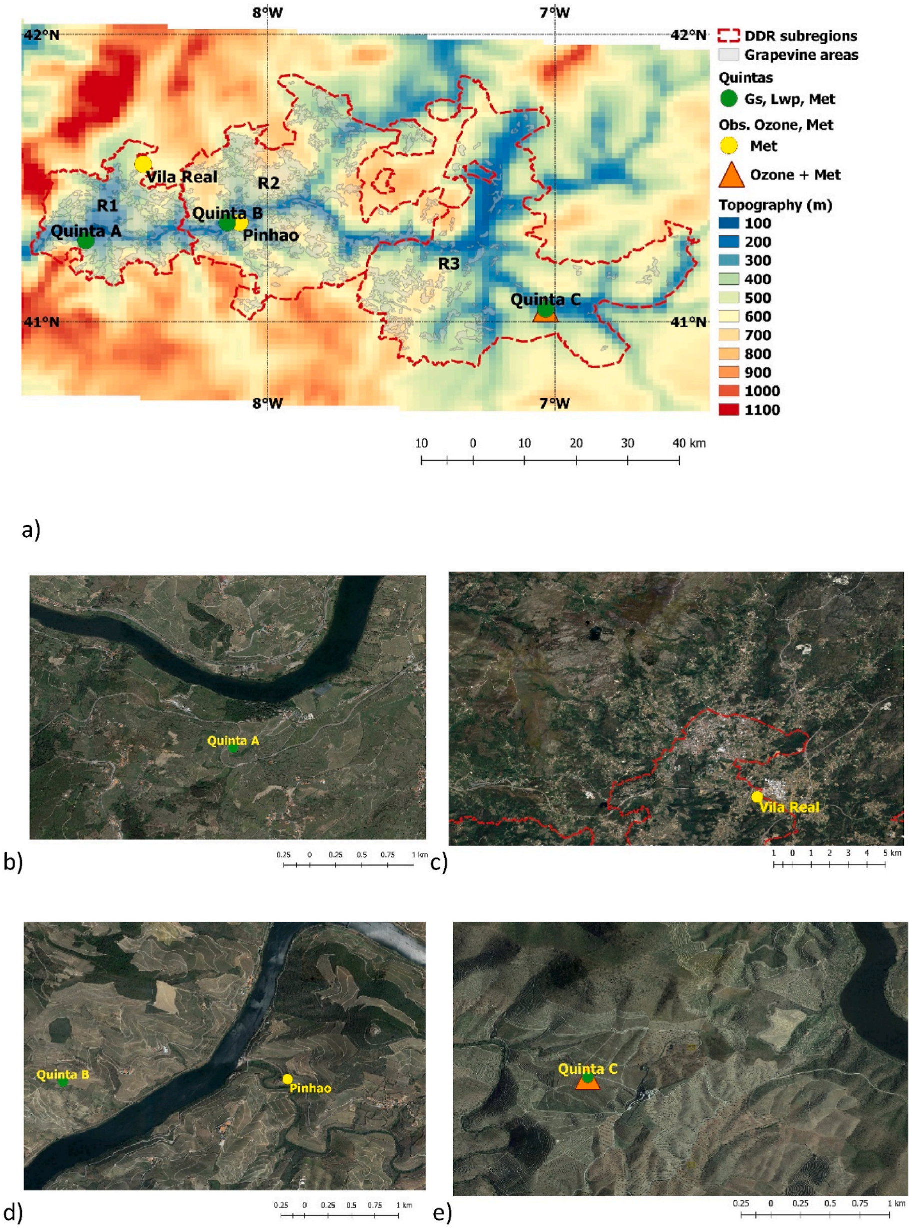


Fig. 2. a) Subregions "Baixo Corgo" (R1), "Cima Corgo" (R2) and "Douro Superior" (R3), along vineyard areas and observational sites. b, c, d, e) Details on field measurement locations of ambient ozone, meteorology and grapevine physiology.

The westernmost region is located 70 km away from the Atlantic Ocean. The landscape is characterized by mountainous terrain, rising above the Douro river and its tributaries, with moderate to steep slopes and different expositions. The average elevation in the region is 443 m, but varies from about 40 m to a maximum of more than 1400 m. The Region covers about 250 thousand hectares with vineyard areas representing 43,480 ha, 17.4% of the total area. It is divided into three subregions: Baixo Corgo with the smaller area (45,000 ha), Cima Corgo, with intermediate extension (95,000 ha), and Douro Superior with the greatest extension (110,000 ha). The vineyard area for these subregions is 13368, 20270 and 9842 ha, respectively (IVDP, 2017). According to the last published reports, the wine produced in the DDR represents more than one fifth of all wine produced in Portugal (IVV, 2017, 2018). The *Touriga Nacional*, *Touriga Franca* and *Tinta Roriz* (*Tempranillo*) grapevine cultivars are the most common varieties in the DDR, but many other regional varieties are also present in the region (Corte-Real, 2014; Santos et al., 2013).

The DDR presents a warm Mediterranean climate with hot summers (Köppen Csa) (Andrade et al., 2021; Climaco et al., 2012). The region is protected from the humid and cold winds of the Atlantic Ocean by two mountain ranges, Marão and Montemuro, which are located on its western border. The temperature increases and precipitation decreases from west to east. The westernmost sub-region of the Douro Valley (Baixo Corgo) is closer to the Atlantic Ocean and therefore more affected by the moist sea winds. The easternmost sub-regions are further away from the Atlantic Ocean, thus having a more continental climate (Corte-Real, 2014; Corte-Real et al., 2016). Low precipitation values, together with high temperatures and high radiation exposure, give rise to intense water and thermal stresses, particularly in the Cima Corgo and Douro Superior subregions (Jones and Alves, 2012). Particularly, the 2017 April to September grape growing season, when the field campaign was developed, was categorized as extremely hot and dry in comparison with 1971–2000 climatological observations (ADVID., 2017).

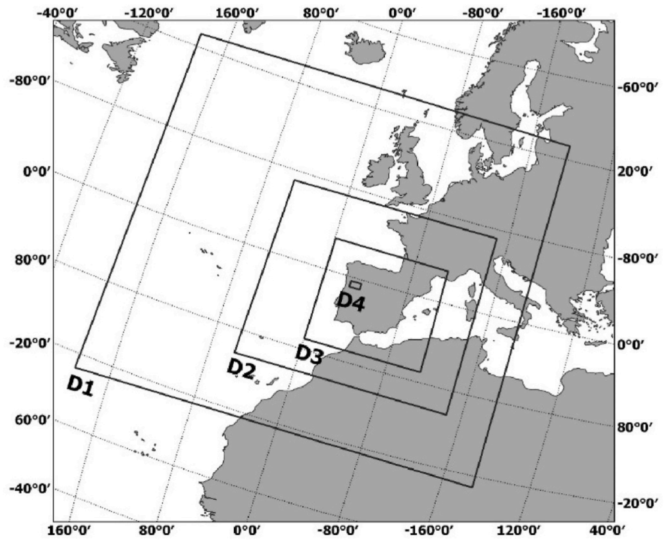


Fig. 3. Nested modelling domains implemented for the WRF-CHIMERE simulations.

3. Methodology

Based on data from a field campaign, local parameterizations were included in the model setup and were evaluated by comparing modelling results with measured data for grapevine phenological development, stomatal conductance and estimated POD. This section describes the field campaign, the modelling system and the POD standards to assess O_3 phytotoxic risk for the grapevine in the study area.

3.1. Field campaign

Data for ozone phytotoxic risk assessment were gathered at three main sites (Fig. 2), named Quinta A (Baixo Corgo), Quinta B (Cima Corgo) and Quinta C (Douro Superior), during the grapevine growing season from April to September 2017. The April to September growing season length is commonly taken as a valid reference grapevine growing season in the Northern Hemisphere (Tonietto and Carbonneau, 2004) and is also used concerning O_3 risk assessment for perennial crops and deciduous trees (Mills et al., 2018).

Furthermore, meteorological data were obtained from two meteorological stations (Pinhão and Vila Real) from the Portuguese Institute for the Sea and the Atmosphere, and three meteorological stations located at the selected places (Quinta B and Quinta C) or nearby (Cambres from the Association for the Development of Viticulture in the Douro Region, ADVID, which is located close to Quinta A) (Fig. 2). Cambres (136 m), Quinta B (174 m), Pinhão (130 m) and Quinta C (228 m) are located in the Douro valley under Mediterranean climate conditions, whereas Vila Real (561 m) represents plateau conditions where there is a stronger sub-Atlantic oceanic influence (Ribeiro, 2000).

3.1.1. Grapevine phenological and physiological data

The phenological development of two grapevine cultivars characteristic of the DDR, *Touriga Franca* (TF) and *Touriga Nacional* (TN), was monitored once per week across Quinta A, Quinta B and Quinta C according to the *Biologische Bundesanstalt, Bundessortenamt und CHemische Industrie* (BBCH) phenological scale from early March to the beginning of October 2017. Six representative plants per cultivar were chosen for Quinta A and Quinta C and three for Quinta B.

Physiological measurements, namely predawn leaf water potential (Ψd) and stomatal conductance (gs), were also measured at the three sites on two dates, July 6th and August 1st, 2017, which were representative of the onset of the ripening and ripening phenological stages, respectively. Predawn leaf water potential was monitored using a Scholander pressure chamber (Model 1000, PMS Instrument Company, Albany, USA) and measurements were performed in four fully expanded leaves of four representative plants per variety and location (16 per treatment). Stomatal conductance was measured using a portable infrared analyzer (IRGA-LCA-4, Analytical Development Co., Hoddesdon, England). Measurements were performed in eight fully expanded leaves per variety and location at 11- and 15-h solar time. For Quinta C, measurements on plants subjected to deficit irrigation equivalent to the 25% daily reference evapotranspiration (ET_0) of the site were also performed.

3.1.2. Meteorological and ambient ozone observations

Daily data on temperature, relative humidity, incoming solar radiation and wind speed from Vila Real, Pinhão and Quinta C meteorological stations were used to estimate reference ET_0 according to the FAO Penman-Monteith method (Allen et al., 1998), whereas the temperature records from Cambres, Quinta B and Quinta C were used to derive grapevine phenological thermal requirements. Moreover, an observational site for ambient O_3 was also available at Quinta C (Fig. 2), which was made operative for this study, from April to September 2017.

3.2. Modelling

3.2.1. Modelling system

The chemical transport model CHIMERE 2016a (Mailler et al., 2016; Menut et al., 2013) was used to estimate ground-level O_3 exposure while the dose of O_3 entering the plant was calculated based on the dry deposition of O_3 for stomatal exchange (DO3SE) model of the European Monitoring and Evaluation Programme for long-range transmission of air pollutants (EMEP) (Emberson et al., 2000b), updated according to the last parametrizations available for grapevine (CLRTAP, 2017b; Emberson et al., 2005). CHIMERE simulations were implemented for four nested domains with increasing horizontal resolution, namely 81 (D1), 27 (D2), 9 (D3), and 1 km (D4) (Fig. 3).

The initial and boundary conditions for the first domain where those from the LMDz-INCA model for gases and non-dust aerosols and from the GOCART model for dust. Anthropogenic atmospheric emission data from the emission database of EMEP were pre-processed for the simulation domains, as well as biogenic emissions, which were computed using the global Model of Emissions of Gases and Aerosols from Nature (MEGAN). Land use types needed by CHIMERE to calculate biogenic emissions, as well as other processes such as deposition, were derived from the U.S. Geological Survey (USGS) 1 km resolution land cover database. The CHIMERE chemical mechanism is based on the MELCHIOR scheme (Mailler et al., 2016). Hourly ozone results were simulated for the period between April 1st to September 30th, 2017, using as meteorological inputs values calculated by the Weather Research and Forecasting (WRF) 3.5 model with the same set of physical parametrizations as in Marta-Almeida et al. (2016). Ozone and meteorological simulations were successfully validated against measured data as described by Blanco-Ward et al. (2021b).

3.2.2. DO3SE parametrization for a representative grapevine cultivar in the DDR

The DO3SE model was parametrized both for a generic grapevine and for the *Touriga Nacional* (TN) as a representative Portuguese grapevine cultivar present in the DDR. This model makes use of a semi-empirical multiplicative function and includes the modifying influence on leaf-level stomatal conductance of the phenological stage (*fphen*) and four environmental variables: photosynthetic active radiation (*flight*), temperature (*ftemp*), vapour pressure deficit (fvpd) and plant available water (*fpaw*), which can be related to soil water potential (*fswp*) or leaf water potential (*flwp*), as is the case in this study (CLRTAP, 2017a):

$$gs = gmax * fphen * flight * \max\left\{\mathrm{fmin}, (ftemp * fvpd * flwp)\right\} \tag{1}$$

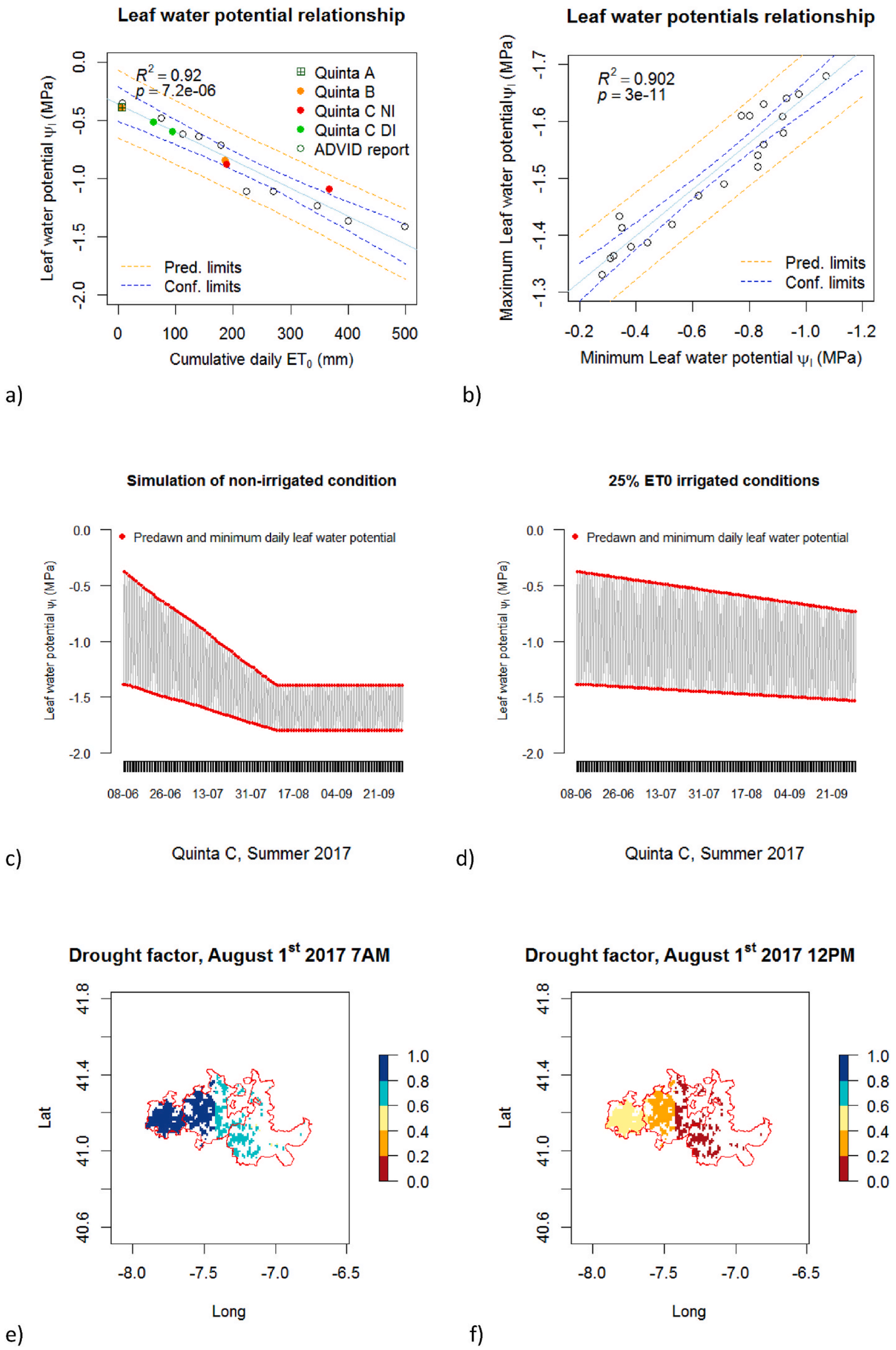


Fig. 4. a) Relationship between cumulative daily ET_0 and grapevine leaf water potential; b) Relationship between predawn and midday leaf water potential; c) Simulated hourly evolution of leaf water potential at Quinta C for unirrigated conditions during the 2017 summer drought season; d) Simulated hourly evolution of leaf water potential at Quinta C for 25% ET_0 deficit-irrigated conditions through the 2017 drought season; e) and f) Examples of hourly drought DDR factor maps derived for August 1st, 2017 at 7AM and 12 p.m. respectively.

Table 1
Comparison between phenological dates (day of year, *DOY*) observed at the three field sites and simulated by coupling WRF daily temperatures with phenological modelling.

	Quinta A		Quinta B		Quinta C	
	Field	Simulations	Field	Simulations	Field	Simulations
Budburst	81	82	81	88	88	95
Flowering	123	135	123	136	123	140
Grape colour onset	186	194	186	193	186	193
Maturity	235	232	235	230	235	229

f_{min} is the relative minimum stomatal conductance that occurs during daylight hours. The parameters *fphen*, *flight*, *ftemp*, *fvpd*, *flwp* and f_{min} range between 0 and 1, as a proportion of the species specific maximum stomatal conductance (g_{max}), expressed as mmol O_3 m^{-2} PLA s^{-1}, where the projected leaf area, PLA, is the total area of sunlit leaves. A top-leaf stomatal flux (*Fst*) can then be estimated from (CLRTAP, 2017a):

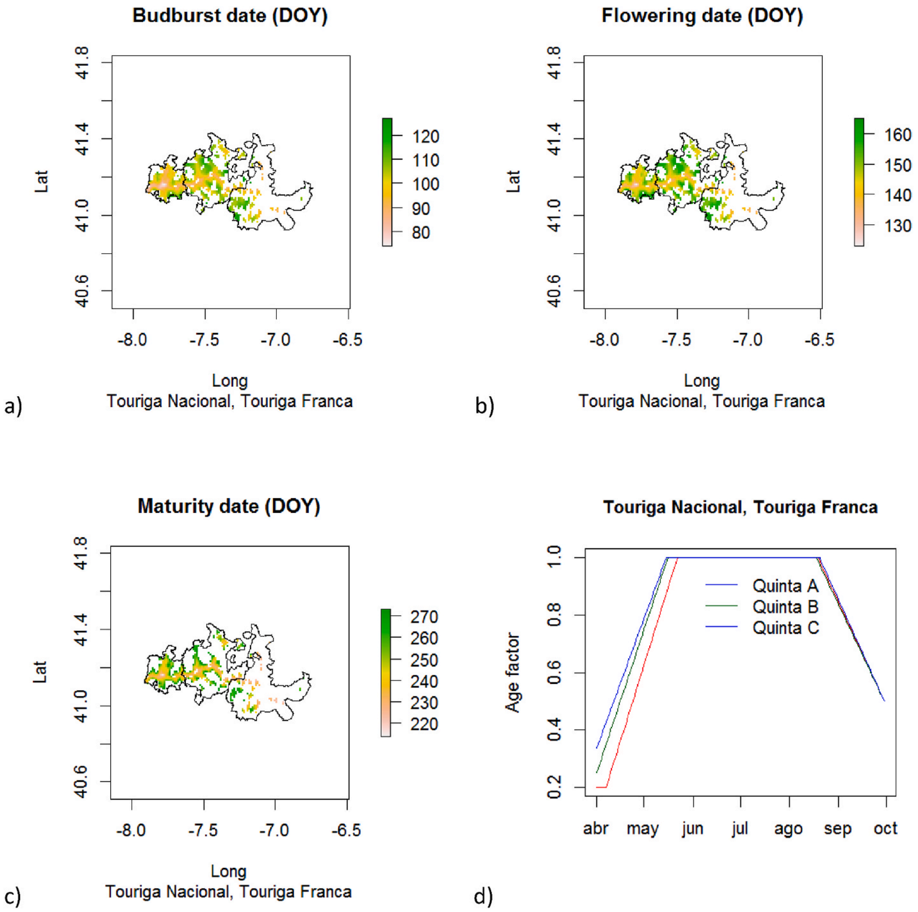


Fig. 5. Spatial phenological maps as derived from the phenological model applied to the WRF simulations for budburst date (a), flowering date (b), and maturity (c) in two cultivars, where the units given are day of year (*DOY*), along with the respective phenological factors for the three vineyard sites (A, B and C) as derived from those maps (d).

$$Fst = gs * [O_3] * \frac{r_c}{r_b + r_c} \tag{2}$$

where *Fst* has units of nmol m^{-2} s^{-1} and represents the instantaneous flux of O_3 through the stomatal pores per unit of projected leaf area. It refers specifically to the sunlit leaves at the top of the canopy and is regarded as the hourly mean flux of O_3 into the stomata. $[O_3]$ is ambient ozone at the canopy top, and r_b and r_c represent the leaf quasi-laminar and surface resistances, respectively. According to CLRTAP (2017a), r_b and r_c are given by:

$$r_b = 1.3 * 150 * \sqrt{\frac{L}{u(Z_1)}} \tag{3}$$

where r_b has units of s m^{-1}, 1.3 accounts for the differences in diffusivity between heat and O_3, 150 is a constant, L is the cross-wind leaf dimension which is taken as 0.15 m for the grapevine, and $u(z_1)$ is the wind speed at z_1 or surface layer.

$$r_c = \frac{1}{gs + ge} \tag{4}$$

Where r_c has also units of s m^{-1}, *gs* accounts for stomatal conductance, as presented previously, and *ge* being the leaf cuticular resistance which is given a constant value of 0.0004 m s^{-1}.

The generic grapevine DO3SE parametrization (CLRTAP DO3SE parametrization) for *flight*, *ftemp*, *fvpd* was implemented according to the last published data for this crop (CLRTAP, 2017b) and does not take into account *fpaw* through the growing season ($fpaw = 1$). The required data to configure the DO3SE model with parameters *flight*, *ftemp*, *fvpd* and *flwp* for *Touriga Nacional* (TN DO3SE parametrization) through boundary non-linear regression analysis were obtained from a three-year study performed on a representative vineyard in the DDR as compiled by Moutinho-Pereira et al. (2001) and Moutinho-Pereira (2000). For *flight*, *ftemp* and *fvpd*, 134 mean stomatal conductance values systematically collected at the upper grapevine canopy through different day timings (i. e. 9:00–10:30AM, 14:00–18:30PM, 17:300–18:30PM) from the end of June to mid- September were compiled from that study. The maximum (g_{max}) and the minimum stomatal conductance required to derive the minimum fraction (f_{min}) were derived from the 97th and 5th percentiles of the available mean stomatal conductance observations from that stomata conductance dataset. In a similar way, 64 mean leaf water potential observations collected through the day (i.e, before sunrise, 10AM, 12PM and 18PM) were selected to derive the *flwp* factor, as in Alonso et al. (2008a). The age component or phenological factor, *fphen*, was adjusted for the two cases, CLRTAP and TN, by phenological modelling as explained in the next section. Finally, the DDR grapevine-cultivated areas where allocated by means of CORINE 2006 (Caetano et al., 2009).

3.2.2.1. Inclusion of daily phenological factor into DO3SE.

The age component was derived from the relationship between the development rate of the grapevine and temperature as a sum of heat degrees or growing degree days (*GDD*, °C units), which were estimated as a daily temperature summation above a temperature base required for a given crop to complete a specific phenological stage:

$$\Theta = \int (T - Tb)dt \tag{5}$$

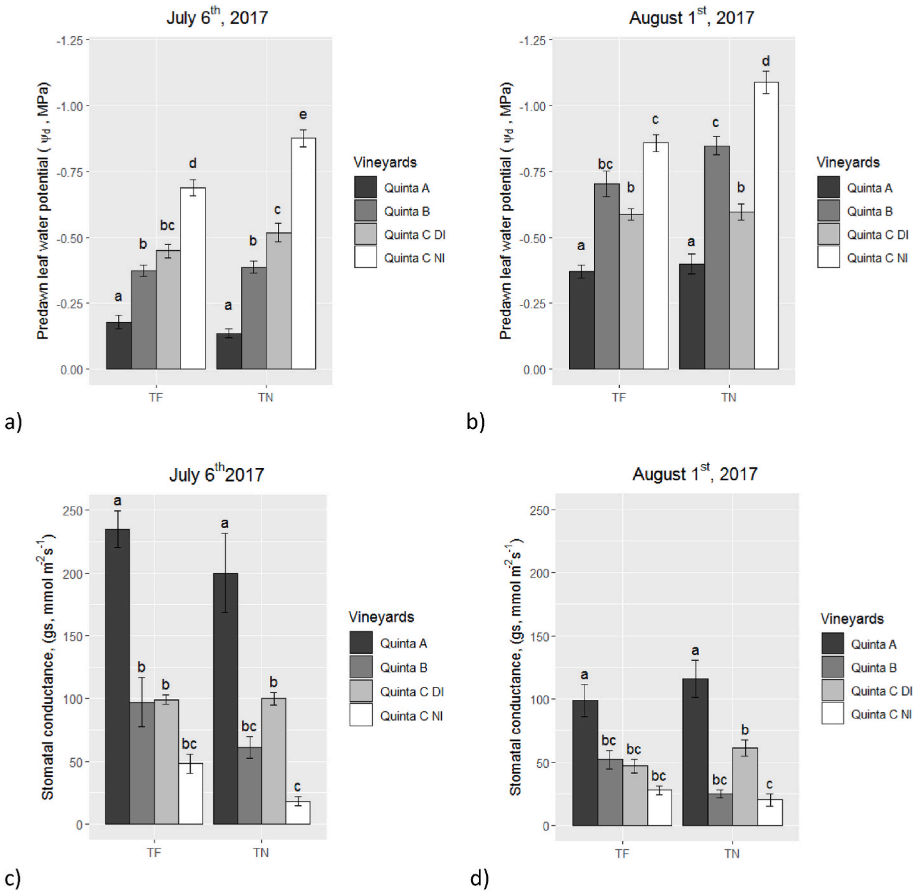


Fig. 6. Statistical analysis summary of a) leaf water potential on July 6th, 2017, b) leaf water potential August 1st, 2017, c) stomatal conductance to water vapour (gs_{H2O}) on July 6th, 2017 and (d) stomatal conductance to water vapour (gs_{H2O}) on August 1st, 2017. Different letters indicate significant differences between treatments ($p < 0.05$) for each day of measurement.

where Θ (°C days) represents the thermal duration of a specific phenological stage, T is the daily average temperature, Tb is a threshold above which there is plant development within that phenological stage and dt represents a daily temporal scale. A specific phenological scheme partitioning the annual development cycle of the grapevine into three major phases (b – budburst-early leaf development to flowering, f – flowering to grape colour onset, and g – grape colour-ripening onset to maturity) was therefore proposed for *Touriga Nacional* (TN) and also *Touriga Franca (TF)* cultivars, as both are early varieties at the budburst and flowering stages and middle-season ones at the maturity stage and therefore have similar thermal requirements (Lopes et al., 2008). This phenological model was used to define the required *GDD* to reach budburst, flowering, grape colour onset and maturity. This work makes use of the specific varietal *GDD* requirements as observed at the Portuguese National Ampelographic Collection (Lopes et al., 2008) for maturity and later observations made available specifically for the Douro Valley region (Alves et al., 2013).

3.2.2.2. Inclusion of hourly leaf water potential factor into DO3SE. Under sustained drought conditions, such as those found in 2017 in the DDR, it is possible to find a strong association between accumulated daily reference evapotranspiration (ET_0) and predawn leaf water potential in grapevines (Gaudin et al., 2017). This relationship was tested both with the observed data collected in the field campaign for the three vineyards across the DDR under non-irrigated (NI) conditions and also for 25% ET_0 deficit-irrigated (DI) conditions at Quinta C, and supplementary leaf water potential data reported for the Cima Corgo subregion through the same summer field campaign season by ADVID (2017) (Fig. 4a). From the same bibliographic sources used to derive the DO3SE parametrization for the *Touriga Nacional* grapevine cultivar (i.e. Moutinho-Pereira et al., 2001 and Moutinho-Pereira, 2000), it was also possible to derive a relationship between predawn leaf water potential and midday leaf water potential (Fig. 4b). Subsequently, a circadian function was fitted to simulate the hourly evolution of the grapevine leaf water potential factor under both non-irrigated and 25% ET_0 deficit-irrigated conditions by setting predawn and midday leaf water potential to happen at 3AM and 3PM, respectively, as in Carbonneau et al. (2004) (Fig. 4c and d). Finally, a simple zoning of the grapevine leaf water potential as surrogate of a drought factor across the DDR was made according to the seasonal evolution observed at the different vineyards and literature sources that also indicated frequent insufficient rainfall and earlier offset of summer drought from the more eastern side of the Cima Corgo subregion and all of the Douro Superior subregion (Jackson, 2008; Jones, 2013; Jones and Alves, 2012) (Fig. 4e and f).

3.3. O_3 Phytotoxic Ozone Dose (POD) standards

The ground-level vegetation risk assessment standards selected for the evaluation of the simulated results were: CLRTAP-based April to September POD0 (Apr–Sep POD0); June to September POD0 (Jun–Sep POD0) as proposed by Soja et al. (2003) and Fumagalli et al. (2019) for the grapevine; CLRTAP-based April to September POD6 (Apr–Sep POD6); June to September POD6 (June–Sep POD6) as proposed by (Soja et al., 2004) for the grapevine. PODY is defined as (CLRTAP, 2017a):

$$PODY = \sum_{accumulation\ period} max(0; \mathrm{Fst} - Y)\Delta t \tag{6}$$

Table 2
DO3SE parameters and functions for a generic grapevine, as available in CLRTAP (2017b), and the *Touriga Nacional* (TN) cultivar, as parameterized from data compiled in the DDR by Moutinho-Pereira et al. (2001) and Moutinho--Pereira (2000). The age component, fphen, was adjusted for the two cases, CLRTAP and TN, by means of the field phenological observations and phenological modelling as explained in section 3.2.1.

Parameter	Unit	*Vitis vinifera*	*Touriga Nacional*	Function
g_{max}	mmol O_3 m^{-2} PLA s^{-1}	229	250	
f_{min}	fraction	0.01	0.05	
light	Unitless	0.0076	0.0046	$flight = 1 - \exp(light*PPFD)$ where *PPFD* is the photosynthetic photon flux density
T_{min}	°C	9	9	$T_{min} > T > T_{max}$; ftemp = f_{min}
T_{opt}	°C	30	30.3	
T_{max}	°C	43	44.5	$T_{min} < T < T_{max}$; $ftemp = \max\{f_{min}, [(T-T_{min})/(T_{opt}-T_{min})]*[(T_{max}-T)/(T_{max}-T_{opt})]^{bt}\}$ $bt = (T_{max} - T_{opt})/(T_{opt} - T_{min})$
VPD_{max}	kPa	1.6	1.4	$fvpd = \min\{1, \max\{f_{min},((1-f_{min})*(VPD_{min}-VPD)/(VPD_{min} - VPD_{max}))+f_{min}\}\}$
VPD_{min}	kPa	6.2	7.4	
LWP α	Unitless	——	−1.36	$flwp = 1/(1 + \exp(\alpha - lwp)/\beta)$
LWP β	Unitless	——	0.14	
fphen_a	Unitless	0.2	0.2	
fphen_1_FD	°C days	523	523	
fphen_b	Unitless	1	1	
fphen_2_FD	°C days	360	360	
fphen_d	Unitless	1	1	
fphen_3_FD	°C days	1573	1573	
fphen_e	Unitless	0.5	0.5	
fphen_4_FD	Days	273	273	

where *Fst* is the instantaneous flux of O_3 through the stomatal openings per unit projected leaf area (PLA) and Δt is the time scale in seconds. It refers specifically to the sunlit leaves at the top of the canopy. It is regarded here as the hourly mean flux of O_3 into the stomata. Y is the threshold stomatal flux per PLA and it can be related to plant defence, repair and detoxification processes (De Marco et al., 2016; Soja et al., 2004). Both parameters have units of nmol O_3 $m^{-2}s^{-1}$. Critical levels based on stomatal flux (Clef) are then cumulative stomatal fluxes above which adverse effects may occur according to present knowledge (CLRTAP, 2017a).

4. Results

Results presented and analysed here are organized based on the needed information for the local parametrization, the calculation, and the validation of the stomatal conductance values, namely the phenological stage and the grapevine physiology (i.e. predawn leaf water potential and stomatal conductance to water vapour). Comparison between values estimated by the CLRTAP DO3SE model and the local TN DO3SE model are also presented.

4.1. Grapevine phenology

Grapevine phenology was estimated using field measured data and meteorological WRF results. Table 1 illustrates the dates of the main phenological phases observed in the field and derived from the phenological thermal modelling applied to the WRF simulations for the three vineyard sites (Quintas). A more detailed description on how the dates for the main phenological stages were derived from the field observations can be found in the supplementary materials (Table 1S).

It can be observed that the phenological thermal model is quite accurate concerning the bud burst at Quinta A with only one day of delay, but that this model delay increases to 7 days at Quinta B and Quinta C. The phenological model flowering date delays between 12 and 13 at Quinta A and Quinta B and up to 17 days at Quinta C. There is a decrease in model delay in relation to the onset of grape colour oscillating between 7 days at Quinta B and Quinta C and 8 days at Quinta A. The opposite happens with maturity, where the dates derived from the phenological simulations are ahead 3 days at Quinta A, 5 days at Quinta B and 6 days at Quinta C.

Fig. 5 (a,b,c) illustrates the dates of main phenological stages as derived from the thermal models applied to the WRF simulations for both *Touriga Nacional* and *Touriga Franca* for the main areas cultivated with grapevine within the DDR. As expected, earlier dates are related to sheltered sites provided by the Douro river course and its tributaries and the more thermic locations toward the west in the Douro Superior subregion. Fig. 5 (d) shows the age factor for the three vineyards as derived from the phenological thermal model where it can also be observed that Quinta C has a later budburst date, as reported in the field.

The delays of the phenological dates for bud break, flowering and grape colour onset can be related with the negative bias present on the WRF temperature simulations which were in the range of −1.8 °C for hourly mean temperature and −3.1 °C for daily maximum temperature at Quinta C and within the range of other studies concerning validation of WRF simulations in the Iberian Peninsula (Blanco-Ward et al., 2021b). Errors in the range of up to 8 days for budbreak, 6 days for flowering, 12 days for grape colour onset have been reported for grapevine using the type of phenological model used in this work (Moncur et al., 1989; Zapata et al., 2017). The change in the error from delay to advancement of the date compared to the field observations in the maturation stage can be related to an inhibition of the physiological development of the grapevine due to high temperatures (i.e. $T > 35$ °C), light and water deficit (Bernardo et al., 2018). Such conditions were reached during the summer of 2017 in the Douro region (ADVID, 2017).

4.2. Grapevine physiology

The statistical analysis of physiological measurements taken in the field are summarized in Fig. 6. It can be observed that predawn leaf water potential (Ψd) and stomatal conductance to water vapour (gs_{H2O}) follow a similar pattern with an increase of the summer stress conditions from Quinta A within the Baixo Corgo subregion or under deficit-irrigated conditions to the higher ones at Quinta C within the Douro Superior subregion. Under sustained drought conditions, grapevine leaf water potentials become more negative through the summer whereas there is also a reduction on leaf stomatal conductance.

According to commonly used Ψd threshold values such as those proposed by Carbonneau et al. (2004) and Deloire et al. (2005) and the mean predawn leaf water potential values observed at the three vineyards, there was no sign of water deficit in the grapevines sampled at Quinta A on July 6th ($\Psi d > -0.2$ MPa), a mild to moderate water deficit was present in the grapevines sampled at Quinta B and under 25% ETP_0 deficit-irrigated conditions at Quinta C (-0.4 MPa $< \Psi d < -0.2$ MPa), whereas the water deficit reached moderate to severe conditions (-0.6 MPa $< \Psi d < -0.4$ MPa) at this last location under unirrigated conditions. As the dry and hot 2017 summer progressed, the grapevines sampled at Quinta A reached a mild to moderate water deficit condition while those sampled at Quinta B and Quinta C displayed a severe to high water deficit ($\Psi d <$- 0.6 MPa) where vegetative growth was reduced or inhibited except for those plants under deficit-irrigated conditions, which continued within the moderate to severe Ψd range of values.

Consistent with the works of Cifre et al. (2005), Flexas and Medrano (2002) and Medrano et al. (2002), it is also possible to relate gs_{H2O} to the degree of water stress and its effects on photosynthesis limitations. As it happened with Ψd, the measured July 6th gs_{H2O} values indicate that: there is mild or no water stress at Quinta A (150 mmol H_2O m^{-2} $s^{-1}<$ gs_{H2O} $<$ 500 mmol H_2O m^{-2} s^{-1}) where gs_{H2O} would probably be the

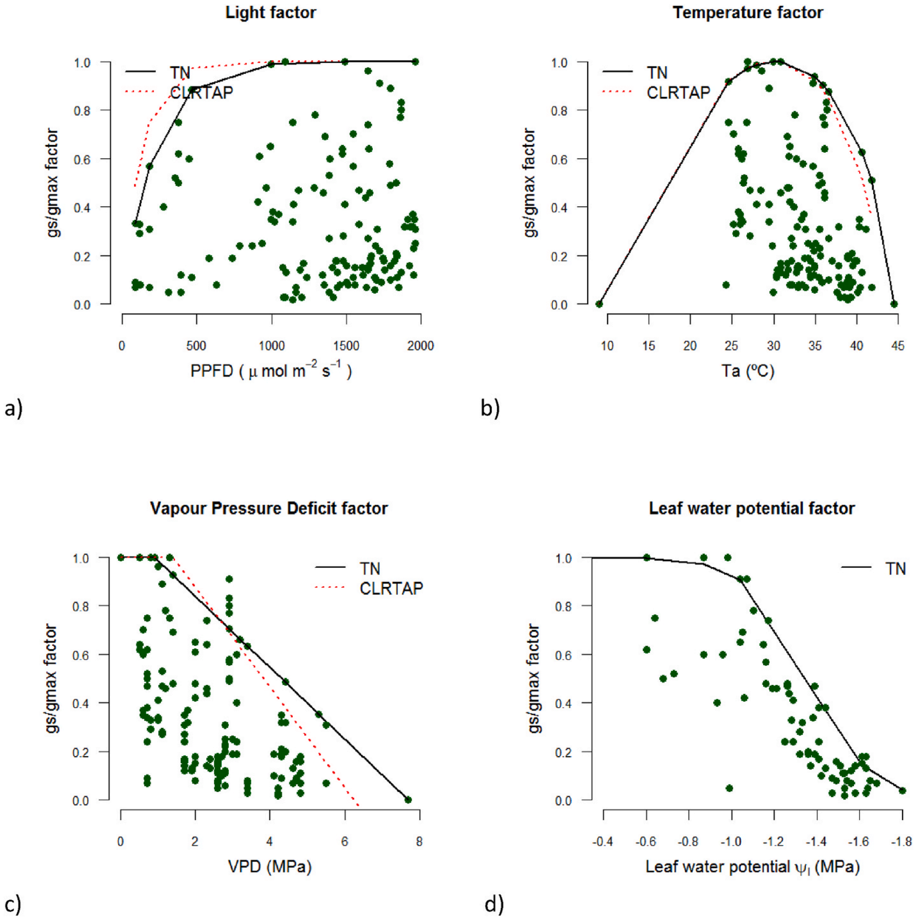


Fig. 7. DO3SE parametrizations used in the last revised CLRTAP DO3SE model for *Vitis vinifera* L. and obtained for *Touriga Nacional* (TN) in the DDR: a) light factor, b) temperature factor, c) vapour pressure deficit factor, and d) leaf water potential factor. Dots represent the data compiled from Moutinho-Pereira et al. (2001) and Moutinho-Pereira (2000) for the DDR, whereas the black thick line represents the TN factor functions fitted by boundary non-linear regression analysis.

only limitation to photosynthesis; there is mild to moderate water stress (50 mmol H_2O m^{-2} s^{-1}$<$ gs_{H2O} $<$ 150 mmol H_2O m^{-2} s^{-1}) at Quinta B and under deficit-irrigated conditions at Quinta C where stomatal limitations would then still be dominant and photosynthesis could be rapidly reversed upon re-watering although non-stomatal limitations (reduced photochemistry and carboxylation efficiency and, eventually, photoinhibition) could also develop; and there is severe water stress at Quinta C under non-irrigated conditions (gs_{H2O} $<$ 50 mmol H_2O m^{-2} s^{-1}) where non-stomatal limitations to photosynthesis would prevail and photosynthesis would not recover after irrigation if the drought is prolonged. By August 1st, mild to moderate water stress is already present at the monitored grapevines at Quinta A, where those located at Quinta B are close to (TF) or present (TN) severe water stress which is definitely present at Quinta C under non-irrigated conditions for both cultivars. Under 25% *ET0* deficit-irrigated conditions at Quinta C, the *Touriga Franca* cultivar mean gs_{H2O} is under the 50 mmol H_2O m^{-2} s^{-1} severe water stress threshold while *Touriga Nacional* is slightly above it.

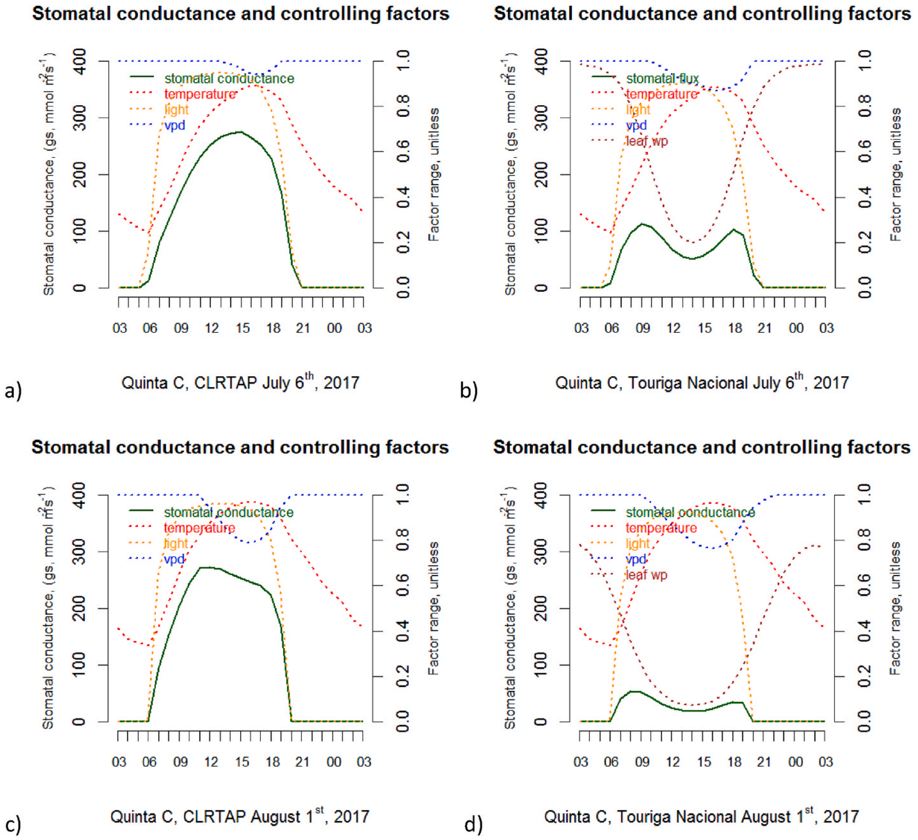
The observed Ψd and gs_{H2O} have a good degree of coincidence in highlighting the existence of severe water stress condition which could inhibit photosynthesis and vegetative growth for the grapevines sampled at Quinta C under non-irrigated conditions from about June 6th, with that condition intensifying and also spreading to unirrigated grapevines at Quinta B from about August 1st. This coincidence was expected due to the strong correlation existing between these parameters (Williams and Araujo, 2002) which for both varieties reached the same Pearson correlation coefficient (0.88, p-value = 0.004). Fig. 1S (in supplementary material) show the strong exponential observed between predawn leaf water potential and mid-day stomatal conductance for *Touriga Nacional* and *Touriga Franca* across the DDR during the 2017 summer season.

As it was hypothesized before, the photosynthetic and vegetative inhibition of the grapevines due to water stress, extreme temperatures and strong light conditions could contribute to the advancement of the phenological thermal model in comparison to the observed maturity dates. In fact, the advancement increases from three days of advancement, to five at Quinta B and six at Quinta C (without no distinction there between non-irrigated or deficit-irrigated conditions). A similar spatial and temporal pattern for Ψd and gs_{H2O} was already observed in the DDR by Moutinho-Pereira et al. (2004).

4.3. DO3SE parametrization

The specific parameters and resulting functions used for the generic grapevine and for the *Touriga Nacional* DO3SE grapevine parametrizations can be found in Table 2 and Fig. 7. The dots in the figure represent the data compiled from Moutinho-Pereira et al. (2001) and Moutinho-Pereira (2000) for the DDR, whereas the black thick line represents the TN factor functions fitted by boundary non-linear regression analysis.

It can be observed that g_{max}, T_{max}, and VPD_{min} parameters are greater for the TN parametrization compared to the CLRTAP one whereas the light factor and VPD_{max} are lower. The TN parametrization reflects a greater adaptation to maintain a higher stomatal conductance at higher temperatures and lower VPDs although it also tends to decrease activity at higher VPDs and lower light flux densities than the more general CLRTAP grapevine parametrization. T_{min} was set to 9 °C, in common



Quinta C, CLRTAP July 6^{th}, 2017

Quinta C, Touriga Nacional July 6^{th}, 2017

Quinta C, CLRTAP August 1^{st}, 2017

Quinta C, Touriga Nacional August 1^{st}, 2017

Fig. 8. Daily profile of stomatal conductance and environmental control factors on July 6th (grape colour onset phenological stage) and August 1st, 2017 (maturity). Quinta C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

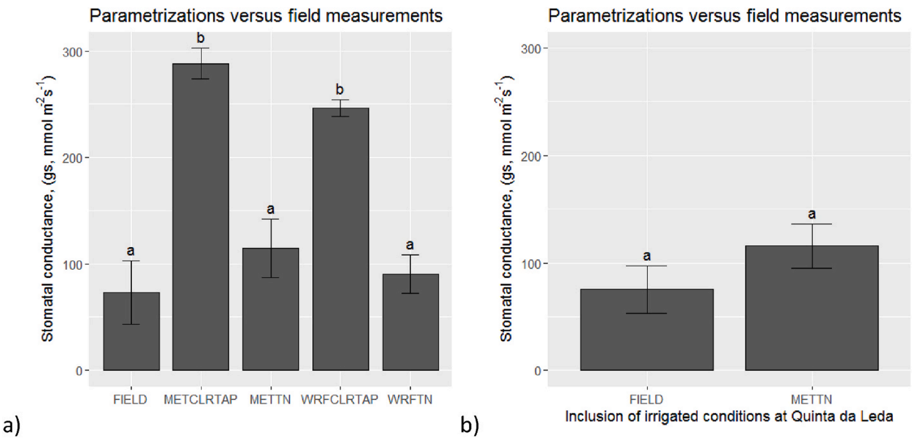


Fig. 9. a) Statistical summary of mean group comparisons among 11AM-15PM solar time gs_{H20} values collected in the field through the three vineyard sites and those derived from CLRTAP and TN DO3SE-based parametrizations feed by on site meteorological observations (MET) and WRF simulations (WRF). b) Mean group comparisons in the field and derived from TN DO3SE-based parametrizations feed by on site meteorological observations (MET) at Quinta C under 25% ET_0 deficit-irrigated conditions.

with the CLRTAP parametrization, as the available stomatal conductance measurements taken both from the field campaign and from bibliographic sources would not cover the colder periods of the growing period being a value close to the commonly accepted 10 °C base temperature for grapevine development activity (Corte-Real et al., 2015). The phenological growth component is the same for CLRTAP and TN parametrizations and is based on the thermal requirements and phenological observations derived from the April–September field campaign. The CLRTAP parametrization lacks the factor related with leaf water potential component as this factor is associated to specific observations made for the *Touriga Nacional* grapevine cultivar in the Douro Demarcated Region (DDR).

Furthermore, Fig. 8 illustrates the daily profile of gs_{H20} and controlling factors at Quinta C for both the WRF CLRTAP and TN DO3SE parametrizations. The gs_{H20} values remain quite stable, increasing along the daylight hours and decreasing in the afternoon, in the CLRTAP DO3SE with the temperature factor exerting the greatest control on July 6th, whereas the vapour pressure factor does so on August 1st.

For both the temperature and the vapour pressure factor, the TN DO3SE parametrization shows a similar hourly pattern to the CLRTAP DO3SE, but the leaf water potential factor, which is not included in the CLRTAP DO3SE parametrization, exerts a much greater control over gs_{H20}, which increases through the summer. Fig. 3S and 4S (in supplementary material) show the same type of results for the other two vineyard sites.

Table 3
POD0 and POD6 field-based estimates from CLRTAP and TN DO3SE parametrizations. Values in bold indicate ozone phytotoxic risk according to the Jun–Sep POD0 standards set by Soja et al. (2003, 2004).

April to September POD0 (mmol m^{-2})			April to September POD6 (mmol m^{-2})		
MET-CLRTAP	MET-TN	MET-TN-25% ET_0	MET-CLRTAP	MET-TN	MET-TN-25% ET_0
28.3	16.8	23.4	1.2	0.1	0.1
WRF-CLRTAP	WRF-TN		WRF-CLRTAP	WRF-TN	
28.6	13.5		0.9	0.2	
June to September POD0 (mmol m^{-2})			**June to September POD6 (mmol m^{-2})**		
MET-CLRTAP	MET-TN	MET-TN-25% ET_0	MET-CLRTAP	MET-TN	MET-TN-25% ET_0
17.8	7.8	**14.3**	0.4	0.1	0.1
WRF-CLRTAP	WRF-TN		WRF-CLRTAP	WRF-TN	
22.9	8.5		0.8	0.1	

4.4. DO3SE stomatal conductance validation

The stomatal conductance to water vapour, gs_{H2O}, as derived from the TN DO3SE parametrization both through the use of meteorological station (MET) or WRF-simulated meteorological data is closer to the values and ranges measured in the field in the three non-irrigated vineyard sites than the respective results estimated by the CLRTAP DO3SE parametrization. No significant difference was found between the WRF and the MET fed DO3SE simulations (Fig. 9a). For the deficit-irrigation conditions at vineyard C, no significant differences were found either between gs_{H2O} field observed values and those derived from MET fed TN DO3SE simulations (Fig. 9b).

4.5. DO3SE POD

For the eastern most vineyard, Quinta C (Douro Superior), where an observational site for ambient O_3 was also available from April to September 2017, the TN DO3SE parametrization yielded lower April to September and June to September POD0 values than the ones derived from the CLRTAP DO3SE model (Table 3). This was expected as stomatal conductance values had lower values during the dry season in the TN DO3SE parametrization, as it has been seen previously. However, the results for 25% *ET0* deficit-irrigated conditions were close to the CLRTAP parametrization. When a 6 nmol m^{-2} s^{-1} detoxification threshold was introduced, as in Soja et al. (2004), the TN parametrization gave much lower values than the CLRTAP ones, and no difference was observed between the deficit-irrigated and non-irrigated conditions for the TN case. This indicates that, according to the DO3SE TN parametrization, the site O_3 stomatal fluxes into the grapevine do not exceed often the 6 nmol m^{-2} s^{-1} detoxification threshold and that the higher the Y threshold the lower the sensitivity to appreciate change in the results concerning the inclusion to the leaf water potential factor. Similar results to these had been already pointed out for forest species in Europe by De Marco et al. (2016).

The maps derived from the WRF-CHIMERE simulations involving the CLRTAP and TN DO3SE parametrizations for the grapevine cultivated areas in the DDR can be found in Fig. 10.

Whereas the CLRTAP DO3SE parametrization shows values above 20 and 30 nmol m^{-2} along all the DDR for the POD0 April to September standard, the higher values derived from the TN DO3SE model do not exceed 30 nmol m^{-2} and those exceeding 20 nmol m^{-2} are mainly located in the western Baixo Corgo subregion with some minor areas in the Cima Corgo subregion. For the June to September POD0 standard, values between 20 and 30 nmol m^{-2} can be found across all the DDR for the CLRTAP DO3SE parametrization but they are not above 20 nmol m^{-2} for the TN DO3SE model, which shows the higher values located almost exclusively in the Baixo and Cima Corgo subregions. Finally, the POD6 April to September standard shows values between 1 and 2 nmol m^{-2} across all the DDR for the CLRTAP DO3SE parametrization but are below 1 nmol m^{-2} for the TN DO3SE one. The POD6 June to September maps are very similar in figure and patterns to the POD6 April to September maps, as it could anticipated from results in Table 3. They can be found in Fig. 5S in the supplementary materials.

5. Discussion

Leaf water potential measurements are regularly used by the wine industry to monitor grapevine water stress and can be empirically related with meteorological variables, such as reference evapotranspiration, through the dry summers common in rain-fed Mediterranean environments (Bernardo et al., 2018; Gaudin et al., 2017). Thus, leaf water potential can be a very valuable proxy to include the soil drought factor into the DO3SE parametrization and it has also been already used in other POD assessment research studies including Mediterranean environments as in Alonso et al. (2008)a,b, and Büker et al. (2012). The TN DO3SE model results did not present significant differences with the gs_{H2O} observed ones in the field through the summer season while the DO3SE CLRTAP model overestimated these observations. This is mainly due to inclusion of the leaf water potential factor as a proxy of soil drought in the DO3SE TN parametrization. The same type of observation has been made with forest species in Mediterranean environments (De Marco et al., 2016).

Although the greater proportion in the difference in the estimation of the standard POD values is related to the inclusion of the leaf water potential factor since early June, a cultivar effect can also be appreciated from before, as it can be observed in Fig. 11.

To perform a POD-based risk assessment at the regional or local scale, it is also necessary to consider the adaptation to the niche of the cultivars present in the study area. In this case, *Touriga Franca*, which was also present in the DDR, had slightly higher values of Ψd and gs_{H2O} under the more severe non-irrigated water stress conditions, but the interpretation of the possible effects in terms of the inhibition of growth and photosynthesis according to the keys commonly used for irrigation management, has been practically the same for the two grapevine varieties, as it has been previously explained.

Phenology is also important in terms of which interval of the vegetative cycle is selected to estimate POD. In this regard, *Touriga Franca* and *Touriga Nacional* have also been classified in the same interval corresponding to cultivars of early budburst and intermediate maturity range (i.e. within 2068 °C – 2190 °C day to achieve the maturity stage in comparison to other early or late to mature cultivars) in an extensive field study involving 16 years of phenological observations among 34 grapevine cultivars in an experimental site at Lisbon (Lopes et al., 2008).

As can also be seen in Fig. 11, a too short phenological window from developed stages well after flowering from June or with low physiological activity along summers with high temperatures, strong light and dry conditions, characteristic in Mediterranean environments, could underestimate the risk. In the present study, the relevance of POD flux from early stages makes more advisable to use wider Apr–Sep intervals similarly to what has been made to assess POD risk for forest species also in Mediterranean environments. On the other hand, it is also known that the flowering stage is very sensitive for the grapevine and with effects that determine the subsequent phases or the harvests of future years, so it is also convenient to carry out studies that include more than one growing season (Guilpart et al., 2014; Soja et al., 1997).

Although the present work was limited to a single year of observation, there is some indication for the TN DO3SE adapted model for the DDR that both Apr–Sep and Jun–Sep POD could exceed Cle_f associated with grapevine yield and quality as it ranges between 10 and 20 mmol O_3 PLA m^{-2} for many areas, specially towards the west in the Baixo Corgo and Cima Corgo subregions. It has also been shown for Quinta C in the eastern Douro Superior subregion of the DDR, which is often severely affected by summer drought, that moderate irrigation (25%

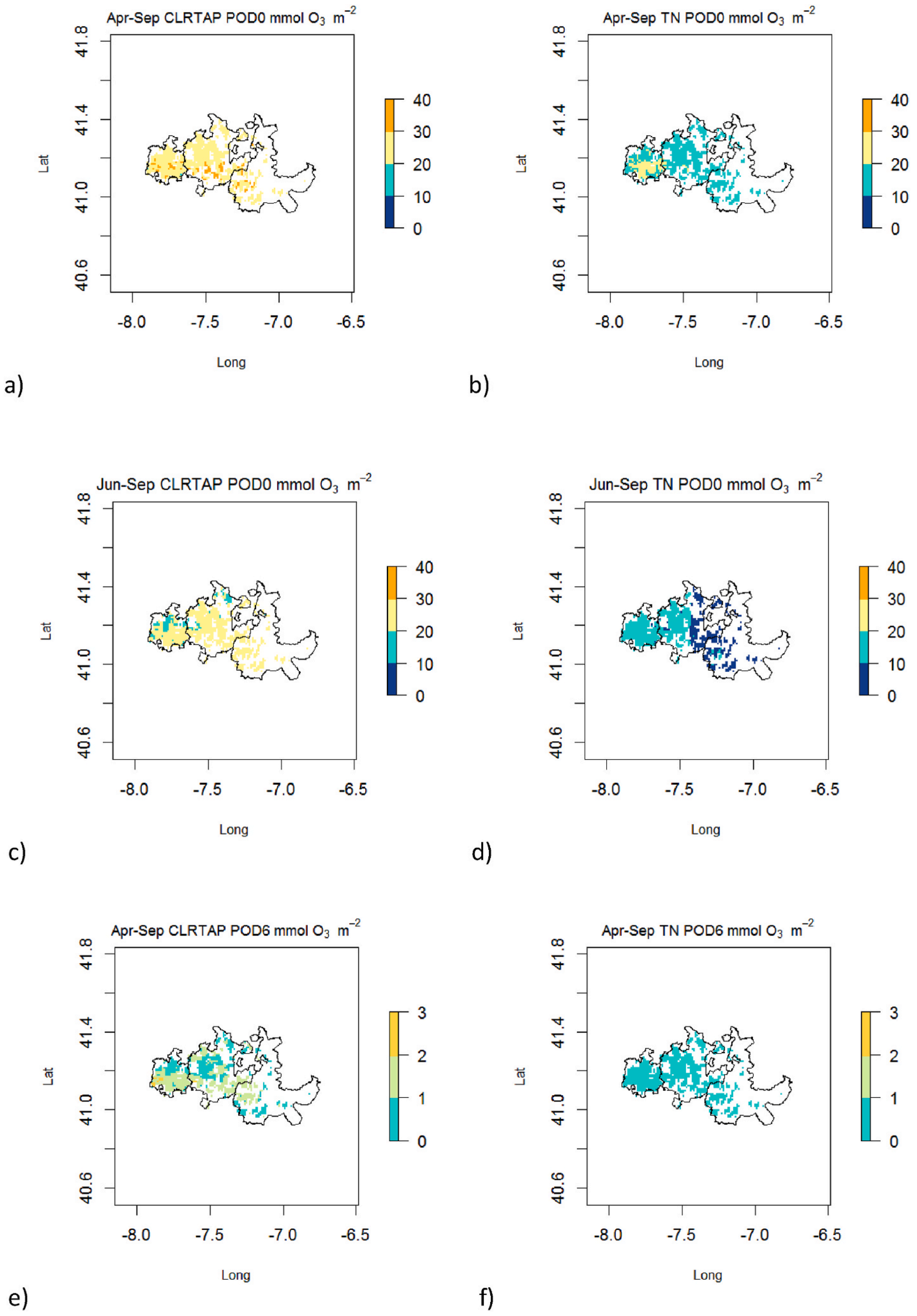


Fig. 10. Apr–Sep and June–Sep POD0 and POD6 maps for non-irrigated cases, for CLRTAP and TN DO3SE parametrizations.

ET_o) can increase the value of POD substantially, and therefore also increase the risk of O_3 phytotoxic damage for this area. However, the information to assess if there is ozone phytotoxic risk for the grapevine in the study area in relation to grape yield and quality based on POD standards is currently limited by the fact that there are only two open top chamber (OTC) O_3 fumigation experiments that were performed in continental Austria and northern Italy for two varieties which are not currently grown in the DDR. For the Jun–Sep POD0 standard, Soja et al. (2003) referred that a 10% reduction in yield is expected if the uptake exceeds 12.5 mmol m^{-2} for two consecutive years; they also noticed that sugar yield was more sensitive than yield with a Clef of 12.0 mmol m^{-2} although these results were limited to a three-year OTC experiment over *Vitis vinifera* cv. Welschriesling three-year old plants grafted on Kober 5BB rootstock under irrigated conditions 30 km south of Vienna, Eastern Austria. In a later work based on the same fumigation experiment, Soja et al. (2004) also published Clef values for grapevine associated with the Jun–Sep POD6 index (stomatal O_3 flux above a Y threshold of 6 nmol O_3 $m^{-2}s^{-1}$). A Jun–Sep POD6 Clef of 3.5 mmol m^{-2} for a 10% reduction of grape yield was established for the first experimental year and 2.2 mmol m^{-2} for the second year, whereas the values associated with a 10% reduction in grape monosaccharide yield were 2.3 mmol m^{-2} in the first year of the experiment and 1.1 mmol m^{-2} in the second year. In addition to the work of Soja et al. (2003, 2004), a Jun–Sep POD0 exceeding 32 mmol m^{-2} was reported by Fumagalli et al. (2019) to have an effect on yield and polyphenols for cv. Merlot, which is considered a global variety as it is extensively cultivated through the world (OIV, 2017).

The use of PODY thresholds has to be done carefully, because the variability of the POD standards calculated by the different DO3SE formulations is greater as the thresholds increase. The variability in the estimation of POD with thresholds with respect to variations in the

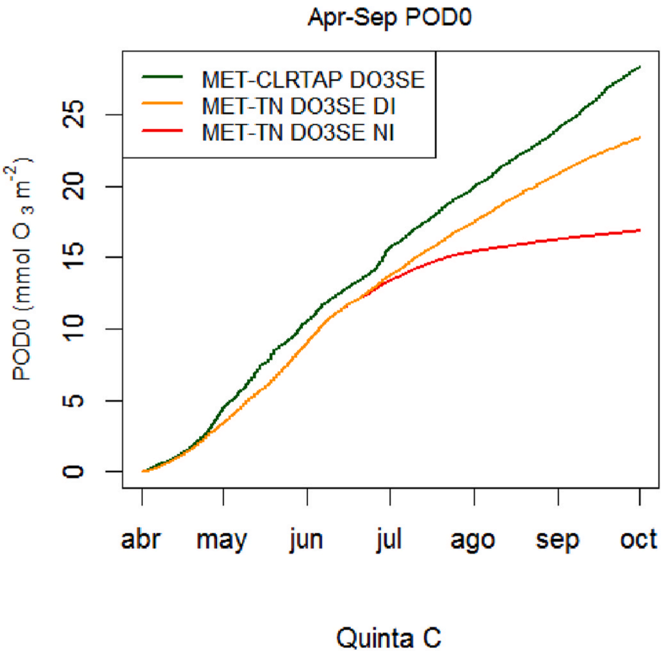


Fig. 11. April to September POD0 cumulative increase for the CLRTAP DO3SE and the TN-DO3SE parametrizations at Quinta C (Douro Superior).

formulation of the DO3SE model has also been observed by De Marco et al. (2016) and currently low threshold standards such as POD1 and POD2 are being considered for forest species in Mediterranean environments.

With all of the above, the value given by the default grapevine CLRTAP DO3SE based parametrization can be considered a worst-case scenario where there is no limitation of the water available in the soil, while the refined TN DO3SE based model would be better adjusted to the local conditions for the studied varieties, *Touriga Nacional* and *Touriga Franca*. Although detailed parametrization of the DO3SE model for the local DDR grapevine cultivars was only possible for the *Touriga Nacional* (TN) case, the field campaign measurements indicated that the *Touriga Franca* (TF) cultivar stomatal fluxes fluctuate within the same range of values in response to drought. As both varieties share similar thermal requirements for phenological stage development and present similar response in parameters such as leaf water potential and stomatal conductance, it could also be expected a similar rate of POD accumulation through the growing season. Both varieties are commonly grown (Corte-Real, 2014; Santos et al., 2013) and appreciated due to its good niche adaptation and high oenological potential in the DDR.

Finally, climate change forecasts for the DDR indicate a reduction in cold periods and precipitation, in addition to an increase in temperatures, and heat waves with the consequent advance in the phenology of the grapevine and the accentuation of its water stress within this century. Traditionally, irrigation has not been allowed in the Douro region in order to maintain the typicity of the wines, but these conditions could favour a change so that the use of precision irrigation strategies becomes more extensive in order to maintain profitability especially in the innermost regions of the DDR, such as the Douro Superior subregion. The results of this study indicate that the use of precision irrigation could increase the phytotoxic risk of ozone for the vineyard. These results could also be relevant to other renowned grape growing regions of the world which have been described with a similar climate (Tonietto and Carbonneau, 2004), such as the Napa Valley (US) in California, where yield impacts reductions for grapes in relation to ambient ozone have already been reported (Hong et al., 2020), or La Mancha (Spain), which is considered the greatest DO in the world, and where high levels of ambient ozone are also present (MITECO, 2021). It is also worth to note that many renowned areas for wine production have been traditionally located within relatively narrow latitudinal bands between 30° and 50° N where exposure levels to ambient ozone also indicate potential risk, although there are not yet corresponding exposure/dose-response studies for representative cultivars under Mediterranean conditions (Blanco-Ward et al., 2021a).

6. Conclusions

The results of this research illustrate the relevance of including a specific parametrization for autochthonous grapevine varieties, with leaf water content as a proxy of the soil water balance, to perform an O_3 phytotoxic risk assessment. Adapting the methodology for a renowned wine producing area, the Demarcated Douro Region of Portugal, not only has a relevant effect on the POD, but it also modifies substantially the spatial patterns of the POD maps produced for phytotoxic risk assessment. Both the field measurements and the TN DO3SE POD model estimates indicate that considerable areas in the Demarcated Douro Region can still exceed critical dose values for the grapevine, although with a lower extent when compared to the default CLRTAP DO3SE which does not include any soil water component for the grapevine. 25% ET_0 deficit-irrigated conditions increase the fine-tuned TN DO3SE POD values close to the default grapevine CLRTAP DO3SE results. Thus, notwithstanding the information available to derive dose-response functions can only be approximated by limited OTC research performed with other varieties and agro-climatological niches, a higher ozone risk of yield and quality loss is expected for deficit-irrigated conditions.

Developments in viticulture increasingly involve the systematic collection of phenological and physiological data for agronomic purposes. As such, similar procedures as those developed in this work can also be applied to other renowned grape growing areas where there is already concern in relation to ozone phytotoxic risk. Although deriving ozone exposure and dose standards for vegetation and also crop protection is becoming increasingly feasible both on a global and local scale, its true usefulness still depends on developing appropriate dose-response studies which, for this crop, are still not available for representative cultivars under Mediterranean conditions. Overall, the research results indicate that air quality management, in particular the reduction of ozone levels in the ambient air, must also be considered to define sustainable grape and wine production strategies in the context of climate and wine production management change.

CRediT authorship contribution statement

D. Blanco-Ward: Conceptualization, Methodology, (WRF-CHIMERE simulations and postprocessing, field campaign data postprocessing), Writing – original draft, Writing – review & editing, Coordination. **A.C. Ribeiro:** Field campaign data collection and manuscript reviewing. **M. Feliciano:** Field campaign data collection and manuscript reviewing. **D. Barreales:** Field campaign data collection and manuscript reviewing. **E. Paoletti:** Conceptualization, Supervision. **A.I. Miranda:** Conceptualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2022.119538.

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