Article

Ozone Effects on Douro Vineyards under Climate Change

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Abstract: Tropospheric ozone (O_3) levels in southern Europe have an increasing tendency, in close relation with the higher incidence of hot summers and heatwaves. Given that O_3 is one of the most damaging pollutants for vegetation, known to affect productivity and quality of crops, it is necessary to develop more rigorous and consistent methods of risk assessment that consider climate change conditions. Studying the O_3 deposition over the Douro Demarcated Region (DDR), which is one of the most productive wine areas in Portugal, and assessing its potential effects under a climate change scenario, was the purpose of this study. To that end, the chemical transport model CHIMERE, with a spatial resolution of 1 km^2, fed by meteorological data from the WRF model, was applied for a recent past climate (2003 to 2005) and future mid-term (2049 and 2064) and long-term (2096 and 2097) scenarios. Simulations for future climate were performed considering: (i) only the climate change effect, and (ii) the effect of climate change together with future air pollutant emissions. The assessment of the potential damage in terms of wine productivity and quality (sugar content) was performed through analysis of O_3 deposition and the application of concentration–response functions, based on AOT40 values. Modeling results show that a reduction in emission of O_3 precursors can successfully decrease AOT40 levels in the DDR, but it is not enough to accomplish the European Commission target value for the protection of vegetation. If the emissions remain constant, the exposure–response functions indicate that, in the long-term, AOT40 levels could worsen wine productivity and quality.

Keywords: tropospheric ozone; grapevine (*Vitis vinifera* L.); air-quality modeling; AOT40; dry deposition; climate change

1. Introduction

Air pollution and climate change are closely related. Air pollutants and their precursors are often co-emitted with carbon dioxide (CO_2) or other Green House Gases, and air pollutant emissions can cause warming or cooling effects on the climate. In turn, climate change influences air pollution by altering the frequency, severity, and duration of heatwaves, air-stagnation events, precipitation, and other weather changes that result in pollutant accumulation [1–6]. Identifying the co-benefits of reducing air pollutants that also reduce the impacts of climate change is an important contribution to climate change research and mitigation.

Tropospheric ozone (O_3) levels in southern Europe have an increasing tendency, which is related to the higher incidence of hot summers and heatwaves [1,7–9]. Modeling results indicate that climate change alone will cause O_3 concentrations to increase in many regions in the world [10–12]. For instance, under the RCP8.5 scenario, Lacressonnière et al. [10] estimated an increase in O_3 levels of approximately 1.5 ppb per decade, during the summer in Europe. Similarly, Sá et al. [11] estimated an increase in the occurrence, duration, and

intensity of extreme O_3 values in Northern Portugal. In addition to weather conditions, such as temperature, humidity, cloud cover, and winds, O_3 concentrations depend on emissions of its precursors as well as long-range transport [13].

Working towards a reduction in O_3 concentrations is very important due to the effects of O_3 on human health and vegetation. However, due to the complex and non-linear chemistry of O_3, reducing the emissions from its precursors may not lead to a decrease in its concentrations. A specific study for Portugal [14] showed that, despite the reduction in O_3 precursors' emissions imposed by the National Emission Ceilings Directive, mean tropospheric ozone concentrations significantly increased between 2003 and 2007 although the number of exceedances to the information threshold (180 $\mu g \cdot m^{-3}$) decreased. O_3 is the most damaging air pollutant to crop yield quantity and quality [15–18]. Avnery et al. [19,20] estimated that, globally, surface O_3 reduced the yields of key crops by up to 15% in 2000 and is projected to cause a 26% reduction in 2030. Blanco-Ward et al. [17], in their review of tropospheric O_3 phytotoxic effects on the grapevine, mention potential yield reductions in the range of 20–31%, as well as damages of grape quality, due to reductions in total polyphenols, in the range of 15–23%. Ascenso et al. [21] estimated that the Douro Demarcated Region (DDR) vineyards' current exposure to O_3 could result in a productivity loss of up to 27%.

Due to its economic interest, the impacts of climate change on wine production have been studied by many authors (e.g., [22–26]), but few address the complex relationship between surface O_3 concentrations, climate change, and grapevine productivity and quality [27]. The DDR is an important wine region in Portugal, where the famous Port Wine is produced. Located within the Douro River basin in the northeastern part of Portugal, the region is known for its deep valleys and mountainous terrain. The main objective of this study was to evaluate Douro vineyards' exposure to tropospheric O_3 in future climates, by assessing O_3 concentrations and deposition in the DDR and then evaluating the potential damage in terms of productivity and quality (sugar loss).

This article is organized as follows: Section 2 describes the air-quality modeling system setup and the working methodology, the modeling results are presented in Section 3, and conclusions are drawn in Section 4.

2. Methodology

O_3 concentration and dry deposition were estimated using the air-quality modeling system WRF-CHIMERE. The simulations were performed for the hottest years of the recent past and mid- and long-term future conditions. The AOT40 (accumulated concentration of O_3 above 40 ppb) indicator, proposed by the European Union to monitor and prevent vegetation damage from O_3 exposure, was calculated and used as input data to estimate the potential loss of productivity and grape sugar content due to climate change, and also considering the projected O_3 precursors' emissions.

2.1. WRF-CHIMERE Modeling System

Climate numerical simulations were performed using the regional high-resolution Weather Research and Forecasting v3.5.1 (WRF) model with two distinct forcings (initial conditions and boundary conditions), namely, ERA-Interim reanalysis [28] and the Max Planck Institute Earth System Model—low resolution (MPI-ESM-LR) [29]. The MPI-ESM-LR model was developed by the MPI with a horizontal resolution of 1.9° [30]. This model participated in the Coupled Model Intercomparison Project Phase 5 (CMIP5) that considered future greenhouse gas emission scenarios defined by the Representative Concentration Pathways (RCP) [31]. In particular, this study considered the RCP8.5 scenario (Radiative Forcing: >8.5 W/m^2 in 2100; Concentration: >~1370 $CO_{2\text{-eq}}$ in 2100; Pathway shape: Rising) [32].

The CHIMERE model (v2016a1) was used in this study. CHIMERE is an open access multi-scale Eulerian chemical transport model (CTM) that applies the integration of the mass continuity equation to estimate the concentrations of several chemical species in each

cell of a given grid. It was developed for simulating gas-phase chemistry [33], aerosol formation, transport, and deposition [34] from regional to urban scales. As input data, the CHIMERE model requires meteorology (from WRF), initial and boundary conditions (from MOZART; [35]), atmospheric emissions (from EMEP; [36]), and land use and topography data (from USGS). For more details on the model parametrizations and input data, see Ascenso et al. [21].

The air-quality simulations for the future climate were two-fold: one was performed considering climate change only, i.e., emissions were kept the same as in recent past climate simulations, to assess the contribution to O_3 levels of meteorological variables alone; the other also included future projected emissions to assess future O_3 levels resulting from both contributions (meteorology and emissions).

The application of the air-quality modeling system WRF-CHIMERE was set up in a one-way hourly nesting configuration with four nested domains with an increasing horizontal resolution. The last domain was focused on the DDR, with a spatial resolution of 1 km^2. For a detailed description of the DDR case study, see Ascenso et al. [21]. The simulation periods were selected based on a climatologic assessment of the region that identified the hottest years from an historical period (1986–2005) and mid- (2046–2065) and long-term (2081–2100) projected scenarios, which were based on the RCP8.5 pathway. The 20-year periods considered for this assessment were the same as those considered in the 5th Intergovernmental Panel on Climate Change (IPCC) Assessment Report [37]. The years 2003 to 2005 were chosen to simulate the recent past climate, 2049 and 2064 for the mid-term future climate, and the years 2096 and 2097 for the long-term future climate.

In addition to meteorological data, emissions are one of the main input data for air-quality modeling, both for the recent past and for the future climate scenarios. For the recent past scenario, 2005 emissions from the EMEP database [36] were used. For future emissions, a methodology to project anthropogenic emissions from the EMEP database was developed. The estimation of future emissions was founded on the RCP8.5 emission scenario [38], keeping therefore consistency between the climate change simulations and the air-quality simulations. This methodology was based on Equation (1):

$$Future\ emissions = EMEP current\ emission \times \frac{RCP8.5\ future\ emission}{RCP8.5\ current\ emission} \tag{1}$$

The EMEP emission inventory for the year 2005 was, therefore, selected to project emissions to the mid- and long-term future scenarios, using RCP8.5 scenario emission data with the same spatial resolution of the EMEP grid (0.5 degrees by grid cell) as a normalization factor to those future projections. A few adjustments between the EMEP and the RCP approaches were performed, namely, correspondence by activity sectors, adopting the Selected Nomenclature for Air Pollution (SNAP): 1—Public power stations, 2—Residential combustion plants, 3—Industrial combustion, 4—Production processes, 5—Extraction and distribution of fossil fuels, 6—Solvent use, 7—Road transport, 8—Other mobile sources. Figure 1 shows the relative differences between 2005 inventory emissions and 2050 and 2100 projected emissions for the O_3 precursors nitrogen dioxide (NO_2) and non-methane volatile organic compounds (NMVOC).

The emission projections for NO_2 and NMVOC indicated a marked reduction in both pollutants (>50%). The main driver for NO_2 emissions reduction was the road transport sector (SNAP 7). In contrast, NO_2 emissions from other mobile sources and machinery (SNAP8) were expected to increase in the future, mainly due to a rise in air and sea traffic [39,40].

Regarding NMVOC, the main emission sectors were solvent and other product use (SNAP6) and road transport (SNAP 7); according to the RCP8.5 future projections, emissions of these chemical compounds will be widely reduced.
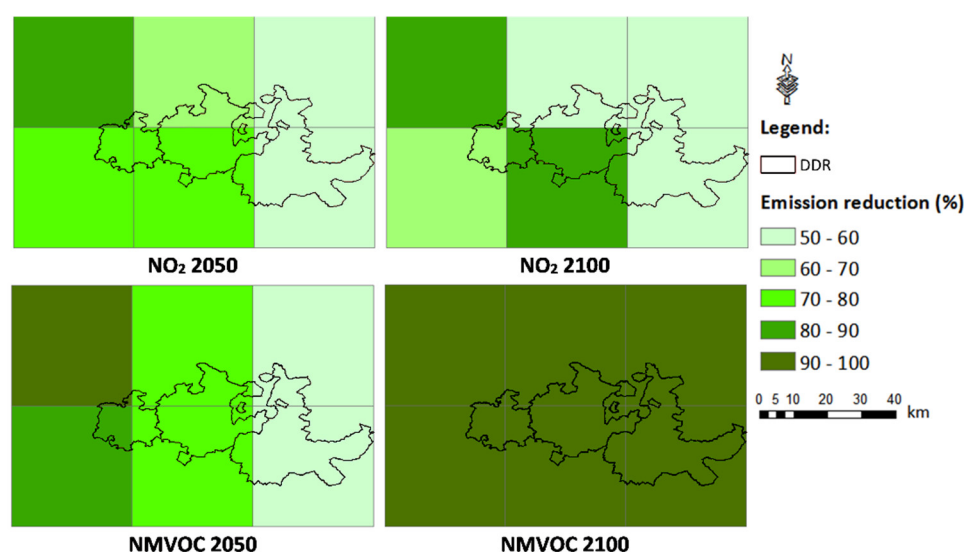
Figure 1. Spatial distribution of NO$_2$ and NMVOC emissions reduction (%) for the DDR EMEP cells in 2050 and 2100.

In summary, a set of five scenarios and a total of 11 yearly simulations were analyzed (Table 1).

Table 1. Summary of the methodology for each scenario assessed in this study. Legend: BASE—Simulation of the recent past climate; MT—Mid-term simulation; MT_emis—Mid-term simulation with projected emissions; LT—Long-term simulation; LT_emis—Long-term simulation with projected emissions.

Scenario	BASE	MT	MT_emis	LT	LT_emis
Years	2003–2005	2049; 2064	2049; 2064	2096; 2097	2096; 2097
Meteorological forcing	ERA-Interim reanalysis	MPI-ESM-LR	MPI-ESM-LR	MPI-ESM-LR	MPI-ESM-LR
Anthropogenic emissions	Base inventory emissions	Base inventory emissions	Projected emissions for 2050	Base inventory emissions	Projected emissions for 2100

2.2. Vineyards' Exposure to Ozone

To evaluate the risk of Douro vineyards' exposure to O$_3$, the accumulated exposure indicator AOT40 was calculated and averaged for the simulated years in each scenario. According to the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (see Annex VII, point A1), "AOT40 (expressed in (μg·m^{-3})·hours) means the sum of the difference between hourly concentrations greater than 80 μg·m^{-3} (= 40 parts per billion) and 80 μg·m^{-3} over a given period using only the one-hour values measured between 8.00 and 20.00 Central European Time (CET) each day". Note that 80 μg·m^{-3} of ozone is approximately 40 ppb because the unit conversion depends on the density of the air. The European and Portuguese target value is 18,000 μg·m^{-3}·h averaged over five years. The long-term objective is 6000 μg·m^{-3}·h. AOT40 quantifies only O$_3$ exposure, i.e., not the effective O$_3$ uptake by (and therefore damage caused to) vegetation. Thus, O$_3$ deposition simulated levels are also presented and discussed.

The assessment of the potential damage in terms of productivity and quality was performed through the application of the exposure–response functions calculated by Soja et al. [41] in their three-year experimental study on the effects of long-term ozone exposure in pot-grown grapevines, regarding fruit yield, noted in Equation (2), and sugar concentrations in juice, noted in Equation (3), wherein grapevines were exposed to different ozone levels in open-top chambers.

$$\text{productivity } (\%) = 102.4 - 2.614 \text{ AOT40} \tag{2}$$

$$\text{sugar } (\%) = 95.4 - 2.456 \text{ AOT40} \tag{3}$$

In these Soja et al. [41] equations, AOT40 is expressed in $\mu mol \cdot mol^{-1} \cdot h$. For this work, the function applied was the one calculated for the last year of the experiment, meaning that this exposure–response function assumed that grapevines were exposed to constant levels of ozone for three years.

3. Effects of Ozone on Vineyards

The effects of O_3 on the vineyards were based on the AOT40 indicator, productivity and quality losses, and dry deposition estimated values, for the different simulated scenarios.

3.1. AOT40

Figure 2 shows the BASE scenario AOT40 simulated values based on the modeling results averaged over the three recent past simulation years (2003–2004–2005).
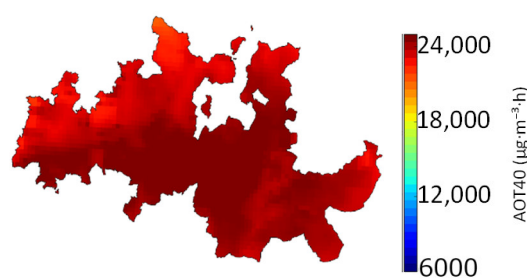
Figure 2. AOT40 levels ($\mu g \cdot m^{-3} \cdot h$) in the DDR for the BASE scenario, averaged over the three recent past years (1×1 km^2 horizontal resolution).

Exceedances of the target value for vegetation protection (18,000 $\mu g \cdot m^{-3} \cdot h$) occurred throughout the DDR area for the recent past conditions. The average AOT40 level for the recent past was 22,500 $\mu g \cdot m^{-3} \cdot h$. This area of Portugal is known for its high O_3 values, observed at the Douro Norte air-quality monitoring station and estimated through modeling approaches [42–44]. The average O_3 concentration in the Douro Norte monitoring station for 2003–2005 was 106 $\mu g \cdot m^{-3}$ with an hourly maximum of 361 $\mu g \cdot m^{-3}$. The high values were related to high altitudes, long-range transport (eastern synoptic forcing), and sea-breeze circulation [45,46].

The maximum level, calculated (24,000 $\mu g \cdot m^{-3} \cdot h$) in the central area of the DDR, was about 1.3 times higher than the target value. This zone also has the lowest wine production per unit of area in the DDR [47].

Figure 3 shows the AOT40 results for the climate change scenarios, with and without emission projected changes.

For the MT scenario, no relevant differences were estimated in relation to the BASE scenario, with an average reduction of 1% in AOT40 levels, due to the small changes in meteorological conditions. On the other hand, AOT40 levels decreased by 20% in the MT_emis scenario, indicating that the reduction in AOT40 levels was mainly influenced by the reduction in emissions.

The greatest differences in AOT40 levels were estimated to occur in the long-term future. In the LT scenario, the model results showed that the impact of climate change on the O_3 concentration would result in a 7% increase in AOT40 levels (Figure 3). Although AOT40 levels would continue to exceed the target value for vegetation protection, when projected emissions were considered (LT_emis scenario), AOT40 levels would decrease by an average of 8% in relation to the BASE scenario.
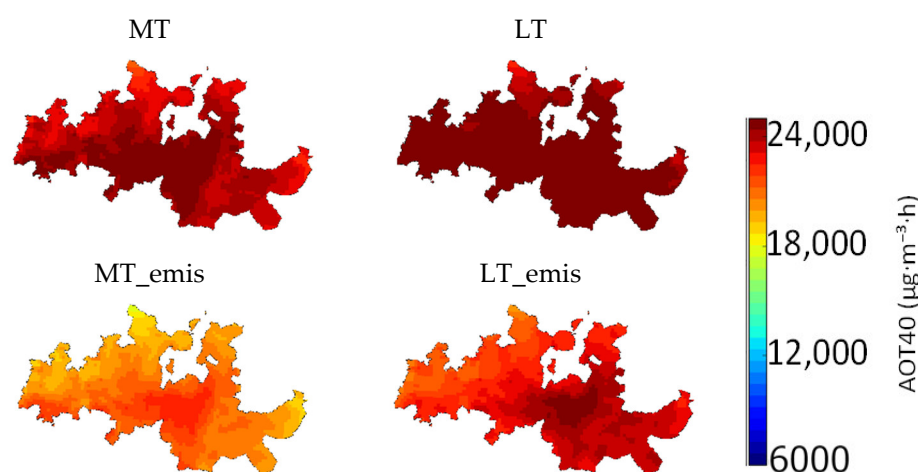
Figure 3. AOT40 values ($\mu g \cdot m^{-3} \cdot h$) for mid-term and long-term climate change scenarios in the DDR (1×1 km^2 horizontal resolution). Legend: MT—Mid-term simulation; MT_emis—Mid-term simulation with projected emissions; LT—Long-term simulation; LT_emis—Long-term simulation with projected emissions.

3.2. Productivity and Quality Losses

Figure 4 shows the BASE values for grapevine productivity and quality loss due to O$_3$ exposure. The impact on quality was calculated through the changes in the grape's sugar content, an important indicator for wine quality.
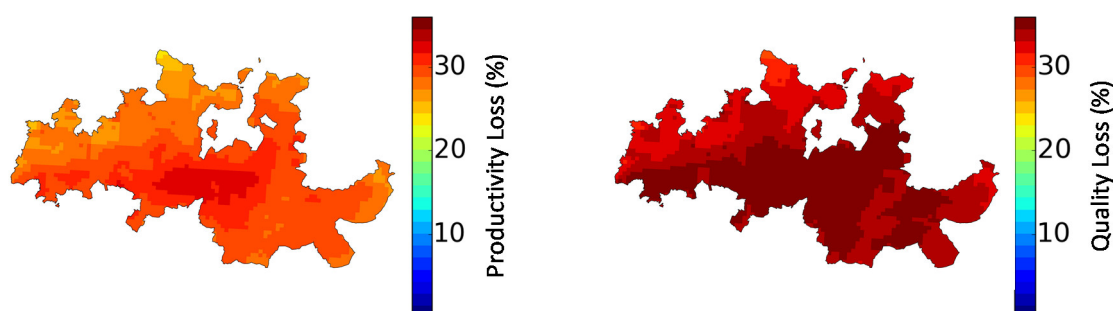

Figure 4. Productivity change (%) (**left**) and quality change (%) (**right**), for the BASE scenario, based on Soja et al. [41] exposure–response functions.

In the BASE scenario, the exposure to high AOT40 levels led to an average productivity loss of 27% and a quality loss of 32%, following Soja et al. [41] response functions. The spatial distribution was similar to that in the AOT40 maps since this indicator was the only variable in the exposure–response functions. These results show that the quality indicator was more sensitive to O$_3$ exposure when compared to productivity; O$_3$ decreased the photosynthetic capacity of leaves and shifted the partitioning of available carbohydrates [41].

The climate change and emission reduction impact on productivity and quality loss for the mid-term and long-term future is presented in Figures 5 and 6, respectively.

Akin to the previous discussed AOT40 levels, relative differences between future scenarios and the BASE case showed an average reduction of 1% in productivity and quality for the MT scenario. For the MT_emis scenario, the 20% decrease in AOT40 levels would lead to a reduction of 5% in productivity losses and 6% in sugar content (grape quality). In the LT scenario, the model results show that the impact of climate change on the O$_3$ concentration would result in a 9% and 7% increase in productivity and quality losses, respectively. However, if the projected emissions reduction were to happen, a decrease of 8% in productivity losses and 7% in quality losses would be expected, relatively to the BASE scenario.
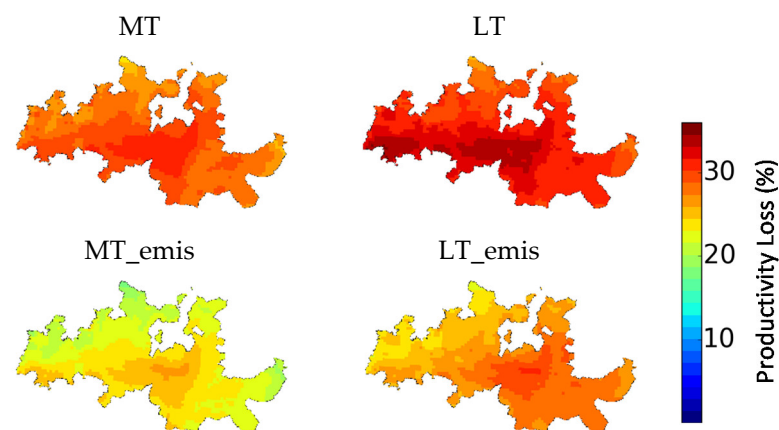
Figure 5. Productivity Loss (%) for mid-term and long-term climate change scenarios in the DDR (1×1 km^2 horizontal resolution). Legend: MT—Mid-term simulation; MT_emis—Mid-term simulation with projected emissions; LT—Long-term simulation; LT_emis—Long-term simulation with projected emissions.
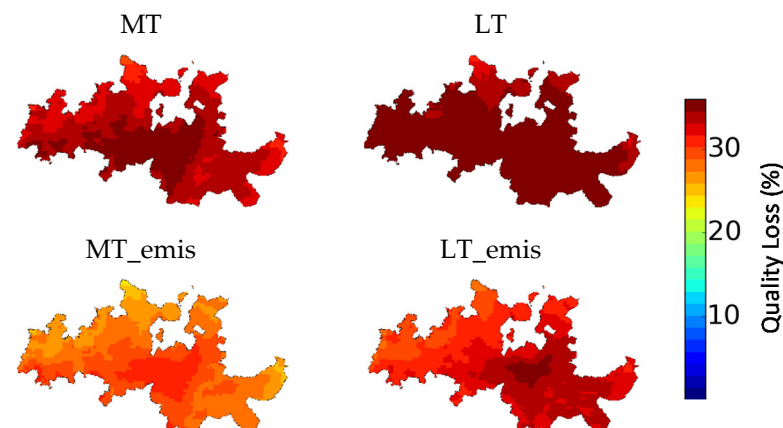
Figure 6. Quality loss (%) for mid-term and long-term climate change scenarios in the DDR (1×1 km^2 horizontal resolution). Legend: MT—Mid-term simulation; MT_emis—Mid-term simulation with projected emissions; LT—Long-term simulation; LT_emis—Long-term simulation with projected emissions.

When discussing these outcomes, it is important to take into account that extrapolating Soja et al. [41] functions to the Douro vineyards has some limitations. The functions were based on a reduced number of replicated experiments with only one cultivar (which is different from DDR's cultivars), and maximum stomatal conductances can differ with age and variety for the grapevine, and can also differ between control studies and the field. Moreover, inferring empirical information obtained under current climatic conditions to assess future risks also brings uncertainty as quality and productivity also change in response to climate change and technological development.

Balancing these results with the reported wine production over the years in the DDR (Figure 7), a reduction in the production of wine is visible a couple of years after the study period (hot years compared to the climatological normal of the recent past). This indicates that environmental stresses can cumulatively affect vineyards. However, it is not possible to compare such values with the study results, since many factors can influence wine production and, in this study, the effect of O$_3$ exposure was assessed isolated from other variables. While O$_3$ could have been reducing productivity, other factors such as temperature, precipitation, and humidity could improve it.
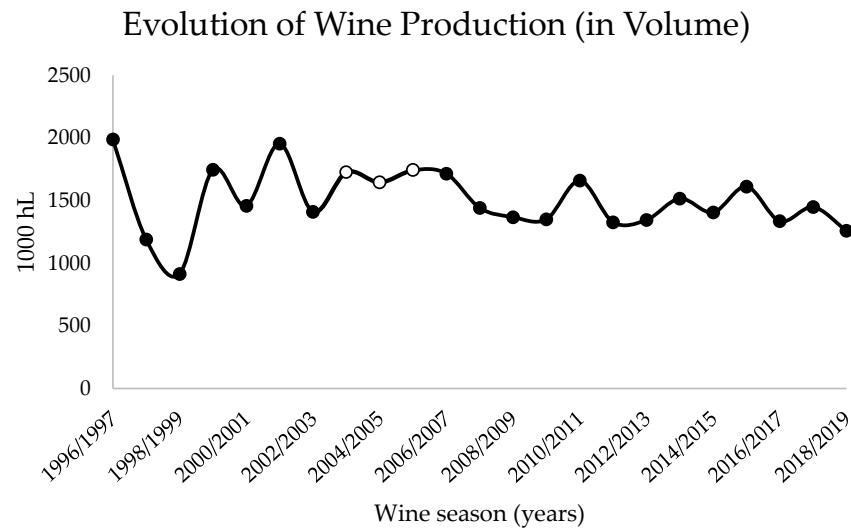
Figure 7. Evolution of wine production in the Douro wine region from 1996 to 2018, according to *Instituto da Vinha e do Vinho*, *I.P* annual reports [48]. The study period (2004 to 2005) is highlighted in white.

3.3. Ozone Dry Deposition

The deposition level results were based on the total O_3 dry deposition accumulated over May to July, the same period established in the Air Quality Framework Directive 2008/50/CE for the calculation of the AOT40 indicator [21]. Figure 8 shows the BASE scenario O_3 dry deposition values, and in Figure 9 the results for the future climate scenarios are presented.
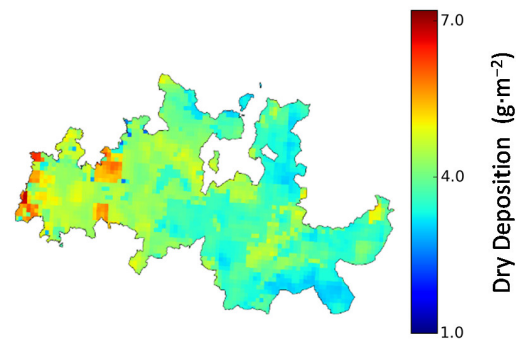
Figure 8. BASE O_3 dry deposition (g·m^{-2}) in DDR (1 × 1 km^2 horizontal resolution), accumulated from May to July and averaged for the three simulation years.
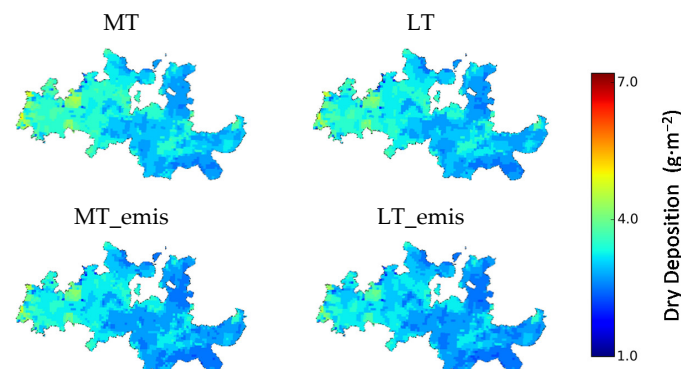
Figure 9. O_3 dry deposition (g·m^{-2}) results for mid-term and long-term future climates. Legend: MT—Mid-term simulation; MT_emis—Mid-term simulation with projected emissions; LT—Long-term simulation; LT_emis—Long-term simulation with projected emissions.

The average BASE value of O_3 dry deposition was approximately 4 g·m^{-2} (deposition velocity ~0.64 cm/s). Higher values were observed over the west side of the DDR, due to the higher precipitation and lower temperatures observed in this area. The spatial distribution of AOT40 and deposition values were distinct, suggesting that exposure-based indicators were not the best approach to assess O_3 damage to vegetation [21].

The dry deposition values of O_3 for the MT and MT_emis scenarios were similar, decreasing 33% and 37% in relation to the BASE scenario. The same was seen for LT and LT_emis scenario results, where decreases of 30% and 34%, respectively, are estimated. These results indicate that, unlike AOT40 levels, dry deposition was mostly influenced by meteorological factors. Therefore, even with an increase in O_3 concentrations, the risk of damage to vegetation is expected to decrease. Analogous conclusions were drawn by Klingberg et al. [49].

The projected reduction in O_3 dry deposition was mostly related to increasing stress factors on the stomata, such as drier conditions and higher temperatures. The modeling results show that, for both future scenarios, an increase in temperature is expected in the DDR, in particular for maximum temperatures during the summer season. This warming trend will lead to a substantial increase in tropical nights. Moreover, for the long-term climate, it is predicted that the majority of the summer season will be under heatwave conditions. A decrease in precipitation is also expected, leading to a large increase in the number of consecutive dry days and a decrease in consecutive wet days, particularly for the long-term climate.

4. Summary and Conclusions

The complex interactions of natural variability and changes in climate and emissions pose a significant challenge for air-quality management. Some approaches to mitigate climate change could result in large near-term co-benefits for air quality. Moreover, given the effects of ambient O_3 on crops and natural vegetation, it becomes necessary to develop more reliable methods of risk assessment that consider the specific environmental conditions of these areas.

This work aimed to estimate O_3 concentration and deposition over the DDR for the recent past, mid- and long-term future, to assess the potential effects of Douro vineyards' exposure to O_3. Simulations for the future climate were performed only considering the climate change impact in O_3 concentrations and considering projected emissions as well. Table 2 summarizes the O_3 effects on Douro vineyards for the mid-term and long-term future, based on RCP8.5 climate projection.

Table 2. Summary of O_3 effects on Douro vineyards for mid-term and long-term climate, based on RCP8.5 climate projection. Legend: BASE—Simulation for the current climate; MT—Mid-term simulation; MT_emis—Mid-term simulation with projected emissions; LT—Long-term simulation; LT_emis—Long-term simulation with projected emissions.

Indicator	Statistic	BASE	MT	MT_emis	LT	LT_emis
AOT40 (µg·m^{-3}·h)	max	26,685	26,473	22,517	29,981	25,118
	min	17,373	17,469	7784	18,578	9801
	avg	22,569	22,237	17,925	24,231	20,702
Productivity Loss (%)	max	32.5	32.2	27.0	36.8	30.4
	min	20.3	20.4	7.8	21.9	10.4
	avg	27.1	26.7	21.0	29.3	24.7
Quality Loss (%)	max	37.4	37.1	32.3	41.4	35.4
	min	25.9	26.1	14.2	27.4	16.6
	avg	32.3	31.9	26.6	34.4	30.0
O_3 Dry Deposition (g·m^{-2})	max	0.8	0.5	0.5	0.6	0.5
	min	0.1	0.0	0.0	0.0	0.0
	avg	0.4	0.3	0.3	0.3	0.3

Modeling results show that a reduction in emission of O_3 precursors can successfully decrease the AOT40 levels in the Douro Region. Nonetheless, the emission reduction projected by RCP8.5 would not be enough to accomplish the target value for the protection of vegetation established in the Air Quality Framework Directive since this value is exceeded over the entire region, suggesting a likely negative impact for crops. If the projected emissions are considered, the exposure–response functions indicate that, in the long-term, AOT40 levels can represent potential damage to the grapevines causing over 30% loss in quality, which is less than the estimated impact in the recent past scenario.

The O_3 dry deposition levels also suggest a decrease in the potential damage to the DDR's vineyards, however, these results were observed for all scenarios, unlike the AOT40 indicator. Thus, the O_3 effects on Douro vineyards based on the AOT40 may be overestimated. It is important to define a threshold for the protection of vegetation that considers the potential uptake using dry deposition levels and developing crop-specific dose–response functions.

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Informed Consent Statement: Not applicable.

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Conflicts of Interest: The authors declare no conflict of interest.

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