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Foliar Silicon Application in the Era of Climate Change as a Part of Strategy to Reduce Water Requirements in Mediterranean Viticulture

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Abstract: Rising temperatures and water scarcity due to climate change are significant challenges for Mediterranean viticulture, particularly in the Douro Valley, a prominent winemaking region. Silicon (Si) has gained attention as a potential solution for mitigating these environmental stresses, especially in areas with limited water resources. This study explores the foliar application of Si as a promising strategy to reduce water requirements in vineyards, specifically for the Touriga Franca variety, thereby supporting more sustainable water use. Four treatments were tested: non-irrigated control (C−), an irrigated control under a deficit irrigation regime (25% ETc; C+), and two Si concentrations (7% Si-Si1 and 20% Si-Si2) applied to non-irrigated plants. Results demonstrate that Si-treated plants improved physiological resilience, as evidenced by enhanced photosynthetic efficiency, greater water-use efficiency, and higher biochemical quality in both leaves and berries. Additionally, Si application increased leaf flavonoids and simultaneously improved must composition due to its overall influence on vine physiology, indicating its potential as a sustainable alternative to irrigation for reducing summer stress. This research suggests that foliar Si application could be a valuable, eco-friendly strategy to support sustainable viticulture under increasingly arid conditions, reducing the irrigation needs.

Keywords: silicon (Si); water stress; viticulture; climate change adaptation; *Vitis vinifera* L.

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1. Introduction

The ongoing trend of warmer and drier climates, driven by climate change, is expected to aggravate, presenting significant challenges to Portuguese viticulture, particularly in renowned winemaking regions like the Douro Demarcated Region (DDR). Among the three sub-regions of the Douro, the Douro Superior stands out as the most vulnerable to extreme weather conditions, especially in summer, characterized by intense radiation, high temperatures, and low precipitation. Future climate projections for this region [1] (https://www.advid.pt/uploads/DOCUMENTOS/Subcategorias/Comunicacao/The%20climate%20of%20the%20Douro-%20Structure,%20trends%20and%20mitigation%20and%20adaptation%20responses%20to%20a%20changing%20climate.pdf, accessed on 13 November 2024) predict shifts in precipitation patterns, rising temperatures and radiation levels, and more frequent severe drought events, which could negatively impact grape productivity, quality, and the distinct typicity of wines from this area. This scenario suggests that a reshaping of the main Portuguese winemaking regions may be inevitable in the coming decades. Therefore, it is imperative to develop and implement appropriate cultural practices to adapt to these climatic changes, thereby preserving the typicity and styles of wine [1].

Numerous studies have documented the adverse effects of water deficit and heat stress on vines and their fruits. These severe conditions can induce earlier phenology and short phenological intervals [2,3], disrupt vine metabolism [4], and increase transpiration [5,6]. Additionally, they can lead to a decline in photosynthesis due to stomatal and non-stomatal limitations, cause leaf damage and sunburn, inhibit anthocyanin synthesis, reduce volatile thiol precursors in berries, decrease yields due to smaller berry size, and heighten susceptibility to vine-related pests and diseases [7–11].

To address summer stress in viticulture, some winegrowers have implemented deficit irrigation strategies. These techniques are designed to maintain yields while preserving or even enhancing the quality of the berries. However, the inherent limitations of water resources in the region, coupled with the high costs and environmental unsustainability of large-scale water capture and distribution systems, underscore the need for low-cost, environmentally friendly adaptation strategies to minimize the negative impacts of climate change [12]. Silicon (Si) has emerged as a potential solution, acting as a leaf protector, biofilm, nutrient, or biostimulant. It can modulate plant responses, improving balance, growth, and development under abiotic and biotic stress conditions [12–17]. The benefits of Si in agriculture have been widely documented, with studies showing its ability to enhance growth, yield, and quality in various crops, including olive trees, tomatoes, corn, rice, and grapevines [18–21]. Si can induce multiple stress response mechanisms, including enhanced heat and drought tolerance, antioxidant defenses, and protection against pests and diseases [17,22–27]. Given its potential and considering the scarcity of water resources and the efforts to maintain unirrigated vineyards in the Douro region, we hypothesize that Si application could offer a viable alternative to deficit irrigation. Therefore, this study aims to evaluate the effects of foliar Si application on the physiological and biochemical behavior of Touriga Franca grapevine variety, comparing these effects with a deficit irrigation regime (25% of crop evapotranspiration, ETc) under Mediterranean climate conditions. The ultimate goal is to determine whether Si application can serve as an effective strategy for mitigating summer stress in viticulture, particularly in the challenging environmental conditions of the Douro Valley.

2. Materials and Methods

2.1. Climate Conditions

The experiment was carried out in 2021 in a commercial vineyard "Caves da Quinta do Pocinho" (41.129971094079046, −7.124811540877517), located in Santa Comba da Vilariça, the Douro Superior sub-region, considered the hottest and driest sub-region in the DDR [1]. The climate is typically Mediterranean-like, with a warm-temperate climate and dry and hot summers [28], with moderate precipitation during the winter and very low during the summer. Meteorological conditions (precipitation, and average and maximum temperature) prevailing during the experimental period are presented in Figure 1.

Climate data from 2021 (Figure 1) showed that the average temperature gradually increased from approximately 5 °C in January, peaking around 25 °C in July and August, before decreasing toward 9 °C by December. Maximum temperatures followed a similar pattern, reaching a peak of about 42 °C in August. Precipitation was highest in February, reaching around 96 mm, with a particularly dry period between July and August where rainfall was nearly absent. This dry period, coupled with high temperatures, suggests potential water stress for the grapevines, influencing irrigation requirements and physiological responses.

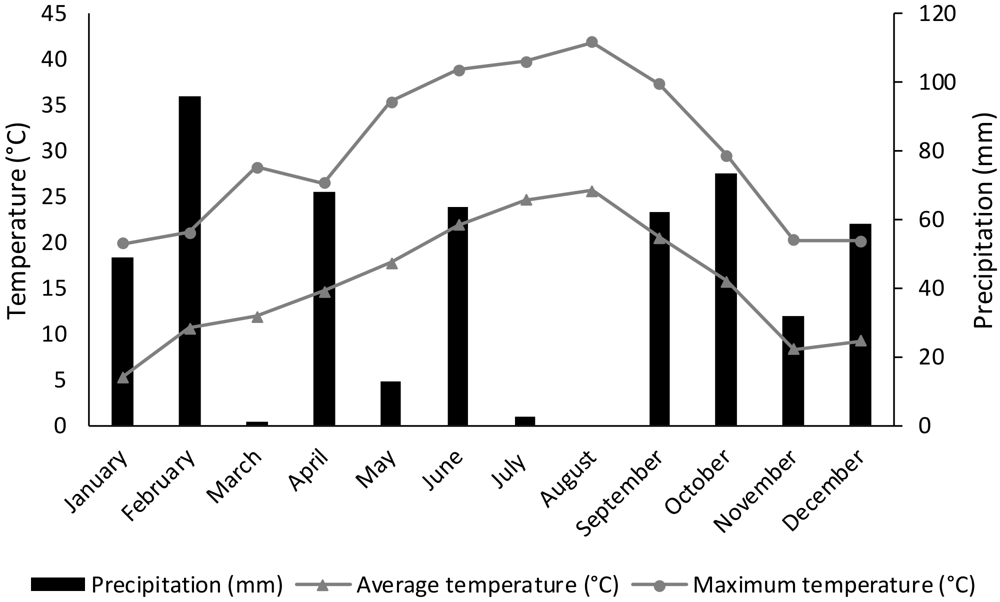

Figure 1. Climatic conditions (total precipitation and average and maximum temperature) of the experimental site during the year of 2021.

2.2. Plant Material and Experimental Design

The grapevine variety used was "Touriga Franca" (*Vitis vinifera* L.), a native Portuguese variety considered well adapted to drier environments with high incident solar radiation, trained in a Guyot pruning system with a N–S orientation, with a 90 cm intra-row distance and 2 m inter-row distance. During pruning, between 10 and 12 buds were left per spur and arc. Vineyard was planted in 2016 (5 years old) and rootstock 1103P was used. Plants were exposed to two levels of soil water availability throughout the growing season: (i) no irrigation and (ii) deficit irrigation (25% of crop evapotranspiration, ETc). Four distinct treatments were established as follows: (1) a non-irrigated control without Si application (C−, negative control); (2) a deficit-irrigated control receiving irrigation at 25% of crop evapotranspiration (ETc) without Si application (C+, positive control); (3) a non-irrigated treated with 7% Si solution, formulated with 15% SiO_2 (Si1); and (4) a non-irrigated treated with 20% Si solution, formulated with 22% SiO_2 and 10% elemental Si (Si2). The experimental set-up was designed to align with the specific characteristics of the commercial vineyard, ensuring uniform soil and climate conditions as well as consistent sunlight exposure across all treatments. A randomized block design was used, with each treatment applied to 3 blocks, each consisting of 10 grapevine plants. This design was chosen to minimize variability and ensure the reliability of the results.

Two Si foliar applications were carried out in different berry growth phenology stages, one at the pre-veraison stage (BBCH scale 71, 1 July 2021), and the second in the veraison stage (BBCH scale 81, 22 July 2021), for a total of 7.5 L for each treatment (approximately 1388 L per hectare). The ecophysiological measurements were carried out in two or three phenological stages: pre-veraison (1 July 2021), veraison (22 July 2021), and maturation (24 August 2021), while the material collection took place only at veraison and maturation stages. A schematic representation of the analysis performed in leaf and berry tissues is presented in Figure 2.

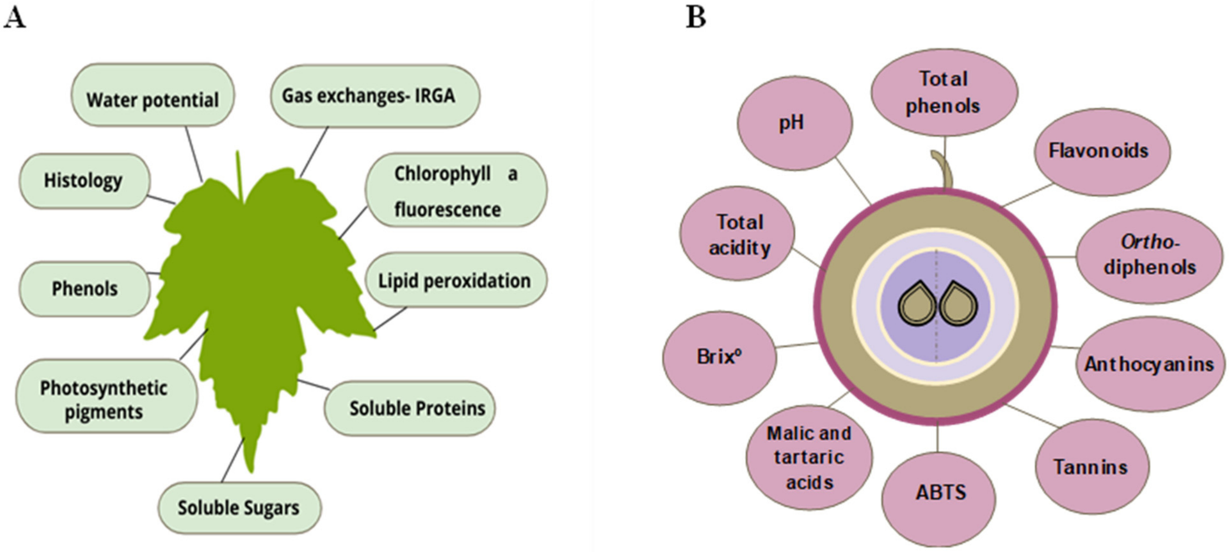

Figure 2. Parameters analyzed in the present study in both leaves (**A**) and fruits (**B**).

2.3. Ecophysiological Procedures

2.3.1. Leaf Water Potential

Leaf water potential (Ψ) was measured using a pressure chamber (Model 1000, PMS Instrument Company, Albany, NY, USA) [29]. For this, an adult leaf was selected from the middle third of the plant. Then, the end of the petiole was cut, and the leaf was introduced into the pressure chamber, leaving the end of the petiole outside the chamber. This chamber was hermetically closed as nitrogen was injected and the pressure increased. The moment the xylem flow reached the cut end was the moment the reference point was reached. At this stage, the gas input was stopped and the pressure value marked on the manometer was recorded. The value was expressed in Bars, displaying a negative value that characterizes the water retention forces, and was subsequently converted into megaPascal (MPa) [30].

Six leaves per treatment (two per block) were used in measurements carried out before dawn, that is, before the stomata opened, to assess the predawn water potential ($\Psi 0$). The leaf water potential at baseline ($\Psi 0$) was measured in the early morning (between 5 and 6 a.m.) for each of the four treatments (C−; C+; Si1 and Si2) at veraison (22 July 2021) and post-harvest (31 August 2021).

2.3.2. Leaf Gas Exchange and Chlorophyll a Fluorescence

Gas exchange parameters were determined in the morning (9:00–10:30 a.m.) and at midday (2:00–3:30 p.m.), in veraison and maturation stages, using an IRGA (InfraRed Gas Analyzer) model LCpro+, ADC, Hoddesdon, England. Net CO_2 assimilation rate (A), stomatal conductance (gs), transpiration rate (E), and internal CO_2 concentration/ambient CO_2 ratio (Ci/Ca) were calculated [31]. The A/gs ratio was used to estimate the intrinsic water use efficiency.

The chlorophyll a fluorescence measurement was evaluated only in the afternoon on the same leaves and stages used for gas exchange measurements (n = 6 per treatment). A pulse amplitude modulated fluorimeter was used (Mini-PAM, Photosynthesis Yield Analyzer; Walz, Effeltrich, Germany). The maximum quantum efficiency of photosystem II ($PSII$) was calculated as $Fv/Fm = (Fm - F0)/Fm$ by measuring the fluorescence signal from a dark-adapted leaf when all reaction centers are open using a low-intensity pulsed measuring light source ($F0$) and during a pulse saturating light (0.7 s pulse of 15,000 mol photons m^{-2} s^{-1} of white light) when all reactions centers are closed (Fm). Leaves were dark-adapted for 30 min using dark-adapting leaf-clips for these measurements. Following Fv/Fm estimation, after a 20 s exposure to actinic light (1500 mol m^{-2} s^{-1}), light-adapted steady-state fluorescence yield (Fs) was averaged over

2.5 s, followed by exposure to saturating light (15,000 µmol m^{-2} s^{-1}) for 0.7 s to establish Fm'. The sample was then shaded for 5 s with a far-red light source to determine $F0'$. From these measurements, several fluorescence attributes were calculated [32,33]: photochemical quenching ($qP = (Fm' - Fs)/(Fm' - F0')$), non-photochemical quenching ($NPQ = (Fm - Fm')/Fm$) and efficiency of electron transport as a measure of the quantum effective efficiency of $PSII$ ($\Phi PSII = \Delta F/Fm' = (Fm' - Fs)/Fm'$). The apparent electron transport rate [34] was estimated as $ETR = (\Delta F/Fm') \times PPFD \times 0.5 \times 0.84$, where PPFD is the photosynthetic photon flux density incident on the leaf, 0.5 is the factor that assumes the equal distribution of energy between the two photosystems, and the leaf absorbance used was 0.84 because this is the most common value for C3 plants [32].

2.4. Structural Traits

Leaves with the same attributes as those used for leaf gas exchange analysis were harvested for anatomical tissue assessments in the veraison and maturation stages. Leaf segments were taken from the middle of the leaves to ensure consistent thickness along the segments. These segments were subjected to a process that involved dehydration, clearing, and embedding in paraffin. Cross-sections of 4 µm were obtained using a rotary microtome, mounted on slides, and stained with toluidine blue. The thicknesses of various components, including the total lamina, palisade and spongy parenchyma, upper and lower epidermis, and cuticles were determined in the leaf cross-sections using an inverted optical microscope (Olympus IX51, Olympus Corporation, Tokyo, Japan) equipped with the image analysis software Cell^A, https://www.electrooptics.com/press-releases/cella-and-cellb accessed on 13 November 2024).

2.5. Leaf Metabolic Assays

Six leaves were randomly collected for each treatment at veraison and maturation stages and immediately stored in liquid nitrogen. In the laboratory, the leaves were macerated with liquid nitrogen and stored at −80 °C until analysis.

2.5.1. Photosynthetic Pigments

To quantify the photosynthetic pigments, 10 mg of sample (fresh weight—FW) and 4 mL of 80% acetone were used. The solution was then centrifuged at 1753× g at 4 °C for 10 min. After centrifugation, the absorbance was read at wavelengths of 663 nm, 645 nm, and 470 nm on a spectrophotometer (SPECTRUM star Nano, BMG Labtech GmbH, Ortenberg, Germany). As the pigments are photo and thermo-sensitive, the entire extraction and quantification process was carried out away from light and on ice. The photosynthetic pigments (chlorophyll *a*, *b*, and total; carotenoids; and the ratios between chlorophyll *a* and *b* and between total chlorophylls and total carotenoids) were calculated according to Arnon [35] and Lichtenthaler [36]. The results were expressed in µg mg^{-1} FW.

2.5.2. Lipid Peroxidation

The TBARS method (thiobarbituric acid reactive substances) was used for lipid peroxidation evaluation. Initially, two reagents were prepared for this method: 20% trichloroacetic acid (TCA) and the TBARS reagent. After that, 10 mg of sample (FW) and 3 mL of 20% TCA were added to each test tube. The sample was homogenized and centrifuged at 1753× g for 20 min at 4 °C. For the experimental procedure, 500 µL of supernatant, 500 µL of TBARS reagent, and 50 µL of 4% butylated hydroxytoluene (BHT) were used. As TBARS is photosensitive, the procedure was carried out away from light. The tubes were placed at 95 °C in a water bath for 30 min and then cooled on ice for 10 min. They were centrifuged again at 1342× g at 4°C for 20 min, and then the absorbances were read at 600 nm, 532 nm, and 440 nm [37–39].

2.5.3. Soluble Proteins

The soluble proteins were extracted using an extraction buffer containing phosphate (Fisher Scientific, Loughborough, UK) of pH 7.5 mixed with EDTA (ethylenediaminetetraacetic acid) (Panreac, Barcelona, Spain). The work solution included the extraction buffer described above, PMSF (Phenylmethanesulfonyl fluoride) (Panreac, Barcelona, Spain), and PVP (Polyvinylpyrrolidone) (Sigma, St. Louis, MO, USA), according to the method of Bradford [40] at 595 nm. The soluble proteins were expressed as milligram bovine serum albumin equivalents per gram of extract (mg BSAE g^{-1} FW).

2.5.4. Soluble Sugars

To determine the soluble sugars, 10 mg of each sample was extracted in 5 mL of 80% ethanol. The extract was homogenized and heated for 60 min at 80 °C in a water bath. The extracts were centrifuged at 15,777× *g*, and the supernatant was collected. In the next step, 250 µL of sample and 750 µL of anthrone were mixed, the tubes were refrigerated for 10 min at 4 °C and then incubated for 20 min at 100 °C. The absorbance was read at 625 nm [41]. The standard curve was made with glucose, and the values were expressed in mg g^{-1} of FW.

2.6. Fruit Phytochemical Analysis

In the veraison and maturation stages, 100 berries were randomly picked up from different branches (in triplicate, 100 berries per block, in a total of 300 berries per treatment) per treatment. In the laboratory, the berries were lyophilized (SCANVAC CoolSafe 55-4 Pro, LaboGene, Lynge, Denmark) for 120 h. Berries were grounded using liquid nitrogen until they formed a powdery texture and then stored for future analysis. The extraction was performed with 70% methanol, according to the protocol of Lemos et al. [42], resulting in a sample concentration of 4 mg mL^{-1}. The methanolic extracts will be used to determine the total phenols, *ortho*-diphenols, flavonoids, tannins, and total anthocyanins content.

2.6.1. Total Phenols

The total phenols were determined by the Folin–Ciocalteu method, and the absorbance was read at 725 nm [43]. It was expressed as mg gallic acid equivalents per gram of extract (mg GAE g^{-1} of dry weight, DW).

2.6.2. *Ortho*-Diphenols

For measuring the *ortho*-diphenols, the absorbance was read at 370 nm, according to the method by Granato et al. [44]. The standard curve was performed with gallic acid, and the values were expressed in mg g^{-1} DW.

2.6.3. Total Flavonoids

The aluminum chloride ($AlCl_3$) complex method at 510 nm, as described by Rodrigues et al. [43], was used for the quantification of the total flavonoids content of extracts. It was expressed as mg of catechin equivalents per gram of extract (mg CAE g^{-1} DW).

2.6.4. Total Tannins

The total tannins content was determined at 280 nm in UV-adapted microplates according to the methyl cellulose precipitable assay [45]. The concentration of tannins was obtained by subtracting the absorbance of methyl cellulose-treated samples and using epicatechin as standard. All measurements were performed in triplicate, and the results were expressed as mg ECE g^{-1} DW.

2.6.5. Total Anthocyanins

The total anthocyanins were quantified according to the differential pH method [46] and expressed as mg malvidin-3-*O*-glucoside equivalents (MVE) per gram of extract (mg MVE g^{-1}, DW). The absorbances were read at 520 nm and 700 nm.

2.7. Antioxidant Activity Analysis

The antioxidant activity of fruit samples was evaluated through ABTS method. The day before carrying out this protocol, a 7.4 mM ABTS radical solution was prepared with a 2.45 mM potassium persulfate solution, according to the protocol of Rodrigues et al. [43]. The following day, the ABTS radical was diluted in acetic acid solution (pH 4.5; 20 mmol) to obtain an absorbance of 0.700 at 734 nm. The values were determined at 734 nm and expressed in mmol g^{-1} DW.

2.8. Vegetative Growth Evaluation

2.8.1. Yield

The yield was obtained at full grape maturity (31 August 2021) from 15 vines per treatment (5 per block). The bunches per vine were weighed.

2.8.2. Ravaz Index

Using the results of the weight of pruning wood and yield, it is possible to calculate the Ravaz Index (RI). This parameter is usually used to quantify the vine balance, through the ratio between yield per vine (kg) and the weight of pruning wood. This index was calculated as follows:

$$\text{RI (kg)} = \text{Yield (kg)}/\text{Weight of pruning wood (kg)}$$

2.9. Must Composition Analysis

In order to perform the chemical analysis of grape juice (titratable acidity, pH, malic and tartaric acids, and Brix°), 100 berries per block (in triplicate, for a total of 300 berries per treatment) were randomly picked from different vines per treatment at veraison (one week after the last application, 22 July 2021), at 39 days after the last application (maturation stage, 24 August 2021), and at 46 days after the last application (harvest, 31 August 2021).

Brix° and Acidity Parameters

Brix was measured, using an ATAGO digital refractometer (CO., LTD., Tokyo, Japan). The brix scale or degrees brix° is numerically equal to the percentage of sugar and other dissolved solids in the solution [47]. Physico-chemical parameters, such as pH and titratable acidity, were analyzed according to the OIV methodologies [48]. The tartaric and malic acid were measured enzymatically (Miura One, TDI S.A., Barcelona, Spain), according to the work of Franquès et al. [49] and Escribano-Viana et al. [50].

2.10. Statistical Analysis

Data analysis was performed using the SPSS 20.0 software (SPSS Software, Chicago, IL, USA). After testing for analysis of variance (ANOVA) assumptions, statistical differences among treatments within each developmental stage were evaluated by one-way factorial ANOVA, followed by the post hoc Tukey test. Different lowercase letters represent significant differences ($p < 0.05$) between treatments.

3. Results and Discussion

3.1. Ecophysiological Responses

3.1.1. Leaf Water Potential

To assess the vine water status [51], the leaf water potential (Ψ) was measured, and the results are presented in Figure 3. The measurements of Ψ were taken in the predawn because it is believed that, at this time, there is a narrow equilibrium between the plant and the soil water potential. This occurs due to the absence of solar radiation and minimal leaf transpiration, creating stable conditions for accurate readings. Therefore, the initial water content in the vine is influenced by the water available in the soil, which impacts the leaf water potential [52].

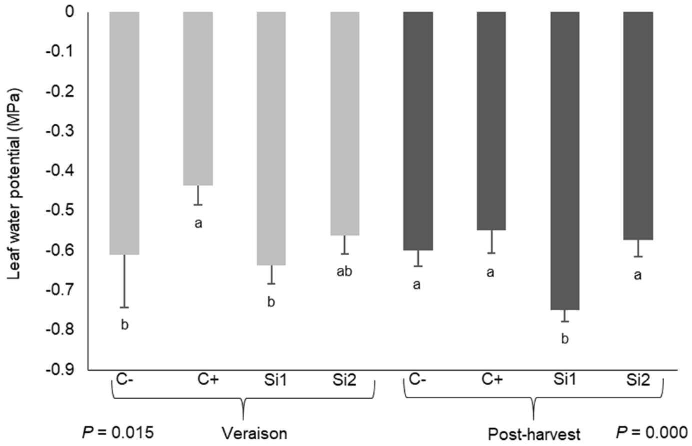

Figure 3. Predawn leaf water potential in Touriga Franca leaves subjected to four treatments: (i) negative control (no irrigation, "C−"), (ii) positive control (irrigation at 25%, "C+"), (iii) silicon 1 (SiO_2; "Si1"), and (iv) silicon 2 (SiO_2+ Si; "Si2") Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

According to Ojeda et al. [53], the level of water stress experienced by the plant can be quantified by the baseline water potential values. Considering this classification, the plants used in this work were under moderate to severe water stress. Indeed, at veraison, the Ψ0 of C+ (−0.43 MPa) was significantly higher than that of the C− and Si-treated plants, corresponding to a moderate stress level [53]. According to Prichard et al. [54], a moderate level of water stress in red wine varieties is considered beneficial for improving must quality since stress during veraison stimulates the synthesis of polyphenols, aromas, and other desirable compounds. If water availability increases, it can disrupt this process by reducing the mobilization of photoassimilates to the berries, potentially compromising fruit quality [55]. On the other hand, the vines with Si2 application exhibited a stress level considered moderate (−0.56 MPa), but close to the limit of severe water stress. In contrast, the Ψ0 of the C− and Si1 groups were statistically lower compared to C+, showing values around −0.61 and −0.63 MPa, respectively (Figure 3). Thus, during veraison, these treatments experienced a level of stress deemed severe, potentially leading to an inhibition of photosynthetic activity due to the reduced hydrolysis of stored starch reserves [55]. The lower Ψ0 values observed in non-irrigated vines in this study align with the findings of Ribeiro et al. [56], where non-irrigated Tinta Roriz vines consistently exhibited lower Ψ0 values compared to those irrigated at 20% and 40% of ET0 during the summer period.

Regarding the post-harvest period, a change in the behavior of Ψ0 between the treatments was observed. The Ψ0 values for the vines treated with Si1 (−0.75 MPa) were at a severe water stress level [53] and were significantly lower than all the other treatments. However, no significant differences were observed between the treatments C+ (−0.55 MPa), Si2 (−0.57 MPa), and C− (−0.60 MPa), which were considered under moderate to severe water stress [53].

Based on the results, plants treated with the highest Si concentration (Si2) showed Ψ0 values comparable to those of irrigated plants, highlighting the potential role of Si in reducing, or even replacing irrigation needs in grapevines. It is important to highlight that the plant's water status is related to its physiological behavior, particularly in gas exchange, as demonstrated by Ribeiro et al. [56], especially in the early morning period.

In general, a decrease in Ψ0 is observed from veraison to the post-harvest period, which may be related to the fact that post-harvest measurements were taken at the end of August, during the height of summer, when temperatures in the Douro Superior region are extremely high, reducing the vines' ability to restore their water status during the night.

3.1.2. Gas Exchange Parameters and Chlorophyll a Fluorescence

The gas exchange parameters of vines subjected to different irrigation regimes and Si applications are presented in Table 1. According to the results, statistically significant differences were only observed in the final stage of maturation during the morning. The Si2-treated plants showed significantly better behavior for net CO_2 assimilation rate (A) at maturation, indicating an increase of around 52% in the rate of photosynthesis compared to the control with irrigation (C+). This increase may be associated with the concentration of Si and the plant's ability to absorb and/or acquire this nutrient [57]. This potentially has a positive effect on photosynthesis and consequently contributes to better CO_2 fixation [58,59]. Pilon et al. [60] associated an increase in A in silicon-treated samples with an increase in the stomatal conductance (gs) and concentrations of chlorophyll *a* and carotenoids. In fact, in the present study, a significant increase in gs was also observed in plants with the application of the highest Si concentration (Si2), with a 70% increase compared to the control with irrigation (C+). When stomatal conductance increases, stomata open wider, allowing more CO_2 assimilation. This greater CO_2 uptake boosts photosynthesis, as CO_2 is essential for producing glucose in the Calvin cycle. While this increase in photosynthesis is beneficial, it also leads to higher water loss through transpiration (E), also observed in this work (an increase of approximately 43.5% compared to the vines with irrigation), which plants must manage to maintain water use efficiency. In fact, increased stomatal conductance enhances photosynthesis by improving CO_2 intake as long as plants can balance the resulting water loss [61]. Si could have influenced the plants to keep their stomatal flow active, increasing transpiration and consequently enabling greater gas exchange. According to Yin et al. [62] and Liu et al. [63], under stress conditions, this micronutrient can promote changes in the gas exchange, increasing stomatal conductance, transpiration rate, and CO_2 fixation. Such changes were also observed in table grapes treated with silicon in the Brazilian semi-arid region, in which the application of Si to the soil increased the photosynthetic efficiency of the grapevine by 5 to 33% compared to the control [64].

Vines treated with the lower Si concentration (Si1) exhibited significantly higher A/gs values compared with all the other plants. This behavior, only observed at morning period of maturation stage, suggests that lower Si concentrations may induce a mild stress response (corroborated by the lower $\Psi 0$ values observed in that plants), prompting the plant to adapt in ways that enhance water use efficiency. Specifically, these vines might be optimizing water use through mechanisms such as reduced transpiration or improved water conservation strategies. This adaptive response under lower silicon conditions can lead to more efficient utilization of water despite the lower overall photosynthetic activity. Other studies have demonstrated changes in gas exchange due to the effect of Si on wheat, rice, and sugar cane plants [65–67]. The results of these studies pointed to an increase in A, gs, E, and A/gs, thus alleviating the effects of limited irrigation and drought. In fact, the possible improvement by Si in these variables can be associated with the protective film formed by this nutrient, which protects the leaves from excessive radiation [24,25,68].

The chlorophyll *a* fluorescence results (Table 2) showed no statistical differences, except only for the photochemical quenching (qP) at veraison, and for the basal fluorescence (F_0) in the maturation stage.

At veraison, plants treated with Si2 treatment showed an increase of around 12% in the qP parameter, compared to the negative control. Although no significant differences were observed, these plants also exhibited slightly higher qP values compared to the irrigated plants (positive control). This parameter refers to the process by which light energy absorbed by chlorophyll is used in photosynthesis, specifically for the photochemical reactions in PSII [69]. Therefore, the vines treated with Si2 were more effective at using the absorbed light energy for photosynthetic processes rather than being dissipated as heat or re-emitted as fluorescence. This improvement could be due to silicon's role in enhancing the efficiency of the photosynthetic machinery, possibly by stabilizing the chloroplasts, improving the structure of the photosynthetic membranes, or protecting against stress conditions that could otherwise impair photosynthesis [70,71]. In the study conducted by

Maghsoudi et al. [72], the results of chlorophyll a fluorescence analysis revealed that Si application alleviated the adverse effects induced by water deficit by increasing F_v/F_m and qP, improving light use efficiency in the four wheat cultivars under stress.

Table 1. Gas exchange parameters (mean ± SD), namely transpiration rate (E, mmol m^{-2} s^{-1}), stomatal conductance (gs, mmol m^{-2} s^{-1}), intercellular carbon (Ci, µmol mol^{-1}), net CO_2 assimilation rate (A, µmol m^{-2} s^{-1}), intrinsic water use efficiency (A/gs, µmol mol^{-1}), and intercellular/atmospheric CO_2 concentration ratio (Ci/Ca), in veraison and maturation (morning and afternoon) in Touriga Franca leaves subjected to four treatments: (i) negative control (no irrigation, “C−”), (ii) positive control (irrigation at 25%, “C+”), (iii) silicon 1 (SiO_2; “Si1”), and (iv) silicon 2 (SiO_2+ Si; “Si2”). Different letters represent significant differences between the treatments at the same time of day and within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

	Veraison				
	C−	C+	Si1	Si2	p Values
	Morning				
E	2.36 ± 0.764	2.90 ± 0.100	2.35 ± 0.780	2.75 ± 0.406	0.511
gs	85.4 ± 35.2	99.4 ± 39.4	84.5 ± 36.7	94.3 ± 17.7	0.839
Ci	245.5 ± 18.3	240.9 ± 21.0	252.6 ± 23.6	254.5 ± 16.6	0.622
A	7.70 ± 3.64	8.89 ± 3.79	7.22 ± 3.73	7.75 ± 1.56	0.841
A/gs	88.1 ± 7.45	88.8 ± 10.3	83.7 ± 11.4	82.3 ± 9.53	0.596
Ci/Ca	0.592 ± 0.045	0.581 ± 0.051	0.611 ± 0.058	0.613 ± 0.041	0.601
	Midday				
E	1.36 ± 0.42	1.98 ± 0.651	1.14 ± 0.432	1.84 ± 0.522	0.062
gs	36.7 ± 11.5	53.9 ± 21.5	30.3 ± 12.2	51.1 ± 17.4	0.055
Ci	234.4 ± 41.9	216.9 ± 19.8	233.9 ± 34.5	233.7 ± 19.2	0.653
A	3.82 ± 1.62	5.84 ± 2.64	3.21 ± 1.92	4.94 ± 1.62	0.122
A/gs	98.5 ± 25.2	106.8 ± 10.3	99.6 ± 19.5	97.9 ± 12.0	0.768
Ci/Ca	0.563 ± 0.102	0.520 ± 0.047	0.562 ± 0.083	0.560 ± 0.047	0.652
	Maturation				
	C−	C+	Si1	Si2	p Values
	Morning				
E	2.14 ± 0.581 ab	1.95 ± 0.564 b	2.03 ± 0.526 ab	2.80 ± 0.384 a	0.027
gs	73.3 ± 18.5 b	66.7 ± 12.7 b	91.8 ± 19.0 ab	112.8 ± 20.7 a	0.034
Ci	245.2 ± 9.36	251.0 ± 12.8	238.8 ± 11.1	253.4 ± 7.20	0.080
A	7.53 ± 2.00 ab	6.15 ± 1.93 b	8.75 ± 1.65 ab	9.34 ± 1.61 a	0.066
A/gs	91.4 ± 7.14 ab	87.3 ± 7.51 ab	94.6 ± 5.62 a	82.9 ± 4.03 b	0.014
Ci/Ca	0.589 ± 0.023	0.605 ± 0.031	0.572 ± 0.028	0.608 ± 0.018	0.070
	Midday				
E	1.73 ± 0.310	2.69 ± 0.640	1.94 ± 0.939	1.77 ± 0.600	0.493
gs	39.1 ± 7.24	61.3 ± 17.5	37.9 ± 13.4	38.7 ± 14.2	0.559
Ci	246.9 ± 56.4	226.1 ± 19.7	223.7 ± 61.3	227.8 ± 36.9	0.815
A	3.92 ± 0.960	5.77 ± 1.44	5.00 ± 1.06	4.14 ± 1.10	0.431
A/gs	101.6 ± 20.4	100.1 ± 14.5	102.9 ± 40.1	100.3 ± 25.2	0.874
Ci/Ca	0.593 ± 0.137	0.544 ± 0.049	0.540 ± 0.149	0.549 ± 0.091	0.833

In the maturation stage, C− plants showed an increase of around 30% in the F_0 parameter, compared to Si2 treatment. This increase in F_0 indicates that these plants were likely experiencing stress, which led to a reduction in the efficiency of PSII [73]. When PSII is less efficient, more energy is released as fluorescence rather than being used for photosynthesis, leading to higher F_0 levels. The increase in this parameter suggests that the photosynthetic apparatus in the control plants was less functional, possibly due to stress factors like drought, which can damage or impair the PSII complexes [74,75]. On the other hand, Si2 plants presented the lowest values for F_0 parameter, indicating that this concentration of Si may have helped protect or stabilize the PSII reaction centers, allowing the plants to maintain better photosynthetic efficiency [69].

Table 2. Chlorophyll *a* fluorescence parameters: basal fluorescence (F_0), maximum quantum efficiency of photosystem II (F_v/F_m), effective efficiency of PSII ($\Phi PSII$), photochemical (qP), and non-photochemical (NPQ) quenching and electron transport rate (ETR, µmol m^{-2} s^{-1}), in the afternoon at the pre-veraison, veraison, and maturation stages, in Touriga Franca leaves subjected to four treatments: (i) negative control (no irrigation, "C−"), (ii) positive control (irrigation at 25%, "C+"), (iii) silicon 1 (SiO_2; "Si1"), and (iv) silicon 2 (SiO_2+ Si; "Si2"). Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

Pre-veraison					
	C−	C+	Si1	Si2	p Values
F_0	385.0 ± 66.1	327.3 ± 116.4	358.1 ± 58.2	348.5 ± 76.2	0.825
F_v/F_m	0.803 ± 0.03	0.827 ± 0.053	0.806 ± 0.042	0.801 ± 0.044	0.645
$\Phi PSII$	0.259 ± 0.08	0.252 ± 0.089	0.239 ± 0.072	0.213 ± 0.099	0.876
qP	0.664 ± 0.06	0.565 ± 0.121	0.642 ± 0.087	0.634 ± 0.075	0.196
ETR	82.8 ± 36.7	64.1 ± 37.8	52.8 ± 38.9	45.8 ± 27.4	0.326
NPQ	2.77 ± 0.90	3.00 ± 0.306	2.72 ± 0.466	3.15 ± 1.07	0.675
Veraison					
	C−	C+	Si1	Si2	p Values
F_0	313.8 ± 72.6	273.9 ± 76.8	334.9 ± 95.7	286.7 ± 78.6	0.302
F_v/F_m	0.809 ± 0.058	0.823 ± 0.046	0.776 ± 0.064	0.816 ± 0.050	0.201
$\Phi PSII$	0.128 ± 0.04	0.136 ± 0.036	0.147 ± 0.045	0.148 ± 0.021	0.491
qP	0.616 ± 0.069 b	0.667 ± 0.052 ab	0.678 ± 0.071 ab	0.687 ± 0.055 a	0.046
ETR	70.2 ± 23.9	74.9 ± 20.3	81.6 ± 27.5	80.3 ± 9.80	0.571
NPQ	4.69 ± 0.924	4.44 ± 0.76	4.55 ± 0.68	4.79 ± 0.530	0.684
Maturation					
	C−	C+	Si1	Si2	p Values
F_0	406.0 ± 108.0 a	344.0 ± 81.4 ab	362.4 ± 34.3 ab	314.3 ± 36.0 b	0.058
F_v/F_m	0.724 ± 0.125	0.784 ± 0.077	0.769 ± 0.042	0.791 ± 0.056	0.253
$\Phi PSII$	0.099 ± 0.051	0.143 ± 0.052	0.110 ± 0.054	0.121 ± 0.034	0.169
qP	0.597 ± 0.091	0.662 ± 0.126	0.638 ± 0.122	0.620 ± 0.113	0.562
ETR	53.1 ± 26.4	66.6 ± 30.1	59.4 ± 26.1	71.1 ± 16.9	0.397
NPQ	4.91 ± 1.73	3.67 ± 1.00	4.89 ± 1.00	4.69 ± 1.89	0.144

Although there were no statistically significant differences between treatments for the F_v/F_m parameter, it is notable that at the maturation stage, the F_v/F_m ratio of C− plants (0.724) falls below the optimal range of 0.75 to 0.85, as established by Bolhar-Nordenkampf et al. [76]. Therefore, when the F_v/F_m ratio falls within this optimal range, it indicates that the plant's photosynthetic apparatus is functioning properly and remains intact. However, a decrease in this ratio below the established limits, as observed in C− plants, suggests the presence of photoinhibitory damage to the PSII reaction centers, indicating that the plant is under stress and that its photosynthetic efficiency has been compromised [74,76,77]. Additionally, the trend of higher F_v/F_m values observed in Si2 plants (despite no significant difference being found) may be related to the protection of the photosynthetic apparatus [78]. Recent studies conducted on table grapes and wheat in dry and arid climates have confirmed the beneficial effects on fluorescence parameters after the application of Si [64,72]. Indeed, both studies revealed that the plants suffered less damage to the photosynthetic apparatus, improving their performance when subjected to water and heat stress conditions.

3.2. Leaf Structural Traits and Biochemical Parameters

According to the results of leaf histological evaluation (Table 3), in the veraison stage, the Si-treated plants (Si2) showed a significantly higher thickness of the upper cuticle, with an increase of approximately 50% and 15.2% over the C+ and C−, respectively. At the maturation stage, these plants also presented a significantly higher thickness of the upper cuticle and epidermis and palisade parenchyma. Moreover, in relation to the thickness of upper cuticle, at maturation stage, plants with applications of both Si2 and Si1 presented increases of around 45.5% and 34%, respectively, compared to the irrigated plants (C+ treatment).

Table 3. Values (mean ± SD) of the length of total leaf thickness (µm), upper cuticle (µm), upper epidermis (µm), palisade parenchyma (µm), spongy parenchyma (µm), and lower epidermis (µm) in Touriga Franca leaves harvested at veraison and maturation stages, leaves subjected to four treatments: (i) negative control (no irrigation, “C−”), (ii) positive control (irrigation at 25%, “C+”), (iii) silicon 1 (SiO_2; “Si1”), and (iv) silicon 2 (SiO_2+ Si; “Si2”). Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

	Veraison				
	C−	C+	Si1	Si2	*p* Values
Total lamina	181.8 ± 13.1	178.6 ± 17.6	171.0 ± 16.7	175.8 ± 23.6	0.295
Upper cuticle	1.91 ± 0.271 b	1.47 ± 0.279 c	2.08 ± 0.382 ab	2.20 ± 0.360 a	<0.001
Upper epidermis	17.3 ± 3.07 a	16.2 ± 1.95 ab	14.8 ± 3.21 b	16.8 ± 2.09 ab	0.028
Palisade parenchyma	55.7 ± 9.38	55.6 ± 6.30	58.8 ± 7.91	59.3 ± 11.7	0.332
Spongy parenchyma	84.3 ± 12.3 a	76.2 ± 11.6 b	77.7 ± 11.1 ab	71.3 ± 10.8 b	0.001
Lower epidermis	18.2 ± 2.13	17.3 ± 2.70	17.1 ± 4.91	19.1± 3.22	0.193
	Maturation				
	C−	C+	Si1	Si2	*p* Values
Total lamina	170.8 ± 16.7	167.8 ± 13.9	175.1 ± 11.5	179.7 ± 12.8	0.381
Upper cuticle	1.80 ± 0.322 ab	1.43 ± 0.261b	1.91 ± 0.240 a	2.08 ± 0.310 a	0.002
Upper epidermis	13.7 ± 1.63 b	17.2 ± 1.79 a	15.3 ± 1.87 ab	16.7 ± 1.90 a	0.002
Palisade parenchyma	58.9 ± 9.78 ab	56.3 ± 7.1 b	60.2 ± 6.11 ab	68.4 ± 3.32 a	0.052
Spongy parenchyma	83.7 ± 10.4	77.4 ± 8.00	84.6 ± 9.75	76.8 ± 10.8	0.300
Lower epidermis	15.1 ± 2.33	18.1 ± 1.63	17.7 ± 1.99	17.9 ± 2.69	0.064

At the maturation stage, in addition to the increase in the thickness of the upper cuticle, the leaves from C+- and Si2-treated vines presented significantly higher thickness of the epidermis than the negative control plants (C−), with increases of around 26 and 22%, respectively (Table 3). The palisade parenchyma measurements of the leaves of Si2-treated plants showed an increase of 21.5% compared to the C+-treated plants. No significant differences were observed in the measurements of the spongy parenchyma and lower epidermis. These results also highlight the ability of Si (especially when applied at higher concentrations) to match or even exceed the benefits of irrigation.

The increase in the thickness of leaf cuticles after Si application was also observed in the studies developed by Ferrón-Carrillo and Urrestarazu [79] and Pozo et al. [80] on cucumber, pepper, melon, tomato, and lettuce. Based on the evidence, this nutrient can accumulate beneath the leaf cuticle, forming a double layer (cuticle–silicon) on the leaf surface, which may have contributed to the increased cuticle thickness observed in the Si-treated samples [17,22]. Consequently, this increase in cuticle thickness can prevent water loss through transpiration because the Si creates a physical/mechanical barrier in the leaves, limiting the transmission of UV-B radiation preventing radiative and thermal stress [57,81–84]. The increase in the thickness of the palisade parenchyma may be associated with improvements in photosynthetic efficiency. According to Castro et al. [85], the plant’s photosynthetic capacity is related to the amount of photosynthetic pigments present in the leaf tissues. Thus, the increase in the thickness of the palisade parenchyma following Si application may be linked to the enhanced rate of photosynthesis observed in the Si2-treated plants (Table 1). This increase in photosynthetic efficiency likely led to anatomical changes in the leaf, potentially optimizing CO$_2$ flow and improving water utilization [86,87].

The photosynthetic pigments quantified in the leaves of the different treatments are presented in Table 4. During the veraison stage, the Si1-treated plants showed significantly higher values for the parameters Chl *a*, Chl *b*, total Chl, and total Car. However, in the maturation stage, the results for the same parameters were the opposite from that obtained at the veraison stage. Indeed, at maturation, both control groups exhibited significantly higher values for all the analyzed parameters except for total Car, where Si2-treated plants showed the highest values. The increase in chlorophyll pigments after Si application observed at veraison stage was also observed in other studies with chestnuts [60], potatoes [88], and sugarcane [89], where they showed increases in Chl *a*, Chl *b*, the Chl *a*/*b* ratio, and carotenoids in plants under water stress conditions. This nutrient may have caused an increase in tolerance to UV-B stress and the production of chlorophylls a and b in these plants [24]. Additionally, Si can reduce the impact of oxidative stress by increasing the synthesis of protective pigments like carotenoids, which act as antioxidants. This overall enhancement in photosynthetic pigments reflects silicon's role in boosting the plant's ability to capture and utilize light energy more effectively, leading to improved growth and development.

Table 4. Concentrations of soluble sugars (mg g^{-1}), total phenols (mg g^{-1}), proteins (mg g^{-1}), thiobarbituric acid reactive species (TBARS, mmol eq. MDA g^{-1}), and photosynthetic pigments—Chlorophyll *a* (Chl *a*; µg mg^{-1}); chlorophyll *b* (Chl *b*; µg mg^{-1}); total chlorophyll (Total Chl; µg mg^{-1}); total carotenoids (Total Carot; µg mg^{-1}); ratio of Chl *a*/Chl *b*; and ratio of total chlorophyll/total carotenoids (Total Chl/total Car)—in Touriga Franca leaves subjected to four treatments: (i) negative control (no irrigation, "C−"), (ii) positive control (irrigation at 25%, "C+"), (iii) silicon 1 (SiO$_2$; "Si1"), and (iv) silicon 2 (SiO$_2$+ Si; "Si2"). Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

Veraison					
	C−	C+	Si1	Si2	*p* Values
Sugars	87.9 ± 6.03 b	112.4 ± 12.1 a	108.5 ± 14.3 a	92.0 ± 2.63 b	0.001
Phenols	484.4 ± 22.8 c	547.4 ± 37.8 b	657.9 ± 26.4 a	663.8 ± 36.0 a	0.000
Proteins	1.40 ± 0.31 b	2.10 ± 0.152 a	2.25 ± 0.270 a	1.58 ± 0.132 b	0.000
TBARS	2.13 ± 0.388 b	1.59 ± 0.348 b	6.30 ± 1.07 a	6.81 ± 1.24 a	0.000
Chl *a*	0.785 ± 0.077 bc	0.863 ± 0.032 b	0.960 ± 0.047 a	0.708 ± 0.056 c	0.000
Chl b	0.678 ± 0.085 a	0.548 ± 0.024 b	0.726 ± 0.021 a	0.518 ± 0.040 b	0.000
Total Chl	1.33 ± 0.137 b	1.38 ± 0.095 b	1.68 ± 0.059 a	1.22 ± 0.092 b	0.000
Totals Car	0.256 ± 0.011 b	0.288 ± 0.015 a	0.275 ± 0.018 ab	0.220 ± 0.008 c	0.000
Chl *a*/Chl *b*	1.39 ± 0.024 b	1.52 ± 0.058 a	1.29 ± 0.058 c	1.38 ± 0.016 b	0.000
Total Chl/ total Car.	5.54 ± 0.163 bc	5.02 ± 0.251 c	6.46 ± 0.396 a	5.64 ± 0.531 b	0.000
Maturation					
	C−	C+	Si1	Si2	*p* Values
Sugars	41.6 ± 4.03 c	59.7 ± 5.68 b	47.7 ± 2.11 c	71.9 ± 6.84 a	0.000
Phenols	336.2 ± 41.9 c	347.1 ± 30.3 c	742.8 ± 31.9 a	466.8 ± 30.7 b	0.000
Proteins	1.38 ± 0.188 b	2.39 ± 0.159 a	2.39 ± 0.139 a	2.42 ± 0.223 a	0.000
TBARS	3.54 ± 0.387 b	3.34 ± 0.330 b	20.8 ± 3.34 a	23.1 ± 1.99 a	0.000
Chl *a*	1.11 ± 0.010 a	1.11 ± 0.045 a	0.610 ± 0.009 b	0.598 ± 0.045 b	0.000
Chl *b*	0.783 ± 0.038 a	0.771 ± 0.059 a	0.533 ± 0.037 b	0.566 ± 0.034 b	0.000
Total Chl	1.93 ± 0.027 a	1.90 ± 0.100 a	1.16 ± 0.078 b	1.12 ± 0.065 b	0.000
Totals Car	0.340 ± 0.007 a	0.308 ± 0.010 b	0.151 ± 0.008 c	0.151 ± 0.012 c	0.000
Chl *a*/Chl *b*	1.36 ± 0.006 a	1.33 ± 0.023 a	1.11 ± 0.015 b	1.05 ± 0.033 c	0.000
Total Chl/ total Car.	5.81 ± 0.075 c	6.11 ± 0.136 c	7.57 ± 0.288 b	8.10 ± 0.326 a	0.000

At the harvest stage (31 August 2021), the degradation in the levels of photosynthetic pigments may be associated with a higher water deficit associated with high light intensity, which caused an increase in chlorophyll excitation states. This can reduce photosynthetic efficiency through photoinhibition, preventing the synthesis of new chlorophyll [90].

In addition, at both stages of development, TBARS levels were significantly higher in the Si-treated plants (both Si1 and Si2) (Table 4). This behavior may also be associated with deterioration in the amount of chlorophyll, induced by environmental stresses that generate reactive oxygen species (ROS) [91–93], which can cause oxidative damage to lipids, proteins, pigments, and nucleic acids [94,95].

However, while the Si1- and Si2-treated vines produced higher levels of TBARS, these treatments also showed statistically significant increases for sugars, phenols, and proteins, as shown in Table 4. One possible explanation for the higher TBARS levels in Si-treated plants could be that the Si treatment induces oxidative stress in the plants, leading to increased lipid peroxidation, as reflected by the higher TBARS levels. This stress might be a response to the treatment itself, or it could be part of a defense mechanism activated by the plant. However, the increase in phenols and proteins suggests that the plants are also engaging in stress response mechanisms to cope with the oxidative stress. Sugars might be elevated as a result of enhanced metabolic activity or as an energy reserve in response to stress. Because sugars are essential elements produced by plants, they are crucial for photosynthetic processes and for the composition of the berry [55]. Phenols, in general, are often involved in plant defense mechanisms and could be increasing as the plant tries to counteract the oxidative damage. Proteins, including stress-related ones, might be upregulated to help mitigate the damage and repair cellular components.

The biochemical parameters of the berries from plants subject to the different treatments were also assessed at the veraison and maturation stages, and these results are presented in Table 5. The results showed that Si1 and C+ plants presented similar levels of phenols and *ortho*-diphenols, showing a significant increase comparing with C−, with increases of around 24% for phenols and 12% for *ortho*-diphenols. Moreover, plants treated with the Si1 application exhibited significantly higher flavonoid levels compared to Si2, and this effect persisted throughout the ripening process.

Table 5. Concentrations of phenolic compounds (mg g^{-1}), antioxidant activity by the ABTS method (mg g^{-1}), anthocyanins (mg g^{-1}), and tannins (mg g^{-1}) of Touriga Franca berries subjected to four treatments: (i) negative control (no irrigation, "C−"), (ii) positive control (irrigation at 25%, "C+"), (iii) silicon 1 (SiO_2; "Si1"), and (iv) silicon 2 (SiO_2+ Si; "Si2"). Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

			Veraison		
	C−	C+	Si1	Si2	*p* Values
Phenols	23.9 ± 1.17 b	30.9 ± 2.67 a	28.3 ± 2.46 a	24.5 ± 0.941 b	0.000
Ortho-diphenols	25.1 ± 0.951 b	28.1 ± 1.78 a	27.7 ± 2.07 a	27.0 ± 0.758 ab	0.010
Flavonoids	18.6 ± 5.85 ab	17.8 ± 5.66 ab	20.1 ± 3.19 a	12.6 ± 0.452 b	0.043
ABTS	22.7 ± 8.19 c	52.4 ± 6.85 a	47.2 ± 11.6 ab	34.9 ± 6.94 bc	0.000
Anthocyanins	5.20 ± 0.26 a	4.56 ± 0.140 b	4.32 ± 0.300 bc	4.04 ± 0.480 c	0.000
Tannins	21.0 ± 2.61 b	29.9 ± 3.75 a	22.2 ± 2.32 b	23.5 ± 2.32 b	0.001
			Maturation		
	C−	C+	Si1	Si2	*p* Values
Phenols	25.3 ± 2.88 a	21.1 ± 1.42 b	18.1 ± 0.571 c	16.3 ± 1.02 c	0.000
Ortho-diphenols	24.2 ± 0.900 ab	25.2 ± 0.629 a	23.9 ± 0.430 b	25.0 ± 0.910 ab	0.021
Flavonoids	8.30 ± 1.63 ab	9.82 ± 3.23 ab	14.6 ± 8.10 a	6.88 ± 1.46 b	0.037
ABTS	29.1 ± 5.86 ab	32.8 ± 4.87 a	31.2 ± 2.73 ab	25.4 ± 1.69 b	0.032
Anthocyanins	4.48 ± 0.156 b	5.45 ± 0.300 a	5.27 ± 0.310 a	3.61 ± 0.127 c	0.000
Tannins	7.60 ± 3.62 b	8.99 ± 1.23 ab	3.57 ± 1.88 c	11.3 ± 1.36 a	0.000

At the veraison stage, the concentrations of ABTS, tannins, and anthocyanins did not present improvements due to Si application (Table 5).

However, at the maturation stage, Si1 plants showed a 17.7% increase in the concentration of anthocyanins compared to C−, and Si2 treatments exhibited a 48.7% increase in the concentration of tannins, compared with the same group.

In general, the application of Si led to notable increases in phenolic compounds, especially during the veraison stage, which is a crucial period when grapes begin to change color and develop flavor.

As the berries advanced to the maturation stage, the silicon treatment continued to positively influence the levels of flavonoids, anthocyanins, and tannins. Flavonoids, which include a range of compounds, are crucial for various taste sensations and play a significant role in the evolution of wine [96–98]. Additionally, flavonoids, anthocyanins, and tannins are vital for the color, flavor, and overall quality of both the berries and the resulting wine quality [99]. This suggests that silicon not only boosts the initial accumulation of phenolic compounds but also enhances the development of key compounds throughout the later stages of berries ripening, ultimately benefiting the wine's quality. Despite that, the observed decrease in flavonoids and stable anthocyanin levels from veraison to maturity could reflect a partial response to environmental conditions rather than complete pigment development in the berries.

3.3. Yield and Ravaz Index (RI)

The cluster weight from vines subject to the different treatments is presented in Figure 4A. The results show that the values were similar across the treatments, with no significant differences observed. This suggests that neither the silicon-based treatments nor irrigation had a significant impact on cluster weight or overall yield.

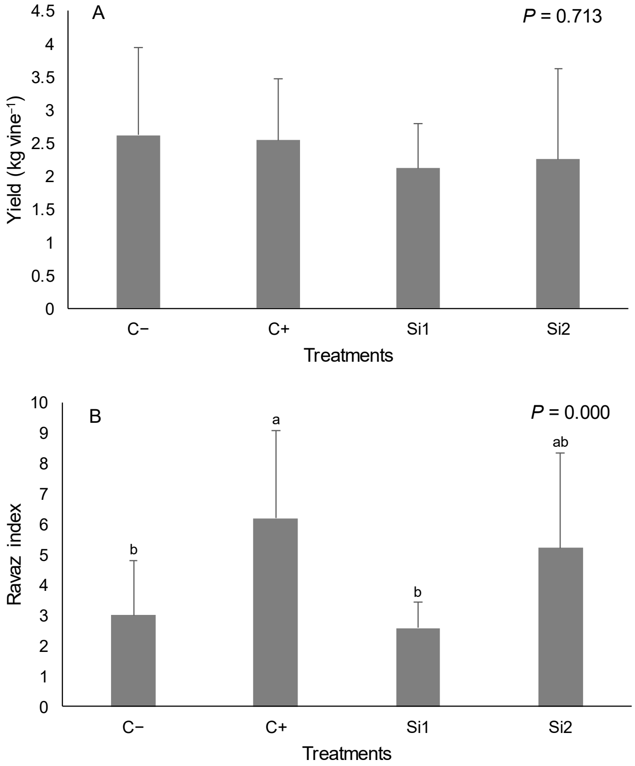

Figure 4. (**A**) Yield (kg vine^{-1}) and (**B**) Ravaz Index of Touriga Franca vines subjected to four treatments: (i) negative control (no irrigation, "C−"), (ii) positive control (irrigation at 25%, "C+"), (iii) silicon 1 (SiO_2; "Si1"), and (iv) silicon 2 (SiO_2+ Si; "Si2"). Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

The Ravaz Index (RI) is a widely used metric in viticulture that assesses the balance between the vegetative growth and the yield per vine. It is calculated as the ratio of yield (cluster mass/vine) to pruning shoot weight (vegetative growth). The RI is an important indicator of vine vigor and its balance, with different ranges suggesting varying levels of vine health and productivity. In the RI calculations presented in Figure 4B, it was observed that plants with irrigation (C+) and with the application of the highest Si concentration (Si2) exhibited the highest RI values. According to the reference values established by Smart and Robinson [100] and Bravdo et al. [101], an RI value below 5 may indicate excessive vigor, where the vine's energy is overly directed toward vegetative growth at the expense of fruit production. Conversely, an RI value above 10 can suggest underproduction, where the vine is producing less fruit yield relative to its vegetative growth, potentially leading to lower overall productivity. The results from this study indicate that the vines in the Si2 treatment achieved an RI of approximately 5.1, positioning them near the lower limit of the ideal range (5 to 10), suggesting a balanced growth-to-production ratio. On the other hand, the C+ treatment showed an RI of 6.6, indicating a relatively balanced vine balance between yield and pruning weight.

These findings suggest that the Si2 and C+ treatments produced the most favorable RI values, indicating a better balance between vegetative growth and yield, which is often associated with optimal vine performance under these conditions. This balance is crucial for producing high-quality grapes, as it ensures that the vine is neither overly vegetative nor underproductive, leading to better overall vineyard management and potentially higher-quality wine production.

3.4. Must Composition

The composition of the must derived from grapes subject to the different treatments is detailed in Table 6.

Table 6. Chemical analysis of grape juice (titratable acidity, pH, malic and tartaric acid, and Brix°) of Touriga Franca berries subjected to four treatments: (i) negative control (no irrigation, "C−"), (ii) positive control (irrigation at 25%, "C+"), (iii) silicon 1 (SiO_2; "Si1"), and (iv) silicon 2 (SiO_2+ Si; "Si2"). Different letters represent significant differences between the treatments within the same phenological stage. The absence of letters indicates that there are no significant differences between treatments.

			Veraison		
	C−	C+	Si1	Si2	*p* Values
Titratable acidity	11.7 ± 0.520 a	11.0 ± 1.06 ab	9.88 ± 0.433 bc	9.25 ± 0.434 c	0.006
pH	2.94 ± 0.021 c	2.98 ± 0.021 bc	3.04 ± 0.027 ab	3.06 ± 0.027 a	0.001
Malic acid	4.52 ± 0.243	4.36 ± 0.675	4.39 ± 0.254	4.68 ± 0.151	0.750
Tartaric acid	5.86 ± 0.209 a	4.96 ± 0.379 b	4.40 ± 0.344 b	3.60 ± 0.200 c	0.000
Brix°	13.7 ± 0.200 b	13.1 ± 0.289 b	15.1 ± 0.612 a	16.0 ± 0.436 a	0.000
			Maturation		
	C−	C+	Si1	Si2	*p* Values
Titratable acidity	5.39 ± 0.140 a	4.71 ± 0.195 b	5.25 ± 0.076 a	5.00 ± 0.192 ab	0.004
pH	3.62 ± 0.038	3.55 ± 0.020	3.61 ± 0.037	3.57 ± 0.016	0.061
Malic acid	1.70 ± 0.122 ab	1.37 ± 0.165 b	1.79 ± 0.187 a	1.67 ± 0.147 ab	0.054
Tartaric acid	2.96 ± 0.105 a	2.71 ± 0.058 ab	2.83 ± 0.077 ab	2.63 ± 0.176 b	0.031
Brix°	18.6 ± 0.306 b	19.1 ± 0.400 b	20.1 ± 0.405 a	20.1 ± 0.207 a	0.002
			Harvest		
	C−	C+	Si1	Si2	*p* Values
Titratable acidity	4.75 ± 0.156 ab	4.18 ± 0.131 c	4.43 ± 0.046 bc	4.96 ± 0.191 a	0.001
pH	3.63 ± 0.033	3.55 ± 0.036	3.58 ± 0.082	3.65 ± 0.040	0.155
Malic acid	1.52 ± 0.229	1.42 ± 0.143	1.51 ± 0.203	1.46 ± 0.159	0.905
Tartaric acid	2.73 ± 0.141	2.78 ± 0.111	2.78 ± 0.111	2.78 ± 0.111	0.934
Brix°	21.1 ± 0.500 b	20.9 ± 0.153 b	22.8 ± 0.405 a	22.8 ± 0.100 a	0.000

At the veraison stage, C− plants showed significantly higher levels of tartaric acid (5.86 g L^{-1}) and titratable acidity (11.7 g L^{-1} eq. tartaric acid) compared to the silicon-based treatments, representing an increase in the acidity of approximately 18.5% and 26.5% compared to plants treated with Si1 and Si2, respectively. The acidity present in grape berries is one of the main characteristics that influence the organoleptic quality of berries and wine [102]. Variations in titratable acidity occur mainly due to the degradation of malic and tartaric acids, which account for about 90% of the titratable acidity in the berries [55]. However, in terms of Brix measurements, the plants treated with both concentrations of Si (Si1 and Si2) presented significantly higher values than the other plants, showing increases of about 16% compared to C− and C+. Additionally, significant differences in pH levels were observed only at veraison, where the must from plants subject to the application of Si2 exhibited a higher average pH (3.06) compared to the other plants, which is also corroborated by the lowest acidity level observed in Si2-treated plants. pH is considered one of the most important parameters to evaluate wine quality and stability in aging [103]. According to Champagnol [104], reference values should range between 2.3 and 2.9 during veraison and between 3.5 and 3.6 at the full maturity. Observing the obtained data, the values exceeded the reference threshold at veraison but remained within the reference threshold during ripening, ranging between 3.55 and 3.62.

No significant differences in malic acid content were observed at the veraison. However, we found that as the berries matured, there was a reduction in its levels, which is common since, at full maturity, this acid is very unstable. Indeed, in regions characterized by high temperatures, such as the Douro region, malic acid degradation can occur, resulting in grapes with lower acidity and higher pH [105–108]. Under high-temperature conditions, not only does malic acid degrade, but tartaric acid accumulation is also minimal. As a result, wine quality is significantly diminished.

At maturation stage, soluble solids levels (Brix°) were significantly higher in plants with application of Si (Si1 and Si2), compared to both control groups. Simultaneously, plants treated with Si1 also presented significantly higher levels of malic acid (increase of 30.7%), which is very important for wine quality and stability, and consequently higher acidity (increase of 12.9%), compared to C+ plants.

Regarding the harvest stage, the plants with Si2 application presented significantly higher titratable acidity and Brix degree compared to the control samples. Some studies also have demonstrated the positive effects of silicon-based foliar sprays, revealing an increase in titratable acidity and the concentrations of tartaric and malic acids, which can be positive in some varieties, especially the white ones, as well as an increase in fruit weight and total sugar content [64,109]. Additionally, in the same phenological stage, plants treated with Si1 only showed a higher Brix degree.

Among all the grape juice chemical parameters evaluated, the Brix degree was the only one that showed statistically higher values under the influence of the Si2 and Si1 treatments during all three developmental stages (Table 6). According to Magalhães [55], the most important phenomenon influencing ripening is the accumulation of sugars in the berry, which is mainly associated with photosynthetic activity, water availability, and temperature. Sugar content influences the final alcohol content of the wine and serves as precursors for the synthesis of organic acids, phenolics, and aromatic compounds [102,110]. Other studies have attributed the increase in sugar content in leaves and berries to the application of silicon in vines [78,111]. This effect may be associated with improved photosynthetic performance combined with the transport of solutes in the phloem from source to sink, resulting in greater carbohydrate accumulation in the berries [64]. Thus, we can assume that silicon-based foliar treatment, especially with the highest dose applied in the present study, contributed to fruit quality, particularly in regions marked by severe environmental conditions, emphasizing its role in reducing the water requirements, and the associated costs of irrigation.

4. Conclusions

This study highlights the promising role of foliar silicon (Si) applications in reducing water requirements and mitigating climate-induced stress in Mediterranean viticulture, particularly in the water-scarce Douro Valley. By comparing non-irrigated and irrigated controls with two Si treatments (7% and 20%), the findings reveal that Si application significantly enhances vine performance under limited water conditions. Si-treated vines exhibited physiological responses, photosynthetic efficiency, and stress resilience comparable to, and in some cases exceeding, those of deficit-irrigated plants, demonstrating that Si can effectively supplement or even replace irrigation needs. The foliar application of Si not only improved water-use efficiency but also increased levels of key phenolic compounds, sugars, and flavonoids in the berries, contributing to higher fruit quality. These results underscore Si's potential as an eco-friendly and cost-effective alternative to traditional irrigation practices, addressing both current and projected water scarcity challenges in viticulture. Future research is encouraged to investigate the long-term impacts and optimize Si use across different grape varieties and environmental conditions. Overall, foliar Si treatments present a sustainable adaptation strategy that can enhance resilience, reduce water dependency, and maintain high product quality in Mediterranean vineyards facing increasing environmental stress.

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