Long-Term Correlation between Water Deficit and Quality Markers in HydroSOStainable Almonds

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Abstract: Global warming enhances the rainfall and temperature irregularity, producing a collapse in water resources and generating an urgent need for hydro-sustainable thinking in agriculture. The aim of this study was to evaluate the correlation between the water stress of almond trees and quality parameters of fruits, after 3 years of experiments, with the objective of establishing quality markers necessary in the certification process of hydroSOStainable almonds. The results showed positive correlations among the stress integral (SI) and dry weight, color coordinates ($L^*$, $a^*$ and $b^*$), minerals (K, Fe, and Zn), organic acids (citric acid), sugars (sucrose, fructose, and total sugars), antioxidant activity, and fatty acids [linoleic acid, polyunsaturated (PUFA)/monounsaturated (MUFA) ratio, PUFA and SFA, among others]. As well as negative correlations of SI with water activity, weight (almond, kernel, and shell), kernel size, minerals (Ca and Mg), fatty acids (oleic acid, oleic/linoleic ratio, MUFA, and PUFA/SFA ratio), and sensory attributes (size, bitterness, astringency, benzaldehyde, and woody). Finally, this research helped to prove key quality parameters that can be used as makers of hydroSOStainable almonds. In addition, it was demonstrated that controlling water stress in almond trees by using deficit irrigation strategies can lead to appropriate yields, improve the product quality, and consequently, lead to a final added value.

Keywords: Prunus dulcis; Vairo; water stress; regulated deficit irrigation; sustained deficit irrigation; quality markers

1. Introduction

Almonds [Prunus dulcis (Mill.) D.A. Webb] are an economically and nutritionally important agricultural good, widely consumed in the Mediterranean diet either as a snack or as an ingredient for confectionery (turrón) and baking [1]. Almond consumption increased by 1.9% at the end of 2018.
in Spain, indicating that consumer appreciation for this nut is high and constantly increasing due to its nutrition values, pleasant flavor, and healthy properties [2,3]. Moreover, raising the number of health-conscious consumers, together with environmental and animals care, lactose intolerance, and hypercholesterolemia in consumers, plant-based milk, yogurt, and cheese has grown over the last decade [4]. For instance, the global almond milk market is predicted to expand 14.3% by 2025; this product being considered a dairy alternative rich in vitamin E and omega 3 and 6 fatty acids. After all, this might be also an important reason that led to almond consumption growth [4–6].

Almond is the third largest crop in terms of surface and the most cultivated tree nut in Spain [7]. Besides, Spain is the main European almond producer and the second-largest in the world (339,033 t in-shell almonds), after the United States of America (1,872,500 t) [8]; Andalusia (111,877 t), Aragon (63,235 t), Castilla La-Mancha (53,201 t), and Valencian Community (40,875 t) are the main producing regions [9]. However, almond production in Spain is relatively low because this crop has been mainly grown in marginal areas where it has traditionally cultivated under restrictive conditions [7]. The almond tree is a drought-tolerant species, but due to the low yield in rainfed conditions (380 kg ha$^{-1}$), irrigation water is necessary to increase its productivity (1842 kg ha$^{-1}$) [9].

The Mediterranean regions are the most affected areas by water stress due to the scarcity and irregularity of rainfall. Moreover, the highest crop water needs are found in areas that are hot, dry, windy, and sunny due to the growth needs of the plant (foliage expansion, vegetative growth, and fruit yield) [10]. The water scarcity crisis is considered the biggest global risk for the world economy and it is affecting every continent [11]. Regarding agricultural sector, there is a consensus about the inadequate management of water resources and the need of achieving an equilibrium between rural development, food security, and environment protection [12]. The population growth leads to an expansion in intensive food production that alters the environment due to greenhouse gas emissions, soil deterioration, and water stress [13]. The main impact produced by climate change includes significant alteration in the average temperature and the rainfall irregularity [14], which leads to a substantially increase in irrigation water demand. In almond farming, climate change can provoke phenological variations on fruit, which may affect the final yield, quality, and marketability [15]. Consequently, all these changes might lead to a reduction in the productivity of agro-ecosystems, a progressive decline of rural areas, and even, land abandonment [16].

The implementation of sustainable irrigation strategies is an important tool to attenuate these negative aspects. However, these strategies must fulfill two important requirements: (i) causing minimal production losses and (ii) ensuring the final quality of the fruits. Regulated deficit irrigation (RDI) is one of these strategies meant to increase the water productivity with minimal yield losses and consists of reducing the amount of water during the kernel-filling stage in almond orchards [17]. Sustained deficit irrigation (SDI) is another strategy, which consists of applying a uniform and reduced amount of water during the whole growing cycle, creating a progressive stress in plants throughout the season [18].

Recently, new research lines focused on water resources sustainability have been developed for different crops (almonds, pistachios, olives, etc.), and the foodstuffs produced under controlled water stress conditions are called hydroSOStainable foods [19–21]. However, a variability in crop responses to water stress was reported for these products with the quality parameters being cultivar-, crop-, and year-dependent. Therefore, long-term research to decide which quality parameters are really affected by the waters stress conditions is needed.

Consequently, the aim of this study was to correlate water deficit response with quality parameters after 3 years of experiments (2017, 2018, 2019) to identify those parameters that behave in the same way throughout the trials. These results are essential to establish the future hydroSOStainable markers.
2. Materials and Methods

2.1. Plant and Experimental Conditions

The experiment was performed during 3 growing cycles (2017, 2018, and 2019) in a commercial orchard “La Florida” (37.23° N, −5.91 W, Dos Hermanas, Seville, Spain). The almond [P. dulcis (Mill.) D.A. Webb cv. Vairo] orchard was 7 years old at the beginning of the experiment. The tree spacing was an 8 m × 6 m square pattern, while the irrigation system used a drip irrigation line (3.8 L h⁻¹) with drippers separated at 0.4 m distance.

The weather data for each season were obtained from the “Instituto de Investigación y Formación Agraria (IFAPA) Los Palacios” station in the Andalusian weather stations network (Figure 1) located about 6 km away from the experimental orchard.

![Figure 1. Climatic conditions during the three experimental seasons (2017–2019). (a) Seasonal daily reference evapotranspiration (circles) and rain (bars). (b) Seasonal daily maximum air temperature (white circles) and maximum vapor pressure deficit (VPD) (black circles). Vertical dots lines indicated from right to left each season, the beginning of pit hardening, early recovery, and regular recovery. DOY: day of the year.](image-url)
The data for all 3 seasons were typical of Mediterranean zones, with null rainfall during the summer period and warm winters. The threshold values of midday stem water potential (SWP) were measured weekly, most of the dates, or every ten days using a pressure chamber (PMS Instrument Company, Albany, OR, USA). These values were used for the irrigation schedule by evaluating the stress level in the plant with the methodology proposed by Myers [22] according to the following expression Equation (1):

$$SI = \sum (\psi_{stem} - (-0.2)) \times n$$  \hspace{1cm} (1)

where $SI$ was the stress integral, $\psi_{stem}$ is the average midday stem water potential for any interval, and $n$ is the number of days in the interval. Most of the measurements were weekly.

### 2.2. Irrigation Treatments

Four irrigation treatments were applied to the experimental plots. Each treatment represents different strategies of farmers in conditions of water scarcity. Moderate RDI is a controlled deficit irrigation in which applied water is lower than full irrigation but restricted considering an accurate water management. Severe RDI (was considered due to the low water availability) represents concentrated irrigation mainly during postharvest. Finally, SDI, is a strategy that was not considered in the phenological stages, and then, postharvest irrigation was very limited. These treatments are described in detail below:

- **Full irrigation (T1):** irrigated to assure the crop needs. Irrigation was daily and irrigation scheduling was performed every week. Water needs were estimated with the crop evapotranspiration ($ETc$) approach according to Steduto et al. [23] using reduction coefficients ($Kr$) around 0.6. In addition, water status was evaluated using midday stem water potential and compared to the McCutchan and Shackel [24] baseline. When water status was more negative than expected, irrigation was increased by 150% $ETc$.

- **Moderate RDI (T2):** the water stress was imposed during the kernel-filling period; almond trees were irrigated when $SWP$ was below $-1.5$ MPa, and for the rest of the time, trees were irrigated to keep an $SWP$ as the baseline proposed by McCutchan and Shackel [24]. Equation (2) estimated optimum midday stem water potential in relation with vapor pressure deficit (VPD):

$$SWP = (-0.41) \times (-0.12VPD)$$  \hspace{1cm} (2)

where: $SWP$ is optimum midday stem water potential (MPa) and $VPD$ is vapor pressure deficit (KPa).

- **Severe RDI (T3):** the same as T2, except that trees were irrigated when SWP was below $-2.0$ MPa during kernel filling and maximum seasonal water was considered (120 mm, around 20% $ETc$). Therefore, after harvest, when total applied water was reached, irrigation stopped.

- **SDI (T4):** the same as T3, but tree water status was not considered. Irrigation was applied in a constant daily rate around 1–2 mm per day. The main differences between both strategies (T3 and T4) was that T4 limited postharvest irrigation more than T3.

Harvesting was done with a self-propelled trunk shaker with collector in the mid of August (28 weeks after blossom). The treatments were separately harvested, and almonds were sun-dried until a moisture content lower than 5% was achieved. Later, in-shell almonds were delivered to Miguel Hernández University (Orihuela, Alicante, Spain) for analysis.

### 2.3. Physical Parameters

#### 2.3.1. Kernel Ratio

The ratio between the mass of in-shell almonds and kernel was calculated from 12 kg of whole fruit per treatment and year.
2.3.2. Dry Weight and Water Activity

For the dry weight content (%) analysis, 2 g of ground almonds (Moulinex grinder AR110830, Alençon, France) were added to an aluminum tray and dried in an oven at 60 °C until a constant weight was reached, while water activity (a_w) was measured by placing the cups with almond (2 g) into an a_w meter (Novasina aw-Sprint TH500; Pfaffikon, Zurich, Switzerland) and reading the value. The experiments were done in quadruplicate.

2.3.3. Weight and Size

For the morphological parameters, 100 almonds per treatment (25 almonds × 4 trees × treatment × year) were randomly selected and measured in terms of weight and size (length, width, thickness) of both in-shell almond and kernel using a digital caliper (Mitutoyo 500-197-20, Kawasaki, Japan) and a precision scale (Mettler Toledo model AG204, Barcelona, Spain), respectively.

2.3.4. Instrumental Color

Color measurements were performed at 25 ± 1 °C using a Minolta Colorimeter CR-300 (Osaka, Japan). Outside color was directly measured on the skin of 100 individual almond kernels per treatment each year. Results were presented as international commission on illumination (CIE) L*, a* and b* color coordinates describing the color in a three-dimensional space as following: L* for the lightness (L* = 0 black; L* = 100 white), a* for the green-red (a* = red; −a* = green), and b* for the blue-yellow components (b* = yellow; −b* = blue).

2.3.5. Instrumental Texture

The texture of 100 almonds per treatment and year was measured using a texture analyzer (Stable Micro Systems, model TA-XT2i, Godalming, UK) with a 30 kg load cell and a probe Volodkevich Bite Jaw (HDP/VB) as following: trigger was placed at 15 g, test speed was 1 mm s⁻¹ over a specific distance of 3 mm. Fracturability (mm), hardness (N), work done to shear (Ns), average force (N), and number of fractures (peaks count) were the parameters analyzed.

2.4. Chemical and Functional Analysis/Parameters

2.4.1. Mineral Content Determination

The digestion of 0.5 g of sample with 8 mL of concentrated HNO₃ and 2 mL H₂O₂ (30%) using a START D Medium Microwave Digestion (SK-10) was first carried out [25]. Followed by the determination of macro-nutrients (Ca, Mg, and K) and micro-nutrients (Fe, Cu, Mn and Zn) with a Unicam Solaar 969 atomic absorption–emission spectrometer (Unicam Ltd., Cambridge, UK). Calcium, Mg, Fe, Cu, Mn, and Zn was determined by atomic absorption and K by atomic emission.

2.4.2. Organic Acids and Sugars

High-performance liquid chromatography (HPLC) was used for organic acids and sugars identification and quantification, as previously described [26]. For this, 1 g of ground almond was homogenized (Ultra Turrax T18 Basic, IKA®-Werke GmbH & Co. KG Janke & Kunkel, Staufen, Germany) with 5 mL of 50 mM phosphate buffer (pH = 7.8) for 2 min at 11,300 rpm, centrifuged (Sigma 3−18 K; Sigma Laborzentrifugen, Osterode and Harz, Germany) at 4 °C and 15,000 rpm for 20 min and filtered (0.45 μm Millipore membrane filter, Billerica, MA, USA). The supernatant was injected (10 μL) into a Hewlett Packard (Wilmington, DE, USA) series 1100 (HPLC) using as mobile phase 0.1% orthophosphoric acid elution buffer. Sugars were analyzed using a Supelcogel TM C-610H column (30 cm × 7.8 mm) with a precolumn (Supelguard 5 cm × 4.6 mm; 219 Supelco, Bellefonte, PA, USA) and detected with a refractive index detector (RID). Organic acids were separated as sugars using a diode-array detector (DAD) at 210 nm for the absorbance measurements. Analyses were run in quadruplicate, and results were expressed as g kg⁻¹ dry weight (dw).
2.4.3. Antioxidant Activity and Total Phenolic Content

The antioxidant activity and total phenolic content was carried out both for whole kernel and its blanched skin. For the extraction 0.5 g of finely ground almond were sonicated with 10 mL of extractant [MeOH/H$_2$O$_2$ (80:20, v/v) + 1% HCl at 20 °C] for 15 min and stored at 4 °C overnight. The mixture was sonicated again under the same conditions and centrifuged at 10,000 rpm for 10 min. The antioxidant activity of the obtained extract was measured using 3 methods: ABTS** [2,2-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid)], DPPH* (2,2-diphenyl-1-picrylhydrazyl), and FRAP (ferric reducing antioxidant power), as previously described by Brand-Williams et al. [27]. The results were calculated according to the Trolox calibration curve and were expressed as mmol Trolox kg$^{-1}$.

For total phenolic content (TPC) 100 µL of supernatant was mixed with 200 µL Folin-Ciocalteu reagent and 2 mL of H$_2$O$_2$ and was stored at 22 °C for 3 min. Then, 1 mL of 20% Na$_2$CO$_3$ was added, followed by 1 h of incubation at room temperature. The results were calculated with the gallic acid calibration curve and expressed as gallic acid equivalents (GAE), g GAE kg$^{-1}$. All measurements were performed in an ultraviolet-visible (UV-vis) spectrophotometer (Helios Gamma model, UVG 1002E; Helios, Cambridge, UK).

2.4.4. Fatty Acids

Ground almond (40 mg) was saponified with 100 µL of dichloromethane (Cl$_2$CH$_2$) and 1 mL of sodium methoxide solution and refluxed for 10 min at 90 °C. Later, 1 mL of BF$_3$ methanolic was added followed by 30 min rest in dark for reaction [25]. The fatty acids methyl esters (FAMEs) were separated in a Shimadzu GC17A gas chromatography coupled with a flame ionization detector and a DB-23 capillary column (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness) J&W Scientific, Agilent Technologies using the same conditions, as previously described by Lipan et al. [25]. The identification of FAMEs peaks was done by comparing the retention times of the FAME Supelco MIX-37 standards. Analysis were carried out in quadruplicate, and the results were expressed as g kg$^{-1}$ concentration, using methyl nonadecanoate (C19:0) as internal standard.

2.5. Descriptive Sensory Analysis

Descriptive sensory evaluation was performed following the steps previously published in literature using a trained panel [19]. Ten highly trained panelists from the Food Quality and Safety Group (Miguel Hernández University of Elche, Orihuela, Alicante, Spain) with ages between 25–62 years (5 women and 5 men) conducted the descriptive analysis. Once the orientation sessions were finished (4), the panel was asked to evaluate the 4 samples corresponding to the irrigation treatments in terms of appearance, basic tastes, and flavor intensities of almond. For this, a structured scale from 0 to 10 (0.5 increments) was used to quantify the intensity of the almond attributes, where 0 represents no intensity and 10 extremely strong. The samples were presented using a randomized block design to avoid biases in individual tasting booths (controlled temperature of 21 ± 2 °C and combined natural/artificial light) equipped with water and unsalted crackers for palate cleaning among samples. The analysis was run in triplicate.

2.6. Statistical Analysis

Two-way analysis of variance (ANOVA), using “irrigation treatment” and “year” as factors, followed by Tukey’s multiple range test were carried out in order to decide the parameters to be used for the correlations. Two supplementary tables were added with the mean values of 3 years (Tables S1 and S2). Only those parameters significantly different among treatments were considered for Pearson’s correlations. All statistical analyses were performed using XLSTAT Premium 2016, while Sigma Plot 11 software was used for figures preparation. Statistically differences were considered significant when $p < 0.05$. 
3. Results and Discussion

3.1. Agronomic Parameters

Tables S1 and S2 contains supplementary information about the mean values of 3 years study for all the parameters. As observed, a lower amount of irrigation water was received by the trees’ growth under deficit irrigation strategies, being T3 and T4 the treatments, which received the less amount of irrigation water; this rebound in the plant status can be observed from the stress integral values. Almond trees from T3 and T4 were the most stressed, although the latter (T4) was statistically significant to T2. During the first season, T2 and T3 were the most stressed treatments followed by T4, which was statistically similar to T2. In 2018, lower values of SI were shown for all treatments, which means that the stress in plant was less severe than the other seasons. T3 and T4 were the most stressed treatments, followed by T2, which was statistically correlated with the control and to the other deficit irrigation treatments. Finally, 2019 was the season in which almonds trees met the highest values of water stress, with T3 and T4 having the highest values, followed by T2. As observed, the SI behaved different yearly, however in the last two seasons, T3 and T4 were similar in terms of water stress in plant. The difference between these treatments is that in the former (T3) the stress was applied in the kernel-filling period, while in the latter (T4), the stress was imposed throughout the whole growing cycle, creating a progressively stress in plant rather than in a single phenological phase (kernel filling). Supplementary data also showed the mean values of kernel yield of all 3 seasons to check how the previous parameters (SI and applied water) influenced the fruit yield. A reduction of this parameter was observed in all the treatments growth under DI conditions with no significant differences among them. If each year production is analyzed, no differences among control and DI treatment was registered in the first season. However, a decrease of 2.4-fold was found for these treatments (T2, T3, T4) regarding the control in the second season (with no significant differences among them) and in the third season. A reduction in kernel yield in deficit irrigation treatments was also observed in 2019 season (1.2-fold in T2 and 1.5-fold in T3 and T4), although this time was lower than in 2018 and T2 was significantly similar to the control. Is important to highlight that in 2018, even though T3 and T4 received a lower amount of water than T2, the kernel yield was similar among them, and that in 2019, although T2 received lower amount of water than the control (T1), the kernel yield was significantly similar between them.

Pearson’s correlation coefficients (R) among SWP and SI with agronomical and physical parameters is shown in Figure 2. A negative and significant correlation was found between SI and (i) SWP (R = −0.67; p < 0.001) and (ii) water activity (R = −0.39; p < 0.01); this means that at higher waters stress values, lower SWP and aw values are obtained. On the other hand, a positive and significant correlation was observed between SI and dry weight (R = 0.53; p < 0.001) as well as between kernel ratio and applied water (R = 0.36; p < 0.05). Regarding the water stress effect on kernel yield, the results showed that in the first year it was not affected (R = 0.11; p > 0.05); however, kernel yield was reduced with water stress during 2018 and 2019 seasons demonstrated by the negative correlations of R = −0.50; p < 0.05 * and R = −0.79; p < 0.001 ***, respectively.
Overall, these results showed that after long-term experiment (3 years), the water stress in almond trees negatively affected the yield but enhanced dry weight. These results suggest that yield differences were related to the number of nuts. Such response could be associated with a postharvest water stress in deficit treatments [18]. However, it was observed that, depending on the treatment, it can lead to yields statistically similar to the control, which might be a good alternative when water restrictions are below the crop needs. In this way, Moderate RDI (T2) could balance water stress effects, because this treatment could secure enough crown volume, which is very important in the tree yield capacity [10] and postharvest recovery, which is according to the current data, the most important effect. On the contrary, T3 and T4 results suggest that water status in postharvest would be better. Then, in conditions of very low water availability, irrigation in this period should be preferential and greater than the ones of T3. Besides, the reduction in the moisture content and water activity with water stress are also important outcomes for food industry, because lower values of these parameters help to maintain at minimum the biological reactions, which essential to increase the almonds shelf life [28]. The obtained

![Heat map of correlation matrix of agronomical parameters](image-url)

**Figure 2.** Heat map of correlation matrix of agronomical parameters. Each square indicates Pearson’s correlation coefficient for a pair of data and the color represents the positive or negative correlation as:

- **R = 1.00;** significant ($p < 0.05$) positive correlation;
- **R = 0.64;*** negative but not correlated;
- **R = 0.36;** significant ($p < 0.05$) negative correlation;
- **R = 0.04;** positive but not correlated;
- **R = -0.28;** negative but not correlated.

* *, **, ***, significant at $p < 0.05, 0.01, and 0.001$, respectively. SWP = minimum stem water potential; SI = stress integral; AW = applied water; KR = kernel ratio; DW = dry weight; aw = water activity.
results indicate that the use of deficit irrigation in almond trees water management can improve yield and reduce water use. Thus, it contributes to reduce water consumption for irrigation purposes.

3.2. Morphological Parameters

Table 1 shows the Pearson’s correlation coefficients (R) between SWP and SI with morphological parameters. The SI was negatively correlated with almond, kernel, and shell weight, with kernel length and width, and with almond thickness. This means that weight and size were reduced with the water stress in plant. The conclusions regarding the effect of deficit irrigation on the morphological parameters are widely spread throughout the literature. For instance, similar results were obtained in almond cultivar (cv.) Nonpareil [18], and no differences were reported for almond cultivars Marta, Guara, Lauranne, Ferragnes, and Texas [29,30]. Additionally, no differences on the morphological parameters were also reported for other crops such as pistachio cv. Kerman and olives cv. Manzanilla if the stress was applied during shell and pit hardening, respectively [21,31]. Finally, an increase in weight and equatorial diameter but a decrease in longitudinal diameter were observed for olives cv. Manzanilla growth under the following RDI conditions: (i) stage I, trees irrigated under non-limited conditions; (ii) stage II, trees under moderate water deficit conditions, they were no irrigated during this period; and (iii) stage III, water applied in order to provide a water status similar to a full irrigated treatment [32].

A significant positive correlation was observed between the SI and color parameters, showing that a higher stress level leads to higher values of $L^*$, $a^*$, and $b^*$ coordinates. This means that hydroSOSTainable almonds have a lighter color with reddish and yellowish notes (more intense brown color). As the almond color skin is given by the polyphenol profile, which is unique for each cultivar [33], the increase in color coordinates under water stress conditions might be related to a potential increase in polyphenols. For instance, almond flavonoids have been extensively studied in different plants, and it was concluded that they are decisive pigment in color plants [34]. The brown almond skin pigment is largely concentrated in the high-molecular weight fraction such as proanthocyanidins, which are the main polyphenols found in almonds that can impart color formation [35]. A positive correlation between SI and proanthocyanidins ($R = 0.73; p = 0.001$) was previously reported in almonds cv. Vairo after one season of experiment. Besides, $a^*$ values were also reported to be higher in almonds cv. Vairo, Marta, Guara, Lauranne growth under deficit irrigation conditions after one season [25,29]. Finally, $a^*$ was reported to be positively correlated with the contents of nine individual flavonols, total kaempferols, and total flavonols in a study about the relationship between rose petals’ (*Rosa* spp.) color and polyphenols content [36].
### Table 1. Pearson’s correlation coefficients (R) among stem water potential and stress integral with morphological parameters.

|       | SWP   | SI     | AWe    | KWe    | SHWe   | AL     | KL     | AWi    | KWi    | ATi    | KTi    | L*     | a*     | b*     | Hue    | C     | H     |
|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|
| SWP   | 1.00  |        |        |        |        |        |        |        |        |        |        |        |        |        |        |       |       |
| SI    | −0.67*** | 1.00  |        |        |        |        |        |        |        |        |        |        |        |        |        |       |       |
| AWe   | 0.17  | −0.39** | 1.00  |        |        |        |        |        |        |        |        |        |        |        |        |       |       |
| KWe   | 0.35* | −0.56*** | 0.85*** | 1.00  |        |        |        |        |        |        |        |        |        |        |        |       |       |
| SHWe  | 0.11  | −0.32*  | 0.99*** | 0.75*** | 1.00  |        |        |        |        |        |        |        |        |        |        |       |       |
| AL    | 0.05  | 0.08  | 0.75*** | 0.43**  | 0.80*** | 1.00  |        |        |        |        |        |        |        |        |        |       |       |
| KL    | 0.26  | −0.57*** | 0.84*** | 0.91*** | 0.77*** | 0.40** | 1.00  |        |        |        |        |        |        |        |        |       |       |
| AWi   | 0.08  | −0.17  | 0.90*** | 0.64*** | 0.92*** | 0.89*** | 0.60*** | 1.00  |        |        |        |        |        |        |        |       |       |
| KWi   | 0.18  | −0.51*** | 0.92*** | 0.88*** | 0.87*** | 0.55*** | 0.86*** | 0.79*** | 1.00  |        |        |        |        |        |        |       |       |
| ATi   | 0.33* | −0.41** | 0.80*** | 0.63*** | 0.80*** | 0.68*** | 0.61*** | 0.81*** | 0.70*** | 1.00  |        |        |        |        |        |       |       |
| KTi   | 0.32* | 0.07  | −0.36*  | −0.04  | −0.44*** | −0.30*  | −0.16  | −0.41** | −0.30*  | −0.15  | 1.00  |        |        |        |        |       |       |
| L*    | −0.20 | 0.61*** | −0.65*** | −0.55*** | −0.64*** | −0.38** | −0.61** | −0.59*** | −0.64*** | −0.59*** | −0.64*** | −0.47*** | 1.00  |        |        |       |       |
| a*    | −0.30* | 0.80*** | −0.41**  | −0.57*** | −0.34*  | 0.14  | −0.69*** | −0.13  | −0.55*** | −0.29*  | 0.19  | 0.65*** | 1.00  |        |        |       |       |
| b*    | −0.21 | 0.72*** | −0.53*** | −0.55*** | −0.50*** | −0.10  | −0.67*** | −0.36  | −0.61*** | −0.49*** | 0.37*  | 0.87*** | 0.90*** | 1.00  |        |       |       |
| Hue   | 0.07  | 0.02  | 0.32*** | −0.04  | 0.40*** | 0.59*** | −0.06  | 0.53*** | 0.16  | 0.48*** | −0.50*** | −0.42*** | 0.27  | −0.05  | 1.00  |        |       |
| C     | −0.09 | 0.10  | −0.40*  | −0.06  | −0.48*** | −0.59*** | −0.06  | −0.60*** | −0.26  | −0.56*** | 0.55*** | 0.56*** | −0.12  | 0.23  | −0.98*** | 1.00  |
| H     | 0.06  | −0.40  | 0.61*** | 0.60*** | 0.58*** | 0.31*  | 0.67*** | 0.48*** | 0.63*** | 0.52*** | −0.32*  | −0.56*** | −0.56*** | −0.63*** | −0.04  | −0.08  | 1.00  |

*, **, *** significant at p < 0.05, 0.01, and 0.001, respectively. SWP = minimum stem water potential; SI = stress integral; AWe = almond weight; KWe = kernel weight; SHWe = shell weight; AL = almond length; KL = kernel length; AWi = almond width; KWi = kernel width; ATi = almond thickness; KTi = kernel thickness; L*, a*, b* = color coordinates; C = Chroma; H = hardness.
3.3. Mineral, Organic Acids, and Sugars Content

The minerals contained in plant tissue are taken by plants from soil and from the water received in production [34]. For this reason, environmental factors, agronomical practices (location, soil composition, water source, irrigation, and fertilizer) and cultivar are responsible for the final mineral content in kernel. Potassium, Ca, Mg, Fe, P, S, and N are the main elements found in plants mainly accumulated during fruit growing and ripening [37]. It was reported that drought conditions reduces the mineral content transport from root to shoot; however, there are plants with a better water use efficiency (WUE) and consequently with greater drought tolerance [38].

In order to analyze the relationship between SWP and SI with minerals, organic acids, and sugars, Pearson’s correlation coefficients (R) were calculated and are displayed in Table 2. Calcium (R = −0.60; p < 0.001) and Mg (R = −0.35; p < 0.01) showed significant negative correlations with the SI, and the latter was also positively correlated with SWP (R = 0.71; p < 0.01). However, if each year is considered both minerals presented significant difference in only one season. Magnesium is a macro element essential component of the chlorophyll molecule, which is necessary in the photosynthesis process [38]. Besides, Mg plays a role in energy preservation and protein synthesis being a cofactor for many enzymes associated with de-phosphorylation, hydrolysis, and in stabilizing the structure of nucleotides and sugar accumulation.

Potassium (R = 0.60; p < 0.001), Fe (R = 0.64; p < 0.001), and Zn (R = 0.44; p < 0.01) were the elements positively correlated with the water stress. Similar results were also reported by other researchers in almonds in which a higher amount of K was reported in moderate RDI attributed to the relationship between water availability and minerals absorption [25]. The authors explain that the excess of water might be the responsible for mineral leaching and also that drought stress could contribute to the saturation of minerals in the rootzone. Potassium is the most important element, after N and P, helping to maintain the plant water status being involved in physiological and molecular mechanisms needed to increase the plant tolerance to stress [38]. Potassium has been reported to be the major mineral cation in almonds kernels (717 mg/100 g in cv. Vairo); in this way, almonds are considered a food high/rich in K because its content is above the minimum threshold (600 mg K/100 g) established in the Regulation (EU) No 1169/2011 of the European Parliament and of the Council [25,39].

Iron and Zn also presented a positive correlation with water stress and these results agreed with other authors reporting that this microelement helps to improve the WUE and the crop yield [38]. Usually, drought induces Fe deficiency with a negative effect on plant tree, causing chlorosis due to low levels of chlorophyll. This microelement is also necessary for an effective function of the antioxidant enzymes because a Fe deficiency reduces the enzymes activity, enhances the ROS production, and reduces the bioactive compounds biosynthesis [38]. The present results might reveal that this controlled stress was below the limit needed to reduce the microelements production; in fact, an opposite phenomenon was observed. Studies in wheat growth in fields under water stress conditions also reported a higher Zn content in grains growth under water stress conditions but not that grown in greenhouses [40].

Positive correlation was shown for citric acid and SI (R = 0.65; p < 0.001), which was confirmed by studies in almonds of cv. Marta, Guara, and Lauranne growth under RDI versus full irrigated and over irrigated conditions [29] and other crops such as thyme [41]. However, in studies of cv. Guara under non-irrigated almonds versus drip-irrigated, the citric acid was higher in almonds growth in drip-irrigated conditions [42]. In addition, no differences were reported in cv. Vairo [25] and cv. Marta [43]. These differences could be attributed to the irrigation strategies and the levels of stress created in each experiment. The increase in citric acid in response to drought may result from the larger inhibition of the citrate degrading system relative to citrate synthesis as previously reported in CAM plant (Aptenia cordifolia), although the capacity for citric acid oxidation and the citrate synthetase activity decreased during drought [44].
Table 2. Pearson’s correlation coefficients (R) among stem water potential and stress integral with minerals, organic acids, and sugars.

|       | SWP | SI  | Ca  | Mg  | K   | Fe  | Mn  | Zn  | Cit | Tar | Mal | ΣOA | Suc | Glu | Fru | SS  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| SWP  | 1.00|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| SI    | 1.00|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ca    | -0.67 *** | 1.00 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Mg    | 0.14 | -0.60 *** | 1.00 |     |     |     |     |     |     |     |     |     |     |     |     |     |
| K     | -0.06 | 0.60 *** | -0.79 *** | 0.39 ** | 1.00 |     |     |     |     |     |     |     |     |     |     |     |
| Fe    | -0.18 | 0.64 *** | 0.79 *** | -0.20 | -0.65 *** | 1.00 |     |     |     |     |     |     |     |     |     |     |
| Mn    | 0.13 | -0.05 | -0.51 *** | -0.46 *** | 0.44 ** | -0.40 ** | 1.00 |     |     |     |     |     |     |     |     |     |
| Zn    | -0.41 ** | 0.44 ** | -0.26 | -0.15 | 0.40 ** | 0.11 | 0.29 * | 1.00 |     |     |     |     |     |     |     |     |
| Cit   | -0.19 | 0.65 *** | -0.61 *** | 0.34 * | 0.58 *** | -0.58 *** | 0.10 | 0.02 | 1.00 |     |     |     |     |     |     |     |
| Tar   | -0.07 | 0.35 | 0.07 | 0.75 *** | 0.04 | -0.05 | -0.80 | -0.24 | 0.41 ** | 1.00 |     |     |     |     |     |     |
| Mal   | -0.01 | -0.17 | -0.23 | -0.56 *** | 0.07 | -0.01 | 0.68 *** | 0.22 | -0.22 | -0.74 *** | 1.00 |     |     |     |     |     |
| ΣOA   | -0.04 | -0.09 | -0.29* | -0.49 *** | 0.13 | -0.07 | 0.67 *** | 0.21 | -0.10 | -0.66 *** | 0.99 *** | 1.00 |     |     |     |     |
| Suc   | -0.42 ** | 0.71 *** | -0.62 *** | 0.06 | 0.52 *** | -0.43 ** | 0.17 *** | 0.19 | 0.71 *** | 0.20 | -0.05 | 0.02 | 1.00 |     |     |     |
| Glu   | -0.02 | 0.26 | 0.03 | 0.57 *** | 0.12 | -0.07 | -0.51 *** | -0.02 | 0.13 | 0.63 *** | -0.53 *** | -0.50 *** | 0.03 | 1.00 |     |     |
| Fru   | -0.36 * | 0.30 * | 0.21 | 0.28 * | -0.24 | 0.28 | -0.55 *** | -0.14 | 0.16 | 0.51 *** | -0.38 ** | -0.34 * | 0.19 | 0.24 | 1.00 |     |
| SS    | -0.39 ** | 0.70 *** | -0.36 * | 0.44 ** | 0.37 * | -0.27 | -0.31 * | 0.09 | 0.60 *** | 0.62 *** | -0.43 ** | -0.35 * | 0.75 *** | 0.64 *** | 0.50 *** | 1.00 |

*, **, ***: significant at $p < 0.05, 0.01$, and 0.001, respectively. SWP = minimum stem water potential; SI = stress integral; Cit = citric; Tar = tartaric; Mal = malic; ΣOA = total organic acids; Suc = sucrose; Glu = glucose; Fru = fructose; SS = total sugars.
Finally, sucrose, fructose, and total sugars were also positively correlated with the water SI sucrose (R = 0.71; p < 0.001), fructose (R = 0.30; p < 0.05), and total sugars (R = 0.70; p < 0.001), and these results agreed with those of other authors in almonds cv. Marta, Guara, and Lauranne [29], with almonds being grown under RDI circumstances. Authors working with cv. Vairo under RDI and SDI conditions reported no differences for total sugars and sucrose in the first year of water deficit; however, a reduction in glucose was reported for the most stressed treatments [25,26]. Lower amounts of sucrose and glucose were reported in cv. Guara growth under non-irrigated conditions when compared to drip-irrigated, while fructose was not affected [42]. Lower values of sucrose with no differences in glucose, fructose, and the total sugars were also reported for cv. Marta under RDI and partial rootzone drying (PRD) in different levels [43]. Although, sucrose started to increase for the most severe treatment of PRD. Moreover, sucrose was reported to increase in non-irrigated conditions for cv. Ferragnes in early harvest, and the opposite was observed for the same cv. in late harvest, while non-irrigation decreased this sugar in cv. Texas in both situations, with the total sugars not affected [30]. If other crops are considered, sugars were also increased in tomatoes under water stress conditions [17], thyme (Thymus vulgaris as drought-tolerant and T. kotschyanus as drought-tolerant species) under drought stress [41], and peaches in which experiment it was demonstrated that deficit irrigation can enhance both total and individual sugars, if proper water stress is established for each cultivar [45]. A different behavior was reported for each peach cultivar; therefore, it is essential to establish specific conditions not only for each plant species but for each cultivar.

The sugars’ enhancement under stress conditions was related to the osmotic adjustment, activated by accumulation of solutes rich in hydroxyl (–OH) groups (sugars, proline, etc.) in the cytoplasm [26]. Osmotic adjustment is a biochemical mechanism that helps plants to adapt to dry and saline conditions by protecting the cellular membrane, protein, and enzymes against dehydration [26]; thus, it enhances the capacity to maintain positive turgor, increasing the sugars and organic acid. Another reason of the sugars accumulation during stress might be the induction of the growth inhibitor abscisic acid (ABA) by plants under stress conditions, which activates the sugar accumulation as an adaptation to stress [46]. Drought increases the biosynthesis and accumulation of ABA, which is considered the main regulator of drought stress response inducing the accumulation of osmotically active compounds, which protect cells from damage [38]. Under stress conditions, this phyto-hormone reduces plant growth and enhances desiccation tolerance by inducing de accumulation of stress-associated transcripts such as low-molecular-weight soluble sugars(sucrose) [47].

In summary, K, Fe, Zn, sucrose, fructose, and total sugars can be considered as good quality markers for hydroSOStainable almonds.

3.4. Antioxidant Activity (AA) and Total Phenolic Compounds (TPC)

The antioxidants are important compounds necessary to inhibit the process of oxidation acting like radical scavengers and converting these pro-oxidants to less reactive species. Antioxidants have attracted considerable consumer interest due to their potential preserving, nutritional, and therapeutic effects. For these reasons, the correlations among SWP and SI with antioxidant activity of almond kernel and kernel skin are important and were evaluated within this study along 3 seasons (Table 3). ABTS** (R = 0.79; p < 0.001 and R = 0.44; p < 0.01) and FRAP (R = 0.34; p < 0.05 and R = 0.41; p < 0.01) in both whole kernel and kernel skin showed a significant and positive correlation with the SI, and only ABTS** (R = −0.44; p < 0.01 and R = −0.30; p < 0.05) in both matrices was negatively correlated with the SWP. This showed that the induced water stress led to almonds with a higher antioxidant activity.
Table 3. Pearson’s correlation coefficients (R) among stem water potential and stress integral with antioxidant activity of almond kernel and kernel skin.

|       | SWP   | SI     | ABTS* K | DPPH* K | FRAP K | TPC K | ABTS* S | DPPH* S | FRAP S | TPC S |
|-------|-------|--------|---------|---------|--------|-------|---------|---------|--------|-------|
| SWP   | 1.00  |        |         |         |        |       |         |         |        |       |
| SI    | -0.67 *** | 1.00  |         |         |        |       |         |         |        |       |
| ABTS* K | -0.44 ** | 0.79 *** | 1.00  |         |        |       |         |         |        |       |
| DPPH* K | -0.09 | -0.25 | -0.46 *** | 1.00  |        |       |         |         |        |       |
| FRAP K | -0.07 | 0.34 * | 0.57 *** | -0.54 *** | 1.00  |       |         |         |        |       |
| TPC K | 0.05  | -0.14 | 0.21   | -0.75 *** | 0.38 ** | 1.00  |         |         |        |       |
| ABTS* S | -0.30 * | 0.44 ** | 0.12  | 0.50 *** | -0.20 | -0.82 *** | 1.00  |         |        |       |
| DPPH* S | -0.07 | 0.10  | -0.20 | 0.80 *** | -0.46 *** | -0.95 *** | 0.82 *** | 1.00  |         |       |
| FRAP S | -0.19 | 0.41 ** | 0.14  | 0.24   | -0.17 | -0.63 *** | 0.87 *** | 0.62 *** | 1.00  |       |
| TPC S | -0.11 | 0.16  | -0.15 | 0.72 *** | -0.43 *** | -0.92 *** | 0.88 *** | 0.94 *** | 0.73 *** | 1.00  |

*, **, *** significant at $p < 0.05, 0.01,$ and 0.001, respectively. SWP = minimum stem water potential; SI = stress integral; ABTS* = 2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid); DPPH* = (2,2-diphenil-1-picrylhydrozayl); FRAP = ferric reducing ability of plasma; TPC = total phenolic content; K = kernel; S = skin.
An increase in AA under water stress conditions was previously reported in many crops, including (i) almonds cv. Vairo, in which the stress was imposed in the kernel-filling phase using RDI and SDI strategies, (ii) olives cv. Manzanilla, when the stress was created just before harvest without re-hydration [48], and (iii) pistachios cv. Kerman, where the stress was imposed at stage II, which corresponds to shell hardening [49]. During the water stress, the turgor pressure is decreased, the ion toxicity is increased, and the photosynthesis is inhibited [50]. This increase in AA during stress conditions can be related to the antioxidant defense system used by plants to cope with reactive oxygen species (ROS) and also to the phytohormones accumulation by plants in water stress conditions. Phytohormones, as above mentioned, are responsible for the initiation of many defense mechanisms, including the increase in antioxidants to enhance plant tolerance to water stress. Jasmonate (JA), which is a phytohormone involved in sensing and signaling during the stress response, helps with the alleviation of plant to drought stress by increasing total carbohydrates, polysaccharides and soluble sugars by activating the enzymatic and non-enzymatic antioxidative system [50].

However, no correlation was found between the TPC and SI after 3 seasons, being in contrast with results previously reported by Lipan et al. (2019) [26] for almonds grown in the same conditions but in the first year of study. Several studies are reporting an increase in TPC values in plants grown under stress conditions, due to their role as plant molecules in response to biotic and abiotic stress, because when the carbohydrates exceed the amount used for growth needs, the excess of CO₂ assimilated in stress conditions is used for the biosynthesis of carbon secondary metabolites. Thus, not finding a correlation between SI and TPC may happen due to the level of stress applied, which perhaps was not strong enough to affect the TPC accumulation.

On the other hand, the positive correlation between SI and AA, and the no correlation or negative correlation of TPC with ABTS•⁺ (R = −0.15; p > 0.05) and FRAP (R = −0.43; p < 0.01) shows that other compounds with antioxidant effect might be responsible for the AA increase observed under water stress rather than only polyphenols. For instance, besides polyphenols, vitamins C and E and carotenoids have been thought to be responsible for most of the AA in foods [41]. Authors reported that, almonds are a valuable source of dietary lipids and have been suggested as a potential source of dietary antioxidants [51]. The same authors in their study about the AA and TPC in 100 different products reported that products with high AA tended to have a higher AA/TPC ratio; thus, this increase may result from compounds with AA that are not phenolic, or some phenolic compounds were more effective than others or with a greater reactivity with peroxyl free radicals (the AA method was an Oxygen Radical Absorbance Capacity (ORAC) Assay on a Plate Reader). Almonds are high rich in vitamin E (25.6 mg/100 g) [52] because its content is above the minimum threshold (3.6 mg/100 g) established by the European Parliament and Council [39]; thus, this might be a compound contributing to the AA enhancement.

For instance, authors working with almonds cv. Nonpareil under water stress conditions reported higher values of tocopherols when RDI and SDI strategies were applied [53], as well as in sunflower seeds (cvs. Gulshan-98 and Suncross), particularly if the water stress was imposed at the reproductive stage [54]. These results led us to the conclusion that after long term study (3 years), antioxidant activity can be considered an important marker in hydroSOStainable almonds detection, while TPC is not a good indicator, presenting no correlation with water stress.

### 3.5. Fatty Acids

Pearson’s correlation coefficients (R) between SWP and SI integral with fatty acids is showed in Table 4. Polysaturated/saturated fatty acids ratio (PUFA/SFA), oleic acid, and consequently, oleic/linoleic ratio (O/L) and monounsaturated (MUFA) fatty acids were significantly negatively correlated with the SI. On the other hand, myristic, palmitic, palmitoleic, lauric, cis-heptadecenoic, stearic, cis-vaccenic, linoleic, saturated (SFA), polyunsaturated (PUFA) fatty acids, and PUFA:MUFA ratio were positively correlated with the SI. Only linoleic, SFA, and PUFA fatty acids were also correlated in a negative way with the SWP, which helped to confirm the statement that these compounds increased with the water stress in almond trees.
### Table 4. Pearson’s correlation coefficients (R) among stem water potential and stress integral with fatty acids.

|          | SWP   | SI    | C14:0 | C16:0 | C16:1 | C17:0 | C17:1 | C18:0 | C18:1n9 | C18:1n7 | C18:2 | O/L   | SFA   | MUFA  | PUFA  | PUFA/SFA | PUFA/MUFA |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|---------|---------|-------|-------|-------|-------|-------|----------|----------|
| SWP      | 1.00  |       |       |       |       |       |       |       |         |         |       |       |       |       |       |          |
| SI       | 0.67 *** | 1.00 |       |       |       |       |       |       |         |         |       |       |       |       |       |          |
| C14:0    | 0.13  | 0.73 *** | 1.00 |       |       |       |       |       |         |         |       |       |       |       |       |          |
| C16:0    | 0.20  | 0.51 *** | 0.95 *** | 1.00 |       |       |       |       |         |         |       |       |       |       |       |          |
| C16:1    | 0.13  | 0.75 *** | 0.92 *** | 0.96 *** | 1.00 |       |       |       |         |         |       |       |       |       |       |          |
| C17:0    | 0.14  | 0.69 *** | 0.96 *** | 0.97 *** | 0.95 *** | 0.90 *** |       |       |         |         |       |       |       |       |       |          |
| C17:1    | 0.06  | 0.65 *** | 0.90 *** | 0.85 *** | 0.84 *** | 1.00 |       |       |         |         |       |       |       |       |       |          |
| C18:0    | 0.20  | 0.80 *** | 0.91 *** | 0.97 *** | 0.95 *** | 0.86 *** | 0.86 *** | 1.00 |         |         |       |       |       |       |       |          |
| C18:1n9  | 0.22  | 0.82 *** | 0.90 *** | 0.95 *** | 0.95 *** | 0.90 *** | 0.98 *** | 1.00 |         |         |       |       |       |       |       |          |
| C18:1n7  | 0.17  | 0.48 *** | 0.51 *** | 0.55 *** | 0.40 *** | 0.47 *** | 0.62 *** | 0.57 *** | 0.60 *** | 1.00 |       |       |       |       |       |          |
| C18:2    | 0.32 * | 0.82 *** | 0.86 *** | 0.91 *** | 0.86 *** | 0.76 *** | 0.75 *** | 0.88 *** | 0.93 *** | 0.46 *** | 1.00 |       |       |       |       |          |
| O/L      | 0.24  | 0.82 *** | 0.90 *** | 0.97 *** | 0.93 *** | 0.84 *** | 0.84 *** | 0.95 *** | 0.98 *** | 0.93 *** | 0.90 *** |       |       |       |       |          |
| SFA      | 0.21  | 0.83 *** | 0.84 *** | 0.90 *** | 0.88 *** | 0.88 *** | 0.89 *** | 0.89 *** | 0.89 *** | 0.89 *** | 0.93 *** | 0.90 *** | 1.00 |       |       |          |
| MUFA     | 0.27  | 0.84 *** | 0.92 *** | 0.97 *** | 0.93 *** | 0.84 *** | 0.83 *** | 0.95 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 1.00 |       |       |          |
| PUFA     | 0.32 * | 0.83 *** | 0.86 *** | 0.91 *** | 0.86 *** | 0.96 *** | 0.97 *** | 0.98 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 1.00 |       |          |
| PUFA/SFA | 0.05  | 0.45 *** | 0.89 *** | 0.96 *** | 0.83 *** | 0.91 *** | 0.96 *** | 0.96 *** | 0.96 *** | 0.96 *** | 0.96 *** | 0.96 *** | 0.96 *** | 0.96 *** | 1.00 |          |
| PUFA/MUFA| 0.32 * | 0.85 *** | 0.89 *** | 0.94 *** | 0.88 *** | 0.80 *** | 0.97 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 0.99 *** | 1.00 |          |

*, **, *** significant at p < 0.05, 0.01, and 0.001, respectively. SWP = minimum stem water potential; SI = stress integral; C16:0 (palmitic); C16:1 (palmitoleic); C17:0 (margaric); C17:1 cis (heptadecenoic); C18:0 (stearic); C18:1n9 (oleic); C18:1n7 (cis-vaccenic); C18:2n6 c9,12 (linoleic); O/L (oleic/linoleic); SFA (saturated fatty acids); MUFA (monounsaturated fatty acids); PUFA (polyunsaturated fatty acids).
A reduction in oleic, MUFA, and O/L ratio and an increase in linoleic, PUFA, and PUFA/MUFA ratio was also reported in almond cv. Marta, Guara, Lauranne, Ferragnes, Texas; olives cv. Mazanilla; pistachio cv. Kerman; and sunflower cv. Suncross [29,30,42,49,54,55].

The decrease in oleic and increase in linoleic in drought conditions was reported in many studies in different crops, although sometimes was cultivar dependent [54]. This effect of water stress on these two fatty acids was attributed to the enzyme Δ12 desaturase, which is responsible for the conversion of oleic acid in linoleic under water stress conditions [56].

As observed, PUFA is increased under water stress and similar results were reported in olives cv. Manzanilla [57] after two years of deficit irrigation. The authors reported that the higher the stress applied during stage III in olives, the greater the linoleic acid concentration and, consequently, (PUFA + MUFA)/SFA ratio, with a correlation of $R^2 = 0.71$ and $R^2 = 0.84$, respectively. An increase in linoleic acid may play an important role in the death of cardiac cells and is an essential fatty acid, which cannot be synthesized by human body [29]. It was reported that consuming 50 g of almonds under RDI conditions can cover approximately 33% of the daily intake of linoleic acid recommended by the European Food Safety Authority [29]. The present study showed an increase in PUFA and a decrease in MUFA with water stress, and this led to a low O/L rate. It is well known that a low O/L rate means almonds are more susceptible to oxidation, because this is initiated in the double bonds of PUFA [58]. However, it was also observed that water stress also enhances compounds with antioxidant activity (polyphenols, α-tocopherol, phytoprostanes, phytofurans, jasmonates, abscisic acid, etc., that are also enhanced by water stress) that might help in maintaining the PUFA in a cell’s membrane, preserving its bioactivity [59].

Saturated fatty acids were also observed to increase in almonds under water stress conditions, and the American Heart Association (AHA) encourages people to replace SFA with MUFA for a healthy lifestyle and low-density lipoprotein (LDL) cholesterol levels reductions. Thus, controlling the stress in almond trees might help to reduce the SFA content, because other studies reported that moderate deficiency did not negatively affected SFA content in almond [25,29,53]. Moreover, the levels of SFA in almonds are so low that almonds as well as other nuts fits well in AHA guidelines [60]. In fact, Food and Drug Administration (FDA) implemented a healthy claim regarding the almonds and other nuts consumption, stating that diets containing ~42.5 g of almonds per day as part of a diet low in saturated fat, and cholesterol may reduce the risk cardiovascular diseases [61].

To conclude this section, the fatty acids were significantly affected by water stress and are good markers of the hydroSOStainable almonds.

3.6. Descriptive Sensory Analysis

Table 5 shows the Pearson’s correlation coefficients (R) between SI and SWP with sensory attributes. These results highlighted strong negative correlations for the size, bitterness, astringency, benzaldehyde, and woody flavors. Previous studies reported that water stress might enhance the sweetness, nutty, almond ID, and crispiness in almonds cv. Lauranne and pistachio cv. Kerman [29,31]. Thus, an increase in sugars and a decrease in bitterness and astringency with water stress conditions as shown in this study might lead to sweeter almonds.

As previously described by Lipan et al. (2019) [19] and Carbonell-Barrachina et al. (2015) [31], the purchase choice of international consumers was based on sweetness, almond ID, pistachio ID, and crispiness. These findings together with those that consumers were willing to pay more for hydroSOStainable almonds [19], pistachios [20], and table olives [62], and the functional properties of the bioactive compounds described here encourage the almond farming sector to bet on deficit irrigation strategy to reduce irrigation water and simultaneously increase the functional and sensorial quality of almonds.
Table 5. Pearson’s correlation coefficients (R) among stem water potential and stress integral with sensory analysis parameters.

|       | SWP | SI  | Color | Size | Sweet | Bitter | Astr | Nutty | Al ID | Benz  | Woody | Hardness | Crispiness | Aftertaste|
|-------|-----|-----|-------|------|-------|--------|------|-------|-------|-------|-------|----------|------------|-----------|
| SWP   | 1.00|     |       |      |       |        |      |       |       |       |       |          |            |           |
| SI    | 0.24| 0.04| 1.00  |      |       |        |      |       |       |       |       |          |            |           |
| Color | 0.35| 0.35| 0.35  | 0.35 | 0.24  | 0.27   | 0.77 | 0.32  | 0.04  | 0.09  | 0.09  | 0.09     | 0.36       | 0.29      |
| Size  | 0.35| 0.35| 0.35  | 0.35 | 0.24  | 0.27   | 0.77 | 0.32  | 0.04  | 0.09  | 0.09  | 0.09     | 0.36       | 0.29      |
| Sweet | −0.43| 0.35| 0.35  | 0.35 | 0.24  | 0.27   | 0.77 | 0.32  | 0.04  | 0.09  | 0.09  | 0.09     | 0.36       | 0.29      |
| Bitter| 0.12| 0.62 | 0.62  | 0.62 | 0.35  | 0.70   | 0.12 | 0.32  | 0.04  | 0.09  | 0.09  | 0.09     | 0.36       | 0.29      |
| Astr  | 0.04| 0.39 | 0.39  | 0.39 | 0.04  | 0.32   | 0.12 | 0.32  | 0.04  | 0.09  | 0.09  | 0.09     | 0.36       | 0.29      |
| Nutty | 0.04| 0.39 | 0.39  | 0.39 | 0.04  | 0.32   | 0.12 | 0.32  | 0.04  | 0.09  | 0.09  | 0.09     | 0.36       | 0.29      |
| Al ID | −0.09| 0.34| 0.34  | 0.34 | −0.09 | 0.34   | 0.34 | 0.34  | 0.34  | 0.34  | 0.34  | 0.34     | 0.34       | 0.34      |
| Woody | 0.16| 0.71 | 0.71  | 0.71 | 0.16  | 0.71   | 0.71 | 0.71  | 0.71  | 0.71  | 0.71  | 0.71     | 0.71       | 0.71      |
| Hardness | −0.32| 0.03| 0.03  | 0.03 | −0.32 | 0.03   | 0.03 | 0.03  | 0.03  | 0.03  | 0.03  | 0.03     | 0.03       | 0.03      |
| Crispiness | −0.17| 0.12| 0.12  | 0.12 | −0.17 | 0.12   | 0.12 | 0.12  | 0.12  | 0.12  | 0.12  | 0.12     | 0.12       | 0.12      |
| Aftertaste | −0.15| 0.29| 0.29  | 0.29 | −0.15 | 0.29   | 0.29 | 0.29  | 0.29  | 0.29  | 0.29  | 0.29     | 0.29       | 0.29      |

*, **, ***: significant at p < 0.05, 0.01, and 0.001, respectively. SWP = minimum stem water potential; SI = stress integral; Sweet = sweetness; Bitter = bitterness; Astr = astringency; Al ID = almond ID; Benz = benzaldehyde like.
4. Conclusions

Globally, data presented here showed that water stress affected the functional and sensorial parameters of hydroSOStainable almonds showing positive correlations with dry weight, color coordinates ($L^*$, $a^*$, and $b^*$), minerals (K, Fe, and Zn), organic acids (citric acid), sugars (sucrose, fructose, and total sugars), antioxidant activity, and fatty acids (linoleic, PUFA, SFA, PUFA/MUFA, among others). On the other hand, the water stress in almonds was negatively correlated with kernel yield, water activity, weight (almond, kernel, and shell), size, minerals (Ca and Mg), fatty acids (oleic acids, oleic/linoleic ratio, MUFA, and PUFA/SFA), and sensory attributes (size, bitterness, astringency, benzaldehyde, and woody). Considering that moderate RDI led to kernel yields similar to the control, agricultural sector can save approximately 45% of the irrigation water obtaining high-quality products. The current long-term research helped to demonstrate which quality parameters are really affected by water stress conditions and to clarify which may be essential markers to distinguish hydroSOStainable almonds from other types of almonds. All these findings help the agro-food sector to understand (i) that is possible to increase the water use efficiency generating products with high functional and sensory quality; (ii) the need of controlling the water stress in plants for the best agronomical and quality responses; and (iii) to set up key agronomic and quality markers to control and establish whether the water stress created at the field/orchard significantly affected the quality and functionality of the final edible nuts.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4395/10/10/1470/s1. Table S1: Mean values of morphological and chemical parameters of irrigation treatments (T1, T2, T3, and T4) for 3 years (2017, 2018, and 2019) and Table S2: Mean values of functional and sensorial parameters of irrigation treatments (T1, T2, T3, and T4) for 3 years (2017, 2018, and 2019).

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