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Preharvest Foliar Application of Si–Ca-Based Biostimulant Affects Postharvest Quality and Shelf-Life of Clementine Mandarin (*Citrus clementina* Hort. Ex Tan)

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Abstract: Citriculture and the postharvest industry are in the quest for biostimulants that favour fruit quality and extend shelf-life. Recently, Si has emerged as a biostimulant and its impact on fruit quality and postharvest shelf-life needs to be elucidated. The experiment is conducted for two consecutive years (2019 and 2020) in a commercial citrus orchard. In the present study, a Si–Ca-based product (Gravital® Force SC, AGROLOGY SA, Sindos, Greece) is foliar sprayed upon clementine mandarin (*Citrus clementina* Hort. Ex Tan cv. SRA 63) trees from August to November, while unsprayed trees are kept as controls. At commercial maturity, both sprayed and unsprayed fruits are harvested and stored for thirty (30) days at 5 °C with 90–95% relative humidity. Afterwards, they are kept at shelf temperature (20 °C) for six (6) days (shelf-life). At different intervals [at harvest, after cold storage (30 d at 5 °C), at the third day of shelf-life (30 d at 5 °C plus 3 d at 20 °C) and sixth day of shelf-life (30 d at 5 °C plus 6 d at 20 °C)], fruits are sampled and analysed for their qualitative characteristics. According to the results, the preharvest foliar application of the Si–Ca-based product delayed fruit maturation, increased peel firmness, total soluble content, total acidity, ascorbic acid, total phenols and antioxidant capacity, and reduced fruit decay during shelf storage. Results suggest that the preharvest foliar spray of Si–Ca products is able to maintain the postharvest quality of mid-ripening mandarin fruit.

Keywords: citrus; biostimulants; postharvest; fruit quality; phytochemicals

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1. Introduction

Citrus is cultivated in more than 140 countries worldwide for its nutritional properties, flavour and by-products, reaching an annual production of more than 146 million tonnes [1]. Mandarins (*Citrus reticulata* Blanco) are among the most important citrus fruits since, in 2020, 30.86 million tonnes were produced globally [2]. In Greece, mandarins are the second most important citrus fruit, with an annual production of over 171,870 tonnes in 2020/2021 [2]. Among the most cultivated mandarin cultivars in Greece, Clementine mandarin cv. SRA 63 (*C. clementina* Hort. Ex Tan) is one of them due to its seedless characteristic and superior taste. In Greece, SRA 63 fruit ripe from mid-December to mid-January, while it is a common practice to store fruits at cold storage facilities in order to extend their market availability and commercial value.

Citriculture and postharvest distribution facilities are searching for compounds that can limit the use of hazardous chemical substances. Furthermore, consumers' awareness towards food safety and nutritional value has increased the demand for excellent-quality fruit [3]. During postharvest storage, it is important to sustain the quality attributes and reduce the use of hazardous chemicals, which could leave harmful residues and negatively affect public health and environmental security [3]. When citrus fruits are subjected to

postharvest storage conditions, several biotic or abiotic stress conditions occur, which modify metabolic cascades, leading to the loss of fruit quality, nutrient deprivation and decay syndromes [4].

It is well known that many factors influence the quality of citrus fruit, such as cultivar and harvest day [5], fruit canopy position [6] and mineral nutrition [7]. Nowadays, there is a growing interest in the potential of foliar application of biostimulants towards the enchantment of tree characteristics [8] and to achieve better crop management [9]. Silicon (Si) is the second most abundant element on the earth, after oxygen. Even though Si is not an essential element for plant growth, in its classical term, according to Epstein [10], it can act as a biostimulant since it can modulate the growth, development and stress response of plants [11]. Plants uptake some amount of Si from the soil in the form of silicic acid [$Si(OH)_4$] and distribute it to plant tissues [12–14]. Furthermore, Si participates in the modulation of various metabolic cascades, or the change of gene expression that alleviates plant tissues or fruits from deleterious abiotic stress conditions [15].

Additionally, calcium (Ca) is an important macro-element in plant nutrition, which acts as a signalling molecule in various metabolic cascades and is a critical component of the cell wall structure. It participates in multiple biochemical processes in plants and fruits, including respiration, development of chlorophyll, senescence, ethylene production, fruit firmness and prevention of rot incidents [16,17]. It has been reported that preharvest Ca spray upon fruits minimises postharvest decay syndromes and minimises the appearance of physiological disorders [18,19]. In Verna lemons, Ca application increased fruit firmness and prevented colour break for 21 days of storage at 15 °C [20]. Moreover, in the work of Cid-López et al. [21], the application of calcium oxide (CaO) nanoparticles to polymeric coatings, increased the shelf life of cucumbers by up to 24 days and improved quality attributes such as appearance, colour and antioxidant activity.

Concerning the impact of Si–Ca on plant physiology, previous studies mainly focused on its role as a biotic or abiotic stress tolerance [22–24]. In the work of Wutscher et al. [25], Si application (66 mg/L) as a nutrient solution enhanced the growth of young orange trees [*C. sinensis* (L.) Osbeck cv. Valencia]. Moreover, in grapefruit trees, supplementation of monosilicic acid in the irrigation water increased root weight by 40% [26]. So far, the combined action of Si and Ca is not yet elucidated, particularly for citrus. The scope of the current work was to investigate the impact of the preharvest foliar application of Si–Ca biostimulant upon the postharvest quality and shelf-life behaviour of mandarin fruit.

2. Materials and Methods

2.1. Plant Material and Treatments

The experiment was performed on thirty-five years-old citrus trees (*C. clementina* Hort. Ex Tan, cv. SRA 63), planted at 5 m × 5 m spacing between rows and along the row, grafted upon sour orange (*C. aurantium* L.). The soil type of the citrus grove was deep, well-drained and sandy loam. At the end of January (2019 and 2020), 1.5 kg of 20-20-20 NPK fertilizer was applied to the roots of each tree. Moreover, at the end of August, 0.5 kg of potassium nitrate fertilizer was also applied to the roots of each tree. Experimental trees were selected from a commercial citrus grove located in Corinth, Greece. For the experimental needs, for each treatment (Control and Si–Ca-Based compound) five (5) trees were used for each replication (three replications), counting a total number of 30 trees. Additional 10 trees were used as border trees for each replication of each treatment, in order to isolate each replication since all trees were within the same citrus grove (60 trees in total). During the years 2019 and 2020, a novel Si–Ca-based compound, (Gravital® Force SC, 35% *w*/*v* SiO_2, 35% *w*/*v* CaO and 30% *w*/*v* inactive compounds, originated from pulverized rock, creating a particle film of Si–Ca, being certified for organic farming use and commercially available by AGROLOGY SA, Sindos, Greece), was sprayed on fifteen trees at the rate of 10 g/L water, while another set of fifteen trees was unsprayed and served as control (five trees per replication). Overall, three sprays were performed each year as follows: at the beginning of August, mid-September and late November.

When the fruit reached commercial maturation (12 January 2020 and 22 December 2020, experimental years 2019 and 2020, respectively), one hundred and twenty (120) healthy and uniform size fruits were collected from each treatment and divided into three lots, forty (40) fruits in each. After harvest, the fruits were transferred into a cold storage facility (5 °C temperature and 90–95% relative humidity) for thirty days. After cold storage, the fruits were moved out and transported to the lab where they remained for 6 days at 20 °C, to stimulate shelf-life environment conditions. In total, thirty (30) fruits (ten in each replication) of each treatment were sampled at four (4) time points i.e., at harvest day, day 0 (exit from cold storage), day 3 of shelf-life and day 6 of shelf-life and used for the determination of qualitative physicochemical parameters.

2.2. Fruit Characteristics (Weight, Juice Content, Peel Thickness and Peel Colour)

Fruit weight (g) and juice content (%) was measured on an electronic precision balance (Kern 440-47 N, Kern, Germany). The peel thickness was measured with an electronic digital slide gauge (Parkside, Germany) with 0.01 mm accuracy. Peel colour was measured on two opposite portions of the equatorial area of each fruit via the use of a Minolta CR-300 chroma-meter. Values L*, a* and b* were converted to the Citrus Color Index (CCI) by the use of the formula CCI = (a* 1000)/(b*L*) [27].

2.3. Fruit Firmness

Fruit firmness was determined by a stable GY-4 Digital Fruit sclerometer (Beijing Channel Scientific Instruments Co., Ltd., Beijing, China), equipped with a flat compression plate. For each fruit, two opposite areas were penetrated and the resistance to compression of 10 mm was recorded and expressed as kg [28].

2.4. Juice Chemical Parameters (Juice pH, Total Soluble Solids, Total Acidity, Ascorbic Acid Content)

The juice pH was determined by using a potentiometer (Thermo Scientific ORION STAR A211, Waltham, MA, USA). Total soluble content (TSS) and total acidity (TA) were measured at 25 °C with a refractometer PAL-BX/ACID 1 Master Kit (Atago CO. Ltd., Tokyo, Japan), and expressed as °Brix and % citric acid, respectively, according to the manual of the instrument.

For the determination of ascorbic acid, total phenolics and antioxidant activity, the juice sample was centrifuged at 1650× *g* for 10 min at 4 °C. The quantification of ascorbic acid was performed according to the AOAC method [29]. Briefly, a 1 mL centrifuged juice sample was mixed with 1 mL of extraction solution (HPO_3-acetic acid). The mixture was used for the determination of the ascorbic acid content by titration with 2,6-dichlorophenolindophenol sodium salt hydrate (2,6-DCPI). The results were expressed as mg ascorbic acid/100 mL juice.

2.5. Total Phenolic Content

Total phenolic content was determined according to Singleton et al. [30]. In detail, in order to extract the juice phenolic content, 1 mL juice sample was mixed with 9 mL 80% (*v*/*v*) methanol and the mixture was incubated for 24 in 4 °C. Afterwards, the mixture was centrifuged at 4 °C for 15 min at 5000 rpm and an aliquot of the supernatant was used for the determination of total phenolics via the Folin-Ciocalteu method. Total phenolics were measured at 760 nm. The results were expressed as Gallic Acid Equivalent (GAE) (mg GAE/mL juice).

2.6. Total Antioxidant Capacity (FRAP Assay)

The antioxidant capacity of the juice was estimated according to Benzie and Strain [31], with some modifications. For the Ferric Reducing Antioxidant Power (FRAP) assay, fresh FRAP reagent solution (300 mM sodium acetate buffer, pH 3.6, 10 mM Fe (II)-TPTZ prepared in 40 mM HCl, 20 mM $FeCl_3 \cdot H_2O$ (10:1:1)) was freshly prepared prior to analysis. An aliquot of the supernatant was mixed with the FRAP reagent and the absorbance was

measured at 593 nm after 30 min incubation at 37 °C. The ascorbic acid solution was used to express the antioxidant capacity as µmol Ascorbic acid/mL juice.

2.7. Fruit Decay during Storage

For the determination of fruit decay during shelf storage, forty-five fruits were randomly selected at the harvest date from each treatment. All collected fruits were divided into 3 replications, each replication was comprised of fifteen fruits. Fruit decay was counted after the 30 days of cold storage, at the 3rd and 6th day of shelf storage at 20 °C. The number of fruits that showed any sign of surface rot by mycelia development (*Penicillium* sp.) was counted [32]. Fruit decay was expressed as a percentage (%).

2.8. Statistical Analysis

The two-year data were analysed by using year and treatment as fixed effects in ANOVA models. In all tables, each year's data are presented along with pooled data since a similar trend was observed between the two years. Since for all measurements there was a similar trend between the years (2019 and 2020), in the results section and during the discussion section, the mean values of each measurement are presented and analysed. The data reported are the mean of replicates and expressed as mean ± standard deviation. Statistical analysis was performed via the use of the SPSS v.27 package (SPSS Inc., Chicago, IL, USA), with the use of a one-way analysis of variance (One-way ANOVA), with six replicates for each treatment. When there was a significant difference ($p < 0.05$), means were separated using Duncan's test.

A principal component analysis [33] was applied via the use of the SPSS v.27 package (SPSS Inc., Chicago, IL, USA). Principal component analysis (PCA) is used as a protocol for the determination of variables or as a tool to pinpoint factors that provide a better explanation of the correlation or covariance matrix of several attributes.

3. Results

3.1. Fruit Parameters and Fruit Decay

The weight of the citrus fruit is one of the basic quality attributes since it affects the overall tree productivity measurement. In our work, the mean fruit weight of the mandarin fruits was not affected by the preharvest foliar application of Si–Ca at all four postharvest time points (Table 1). However, irrespective of foliar treatments, a significant reduction in fruit weight was observed after one month of cold storage.

The CIE L*, a*, b* colour scale was used for the evaluation of peel colour during harvest, cold storage and ambient room storage. In this study, it was observed that Si–Ca spray did not significantly affect the fruit skin colour (CCI) at the harvest date and after one-month cold storage (30 d at 5 °C). During shelf storage, at day 3 (30 d at 5 °C plus 3 d at 20 °C), Si–Ca treated mandarin fruit exhibited a 14.37% higher CCI value than control fruit, whereas, at day 6 (30 d at 5 °C plus 6 d at 20 °C), no difference of CCI value was observed between treatments (Table 1).

Skin firmness is also an important attribute for the determination of citrus fruit quality and is tightly related to their ability to travel long distances. Si–Ca treated mandarin fruit exhibited a significant increase in fruit firmness values by 14.2% at harvest date, by 19.3% after one-month cold storage, by 16.28% on the third day (30 d at 5 °C plus 3 d at 20 °C) of shelf storage and by 10.95% on the sixth day of shelf storage (30 d at 5 °C plus 6 d at 20 °C), as compared to their respective control fruits (Table 1).

Peel thickness is a significant quality attribute of citrus fruit. In the current work, the foliar spray of Si–Ca significantly increased the peel thickness by 11.44% on the harvest day. After one-month cold storage (30 d at 5 °C) and at both shelf storage intervals (30 d at 5 °C plus 3 d at 20 °C and 30 d at 5 °C plus 6 d at 20 °C), Si–Ca treated mandarin fruits had no significant changes in peel thickness over their respective control (Table 1).

Table 1. Effect of preharvest Si–Ca foliar application on physical attributes of mandarin fruit. Means ± S.D. different letters indicate that there are statistically significant differences ($p < 0.05$) between the values of each treatment at each time point.

	Postharvest Time Point	**2019**		**2020**		**Mean**	
		Control	**Si–Ca**	**Control**	**Si–Ca**	**Control**	**Si–Ca**
Fruit weight (g)	Harvest day	95.13 ± 12.93 b	90.46 ± 17.45 b	75.67± 2.96 b	77.45 ± 2.00 b	85.4 ± 5.08 c	83.95 ±7.77 c
	30 d at 5 °C	53.10 ± 2.53 a	61.41 ± 5.43 a	67.48 ± 1.7 a	67.56 ± 1.05 a	60.29 ± 0.71 ab	64.49 ± 2.66 b
	30 d at 5 °C plus 3 d at 20 °C	50.01 ± 2.76 a	60.91 ± 0.31 a	66.32 ± 1.77 a	67.43 ± 1.36 a	58.17 ± 0.66 ab	64.17 ± 0.71 b
	30 d at 5 °C plus 6 d at 20 °C	48.52 ± 3.05 a	61.27 ± 0.22 a	65.17 ± 1.89 a	63.71 ± 1.61 a	56.84 ± 0.81 a	62.49 ± 0.77 ab
CCI	Harvest day	11.32 ± 1.40 a	10.76 ±0.86 a	12.39 ±0.92 a	14.04 ± 0.28 b	11.85 ± 0.26 a	12.40 ± 0.57 a
	30 d at 5 °C	10.56 ± 1.33 a	12.07 ± 1.56 a	13.31 ± 0.62 ab	12.33 ± 0.54 a	11.93 ± 0.36 a	12.20 ± 0.54 a
	30 d at 5 °C plus 3 d at 20 °C	11.24 ± 3.82 a	15.53 ± 1.33 b	13.11 ± 0.37 ab	12.32 ± 0.57 a	12.17 ± 1.74 a	13.92 ± 0.88 b
	30 d at 5 °C plus 6 d at 20 °C	10.55 ± 1.42 a	13.56 ± 0.45 ab	12.74 ± 0.57 a	12.34 ± 0.26 a	11.64 ± 0.71 a	12.96 ± 0.23 ab
Skin Firmness (kg)	Harvest day	2.78 ± 0.07 ab	3.36 ± 0.34 de	3.04 ± 0.12 bc	3.30 ± 0.18 cd	2.91 ± 0.09 ab	3.33 ± 0.26 cd
	30 d at 5 °C	2.81 ±0.12 abc	3.09 ± 5.00 cde	2.71 ± 0.14 a	3.50 ± 0.10 c	2.76 ± 0.1 a	3.3 ± 0.05 cd
	30 d at 5 °C plus 3 d at 20 °C	2.74 ± 0.12 a	3.20 ± 0.09 de	2.83 ± 0.08 ab	3.27 ± 0.14 cd	2.78 ± 0.10 a	3.24 ± 0.11 cd
	30 d at 5 °C plus 6 d at 20 °C	3.07 ± 3.38 bcd	3.38 ± 0.18 e	3.08 ± 0.08 bc	3.44 ± 0.23 c	3.07 ± 0.10 bc	3.41 ± 0.20 d
Rind Thickness (mm)	Harvest day	3.00 ± 0.38 b	3.52 ± 0.14 c	3.40 ± 0.10 c	3.61 ± 0.10 d	3.20 ± 0.24 b	3.57 ± 0.12 c
	30 d at 5 °C	2.29 ± 0.12 a	2.31 ± 0.15 a	2.47 ± 0.13 ab	2.56 ± 0.15 b	2.38 ± 0.12 a	2.44 ± 0.15 a
	30 d at 5 °C plus 3 d at 20 °C	2.10 ± 0.2 a	2.24 ± 0.08 a	2.32 ± 0.13 ab	2.37 ± 0.07 ab	2.21 ± 0.16 a	2.31 ± 0.07 a
	30 d at 5 °C plus 6 d at 20 °C	2.13 ± 0.06 a	2.41 ± 0.35 a	2.26 ± 0.07 a	2.54 ± 0.34 ab	2.20 ± 0.06 a	2.48 ± 0.35 a
Juice Content (%)	Harvest day	31.89 ± 1.64 a	32.60 ± 2.95 a	34.23 ± 2.00 a	35.08 ± 2.40 a	33.06 ± 1.81 a	33.84 ± 2.61 a
	30 d at 5 °C	37.01 ± 7.04 a	35.64 ± 3.69 a	40.76 ± 6.08 a	37.88 ± 3.26 a	38.88 ± 6.53 a	36.76 ± 3.35 a
	30 d at 5 °C plus 3 d at 20 °C	34.36 ± 3.16 a	33.03 ± 3.27 a	35.49 ± 3.85 a	35.98 ± 2.08 a	34.92 ± 3.49 a	34.51 ± 2.67 a
	30 d at 5 °C plus 6 d at 20 °C	36.00 ± 2.69 a	37.40 ± 1.98 a	37.50 ± 3.88 a	39.46 ± 0.81 a	36.75 ± 3.27 a	38.43 ± 1.24 a
Fruit Decay (%)	Harvest day	-	-	-	-	-	-
	30 d at 5 °C	33.49 ± 1.41 a	32.94 ± 2.68 a	34.66 ± 2.69 a	34.57 ± 2.26 a	34.07 ± 1.89 a	33.75 ± 2.47 a
	30 d at 5 °C plus 3 d at 20 °C	40.70 ± 1.46 b	34.80 ± 1.90 a	42.82 ± 1.62 cd	37.70 ± 1.69 ab	41.76 ± 1.54 cd	36.25 ± 1.79 ab
	30 d at 5 °C plus 6 d at 20 °C	43.90 ± 1.71 c	38.14 ± 0.65 b	46.21 ± 2.97 d	39.36 ± 0.93 bc	45.05 ± 2.32 d	38.75 ± 0.78 bc

In addition, the juice content did not show any significant change between the examined treatments at all four time points (Table 1).

Postharvest fruit decay incidence during shelf storage was significantly decreased by the preharvest foliar spray of Si–Ca (Table 1). After one month of cold storage (30 d at 5 °C), no significant difference in fruit decay was observed between treatments. During shelf storage (30 d at 5 °C plus 3 d at 20 °C and 30 d at 5 °C plus 6 d at 20 °C), preharvest foliar sprayed Si–Ca mandarin fruit exhibited a significant lower fruit decay by 13%, as compared to the control (Table 1).

3.2. Juice Parameters (Total Soluble Solids Content, Total Acidity, TSS/TA Ratio and pH)

TSS and acidity are very important quality indexes since they determine the taste of mandarin fruit. In our study, TSS and TA were determined at harvest day, one month after cold storage (30 d at 5 °C) and during shelf storage (30 d at 5 °C plus 3 d at 20 °C and 30 d at 5 °C plus 6 d at 20 °C). In the present study, it was observed that preharvest foliar Si–Ca spray significantly increased the fruit TSS content by 19.70% at harvest date, by 35.47% after one month of cold storage (30 d at 5 °C), by 40.18% at the third day of shelf storage (30 d at 5 °C plus 3 d at 20 °C) and by 32.10% at the sixth day of shelf storage (30 d at 5 °C plus 6 d at 20 °C), with respect to their control fruits (Table 2).

Moreover, preharvest foliar Si–Ca application significantly increased fruit TA by 40.74% at harvest date, by 81.65% after one-month cold storage (30 d at 5 °C), by 75% at the third day of shelf storage (30 d at 5 °C plus 3 d at 20 °C) and by 76.34% at the sixth day of shelf storage (30 d at 5 °C plus 6 d at 20 °C), with respect to their control fruits (Table 2).

Furthermore, the ratio of TSS/TA is used in order to determine the taste of citrus fruits, and mandarin fruits as an indicator of the fruit's maturity stage. In the current work, Si–Ca treated fruit exhibited a significantly lower ratio of TSS/TA by 14.6% at the harvest date, by 25.40% after one month of cold storage (30 d at 5 °C), by 19.66% at the third day of shelf storage (30 d at 5 °C plus 3 d at 20 °C) and by 24.81% at the sixth day of shelf storage (30 d at 5 °C plus 6 d at 20 °C), with respect to their control fruits (Table 2).

Juice pH is a significant quality attribute of citrus fruit. In the current work, Si–Ca treated fruit exhibited a significantly lower ratio of juice pH by 10.99% at the harvest date, by 10.17 % after one month of cold storage (30 d at 5 °C), by 11.06% on the third day of shelf storage (30 d at 5 °C plus 3 d at 20 °C) and by 14.57% on the sixth day of shelf storage (30 d at 5 °C plus 6 d at 20 °C), with respect to their control fruits (Table 2).

3.3. Juice Ascorbic Acid Content, Phenolics and Antioxidant Capacity

Ascorbic acid (AA) content and total phenolic content, along with the determination of the total antioxidant capacity, are crucial factors that link the consumption of fruit for health-related benefits. In our study, the preharvest foliar spray of Si–Ca significantly affected the AA content of mandarin fruit at the harvest date. After one-month cold storage (30 d at 5 °C) of Si–Ca treated fruit, a significant change of AA content by 69.63% was observed over control ones. During shelf storage, at day 3 (30 d at 5 °C plus 3 d at 20 °C), Si–Ca treated fruit exhibited 55.76% higher AA content than control fruit, whereas, at day 6 (30 d at 5 °C plus 6 d at 20 °C), a significant increase of 51.76% AA content was observed in Si–Ca treated fruit (Table 3).

Moreover, in our study, preharvest Si–Ca foliar spray on mandarin trees significantly affected the total phenolic (TP) content at harvest date by 21.90% with respect to control fruits. After one-month cold storage (30 d at 5 °C) upon Si–Ca treated fruits, a significant change of TP content by 39.45 % was observed over control ones. During shelf storage, at day 3 (30 d at 5 °C plus 3 d at 20 °C), Si–Ca treated mandarin fruit exhibited 30.53% higher TP content than control fruit, whereas, at day 6 (30 d at 5 °C plus 6 d at 20 °C), 32.17% more TP content was observed in Si–Ca treated mandarin fruit (Table 3).

Table 2. Effect of preharvest Si–Ca foliar application on quality attributes of mandarin fruit. Means ± S.D. different letters indicate that there are statistically significant differences ($p < 0.05$) between the values of each treatment at each time point.

	Postharvest Time Point	2019		2020		Mean	
		Control	Si–Ca	Control	Si–Ca	Control	Si–Ca
Total Soluble Solids (°Brix)	Harvest day	10.80 ± 0.56 a	13.43 ± 0.81 b	11.53 ± 0.21 a	13.30 ± 0.17 bc	11.17 ± 0.35 a	13.37 ± 0.49 b
	30 d at 5 °C	11.05 ± 2.15 a	15.95 ± 0.94 c	11.89 ± 1.14 ab	15.12 ± 0.89 d	11.47 ± 0.50 a	15.53 ± 0.12 d
	30 d at 5 °C plus 3 d at 20 °C	10.54 ± 0.27 a	16.13 ± 2.19 c	11.86 ± 0.85 ab	15.27 ± 1.21 d	11.20 ± 0.53 a	15.70 ± 0.52 d
	30 d at 5 °C plus 6 d at 20 °C	10.10 ± 0.56 a	15.01 ± 1.82 b	11.50 ± 0.56 a	13.52 ± 0.81 c	10.80 ± 0.44 a	14.27 ± 0.55 c
Acidity (% citric acid)	Harvest day	0.62 ± 0.02 b	0.93 ± 0.17 d	0.53 ± 0.02 b	0.69 ± 0.02 c	0.58 ± 0 b	0.81 ± 0.08 de
	30 d at 5 °C	0.39 ± 0.01 a	0.86 ± 0.12 cd	0.54 ± 0.03 b	0.83 ± 0.04 d	0.47 ± 0.02 a	0.84 ± 0.06 e
	30 d at 5 °C plus 3 d at 20 °C	0.40 ± 0.04 a	0.78 ± 0.16 bcd	0.46 ± 0.02 a	0.71 ± 0.01 c	0.43 ± 0.03 a	0.75 ± 0.09 cd
	30 d at 5 °C plus 6 d at 20 °C	0.35 ± 0.02 a	0.72 ± 0.14 bc	0.45 ± 0.02 a	0.68 ± 0.06 c	0.40 ± 0 a	0.70 ± 0.04 c
TSS/Acidity	Harvest day	17.45 ± 0.32 a	14.71 ± 1.97 a	21.65 ± 1.10 b	19.20 ± 0.70 ab	19.39 ± 0.61 ab	16.56 ± 1.08 a
	30 d at 5 °C	28.40 ± 6.02 cd	18.75 ± 1.54 a	21.98 ± 0.92 b	18.18 ± 1.56 a	24.71 ± 2.09 c	18.44 ± 1.13 ab
	30 d at 5 °C plus 3 d at 20 °C	26.79 ± 3.30 bcd	20.80 ± 1.92 ab	26.02 ± 2.36 c	21.53 ± 2.00 b	26.33 ± 2.22 c	21.15 ± 1.62 b
	30 d at 5 °C plus 6 d at 20 °C	29.23 ± 3.03 d	21.75 ± 7.05 abc	25.74 ± 0.40 c	20.05 ± 2.82 ab	27.22 ± 1.10 c	20.47 ± 2.00 b
Juice pH	Harvest day	3.62 ± 0.05 cd	3.30± 0.18 a	3.72 ± 0.14 c	3.23 ± 0.06 a	3.67 ± 0.05 d	3.27 ± 0.07 a
	30 d at 5 °C	3.79 ± 0.12 d	3.33 ± 0.05 ab	3.75 ± 0.06 c	3.44 ± 0.07 b	3.77 ± 0.03 e	3.39 ± 0.04 b
	30 d at 5 °C plus 3 d at 20 °C	4.02 ± 0.08 e	3.53 ± 0.12 bc	3.94 ± 0.06 d	3.55 ± 0.12 b	3.98 ± 0.02 f	3.54 ± 0.08 c
	30 d at 5 °C plus 6 d at 20 °C	3.99 ± 0.07 e	3.39 ± 0.14 ab	3.97 ± 0.12 d	3.41 ± 0.05 b	3.98 ± 0.03 f	3.40 ± 0.07 b

Table 3. Effect of preharvest Si–Ca foliar application on phytochemical attributes of mandarin fruit. Means ± S.D. different letters indicate that there are statistically significant differences ($p < 0.05$) between the values of each treatment at each time point.

	Postharvest Time Point	2019		2020		Mean	
		Control	Si–Ca	Control	Si–Ca	Control	Si–Ca
Ascorbic Acid (mg/100 mL)	Harvest day	40.57 ± 9.45 a	58.33 ± 6.56 b	73.90 ± 4.51 b	86.06 ± 3.40 c	57.24 ± 4.91 b	72.20 ± 3.90 c
	30 d at 5 °C	36.58 ± 4.68 a	85.71 ± 17.19 c	74.15 ± 3.38 b	102.11 ± 2.98 d	55.36 ± 1.33 ab	93.91 ± 8.56 d
	30 d at 5 °C plus 3 d at 20 °C	30.61 ± 7.21 a	59.23 ± 4.71 b	65.04 ± 2.98 a	89.76 ± 7.04 c	47.83 ± 3.01 a	74.49 ± 5.52 c
	30 d at 5 °C plus 6 d at 20 °C	36.11 ± 5.21 a	61.76 ± 3.41 b	62.44 ± 1.95 a	87.80 ± 5.16 c	49.28 ± 1.81 ab	74.78 ± 1.74 c
Total Phenols (mg GAE/ mL)	Harvest day	0.83 ± 0.03 abc	0.96 ± 0.08 bcd	0.48 ± 0.04 a	0.63± 0.01 c	0.65 ± 0.03 a	0.80 ± 0.04 b
	30 d at 5 °C	0.75 ± 0.09 a	1.20 ± 0.11 e	0.58 ± 0.02 b	0.64 ± 0.01 c	0.66 ± 0.04 a	0.92± 0.05 d
	30 d at 5 °C plus 3 d at 20 °C	0.82 ± 0.08 abc	1.10 ± 0.24 de	0.58 ± 0.01 b	0.73 ± 0.03 d	0.70 ± 0.04 a	0.92 ± 0.11 cd
	30 d at 5 °C plus 6 d at 20 °C	0.77 ± 0.05 ab	1.02 ± 0.07 cde	0.48 ± 0.04 a	0.63 ± 0.01 c	0.63 ± 0.01 a	0.83 ± 0.04 bc
FRAP (μmole Asc.Acid/mL)	Harvest day	5.09 ± 0.70 ab	5.94 ± 0.48 ab	5.14 ± 0.08 a	6.53 ± 0.50 b	5.11 ± 0.31 a	6.23 ± 0.37 bc
	30 d at 5 °C	5.57 ± 0.60 ab	7.73 ± 0.90 c	5.22 ± 0.08 a	7.32 ± 0.26 c	5.40 ± 0.30 ab	7.53 ± 0.43 d
	30 d at 5 °C plus 3 d at 20 °C	5.46 ± 0.75 ab	6.35 ± 1.62 bc	5.24 ± 0.10 a	7.64 ± 0.49 c	5.35 ± 0.42 ab	6.99 ± 1.05 cd
	30 d at 5 °C plus 6 d at 20 °C	4.60 ± 0.59 a	6.27 ± 0.64 bc	5.10 ± 0.10 a	6.57 ± 0.25 b	4.85 ± 0.26 a	6.42 ± 0.44 c

Furthermore, in our study, a significant improvement in the overall antioxidant capacity was observed in the Si–Ca-treated mandarin fruit over untreated ones. In detail, Si–Ca spray on fruit significantly increased the antioxidant capacity (FRAP value) of the juice at harvest date by 21.90% with respect to control fruits. After one-month cold storage (30 d at 5 °C) of Si–Ca treated mandarin fruits, a significant increase of FRAP value by 39.45%, was observed over control ones. During shelf storage, at day 3 (30 d at 5 °C plus 3 d at 20 °C), Si–Ca treated mandarin fruit exhibited 30.72% higher FRAP values than control fruit, whereas, at day 6 (30 d at 5 °C plus 6 d at 20 °C), 32.18% more TP content was observed in Si–Ca treated mandarin fruit (Table 3).

In the end, principal components analysis (PCA) was used to detect possible patterns, groupings and differences in the Si–Ca treated mandarin fruit, at harvest and post-harvest period. A PCA analysis was conducted using 14 variables related to mandarin physiology and quality (Figure 1). The variance of data that was explained by the PCA model was 77.2%, where PC1 explained 49.4% and PC2 27.8% of the total variance. The Kaiser Meyer Olkin measure of sampling adequacy (KMO) on the data was 0.657. A clear separation between the Si–Ca treated mandarins (positive values) and control mandarins (negative values) was observed. Moreover, PC1 construction was closely related to total phenols content, FRAP, TSS, TA, AA content and peel firmness that increased in Si–Ca treated mandarins while it was decreased in the pH and TSS/TA. PC2 was more closely linked to stage separation between harvest and post-harvest storage. PC2 construction is related to fruit decay, fruit weight and rind thickness where these variables are mainly involved in the separation of harvest from post-harvest storage (Figure 1).

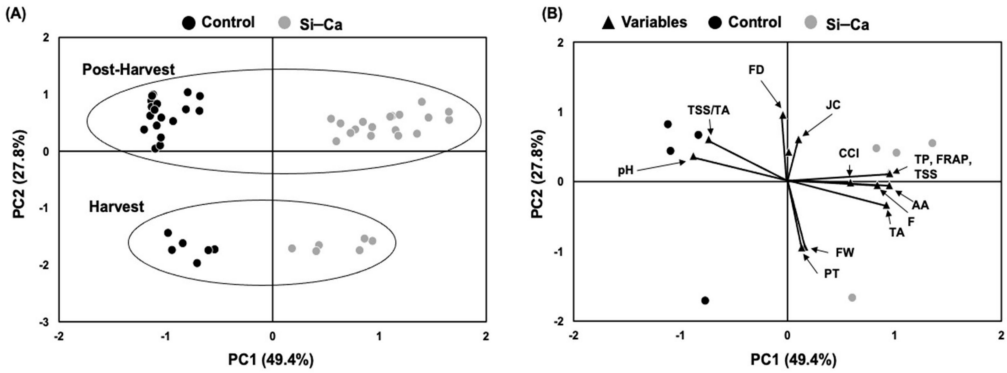

Figure 1. Principal component analysis (PCA) of physiological and quality traits is illustrated in mandarins treated with Si–Ca at harvest and post-harvest, using a score plot (**A**) and a biplot (**B**). Control: black circle, Si–Ca: grey circle. Variables are represented with a black triangle: fruit weight (FW); peel thickness (RT); colour index (CCI); flesh firmness (F), juice content (JC); total soluble solids (TSS); titratable acidity (TA); fruit decay (FD); ascorbic acid content (AA); total phenols content (TP), antioxidant activity (FRAP).

4. Discussion

Nowadays, there is a shift in agriculture towards the implementation of agricultural practises that preserve fruit quality attributes [34]. Fruit sprayed with biostimulants can sustain the quality attributes for an extensive period of shelf storage [34]. However, limited data are currently available regarding the effect of applied biostimulants towards the quality attributes of perennial tree crops [11].

In the present study, fruit weight was not significantly affected by the preharvest foliar application of Si–Ca biostimulant (Table 1). This result is aligned with that of Omar and El-Enin [35], who demonstrated that the foliar application of Ca did not significantly affect citrus fruit weight. Likewise, the application of Si to hydroponically cultivated strawberries, under Fe deficiency, did not alter fruit weight [36]. However, when lemon fruits were dipped in Si solution, a significant reduction in weight was recorded due to the proposed reduction of membrane permeability and increased membrane stability and integrity [37].

The difference in the effect of Si–Ca upon fruit commodities could be attributed to the method of application (fruit coating, fertigation, foliar spray) and time of application.

The colour of the mandarin fruit is a crucial quality attribute since it determines consumer choice [38]. In the current work, no significant differences in mandarin skin CCI were recorded at the various studied time intervals (Table 1). This result is in accordance with Bang et al. [39] and Peris-Felipo et al. [36], who demonstrated that the application of CaO or Si, respectively, did not influence the peel colour of the examined fruit. In the work of D' Aguino et al. [40], the application of the commercial compound surrounding WP (a Kaolin-Si-based compound) delayed cactus pear fruit colouration at harvest. Furthermore, in the work of Karagiannis et al. [14], foliar spray of a commercial Si-based biostimulant favoured the development of red colour on the peel of apples at harvest. These results demonstrate that the impact of Si on the development of colour peel during fruit ripening is contradictory and rather limited, as stated by several research groups [36,41,42].

In the current study, it was demonstrated that the preharvest foliar spray of the Si–Ca-based compound improved the postharvest fruit firmness (Table 1). This result is in line with the data from Weerahewa and David [43], who witnessed a significant increase in fruit firmness when Si was applied during flowering. Moreover, in the work of Yavad and Varu [44], the addition of Ca to papaya fruits resulted in the maintenance of fruit firmness during storage. The beneficial effect of foliar Si–Ca application upon tomato fruit firmness was demonstrated by Jing et al. [45]. The current beneficial effect of preharvest foliar Si–Ca spray could be linked with the ability of Ca to protect membranes from disorganization [16] and the ability of Si to stabilize the cell wall, via its protection from degradative enzymes [14], and the stimulation of the deposition of cellulose and hemicellulose [46].

In citrus fruit, it has been proposed that foliar application of Ca along with biostimulants and bioregulators is the most optimum method to alleviate fruit cracking and affect fruit rind thickness [47]. In the current study, preharvest spray of a Si–Ca-based compound resulted in increased rind thickness, only at harvest time, while no significant differences were recorded during postharvest cold storage and shelf storage (Table 1). This finding is in line with that of Hoda et al. [48], who demonstrated that the preharvest foliar application of Ca- or Si-based compounds can increase the mandarin peel thickness at harvest time. In another study by Hoda et al. [49], preharvest foliar application of diatoms (a source of Si) on Valencia orange fruit increased citrus peel thickness. It can be proposed that the preharvest foliar spray of Si–Ca compound provides the proper time interval for the plant leaves to absorb Si and Ca, translocate them into the fruit peel tissue, thus increase their tissue concentration and participation in the build-up of the mesocarp and epicarp of the fruit peel [48]. These findings support the role of Ca and Si in the citrus rind's development and rigidity when Ca and Si are applied at the pre-harvest stage [50].

It has been reported that the use of Si and Ca is beneficial towards the control of citrus fruit decay caused by *Penicillium spp.* [32,51]. In our work, mandarin fruit sprayed with a Si–Ca-based compound exhibited lower fruit decay than the control (Table 1). These data are in accordance with those observed by Moscoso-Ramírez and Palou [32], who found significant preventive (treatment before fungal inoculation) and curative (treatment after inoculation) activities of Si against *Penicillium spp.* after 6 days at 20 °C. Moreover, in the work of Weerahewa and Somapala [52], it is well documented that the application of Si can enhance the biotic resistance of tropical fruits. This beneficial role of Si was also supported by Mvondo-She et al. [53], who provided evidence that Si treatment can mitigate biotic stress syndromes in citrus fruits. It has been proposed that Si–Ca application in citrus fruit decreases fruit spoilage due to the ability of Ca to maintain cell wall structure and cell membrane integrity [16] and the ability of Si to act as a physical barrier against pathogen penetration or as a stimulant of defence responses [54]. It is known that Si's ability to initiate defence responses in plant pathosystems is linked with the ability of Si to induce physical resistance via reduced penetration and/or increased hardness and abrasiveness of the fruit tissue due to Si deposition when applied at preharvest time points [52]. Si can also induce chemical resistance via the enhanced production of defensive enzymes and

the production of antifungal compounds such as phenolic compounds [52], a fact that was witnessed in the current work (Table 3).

It is well documented that in citrus fruit, sugars and especially organic acids are detrimental compounds for the determination of fruit taste quality [55]. It is stated that a high concentration of organic acids or a rather low pH value is an indicator of delayed senescence procedures [56], while the ratio between TSS and TA (which refers to maturity index) determines fruit sweetness [21]. In our work, the preharvest foliar spray of a Si–Ca-based compound increased TSS, TA and juice pH during postharvest treatments (Table 2). The positive impact of Si or Ca application upon TSS was also demonstrated by Mounika et al. [16]. In the work of Matichenkov and Calvert [26], the supply of Si in orange trees significantly increased fruit sugar content. Moreover, in the work of Sharma et al. [57], the application of kaolin (a Si-containing compound) improved or had no adverse effect on the TSS of pomegranate fruit during postharvest storage. Similar positive results, upon the TSS content, were also accounted via the application of Ca to cucumber fruit during postharvest storage [21]. In our work, the increased amount of TA and decreased pH values, along with lower TSS/TA values, at all-time points of the analysis, indicate that the preharvest foliar application of the Si–Ca compound delayed the maturation of the mandarin fruit at harvest time and during postharvest storage (Table 2).

The basic phytochemicals of citrus juice are ascorbic acid (AA) and phenolic compounds, as it has been well documented in various citrus species such as blood oranges [58], pomelo [59] and lemons [60]. It is stated that the application of Si or Ca-based fertilizers exerts a positive impact upon the concentration of AA and fruit sugars [61]. In our work, the foliar application of a Si–Ca-based compound increased the concentration of AA content when compared to the control (Table 3). The positive impact is in line with the work of Bang, Kim and Min [39], who demonstrated that the application of Ca (CaO) increased the concertation of AA in mandarin fruit. This Ca effect could be attributed to the movement of Ca within the mandarin tissue, which modulated the oxidation of AA, thus preventing its loss [62]. Furthermore, in the work of Ibrahim and Al-Wasfy [63], the preharvest foliar spray of potassium silicate upon Valencia orange trees resulted in enhanced levels of AA, TSS and total sugars. Additionally, the preharvest application of nano-silicon to soybean seedlings was able to increase the AA levels [64]. The increased levels of AA could be regulated by the increased levels of sugars since D-glucose is a precursor in the pathway of AA biosynthesis [65].

It has been proposed that Si and Ca induce the production of phenolics and enhance the antioxidant capacity of citrus juice [39,66]. In the current work, it was demonstrated that preharvest foliar application of Si–Ca-based compounds increased the total phenolic concentration of the juice along with the antioxidant capacity (FRAP values) of mandarin fruits examined at postharvest time intervals (Table 3). These results are in accordance with the work of Bang et al. [39], in which the application of Ca halted the loss of total phenolics and antioxidant capacity in mandarin fruit stored at cold temperatures or when exposed to shelf storage conditions. The beneficial impact of Ca on the preservation of phenolics was attributed to the ability of Ca to penetrate mandarin tissues and diminish the potent contact of polyphenol oxidase with its substrate [67]. Furthermore, the increased antioxidant capacity of mandarin fruits, under the effect of Ca, was linked also to the ability of Ca to penetrate the citrus tissue, resulting in a decreased amount of free radicals in the fruit tissue [68], thus preserving the antioxidant capacity at higher levels. In parallel, the ability of Si to exert a positive action towards the induction of total phenolic production and high antioxidant capacity in citrus fruit (lemons) was reported by Mditshwa et al. [37]. Furthermore, potassium silicate application to avocado fruit increased total phenolic concertation and the activity of antioxidant enzymes such as polyphenol oxidase and catalase [34]. Our results are in accordance with those of Mditshwa et al. [37], who proposed that Si can induce the production of phenolics and flavonoid content in the peel of lemon fruits. Additionally, Karagiannis et al. [14] demonstrated that the preharvest foliar application of a similar Si-based commercial compound (AGROLOGY SA) can induce the accumulation

of total phenolics and total anthocyanin compounds in various tissues of apple fruit. The observed data in the current work can be attributed to the ability of Si to increase the photosynthetic active radiation of the fruit [69,70], which increases the enzymatic activity of phenyl ammonia lyase (PAL), and thus the concentration of the total phenolics within the fruit tissues [57].

5. Conclusions

From the current study, the extracted data revealed that the preharvest foliar spray of Si–Ca can positively change the postharvest quality traits of mandarin clementine cv. SRA 63 fruits. At harvest, TSS and TA content were increased, and the fruit maturation of this mid-ripening variety was delayed while ascorbic acid, total phenolics and antioxidant capacity were increased. This increase in quality attributes was preserved even after cold storage for 30 days (30 d at 5 °C) and after the exposure of the fruit at room temperature (30 d at 5 °C plus 3 d at 20 °C and 30 d at 5 °C plus 6 d at 20 °C). The beneficial impact of the Si–Ca-based compound (Gravital® Force SC, AGROLOGY SA, Sindos, Greece) application was also exerted via the decreased fruit decay syndromes during fruit shelf storage. Our results add valuable information regarding the effect of a Si–Ca-based biostimulant on fruit quality and postharvest manipulation of citrus fruit. Overall, this work provides valuable data for understanding metabolic cascades, which are triggered via the application of Si and Ca.

Author Contributions: V.Z. and N.B. conceived and designed the project and its components. V.Z. and N.B. collected the samples and performed the laboratory analysis. V.Z. analysed the data and wrote the initial draft of the manuscript. S.B.H. revised the manuscript and provided technical support. All authors have read and agreed to the published version of the manuscript.

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