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Effect of Preharvest Treatments with Sodium Bicarbonate and Potassium Silicate in Navel and Valencia Oranges to Control Fungal Decay and Maintain Quality Traits during Cold Storage

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Abstract: The quality of sweet orange (*Citrus sinensis* L.) is determined by the presence of decay caused by phytopathogenic fungi. This can develop in the field and rapidly spread among oranges during postharvest storage. Currently, the conventional treatments applied to control this problem are chemical fungicides. However, consumers demand eco-friendly and non-polluting alternatives with low chemical residues. Therefore, the aim of this work is the preharvest application of sodium bicarbonate (SB) and potassium silicate (PS) solutions at 0.1 and 1% to Navel and Valencia oranges to elucidate the effect on fruit quality and fungal decay at harvest and after 42 days of storage at 8 °C. Results showed that oranges treated with SB 0.1%, PS 0.1, and PS 1% maintained quality traits at similar levels to the control ones. However, SB 1% reduced firmness and increased weight loss, respiration rate, maturity index, and citrus color index. The total carotenoid content significantly increased in oranges treated with SB 1%, and no differences were observed in the other treatments compared to the control. Total antioxidant activity and total phenolic content decreased in oranges treated with SB at 0.1 and 1%, contrary to the results observed in oranges treated with PS, where both parameters increased. Regarding fungal decay, the best results were obtained in oranges treated with the highest doses of SB and PS. Therefore, the use of SB and PS in preharvest sprays could be an alternative to control fungal decay without affecting orange quality.

Keywords: sodium bicarbonate; potassium silicate; preharvest; quality; decay

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1. Introduction

Sweet oranges (*Citrus sinensis* L.) are the most important citrus fruit produced worldwide, with a global production of 76 million tons in the 2019/2020 season [1]. Consumers demand oranges with high-quality traits, contributing to their purchasing decisions. In this sense, firmness, freshness, and visual appearance are key parameters in the context of commercial quality [2]. Oranges are non-climacteric fruits with low respiration rates and ethylene production during storage, which results in a slow ripening process during their postharvest storage [3]. However, oranges are susceptible to different physiological and pathological disorders. Currently, the main cause of economic losses in the citrus industry is decay produced by pathogen infections in the fruit. *Penicillium digitatum* (green mold) and *Penicillium italicum* (blue mold) are the most important citrus pathogens, representing 80% of the total rot decay. Both fungi are wound pathogens that produce a high number of spores. Their control is currently managed by the pre- and post-harvest application of chemical fungicides, such as imazalil, pyrimethanil, or thiabendazole [4]. However, consumers are demanding fruits free of any chemical fungicides due to their direct association with human health issues and environmental pollution from chemical residues. Additionally, the use of high quantities of chemical fungicides with low control produces

pathogen strains resistant to the active compounds of the fungicides. Therefore, legislative updates are requesting a reduction in the use of those chemical fungicides. Thus, there is a need to develop new, alternative treatments with low toxicity to control postharvest decay in fruits [5].

Among 'Generally Recognised As Safe' (GRAS) compounds, inorganic and organic salts have been used in the food industry as antimicrobial agents because their manipulation and application allow an easy transfer to the citrus packinghouse as a postharvest treatment. The antifungal activity of salts is mainly related to changes in pH (acid or alkaline) and the presence of cations such as Na^+, $K^{+,}$ or $NH_4{}^+$, which promotes the generation of reactive oxygen species (ROS) [6]. There are many examples in the literature showing the effect of salts applied postharvest to control decay in lemons, oranges, and mandarins [7]. However, very little research has been conducted on preharvest salt application, only in table grapes [8,9] and strawberries [10], to control postharvest decay. It is well-known that salt treatments do not protect the fruit for long periods or from re-infection. Hence, the application time and optimization of the application methodology are important factors for achieving the best results for protecting the fruit. Thus, salts applied in the field could be an interesting strategy to guarantee the maximum interaction with the pathogen, altering the inoculum density and the conditions of the wounds colonized by the pathogen [11].

Sodium bicarbonate (SB) belongs to the carbonic salts. It is reasonably priced and can be used without any risk of damage to the fruit. SB has been used widely as a postharvest treatment to control fruit decay. The application of SB solutions from 0.5 to 2% effectively controlled the mycelium growth and spore production of *P. digitatum*, *P. italicum,* and *G. citri-aurantii* in in vitro assays [12]. Regarding in vivo assays, SB solutions effectively controlled grey mold in tomatoes and black rot in yellow pitahaya [13,14]. Palou et al. [15,16] showed that SB treatments effectively controlled postharvest blue and green molds in oranges [15] and mandarins [16]. Potassium silicate (PS) is a salt with many uses in agriculture because silicon (Si) is considered a functional plant nutrient that plays an important role in cellular integrity. Therefore, Si treatments have been used to mitigate some physiological disorders produced postharvest in long-term cold-storage fruits [17]. Recently, the use of PS has been promoted to control mildew in cucumber, and its mode of action, produced by Si and a direct effect of K^+ toxicity, has been associated with the induction of the defense response in plants [18]. The antifungal activity of PS has been mainly studied in the field. However, in postharvest assays with bananas treated with a solution of PS 2% the appearance of fungal decay was delayed [19]. Several studies have shown the effect of SB and PS on the host and their potential to activate its defense response against fungal attack, inducing the synthesis of phytoalexins, increasing the activity of the phenylalanine ammonia-lyase, and promoting the synthesis of peroxidases in the tissues [20,21]. All those strategies play a role in enhancing cellular resistance against multiple pathogens. The aim of the present study is to elucidate the effect of sodium bicarbonate (SB) and potassium silicate (PS) applied preharvest to control fungal decay in oranges and the effect of these treatments on fruit quality parameters and antioxidant systems at harvest and after 42 days of storage at 8 °C.

2. Materials and Methods

2.1. Plant Material, Experimental Design, and Sample Preparation

Experiments were carried out during the 2022–2023 season in a commercial field located in Alhama de Murcia (Murcia, Spain). Two different 8-year-old orange cultivars were selected for these experiments, 'Chislett' (Navel) and 'Salustina' (Valencia), grafted on *Citrus macrophylla* and Carrizo citrange, respectively. Both cultivars' trees were planted at 7 × 5 m. For each cultivar, three blocks of three orange trees were randomly selected for each treatment. Navel and Valencia oranges were treated with sodium bicarbonate (SB) and potassium silicate (PS) at 0.1 and 1%. Those concentrations were selected according to non-published previous results. All salt treatments were prepared by diluting SB and PS (Sigma-Aldrich, Madrid, Spain) in distilled water with 0.1% of Tween 20 as a surfactant. Control trees were treated with 0.1% of Tween 20 dissolved in an aqueous solution. Orange

trees were treated with 5 L of the solution through foliar spraying using a mechanical system. These treatments were applied three times: the first application was conducted when the final orange sets were on the tree, the second one month later, and the last one after one month, 3 days before harvest. Navel and Valencia oranges were harvested in February and May 2023, respectively, once they achieved the commercial ripening stage requested by the market. Then, oranges were transferred to the lab within 2 h, and seven lots of 15 oranges (3 replicates of 5 fruits each) uniform in size, color, and without any physical damage, were selected and stored for 42 days at 8 °C and 85% relative humidity (RH). Weekly, one lot from each treatment was randomly selected for the analytical determinations. However, the results were focused on day 0 and day 42, as they represented the start and the end of the storage period.

2.2. Decay Incidence of Oranges

In a parallel experiment, 10 boxes of 100 oranges from each treatment and cultivar were stored in commercial storage at 8 °C and 85% RH. Decay incidence was evaluated every 7 days during the whole storage of 42 days, identifying and discarding oranges with disease symptoms. Furthermore, those fruits were categorized depending on the fungal growth stage at three levels: peel softening, mycelial growth, and the presence of spores. Those parameters were determined visually while the decayed fruit was removed. Fungal decay was expressed as a percentage (%) of accumulated decay and was calculated using the following Formula (1):

$$\text{Decay (\%)} = (\text{decayed fruits}/\text{total evaluated fruits}) \times 100 \quad (1)$$

2.3. Fruit Quality Evaluation

Weight loss (WL) was measured by weighing each individual fruit at day 0 and after 42 days of storage. WL results were expressed in percentage (%). The respiration rate was determined by placing four fruits in a 0.5 L glass jar for an hour. Then, 1 mL of headspace atmosphere was taken and injected into a gas chromatographer (Shimadzu 14B-GC, Kyoto, Japan) coupled to a thermal conductivity detector. Results were expressed as CO_2 kg^{-1} h^{-1} [22]. Firmness was measured individually on each fruit using a TX-XT2i texture analyzer (Stable Microsystems, Godalming, UK) coupled to a steel plate, which applied a deformation force of 5% in the equatorial zone. Firmness was expressed in N mm^{-1}. Total Soluble Solids (TSS) were measured using a digital refractometer (Hanna Instruments, Woonsocket, RI, USA), and Titratable Acidity (TA) with automatic titration (785 DMP Titrino, Metrohm AG, Herisau, Switzerland), where 1 mL of juice was neutralized with NaOH 0.1 mM. Results were expressed as °Brix and grams of citric acid equivalent 100 mL^{-1}, respectively. The maturity index (MI) of oranges was presented as an absolute value obtained from the ratio between TSS and TA. Citrus color index (CCI) was calculated from the data obtained from a Minolta colorimeter (CRC200; Minolta, Osaka, Japan), measuring different points of the equatorial perimeter and applying Formula (2) presented below:

$$\text{CCI} = (1000 \times \text{a})/(\text{L} \times \text{b}) \quad (2)$$

2.4. Total Carotenoids, Total Phenolics, and Total Antioxidant Activity

The extraction was carried out by homogenizing 1 g of flavedo in 10 mL of potassium phosphate buffer 50 mM pH 7 and ethyl acetate (2:1 v/v). The resulting extracts were centrifugated at 10,000× g for 12 min at 4 °C. Total carotenoid content (TCC) was directly measured in the hydrophobic phase at 450 nm in a spectrophotometer, as previously reported [23]. Results were expressed as mg of carotene equivalent to 100 g of fresh weight (FW). Total phenolic content (TPC) was measured in the hydrophilic phase using the Folin–Ciocalteau reagent, as previously reported [24]. Results were expressed as mg of gallic acid equivalent to 100 g of FW. The antioxidant activity was measured in the hydrophobic and hydrophilic phases using the ABTS-peroxidase system as described [25]. The total

antioxidant activity (TAA) was the sum of both phases, and results were expressed as mg of Trolox equivalent to 100 g FW.

2.5. Statistical Analysis

Results were expressed as the mean ± SE of three randomized replicates. Data were subjected to an analysis of the variance (ANOVA), and a multiple-range test (Tukey's test) was applied to determine significant differences between treatments (p-value < 0.05). Those statistical analysis were performed using SPSS, version 22 (IBM Corp., Armonk, NY, USA). The PCA model was constructed with normalized data using Unscrambler 11 software (CAMO AS, Oslo, Norway).

3. Results

Preharvest treatments with SB and PS at 0.1 and 1% reduced the decay incidence in both cultivars compared to the control ones. However, the best results were obtained when the higher concentrations of both salts were applied. BS and PS at 1% showed a decay incidence of 2.5% and 2%, respectively, in Navel oranges and 8% and 5%, respectively, in Valencia oranges (Figure 1). When those results were compared to the control, a 3-fold reduction in decay incidence was achieved. Meanwhile, those treatments with the lowest concentrations of SB and PS achieved a reduction in the decay incidence of 1.5 to 2-fold in both cultivars (Figure 1). Furthermore, the effect of preharvest treatments with SB and PS on mold development was measured, and three levels of mold development were defined: peel softening, mycelial growth, and the presence of spores. Thus, control oranges showed the highest spore presence, with 75% of the total oranges presenting fungal decay symptoms, followed by SB and PS at 0.1%, with 40% of the total, and SB at 1%, with 15% of the total. It is important to mention that the treatment with PS 1% did not show any oranges with spores on their surface during the cold storage (Figure 1). Finally, the peel softening and mycelial growth were not controlled as efficiently as the spore germination by SB and PS preharvest treatments.

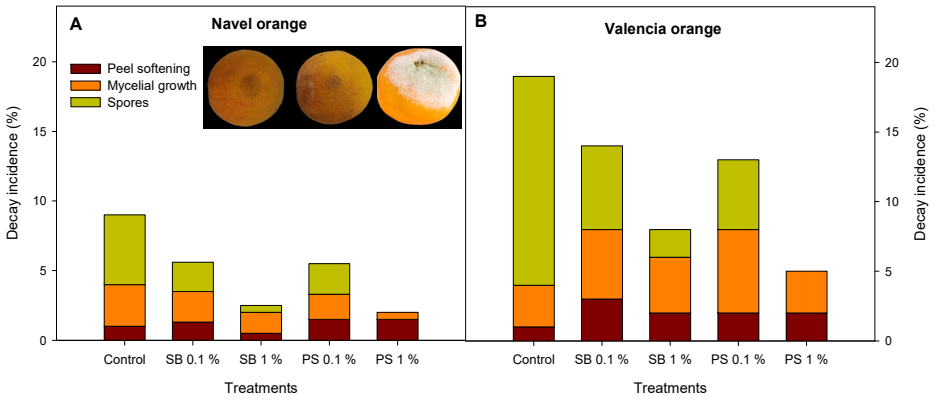

Figure 1. Effect of preharvest treatments with sodium bicarbonate (SB) and potassium silicate (PS) at 0.1 and 1% in the fungal decay incidence and the fungal development (peel softening, mycelial growth, spore production) in Navel (**A**) and Valencia (**B**) oranges after 42 days of storage at 8 °C.

Fruit quality parameters were evaluated at harvest and after 42 days of cold storage (Table 1). Weight loss of Navel and Valencia oranges increased during cold storage in all treatments. The preharvest treatment with SB 1% significantly increased ($p < 0.05$) 60% and 35% WL of Navel and Valencia oranges, respectively, compared to the control ones. Meanwhile, controls and treatments with SB 0.1% and PS 0.1 and 1% did not show any significant differences ($p < 0.05$). A 35 and 18% firmness decrease, on average, was observed in Navel and Valencia oranges, respectively, during the cold storage period. Navel oranges treated with SB 1% presented a 15% reduction in firmness compared to the controls after 42 days of cold storage. This effect was also observed in Valencia oranges at harvest and

after 42 days of storage, with a reduction of 10% and 37%, respectively. Therefore, SB 0.1% and PS 0.1% and 1% preharvest treatments did not present any negative effect on orange firmness (Table 1). The respiration rate was significantly ($p < 0.05$) higher in Navel oranges treated with SB 1% at harvest and after 42 days of cold storage, with an increase of 19% and 38%, respectively. A similar effect was observed in Valencia oranges treated with SB 1%. Oranges treated with SB 0.1% and PS 0.1 and 1% did not show any significant differences ($p < 0.05$) in respiration rate compared to the control ones. The maturity index increased during cold storage in all treatments, 20% on average. In this sense, MI was significantly higher in Navel and Valencia oranges treated with SB 1% than control ones at harvest and after 42 of cold storage (15% and 10%, respectively). The citrus color index was lower in Navel oranges treated with PS 0.1 and 1% than in controls and oranges treated with SB 0.1 and 1% at harvest. Those differences changed after 42 days of storage, where the CCI of oranges treated with SB and PS at 1% significantly increased compared to control ones. A similar effect was observed in Valencia oranges, where the CCI of oranges treated with SB and PS 1% were significantly higher than the control, SB and PS 0.1% oranges at harvest and after 42 days of cold storage (Table 1).

Table 1. Effect of preharvest treatments with sodium bicarbonate (SB) and potassium silicate (PS) at 0.1 and 1% on weight loss, firmness, respiration rate, maturity index, and citrus color index in Navel and Valencia oranges at harvest and after 42 days of storage at 8 °C. Significant differences are presented with the F-value and asterisks (* $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$). When no significant differences were found, 'ns' is used. Different capital letters indicate significant differences between treatments according to Tukey's multiple range test at the 95% confidence level.

Cultivar (C)	Storage Day (S)	Treatment (T)	Weight Loss (%)	Firmness (N mm^{-1})	Respiration Rate (mg CO_2 Kg^{-1} h^{-1})	Maturity Index (°Brix/% TA Ratio)	Citrus Color Index (CCI)
Navel oranges	0	Control		7.00 ± 0.26	21.39 ± 0.52	5.78 ± 0.13	6.09 ± 0.22
		SB 0.1%		7.54 ± 0.14	21.98 ± 0.61	5.43 ± 0.13	5.92 ± 0.14
		SB 1%		7.39 ± 0.23	25.23 ± 0.42	6.33 ± 0.10	6.21 ± 0.11
		PS 0.1%		6.95 ± 0.26	20.93 ± 0.58	5.34 ± 0.12	5.23 ± 0.15
		PS 1%		7.02 ± 0.20	21.66 ± 0.53	5.42 ± 0.14	5.41 ± 0.15
	42	Control	4.28 ± 0.18	4.55 ± 0.14	13.43 ± 0.32	6.97 ± 0.12	7.19 ± 0.13
		SB 0.1%	3.93 ± 0.14	4.40 ± 0.20	13.16 ± 0.38	6.85 ± 0.11	6.98 ± 0.19
		SB 1%	7.02 ± 0.15	3.80 ± 0.25	18.14 ± 0.40	7.06 ± 0.14	7.96 ± 0.24
		PS 0.1%	3.98 ± 0.14	4.41 ± 0.20	13.13 ± 0.32	6.92 ± 0.14	7.11 ± 0.13
		PS 1%	4.13 ± 0.14	4.24 ± 0.16	13.25 ± 0.34	6.97 ± 0.10	7.81 ± 0.20
Valencia oranges	0	Control		7.04 ± 0.15	25.91 ± 0.52	4.47 ± 0.09	4.23 ± 0.11
		SB 0.1%		7.17 ± 0.10	25.56 ± 0.49	4.80 ± 0.12	4.88 ± 0.11
		SB 1%		6.36 ± 0.16	30.06 ± 0.53	5.31 ± 0.12	5.64 ± 0.17
		PS 0.1%		7.02 ± 0.15	25.24 ± 0.51	4.55 ± 0.10	4.89 ± 0.14
		PS 1%		6.80 ± 0.13	25.49 ± 0.38	4.67 ± 0.11	4.79 ± 0.12
	42	Control	3.36 ± 0.14	5.81 ± 0.11	15.56 ± 0.49	5.50 ± 0.11	5.24 ± 0.18
		SB 0.1%	3.23 ± 0.15	5.60 ± 0.16	15.16 ± 0.20	5.67 ± 0.13	5.36 ± 0.17
		SB 1%	4.53 ± 0.12	3.61 ± 0.14	21.22 ± 0.29	6.25 ± 0.15	6.20 ± 0.20
		PS 0.1%	3.30 ± 0.14	5.24 ± 0.17	14.79 ± 0.12.	5.46 ± 0.12	5.27 ± 0.18
		PS 1%	3.26 ± 0.14	5.02 ± 0.17	15.26 ± 0.26	5.65 ± 0.12	5.19 ± 0.16
ANOVA							
S			-	880.60 ***	2218.92 ***	441.85 ***	226.56 ***
C			150.01 ***	8.78 **	277.99 ***	407.26 ***	379.28 ***
T			82.19 ***	15.70 ***	100.91 ***	20.00 ***	19.03 ***
S × C			-	46.15 ***	28.37 ***	10.41 **	53.47 ***
S × T			-	7.91 **	2.13 ns	2.14 ns	1.91 ns
C × T			13.70 ***	7.78 **	1.17 ns	2.71 ns	4.24 *
S × C × T			-	0.85 ns	0.27 ns	2.34 ns	5.40 **
Tukey's test							
Control			A	A	BC	A	A
SB 0.1%			A	A	C	A	A
SB 1%			B	B	A	B	B
PS 0.1%			A	A	BC	A	A
PS 1%			A	A	B	A	A

Total carotenoid content significantly increased ($p < 0.05$) during the storage period, around 20%, on average, in each treatment and in both oranges (Figure 2). Navel oranges treated with SB 1% and PS 0.1 and 1% showed the highest quantity of TCC at harvest, with an increase of 110%, 15%, and 45%, respectively, compared to the control ones (4.54 ± 0.26 mg 100 g^{-1}) (Figure 2A). A similar effect was observed in Valencia oranges (Figure 2B). These differences observed at harvest were maintained after 42 days of cold storage in Navel oranges but not in Valencia oranges. The TCC in oranges treated with BS 0.1% and PS 0.1 and 1% did not show any significant ($p < 0.05$) differences from the control oranges.

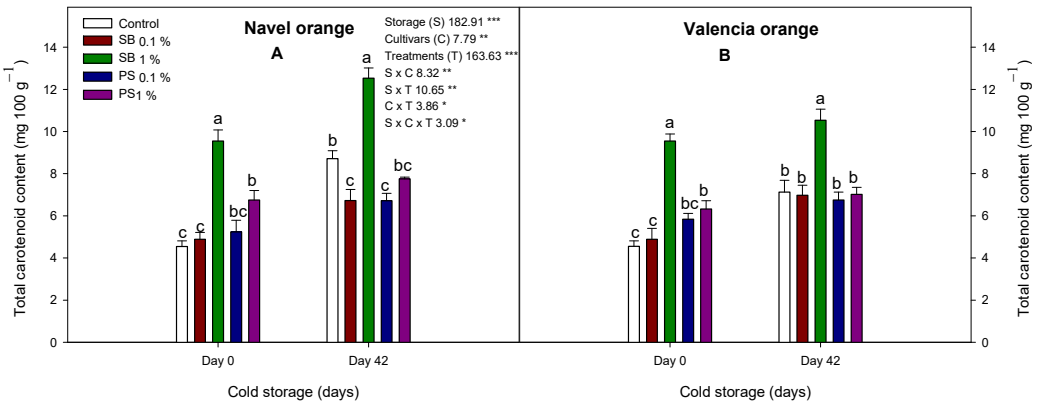

Figure 2. Effect of preharvest treatments with sodium bicarbonate (SB) and potassium silicate (PS) at 0.1 and 1% in the total carotenoid content of Navel (**A**) and Valencia (**B**) oranges at harvest and after 42 days of storage at 8 °C. Significant differences are presented with the F-value and asterisks (* $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$). Different letters indicate significant differences according to Tukey's test at the 95% confidence level.

The bioactive content of oranges was evaluated in both orange cultivars at harvest and after 42 days of storage (Figure 3). In Navel oranges, the TAA decreased significantly ($p < 0.01$) during cold storage. At harvest, Navel oranges treated with SB 1% showed the lowest TAA, 12% lower than the control ones (Figure 3A). Furthermore, oranges treated with SB 0.1% and PS 0.1 and 1% showed a TAA similar to the controls, without any significant ($p < 0.05$) differences among those treatments. After 42 days of cold storage, Navel oranges treated with SB 0.1 and 1% showed a decrease in the TAA of 17% and 20%, respectively, compared to control ones. Navel oranges treated with PS 0.1 and 1% maintained a TAA similar to the control (Figure 3A). The TAA in Valencia oranges showed a slight decrease during cold storage, and some of the treatments increased the TAA (Figure 3B). However, the effect of the treatments was similar to those previously described in Navel oranges. Oranges treated with SB 1% showed a 10% decrease in the TAA, on average, at harvest and after 42 of cold storage compared to the control ones. On the contrary, Valencia oranges treated with SB 0.1% and PS 0.1 and 1% showed a TAA similar to controls at harvest. Oranges treated with PS 0.1 and 1% showed an increase in the TAA of 17% and 27%, respectively, after 42 days of cold storage (Figure 3B). Total phenolic content is an important part of the TAA in oranges. TPC decreased in Navel and Valencia oranges by 15% and 10%, on average, respectively, during the storage period (Figure 3C,D). Navel oranges treated with SB 1% showed a 10% decrease compared to the control ones at harvest. Furthermore, Navel oranges treated with SB 0.1% and PS 0.1 and 1% did not show any significant differences ($p < 0.05$) in the TPC compared to the control. After 42 days of cold storage, Navel oranges treated with SB 1% and PS 1% showed a decrease of 25% and 19%, respectively. However, Navel oranges treated with SB and PS 0.1% maintained their TPC similar to the control ones, without any significant differences among those treatments (Figure 3C). The TPC of Valencia oranges treated with BS 1% decreased by 15%, on average, at harvest and after 42 days of cold storage compared to the control ones. Furthermore,

Valencia oranges treated with PS 0.1% showed an increase in their TPC of 11% and 16%, respectively, at harvest and after cold storage. Valencia oranges treated with BS 0.1%, PS 1%, and controls did not show any significant differences ($p < 0.05$) (Figure 3D).

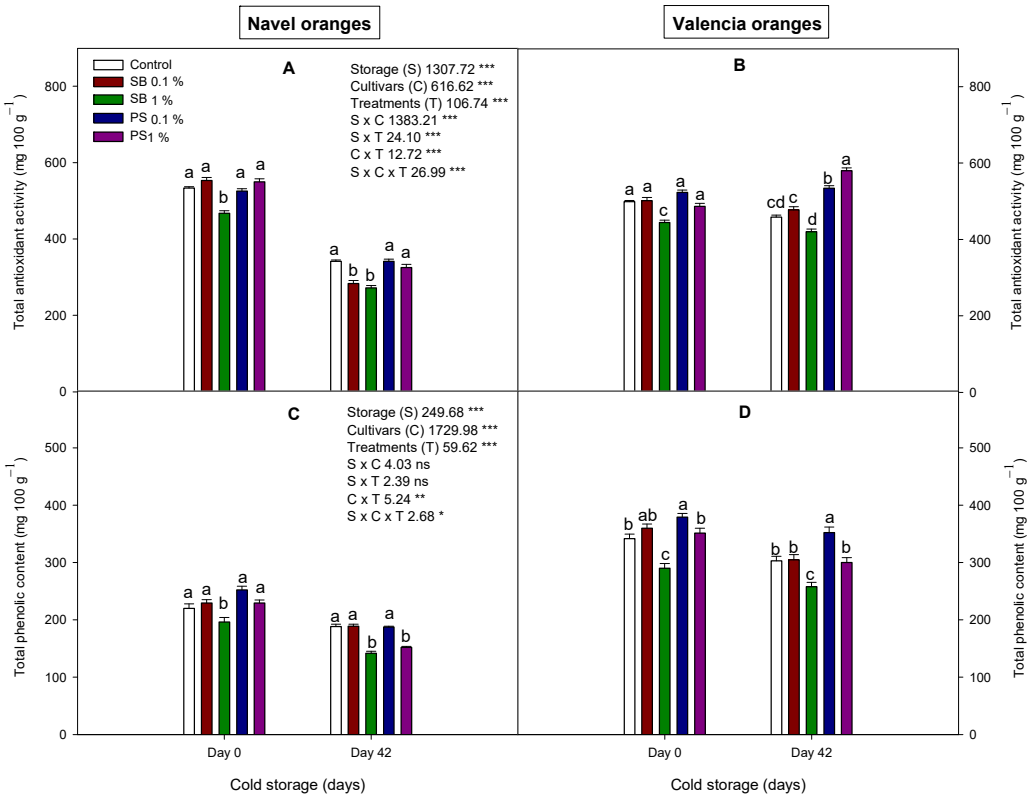

Figure 3. Effect of preharvest treatments with sodium bicarbonate (SB) and potassium silicate (PS) at 0.1 and 1% in the total antioxidant activity (**A**,**B**) and total phenolic content (**C**,**D**) in Navel and Valencia oranges at harvest and after 42 days of storage at 8 °C. Significant differences are presented with the F-value and asterisks (* $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$). When no significant differences were detected, 'ns' is used. Different letters indicate significant differences according to Tukey's test at the 95% confidence level.

Principal component analysis (PCA) was applied to all data to determine the effect of the preharvest treatments with SB and PS at 0.1 and 1%, the importance of the cultivar, and the storage period. The variance of the first (PC-1) and the second (PC-2) principal components was 65% and 18%, respectively, and the accumulative variance contribution was 83%. PC-1 is clearly identified with MI, CCI, TAA, and TPC, while PC-2 is related to WL, RR, and decay. The factor contributing the most to the positive side of PC-1 was TAA and TPC, while CCI and MI contributed to the negative side. Regarding PC-2, on the positive side, WL and RR were the most relevant parameters, and on the negative side, decay was the most important. Thus, PC-2 allowed the discrimination of the preharvest treatments applied, showing that controls, SB 0.1% and PS 0.1 and 1%, were closer than SB 1% (Figure 4), independent of the storage time and cultivar. Finally, storage time and cultivar were more dependent in PC-1.

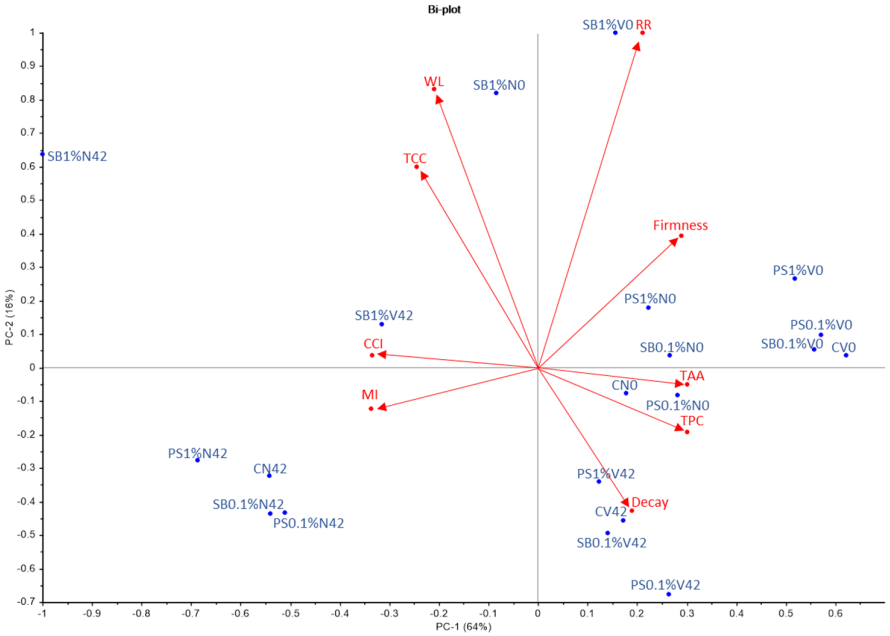

Figure 4. Principal component analysis (PCA) biplot of the physico–chemical traits analyzed, expressed as vectors, showing the relationship among Navel (N) and Valencia (V) oranges treated with sodium bicarbonate (SB) and potassium silicate (PS) at 0.1 and 1% and controls (C) at harvest (D0) and after 42 days of storage at 8 °C (D42). The two principal components of the PCA explained 83% of the variation in the measured data.

4. Discussion

The use of generally recognized as safe (GRAS) compounds, such as acetic acid, electrolyzed water, ethanol, and inorganic and organic salts, has been widely applied to extend the postharvest storage of citrus [26]. GRAS salts are classified as chemicals with low toxicity for human health and the environment. Inorganic and organic salts, such as carbonates, sorbates, benzoates, and silicates, show great potential to become commercial products due to their availability, low cost, and high solubility in water [11]. The use of GRAS salts in the citrus industry to control the main fungal phytopathogens has been extensively applied postharvest. Previous studies carried out postharvest have applied SB and PS to efficiently control *P. digitatum* and *P. italicum* in oranges and mandarins [27,28]. Nevertheless, there is limited research on the use of these salts preharvest in citrus. In the present study, results showed that the use of SB and PS preharvest allowed the control of fungal growth and development in Navel and Valencia oranges stored for 42 days at 8 °C, reducing the decay incidence. The antifungal activity of these salts has been widely studied, although the mode of action is not fully understood. The use of salts changes the pH of the fruit peel surface and delays the activity of cell wall-degrading enzymes (polygalacturonase, pectin lyase, and pectin methyl esterase) synthesized by the pathogen in the early stages of the infection [29]. Additionally, SB and PS salts release Na^+ and K^+ ions that modify the osmotic balance of the cell, the ion transport, induce ROS metabolism, and the toxicity through Na^+ K^+/Cl^- in the cytoplasm [30]. This mode of action would explain the fact that SB and PS salts applied preharvest control the mycelium growth and spore formation in decayed fruit. Furthermore, Navel and Valencia oranges treated with PS 1% did not show any spores during the whole cold storage period. The differences between treatments suggest the importance of optimizing the salt and concentration used for each fruit and the conditions to control the influence of additional factors related to the infection site or the pathogenicity of the fungi. Inorganic salts have been described as compounds that possess fungistatic properties [6]. Thus, the inhibitory effect of SB and PS is directly related to the presence of salt residues in the wounds occupied by the fungi.

Most studies about the effect of inorganic salts on fruits have been carried out to explain the ability of those salts to enhance the defense mechanism of fruits against molds and have not been focused on the final fruit quality [31]. In this study, the influence of the preharvest treatments with SB and PS treatments on Navel and Valencia oranges on quality parameters was evaluated. Results showed that SB at 1% increased significantly ($p < 0.05$) the WL, respiration rate, MI, and CCI and reduced the firmness of oranges. Contrarily, oranges treated with SB 0.1% and PS 0.1 and 1% maintained similar quality parameters as control ones. Thus, WL is mainly related to the transpiration through the fruit peel. Therefore, the increase in the WL observed in Navel and Valencia oranges treated with SB 1% was in accordance with the increase observed in the respiration rate. Those results showed that oranges treated with SB at 1% increased their metabolism due, presumably, to the toxicity of the salt. For maintaining normal cell homeostasis, energy is required for ion transport and for combating the oxidative stress produced in the presence of the reactive oxygen species (ROS) [32]. Firmness is one of the most important quality traits for the orange market. Results showed that in Navel and Valencia oranges treated with SB 1%, firmness significantly decreased ($p < 0.001$) during cold storage. Firmness is related to the cell turgidity and thickness of the peel, and it depends on the activity of cell wall-degrading enzymes, which directly affects fruit softening. Previous results have shown that the activity of pectin methyl esterase could increase in alkaline conditions to promote the hydrolysis of methyl esters along the pectin backbone and lower the pH of the skin [33,34]. MI is an important parameter, calculated as the ratio of total soluble solids:titratable acidity, providing information about the maturity stage of orange fruits at harvest and after 42 days of storage. Results showed that this parameter increased during the whole storage period in all treatments. However, it was observed that Navel and Valencia oranges treated with SB 1% had the highest MI. Those differences in the MI could be explained by the sugar accumulation produced with the increase in the sucrose-synthesizing activity and the acidity loss produced by the use of organic acids as an intermediary compound in carbon metabolism and a key component in the stress response [35]. The CCI was clearly affected by SB and PS at 1% treatments, promoting orange degreening. In the early stages, the main pigments in the peel of oranges are chlorophylls, which, through the maturation of the tree, are degraded and allow the down-layer composed of carotenoids to appear. These results are in accordance with the higher TCC observed in the Navel and Valencia oranges treated with SB and PS at 1%. Carotenoids act as an antioxidant layer that alleviates the effects of the produced ROS due to the salt application [36]. The presence of ROS compounds could promote the expression of phytoene synthase, phytoene desaturase, carotene desaturase, and lycopene β-cyclase genes that regulate the accumulation of the main carotenoids in Navel and Valencia oranges, violaxantine and phyotoene, respectively [37].

The total antioxidant activity was dependent on the salt applied, decreasing when oranges were treated preharvest with SB and increasing with PS. Similar results were obtained in the TPC. In this sense, Navel and Valencia oranges treated with BS 0.1 and PS 0.1 and 1% maintained a slight increase in the TPC compared to the control ones; meanwhile, the TPC of oranges treated with SB 1% drastically decreased. Therefore, Na^+ release from SB was more toxic than K^+ release from PS for the fruit cell membrane. This effect can be associated with the fact that ROS compounds increase membrane permeability, allowing an increase in the cytosolic concentration of Na^+ and K^+. In this sense, the stability of DNA structures is greater when the amount of cytosolic K^+ is higher than Na^+ [30]. The normal cytosolic rate of K^+:Na^+ is 1:0.5. Moreover, previous results in peaches and nectarines treated preharvest with PS significantly improved the fruit quality and enhanced the antioxidant systems [38]; those results are similar to the results obtained in the present study. Therefore, the salt toxicity is focused on Na^+, which could induce a low cytoplasmatic K^+, increase the Cl^- toxicity, promote a disbalance in the water management, and deficiency in $Ca_2{}^+$ and $Mg_2{}^+$, increasing ROS damage, and therefore, induce the use of high amounts of energy for ion transport in the plant cell [39]. Additionally, high cytosolic Na^+ concentrations promote the mitochondria to generate less ATP and are more likely to

absorb Na^+, which is the cause of the cell having less energy available. Thus, Navel and Valencia oranges treated with SB 1% showed the lowest TAA and TPC, because the cell is using all of its mechanisms to reduce the cytosolic Na^+ concentration. Therefore, the cell does not have the necessary energy to maintain or increase the antioxidant compounds.

In the present study, multivariable analysis was applied to determine the effect of SB and PS treatments, the influence of the cultivar, and the storage time. The PCA indicated that cultivar and storage time significantly influence orange quality. The major contributors to differentiate the cultivars and storage time were TPC, TAA, MI, and CCI, which is in line with previous results published on mandarins and oranges [40]. Regarding treatments, the oranges treated with SB 0.1% and PS 0.1 and 1% were close to the control ones. Meanwhile, the PCA analysis indicated that SB 1% treatment significantly influenced the orange quality and was the most important contributor to the TAA and the respiration rate.

5. Conclusions

The present study showed that preharvest treatments with SB and PS at 0.1 and 1% contributed to the most effective control of postharvest rot decay in Navel and Valencia oranges. However, the application of SB 1% reduced the quality traits TAA and TPC in both cultivars assessed. On the contrary, preharvest treatments with SB 0.1%, PS 0.1 and PS 1% did not negatively affect the whole fruit quality. Therefore, SB at a low concentration and PS applied preharvest could be recommended for controlling fungal decay without negatively affecting orange quality.

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