Applied Fruit Science
https://doi.org/10.1007/s10341-024-01188-4

ORIGINAL ARTICLE

Effect of Pre-harvest Calcium and Boron Application on the Quality and Shelf-Life of Apple cv. 'Red Delicious'

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Received: 22 January 2024 / Accepted: 12 August 2024

Abstract

Field experiments were conducted to study the effect of calcium chloride (0.4%, 0.6% and 0.8%), boric acid (0.2%, 0.4% and 0.6%) and their combinations on apple trees cv. 'Red Delicious', applied twice (60 days and 30 days before harvest). Results revealed that among different treatments, maximum fruit weight (192.13 g), fruit length (7.49 cm), fruit diameter (7.64 cm) and fruit volume (185.86 cm^3) were observed in treatment T_{10} (0.6% $CaCl_2$ + 0.2% H_3BO_3), and the highest TSS (14.56 °Brix), TSS:acid ratio (80.89), total sugar (11.36%), reducing sugar (9.37%), non-reducing sugar (1.83%), chlorophyll content SPAD value (53.75), firmness (7.62 kg cm^{-2}), shelf life under room temperature (28.20 days), under refrigeration (93.20 days) and under controlled atmosphere (CA) storage (180.50 days), organoleptic rating out of a 9-point hedonic scale (taste: 8.70, flavour: 8.70 and overall acceptability: 8.60), quality grading out of a 9-point hedonic scale (texture: 8.90, aroma: 8.90, appearance: 8.70, colour: 8.40) out of a 9-point hedonic scale and the lowest titratable acidity (0.18%) were recorded with the application of treatment T_{11} (0.6% $CaCl_2$ + 0.4% H_3BO_3). Our results support the use of calcium chloride and boric acid as a promising fertilizer for improving the overall characteristics of apple cv. 'Red Delicious'.

Keywords Apple quality · Fruit longevity · Apple storage · Crop management · Post-harvest quality

Introduction

Apple (*Malus* × *domestica* Borkh.) is one of the most significant crops extensively grown worldwide. Moreover, the customers' acceptance of apples has been expanding specifically with increasing the public health awareness which highlights the demand for superior quality fruits with increased shelf-life. Fruit quality and shelf-life of apple fruits are determined by the nutritional status of fruit trees, particularly boron and calcium. Due to a glut in the market, growers do not obtain better prices. Therefore, there is a need for prolonging the supply of apple fruits by extending the postharvest life. Firmness is one of the most essential properties of apple quality and shelf-life that tends to be greatly influenced by several pre-harvest conditions. Apple consumers desire a crispy flesh. Obtaining and sustaining apple fruit firmness from orchard to consumers tends to be one of the biggest challenges facing apple producers. Indeed, calcium plays a critical role in maintaining and modifying cell activities and the constituents of plant tissues (Elmar et al. 2007). Moreover, calcium has been found to maintain cellular membranes and postpone senescence in horticultural crops (Poovaiah 1988; Hosseini and Thengane 2007). Calcium enters the apoplast and binds, in an exchangeable form, to cell walls and the external surface of the plasma membrane. Furthermore, it combines with pectic acid in the cell walls to create calcium pectate, maintaining fruit cell wall integrity and protecting it from degrading enzymes (White and Broadley 2003). Calcium has long been known to be a vital element for plants time. Calcium is responsible

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for the structural and physiological stability of plant tissues. It occurs in plants predominantly in leaves, seeds and fruits and is a constituent of the middle lamella of the cell walls which assist cells bond together. There is now evidence that auxin-driven H^+ secretion of meristematic cells is connected to the presence of ca^{2+} (Marme 1983). Calcium insufficiency causes the organic components and mineral salts in the cell to quickly leak down through the walls and fruit lose its firmness. Disorders like bitter pit, cork spot and internal disintegration are connected with high rates of respiration and appear due to shortage of calcium (Thakur and Xu 2004). Calcium also improves absorption of magnesium, iron and potassium (Chadha 2001). The direct introduction of calcium to the fruit is the most efficient way for enhancing fruit calcium content is to spray trees with calcium fertilizers (Conway et al. 2002). Production of apples characterized by high Ca content is highly crucial for successful storage and handling. The ideal Ca concentration may be variable for distinct cultivars. In general, it is indicated that a Ca level above 45–60 mg/kg of fresh fruit weight is adequate (Johnson 1980). Firming and resistance to softening resulting from addition of calcium have been attributed to the stabilization of membrane systems and the formation of Ca-pectates, which increase rigidity of the middle lamella and cell wall of the fruit (Jackman and Stanley 1995) and improve the skin strength (Mignani et al. 1995). Boron is vital for glucose metabolism since it helps in translocation of sugars and synthesis of DNA in the meristem. Its deficiency promotes cracking and internal and exterior cork growth in fruit. In addition to alleviating boron deficiency symptoms, boron treatment may affect fruit quality through its effect on fruit calcium nutrition. Application of boron to apple trees low in boron was demonstrated to improve mobility of Ca in the tree. Boron is necessary for optimal yield and quality of apple fruit. Foliar fertilization with micronutrients is often successful since deliverable levels are enough to meet most tree requirements. Boron is engaged in physiological and biochemical processes inside the plant cell, affecting the concentration and transport of nutrients (Tariq and Mott 2007). Different calcium and boron fertilizers are suggested to fruit growers. The goal of our experiment was to assess the influence of pre-harvest calcium and boron treatments on apple quality and shelf-life.

Materials and Methods

The present investigation was carried out during the period 2022–2023 at the Regional Horticulture Research Sub-Station Bhaderwah of SKUAST-Jammu in District Doda, J&K, India. The experimental site is located at Sartangal, about 35 km away from Doda city at an elevation of 1680 m above mean sea level lying between 32° 56′–32° 57′ N latitude and 75°43′–75°43′ E longitude.

Table 1 Treatment details

T_1	(0.4% $CaCl_2$)	×2
T_2	(0.6% $CaCl_2$)	×2
T_3	(0.8% $CaCl_2$)	×2
T_4	(0.2% H_3BO_3)	×2
T_5	(0.4% H_3BO_3)	×2
T_6	(0.6% H_3BO_3)	×2
T_7	(0.4% $CaCl_2$ + 0.2% H_3BO_3)	×2
T_8	(0.4% $CaCl_2$ + 0.4% H_3BO_3)	×2
T_9	(0.4% $CaCl_2$ + 0.6% H_3BO_3)	×2
T_{10}	(0.6% $CaCl_2$ + 0.2% H_3BO_3)	×2
T_{11}	(0.6% $CaCl_2$ + 0.4% H_3BO_3)	×2
T_{12}	(0.6% $CaCl_2$ + 0.6% H_3BO_3)	×2
T_{13}	(0.8% $CaCl_2$ + 0.2% H_3BO_3)	×2
T_{14}	(0.8% $CaCl_2$ + 0.4% H_3BO_3)	×2
T_{15}	(0.8% $CaCl_2$ + 0.6% H_3BO_3)	×2
T_{16}	(control) water spray	×2

Where, × 2, two spray

The present study focused on 'Red Delicious' apple trees with uniform size and vigor, grafted on rootstock (MM-106), spaced at 7 m × 7 m, and trained to a modified central leader system. Throughout the research, the experimental trees were maintained under the same cultural conditions with the exception of varying dosages of boric acid and calcium treatments. With 16 treatments and three replications of each treatment, the experiment was set up in a randomized block design. Both independently and in combination, one commercial-grade calcium formulation ($CaCl_2$) and boric acid (H_3BO_3) at various doses were utilized. Treatments were sprayed on the experiment's chosen trees as foliar sprays. The trees were sprayed twice, i.e., 60 days and 30 days before harvest. The treatment details are mentioned below (Table 1):

Using an electric top balance, the weight was measured in grams per fruit. Fruit length and fruit diameter was measured using a digital vernier caliper and the average was expressed in centimeters. Using the water displacement method, the fruit volume was determined. To achieve a specific graduation, a cylinder with measurements filled with water was submerged in a selection of fruits. The fruit sample volume was calculated by comparing the first and final readings. The data were expressed in milliliters (ml) and averaged.

An Erma hand refractometer (0–32 °Brix) was used to measure the total soluble solids (TSS) content. When the temperature went over or below 20 °C, a temperature adjustment was made. The TSS/acid Ratio was calculated by dividing the value of TSS with titratable acidity (TA). The total TA was determined by titrating the juice with

Table 2 Effect of foliar spraying of calcium chloride and boric acid on fruit weight, fruit length, fruit diameter, fruit volume, total soluble solids (TSS), TSS:acid ratio, titratable acidity, total sugar, reducing sugar and non-reducing sugar of apple cv. 'Red Delicious'

Treatment	Fruit weight (grams)	Fruit length (cm)	Fruit diameter (cm)	Fruit volume (cm^3)	Total soluble solids (°Brix)	TSS:acid ratio	Titratable acidity (%)	Total sugar (%)	Reducing sugar (%)	Non-reducing sugar (%)
T1 (0.4% $CaCl_2$)	184.95	7.44	7.59	182.56	14.29	57.16	0.25 (2.85)	10.57 (18.96)	8.82 (17.27)	1.68 (7.43)
T2 (0.6% $CaCl_2$)	186.55	7.45	7.60	182.69	14.46	65.72	0.22 (2.68)	10.65 (19.04)	8.85 (17.30)	1.71 (7.50)
T3 (0.8% $CaCl_2$)	184.77	7.42	7.57	182.43	14.13	61.43	0.23 (2.74)	10.48 (18.88)	8.75 (17.20)	1.64 (7.33)
T4 (0.2% H_3BO_3)	183.40	7.32	7.47	181.40	14.23	64.68	0.22 (2.67)	10.58 (18.97)	8.81 (17.26)	1.68 (7.44)
T5 (0.4% H_3BO_3)	182.15	7.31	7.46	180.92	14.34	71.70	0.20 (2.53)	10.70 (19.08)	8.89 (17.34)	1.72 (7.52)
T6 (0.6% H_3BO_3)	181.67	7.29	7.44	179.67	14.18	67.52	0.21 (2.61)	10.64 (19.03)	8.83 (17.28)	1.72 (7.53)
T7 (0.4% $CaCl_2$+ 0.2% H_3BO_3)	188.38	7.47	7.62	183.99	14.32	65.09	0.22 (2.66)	10.75 (19.13)	8.91 (17.36)	1.75 (7.59)
T8 (0.4% $CaCl_2$+ 0.4% H_3BO_3)	187.86	7.46	7.61	183.70	14.42	72.10	0.20 (2.53)	10.86 (19.23)	9.01 (17.46)	1.76 (7.60)
T9 (0.4% $CaCl_2$+ 0.6% H_3BO_3)	186.65	7.45	7.60	182.70	14.39	68.52	0.21 (2.60)	10.80 (19.18)	8.97 (17.42)	1.74 (7.57)
T10 (0.6% $CaCl_2$+ 0.2% H_3BO_3)	192.13	7.59	7.78	185.86	14.49	76.26	0.19 (2.48)	10.91 (19.28)	9.04 (17.49)	1.78 (7.66)
T11 (0.6% $CaCl_2$+ 0.4% H_3BO_3)	189.34	7.47	7.63	184.23	14.56	80.88	0.18 (2.41)	11.36 (19.69)	9.37 (17.82)	1.83 (7.77)
T12 (0.6% $CaCl_2$+ 0.6% H_3BO_3)	187.21	7.46	7.61	183.45	14.43	75.94	0.19 (2.46)	11.15 (19.50)	9.24 (17.69)	1.81 (7.71)
T13 (0.8% $CaCl_2$+ 0.2% H_3BO_3)	184.73	7.42	7.57	182.33	14.21	61.78	0.23 (2.72)	10.60 (18.99)	8.83 (17.28)	1.68 (7.42)
T14 (0.8% $CaCl_2$+ 0.4% H_3BO_3)	184.32	7.41	7.56	181.72	14.30	65.00	0.22 (2.66)	10.69 (19.08)	8.89 (17.34)	1.71 (7.50)
T15 (0.8% $CaCl_2$+ 0.6% H_3BO_3)	183.46	7.39	7.54	181.55	14.19	64.50	0.22 (2.68)	10.53 (18.93)	8.76 (17.21)	1.68 (7.43)
T16 (control)	168.23	7.10	7.15	167.78	13.60	50.37	0.27 (2.97)	10.32 (18.73)	8.60 (17.04)	1.63 (7.31)
C.D. (0.05)	0.25	0.11	0.15	0.41	0.08	0.55	0.02 (0.16)	0.10 (0.09)	0.10 (0.09)	0.10 (0.23)

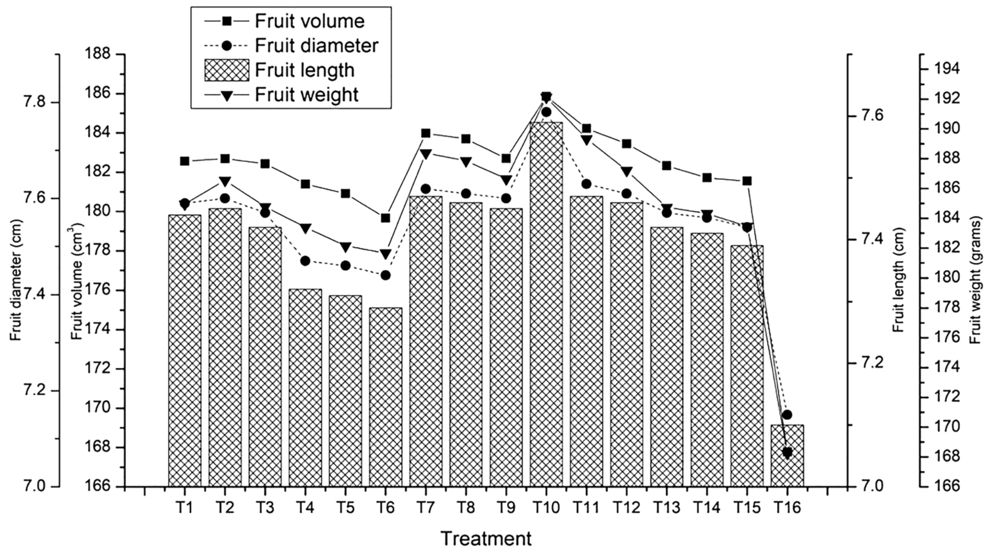

Fig. 1 Effect of foliar spraying of calcium and boron on fruit weight, fruit length, fruit diameter and fruit volume of apple cv. 'Red Delicious'

N/10 NaOH using phenolphthalein as an indicator. The results were expressed as percentage of malic acid. The total sugar, reducing sugar and non-reducing sugar was estimated as per the procedure described by AOAC (1995). The amount of chlorophyll in apple leaves was measured using a chlorophyll meter SPAD-502 made by the Japanese company Konica Minolta Sensing, Inc. (Chiyoda city, Japan) Fruit firmness was determined by a pressure tester (Magness Taylor).

'Red Delicious' apples of proper maturity (180 days after full bloom) and firm texture were harvested from site. After harvesting, the fruit was pre-cooled in order to remove the field heat. The precooled fruit was graded manually for achieving uniformity in size and any blemished or diseased fruits present were discarded. Shelf-life was determined by placing five fruits from each treatment in storage under three distinct conditions: room temperature 25 °C, refrigerator 5 °C, and controlled atmosphere (CA) storage 0 °C. Organoleptic rating and quality grading was recorded by using a 9-point hedonic scale. A score of 5.5 and above was considered acceptable (Amerine et al. 1965).

Results and Discussion

The findings in Table 2 show that in apple cv. 'Red Delicious', treatment T_{10} (0.6% $CaCl_2$ + 0.2% H_3BO_3) produced the highest fruit weight (192.13 g), fruit length (7.59 cm), fruit diameter (7.78 cm), and fruit volume (185.86 cm^3), while control (T_{16}) produced the lowest fruit weight (168.23 g), fruit length (7.10 cm), fruit diameter (7.15 cm), and fruit volume (167.78 cm^3).

The increase may be attributed to higher synthesis of metabolites, increased absorption of water and mobilization of carbohydrates and minerals in the enlarged cells and intercellular gaps due to calcium Solhjoo et al. (2017). Boron either separately or in combination as shown in Table 2 also contributed in maximum growth in fruit weight by increasing the transit of photosynthates from leaf to the growing fruit (Lakshmipathi et al. 2015). Calcium is essential for cell elongation and cell division. There is now evidence that auxin-driven H+ secretion of meristematic cells is connected to the presence of Ca^{+2} (Marme 1983). The dramatic effect of calcium and boron (Fig. 1) in terms of improvement of fruit weight has been thoroughly demonstrated (Mehta and Jindal 1984). These findings are consistent with those of Kadir (2005), Mursec (2004), Asgharzade et al. (2012), and Al-Mayahi (2020), who similarly noted increases in fruit weight and size following calcium and boron applications. They also reported that rise in fruit weight and size was attributable to a linear increase in calcium concentrations of fruits and leaves owing to calcium applications and it may be attributed to quick supply of nutrients for longer period to the growth and development of fruits. The statistical analysis of data revealed best results for the combination of both calcium and boron because of the synergistic effect of the treatment.

In apple cv. 'Red Delicious', the data in Table 2 shows that the maximum TSS (14.56 °Brix), TSS:acid ratio (80.88), total sugar (11.36%), reducing sugar (9.37%), non-reducing sugar (1.83%), chlorophyll content (53.75 SPAD value), firmness (8.47 kg cm^{-2}), and minimum TA (0.18%) were recorded in treatment T_{11} ($CaCl_2$ 0.6% + H_3BO_3 0.4%). The maximum TSS (13.60 °Brix), TSS:acid ratio (50.37), total sugar (10.32%), reducing sugar (8.60%), non-reducing sugar (1.63%), chlorophyll content (47.80 SPAD value), firmness (7.44 kg cm^{-2}) and maximum TA (0.27%) were recorded in control (T_{16}).

The considerable increase in TSS and TSS:acid ratio (Fig. 3) content by calcium and boron treatment can be at-

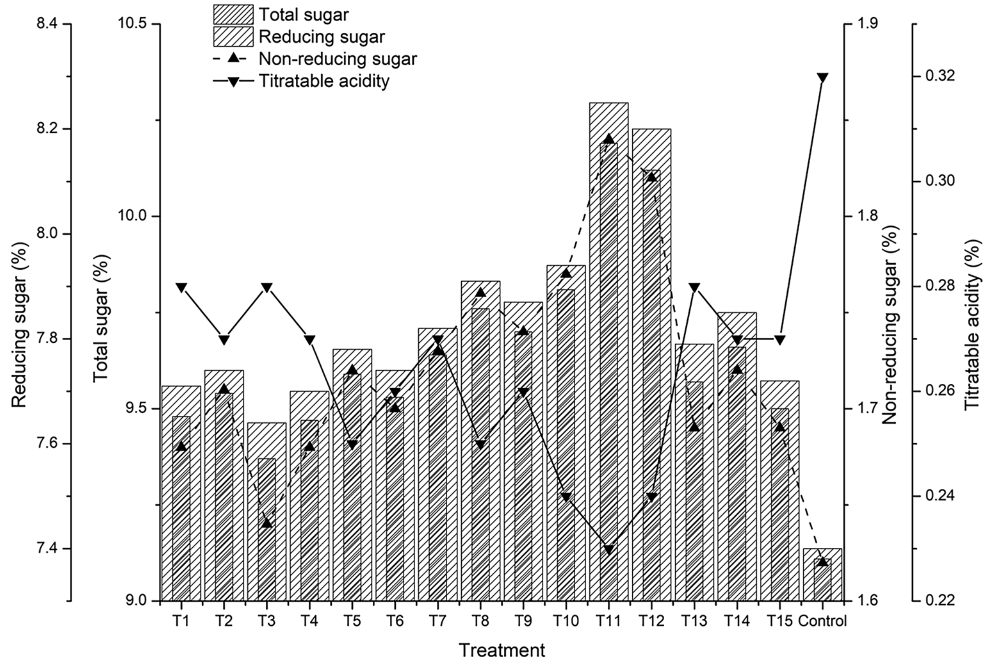

Fig. 2 Effect of foliar spraying of calcium and boron on reducing sugar, total sugar, non-reducing sugar and titratable acidity of apple cv. 'Red Delicious'

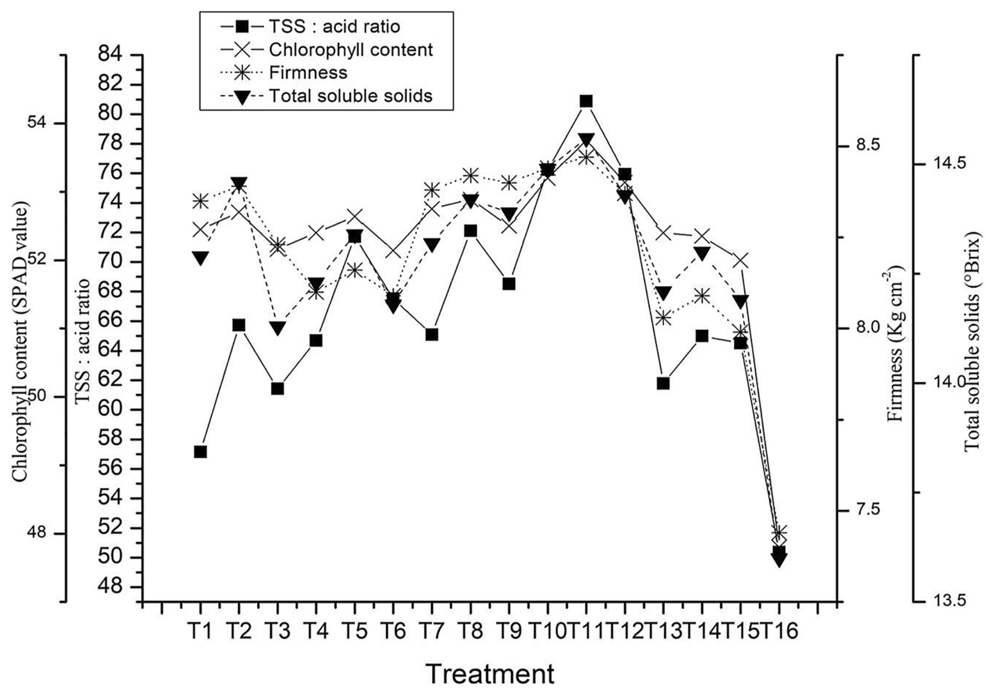

Fig. 3 Effect of foliar spraying of calcium and boron on total soluble solids (TSS):acid ratio, chlorophyll content, firmness and TSS of apple cv. 'Red Delicious'

tributed to decreased consumption of sugars in metabolic processes as a result of reduced respiration, as reported by Tamboli et al. (2015) and Baghdady et al. (2014). Decrease in TA (Fig. 2) owing to calcium chloride and boric acid treatment may be related to use of organic acids as source of energy and synthesis of new molecules during ripening. The results were consistent with those of Bhat and Farooqui (2004), who found that applying calcium chloride and boric acid together reduced the acidity of 'Red Delicious' apples. Increase in sugar content (Fig. 2) may be related to translocation of sugars and transportation of increased amount of assimilates into fruit tissues (Wojcik et al. 2008), which is boosted with calcium and boron administrative law. Enhancement of total sugars by combined applications of nutrients has been also documented in different fruit crops by Gurung et al. (2016) and Wani et al. (2017). The results are in line with Davarpanah et al. (2016).

Increase in chlorophyll content of leaves (Fig. 3) by calcium treatment might be related to maintaining the chloroplast membrane integrity and by retarding the action of

Table 3 Effect of foliar spraying of calcium chloride and boric acid on chlorophyll content, firmness, shelf-life under different storage conditions and organoleptic rating of apple cv. 'Red Delicious'

Treatment	Chlorophyll content (SPAD value)	Firmness (Kg cm^{-2})	Shelf-life under different storage conditions (days)			Organoleptic rating (1–9 point hedonic scale)		
			Room temperature (25 c)	Refrigeration (5 c)	CA storage (0 c)	Taste	Flavour	Overall acceptability
T1 (0.4% $CaCl_2$)	52.45	8.35	25.80	90.80	179.00	7.90	7.40	7.70
T2 (0.6% $CaCl_2$)	52.70	8.39	27.50	92.60	180.50	8.40	8.10	8.20
T3 (0.8% $CaCl_2$)	52.16	8.23	24.30	89.20	177.40	7.30	6.90	7.20
T4 (0.2% H_3BO_3)	52.40	8.10	25.50	90.60	178.20	7.80	7.30	7.60
T5 (0.4% H_3BO_3)	52.64	8.16	26.40	91.30	179.80	8.10	7.90	8.00
T6 (0.6% H_3BO_3)	52.14	8.09	24.60	89.90	177.80	7.40	7.00	7.30
T7 (0.4% $CaCl_2$ + 0.2% H_3BO_3)	52.75	8.38	26.20	91.10	179.50	8.00	7.70	7.90
T8 (0.4% $CaCl_2$ + 0.4% H_3BO_3)	52.89	8.42	26.80	91.80	180.10	8.20	8.00	8.20
T9 (0.4% $CaCl_2$ + 0.6% H_3BO_3)	52.50	8.40	26.60	91.50	179.90	8.10	7.90	8.10
T10 (0.6% $CaCl_2$ + 0.2% H_3BO_3)	53.20	8.44	27.80	92.90	180.90	8.50	8.40	8.30
T11 (0.6% $CaCl_2$ + 0.4% H_3BO_3)	53.75	8.47	28.20	93.20	181.50	8.70	8.70	8.60
T12 (0.6% $CaCl_2$ + 0.6% H_3BO_3)	53.14	8.37	27.20	92.20	180.30	8.30	8.10	8.20
T13 (0.8% $CaCl_2$ + 0.2% H_3BO_3)	52.40	8.03	25.20	90.30	178.40	7.70	7.20	7.50
T14 (0.8% $CaCl_2$ + 0.4% H_3BO_3)	52.35	8.09	26.00	90.90	179.20	7.90	7.60	7.70
T15 (0.8% $CaCl_2$ + 0.6% H_3BO_3)	52.00	7.99	24.80	90.10	178.00	7.60	7.10	7.40
T16 (control)	47.80	7.44	20.20	85.30	171.60	7.00	6.90	7.10
C.D. (0.05)	0.13	0.05	0.07	0.13	0.24	0.11	0.34	0.10

CA Controlled atmosphere

Table 4 Effect of foliar spraying of calcium chloride and boric acid on chlorophyll content, firmness, shelf-life under different storage conditions and organoleptic rating of apple cv. 'Red Delicious'

Treatment	Quality grading (1–9 point hedonic scale)			
	Texture	Aroma	Appearance	Colour
T1 (0.4% $CaCl_2$)	7.30	7.50	7.30	7.50
T2 (0.6% $CaCl_2$)	8.40	8.50	8.20	8.20
T3 (0.8% $CaCl_2$)	6.70	6.90	6.70	6.80
T4 (0.2% H_3BO_3)	7.20	7.40	7.20	7.30
T5 (0.4% H_3BO_3)	7.50	8.00	7.90	7.90
T6 (0.6% H_3BO_3)	6.80	7.20	6.90	7.10
T7 (0.4% $CaCl_2$ + 0.2% H_3BO_3)	7.40	7.90	7.70	7.80
T8 (0.4% $CaCl_2$ + 0.4% H_3BO_3)	7.90	8.20	8.00	8.00
T9 (0.4% $CaCl_2$ + 0.6% H_3BO_3)	7.60	8.10	7.90	7.90
T10 (0.6% $CaCl_2$ + 0.2% H_3BO_3)	8.70	8.70	8.30	8.30
T11 (0.6% $CaCl_2$ + 0.4% H_3BO_3)	8.90	8.90	8.70	8.40
T12 (0.6% $CaCl_2$ + 0.6% H_3BO_3)	8.10	8.20	8.10	8.10
T13 (0.8% $CaCl_2$ + 0.2% H_3BO_3)	7.10	7.30	7.20	7.20
T14 (0.8% $CaCl_2$ + 0.4% H_3BO_3)	7.30	7.70	7.50	7.60
T15 (0.8% $CaCl_2$ + 0.6% H_3BO_3)	7.00	7.20	7.10	7.20
T16 (control)	6.50	6.50	6.30	6.10
C.D. (0.05)	0.20	0.12	0.09	0.10

chlorophyllase and chlorophyll oxidase (Gzink 1996). This finding is in accordance with Jeet (2016), who observed an increase in chlorophyll content of apple leaves with application of calcium. The favorable effects of calcium and boron treatments on fruit firmness could be related to the physiological role of calcium, which performs a binding role in the complex polysaccharides and proteins building the cell wall (Ajender and Thakur 2018). Calcium serves as an intermolecular binding agent that stabilizes pectin-protein complexes of the middle lamella. Calcium also plays an important role in the cell membrane by inducing rigidity at the membrane surface of apple fruit tissue (Fallahi et al. 1997). Fruit firmness (Fig. 3) is directly related to calcium pectate as calcium contact with pectic polymers of cell wall and function as cementing agent which offers strength to the cell wall (Ganai 2006). These results are in accordance with Casero et al. (2004), who observed that foliar treatments of calcium increased the firmness of apple fruits. These outcomes concur with those of Val et al. (2008).

The maximum shelf-life (Table 3) at room temperature of 28.20 days, at refrigeration 93.20 days and at CA storage 181.50 days was found in treatment T_{11} ($CaCl_2$ 0.6% + H_3BO_3 0.4%), which was followed by 27.80 days at room temperature, 92.90 days at refrigeration and 180.90 days at CA storage in treatment T_{10} ($CaCl_2$ 0.6% + H_3BO_3 0.2%), while the minimum shelf-life at room temperature of 20.20 days, at refrigeration 85.30 days and at CA storage 171.60 days was recorded in control (T_{16}).

The statistical analysis of data in Table 3 shows maximum taste (8.70), flavour (8.70) and overall acceptability (8.60) out of a 9-point hedonic scale was found maximum in treatment T_{11} ($CaCl_2$ 0.6% + $H_3BO_3$0.4%), which was followed by taste (8.50), flavour (8.40) and overall acceptability (8.30) out of a 9-point hedonic scale in treatment T_{12} ($CaCl_2$ 0.6% + H_3BO_3 0.6%) and the minimum taste (7.00), flavour (6.90) and overall acceptability (7.10) out of a 9-point hedonic scale was recorded in control (T_{16}).

The data analysed in Table 4 revealed maximum texture (8.90), aroma (8.90), appearance (8.70) and color (8.40) out of a 9-point hedonic scale was found maximum in

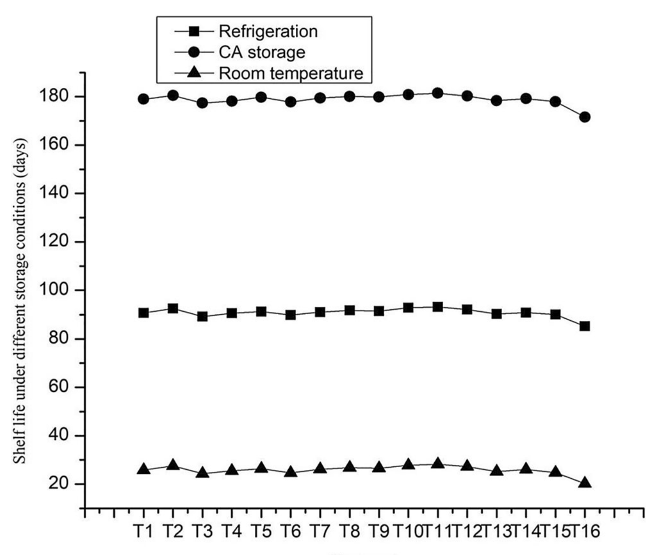

Fig. 4 Effect of foliar spraying of calcium and boron on shelf-life under different storage conditions of apple cv. 'Red Delicious'. *CA* Controlled atmosphere

treatment T_{11} ($CaCl_2$ 0.6% + H_3BO_3 0.4%), which was followed by texture (8.70), aroma (8.70), appearance (8.30) and colour (8.30) out of a 9-point hedonic scale in treatment T_{12} ($CaCl_2$ 0.6% + H_3BO_3 0.6%) and the minimum texture (6.50), aroma (6.50), appearance (6.30) and colour (6.10) out of a 9-point hedonic scale was found in control (T_{16}).

Fruits stored at room temperature (25 °C) exhibited a high concentration of volatile compounds and TSS, but were unable to retain firmness and TA as compared to other treatments. The fruits showed higher respiration and ethylene production (Fig. 4) during shelf-life storage at room temperature (25 °C). In contrast, fruits treated with a combination of calcium and boron maintained higher firmness, TSS, and TA, and inhibited ethylene production during shelf-life storage at 25 °C. This is consistent with findings reported by Khera et al. (2024). Additionally, the shelf-life was shorter at room temperature (25 °C) compared to CA (0 °C) and refrigerated storage (5 °C).

It is possible that the fruits' decreased ethylene concentration contributed to the longer shelf life (Fig. 4), which is in line with research by Fallahi et al. (1997), Saftner et al. (1999), and Sams and Conway (1984). The structure and function of cell membranes are influenced by calcium. It also reduces the activity of ethylene-producing enzymes that are attached to the cell membrane and have a protein structure, slightly delaying the climacteric rise, lowering the climacteric maximum, and preventing softness (Fallahi et al. 1985; Recasens et al. 2004). The hardness of the fruit tissue deteriorated after storage. Mature apples exhibit variations of ripening process during storage, which involve cell wall destruction by the enzymes polygalacturonase and pectin methyl esterase (Knee and Bartley 1981). In fact, storage at low temperatures, due to the destruction of the intermediate membrane and cellular separation, leads to a decline in the fruit tissue firmness. Calcium treatments lowered fruit tissue stiffness less than control fruits. Calcium decreases the vulnerability of the cell wall to enzymatic hydrolysis by reducing the activity of the enzymes polygalactornase and pectin methyl esterase, as well as by binding to cellular polymers, and limits the breakdown and disintegration of cells Fallahi et al. (1997). Calcium binding may reduce the accessibility of cell wall degrading enzymes (Faostat—Food and Agricultural Organization of the United Nations 2020). Moreover, pectin interacts with Ca^{2+} to form calcium-pectin gel, which causes cell-wall stiffening (Gao et al. 2019). Thus, these calcium-pectin structures confer resistance to the cell wall and prevent their degradation and hence their substrates. The fruit stored in controlled atmosphere at 0 °C presented fewer volatile organic compounds.

Fruit firmness was maximum at harvest and subsequently declined as the period of storage advanced however the rate of reduction of fruit firmness was slowed down by calcium treatments. Delayed softening of peach fruit following postharvest administration of calcium has also been recorded by wills and Mahendra (1989). Eksteen, Rhyn, and Villiers (1986) has also found the improvement in calcium content of pear by post-harvest application of 2% and 4% $CaCl_2$. Controlled atmospheres (0 c) can alter the proportion of different fractions of pectic compounds (Płocharski and Lange 1982; Siddiqui et al. 1996), and changes in polyuronides taking place during storage can be influenced by acidity (Murayama et al. 2002). These results are in line with Siddiqui et al. (1996), who observed that after 4 and 6 months of storage, the decrease in total pectins and hemicellulose, and rise in free pectins, were lowest in low oxygen circumstances, higher in CA conditions and maximum in normal atmospheres. The calcium content of the fruit samples increased considerably with refrigerated storage up to 90 days. The higher calcium content of the fruits treated with varied concentrations of $CaCl_2$ is connected to slow cellular deterioration and higher absorption of calcium by the fruits (Tobias et al. 1993).

Respiration rate of apple fruit, under different treatments, during refrigerated storage (5 °c) exhibited an initial increase before declining towards the end of storage. Such changes were relatively faster in control fruits which recorded highest respiration after 90 days of refrigerated storage. Treatment of the fruits with combination of $CaCl_2$ and H_3BO_3 effectively reduced respiration rate of the fruits following 90 days of refrigerated storage. $CaCl_2$ has been reported to control ethylene action by strengthening the pectin framework and making fruit less susceptible to the action of ethylene. A delay in fruit ripening and decrease in rate of respiration of fruits upon calcium treatments has

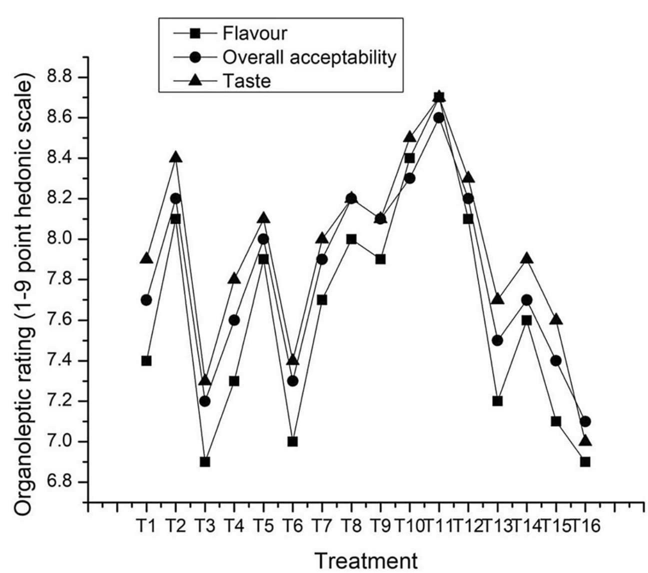

Fig. 5 Effect of foliar spraying of calcium and boron on organoleptic rating (1–9 point hedonic scale) of apple cv. 'Red Delicious'

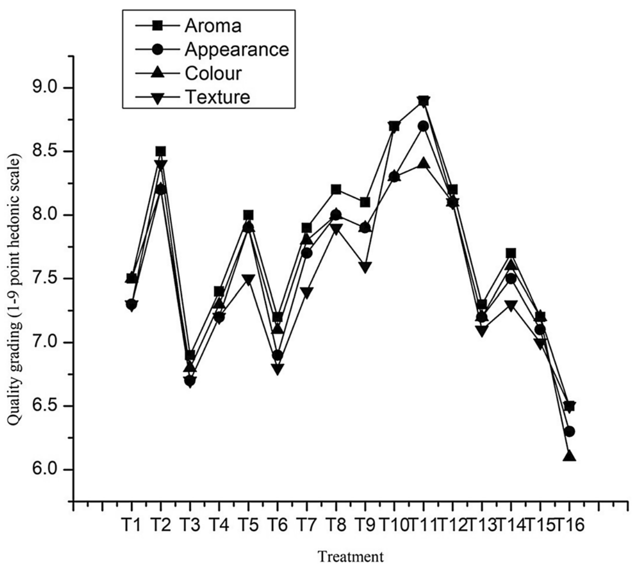

Fig. 6 Effect of foliar spraying of calcium and boron on quality grading (1–9 point hedonic scale) of apple cv. 'Red Delicious'

been reported during storage of peach (Manganaris et al. 2007).

Initially, the variety recorded the highest organoleptic score (Fig. 5) treated with varied combinations of $CaCl_2$ and H_3BO_3 up to 7 days after harvest exhibiting acceptability but afterward significant drop in sensory quality was detected. The organoleptic score of both kinds revealed that the variety having medium to high TSS and total sugars scored higher values, while lower values for either of these traits resulted in lower score.

Quality grading scores were usually highest in fruits treated with different combinations of $CaCl_2$ and H_3BO_3 (Fig. 6), whereas the control fruits exhibited rapid deterioration in quality during storage and were least acceptable. During ripening, degradation of chlorophyll results in exposure of the underlying carotenoids, which is also accompanied by the conversion of starch into sugars and a decrease in acidity resulting in fruits becoming more acceptable. Such changes occurred rapidly in control fruits. Changes in the sensory scores were more gradual under different $CaCl_2$ and H_3BO_3 treatments and thus the initial increase in quality grading scores of the fruits could be due to development of appropriate colour, taste, aroma and appearance, while the decline towards the end of storage could be due to the completion of ripening and initiation of senescence marked by the occurrence of undesirable changes. The findings of the present study where higher sensory scores in apple fruits treated with $CaCl_2$ and H_3BO_3 have been observed are congruous to the results obtained by Gorny et al. (2002) in pear and Conway et al. (2002) in apple fruits.

Conclusions

It is concluded from the experiments conducted that two sprays of calcium chloride (0.6%) + boric acid (0.4%) at 60 days and 30 days before harvest were best in improving the fruit quality at harvest as well as reducing physiological loss in weight and enhancing the shelf-life of apples. The physical parameters of fruits were found to be optimum with two sprays of calcium chloride (0.6%) + boric acid (0.2%). Hence, it is advisable to spray calcium chloride (0.6%) + boric acid (0.2%) and/or calcium chloride (0.6%) + boric acid (0.4%) twice for better quality and improved shelf-life of apples.

Acknowledgements All authors are very thankful to Sher-e-Kashmir University of Agricultural Sciences and Technology of Jammu, Main Campus, Chatha (J&K) for timely support and coordination.

Funding The research received no external funding.

Declarations

Conflict of interest A.B. Zahid, J. Mahital, S. Nirmal, S. Sushma and A.K. Burhan declare that they have no competing interests.

Ethical standards The authors of this article did not conduct any studies involving human participants or animals. All referenced studies were conducted in accordance with the respective ethical standards.

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