Role of Calcium in Maintenance of Postharvest Quality of Horticultural Crops

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Abstract
Horticulture has emerged as one of the major agricultural sectors as there has been a substantial increase both in area and production of horticulture crops. But still the wastage losses in horticulture are major concern. Minimizing these losses can increase their supply without bringing additional land under cultivation is necessary. Preharvest applications of calcium mainly in form of calcium chloride can modify biochemical changes occurring within developing fruits and therefore has a potential to transform its quality at harvest, which can ultimately affect storage quality of fruits. Calcium also has beneficial effects on marketing and storage of fruits through inhibition of abnormal senescence and reduction of respiration rate, ethylene synthesis, protein breakdown, weight loss and rotting. It has also been reported that fruits high in calcium have lower respiration rates.

Keywords: Calcium, calcium chloride, preharvest application, postharvest quality, etc

1. Introduction
Horticulture has emerged as one of the major agricultural activities as there has been a substantial increase both in area and production of horticulture crops. Horticulture crops have the inherent advantage of providing higher productivity per unit area of land as compared to other crops, resulting in higher income and employment generation in rural areas. Fruits and vegetables have been shown to earn 20-30 times more foreign exchange per unit area than cereals due to higher yields and higher prices available in the national or international markets. One important trend observed in the last five years is that horticulture development has gradually moved out of its rural confines into urban areas and from traditional agricultural enterprise to the corporate sector. This trend has led to the adoption of improved technology, greater commercialization and professionalism in the management of production and marketing of different horticulture crops.

On the other hand, postharvest losses in fruits and vegetables are very still very high (2-40%) depending upon the crop. Minimizing these losses can increase their supply without bringing additional land under cultivation is necessary. It will also help keep pollution under control. Improper handling and storage cause physical damages due to tissue breakdown. Mechanical losses include bruising, cracking, cuts, microbial, spoilage by fungi and bacteria, whereas physiological losses include changes in respiration, transpiration, pigments, organic acids and flavour. About 36% of vegetables decay due to soft-rot bacteria, whereas 30% of fruits decay due to *Penicillium* species alone. The losses can be minimized by proper pre- and post-harvest treatments.

A number of preharvest treatments including nutrients, growth regulators and promoters, training and pruning, fungicides, etc., affect fruit quality at harvest and hence their storability. Preharvest applications of these substances can modify the pace and direction of biochemical changes occurring within developing fruits and therefore has a potential to transform its quality at harvest, which can ultimately affect storage quality of fruits. So, in this review paper main emphasis is given on application of calcium which is most important to improve the quality before harvest and maintenance of that quality after harvest.

2. Role of Calcium in Horticultural Crops
Calcium plays an important role in maintaining quality of fruits and vegetables (Huber, 1983). It is essential for maintaining the structure and function of cell wall and membranes as it interacts with pectic acid in the cell wall to form calcium pectate, thereby having a direct influence on fruit firmness. Calcium also has beneficial effects on marketing and storage of fruits through inhibition of abnormal senescence and...
reduction of respiration rate, ethylene synthesis, protein breakdown, weight loss and rotting. It has also been reported that fruits high in calcium have lower respiration rates and a longer shelf life in comparison to fruits low in calcium content (Faust and Shear, 1972). Pre- and postharvest application of calcium delays senescence of muskmelon fruits with no detrimental effect on consumer acceptance (Lester and Grusak, 2004). Gautam et al. (1981) observed that higher concentrations of calcium nitrate (0.6 to 1.0 %) resulted in decrease in TSS and increase in acidity of Kanto-5 peach fruits when the treatments were applied at the pit-hardening stage and again two weeks later.

Different calcium formulations (Calcium nitrate, calcium chloride and calcium amino acid chelate) were applied throughout the peach fruit development and growth period and were assessed for their effect on the quality and shelf life of peach fruit. All the treatments resulted in improvements in fruit firmness and reduced postharvest fruit rots (Taylor and Brannen, 2008).

Pre-harvest calcium sprays with calcium chloride or with a commercial chelated calcium form at equivalent calcium rate were applied to nectarine trees at weekly intervals beginning 4 or 8 weeks before harvest. The fruits were harvested at commercial maturity stage and cold stored (0 °C, 95% RH) for 0, 2, 4 and 6 weeks, prior to their ripening at room temperature (20 °C) for 1 and 5 days. Calcium increased by 14-25 % in the peel and by 8-11 % in the flesh, whereas cell wall calcium increased by 7-17 % in calcium-sprayed fruits after harvest. Cell wall and pectin calcium increased with an increase in storage time in both sprayed and non-sprayed fruits without a corresponding increase of total calcium and uronic acid content, indicating the formation of more sites for calcium binding as storage period increased (Vasilakakis et al. 2006). Further calcium plays a number of roles in maintenance of quality as:

2.1. Physiological loss in weight (PLW)

The physiological loss in weight during storage is generally due to the loss of moisture and respiratory losses occurring in the commodity. Wilkinson (1965) observed that most fruits contain 80-85 % of water by weight, some of which may be lost by evaporation although a major portion of it is lost by transpiration.

Generally, calcium is essential to maintain structural integrity of membranes and cell walls and as such plays an important role in regulating the quality and storage life of fruits (Manganaris et al. 2006). Fruits high in calcium may have potential for better transportation and remains in good condition for longer duration because calcium decreases respiration rate, maintains fruit firmness, delays senescence and thus extends the storage life and reduces the incidence of physiological disorders during storage (Ferguson, 1984). Preharvest treatments with calcium nitrate have been reported to cause a significant reduction in loss in weight of peach fruits during storage. It was also observed that the minimum physiological loss in weight occurred in response to 1.5% calcium nitrate treatment (Gupta et al., 1984) while applying 1.5% calcium chloride as preharvest treatment at weekly intervals in peach cv. Sharbati. Mir et al. (1993) studied the effect of calcium infiltration on the storage behaviour of Red Delicious apples and found that calcium treatment reduced physiological loss in weight during storage. Fruits of peach cv. Earl Grande that were treated with 4 and 6% CaCl₂ for 10 minutes, air dried, packed and cold stored at 0–2 °C and 85–90% relative humidity, exhibited lower PLW and TSS contents under the influence of calcium treatment (Navjot and Gurcharan, 2006).

Foliar application of CaCl₂ at 2000 ppm to peach cv. Surecrop increased fruit firmness and acidity and also delayed fruit ripening (Ochie et al., 1993). Budde et al. (1999) noted an increase in the calcium concentration in the outer two third portion of fruit mesocarp of peach cv. Angelus following preharvest treatment of CaCl₂ @ 0.4% at weekly intervals for 5 weeks. However, the higher concentration of 2.0% CaCl₂ proved toxic and had exerted adverse effect on fruit quality. Yu et al. (2004) reported that peach cv. Qinwang when immersed in 1.0, 3.0 or 5.0 % CaCl₂ for 15 minutes and stored at 0±1°C and 80–95% RH for 35 days, showed a decrease in ethylene production, respiration rate, polyphenol oxidase and peroxidase enzyme activities of fruits especially when treated with 3.0% CaCl₂. They further reported that fruit browning was inhibited and fruit quality improved. Manganaris et al. (2005) found that a total of 6 or 10 preharvest calcium sprays (calcium chloride) were effective in increasing the Ca content in the cell walls of peach fruit, which corresponded to the Ca increase in the insoluble pectin fraction.

2.2. Fruit firmness

Flesh firmness is an important determinant of fruit quality (Martin et al., 1975). Changes in fruit texture with advancement in ripening results from changes in the structure and composition of their cell walls. Softening of fruits is caused by the breakdown of insoluble protopectin into soluble pectin (Mattoo et al., 1975). Rilley and Kolathukudy (1976) reported that Golden Delicious apples when individually sprayed with calcium chloride solutions a week immediately prior to harvest were firmer by 1.0 kg (2.1lb) than untreated fruits at harvest. Raese and Drake (1998) found an increase in firmness of pear fruits during each of the 45, 90 and 145 days storage regimes in response to preharvest treatment of trees with calcium chloride.

2.3. Total soluble solids (TSS)

Salunkhe et al. (1968) reported that soluble solid content increased during ripening of peach fruits on the tree and also during storage. According to Gangwar and Tripathi (1972) total soluble solid contents increased during maturity of peach fruits and they recorded TSS contents of 10.5 and 12.0% in mature and ripened fruits, respectively. Aly et al. (1981) found that
total soluble solids generally increased with storage time and temperature as fruits stored at low temperatures developed lower soluble solids. With the advancement in storage period, starch gets hydrolyzed into mono- and disaccharides which in turn may lead to increase in TSS and sugar contents and on complete hydrolysis of starch no further increase occurs. Subsequently there may be a decline in these constituents especially under prolonged storage as they are the primary substances for respiration (Wills et al. 1989).

2.4. Titratable acidity

Organic acid levels in peaches and nectarines reach a maximum and then decrease as the fruit approach harvest maturity (Ryugo and Davis, 1958). The acidity of fruits is derived from organic acids which are stored principally in cell vacuoles. There is generally a decrease in total acidity with ripening of fruits, though the contents of one or more acids may increase. Scott (1980) observed that with the advancement of storage period acids act as substrates for respiration and therefore, their contents declined towards the end of storage periods. In peaches, the overall acidity declines and pH rises slightly during maturity as reported by Kakiuchi et al. (1981). However, peach fruits stored at low temperature have also been reported to have lower acidity than the fruits stored at higher temperature (Aly et al. 1981). Mehta and Jindal (1984) applied various nutrients like Ca(NO)\textsubscript{3}, KNO\textsubscript{3}, CaCl\textsubscript{2}, and H\textsubscript{2}BO\textsubscript{3} at the preharvest stage to plum cv. Santa Rosa and found the lowest value for titratable acidity in calcium chloride treated fruits.

Farag et al. (2012) investigated the role of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} compounds or sources on firmness and quality of “Anna” apple fruits applied as preharvest or postharvest treatments. During 2009 and 2010 seasons, “Anna” apple trees were sprayed ten days before harvest with Ca\textsuperscript{2+} and, or Mg\textsuperscript{2+} sources in the form of chloride or sulphate in addition to the control. In the postharvest study, apples from untreated trees from the same orchard were dipped in MgCl\textsubscript{2}, CaCl\textsubscript{2} each at 1% or 2% (w/v) alone or in combinations, Ethrel at 100 ppm and then held at room temperature (22±2°C) for 5 days. The preharvest study provided evidence that CaCl\textsubscript{2} alone or combined with MgCl\textsubscript{2} resulted in the highest firmness of apple fruits followed by MgSO\textsubscript{4} plus CaSO\textsubscript{4}. In addition, CaCl\textsubscript{2} alone or plus MgCl\textsubscript{2} resulted in higher acidity and vitamin C than other treatments.

2.5. Sugar contents

In common with other fruits, the sugar content and other constituents of peaches are greatly influenced by maturity at harvest, season and storage conditions. In general, the reducing sugar content in apple tends to increase during the initial periods of storage and thereafter a decline has been reported (Wright and Whitehan, 1955). Dutta et al. (1960) reported that during storage of oranges their reducing sugar contents showed a constant increase. In peaches, the non-reducing sugars increased with maturity by a greater amount than reducing sugars (fructose and glucose), whereas reducing sugars declined at a faster rate than sucrose during storage (Deshpande and Salunkhe, 1964).

Debov and Zadgovski (1970) reported that the total sugar content in peaches and nectarines ranged from 7.73–14.75%, whereas the sucrose levels varied from 4.66–11.6%. An increasing trend in reducing sugar contents of Kinnon fruits has also been reported by various other workers with an increase in storage periods (Mann and Randhawa, 1976). According to Kawamata (1977) peach, plum, apricot, cherry and nectarines contained glucose as the most abundant sugar and fructose and sucrose in traces. At maturity, total sugar content has been reported to range from 5.57–11.61%.

Conway (1998) observed a gradual increase in sugar contents of Red Chief and Granny Smith apples treated with Frutox (3%)+CaCl\textsubscript{2} (100 ppm) during the initial five months of storage under refrigerated conditions, before showing a decline. However, Nickhah et al. (1999) found a decrease in sugar content of pear fruits that were dipped in calcium chloride solution.

2.6. Ascorbic acid

Nutritive value of fruits is largely due to the high vitamin contents especially ascorbic acid (Vit. C). Peaches have been reported to contain 1–12 mg of ascorbic acid 100 g\textsuperscript{-1} of fruit pulp (Floyd and Fraps, 1939). However, Peynaud (1958) mentioned that the ascorbic acid range for 95 peach varieties was 6–59 mg 100 g\textsuperscript{-1} of fresh fruit pulp, individual values depending on the variety and stage of ripening. Also, Wills et al. (1989) noticed that apple and peach fruits contain 10 mg ascorbic acid 100 g\textsuperscript{-1} of fruit pulp. Joshi and Bhutani (1995) reported that the ascorbic acid content in peach fruits varies from 1.0–27.0 mg 100 g\textsuperscript{-1} pulp. Luh and Phithakpol (1972) observed that the ascorbic acid content declined during ripening of fruits.

Bangerth (1976) reported a direct relationship between the calcium treatments, calcium content and ascorbic acid content of apple, pear and tomato fruits as a result of preharvest calcium chloride treatments. In addition, calcium treatment has also been reported to retard the loss of ascorbic acid in grape berries (Lu and Ouyang, 1990). Besides, Gupta et al. (1987) also noted higher ascorbic acid contents in ber fruits treated with calcium chloride as preharvest spray.

2.7. Fruit softening enzymes

The process associated with the ripening of climacteric fruit are under enzymatic control. The dissolution of middle lamella in ripening fruits may be brought about mostly by the action of pectolytic enzymes especially polygalacturonase and pectin methyl esterase (Lesham et al., 1986). The softening of fruit tissue is one of the most important changes associated with ripening and is normally accompanied by an increase in the concentration of soluble pectin polysaccharides (Bartley and Knee, 1982). The enzyme believed to be involved in softening of fruit is D-polygalacturonase (PG). The activity of
this enzyme is low or absent in unripe fruits and increases during the ripening process (Abeles and Takede, 1990). Pollard (1975) observed an increase in pectin methyl esterase and polygalacturonase activity in apple fruits during ripening and pectic substances became water soluble only after PG activity has been initiated. Further, Pressey et al. (1971) found no polygalacturonase activity in unripe peaches but its activity appeared when the fruit began to soften and then increased sharply as ripening proceeded.

Mahajan and Chopra (1994) observed an initial slow increase in PG activity which was followed by a decline towards the end of storage of Red Delicious apple fruits treated with Frutox (6%) as compared to control fruits where faster changes in PG activity were noticed. Lurie and Ben (1990) reported profound polygalacturonase enzymatic activity in Waxol (3%) + DPA (500 ppm) treated Granny Smith apples and a low activity in uncoated fruits.

Schewfelt (1965) reported that pectin methyl esterase (PME) is present in peaches at all stages of development and ripeness and the amount does not differ greatly between clingstone and free stone varieties. PME activity in mature peach fruit is in the range of 15 milliequivalents kg\(^{-1}\) hr\(^{-1}\). They also found an increase in the level of PME activity.

Pre-harvest calcium sprays (7 weekly applications at 1.6%, w/w, 81–123 days after full bloom) were applied to ‘Fuji Kiku-8’ apples, with the purpose of examining treatment effects on cell wall metabolism during on-tree fruit maturation and ripening. Applied calcium improved cell-to-cell adhesion as indicated by better preservation of the middle lamella and by higher contents of ionically bound pectins in treated fruit, leading to higher fruit firmness levels at commercial harvest. Matrix glycan breakdown was also delayed in response to calcium treatment. Calcium applications partially suppressed pectinmethylesterase, pectate lyase, \(\beta\)-galactosidase, \(\alpha\)-L-arabinofuranosidase and \(\beta\)-xylosidase activities, without any apparent relationship with ethylene production rates (Ortiz et al., 2011).

2.8. Spoilage of fruits

Spoilage is an important economic factor in the marketing and storage of fruits. Losses caused during post harvest handling are generally attributed to decay caused by microorganisms, especially fungi (Eckert and Sommer, 1967). Singh (1984) reported that preharvest sprays of calcium compounds reduced decay losses in peach during storage. Moreover, Braret et al. (1998) confirmed that preharvest sprays of calcium nitrate effectively reduced spoilage of peach fruits up to 22 days under cold storage conditions as compared to untreated fruits. Raese (1999) observed lower incidence of external rots of pear fruits treated with calcium chloride.

Peach and nectarine trees were foliar sprayed with a formulation containing \(\text{Ca}^{2+}\), \(\text{Mg}^{2+}\) and \(\text{Ti}^{4+}\). Parameters related to fruit quality were evaluated at harvest, after 7–28 days of cold storage and after subsequent ripening for 4 days at 20 °C (shelf life). At harvest, treated fruits from both cultivars had higher weight and pulp firmness than control fruits, while no effect was observed for either colour, total soluble solid content (TSS) and titratable acidity (TA) or the time required to ripen on the tree. Also, the storability of treated fruits was extended for up to 14 days more than that of control fruits. Even during ripening at 20 °C after different periods of cold storage, parameters related to ripening evolved faster in controls than in treated fruits. Also, the occurrence of the climacteric peak of ethylene production was delayed and its intensity was lower in treated peaches and nectarines (Serrano et al., 2004).

The effect of preharvest calcium foliar application on ethylene production, respiratory rate, soluble pecturonides and fruit firmness of ‘Bebekou’ apricot fruits was determined by Tzoutzoukoua and Bouranisib (1997). Calcium was applied 21, 17, and 13 days before harvest for 1991 at the concentration of 0.5% calcium chloride (\(\text{CaCl}_2\)) each time and 16 and 12 days before harvest for 1992 at the concentrations of 0.8 and 0.7% \(\text{CaCl}_2\), respectively. Calcium treatment resulted in a 30–76% increase in the Ca content of fruit flesh. After four weeks of storage at 0 °C, there was no significant effect of Ca on the respiratory rate. Calcium-treated fruits were about 70 % firmer than the untreated ones at harvest time. Foliar-applied Ca produced a 29% decrease in the soluble pecturonide content of fruits at harvest time, but not after four weeks of storage.

3. Conclusion

Calcium has been recognized as an essential plant nutrient involved in a number of physiological processes involving cell wall, membrane and enzymatic activities. It is also plays an important role in maintaining quality of fruits and vegetables by maintaining the structure and function of cell wall and membranes as it interacts with pectic acid in the cell wall to form calcium pectate, thereby having a direct influence on fruit firmness. External application of calcium strengthen the cell wall structure and helps in maintaining the quality after harvest. A no. of studies above depicted in the review showed that it resulted in lowering the respiration rates and a longer shelf life in comparison to fruits low in calcium content. External application of calcium in the form of calcium chloride also reduces ethylene synthesis, protein breakdown, weight loss and rotting.

4. Further Research

Calcium chloride solution proven to be a true supplier of calcium when applied in the form of dip or spray to the crops. There is still a need of research to be carried out that how it is effectively involved in direct inhibition of ethylene bio-synthesis. Further the interaction between enzymes and calcium inside the fruit is also an area need to be worked thoroughly as only a few studies are carried out on this aspect.
5. References


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