Research Article

Changes in pH, acids, sugars and other quality parameters during extended vine holding of ripe processing tomatoes

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Abstract

BACKGROUND: Two important quality attributes of processing tomatoes are pH and titratable acidity. These and other quality attributes can be affected by tomato fruit maturity and over-maturity. We have determined the magnitude of these maturity effects in four processing tomato cultivars commonly grown in California.

RESULTS: Allowing tomatoes to remain on the vine for up to 4 weeks after ripening resulted in an increase in fruit pH of between 0.01 and 0.02 unit per day for the four cultivars examined. The increase in pH was paralleled by a decrease in titratable acidity, due to a loss of citric acid. Glucose and fructose concentrations also declined with increasing maturity after ripening. Other quality parameters (color, lycopene, total pectin, pectin solubility, and Bostwick consistency) all showed little change.

CONCLUSION: Vine holding of ripe fruit adversely affects quality, especially pH and titratable acidity. Recent problems with high tomato juice pH encountered by tomato processors in California could be the result of increased average fruit maturity at harvest.
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Keywords: tomato; pH; maturity; quality; citric acid

INTRODUCTION

Average annual production of processing tomatoes in California is about 12 million tons per year, accounting for more than 90% of the US crop and about 40% of worldwide production. Since the 1960s harvesting has been by machine where all fruit from an entire field is collected in a single pass. This harvesting system results in a mixture of fruit with a range of maturities. After sorting on the harvester to remove unripe green fruit, the tomatoes are transported by truck to processing plants where they are converted into a variety of products, including whole peeled tomatoes, diced tomatoes, and tomato paste. A major challenge in this production system is to coordinate the timing of the harvests with available processing plant capacity. Often it is necessary to delay harvesting until sufficient processing capacity becomes available. This 'field storage' of ripe fruit can further affect the average maturity of the fruit being processed.

Two important quality attributes of processing tomatoes are pH and titratable acidity (TA). Tomatoes are not a low-acid food and thus require less drastic thermal treatments than foods classified as low acid (pH > 4.6) for the destruction of spoilage microorganisms to ensure food safety. It has been suggested that pH 4.4 is the maximum desirable for safety and the optimum target pH should be 4.25.[1] Industrial processors of tomatoes in California typically specify a pH of 4.2 or 4.3 in their processed products. The pH of tomatoes is determined primarily by the acid content of the fruit. The acidity of the fruit is also important as a contributor to the flavor of the tomato products.

In recent years processors in California have noted that the pH of products such as hot-break tomato paste have been increasing, often requiring the addition of citric acid to obtain the required final pH. While processing conditions can affect the acid content and pH of tomato products,[2,3] changes in processing conditions do not appear to be the cause of this recent pH rise. Rather, the rise in pH can be observed in the raw fruit arriving at the processing plant. Typically each truck-load of tomatoes arriving at the processing plant is sampled and the pH of the fruit determined. These data are available to the public (www.ptab.org). An analysis of this load data collected over the past 9 years (2001–2009) showed that the average pH of fruit arriving at processing plants has been rising by about 0.01 pH unit per year. Significantly, this pH rise can be observed even when the data analyzed are limited to a single cultivar grown in a single county. Thus the overall rise in pH is not due to the introduction of new cultivars or to a geographic shift in production.[4]

Several previous studies have looked at the effects of tomato cultivar and fruit maturity on pH and other quality parameter.[5–10]

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In all tomato cultivars examined, pH increased as the fruit ripened from the green to pink to red stage, and continued to increase as the red ripe fruit remained on the vine. TA was at its maximum at the beginning of the ripening process then decreased as the fruit reached the ripe stage and continued to decrease with over-maturity. Soluble solids have been shown to increase during ripening then remain constant with over-maturity.[7] Contradictory results have been obtained for the effect of maturity on juice consistency where it has been shown that Bostwick values either increase[5,6] or decrease with maturity.[9]

Citric acid is the most abundant acid in tomatoes and the largest contributor to the total TA.[10,11] The decrease in TA with maturity and over-maturity is generally assumed to be due to a loss of citric acid, although direct measurements of changes in citric acid concentrations with maturity have not been reported. Two other acids that contribute significantly to the TA are malic and glutamic acid. Malic acid is typically present at only one tenth the level of citric acid, although the ratio of malic to citric can vary considerably between different tomato cultivars.[10,11] Changes in malic acid levels with maturity and over-maturity have not been reported. Glutamic acid levels have been shown to increase 10-fold as the fruit ripens from the green to the red stage.[12] Further changes in glutamic acid with over-maturity have not been reported. Glutamic acid is also an important contributor to tomato flavor.

Recently, new cultivars of tomatoes have been introduced which have a greater ability to resist decay once fully ripened and can thus be left in the field longer after reaching the red ripe stage. These 'extended field storage' (EFS) cultivars are desirable for the growers and processors because they allow greater flexibility in the timing of harvests once the fruit has reached the ripe stage, which helps in coordinating harvests with processing plant capacity. Changes in fruit quality with EFS are likely to be similar to those seen in older non-EFS cultivars, although this has not been studied. In this study we have examined both EFS and non-EFS cultivars to determine the changes in sugars, acids, and pH that occur when ripe tomatoes are allowed to remain on the vine.

EXPERIMENTAL

Tomato plantings

Two separate field trials were grown. In the first trial, fruit of uniform maturity were obtained by tagging fruit in the field at the pink stage, then this tagged fruit was hand harvested weekly for 5 weeks. In the second trial the entire mass of fruit from a randomly selected 10 foot row section was harvested and sorted weekly for four weeks. Four cultivars of processing tomatoes, Heinz 2401 (H2401), Sun Seeds 6368 (N6368), Heinz 9557 (H9557), and AB2 were examined. Two of these, H2401 and N6368, are considered EFS cultivars.

Four cultivars of processing tomatoes, Heinz 2401 (H2401), Sun Seeds 6368 (N6368), Heinz 9557 (H9557), and AB2 were grown in two separate field trials. Two of these cultivars (H2401 and N6368) are considered EFS cultivars. The first trial was grown in Yolo County, California, at the Vegetable Crops Research Field Station, University of California Davis. Plants were grown from transplants and watered with subsurface drip irrigation using standard commercial practices. At 96 days after transplanting, fruit at the pink stage were identified and tagged with small adhesive stickers. Completely exposed fruit at the top of the canopy was avoided to reduce the incidence of sunburn in the tagged set of fruit. A total of 500 of each variety were tagged. Fruit

were hand harvested weekly beginning 1 week after tagging for a total of 5 weeks. Only undamaged fruit with minimal sunburn were included in the harvest.

The second trial was grown at the University of California West Side Research and Extension Center in Fresno County, California. The same four varieties as in the first trial were grown from transplants and watered with subsurface drip irrigation and standard commercial practices. The first harvest was at 125 days after transplanting with three additional harvests at 1-week intervals. For each harvest four 10-foot sections of the rows were selected at random and the entire mass of tomato fruit in that section collected. This fruit was then sorted by hand into green, marketable red, and unmarketable damaged fruit (culls) and the total mass in each category determined. Yields per acre were calculated from these sample sections. A portion of the marketable red fruit was set aside and transported to UC Davis for juice preparation and analysis.

Preparation and evaluation of juices

Microwave hot-break juice was prepared from 1300 g samples of tomatoes from the field trials as described previously.[13] For each variety at each harvest date three separate juices were prepared. Juices were analyzed for lycopene, color, titratable acidity, and pH as described.[13]

Supernatants were prepared from these juices by centrifuging at $15\,000 \times g$ for 10 min. These supernatants were analyzed for individual sugars and acids using enzyme kits (R-Biopharm, Marshall, MI, USA). It has been shown that acid and sugar levels determined with these kits on crude tomato juice supernatants give excellent agreement with HPLC analysis.[14] Soluble solids contents of the supernatants were determined with an Atago PR-32 refractometer, and phosphate concentrations by the Ames method.[15]

Statistical analysis

Data are presented as means ± SE. An unpaired t-test with equal variance was used to calculate the two-tailed P value to estimate statistical significance of differences between means.

RESULTS

Fruit color and lycopene

To assess the ripeness stage of the fruit the color and lycopene content of hot-break juice prepared from the fruit was determined. The a/b ratio, a measure of redness, increased between the first harvest at 7 days after tagging, and the second harvest at 14 days, indicating that the fruit was not fully ripe until the second harvest (Fig. 1). The lycopene content of the juice similarly did not reach its maximum level until the second harvest. The general correlation between lycopene and a/b ratio has been noted previously.[16] Both the a/b values and the lycopene content of the juice from N6368 fruit were lower than those of the other three cultivars at all stages of maturity.

pH and titratable acidity

The pH of hot-break juice increased with increasing maturity in all 4 cultivars examined (Fig. 2A). The only obvious differences between cultivars were the lower pH values for the H2401 tomatoes at all stages of maturity. Both the EFS cultivars (H2401, N6368) and the non-EFS cultivars (H9557, AB2) showed similar pH increases with maturity. The pH increase between the first harvest at 7 days, and
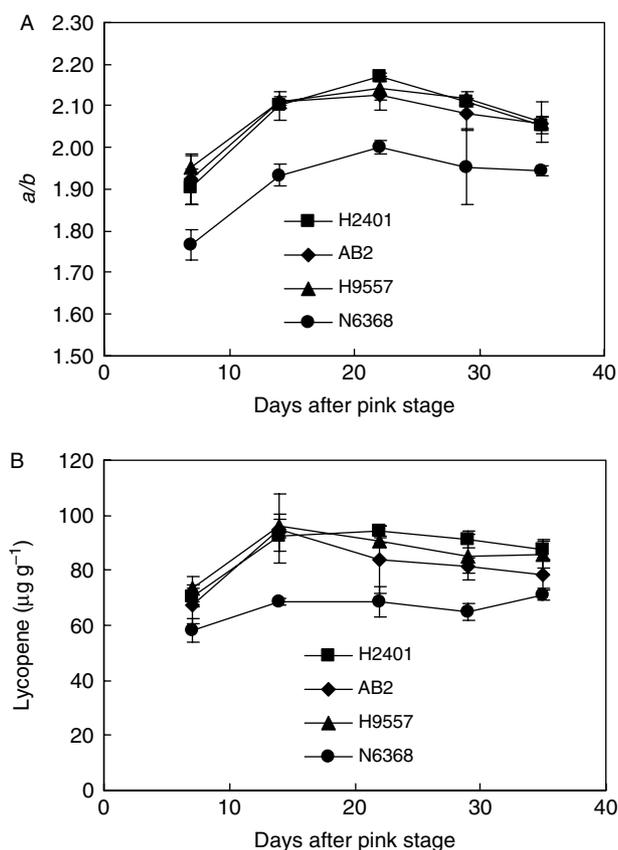
Figure 1. Color and lycopene content of tomato juices prepared from tomatoes of different maturities. (A) Color measured as the Hunter Lab *a/b* ratio. (B) Lycopene content.

the final harvest at 35 days, varied between 0.29 and 0.31 unit for the four cultivars examined. This is equal to a pH increase of approximately 0.01 unit per day.

Total TA of the hot-break tomato juices decreased with increasing tomato maturity (Fig. 2B). This decrease ranged from 17 µeq g^{-1} for the H2401 cultivar to 9 µeq g^{-1} for the AB2 cultivar. The decrease in TA mirrored the increase in pH. The H2401 tomatoes, which had a notably lower pH than the other cultivars, had the highest TA. A plot of pH versus TA for all 124 juice samples prepared in this study showed a clear relationship between pH and TA (Fig. 2C).

Organic acids

The rise in pH and decrease in TA indicates that acid concentrations in the fruit are declining with maturity. The predominant acid in tomatoes is citric acid. Citric acid levels declined with maturity in all four tomato cultivars (Fig. 3A). Citric acid levels were 22–30% lower at the final harvest than at the first harvest, for the four cultivars examined. As with the pH and TA measurements, the H2401 tomatoes were notably higher in acid content than the other three cultivars, but showed a similar decline with maturity. Glutamic acid levels were lower than citric acid and did not show an obvious decline with maturity in any of the cultivars (Fig. 3B). The change from the first to the last harvest ranged from +12% to −16%. Malic acid levels were even lower than glutamic and also did not decline with maturity (Fig. 3C). From the first harvest (day 7) to the third harvest (day 22) malic acid levels actually increased
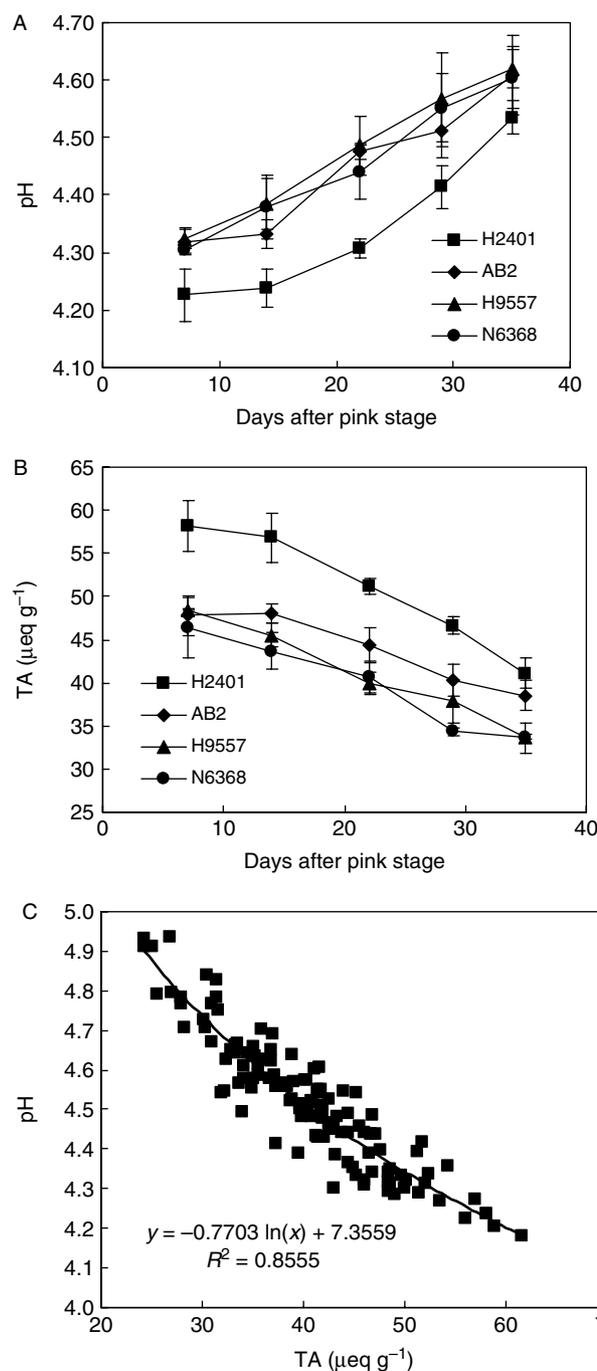

Figure 2. (A) Effect of maturity on tomato juice pH. (B) Effect of maturity on titratable acidity (TA). (C) Relationship between pH and TA.

in all four cultivars then either declined or remained constant at later harvests. Phosphate ions also contribute to the measured TA. Free phosphate concentrations in these tomato juices ranged from 3 to 4 mmol L^{-1} but showed no change with maturity or any consistent difference between cultivars (data not shown). These phosphate concentrations are in line with what has been reported previously.[11]

From the measured tomato juice pH, the expected TA of the juice can be calculated from the measured concentrations of citric acid, glutamic acid, malic acid, and phosphate, and their
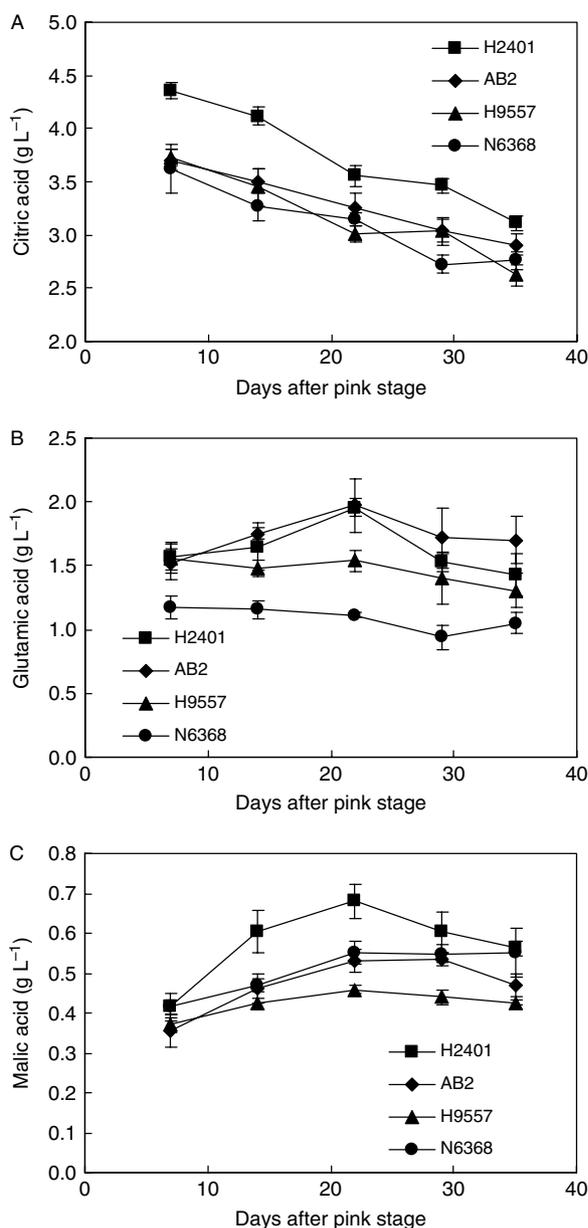
Figure 3. Changes in acids with maturity. (A) Citric acid. (B) Glutamic acid. (C) Malic acid.

Figure 4. Predicted versus measured TA.

known pK_a values. When the predicted TA was compared with the measured TA there was a very good correlation between these two values for all 124 juice samples prepared in this study (Fig. 4). Predicted TA values were equal to 86% of the measured TA values on average, indicating that only 14% of the measured TA acidity was due to other acids not measured. These other acids would include ascorbic, oxalic, as well as numerous amino acids including aspartic and γ-aminobutyric. In some varieties of tomatoes these latter two amino acids have been shown to occur at levels comparable to that of glutamic acid in ripe fruit.[12]

Sugar and soluble solids

Glucose and fructose levels were highest at the second harvest when the fruit reached full ripeness, then declined slightly over the next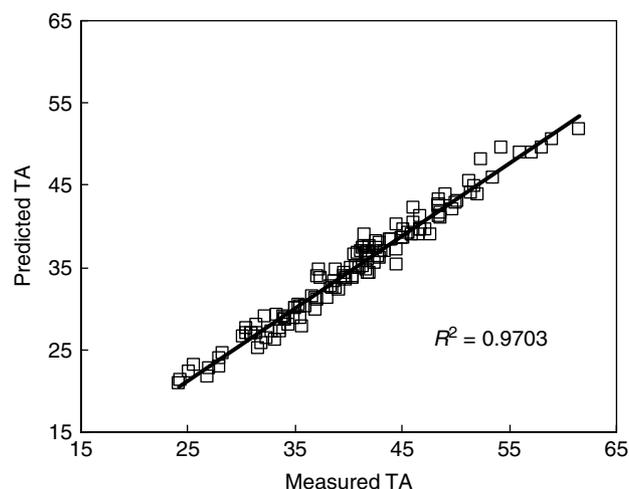 3 weeks of vine holding (Fig. 5A). The decreases between the second and fifth harvests were small but significant ($P < 0.05$) and ranged from 10 to 12% for the four cultivars. Fruit of the AB2 cultivar had the highest sugar levels while H2401 had the lowest.

Soluble solids content, measured with a refractometer and expressed in °Brix, is a commonly used measure for assessing tomato quality. The soluble sugars glucose and fructose are the largest contributor to the total soluble solids. Between the first and last harvests soluble solids declined by between 4% and 7% for the four tomato cultivars, in agreement with the measured declines in glucose and fructose (Fig. 5B). Overall soluble solids showed a good correlation with the sum of glucose plus fructose concentration (Fig. 5C).

Other quality attributes changed relatively little over the 4 weeks of field holding. Consistency, measured as Bostwick values, increased with later harvest times (Fig. 6A). For all four cultivars the average Bostwick values at the fifth harvest were higher than those from the first harvest (6–15% higher depending on the cultivar) but for no individual cultivar was this difference significant at $P < 0.05$. Pectin content and composition are known to be important contributors to the consistency of tomato juice. Between the first and fifth harvests changes in total pectin, measured as galacturonic acid (GalUA), were small ($<5\%$) and not significant at $P < 0.05$ (Fig. 6B). Similarly, no significant changes were found in the water solubility or the degree of methyl esterification of pectin between the first and fifth harvests (data not shown). Although no large change in consistency or pectin content occurred within a cultivar there were obvious differences between cultivars. The cultivars H2401 and H9557 had substantially higher pectin contents and lower Bostwick values than the AB2 and N6368 cultivars. Overall Bostwick consistency showed a significant correlation with pectin content (Fig. 6C), which is in agreement with previous research findings.[9]

Effects of delayed harvesting

By tagging individual fruit it was possible to successively harvest fruit of uniform maturity to determine the effect of maturity on acidity and pH. However, this approach does not address the question of how large a change in pH will occur if an entire field, containing fruits of varying maturities, is harvested at successively later dates. Nor does it allow for determining the effect of extended vine holding on the yield of intact red fruit. To answer these
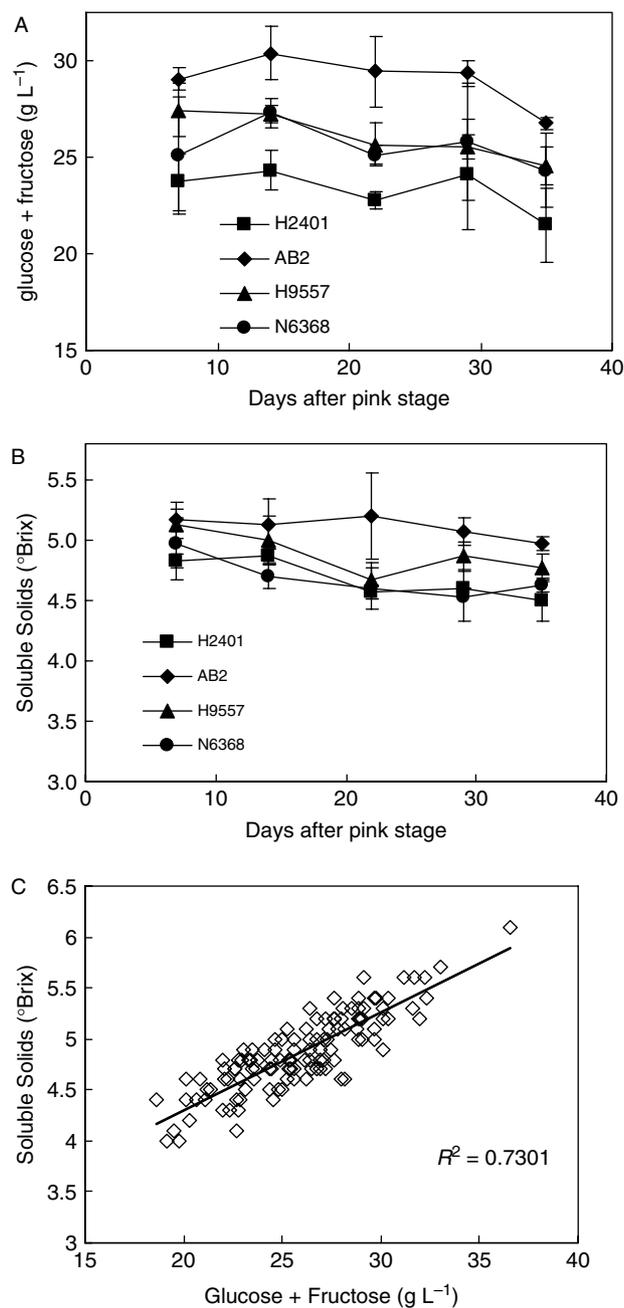
Figure 5. (A) Changes in sugar (glucose + fructose) with maturity. (B) Changes in soluble solids with maturity. (C) Correlation between soluble solids and sugars.
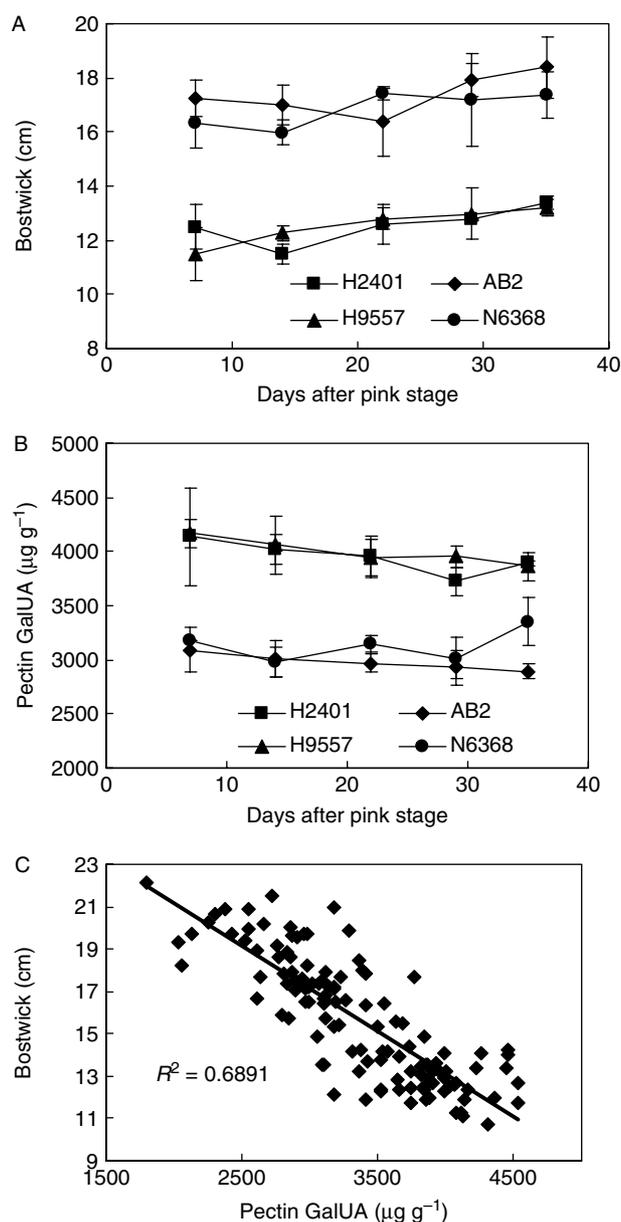

Figure 6. (A) Effect of maturity on Bostwick consistency. (B) Effect of maturity on pectin. (C) Correlation between Bostwick consistency and pectin content.

questions a second field trial with a different protocol was used. In this trial the same four cultivars of tomatoes were grown and entire replicate 10-foot sections of rows were harvested in four weekly harvests. The yield of marketable red fruit was determined and a sample of this red fruit was used to prepare hot-break juice for analysis.

The yield data showed a clear difference between the cultivars (Fig. 7). The two EFS cultivars, H2401 and N6368, had higher yields in all four harvests and showed no decline in yield until the fourth harvest. In contrast, the yield of the non-EFS cultivars, AB2 and H9557, dropped steadily with each harvest reaching near zero

yield by the end of the 4-week period. These results show the superior field-holding ability of the EFS cultivars.

Delayed harvesting resulted in juice with a higher pH in all varieties. Average pH ranged from 4.38 to 4.49 at the first harvest, then increased to a range of 4.70 to 4.89 at the final harvest 21 days later (Fig. 8A). The pH of the final harvest was more than 0.2 unit higher than that in the first trial, which may indicate that the average maturity at the final harvest in the second trial was beyond the range of maturities examined in the first trial. As in the first trial the rise in pH was accompanied by a decline in TA due to a loss of citric acid (Fig. 8B and C). Changes in soluble solids and the concentrations of glucose, fructose, glutamic acid, and malic acid were all similar to what was observed in the first trial (data not shown).
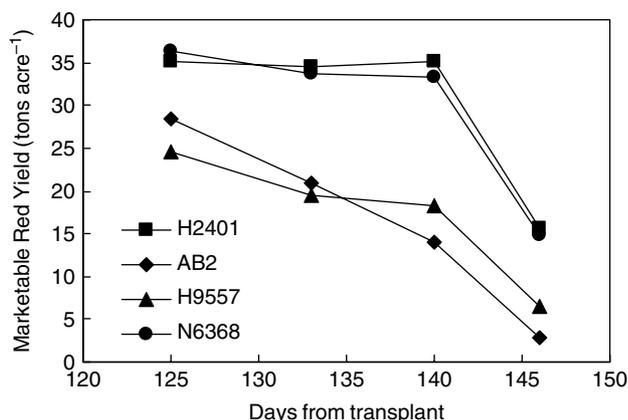
Figure 7. Decrease in yield with later harvest date.

DISCUSSION

The results presented here, in agreement with several earlier reports, show that tomato juice pH increases and TA decreases with extended vine holding after fruit maturity. Hanna[8] found that the average increase in pH was about 0.3 unit over 30 days of vine holding, which is similar to what we found here. Others have also reported increases in pH and declines in TA with increased tomato maturity.[5,6,10] Citric acid is the most abundant organic acid in tomatoes and the decrease in TA measured with increased fruit maturity was due to a loss of citric acid from the fruit. During ripening in tomatoes, as in other fruits, declines in acid levels are accompanied by increases in sugars. At least a portion of this change may be due to the metabolic conversion of acids into sugars by gluconeogenesis.[17] Such a conversion of acids to sugars did not appear to take place during extended vine holding of ripe tomatoes because the decline in citric acid was not accompanied by increases in the concentration of glucose and fructose. Rather the loss of organic acids from the mature fruit appears to be entirely through respiration.

EFS and non-EFS cultivars showed no difference in their loss of citric acid with maturity. Nor was there any other obvious difference between these types of cultivars other than the ability of the EFS fruit to remain intact longer after ripening, allowing for a greater yield of marketable fruit in later harvests. Thus the delayed harvesting made possible by EFS tomatoes will lead to pH increases and possible problems for processors.

The increase in pH with maturity can be compared with the increase in pH observed in recent years at processing plants in California. Data collected on incoming truck-loads of tomatoes arriving at these processing plants has shown that over the 8 year period from 2001 to 2008 the average pH of fruit has increased by about 0.01 unit per year for most common cultivars.[4] For the four cultivars examined here the pH increases with delayed harvest were between 0.01 and 0.02 unit per day. Thus the observed increase in average pH could be explained if the average maturity at harvest has been increasing by only 1 day per year. Over this same time period two new cultural practices have been widely adopted: the use of transplants rather than direct seeding of fields, and drip rather than flood irrigation. While it is possible that these new cultural practices are, by themselves, affecting fruit pH, it seems more likely that their effect is through changes in fruit maturation. This was the case in previous work where it was shown that differences in fruit quality between conventional versus organic production could be explained if one of the principal
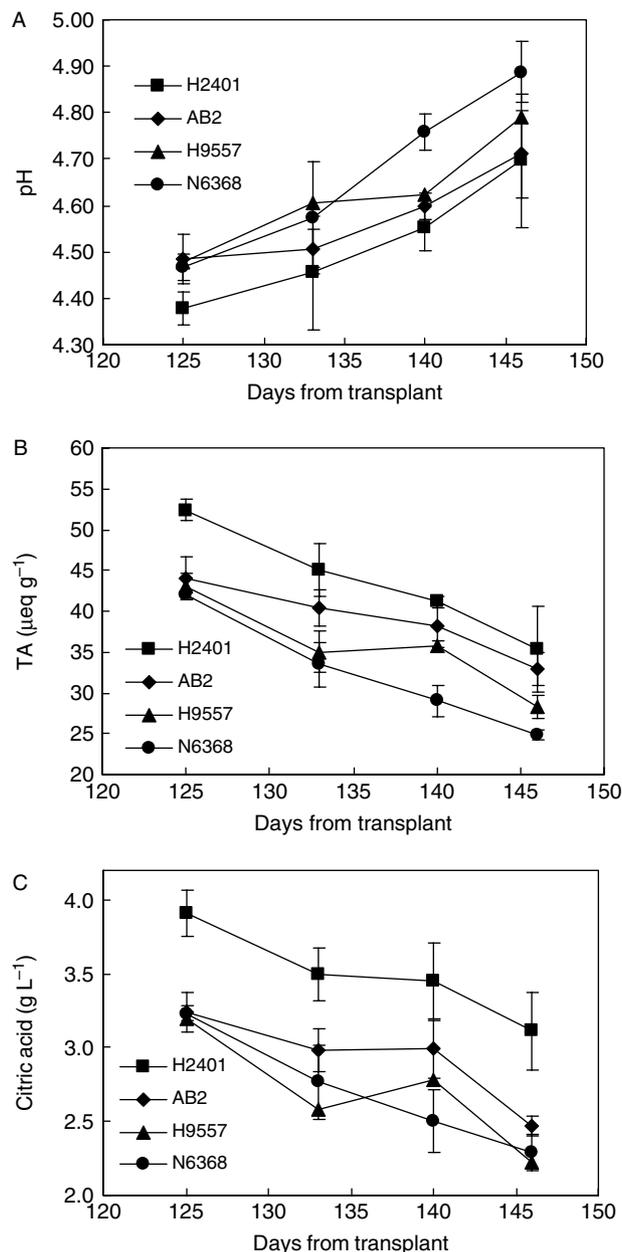

Figure 8. Increase in pH and decreases in TA and citric acid with later harvest date.

differences caused by these cultural practices was a change in the relative maturity of the fruit at harvest.[18] The difficulties in defining harvest maturity and its relationship to environmental conditions and fruit age have been discussed by others.[19]

The obvious approach for minimizing problems with high pH would be to reduce the field holding of ripe fruit as much as possible. This may not be practical given that the advantages field holding allows for coordinating harvests with processing plant capacity. Since the principal change in the fruit causing the undesirable rise in pH is a loss of citric acid, breeding for higher initial citric acid content in the fruit, especially in EFS cultivars where increased fruit maturity is more likely to occur, would be desirable. The higher citric acid content of the H2401 cultivar shows that such an approach is possible. Analysis of pH data collected during commercial production has shown that H2401 typically has

the lowest average pH of any of the major cultivars.[4] Alternatively, the pH in the final product may be reduced by adding citric acid to the tomato juice during processing. Addition of citric acid has been routine for decades in California during production of whole peeled and diced tomato products. The practice has been less common in paste production but may become necessary in the future.

ACKNOWLEDGEMENTS

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