Effect of pre-harvest calcium silicate on post-harvest quality of tomatoes
Efeito do silicato de cálcio em pré-colheita na qualidade pós-colheita de tomates
Efecto del silicato de calcio antes de la cosecha sobre la calidad poscosecha de los tomates

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Abstract
The present work evaluated the influence of calcium silicate on the polygalacturonase enzyme activity, respiration, ethylene, and the physicochemical characteristics on the post-harvest quality of two tomato hybrids. The experimental design was of randomized blocks, with four repetitions in protected cultivation environment. The treatments were distributed in a 2 x 5 factorial scheme, corresponding to the hybrids (Ivety and Natalia) and five doses of calcium silicate (0, 150, 300, 450 and 600 kg ha\(^{-1}\)), which were applied on the same day as the pots were filled. Evaluations were carried out on the fruits, namely: ethylene production, fruit respiration, firmness, number of loculus, polygalacturonase activity, total carotenoids, lycopene, phenolic compounds, soluble solids content, pH, titratable acidity and ascorbic acid content. The application of calcium silicate provided the reduction of ethylene production and fruit respiration. Natalia hybrid showed low polygalacturonase activity, this difference being due to genetic variability. The increase of calcium silicate doses provided the reduction of polygalacturonase enzyme concentration due to its constitution in the cell wall. The concentrations of lycopene, phenolic compounds, soluble solids, pH, titratable acidity and ascorbic acid in the fruits increased in response to the increasing doses of calcium silicate for 'Ivety'. Hybrids present distinct behaviors on the influence of the fertilization of tomatoes with calcium silicate, which can increase the post-harvest conservation and improve the physical-chemical characteristics of tomato fruits.

Keywords: Hybrids; Post-harvest conservation; Respiration, Solanum lycopersicum L.

Resumo
O presente trabalho avaliou-se a influência do silicato de cálcio sobre a atividade da enzima poligalacturonase, respiração, etileno e as características físico-químicas na qualidade pós-colheita de dois híbridos de tomate. O delineamento experimental foi de blocos casualizados, com quatro repetições em cultivo protegido. Os tratamentos foram distribuídos em esquema fatorial 2 x 5, correspondendo aos híbridos (Ivety e Natália) e cinco doses de silicato de cálcio (0, 150, 300, 450 e 600 kg ha\(^{-1}\)), nas quais estas foram aplicados no mesmo dia em que os vasos foram preenchidos. Realizou-se avaliações nos frutos, a saber: a produção de etileno, a respiração dos frutos, a firmeza, o número de lóculos, a atividade da poligalacturonase, os carotenóides totais, o licopeno, os compostos fenólicos, o teor de sólidos solúveis, o pH, a acidez titulável e o teor de ácido ascórbico. A aplicação de silicato de cálcio proporcionou a
redução da produção de etileno e a respiração dos frutos. O híbrido Natália apresentou baixa atividade poligalacturonase, sendo esta diferença devido a variabilidade genética. O aumento das doses de silicato de cálcio proporcionou a redução da concentração da enzima poligalacturonase devido a sua constituição na parede celular. As concentrações de licopeno, compostos fenólicos, sólidos solúveis, pH, acidez titulável e ácido ascórbico dos frutos aumentaram em resposta às doses crescentes de silicato de cálcio para ‘Ivety’. Os híbridos apresentam comportamentos distintos sobre a influência da adubação do tomateiro com silicato de cálcio, podendo aumentar a conservação pós-colheita e melhorar as características físico-químicas de frutos do tomateiro.

Palavras-chave: Híbridos; Conservação pós-colheita; Respiração; Solanum lycopersicum L.

Resumen

El presente trabajo evaluó la influencia del silicato de cálcio sobre la actividad de la enzima poligalacturonasa, la resoiración, el etileno y las características físico-químicas en la calidad poscosecha de dos híbridos de tomate. El diseño experimental fue de bloques al azar, con cuatro repeticiones en cultivo protegido. Los tratamientos se distribuyeron en un esquema factorial 2 x 5, correspondientes a híbridos (Ivety y Natália) y cinco dosis de silicato cálcico (0, 150, 300, 450 y 600 kg ha⁻¹), en el que se aplicaron en el mismo día en que se llenaron los vasos. Se realizaron evaluaciones en los frutos, a saber: producción de etileno, respiración del fruto, firmeza, número de lóculos, actividad poligalacturonasa, carotenoides totales, licopeno, compuestos fenólicos, contenido de sólidos solubles, pH, acidez titulable y contenido de ácido ascórbico. La aplicación de silicato de cálcio proporcionó una reducción en la producción de etileno y la respiración de la fruta. El híbrido de Natália mostró una baja actividad poligalacturonasa, esta diferencia se debe a la variabilidad genética. El aumento de las dosis de silicato de钙cio redujo la concentración de la enzima poligalacturonasa debido a su constitución en la pared celular. Las concentraciones de licopeno, compuestos fenólicos, sólidos solubles, pH, acidez titulable y ácido ascórbico de los frutos aumentaron en respuesta a las dosis crescentes de silicato de calcio para ‘Ivety’. Los híbridos exhiben diferentes comportamientos sobre la influencia de la fertilización del tomate con silicato de cálcio, lo que puede aumentar la conservación poscosecha y mejorar las características físicoquímicas de los frutos del tomate.

Palabras clave: Conservación poscosecha; Híbridos; Respiración; Solanum lycopersicum L.
1. Introduction

Tomato (*Solanum lycopersicum* L.) is considered one of the most important cultivated vegetables worldwide. Its fruit has great commercial and nutritional importance due to its high consumption in natura or as industrialized. Tomatoes occupy the second place among vegetables produced in Brazil, being produced in all regions of the country (Camargo Filho and Camargo, 2017). The productivity and quality of table tomatoes is mainly associated with the fertilization stage, especially when there is a balanced input of minerals that are necessary for the biochemical and physiological processes of the plant and fruits (Kulcheski et al., 2015). Quality characteristics such as titratable acidity, soluble solids content, size, firmness, color, and shine in tomatoes are important for its valorization (Dalastra et al., 2018).

Silicon is not considered an essential nutrient, but it has fundamental importance in physiological and biochemical processes, because although it does not act directly on the main metabolic pathways, it can provide greater tolerance of the plant to biotic and abiotic stresses (Menegale et al., 2015). It has been reported that the deposition of silicon on the cell wall can promote improvements in the physical-chemical quality of tomato fruits (Marodin et al., 2016). In strawberry, the supply of silicon improved the final product with an increase in total sugar contents (Figueiredo et al., 2010), in lettuce there were improvements for ascorbic acid and soluble solids (Lemos Neto et al., 2018). A study conducted by Marodin et al. (2016) showed that silicon provided better post-harvest conservation, as the application of silicon increased the firmness and concentrations of soluble solids, vitamin C and lycopene in tomato fruits.

The change in the cell wall caused by calcium silicate can alter enzymes that act on pectins, being mainly polygalacturonase, methyl esterase pectin, β-galactosidase and pectatoliasis. All these enzymes are part of a multigenic family, which regulate the process of cell wall modification, being that the polygalacturonase is an enzyme with main hydrolytic function, catalyzing the link α 1-4. Its activity is linked to the increase of soluble pectins and softening of fruits, because it is linked to the degradation of the cell wall (Oliveira et al., 2006).

The silicon content in the fruit cell wall can alter its physiological metabolism and influence important changes in some quality standards such as color and firmness. However, the way fertilization with calcium silicate can influence its content in the fruits and, consequently, in the physiological metabolism and conservation of tomatoes needs to be better investigated. Thus, the objective of this research was to evaluate the influence of
calcium silicate on the activity of the enzyme polygalacturonase, respiration, ethylene and the physical-chemical characteristics on the post-harvest quality of two tomato hybrids.

2. Material and Methods

2.1 Conducting the cultivation of tomatoes

This experiment was conducted between the months of August and December 2017 in a protected environment at the Protected Crop and Biological Control Station "Professor Dr. Mário César Lopes" belonging to the Universidade Estadual do Oeste do Paraná, at the Campus of Marechal Cândido Rondon - PR (24º 46' S and 54º 22' W; average altitude 420 m).

According to Köppen's classification, the climate of the region is of type Cfa, subtropical humid mesothermal with dry winters, and with well distributed rains throughout the year and hot summers (Alvares et al., 2013).

The tomatoes were grown in a protected environment on a metallic structure and arch-shaped roof (7 x 30 m and 3.5 m in height). The roof was covered with low density polyethylene film (150 μm and 80% transmissivity) and closed sides with white screen (40% shading). The temperature and air relative humidity were recorded each hour of the day by means of a datalogger (HOMIS, 494), which was positioned in a meteorological shelter at 1.20 m above ground, in the center of the protected environment. The values of temperature, relative humidity and radiation are shown in figure 1.

The experimental design adopted was of randomized blocks in a 2 x 5 factorial scheme, with four repetitions. The first factor consisted of two tomato hybrids of the salad group (Ivety and Natalia), with 'Natalia' presenting in its genetic constitution the rin gene, which is a characteristic of "long-lived" tomatoes, thus characterizing a longer post-harvest life.

The second factor corresponded to five doses of calcium silicate (0; 150; 300; 450 and 600 kg ha⁻¹), where these were applied on the same day that the pots were filled with a mixture of commercial substrate for vegetables and vermicompost in the proportion 1:1. The calcium silicate had 20% silicon and 29% calcium in its composition. The 12 dm³ vessels were arranged in 1.20 x 0.50 m spacing, using one plate per vessel to avoid the loss of nutrients by leaching. Each experimental plot was composed of four vessels, arranged in a single row.
Figure 1. Average, minimum and maximum values of air temperature, average relative humidity per day (A) and solar radiation (B), during tomato cultivation in a protected environment. UNIOESTE - Marechal Cândido Rondon (August to December 2017).

The chemical characterization of the substrate and mixed vermicompost used was: $P = 468.23 \text{ mg dm}^{-3}$, $K = 2.19 \text{ cmol}_c \text{ dm}^{-3}$, $Ca^{2+} = 13.72 \text{ cmol}_c \text{ dm}^{-3}$, $Mg^{2+} = 4.40 \text{ cmol}_c \text{ dm}^{-3}$, $Cu = 1.40 \text{ mg dm}^{-3}$, $Zn = 44 \text{ mg dm}^{-3}$, $Mn = 136.58 \text{ mg dm}^{-3}$, $Fe = 91.10 \text{ mg dm}^{-3}$, $OM = 51.95 \text{ g dm}^{-3}$ and $pH = 6.6$.

The plants were vertically conducted in a single stem, using plastic ribbons up to approximately 1.90 m from the pot. During the whole cycle thinning was performed in order to keep one single stem per plant and all of them were kept with six bunches, allowing the removal of the apical bud after the third leaf above the sixth bunch.

Irrigation was done by drip irrigation four times a day according to the crop needs, being applied around 1 to 2.5 L of water per day in order to keep the substrate humidity above 80%. For this irrigation flexible tape (1.6 L h$^{-1}$) and emitters spaced 0.50 m were used. Fertilization was done via fertirrigation, according to the recommendation of Dalastra (2017), being applied a total of 3084 g of MAP, 3900 g of MgSO$_4$, 1824 g KNO$_3$, 8148 g K$_2$SO$_4$, 7008 g Ca(NO$_3$)$_2$ and 876 g H$_3$BO$_3$, being also applied 320 g micronutrients (Mg 3.8%, S 12%, B 5%, Cu 0.5%, Fe 0.1%, Mn 7%, Mo 0.1%, Zn 7%).

The volume of the solution prepared for fertigation was 20 L per application, in which 45 applications were weekly carried out and, of these, 27 applications were in the phase of full bloom and start of fruiting, applied in this initial phase a percentage between 50-60% of the total amount of macro and micronutrients fertilizers. In full fruitfulness the first and second bunch was already being harvested, in which were applied the rest of the fertilization.
corresponding to a percentage between 40-50% of the macro and micronutrients, being performed the fertirrigation until one week before the last harvest.

The fruits were harvested when they had 90% of red colored surface, allowing to select fruits of homogeneous size and healthy for the post-harvest quality analysis. These were performed at the Food Technology Laboratory of the Unioeste Agricultural Sciences Center, Campus Marechal Cândido Rondon. The fruits were harvested and sent to the laboratory for the analysis of respiration, ethylene production and firmness, for the other analysis the fruits were frozen.

2.2 Post-harvest variables analyzed

2.2.1 Respiration and ethylene production

For respiration and ethylene production third and fourth bunch tomatoes (evaluated by parcel) were used, free of pathogens or any apparent defect. Three harvested fruits were allocated in hermetic plastic flasks with volume of 800 mL and silicone septum in the lid for gas sampling. After 90 minutes of bottle closure, 2.5 mL samples were collected with a gastight syringe from the inner atmosphere of the bottles and immediately injected into a gas chromatograph (Finnigan, 9001) calibrated for column (capillary) temperatures of 80 °C, injector (splitless) 100 °C, detector (flame ionization) 250 °C and methanator 350 °C.

2.2.2 Polygalacturonase activity

The determination of the polygalacturonase activity was performed in fruits of the third bunch, using the methodology described by Pressey and Avants (1973) homogenizing 5 g of vegetal material with 10,4 mL of distilled water. The macerate was centrifuged at 12.000 rpm for 20 minutes at 4 °C. The supernatant was discarded, and the precipitate was solubilized with distilled water and again centrifuged, the same process being repeated twice. The supernatant was again discarded, and the precipitate was solubilized in 10,4 ml of NaCl (1 mol L⁻¹), adjusting the pH with NaOH (1 mol L⁻¹) to 6,0, remaining in the refrigerator for 1 hour. The extract was centrifuged, and the supernatant kept in ice. The enzyme activity was determined by incubating the extract with polygalacturonic acid solution in 100 mmol L⁻¹ NaOAc buffer at pH 5,0 for 30 minutes at 50 °C. The reaction was stopped by the addition of PAHBAH reagent and boiling of the assay tubes for 5 minutes and then routed to ice. The
galacturonic acid production in the reaction was determined by the Lever method (1972). The total protein of the extracts was determined by the Bradford method (1976) using BSA as standard.

2.2.3 Physical-chemical

Firmness was measured in opposite poles in the equatorial region of the fruit in a total of three ripe fruits of the third and fourth bunch evaluated per plot, using the texturometer (CT3 Texture Analyser, Brookfield Engineering) with a tip of 8 mm in diameter and penetration speed of 2.0 mm s⁻¹, which expressed the results in N. After this evaluation, the fruits were cut to count the number of loculus.

For the chemical analyses fruits were collected from all bunches, being sent to the laboratory and frozen, later they were homogenized and the analysis of soluble solids content (SS) and pH were determined by direct reading of the juice extract with the aid of a refractometer and digital pH meter, respectively. The SS content was expressed in ºBrix, the titratable acidity (TA) was determined by the titulometric method according to the methodology proposed by IAL (2008). The ascorbic acid content was determined by titration with 2,6-dichlorophenol-indophenol (DCFI) at 0.01 mol L⁻¹, with results expressed in mg ascorbic acid per 100 mL⁻¹ pulp (Benassi and Antunes, 1988).

The evaluation of the pigment contents was performed with fruits from the third bunch of the plant, where the carotenoids content was performed according to the methodology described by Sims and Gamon (2002). The lycopene content was determined by the method described by Rodriguez-Amaya (2001). The determination was performed in spectrophotometer, with the direct reading of the supernatant in the absorbance of 470 nm and 453 nm, respectively.

The total phenolic compounds were evaluated using the fruits of the third and fourth bunch with the methodology proposed by Georgé et al. (2005), using Folin-Ciocalteu and sodium carbonate solution, where the direct reading of the supernatant obtained in a spectrophotometer at 760 nm was performed.

2.3 Statistical

The experimental data were submitted to the Shapiro-Wilk normality test (p ≤ 0.05). Then, variance and polynomial regression analysis was performed (p ≤ 0.05), using the
statistical software SISVAR (Ferreira, 2014).

3. Results and Discussion

The data of temperature, air relative humidity and radiation throughout the conduction period of the cultivation stage in a protected environment are presented in figure 1. The average temperature varied between 23 and 29 °C, the relative humidity between 45,43 to 81,70% and the solar radiation between 8,88 to 21,13 MJ m$^{-2}$ day$^{-1}$. These climatic data are in accordance with the requirements of the crop because the minimum a plant needs for its maintenance and development is 8,40 MJ m$^{-2}$ day$^{-1}$ of solar radiation (Beckmann et al., 2006). According to Gazolla-Neto et al. (2013), climatic elements play an important role in the physiological reactions of plants, in which they lead to growth and development, thus demonstrating that these climatic data are essential for post-harvest quality characteristics, since the level of radiation that the plant undergoes can alter some biosynthetic pathways involved in the accumulation of sugars, vitamins and antioxidant compounds.

The ethylene production (µg C$_2$H$_4$ kg$^{-1}$ h$^{-1}$) and respiration (mg CO$_2$ kg$^{-1}$ h$^{-1}$) of tomatoes were measured to evaluate the physiological response of the fruits of plants submitted to different doses of calcium silicate, no effect of the interaction between the hybrids and the doses being observed, and the difference between the hybrids was presented only for the respiration of the fruits (Table 1). However, a significant difference was also observed for doses of calcium silicate for ethylene production and for tomato fruit respiration, which made it possible to observe significant decreases in ethylene production and in tomato fruit respiration with increased doses of calcium silicate (Figure 2) suggesting that calcium silicate, when applied at planting, promotes changes in fruit metabolism that may be favorable in the post-harvest stage, since it led to lower ethylene production and lower respiratory intensity.

This reduction in ethylene production and fruit respiration may reflect in the increased post-harvest life of the fruit, because the increase in ethylene production is associated with the activation of important metabolic routes that may accelerate physiological changes that lead to the senescence of the fruit, among them the activation of enzymes responsible for the degradation of the fruit cell wall (Bassan et al., 2013). Ethylene is a secondary metabolism related to the aerobic metabolism of plant tissue and its reduction may be associated, among other factors, with the inhibition of ACC (1-aminoacylciclopropan-1-carboxylic acid) oxidase (Alexander and Grierson, 2002). Islam et al. (2018) studied the foliar application of silicon in
the cultivation of cherry tomatoes and found reduction of ethylene production in the fruits. Still regarding the fruits respiration (Figure 2 - B), the quadratic adjustment equation suggests a minimum respiratory rate estimate of 4.87 mg CO$_2$ kg$^{-1}$ h$^{-1}$ (Figure 2 - B) for a dose of 552.24 kg ha$^{-1}$ of calcium silicate.

**Table 1.** Respiration (CO$_2$), fruit firmness (FF), number of loculus (NL) and polygalacturonase activity (PA) as a function of tomato hybrids. UNIOESTE - Marechal Cândido Rondon, August to December 2017.

| Hybrid     | CO$_2$ mg CO$_2$ kg$^{-1}$ h$^{-1}$ | FF N | NL | PA µg glucose h$^{-1}$ mg$^{-1}$ of protein |
|------------|----------------------------------|------|----|---------------------------------------------|
| Ivety      | 6.82$^a$                         | 2.23$^a$ | 4.24$^a$ | 21.40$^a$                                  |
| Natália    | 4.04$^b$                         | 2.32$^a$ | 3.56$^b$ | 6.14$^b$                                   |
| CV (%)     | 9.25                             | 11.08 | 19.30 | 20.20                                      |

*Significant at 5% probability by F test. Source: Authors.

**Figure 2.** Production of ethylene (A) and respiration (B) of fruits, according to doses of calcium silicate. UNIOESTE - Marechal Cândido Rondon, August to December 2017.

‘Ivety’ showed a higher respiration rate of 6.82 mg CO$_2$ kg$^{-1}$ h$^{-1}$ (Table 1). This difference between hybrids can be explained by the fact that they present a completely different genetic characteristic, where the hybrid Natalia presents the *rin* gene, which is an improved hybrid and present in its natural process the delayed maturation, which prolongs the post-harvest conservation (Benites et al., 2010).
The difference in ethylene production and respiration is a characteristic that is also linked to the cell wall and consequently to the firmness of the fruits, and it did not show any difference in the interaction or factors studied alone (Table 1). This absence of significant effect may have been caused by the difference in the number of loculus or even by the ripening stage of the fruit, and the number of loculus may be modified due to the fruit size (Rodrigues et al., 2010).

Changes in the firmness of the fruit that lead to its softening during ripening involve the loss of turgidity pressure. This process occurs due to the accumulation of osmotic solutes in the apoplast because there are modifications in the simple and apoplast relationship, starch degradation and physiological changes in the composition, structure and dynamics of the cell wall (Bertin and Génard, 2018). Although firmness has not shown significant difference in the present study, it is characterized by delayed degradation in the cell wall.

This absence of difference between hybrids for fruit firmness demonstrates that there was a change in the number of loculus to 'Ivety', which had more loculus (Table 1). The number of loculus is a genetic characteristic that presents a direct correlation with the size of the fruits (Rodrigues et al., 2010).

Although there was no difference for firmness, the 'Ivety' showed the highest softness of tomato fruits, and this increase is linked to PA activity which was 21.40 µg glucose h⁻¹ mg⁻¹ protein (Table 1). This difference between the hybrids is related to the genetic variability between them, because the hybrid that presents the rin gene provides aspects in the alteration of ripeness, in which the fruits are firmer with less response to ethylene, which results in the structural difference of the cell wall (Benites et al., 2010).

The PA activity also showed a difference between the calcium silicate doses, providing a decrease of the PA activity with the increase of the doses (Figure 3). Calcium silicate, as a constituent of the cell wall, plays an important role in the formation of cross bridges between the pectic substances, leading to the stabilization of the fruit cell wall and the protection against the cell wall degradation enzymes, specifically pectolytic enzymes, such as PA, which breaks the glycosidic bonds between units of non-esterified galacturonic acids (Resende et al., 2004). In this way, calcium silicate interacts with these carboxylic groups without esterification, reducing their number and thus the action of PA decreases.

The reduction in the respiration and the production of ethylene according to the calcium silicate doses played an important role in the low activity of PA, providing firmer fruits. The use of silicon in fruit production increases its firmness, although it did not present a difference in the study, this increase was demonstrated in the work of Marodin et al. (2016),
who worked with different sources of silicon in tomato. Islam et al. (2018) compared different ways of applying silicon to cherry tomatoes and obtained increased firmness at harvest time. The firmness and ripeness of the fruits are closely associated, therefore, the prolongation of the firmness of the fruits is desirable to have an extension of storage.

**Figure 3.** Polygalacturonase activity of tomato fruits as a function of calcium silicate doses. UNIOESTE - Marechal Cândido Rondon, August to December 2017.

For the characteristics of fruit pigments there was no interaction between the factors studied, so the levels of total carotenoids and lycopene were evaluated separately (Table 2).

**Table 2.** Total carotenoids, lycopene, and ascorbic acid (AA) content as a function of tomato hybrids. UNIOESTE - Marechal Cândido Rondon, August to December 2017.

| Hybrids  | Carotenoids (mg g⁻¹) | Lycopene (µg 100 g⁻¹) | AA (mg 100 g⁻¹) |
|----------|----------------------|-----------------------|-----------------|
| Ivety    | 0,011ᵃ                | 25,22ᵃ                | 21,96ᵃ          |
| Natália  | 0,010ᵇ                | 20,98ᵇ                | 21,01ᵇ          |
| CV (%)   | 20,08                 | 2,35                  | 1,66            |

*Significant at 5% probability by F test. Source: Authors.

The ripening of the tomato fruit is controlled by ethylene and characterized by a change of color from green to red. However, regarding photosynthetic pigments studied as total carotenoids, there was a significant difference only between hybrids (Table 2), since this
content varies according to species and hybrid, as well as environmental factors and cultural practices before and after harvest.

Carotenoids are accessory pigments responsible for color change, pondering to come from chlorophyll degradation, causing an increase in carotenoids (β-carotenes and lycopene) and anthocyanins (xanthophylls), resulting in red and yellow colored fruits and flowers, besides being the second most important pigment in the photosynthesis process (Su et al., 2015).

Ivety' had higher lycopene content (Table 2). Among the process of decreasing the chlorophyll and xanthophyll content in tomatoes, there is a strong accumulation of lycopene, which is the main carotenoid in tomatoes, representing 71% of the total content in ripe fruits, giving the fruits a reddish color (Del Giudice et al., 2015). The lycopene content also showed a difference between doses of calcium silicate, showing the quadratic behavior during the increase in doses (Figure 4 - A).
Figure 4. Lycopene (A), phenolic compounds (B), soluble solids (C), pH (D), titratable acidity (E) and ascorbic acid (F) of tomato hybrids, depending on different doses of calcium silicate. UNIOESTE - Marechal Cândido Rondon, August to December 2017.

Source: Authors.

The highest accumulation of lycopene content was observed in the 600 kg ha\(^{-1}\) dose of calcium silicate (Figure 4 - A). Lycopene directly interferes with the color of the fruit, which may influence consumer acceptance. Marodin et al. (2016) observed that silicon increased the lycopene content in tomato fruits, reaching 30.13 µg 100 g\(^{-1}\) at the dose 491 kg ha\(^{-1}\), they also observed that calcium and sodium silicate provided higher lycopene concentrations.

Both the hybrid ‘Ivete’ and 'Natalia' had increases in the content of phenolic compounds with increased doses of calcium silicate. However, the quadratic response to
'Natalia' suggests that the highest content of phenolic compounds was 25.89 mg AG/g obtained when the dose 355.68 kg ha⁻¹ was applied (Figure 4 - B). For the ‘Ivete’ hybrid, the increase in the content of phenolic compounds led to the maximum observed value of 26.64 mg AG/g. These results indicate that supplementation with calcium silicate can improve both the antioxidant status of tomatoes, beneficial to the plant metabolism itself, and their nutritional status.

This increase in the content of phenolic compounds in the fruit increases resistance to pathogens in the post-harvest tomatoes, this increase occurs due to the accumulation of silicon in the fruit, because this element is considered a beneficial element for the plants and end up inducing resistance to pathogens in addition to resulting in improved fruit quality (Menegale et al., 2015).

The soluble solids content is one of the most important quality factors for most fruits, and can be altered by several environmental factors before and after harvesting. It was observed in this study that calcium silicate influenced the hybrids tested, providing an increasing increase to 'Ivety', reaching 5.02 °Brix in the maximum calcium silicate dose. Regarding 'Natalia', it showed a quadratic behavior, registered a content of 4.92 °Brix in the dose 287.81 kg ha⁻¹ of calcium silicate (Figure 4 - C). This behavior of SS in 'Natalia' can occur because the ripening process of the fruit is different from the other hybrid, because it presents a reduction of the breathing of the fruit that consequently can increase the shelf life, and it presents less PA activity, thus reducing the degradation process of the cell wall and softening of the fruit.

These results are in accordance with those of Marodin et al. (2016), where an increase in soluble solids content was observed with an increase in the dose of silicon in a ‘Santa Cruz Kada’ tomato hybrid, which does not present a rin gene, showing an increasing increase up to the dose 600 kg ha⁻¹, with a later decrease. Observing this way that the dose of silicon can be different for each hybrid, because one of the beneficial effects of silicon is the association with the increase of photosynthetic efficiency (Murillo-Amador et al., 2007), being the sugar that is produced in the leaf translocated to the fruits, thus demonstrating this increase of soluble solids.

There is an indirect relationship between soluble solids and phenolic compounds because the accumulation of soluble solids occurs due to the conversion of starch into sugars, increasing sweetness, and may also come from the synthesis of secondary compounds such as simple phenolic and the accumulation of organic acids. This characteristic is also dependent on the hybrid, as observed in this work.
The fruits pH varied little, having as maximum and minimum values equal to 4.38 and 4.16, respectively (Figure 4 - D), and this variation is specifically of the Ivety hybrid. For the hybrid that presents the *rin* gene, on the other hand, the variation was much smaller between 4.21 and 4.25. The elevation of the pH value may be due to the synthesis of organic acids, and the same results are below that indicated as optimal for the separation of acidic fruits from non-acidic fruits for tomato (Modolon et al., 2012).

The titratable acidity showed a difference only for calcium silicate doses, presenting linear behavior with the increase of calcium silicate doses, thus producing tomatoes with higher titratable acidity (Figure 4 - E). It has a small variation of 0.30 to 0.33%, being represented by the percentage of citric acid. This increase may have occurred due to the low rate of respiration and ethylene production, and the acidity values are within the expected for salad tomatoes. Similar results were obtained by Islam et al. (2018) who worked with the application of silicon before harvest in cherry tomatoes.

The increase in acidity was also observed by Figueiredo et al. (2010) in the culture of strawberry using foliar spraying and fertirrigation with silicon, with a decrease followed by an increase in the titratable acidity content of the fruits with increased doses of potassium silicate. According to the same author, the form of application of silicon can result in greater absorption of silicon by the plant, which results in fruits with an increase in post-harvest quality.

The ascorbic acid content was influenced by the calcium silicate doses, showing an increasing linear behavior with the increase of doses (Figure 4 - F). It was also observed that the Ivety hybrid presented higher concentrations in relation to 'Natalia', both being within the values normally found in tomato (Table 1). These results corroborate with Marodin et al. (2016), where the ascorbic acid content increased with the addition of silicon in tomato fruits, reaching 21.34 mg 100 g⁻¹ in the 498 kg ha⁻¹ dose.

The hybrids behaved differently in relation to the accumulation of silicon in the fruit, presenting an increasing accumulation until the maximum dose of 5.85 g kg⁻¹ of silicon for 'Natalia' (Figure 5 - A) that presents the *rin* gene, which are fruits that present a longer shelf life, remaining firm and brilliant, because it is a hybrid that presents interference in the ethylene production and in the enzymatic activities involved in the normal ripening process of the fruits (Della Vecchia and Koch, 2000). Although this hybrid did not present any difference in relation to 'Ivety' for the ethylene production, the PA activity was lower for 'Natalia'.
Figure 5. Silicon and calcium content in tomato fruits, as a function of tomato hybrids and doses of calcium silicate. UNIOESTE - Marechal Cândido Rondon, August to December 2017.

'Ivety' showed an increasing behavior caused by the silicon content in the fruit, being observed a considerable difference from dose 0 to 150 kg ha\(^{-1}\) of calcium silicate, presenting a difference of 1.77 g kg\(^{-1}\) of silicon. From this dose the increase of silicon content in the fruit was minimal, but significant around 0.11 g kg\(^{-1}\) of silicon with the increase of doses (Figure 5 - A). This hybrid presented satisfactory results for the physical-chemical standards, being superior in several parameters. The accumulation of silicon is strongly associated with the physiological functions of the plant, improving the quality and shelf life of tomato fruits. The same result was observed in salad and cherry tomatoes (Marodin et al., 2016; Islam et al., 2018).

Regarding the calcium content in the fruit, interaction between the hybrids and doses of calcium silicate was observed, demonstrating that the hybrids showed an increasing behavior, reaching 1.51 and 1.63 g kg\(^{-1}\) of calcium for 'Natalia' and 'Ivety', respectively (Figure 5 - B).

This increase in the calcium content of tomato fruits is important because its mobility in the plant is limited, and some physiological disorders may occur caused by the deficiency of this nutrient, especially in tomato culture and in other crops that present their rapid and continuous development as in horticulture, because the unavailability of it in the tissues may cause the burning of leaves and the cracking of the cell wall of the fruits (Serrano et al., 2002), not being observed this physiological disorder during cultivation.

The fertilization with calcium silicate in tomato plants improves the physic-chemical characteristics because the deposition of these nutrients occurs in different concentrations in
the cellular wall, making the epidermal cell thicker, with distinct responses to the hybrids evaluated.

4. Conclusions

The calcium silicate promoted a reduction in ethylene production and fruit respiration in the maximum dose of calcium silicate 600 kg ha\(^{-1}\), besides presenting low polygalacturonase activity, thus improving the physicochemical characteristics by increasing the levels of lycopene, phenolic compounds, soluble solids, pH, titratable acidity and ascorbic acid of the fruits. Such characteristics contribute to the improvement of post-harvest durability.

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