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EFFICIENCY OF $CaCl_2$ SPRAY AT DIFFERENT FRUIT DEVELOPMENT STAGES ON THE FRUIT MINERAL NUTRIENT ACCUMULATION IN CV. HAYWARD KIWIFRUIT

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Abstract

Despite the importance of calcium in many fruit species and the effects of calcium application, there is little or no reliable information on the effect of $CaCl_2$ spray at different fruit development stages on the fruit mineral nutrient content during the growing season and at harvest. Therefore, this study has been conducted to evaluate the effect of calcium chloride ($CaCl_2$, 15 g L^{-1}) spray at different fruit development stages on the accumulation Ca and other macronutrients in cv. Hayward kiwifruit grown at two locations. In order to find the absorbality of Ca at different spraying times, fruits were harvested 7 days after a Ca treatment. Additionally, the mineral composition of kwifruit was determined at the stage of harvest ripeness. The results showed that the absorbality of Ca by kiwifruit from Ca spray decreased significantly with the progressing fruit development. The highest fruit Ca content was found when the fruit plants were sprayed at 35+80 DAFB and 35+80+120 DAFB, irrespectively of the location of an orchard. At a later Ca spraying application, the N content in kiwifruit significantly decreased, but the K and Mg content slightly increased. In contrast, the K/Ca, N/Ca, Mg/Ca and (K+Mg)/Ca ratios of $CaCl_2$ sprayed fruits was lower than in the control and the ratio values were more balanced in the Ca treated fruit than in the control. Overall, three $CaCl_2$ (15 g L^{-1}) sprays could effectively improve the fruit quality by balancing the Ca ratio to other macronutrients. Therefore, Ca spray treatments could be a recommended treatment in growing cv. Hayward kiwifruit.

Keywords: *Actinidia deliciosa*, seasons spray, fruit development, macronutrient accumulation, calcium absorption.

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INTRODUCTION

There is a growing interest among consumers in kiwifruit (*Actinidia deliciosa*) owing to potential health benefits associated with the rich content and wide range of vitamins, polyphenols, other nutrients, high fiber content as well as the antioxidant capacity of these fruits (Bieniek, Dragańska 2013, Ghasemnezhad et al. 2013, Shiri et al. 2014, 2015*a*).

Samadi Maybodi, Shariat (2003) examined four cultivars of *A. deliciosa* grown in various part of Iran and found the content of micro- and macronutrients to vary from cultivar to cultivar. They also observed large differences between fruit parts and demonstrated that the content of minerals in fruit did not depend on their content in soil.

Fruit growth and development, quality and postharvest storage life are considerably influenced by the mineral nutrient composition (Léchaudel, Joas 2007, Shiri et al. 2015*b*). The content of minerals in fruits of *A. arguta* and *A. purpurea* found by Bieniek (2012) may indicate a significant effect of environmental conditions (cultivation conditions, soil fertility and fertilization) on the level of nutrient accumulation.

Among the mineral nutrients, calcium (Ca) plays an important role in plant cell functions (such as cell elongation and division), nitrogen and carbohydrate metabolism and plant cell membrane integrity (Mengel, Kirkby 2002, Bieniek 2012). Its physiological activity as a second messenger in cellular biochemistry and its contribution to the cell wall structure make it important for the fruit's growth and development (Kadir 2004, Gerasopoulos, Drogoudi 2005, Bieniek 2012). Therefore, improved Ca absorption and accumulation in fruits is an important goal of cultivation technologies, whose aims are to ensure the best nutrient balance and to achieve a better quality product. Moreover, the Ca content and ratio to some other elements are essential for enhanced fruit quality (Sio et al. 1999).

Ca is transported mainly through the xylem by the water potential gradient and hydrostatic pressure (Mengel, Kirkby 2002). High growth rates followed by low transpiration in fruits may result in the Ca content falling below the critical level required for cell wall stabilization and membrane integrity (Himelrick, Mcduffie 1983). Therefore, foliar application of Ca is recommended to increase Ca levels of many fleshy fruits (Manganaris et al. 2006). Moreover, Gerasopoulos et al. (1996) and Gerasopoulos, Drogoudi (2005) reported the benefit of preharvest Ca application on kiwifruit quality and mineral nutrient content.

The effect of a Ca treatment depends on a plant genotype, cultivation system, technique of spraying, salt concentrations, time and number of treatments and the type of fertilizers (Mengel, Kirkby 2002, Lanauskas et al. 2012). Previous research indicated that Ca absorption in apple fruits in response to Ca sprays decreased with the progressing fruit development

(Schlegel, Schonherr 2002), thus suggesting that fruit growers should start Ca sprays early in the growing season, in the hope that they would control bitter pit more effectively. Tomala (1997) recommended performing the first spray of winter apple cultivars with Ca salts at the beginning of June, but no later than in the second half of June. There are numerous studies implicating that foliar application of Ca to apple trees is effective in the second half of the plant growing period, when the delivery of Ca ions to fruits through the uptake by roots decreases rapidly (Casero et al. 2002). In the later period of fruit growth and ripening, the transport of Ca can be limited to phloem (Lang 1990), thus spraying fruits with Ca solution at that time can increase the Ca concentration in these fruit tissues.

There is little information on the effectiveness of $CaCl_2$ sprays applied at different fruit development stages on the Ca accumulation in kiwifruits and their content of other macronutrients during the fruit development and at harvest time. Therefore, the aim of the present investigation has been to evaluate the effect of early-, mid- and late-season sprays of $CaCl_2$, single or in a series, on the calcium absorbality and the accumulation of other macronutrients in cv. Hayward kiwifruit.

MATERIAL AND METHODS

This study was designed to investigate calcium absorbability of kiwifruit and changes in the macronutrient content in response to early-, mid- and late-season single or repeated sprays of $CaCl_2$. Two separate experiments on kiwifruit were conducted. In the first trial, changes in the fruit content of mineral nutrients during fruit development were investigated in response to early-, mid- and late-season sprays of $CaCl_2$ and their combination. In the second study, the effect of different $CaCl_2$ spraying times on the fruit content of mineral nutrients was analysed at harvest.

Plant material and treatments

This experiment was performed during the 2013 growing season, on the kiwifruit cultivar Hayward grown in two commercial orchards in the north of Iran. The two orchards were selected so as to ensure similar climatic conditions, orchard age, plant training and management system, vegetative and reproductive characteristics, although there were some differences because of the geographical distance between the two locations. The first orchard was located in Rasht (latitude of 37°21' N, longitude of 49°57' E, 5 m altitude, 15.9°C mean annual temperature and 1359 mm rainfall per year) and the second one belonged to the Iranian Citrus Research Institute in Ramsar (latitude of 36°90' N, longitude of 50°65' E, 21 m altitude, 21°C mean annual temperature and 1200 mm rainfall per year). Ten-years old vines were

spaced at 6×4 m (417 vines ha^{-1}) and trained on a T-bare system with Tomori grown at a 8:1 ratio as a pollinizer. All the vines and the soil were managed according to standard horticultural practice described by SALE (1990). The results of soil analysis under the vine canopy are shown in Table 1. The vines were regularly drip-irrigated during the season and water was supplied based on the demand due to evaporation. Tilling and mowing kept the alleyways mostly weed-free.

Table 1

Some physical and chemical properties of soil at two experimental sites

Location	Texture	pH	EC ($ds.m^{-1}$)	OC (%)	N ($g\ 100\ g^{-1}DW$)
Rasht					
0-30 cm	sandy loam	7.3	1.2	1.48	0.13
30-60 cm	sandy clay loam	7.5	1.2	1.17	0.10
Ramsar					
0-30 cm	clay	7.2	0.24	2.04	0.19
30-60 cm	clay loam	7.05	0.24	1.65	0.15

EC – electrical conductivity, OC – organic carbon, N – nitrogen

Fifty-four uniform vines were selected from each orchard for a preharvest $CaCl_2$ treatment. According to the three main stages in the metabolism in kiwifruit (RICHARDSON et al. 2004), $CaCl_2$ (15 g L^{-1}) was sprayed three times 35, 80 and 125 day after full bloom (DAFB) during the growing season. A surfactant (0.01% Tween 20) was added to the Ca solution to improve Ca absorption. Treatments were arranged in a completely randomized block design with three replicates, each consisting of three vines. The treatments were identified as follows: 1) control (unsprayed), 2) early-spray: $CaCl_2$ sprayed at 35 DAFB (sprayed in mid-June), 3) mid-spray: $CaCl_2$ sprayed at 80 DAFB (sprayed in late-July), 4) late-spray: $CaCl_2$ sprayed at 125 DAFB (sprayed in early-September), 5) double spray: $CaCl_2$ sprayed at 35 + 80 DAFB, 6) triple spray: $CaCl_2$ sprayed at 35 + 80 + 125 DAFB. All sprays were applied in the afternoon to prevent any sunburn injury.

In order to find the absorbability of Ca by kiwifruit at each spray time, 30 uniform and defect-free fruits were harvested from the sprayed and control vines 7 days after a Ca treatment during fruit development (Experiment 1) and at the harvest ripeness stage, i.e. when total soluble solids (TSS) reached about 6.2-6.5% (Experiment 2). Afterwards, fruits from both orchards were immediately transferred to a laboratory for analyses of the composition of mineral elements.

Determination of the content of mineral nutrients

Before assays of mineral nutrients, fruit samples were washed thoroughly with tap water and subsequently rinsed with deionized water to re-

move all surface residues. After air drying, fruit flesh samples were taken from the equatorial section of each fruit quarter, oven-dried at 70°C for 72 h and hand milled to fine powder passed through a forty-mesh sieve. A portion of fine powder weighing 2 grams was dry ashed in a furnace at 550°C for 4 h and then the ash was dissolved in 10 ml hydrochloric acid (HCl) 2 M. The digested samples were filtered through Whatman No. 40 filter paper and used for phosphorus (P), potassium (K), Ca and magnesium (Mg) analyses.

The nitrogen (N) concentration in samples was determined according to the Kjeldahl method (WALING et al. 1989). Briefly, a 0.3 g sample was digested in concentrated H_2SO_4 and distilled with NaOH (40%), and ammonium N was fixed in H_3BO_3 (2%) and titrated with 0.1N H_2SO_4.

The P content of samples was determined by the vanadate-molybdate colorimetric method (CHAPMAN, PRATT 1982). The absorbance of samples was measured at 470 nm in a UV/Visible spectrophotometer (model PG Instrument $^+$80, Leicester, UK). K was determined by flame photometric method as described by WALING et al. (1989). Digested extract was diluted by caesium chloride (CsCl) at a 1:9 ratio and the absorbance was measured at 766.5 nm (WALING et al. 1989).

Ca and Mg were measured using atomic absorption spectroscopy. Briefly, digested extracts were diluted with distilled water (1:9 v/v), then 4.75 ml lanthanum nitrate [$La(NO_3)_3$] was added to 250 ml of the diluted extract. Finally, the absorbance was measured at 422.7 nm for Ca and 285.2 nm for Mg (WALING et al. 1989). All macronutrients were expressed as g per 100 g of fruit dry weight (g 100 g^{-1} DW).

Statistical analysis

Both experiments were carried out according to a combined analysis across locations based on a completely randomized block design with three replications. The data from the individual experiments were analyzed separately. Proc Anova procedure aided by SAS software (Ver. 9.1 2002-2003, SAS Institute, Cary, NC, USA) was used for statistical data processing. Before Anova, the results were tested for normality and homoscedasticity using the Kolmogorov-Smirnov and Cochran tests, respectively. Least significant difference (LSD) at $P \leq 0.01$ and $P \leq 0.05$ was calculated to compare differences between means following a significant Anova effect. Moreover, for each orchard, the Pearson correlation coefficients were evaluated and calculated separately to correlate between kiwifruit mineral content. It should be noted that slicing was performed based on the orchard location.

RESULTS

Changes in the content of fruit macronutrients 7 days after Ca spray

The fruit content of Ca, Mg, K, N, P and the ratios of these elements were determined 7 days after Ca sprays in both sprayed and control fruits (Table 2). The results showed that the orchard location had a significant ef-

Table 2

Effect of $CaCl_2$ (15 g L^{-1}) spraying times (35, 80, 120 DAFB) on macronutrient content (g 100 g^{-1}DW) and their ratios of cv. Hayward kiwifruit immediately 7 days after treatment

	Ca	N	P	K	Mg	N/Ca	K/Ca	Mg/Ca	K+Mg/Ca
Rasht									
Control	1.67 *b**	1.47 *a*	0.24 *a*	4.12 *b*	0.28 *a*	0.88 *a*	2.47 *a*	0.17 *a*	2.64 *a*
35 DAFB**	2.78 *a*	1.28 *b*	0.25 *a*	4.58 *a*	0.29 *a*	0.45 *b*	1.60 *b*	0.10 *b*	1.70 *b*
Control	1.83 *b*	1.22 *a*	0.28 *a*	4.10 *b*	0.15 *a*	0.67 *a*	2.24 *a*	0.08 *a*	2.33 *a*
80 DAFB	1.94 *b*	1.18 *ab*	0.28 *a*	4.19 *b*	0.16 *a*	0.61 *b*	2.15 *a*	0.08 *a*	2.23 *a*
35+80 DAFB	2.21 *a*	1.11 *b*	0.29 *a*	4.63 *a*	0.16 *a*	0.50 *c*	2.09 *a*	0.07 *a*	2.17 *a*
Control	1.98 *b*	1.02 *a*	0.19 *a*	3.82 *b*	0.14 *b*	0.51 *a*	1.94 *a*	0.07 *a*	2.01 *a*
120 DAFB	2.02 *b*	1.00 *a*	0.19 *a*	3.88 *b*	0.14 *b*	0.51 *a*	1.96 *a*	0.07 *a*	2.03 *a*
35+80+120 DAFB	2.63 *a*	0.88 *b*	0.20 *a*	4.52 *a*	0.17 *a*	0.33 *b*	1.72 *a*	0.06 *a*	1.78 *a*
Ramsar									
Control	1.03 *b*	1.14 *a*	0.22 *a*	3.87 *b*	0.32 *a*	1.10 *a*	3.76 *a*	0.32 *a*	4.08 *a*
35 DAFB	1.53 *a*	0.98 *b*	0.24 *a*	4.35 *a*	0.33 *a*	0.64 *b*	2.85 *b*	0.22 *a*	3.07 *b*
Control	1.48 *b*	0.83 *a*	0.12 *a*	3.63 *b*	0.17 *a*	0.56 *a*	2.46 *a*	0.11 *a*	2.57 *a*
80 DAFB	1.59 *b*	0.82 *a*	0.13 *a*	3.80 *ab*	0.17 *a*	0.51 *b*	2.39 *a*	0.11 *a*	2.50 *a*
35+80 DAFB	1.91 *a*	0.75 *b*	0.13 *a*	4.22 *a*	0.18 *a*	0.39 *c*	2.22 *a*	0.09 *a*	2.31 *a*
Control	1.48 *b*	1.08 *a*	0.15 *a*	3.78 *b*	0.14 *b*	0.73 *a*	2.56 *a*	0.09 *a*	2.64 *a*
120 DAFB	1.57 *b*	1.07 *a*	0.15 *a*	3.81 *b*	0.14 *b*	0.68 *a*	2.43 *a*	0.09 *a*	2.52 *a*
35+80+120 DAFB	2.05 *a*	0.92 *b*	0.16 *a*	4.54 *a*	0.18 *a*	0.45 *b*	2.23 *a*	0.08 *a*	2.32 *a*

* Same letters are not significantly different at $P < 0.05$ according to the LSD test. Slicing was performed based on orchards location and spraying times. ** DAFB means day after full bloom.

fect on the fruit nutrient content. The absorbability of Ca in fruit in response to Ca spraying decreased significantly with the progressing fruit development (Table 2). Therefore, the highest Ca accumulation was found when fruits were sprayed with 15 g L^{-1} $CaCl_2$ at 35 DAFB. For example, the Ca content in sprayed fruits from the Rasht and Ramsar orchards was 41.61 and 32.42% more than in the control, respectively, when sprayed at 35 DAFB (Table 3). In fact, the penetration rate of Ca was significantly affected by the fruit development stage in kiwifruit. A delay in $CaCl_2$ spraying significantly reduced Ca accumulation rates (Tables 2 and 3). Moreover, the fruit

Table 3

The change of N, P, K, Ca, Mg percentage of Ca (with $CaCl_2$ 15 g L^{-1}) sprayed fruits as compared to control immediately 7 days after treatment

	Ca	N	P	K	Mg
Rasht					
35 DAFB	+41.61 *a**	-14.38 *c*	+5.25 *a*	+9.89 *a*	+1.75 *c*
80 DAFB	+5.92 *cd*	-3.22 *a*	+2.39 *a*	+2.03 *b*	+1.95 *bc*
120 DAFB	+0.74 *d*	-1.23 *a*	+0.67 *a*	+1.42 *b*	+0.98 *c*
35+80 DAFB	+17.30 *bc*	-9.74 *b*	+4.02 *a*	+11.54 *a*	+5.99 *b*
35+80+120 DAFB	+24.68 *b*	-15.35 *c*	+4.43 *a*	+15.28 *a*	+18.37 *a*
Ramsar					
35 DAFB	+32.42 *a*	-15.88 *b*	+6.65 *a*	+10.97 *b*	+1.41 *b*
80 DAFB	+7.06 *c*	-1.71 *a*	+2.88 *a*	+4.54 *c*	+2.11 *b*
120 DAFB	+5.78 *c*	-0.58 *a*	+1.92 *a*	+0.83 *c*	+3.10 *b*
35+80 DAFB	+22.42 *b*	-10.97 *b*	+4.22 *a*	+14.11 *ab*	+6.73 *b*
35+80+120 DAFB	+26.84 *ab*	-17.11 *b*	+3.18 *a*	+16.70 *a*	+22.81 *a*

* For each orchard and element, means followed with the same letters are not significantly different at $P < 0.05$ according to the LSD test. Slicing was performed based on orchards location.

Ca concentration increased with a more frequent spray application (Tables 2 and 3). The highest Ca accumulation was found when fruits were treated with $CaCl_2$ three times.

Calcium sprayed fruits showed a lower N content than the control. The lowest N content was found when fruits were sprayed three times, at 35, 80 and 120 DAFB (-15.35 and -17.11% in the Rasht and Ramsar orchards respectively). Contrary to our expectations, the K and Mg content of $CaCl_2$ sprayed fruits slightly increased but no significant difference was found for the P content between $CaCl_2$ sprayed and control fruits (Tables 2 and 3).

In general, the K/Ca, N/Ca, Mg/Ca and (K+Mg)/Ca ratios in $CaCl_2$ sprayed fruits were lower than in the control and the values showed better balance in treated fruit than in the control (Table 2). The lowest N/Ca was found when fruits were sprayed at 35 DAFB, 35+80 DAFB and 35+80+120 DAFB (Table 2). The lowest K/Ca and K+Mg/Ca were obtained at 35 DAFB. The Mg/Ca ratio significantly increased by the 35 DAFB treatment in the Rasht orchard, but was not significantly affected by any $CaCl_2$ sprays in the Ramsar orchard.

Changes of the macronutrient content of harvest mature fruits in response to Ca spray

The fruit Ca, Mg, K, N, P and their ratios were determined in mature, harvested fruits both Ca sprayed and control (Table 4). The determinations showed that fruit macronutrients at the harvest time were significantly af-

Table 4

Effect of $CaCl_2$ (15 g L^{-1}) spraying times (35, 80, 120 DAFB) on macronutrient content (g 100 g^{-1} DW) and their ratios of harvested mature cv. Hayward kiwifruit

	Ca	N	P	K	Mg	N/Ca	K/Ca	Mg/Ca	K+Mg/Ca
Rasht									
Control	2.222 *c**	1.318 *a*	0.270 *a*	3.998 *c*	0.138 *c*	0.592 *a*	1.801 *abc*	0.063 *ab*	1.863 *abc*
35 DAFB	2.153 *c*	1.293 *ab*	0.275 *a*	4.331 *ab*	0.131 *c*	0.602 *a*	2.021 *a*	0.062 *ab*	2.083 *a*
80 DAFB	2.204 *c*	1.316 *a*	0.277 *a*	4.131 *bc*	0.136 *c*	0.607 *a*	1.893 *ab*	0.062 *ab*	1.955 *ab*
120 DAFB	2.177 *c*	1.278 *ab*	0.276 *a*	4.046 *c*	0.158 *b*	0.601 *a*	1.888 *ab*	0.074 *a*	1.962 *ab*
35+80 DAFB	2.622 *b*	1.030 *bc*	0.284 *a*	4.207 *bc*	0.158 *b*	0.393 *b*	1.613 *bc*	0.060 *b*	1.673 *bc*
35+80+120 DAFB	2.970 *a*	0.879 *c*	0.272 *a*	4.580 *a*	0.205 *a*	0.296 *b*	1.542 *c*	0.069 *ab*	1.611 *c*
Ramsar									
Control	1.615 *b*	0.957 *a*	0.140 *a*	3.728 *c*	0.132 *b*	0.597 *a*	2.324 *a*	0.082 *ab*	2.406 *ab*
35 DAFB	1.680 *b*	0.952 *a*	0.143 *a*	3.913 *b*	0.133 *b*	0.568 *a*	2.334 *a*	0.079 *ab*	2.414 *ab*
80 DAFB	1.626 *b*	0.947 *ab*	0.139 *a*	3.979 *b*	0.130 *b*	0.586 *a*	2.462 *a*	0.081 *ab*	2.543 *a*
120 DAFB	1.597 *b*	0.954 *a*	0.142 *a*	3.731 *c*	0.122 *b*	0.560 *a*	2.343 *a*	0.077 *b*	2.420 *ab*
35+80 DAFB	2.045 *a*	0.908 *b*	0.146 *a*	4.053 *b*	0.206 *a*	0.448 *b*	1.999 *b*	0.102 *a*	2.101 *bc*
35+80+120 DAFB	2.482 *a*	0.844 *c*	0.148 *a*	4.587 *a*	0.231 *a*	0.341 *c*	1.853 *b*	0.94 *ab*	1.946 *c*

* For each orchard, element and sampling time, means followed with the same letters are not significantly different at $P < 0.05$ according to the LSD test. Slicing was performed based on orchards location.

fected by a preharvest Ca spray application (Table 4). In both orchards, the Ca content in mature, harvested fruits increased under the influence of more frequent spray applications, as the highest Ca was found in 35+80+120 DAFB sprays (2.97 and 2.48 g 100 g^{-1} DW in the Rasht and Ramsar orchards respectively) (Table 4). The highest Ca accumulation in harvest ripe fruits was found when spraying was carried out at both 35+80 DAFB and 35+80+120 DAFB, independently of the orchard location (Table 5).

No significant difference was found between Ca sprayed and control fruits in the P content at the harvest ripeness stage (Table 4). By contrast, the fruit N, Mg and K content was affected by the $CaCl_2$ spraying timing and frequency. At a higher treatment frequency, the N content in fruits significantly decreased. The lowest N content was found when fruits were sprayed three times: at 35, 80 and 120 DAFB (-50.10 and -13.63 in the Rasht and Ramsar orchards respectively). Unexpectedly, Ca spraying increased the fruit content of K and Mg. The highest K and Mg accumulation in kiwifruit at harvest time was found when fruits were sprayed with $CaCl_2$ three times: at 35+80+120 DAFB (Tables 4 and 5).

The K/Ca, N/Ca, Mg/Ca and (K+Mg)/Ca ratios in $CaCl_2$ sprayed fruits was lower than the control in Ramsar. However, there was no significant difference for the K/Ca and (K+Mg)/Ca ratios between Ca sprayed and control fruits in the Rasht orchard (Table 4). The lowest N/Ca ratio in mature

Table 5

The change of N, P, K, Ca, Mg percentage of Ca (with $CaCl_2$ 15 g L^{-1}) sprayed fruits as compared to control in mature harvested cv. Hayward kiwifruit

	Ca	N	P	K	Mg
Rasht					
35 DAFB	+3.73 *c**	-2.16 *a*	+1.95 *a*	+7.53 *b*	-5.56 *c*
80 DAFB	+0.65 *c*	-0.17 *a*	+2.64 *a*	+3.14 *cd*	-2.40 *c*
120 DAFB	-1.88 *c*	-3.13 *a*	+2.11 *a*	+1.10 *d*	+12.45 *b*
35+80 DAFB	+20.09 *b*	-27.84 *b*	+4.78 *a*	+4.96 *bc*	+11.92 *b*
35+80+120 DAFB	+34.65 *a*	-50.10 *c*	+0.47 *a*	+12.71 *a*	+32.29 *a*
Ramsar					
35 DAFB	-3.72 *c*	-0.53 *a*	+2.66 *a*	+4.73 *b*	+0.86 *b*
80 DAFB	-1.90 *c*	-1.11 *a*	-0.20 *a*	+6.27 *b*	-1.37 *b*
120 DAFB	-4.01 *c*	-0.31 *a*	+1.39 *a*	+0.06 *c*	-12.86 *b*
35+80 DAFB	+14.93 *b*	-5.40 *a*	+4.22 *a*	+7.99 *b*	+35.70 *a*
35+80+120 DAFB	+25.18 *a*	-13.63 *b*	+5.49 *a*	+18.65 *a*	+42.93 *a*

* For each orchard and element, means followed with the same letters are not significantly different at $P < 0.05$ according to the LSD test. Slicing was performed based on orchards location.

fruits was found when fruits had been sprayed with $CaCl_2$ twice (35+80 DAFB) and thrice (35+80+120 DAFB). Furthermore, the lowest K/Ca, Mg/Ca, K+Mg/Ca ratios were determined in the fruits sprayed thrice, although there was no significant difference versus the kiwifruits in the Ramsar orchard sprayed with Ca twice (Table 4).

The correlation between the cv. Hayward kiwifruit content of minerals in response to $CaCl_2$ spray

There was a negative correlation between the N content in fruit with the content of K, Ca and Mg (Table 6); that meant that the kiwifruit N content significantly decreased following the increasing Ca, K and Mg accumulation in fruits during fruit development and at the harvest time (Tables 3 and 5). No significant correlation was found between P and the other elements in fruits at harvest. Moreover, there was a significant positive correlation between K, Mg and Ca, indicating that an increase in the fruit Ca content was associated with the increasing content of K and Mg ions in the fruits (Table 6). It should be noted that because an of the Ca content in response to $CaCl_2$ spray was higher than in the case of K and Mg, a negative correlation was found between the Ca content and the K/Ca, N/Ca, Mg/Ca and (K+Mg)/Ca ratios (Table 6).

Table 6

The correlation coefficients between fruit mineral content of cv. Hayward kiwifruit at the harvest time in response to Ca spray times at two commercial orchards

	Ca	N	P	K	Mg	N/Ca	K/Ca	Mg/Ca	K+Mg/Ca
Rasht									
Ca	1								
N	-0.71 $^{**\,a}$	1							
P	-0.09 ^{ns}	0.20 ^{ns}	1						
K	0.56 **	-0.36 *	0.05 ^{ns}	1					
Mg	0.74 **	-0.73 **	-0.03 ^{ns}	0.52 **	1				
N/Ca	-0.90 **	0.94 **	0.17 ^{ns}	-0.44 **	-0.73 **	1			
K/Ca	-0.91 **	0.65 **	0.16 ^{ns}	-0.17 ^{ns}	-0.58 **	0.85 **	1		
Mg/Ca	-0.26 *	-0.11 ^{ns}	0.09 ^{ns}	-0.03 ^{ns}	0.45 **	0.13 ^{ns}	0.35 *	1	
K+Mg/Ca	-0.90 **	0.63 **	0.16 ^{ns}	-0.17 ^{ns}	-0.56 **	0.84 **	0.99 **	0.38 *	1
Ramsar									
Ca	1								
N	-0.79 **	1							
P	0.34 *	-0.31 *	1						
K	0.89 **	-0.87 **	0.39 **	1					
Mg	0.83 **	-0.87 **	0.18 ^{ns}	0.79 **	1				
N/Ca	-0.98 **	0.84 **	-0.29 *	-0.88 **	-0.86 **	1			
K/Ca	-0.94 **	0.64 **	-0.22 *	-0.68 **	-0.74 **	0.94 **	1		
Mg/Ca	-0.24 *	-0.52 **	-0.13 ^{ns}	0.31 *	0.73 **	-0.30 *	-0.15 ^{ns}	1	
K+Mg/Ca	-0.93 **	0.62 **	-0.23 *	-0.67 **	-0.70 **	0.93 **	0.99 **	-0.09 ^{ns}	1

^{a} ^{ns}, * or ** indicates non-significant, significant at $P \leq 0.05$ or 0.01, respectively. Slicing was performed based on orchards location.

DISCUSSION

This study has demonstrated that a potential increase in the fruit Ca content by $CaCl_2$ spraying decreased with the progressing development of kiwifruit plants. Furthermore, a single $CaCl_2$ spray at 35 DAFB during fruit development was more effective in modifying the accumulation of other macronutrients; however this effect was less obvious for 80 and 120 DAFB sprays. The importance of starting treatment with Ca early is that in many crops the nutrient maximum uptake occurs after fruit setting and Ca is accumulated principally in leaves during the period of the most intensive leaf growth (BEMADAC et al. 1996).

Many studies reported that the penetration rates of $CaCl_2$ in apples were affected by the fruit development stage; namely, the penetration rate was

higher in early fruit development stages and decreased rapidly in later stages (Michalczuk, Kubik 1984, Schlegel, Schonherr 2002). Moreover, Schlegel, Schonherr (2002) showed that rapid penetration of foliar applied Ca into young apple fruits occurred through trichomes and stomata until 45 DAFB, when fruit shed trichomes and penetration continued mainly *via* lenticels. Neilsen et al. (2005) indicated that $CaCl_2$ spray in the early growing season was as effective as in late season, despite the low Ca concentration in the harvested fruit. This conclusion was drawn despite a minimal impact of the mid- and late-season applications on the whole fruit Ca concentration at the harvest time (Neilsen et al. 2005).

In kiwifruit, the xylem functionality, fruit transpiration, fruit hair viability and fruit hydraulic conductance showed significant changes during the first 8 to 10 weeks after full bloom (Xiloyannis et al. 2008). Xylem transport occurs only in the acropetal direction and is of some importance for the Ca supply to young fruits, which continue to transpire in the early phase of their development (Xiloyannis et al. 2008). At a later stage, fruits almost exclusively feed through the phloem (Mengel, Kirkby 2002). The phloem transport system is through the cytoplasm, which has low concentrations of Ca (Raven 1977).

Gerasopoulos et al. (1996) concluded that later applications (e.g. at 143 DAFB) added to early ones (93 and 118 DAFB) enhanced the Ca content, and in many cases doubled the fruit Ca content. This may be attributed to the loosening of the cell wall in kiwifruit during fruit development, which in turn facilitates the penetration of Ca ions (Hardenburg, Anderson 1979).

In contrast, Casero et al. (2002) concluded that late Ca sprays increased the Ca absorption rate and accumulation in apple fruit and improved fruit quality. Moreover, Zavalloni et al. (2001) showed that fruit Ca increased progressively during the season in a linear pattern. It is probable that calcium sprays at the end of fruit growth are most effective, since the total surface of a fruit is larger and the liquid can move through channels of discontinuity and openings that appear in fruits during on-tree ripening (Benavides et al. 2001).

The frequency of applications is also a very important factor for the penetration of Ca into the fruit. Our results revealed that the fruit Ca concentration increased with an increasing frequency of $CaCl_2$ spray applications, for instance a series of three $CaCl_2$ sprays was more effective in changing the fruit mineral content (Tables 2 and 4). It appears that an increase in the number of $CaCl_2$ applications during the second half of the growing cycle raises calcium levels in fruit, but does not always induce a proportional raise in Ca with regard to the number of sprays applied (Casero et al. 2009). These results agree with findings by Le Grange et al. (1998), who determined that calcium concentration slightly increased with the number of calcium sprays.

The current results also showed that the fruit mineral composition was significantly affected by Ca spray times and frequency, as Ca concentrations

significantly increased at 35 and 35+80+120 DAFB sprays (Tables 2 and 4). These results are in agreement with Gerasopoulos et al. (1996) who revealed that $CaCl_2$ sprays enhanced fruit pericarp, core, and skin Ca concentration of kiwifruit.

Similar results regarding a decrease in the N content by $CaCl_2$ spraying were obtained by Madani et al. (2013) in papaya. This may be explained by the fact that if calcium is applied beyond precipitation requirements, it stimulates ammonium absorption by plants. Adding supplemental calcium has increased the rate at which plants absorb ammonium by as much as 100 percent. Plant cannot access nitrogen in an environment containing more than 32 percent ammonium (Feagley, Fenn 1998).

The results of this study indicated that $CaCl_2$ foliar spray caused higher K and Mg accumulation in fruits as compared with the control (Tables 2 and 4). These results are in agreement with Perucka, Olszowka (2011), who reported that $CaCl_2$ foliar spray of lettuce caused higher K and Mg concentrations in whole leaves compared with the control. Additionally, the results for K increase are supported by Tuna et al. (2007), thus confirming that Ca has a significant role in improving the status of K. Similarly, the K content progressively increased under the other treatments as compared to control plants. Ca improves the nutrient status of plants by increasing the K content of plants (Abbasi et al. 2013). It is known that Ca^{2+} maintains membrane integrity and controls selectivity of ion uptake and transport (Mengel, Kirkby 2002).

In some earlier studies, foliar sprays of Ca had no significant effects on fruit nutrients (Tomala 1997), especially on the P content (Le Grange et al. 1998). Furthermore, Koutinas et al. (2010) mentioned that P, Fe, Mn, and Zn concentrations of kiwifruits were unaffected by Ca foliar sprays. Variations in fruit mineral concentrations are largely influenced by certain differences in growing conditions and climatic factors, or by the rate of fruit development (Tomala 1997, Casero et al. 2009). The effects of foliar Ca application sometimes show inconsistencies in terms of fruit mineral content. There are three possible reasons for inconsistent Ca treatment results: (1) atmospheric effects of Ca absorption, (2) uneven distribution of Ca in fruits within a canopy, (3) condition and management of a tree (Yamane 2014).

Our results indicated that $CaCl_2$ sprays produced fruit with lower N, K, Mg/Ca ratios, as the 35+80+120 DAFB sprays was more effective (Tables 2 and 4). The ratios of mineral nutrients are an important indicator of the nutritive value of a diet. Some researches use N, K, Mg/Ca ratios for prediction of calcium deficiency related disorders in fruits (Sio et al. 1999). Lower N, K, Mg/Ca ratios are desirable. It was found that an application of Ca fertilizers might significantly decrease the N/Ca and K/Ca ratios in fruit (Casero et al. 2009, Lanauskas et al. 2012) as a consequence of the increasing Ca content. Generally, such changes have a positive impact on fruit quality and storability (Winska-Krysiak, Lata 2010).

There was a negative relationship between the N concentration and Ca availability, as the N content significantly decreased with an increasing Ca concentration. This relationship was also reported by Fenn et al. (1987) and Favaro et al. (2007), who observed similar behaviour for N uptake in plant tissue due to Ca nutrition.

CONCLUSION

It can be concluded that the potential of $CaCl_2$ sprays to change the fruit nutrient content decreased significantly with progressing fruit development, as early-season (35 DAFB) $CaCl_2$ spray could change the content of fruit minerals as compared with the mid- and late-season sprays, despite having no significant effect on the content of nutrients at the harvest time. The orchard location had significant effects on the content of fruit nutrients, for example kiwifruits from the Rasht orchard had a higher Ca content than in the Ramsar orchard. Moreover, increasing the frequency of $CaCl_2$ sprays considerably affected the fruit mineral content, namely a series of three (35+80+120 DAFB) $CaCl_2$ sprays was most effective. Overall, we suggest using triple $CaCl_2$ sprays in 6-week intervals from mid-June to early-September as a viable approach to increasing the fruit Ca content and ensuring better fruit mineral nutrient balance.

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