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The Accumulation of Rare Earth Elements Fertilizer and its Subsequent Effects on Apple Fruit Quality at Harvest and During Storage

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Abstract. Rare earth elements fertilizer and Ca were sprayed on eight-year-old 'Fuji'/M.9 apple trees during two consecutive seasons, and fruit quality was quantified at harvest and 5-month long storing in a commercial cooling house at 4°C and 80~85% RH. In the first season, single-sprayed of rare earth elements fertilizer showed appreciable accumulations of its elements (La, Pr, Gd, and Nd) in the fruit. In the following season, application of higher doses accumulated higher amount, indicating that the accumulation of rare earth elements was dose-dependent. However, rare earth elements did not affect the accumulations of Ca, Mg, and K in 'Fuji' apple fruit showed that there was no interaction between rare earth elements and these macronutrients. Double-spray of 0.2% rare earth elements increased fruit redness at harvest and had exhibited better color. Although at harvest it did not show significant effects on fruit weight, pulp firmness and titratable acidity (TA), but had pronounced effects on inhibiting fruit softness and retarded decrease of TA during storing. Furthermore, it reduced respiration rate and inhibited ethylene production during storing indicated that rare earth elements may be an alternative for prolonging the shelf life of 'Fuji'/M.9 apple fruit.

Key words : Ca, firmness, rare earth elements, SSC/TA, TA

Introduction

Rare earth elements belongs to IIIA element family (Henke, 1977), which have characteristics and tend to be present naturally as a group. However, fractionation between light (La from Eu) as well as heavy (Gd from Lu) rare earth elements were observed during transportation in bioaccumulation processes (Xu et al., 2002; Wyttenbach et al., 1998). The property and structure of rare earth elements are very similar to Ca^{2+}. They replace or compete with Ca^{2+} at their low concentration for binding sites and affect the function of some enzymes in cell membrane, enhance absorption, utilization and transformation of nutrients (Brown et al., 1990).

Zhu et al. (1987) reported that rare earth elements acted as nutrients for crops at low levels. Based on this, fertilizers containing rare earth elements have been applied in agriculture since 1980s. Rare earth fertilizer comprises including La, Ce, Pr, and Sm elements, and its stimulation effects are the contribution of all elements. $Re(NO_3)_3$ is an inorganic compound of rare earth fertilizer which is categorized as a kind of microelement by its function, and have been widely applied to agricultural crops (Wang et al., 2001). To date, several considerable researches have been done on the application of rare earth elements for improving wheat (Ding et al., 2006; Zhang and Shan, 2001) and maize (Xu et al., 2002) production.

Pre-harvest calcium applications have been commercially used for delaying senescence and control of many physiological disorders in apple fruit during storing (Conway et al., 1994; Poovaiah, 1986). Although rare earth elements have similar characteristics of Ca^{2+}, there is no report about the effect of rare earth on apple quality. Dose-effect of rare earth elements has been observed in corn (Wang et al., 2001) but not in apple. Therefore, in this study rare earth elements fertilizer was applied as

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foliar spray on ‘Fuji’/M.9 apple during growing season to examine its bioaccumulation and effects on the quality of fruit.

Materials and Methods

The experiments were carried out on eight-year-old ‘Fuji’/M.9 apple trees that were grown in an orchard of Andong Agricultural Technological Center during two consecutive years. A standard randomized block design with six replications was used and tested trees were isolated by one untreated guard trees. All spray applications were performed in the morning by a hand sprayer following doses 20 L/six trees. In the first year, a preliminary experiment was done by applying water (control treatment) and single spray of 0.1% rare earth elements solution.

In the second year, treatments were made with water (control), double-spray of 0.2% rare earth elements solution (in the first two timings), triple-spray of 0.1% and 0.2% rare earth elements solution, triple-spray of 0.2% calcium solution, and the treatments were applied on 10th June, 29th July and 19th September i.e. 40, 90 and 140 days, respectively after anthesis.

The contents of rare earth elements fertilizer used in this study were listed in Table 1. To examine the uptake of minerals in apple, fruits were collected at commercial harvest time and then washed with deionized water. Fruit pulps were dried in an air-forced oven at $65 \pm 3^{o}C$, powdered in a stainless steel mill and then stored in paper bags until analysis. Each sample contained with an amount of 0.5 g powder was burnt in Muffle furnace at $500^{o}C$ for 5 h, and then the ashes were dissolved in 10% HNO_3. Therefore, Ca, Mg, S, and K were analyzed by inductively coupled plasma (ICP), and La, Ce, Pr, Gd, Nd, Sm were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (Yuan et al., 2001).

Fruit firmness was measured by compression of individual fruit with a fruit texture analyzer (GUSS.ZA/GS-14). Apple juice was collected for analysis of soluble solid concentration (SSC) using a digital refractometer (PR-101, Cat. No. 3412, ATAGO, Japan), and titratable acidity (TA) by a digital fruit acidity analyzer (Model: GMK-708, GVK, South Korea). Fruit color was determined by using a Color-Reader (KONICA MINOLTA SENSING, INC. Japan) which recorded the spectrum of reflected light and converted it into a set of color coordinates (Hunter L, a, and b value).

For measurement of CO_2 and ethylene production rate, fruits were incubated in a 2-L sealed plastic jar for 30 min, and therefore, well-mixed headspace gas samples were obtained from the jar and analyzed by GC (5890a Series Π; Hewlett Packard Rockville, MD). The GC column used for CO_2 was CTR 1 (Alltech Associates, Deerfield, Ⅲ) with a thermal conductivity detector (TCD), and an activated alumina column with a flame ionization detector (FID) was used for ethylene. Temperature maintained in the column was $80^{o}C$ and the carrier gas was N_2 at a flow rate of 20 ml/min.

All trials and observations were replicated three times. T-test was carried out for each group of measurements to determine whether there is significant difference between sprayed and control treatments. For the second year, statistical comparisons were made by one-way analysis of variance (ANOVA) followed by Duncan’s multiple range test (DMRT) using SAS 9.1 version (SAS, Inc., Cary, NC, USA).

Results and Discussions

Generally, concentrations of rare earth elements in plants are variable even within the same plant (Ding et al., 2006). In our first year study, rare earth elements fertilizer was sprayed at low concentration (0.1%) only before harvest but significant accumulations of the elements, La, Pr, Gd, Nd and Sm were found in treated fruits (Table 2). However, Ce did not significantly accumulate in fruit, which may be due to its lower absorption efficiency compared to others. Application of rare earth elements at low concentrations on tomato, cucumber,

Table 1. The characteristics of rare earth elements fertilizer used in this study.

Mg (ppm)	S (ppm)	Ca (ppm)	K (ppm)	La (ppb)	Ce (ppb)	Pr (ppb)	Gd (ppb)	Nd (ppb)	Sm (ppb)
2406.3	5287.5	3308.8	94250	890	1161.3	905	784.6	1013.8	918.7

Table 2. The accumulations of rare earth elements in ‘Fuji’ apple sprayed with rare earth elements fertilizer.

Year	Treatment	La (ppb)	Ce (ppb)	Pr (ppb)	Gd (ppd)	Nd (ppb)	Sm (ppb)
2006	Control (water spray)	13.1b	24.4a	2.6b	6.1b	9.5b	0.9b
	RE 0.1% for single spray	15.7a	26.7a	3.2a	7.8a	11.7a	1.1a
2007	Control (water spray)	11.7d	25.0d	3.0c	10.3b	10.3d	1.1b
	RE 0.1% for tri-spray	28.1b	54.6b	6.0b	14.3ab	21.0b	1.7b
	RE 0.2% for double-spray	26.2bc	47.8bc	5.6b	15.8ab	19.5bc	1.6b
	RE 0.2% for tri-spray	44.2a	80.7a	9.3a	27.2a	31.6a	2.9a
	Ca 0.2% for tri-spray	16.8cd	33.3cd	5.5bc	19.7ab	14.2cd	3.2a

*The means within column with the same letter are not significantly different at P = 0.05 according to t-test (2006) and Duncan’s multiple range tests (2007). Data are the mean ± SE of 10 fruits in triplicate.
*RE: rare earth elements fertilizer.

kidney beans, cabbage and Chinese cabbage showed accumulation of its elements (Wen et al., 2001). In the second year, La, Ce, Pr, Gd, Nd, and Sm showed significantly higher accumulations in ‘Fuji’/M.9 fruits compared to control (Table 2). The highest concentration of La, Ce, Pr, Gd, Nd, and Sm elements were observed in ‘Fuji’ apple fruit treated with triple spray of 0.2% rare earth. This indicated that accumulation of rare earth elements in ‘Fuji’/M.9 fruit is dose-dependent. There was no remarkable difference between double and triple spray of 0.2% and 0.1%, respectively. On the contrary, triple-spray resulted in higher accumulations than that of double spray. It showed consistent with the report of Zhang and Shan (2001) who applied rare earth elements on wheat and found that accumulation of La, Ce, Pr, and Nd increased with increasing number of spray.

In both the season, concentrations of Mg and K in ‘Fuji’ apple fruit (Table 3) did not differ significantly which demonstrated that use of rare earth elements fertilizers did not affect the absorption of these nutrients. However in the second year, concentrations of Mg, S, Ca, and K were much lower than that of the first year, which may be due to the heavier rainfall in the second year. In our study, foliar spray of Ca showed its significantly higher absorption which is in agreement with previous results on plum (Alcaraz-Lopez et al., 2003) and apple (Raese and Drake, 2000). There are report on extreme high doses (100 kg/ha) of rare earth elements fertilizer had significant reduction of minerals in maize grains (Xu et al., 2002). In our study foliar spray of rare earth elements did not affect mineral concentration (Ca, Mg, K) indicated that application concentrations were not toxic to ‘Fuji’ apple trees.

Although rare earth elements were accumulated in ‘Fuji’ fruit but no detrimental effects were found on fruit weight (Fig. 1). In 2007, triple spray of 0.2% rare earth elements resulted in better redness with a-value of 27.16 at harvest (Fig. 2). The redness of stored apple fruits was gradually decreased during storage. It is consistent with the findings of Rosso and Mercadante (2007) who observed a decreased a-value during storing of tropical fruits. Results regarding storing intervals showed that double-

Table 3. Effect of rare earth elements or calcium on mineral concentrations of ‘Fuji’ apple.

Year	Treatment	Mg (ppm)	S (ppm)	Ca (ppm)	K (ppm)
2006	Control (water spray)	242.8a	610.2a	293.3a	0.83a
	RE 0.1% for single spray	244.8a	624.4a	293.8a	0.87a
2007	Control (water spray)	188.8a	466.4c	192.6b	0.66a
	RE 0.1% for tri-spray	212.7a	627.4ab	212.8b	0.71a
	RE 0.2% for double-spray	196.7a	595.2b	206.2b	0.70a
	RE 0.2% for tri-spray	199.9a	674.5a	222.3b	0.65a
	Ca 0.2% for tri-spray	197.1a	609.6ab	285.5a	0.68a

*The means within column with the same letter are not significantly different at P = 0.05 according to t-test (2006) and Duncan’s multiple range tests (2007). Data are the mean ± SE of 10 fruits in triplicate.
*RE: rare earth elements fertilizer.

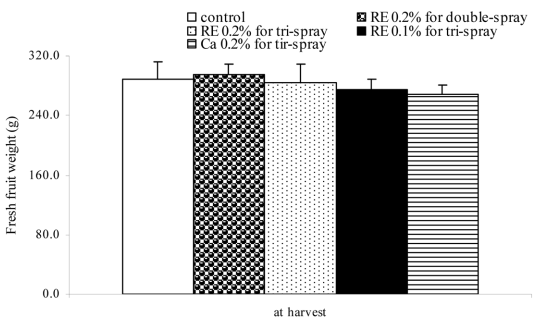

Fig. 1. Individual fruit weight of 'Fuji'/M.9 apple treated foliar spray of rare earth elements, or calcium in growth season in 2007. The bar indicated SE.

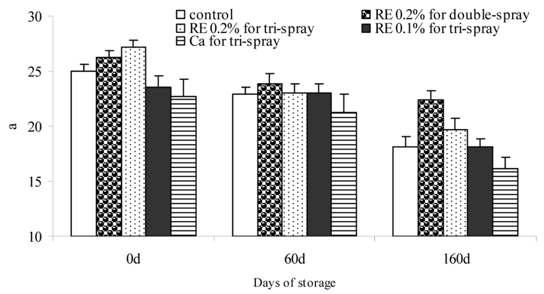

Fig. 2. Fruit redness (Hunter a value) of 'Fuji'/M.9 apple treated foliar spray of rare earth elements, or calcium during 5-month storage in 2007. The bar indicated SE.

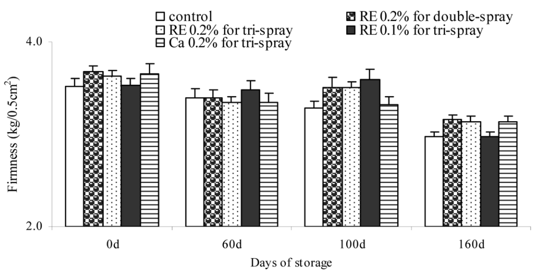

Fig. 3. Fruit firmness of 'Fuji'/M.9 apple treated foliar spray of rare earth elements, or calcium during 5-month storage in 2007. The bar indicated SE.

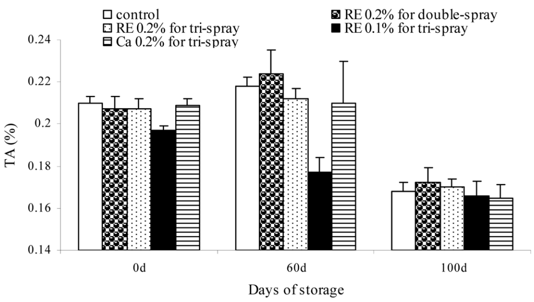

Fig. 4. TA value of 'Fuji'/M.9 apple receiving foliar spray of rare earth elements, or calcium during 5-month storage in 2007. Data are the mean ± SE of 10 fruits in triplicate.

spray of 0.2% rare earth elements exhibited better expression on maintaining redness of 'Fuji' fruit color. However, at the end of storing, triple spray of 0.2% rare earth elements resulted in somehow lower a-value (less redness) than that of double spray, indicated that double spray should be optimal for 'Fuji' fruit.

Rare earth elements or Ca did not affect fruit firmness at the time of harvest but had significant effects on inhibiting fruit softness during storing. Among the treatments, 0.2% rare earth had the best performance in retarding fruit softness and similar effect was also found in Ca treated fruit (Fig. 3). In our study foliar spray of Ca did not increased fruit firmness at the time of harvest which showed agreement with the previous report on peach (Manganaris et al., 2005). On the contrary, Siddiqui and Bangerth (1995) found favorable effect of calcium on 'Golden Delicious' apple firmness. Our results showed that softness of 'Fuji' fruit was retarded during storing, although there was no highly accumulation of Ca in the fruits (Table 3). This indicated that fruit firmness is not always correlated with Ca concentration (Manganaris et al., 2005) but may be caused by the accumulations of rare earth elements, such as La, Ce, Pr, Gd, and Nd. The efficacy of rare earth elements on firmness may be related with competition of La^{3+} and Ce^{3+} with Ca^{2+} for binding sites at low concentrations to form new chemicals (Fedirko et al., 1998), which might strengthen molecular binding between constituents of cell wall.

Rare earth elements or Ca did not show significant effect on titratable acidity (TA) at the time of harvest (Fig. 4) suggested that the foliar spray of rare earth elements or Ca did not affect the fruit ripening on the tree. Whereas storing intervals had a decreasing trend of titratable acidity which showed accordance with the previous report of Hayat et al. (2005) who had observed that acidity percentage decreased with increasing storing period. Among the treatments, double-spray of 0.2% rare earth elements proved powerful for retarding the decrease of TA toward the end of storage.

The ratio between SSC and TA is considered a good

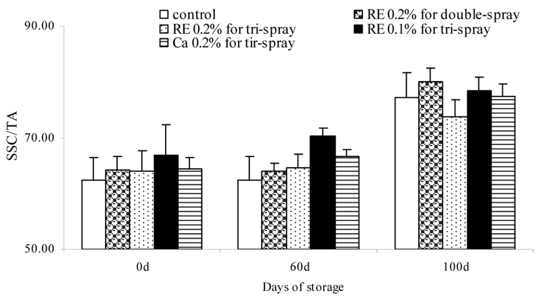

Fig. 5. SSC/TA ratio of 'Fuji'/M.9 apple receiving foliar spray of rare earth elements, or calcium during 5-month storage in 2007. Data are the mean ± SE of 10 fruits in triplicate.

index for the evaluation of fruit quality (Serrano et al., 2004). In our study, 'Fuji' apples that had double sprayed with 0.2% rare earth elements exhibited the highest SSC/TA value at the end of storage (Fig. 5) indicated that this treatment proved better than others.

Ethylene production of 'Fuji' apple fruit was significantly inhibited by foliar spray of rare earth elements at harvest (Table 4). Ca-treated fruits also showed significantly lower ethylene production compared to control. Ferguson (1984) reported that calcium sprays decreased ethylene production in apples, which could be attributed to a decrease in ACC oxidase activity (Guan et al., 1991). At the end of shelf life ethylene production remarkably increased in all treatment groups but rare earth elements maintained the lowest rate. Rare earth elements reduced respiration rate at harvest (Table 4) which is critical in extending shelf-life of 'Fuji' apple (Lee et al., 2003; Surjadinata and Cisneros-Zevallos, 2003). Both rare earth elements and Ca treated fruits showed decreased CO_2 production at the end of shelf life is an agreement with the report that calcium delayed ripening and senescence of fruits by lowering the respiration rate (Singh et al., 1993).

Effects of foliar spray of rare earth elements on 'Fuji' apple indicated improved fruit redness at harvest which strongly favored fruit marketing. Although foliar spray of rare earth elements did not show significant difference on individual fruit weight, mineral accumulations, firmness, SSC/TA ratio, and TA at harvest but retarded the decrease in firmness and TA in the storage. Furthermore, during storing, rare earth elements showed lower respiration rate and ethylene production as Ca indicated that rare earth elements may be an alternative for extending postharvest life of 'Fuji' apple fruit.

Acknowledgement

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Table 4. Effects of rare earth elements or calcium on ethylene production and respiration rate of 'Fuji' apple at harvest and end of shelf life (160 days after harvest).

Treatments	Ethylene Production (ml kg^{-1} h^{-1})		Respiration rate (ml g^{-1} h^{-1})	
	At harvest	End of shelf life	At harvest	End of shelf life
Control	0.62a	31.58a	7.01a	4.84a
Re 0.2% for double-spray	0.30c	28.71c	6.46ab	4.07b
Ca 0.2% for tri-spray	0.48b	30.37b	7.01a	4.36ab

* The means within column with the same letter are not significantly different at P = 0.05 according to Duncan's multiple range tests. Data are the mean ± SE of 10 fruits in triplicate.
*RE: rare earth elements fertilizer.

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Wei-Wei Zheng, Mu-Young Park, Peter Hirst, Tae-Myung Yoon, and Ik-Jo Chun

희토류비료 시비가 사과 과실내 축적과 수확 및 저장 중 사과품질에 미치는 영향

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적 요. 본 연구는 희토류비료 시비가 8년생 '후지'/M.9 사과의 미량원소 변화 및 사과의 수확 품질과 5개월간 4 저장 후 과실 품질에 미치는 영향을 알아보기 위해 수행하였다. 1년차 희토류 비료의 시비는 '후지' 사과 과실내 란타늄, 프라세오디뮴, 가돌리늄 및 네오디뮴을 축적하였다. 또한 2년차 연구에서 높은 농도의 희토류비료 시비는 보다 많은 량의 희토류 성분을 과실에 축적하여 과실내 희토류의 축적은 희토류비료의 시비량에 비례하였다. 이러한 희토류비료의 시비는 과실내의 다른 미량원소인 칼슘, 마그네슘과 칼륨의 농도에는 영향을 미치지 않았다. 희토류비료 시비에 따른 과실 품질조사에 있어, 희토류비료 0.2%의 엽면살포는 수확기 사과 과피의 붉은 색을 증가시켰으나, '후지' 과실의 과중, 경도 및 산도는 변화가 없었다. 저장 사과의 희토류비료 시비효과를 조사한 결과, 희토류비료 처리된 사과의 경우 무처리에 비해 5개월 저장 후 과실의 연화 및 적정산도의 감소를 지연시키며, 호흡률과 에틸렌발생을 감소시켰다.

주제어 : 경도, 당산비, 산도, 칼슘, 희토류