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Calcium oxide nanofertilizer as alternative to common calcium products for the improvement of the amount of peel fruit calcium

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ABSTRACT

The necessity to improve the effectivity of fertilizers in agriculture, to be more in agreement with the new ecological trends, is a must nowadays. For this purpose, nanoparticles (NPs) could be an interesting alternative thanks to its enhanced characteristics due to the high surface-to-volume ratio. In this point, the use of NPs as nanofertilizers has been demonstrated that could be an alternative to conventional products using bulk macro and micronutrients. However, the effect of NPs on fruits has not been studied yet, although their effect on plants showed enhanced growth, root, shoot length, higher amount of biomass without phytotoxicity effects. In addition, the study of these nanomaterials directly on field has been avoided until now.

Therefore, in this work the effect of CaO NPs as foliar feeding nanofertilizers was studied directly on field for different fruits (cherries, apples, peaches, pears, tomatoes, grape, Paraguayan and apricots). For this purpose, the NPs size, the effect of the presence of chelate agents in the product and comparison with bulk fertilizers was evaluated.

The results showed that the use of CaO NPs increase the content of Ca^{2+} in the peel fruit and the peel cell width. In addition, the products using CaO NPs showed similar results than those obtained when a bulk Ca^{2+} commercially available product is used but using 20 times less CaO than the commercial product. Therefore, the proposed CaO NPs as foliar fertilizer alternative foliar to improve the peel Ca^{2+} content and the cell width has been demonstrated.

1. Introduction

Inside the agriculture, the farming of vegetables and fruits is quite important since with the global uprising in population and rapid urbanization the average need per country of fruits and vegetables will increase in the following years. Therefore, is important to control adequately the uptake of nutrients in fruits and vegetables. These compounds or chemical elements are divided in two main groups: (i) non-mineral and (ii) mineral nutrients. The first ones are hydrogen, oxygen and carbon which are incorporated by the plants through the photosynthesis since these elements are available in the air and water. However, these elements are not enough, and 13 mineral nutrients are important for plants. These minerals can be divided in macronutrients (nitrogen, phosphorous, potassium as primary macronutrients

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and calcium, magnesium and sulfur as secondary macronutrients) and micronutrients (boron, copper, iron, chloride, manganese, molybdenum and zinc) (Uchida, 2000). Although the absorption of these nutrients can be done through the plant roots, sometimes the lack of these elements in soil led to farmers and gardeners to use fertilizers in soils or even by foliar feeding. Inside these nutrients, one of the most important disorders in fruit and vegetables is the deficiency of calcium, even if foliar feeding application, which is a rapid way to correct of nutrient deficiencies.

The deficiency disorders due to the lack of calcium (Ca^{2+}) has been a challenge for more than 100 years. These disorders are especially important in peel fruits where low content of Ca^{2+} is present in cells and plasma membranes (Suzuki et al., 2003) which could lead to fruit-cracking (citrus), bitter pit (apple) or blossom end rot (tomatoes and peppers) and even tip burn in vegetables (cabbage, lettuce and brussels sprouts) and cavity spot (carrot) among other problems. The deficiencies of Ca^{2+} could be produced by mechanisms that reduce plant calcium uptake from the soil, fruit Ca^{2+} uptake from the plant, and Ca^{2+} translocation within the fruit. One of the biggest problems to overcome the Ca^{2+} deficiency is that the involved mechanisms for the Ca^{2+} distribution along the fruit are not really well explained. In this sense, several different mechanisms can be potentially participate in this process, such as cell wall Ca^{2+}-binding capacity and symplastic Ca^{2+} uptake from peduncle to distal fruit tissue (Tonetto De Freitas and Mitcham, 2012). Also, Ca^{2+} can reach the fruit the cell wall (Ca^{2+} represents about 60%–75% of the total fruit tissue Ca^{2+} amount Demarty et al., 1984; Tonetto De Freitas et al., 2010) through the xylem vessels, where is electrostatically join to the negatively charged particles present in the cell wall of the xylem vessels and apoplastic environment (Ralet et al., 2001; Herbette and Cochard, 2010). However, increasing the amount of Ca^{2+} intake by the fruit or plant do not lead necessarily to an increase in the translocation of Ca^{2+} in the fruit. This behavior can be explained due to higher rates of cell expansion achieved by high Ca^{2+} intake (Cheniclet et al., 2005) that can reduce the tissue Ca^{2+} concentration and increase the susceptibility to deficiency disorders (Ro et al., 1993; Ro and White, 2005; Tonetto De Freitas et al., 2011). In this sense, novel ways to improve the effectiveness of Ca^{2+} intake in fruits and vegetables should be found and, in this sense, the nanotechnology with the use of functional nanomaterials could be an interesting approach to overcome these Ca^{2+} disorders.

Nanotechnology in agriculture can overcome problems such as deficiency disorders and also can control the chronic problem of eutrophication due to the small amount necessary of nanomaterials compared to bulk materials, directly related to the high effectiveness of the nanoscale materials (Raliya et al., 2013). In this sense, the most typical used NPs are the inorganic-based materials, which include metals and metal oxides due to its easy synthesis and small size. However, nanotechnology has been scarcely investigated until now in some reports (Nair et al., 2010) which are demonstrating that there is a vast scope for the formulation of nanomaterials and its high effect by foliar feeding or applications (Raliya and Tarafdar, 2013). For example, the application of carbon nanotubes can improve the tomato growth (Derosa et al., 2010). Other studies using different metal oxides as ZnFeCu-oxides showed increase in root and shoot length and accumulation of higher amount of biomass, in green grams, in the plants treated with the nanoparticles (Dhoke et al., 2013). In addition, some researchers study the phytotoxicity of some nanoparticles as Zn and ZnO at different concentrations (Lin and Xing, 2007). The study showed some negative effects on seed germination and root growth at high concentrations (∼2,000 mg L^{-1}) of these nanoparticles. However, the studies were performed in petri dishes by previous soaking of the seeds in the corresponding solution containing NPs and no crop field studies were performed in order to confirm these results in real conditions. Nevertheless, results based on the use of Ca^{2+} and CaO nanoparticles for the correction of deficiency disorders has been scarcely study (Deepa et al., 2015).

The effect of CaO NPs were study by Deepa et al. (2015) and interesting results were found. In this study, CaO NPs with an average diameter of 70 nm were used at different concentrations (10–1,000 mg L^{-1}) by adding the dispersions by foliar feeding. Deepa et al. demonstrated that the CaO NPs were absorbed by the leaves and stems through the phloem while the bulk sprayed Ca^{2+} showed a restricted mobility in the phloem. In all cases, the application of CaO NPs improves the Ca^{2+} content in the root, stem and leaves and the maximum efficiency was found for relatively high concentrations (500 mg L^{-1}). Also, no phytotoxicity effects were found for the tested concentrations. However, the study did not include the effect on fruits which could be interesting to correct the Ca^{2+} deficiency disorders.

In this work, the improvement uptake of Ca^{2+} content in fruits and peel fruits is proposed by foliar feeding of suspensions containing CaO NPs at different sizes. The study was performed in different fruit species (cherries, apples, peaches, pears, tomatoes, grapes, paraguayans and apricots) at crop field level in order to see the effect in the farmer conditions. Also, the assays were compared with a common commercial product used for correction of Ca^{2+} deficiency. In addition, the effect on the cell wall of the external part of the fruit peel by measuring the cell wall width after the treatment was study.

2. Materials and methods

2.1. Instrumentation

The synthesis of the NPs was performed by using an ultrasonic bath and a muffle (up to 1,100 °C) with temperature programming. The characterization of the NPs was done with a transmission electron microscopy (TEM) from Jeol (Tokyo, Japan) model JEM-1010 microscope operated at 100 kV. For this purpose, the nanoparticles were dispersed in water by sonication, and 0.05 mL of this suspension was placed on a 200-mesh Cu grid coated with a holey amorphous carbon film. The water was evaporated prior to TEM analysis. Images were obtained using a MegaView III camera provided with the AnalySIS® image data acquisition system.

Table 1
Aqueous solutions used along the work to the foliar feeding of the selected crops for the study. The percentage necessary to achieve the 100% was completed with water.

Formulation	NPs size (nm)	CaO NPs[a] (%)	Citric Acid (%)	MSB (%)	AA_v (%)	Ca^{2+},[a] (%)
F0	–	0.0	0.0	0.0	0.0	0.0
F1	–	0.0	0.0	5.0	16.0	0.0
F2	5	1.4	0.0	5.0	16.0	0.0
F3	5	1.4	4.0	5.0	16.0	0.0
F4	20	1.4	4.0	5.0	16.0	0.0
F5	40	1.4	4.0	5.0	16.0	0.0
F6	–	–	–	5.0	16.0	10

[a]Expressed as percentage of CaO in the total aqueous solution.

A flame absorption spectroscopy instrument from Varian (Japan) was used to measure the content of calcium in peel fruits. The cell wall measurements were done with a fluorescence optical microscope from Leica (Barcelona, Spain) using the 40x (oil) lens. It has a digital high-resolution image capture system DFC450C (up to 5 megapixels) controlled through LAS software. The foliar feeding in the fields was done by using a 20 L agricultural piston backpack sprayer.

2.2. Synthesis of CaO NPs

The synthesis of the CaO NPs was adapted from literature (Ghiasi and Malekzadeh, 2012). Thus, 250 mL of an aqueous solution containing 175 mmol Ca^{2+} from $Ca(NO_3)_2 \cdot 4H_2O$ (Sigma Aldrich, Milwaukee, WI, USA) and was mixed with 250 mL of water in absence or in presence of 125 mmol of citric acid (Sigma Aldrich) and subsequently put it in the ultrasonic bath until complete solvation. Then, the solution was placed in a furnace until dryness. Next, the obtained solid was placed in a crucible and calcined at 900 °C for 5 h. After completion of the reaction, the white precipitate was collected and keep it in desiccator until its use. The optimal CaO nanoparticles (40 nm) showed a potential z and polydispersity index of −10.7 mV and 0.61, respectively. The amount of Ca was measured by absorption spectroscopy, previous nitric acid dissolution of the CaO NPs, and a 92.7% of theoretical expected Ca in CaO NPs was obtained.

2.3. Prepared products for the foliar feeding with CaO NPs

In order to study different effects on the selected fruits (*see Section* 2.5) several products were prepared or purchased as shown in Table 1. As can be seen, some of the products contains CaO NPs or bulk Ca^{2+} but some of the products were prepared in absence of Ca^{2+} or neither CaO in their formulations to be used as blank reference. In addition, some of the products contains citric acid, menadione sodium bisulfite (MSB) and amino acids from vegetal origin (AA_v), where at least 80% of the product corresponds to free amino acids, and were kindly donated by Agrostock S.A.

2.4. Selected fruits for the crop field studies

In this work, several fruit species were studied and can be found below.

Cherries: Four cherry varieties were tested along this work. Particularly, the varieties called Irnet, Prime Giant, Rita Grosa and Early Van Compact.

Apples: Two varieties of apples called Golden and Granny Smith were studied.

Peach: The variety called Maura.

Pears: The Spanish variety "Blanquilla" and the Ercolini variety.

Tomatoes: Raf, Bodar and Rosa were the three tomatoes varieties tested.

Grape: The table variety named Crimson.

Paraguayans: The three varieties tested in this work were the ones named Carioca, Platerino and Delfin.

Apricots: Tsunami and Tornado were the studied apricots.

2.5. Crop field studies

All the fruits studied in this work were collected from Fraga (Huesca, Spain). In order to do an adequate sampling, the studies were performed on four different blocks containing each one 5 trees for each treatment tested. The blocks used in these studies were separated between them with a block without treatment to avoid non desired contaminations. The formulations were applied by diluting 2.5 L of the product to 1000 L of water followed by the foliar feeding. In the case of the product F6, the dilution applied for foliar application was 5 L in 1000 L of water, as recommended by the manufacturers. The foliar feeding was performed as 1000 L/ha of crop field. The different studied fruits showed different number of treatments (see Table 2) but all of them were applied with separation of 15 days except for cherries, which the treatments were applied weekly due to the short mellowing time. Finally, the last treatment was sprayed 15 days before the collection of the fruits, except in the cherries where the last treatment was applied one week before the fruit collection. In all cases, 20 fruits per tree were collected for further analysis.

Table 2
Treatment schedule of the different studied fruits.

Fruit	Variety	Days before the fruit collection (Treatment)			
		1	2	3	4
Cherry	Irnet	21	14	7	–
	Prime Giant	21	14	7	–
	Rita Grosa	21	14	7	–
	Early Van Compact	21	14	7	–
Apple	Golden	60	45	30	15
	Granny Smith	60	45	30	15
Peach	Maura	45	30	15	–
Pear	Blanquilla	60	45	30	15
	Ercolini	60	45	30	15
Tomatoes	Raf	45	30	15	–
	Bodar	45	30	15	–
	Rosa	45	30	15	–
Grape	Crimson	45	30	15	–
Paraguayan	Carioca	45	30	15	–
	Platerino	45	30	15	–
	Delfin	45	30	15	–
Apricot	Tsunami	45	30	15	–
	Tornado	45	30	15	–

2.6. Analysis of calcium and cell wall width

2.6.1. Calcium analysis

In order to analyze the calcium content in the complete dry fruit, the procedure was as follows: first, the fruit peel was removed with a knife from the pulp and subsequently, with a razor blade, the residual pulp in the internal part of the peel was removed in order to avoid possible contaminations. Then, around 2 g of peel was weighed in a previously weighed crucible and place it in the muffle for 24 h at 70 °C to calculate the dryness of the fruit. Afterwards, the dry fruit in the crucible was calcined in a muffle for 2 h at 550 °C. Thus, the calcined fruit was dissolved in 10 mL of HCl 0.15 M, filtered and adequately diluted with water. Also, all the solutions contained 0.1% of La(III). Finally, the calcium was measured at 422 nm in the prepared solutions in a flame absorption spectroscopy instrument containing a Calcium hollow cathode lamp. In all the cases, an adequate calibration curve was prepared to interpolate the measurements of the samples.

2.6.2. Cell wall width analysis

The examination of the cell wall width in the external zone of the fruit peel was performed by cryostat with the microtome cut of the frozen fruit peel and the extremely thin slices obtained were stained. Thus, the stained samples were analyzed with an optical microscope at 40x oil submerged lens. Finally, the software ImageJ was used to measure the cell wall width in the different taken pictures.

3. Results and discussion

3.1. Synthesis and characterization of CaO NPs

The synthesis of the CaO NPs was studied in order to obtain different particle sizes. The synthesis was based in previous research performed by Ghiasi and Malekzadeh (2012) and the synthesis procedure is described in *Section* 2.2. The method is based in the thermal decomposition of calcium nitrate (Eq. (1)) in presence or absence of citric acid.

$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2 \quad (1)$$

When acid citric is introduced in the solution, calcium citrate can be formed and, then the $CaCO_3$ is formed after decomposition of the calcium citrate leading to a typical decomposition of $CaCO_3$ to CaO that occurs at 900 °C (Ghiasi and Malekzadeh, 2012; Mansour, 1994), which will be as shown in Eq. (2).

$$Ca_3(C_6H_5O_7)_2 \rightarrow 3CaCO_3 + 5H_2O + 9C(\text{as CO and/or } CO_2) \rightarrow 3CaO + 3CO_2 \quad (2)$$

In this work, three different procedures were tested and characterized. For this purpose, the first tested methodology (S1) was based in the use of citric acid (125 mmol) in water and mix with an aqueous solution containing 175 mmol of calcium nitrate tetrahydrate. Then, the mixture was placed in the ultrasonic bath until complete solvation and led to dryness at 120 °C. Afterwards, the white solid was calcined at 900 °C for 5 h. The second methodology (S2) consisted in

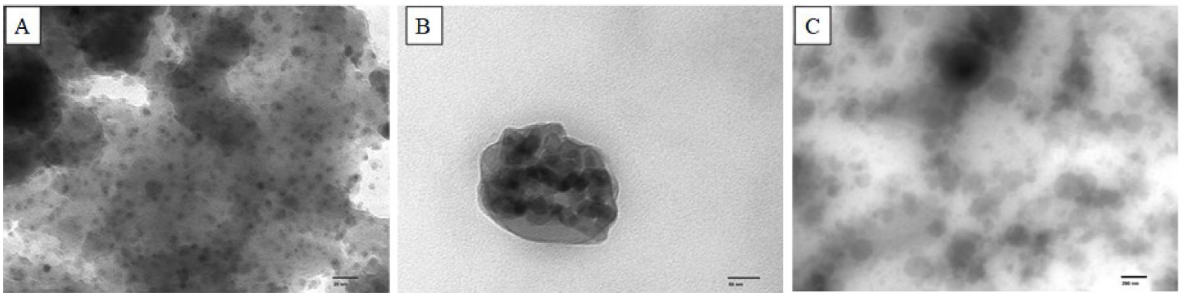

Fig. 1. SEM micrographies of the nanoparticles synthetized by the synthesis (A) S1 (∼5 nm), (B) S2 (∼25 nm) and (C) S3 (∼50 nm).

the elimination of the citric acid but all the other steps were maintained. The last tested methodology (S3) was based on the change in the temperature of the dryness step at 150 °C in order to reduce synthesis time. In all cases, similar white solids were obtained.

The morphology of the synthetized CaO NPs was investigated by TEM (Fig. 1). As shown, the three synthesis (S1, S2 and S3) showed spherical shapes but different particle diameters, from 5 to 50 nm. Particularly, the S1 CaO NPs (Fig. 1A) showed particles diameters around 5 nm while S2 (Fig. 1B) and S3 (Fig. 1C) CaO NPs displayed particle diameters of around 25 and 50 nm, respectively. No differences in size and calcium content were observed after 1 year of the synthesis. The three CaO NPs synthetized offered the possibility to study the effect of the size in the fruit calcium uptake as it would be explained in next chapters.

Another consideration that needs to be taken into account when nanomaterials are used in daily life is their influence in human health. In this sense, a recent review has constated that the cutaneous absorption of nanoparticles is negligible (Saweres-Argüelles et al., 2023). Therefore, the farmers can use this products without any problem.

3.2. Effect of different additives to improve the CaO uptake

As commonly known, the use of some additives that can chelate the ions improves the uptake by the foliar feeding of the leaves where the Ca^{2+} can move in the acropetal direction in non-deficient and in deficient Ca^{2+} plants (Millikan and Hanger, 1965). In this sense, the use of AA_v as Ca^{2+} chelating agent was tested. The addition of a second chelate agent (citric acid) was also studied since has been demonstrated its effectiveness for the stabilization of NP dispersions (Mudunkotuwa et al., 2012; de Sousa et al., 2013). On the other hand, MSB, a derivative of vitamin K3, which acts as plant metabolism stimulator (Borges et al., 2004) was included in the prepared formulations. As shown in Fig. 2, the effect of different formulations containing or not containing CaO NPs was studied on the fruit peel calcium (Fig. 2A) and cell wall width of the peel fruit (Figs. 2B and C). The composition of the different tested formulations (F0, F1, F2 and F3) are described in Table 1. Briefly, F0 was a control formulation containing only water, F1 contains AA_v and MSB, F2 was as F1 but containing also CaO NPs and finally, F3 was as F2 but also containing citric acid. The content of CaO NPs in the formulations was maintained at 1.4% since higher concentrations led to precipitation. In any case, formulations containing 1.4% were stable more than one year.

As can be observed in Fig. 2A, the effect of the addition AA_v and MSB led to a reduction in the content of fruit peel calcium in all the tested fruits (golden apple, prime giant and irnet cherries and crimson grapes). This behavior could be explained by the increase in the movement of Ca^{2+} ions through the fruit due to the presence of the chelate agent and the metabolism stimulation. Probably, the presence of these two compounds in the fruit and the absence of extra Ca^{2+} reorganized the distribution of the Ca^{2+} thanks to the transport through the acropetal. However, no significant changes were found in the cell wall width where also, a small increase in the width was found practically for all the tested fruits.

On the other side, when the fruits are feed up with F2 containing CaO NPs an increase in the fruit peel calcium content compared with F1 was found. However, similar results to those found for the F0 fruits were observed. This increase or similarity of calcium content in the tested fruits showed that the uptake of CaO NPs in the fruits occurs by foliar feeding. Also, some small increases in the cell width were observed for golden apple and crimson grapes. These results are also more evidenced in the fruits treated with formulation F3 where the CaO NPs were stabilized with citric acid. As can be observed, in Fig. 2A, the content of calcium in the fruit peel was increase drastically in the prime giant cherries and crimson grapes and increased for the irnet cherries. However, no increase was observed for the golden apple fruits. In any case, all the tested fruits showed small increases in the cell width, even in the golden apple studies.

Fig. 2C shows the cell width of golden apples for F0 and F3, as can be deduced from the pictures the increase in the cell wall width is enough big (up to 3 μm in the average).

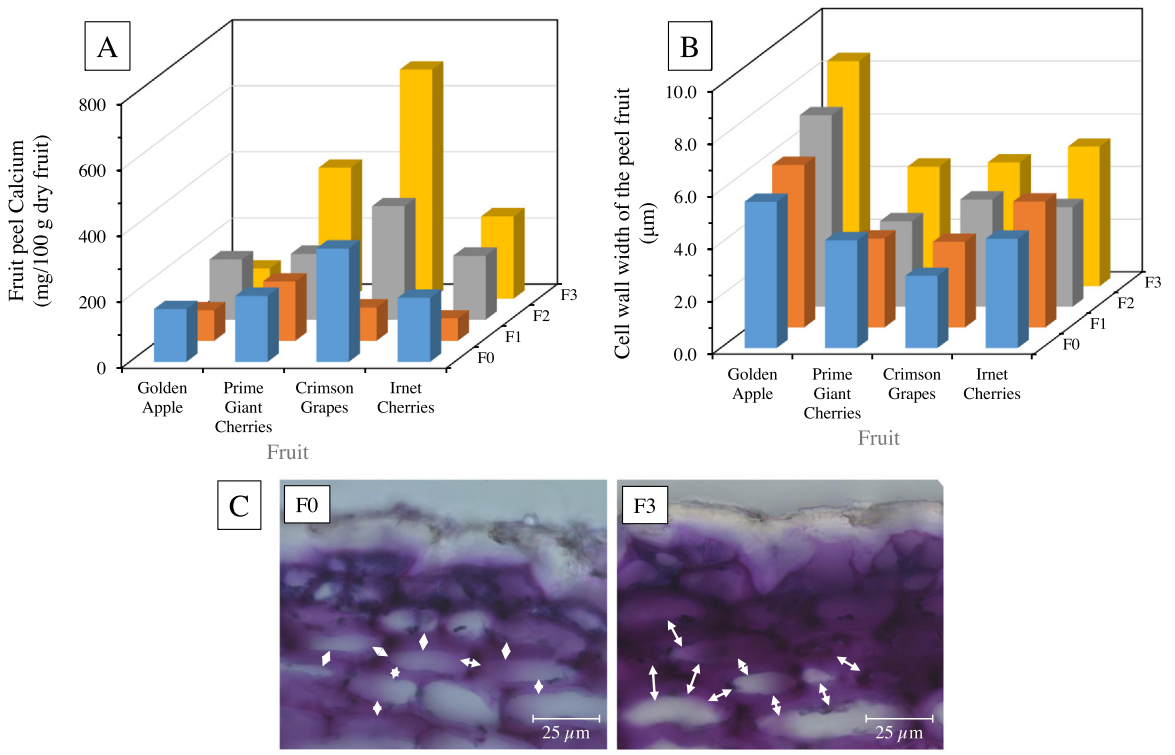

Fig. 2. Effect on fruit peel calcium (A) and cell wall width (B) using different formulations (F0, F1, F2 and F3, see Table 1). In addition, the pictures of the wall cell width in the peel of Golden apples is shown (white arrows indicate the cell wall width).

3.3. Study of the NPs size on the incorporation of CaO NPs to the fruits

Other important parameter, which should be carefully study, is the NP size. In this sense, it is known that the particle size affects the properties of the NPs and therefore, the particle size could modify the calcium plant uptake. For this purpose, in this work, the effect of the NP size was study at three levels (5, 20 and 40 nm) as shown in Fig. 3. The synthesis of the CaO NPs with different diameter size is described in previous sections (*See Sections* 2.2 *and* 3.1). As shown in Fig. 3A, the amount of Ca^{2+} in the fruit peel increases when the 20 nm CaO NPs were used instead the 5 nm in both fruits (Tsunami apricot and Prime giant cherry). However, when the CaO NPs used was increased in particle dimeter to 40 nm only the Tsunami apricot showed a significant increase although not as drastic as from 5 to 20 nm increases. In the case of the Prime giant cherry, similar results were found for 20 and 40 nm NPs. In the case of the cell width, no differences for the Tsunami apricot were observed, while a significant increase of the cell width from 5 to 20 and 40 nm was evidenced (Fig. 3B).

The results evidenced for these fruits are contradictory with the idea of smaller diameter sizes will led to better calcium uptakes. However, in other disciplines was observed that the NPs with diameter sizes higher than 10 nm showed better interactions with other molecules. This behavior could be explained by the large curvature of the small particles that might led to fewer interactions with the uptake of the surface released Ca^{2+} from the CaO NPs (Horie et al., 2016; Khine et al., 2022). Therefore, as the size of the CaO NPs increases, it is easier to find positions to interact with transport molecules (aminoacids, MSB and citric acid, among others) and, therefore higher number of active sites could lead to an easier incorporation to the fruit peel (Lv et al., 2012). Nevertheless, when the particle diameters where more or equal to 20 nm, the observed increases in calcium content were smaller. Therefore, 40 nm (for its faster synthesis) was used for the following studies.

3.4. Comparison of the prepared product containing CaO NPs with a commercial Ca^{2+} product

The product F5, containing CaO NPs of 40 nm was compared with a commercial product containing Ca^{2+} (F6). For this purpose, the Tsunami apricot and the Prime Giant cherry were treated with F5 and F6 products. As can be observed in Fig. 4, both products showed similar results for the fruit peel calcium and a small decrease in the cell wall width for the F6 product, more evidenced in Prime Giant cherry. Although, these results showed that the improvement in the use of CaO NPs against the bulk Ca^{2+} is limited, since similar results were obtained, it needs to be remarked the differences in

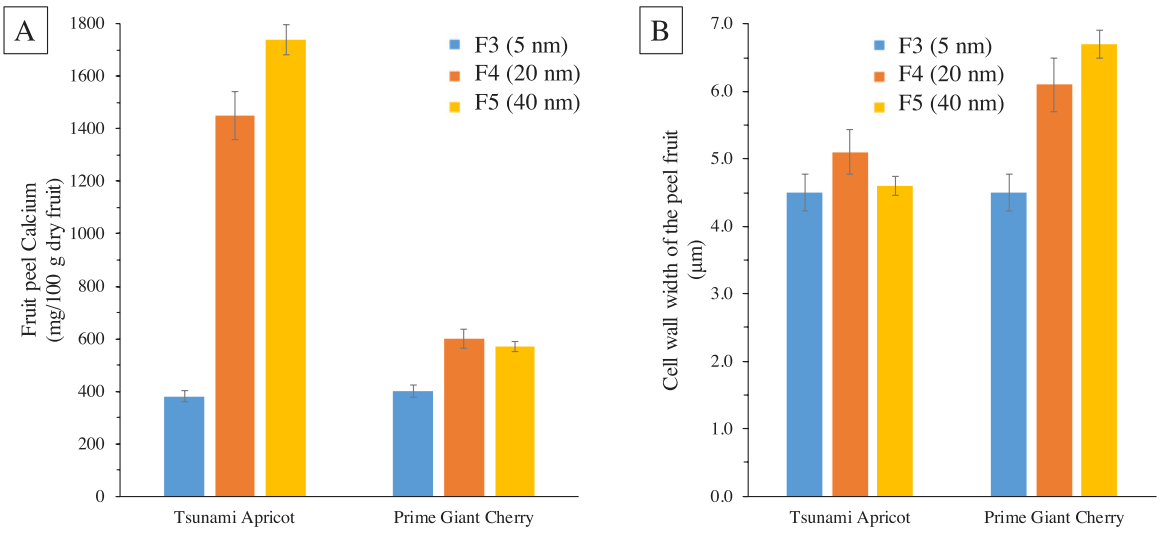

Fig. 3. Effect of NP size (formulations F3 (5 nm), F4 (20 nm) and F5 (40 nm), see Table 1) on fruit peel calcium (A) and cell wall width (B).

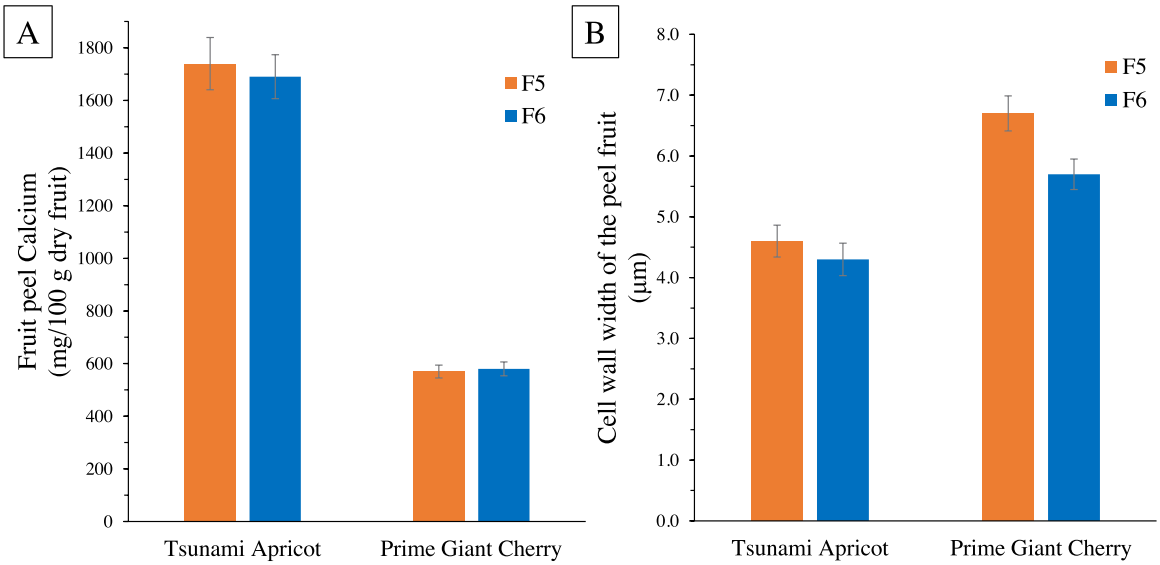

Fig. 4. Comparison of the optimal formulation (F5) versus a commercial formulation containing Ca^{2+} (F6) for the fruit peel calcium (A) and cell wall width (B).

the amount of Ca used by hectare. In this sense, product F5 was using around 35 g of CaO ha^{-1} while the F6 was using 700 g CaO ha^{-1}. Therefore, the F6 product is using 20 times more CaO to obtain similar uptake results, demonstrating the high uptake ratio of the CaO NPs by plants compared to bulk Ca^{2+}. These results also showed that the CaO NPs, citric acid, MSB and AA_v are not only favoring the absorption of CaO NPs and its metabolization, also the products are improving the transport and distribution of Ca^{2+} through the xylem vessels. In addition, as demonstrated by Cheniclet et al. (2005), it is not necessary the use of high amount of Ca^{2+} to increase the intake of Ca^{2+} by the fruit.

3.5. Application of the optimized products to different fruit species

Finally, the formulation F5 was tested with several different fruits and compared with F0. As shown in Fig. 5, the results evidenced the increase in calcium content in peel for all the studied fruits. In addition, in some cases as cherries and apricots the increases are up to 3 times more Ca^{2+} in the fruit peel. This result showed a good translocation of the uptake Ca^{2+} from the CaO NPs through the fruit.

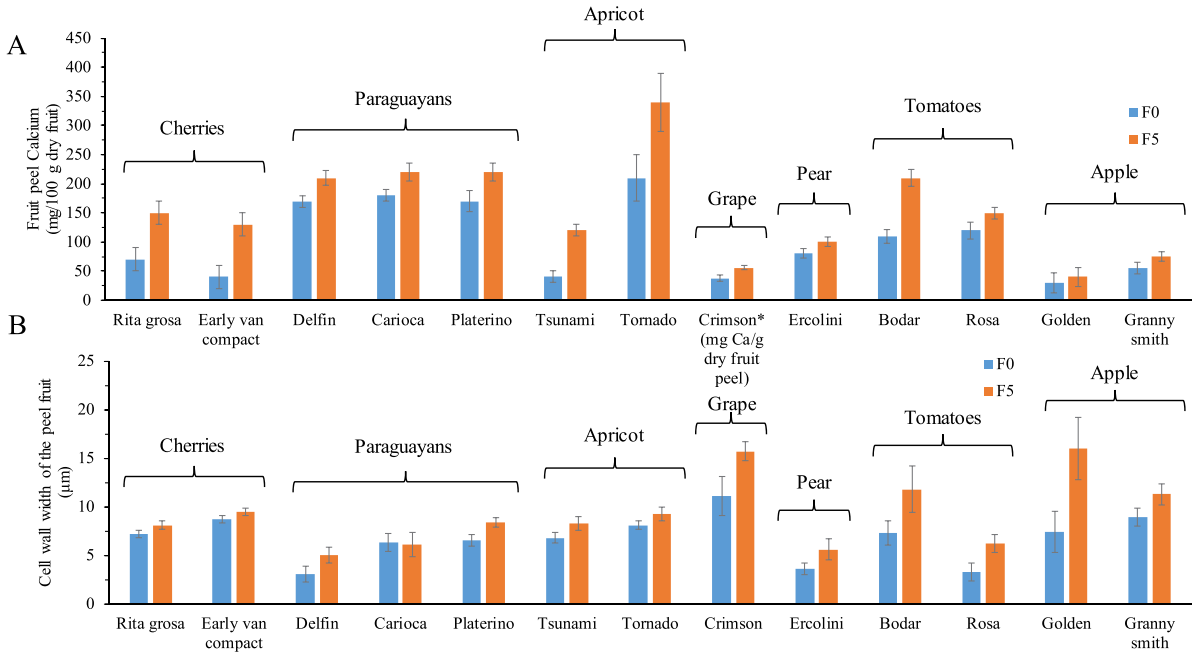

Fig. 5. Comparison on fruit peel calcium (A) and cell wall width (B) for different fruits using the formulations F0 and F5.

In the case of the cell wall width, similar results can be observed in Fig. 5B were all the studied fruits showed higher cell wall widths for the F5 treatment compared to the F0 treatment. However, the higher differences between the F0 and F5 treatments were found for Crimson grapes (1.4 times higher) and Golden apple (2.1 times higher).

4. Conclusions

In the present work, the use of CaO NPs as foliar nanofertilizer for fruits has been demonstrated by its study directly in field on different fruits (cherries, apples, peachs, pears, tomatoes, grape, paraguayan and apricots).

In order to assay the synthetized NPs different formulations were prepared. Firstly, the effect of the chelating agent (citric acid) was tested. In this sense, it was observed that the CaO NPs in presence of citric acid improve the amount of Ca^{2+} as well as the cell wall width on the peel fruit. In addition, the effect of the NP size was examined showing the best effects for the large diameter NPs (25–40 nm). Similar results (Ca^{2+} and cell wall width in peel fruit) were found for commercial products containing bulk Ca^{2+} (20 times more) and the formulations of this works, which demonstrates that the CaO NPs administrated by foliar feeding are more effectively included in the peel fruit than the bulk Ca^{2+}.

In conclusion, in this work has been demonstrated that the use of CaO NPs is an ecological alternative for fertilizers due to its high availability rate, low material consumption, easy preparation and low cost (the actual cost of preparation of these formulations at laboratory is 15 €/Kg of reagents and at industry level the cost is around 0.25 €/Kg of raw materials and 1 € extra/kg regarding personnel cost). On the other side, the uptake of the NPs by plants is not clear, and therefore it is hard to state that these NPs can be present in the final fruit and affect human health. In this case, the increment in Ca^{2+} content in peel and in cell width can be understand as an adequate processing of the NPs by the plants, converting the CaO NPs in a more available source of calcium, limiting the amount of CaO NPs in the final fruit.

Therefore, the employment of these type of nanomaterials could open new avenues in the use of nanofertilizers in agriculture, improving the production rate and helping the supply problem due to the global uprising in population.

CRediT authorship contribution statement

Enrique Javier Carrasco-Correa: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Òscar Mompó-Roselló:** Methodology, Investigation, Writing – original draft. **Ernesto Francisco Simó-Alfonso:** Conceptualization, Methodology, Investigation, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request

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