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Proceeding Paper

Monitorization of Mineral Content and Location after 3 Months of Storage of Naturally Enriched Potato (*Solanum tuberosum* L.) with Calcium †

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Abstract: Potato (*Solanum tuberosum* L.) is one of the most important staple food crops and one of the most consumed worldwide. As such, is a suitable food matrix for biofortification studies, namely with Ca, as it is an essential mineral for plant growth and development, being required for several structural issues. In this context, this study aimed to monitor the mineral content and location of Ca and other essential minerals (K, P, S, Fe, and Zn) and assess some quality parameters (color of the pulp, total soluble solid and dry weigh content) in tubers of *Solanum tuberosum* L. (Agria variety) after three months of storage, submitted to a Ca biofortification process with four foliar sprays with three concentrations of calcium nitrate (0.5, 2 and 4 kg.ha^{-1}) and two concentrations of calcium chloride (3 and 6 kg.ha^{-1}). It was found out that in most treatments, Ca, K, P, S, Fe, and Zn have higher content in the epidermis region and that control tubers showed a lower dry weight content compared to the biofortified ones. Moreover, after three months of storage, naturally enriched tubers maintain a preferential accumulation of Ca in the epidermis region (as seen in harvest) and showed a decrease in the dry weight content in control and biofortified tubers (compared to harvest data). Additionally, no significant differences were observed in the colorimetric parameters of pulp tubers and in the total soluble solid content, presenting similar data to the harvest ones. In conclusion, the storage process of biofortified tubers affected a quality parameter—dry weight content—being relevant for industrial processing and a criterion for potato tubers classification. In this context, only $Ca(NO_3)_2$ 2 kg.ha^{-1}, $CaCl_2$ 3 and 6 kg.ha^{-1} treatments presented suitable for industrial processing after 3 months under storage conditions.

Keywords: calcium biofortification; natural enrichment with calcium; postharvest analysis; *Solanum tuberosum* L.

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1. Introduction

Worldwide population is expected to reach 9 billion by 2050 [1] and to feed the future population, food production must increase by 25 to 70% [2]. As such, it's important to reduce the post-harvest food losses, to avoid waste which are especially high in perishable crops. Potato is a perishable crop and correct post-harvest management is required to reduce food losses [3]. In fact, potato is considered the 3rd most important (non-grain) food crop worldwide and more than a billion people around the world eat potato [4], being widely grown [5]. In Portugal, consumption per capita is around 85 kgs of potato per year [6]. As a perishable commodity, to allow the later use of potatoes, it's important to understand the factors that affect potatoes storage, to ensure a correct storage for 3 to 10 months. Therefore, potato tubers have an active metabolism during post-harvest, leading to losses of mass and quality. The loss of quality during storage depends on storage conditions and on culture management since early stage (seed storage), during growth and harvest [5]. Due to the metabolic process of respiration, potatoes must be under refrigeration or cool temperatures during the post-harvest stage, to slow down this process and maintain tuber quality [7]. Additionally, considering that potato tubers is mainly water (about 80%) and dry matter (around 20%, mostly starch) [8], due to low external vapor pressure or even relative humidity can lead to losing the internal water and starting to shrink [7]. Therefore, two of the major causes of post-harvest losses are the water loss and sprouting (that can decrease nutritive quality of potato tubers) [7].

Nevertheless, the lack of essential nutrients in individuals who are attaining healthy levels of calories are a major world problem [9], so it's important to have more food production and with quality (able to provide the daily nutritional dietary requirements). In this context, the aim of this study is to monitor the mineral content and location of Ca, K, P, S, Fe and Zn and analyze important quality parameters (namely, color of the pulp, total soluble solids and dry weight content) in tubers of *Solanum tuberosum* L. (Agria variety) after three months of storage (under low temperatures), submitted to a Ca biofortification process with four foliar sprays with three concentrations of calcium nitrate (0.5, 2 and 4 $kg.ha^{-1}$) and two concentrations of calcium chloride (3 and 6 $kg.ha^{-1}$), in order to verify if the storage process as any effect on mineral content and location on tuber tissue and in quality parameters.

2. Materials and Methods

2.1. Biofortification Intinearary

The experimental potato-growing field used to growth Agria variety (*Solanum tuberosum* L.) is described in [10]. After harvest, potatoes were stored in cold rooms between 6–8 °C for 3 months.

2.2. Mineral Content in Potato Tissues through Fluorescence Detection

Content and location (in three regions-center, middle region, and peel) of Ca, K, P, S, Fe and Zn in the tissues of tubers after 3 months under storage conditions were determined using the μ-EDXRF system (M4 Tornado™, Bruker, Germany), as previously described in [10], after being sliced transversely (with 4 mm) at the equatorial region and dried at 60 °C. The values of the minerals content were obtained through the average of four readings taken by the device.

2.3. Quality Parameters

Dry weight and total soluble solids content were performed considering four randomized tubers as described in [10]. Colorimetric parameters, using fixed wavelength, followed [11] were carried out in the pulp of four randomized fresh tubers.

3. Results

After three months of harvest, the mineral content and location of tuber tissues under storage conditions were assessed (Figures 1 and 2).

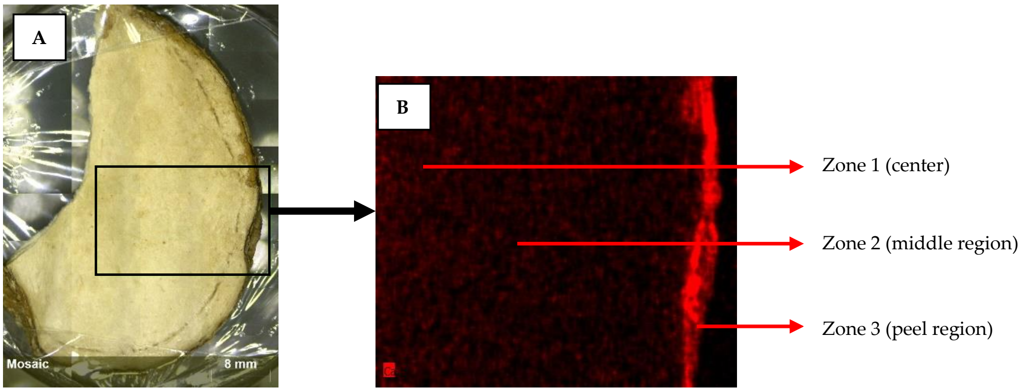

Figure 1. Macroscopic visualization of dry tuber (**A**) and tuber sections (from center to epidermis, 1–3) from the equatorial region (**B**) of *Solanum tuberosum* L., cv. Agria, 3 months after harvest (under storage conditions).

Regarding the most treatments, Ca, K, P, S, Fe and Zn showed a higher content in the epidermis/peel region (zone 3) (Figure 2). Calcium showed a higher content relatively to control, in $CaCl_2$ 6 kg.ha^{-1} and $Ca(NO_3)_2$ 4 kg.ha^{-1} treatments, respectively. Additionally, $Ca(NO_3)_2$ 0.5 kg.ha^{-1} treatment has higher content of Ca in zone 1—center region. In the epidermis region, K presented a higher content in $Ca(NO_3)_2$ 4 kg.ha^{-1} and $CaCl_2$ 6 kg.ha^{-1} treatments, regarding control. Regarding P, this treatment showed oscillations, despite all the remain treatments (control included), had a similar distribution in tuber tissues. Yet, as seen in Ca, also in P, $Ca(NO_3)_2$ 0.5 kg.ha^{-1} treatment showed a higher content in center region and $CaCl_2$ 6 kg.ha^{-1} treatment in the epidermis. Moreover, regarding S, in zone 3, $CaCl_2$ 6 kg.ha^{-1} treatment demonstrated a high levels compared to other treatments and control. Additionally, as seen in P, in S despite some oscillations the remain treatments showed a similar distribution in the three zones. Iron showed the highest contents in zone 3, both in control and in biofortification treatments, compared to the remain tuber tissue regions. However, only $Ca(NO_3)_2$ 4 kg.ha^{-1} treatment showed a higher content than control. As observed in S and Fe, also Zn showed higher contents in zone 3. Yet, only $Ca(NO_3)_2$ 4 kg.ha^{-1} and $CaCl_2$ 6 kg.ha^{-1} treatments presented higher levels than control. Verifying a higher Zn content (in the epidermis region) in $Ca(NO_3)_2$ 4 kg.ha^{-1} treatment.

Some quality parameters were determined in Agria variety tubers after three months under storage conditions. Dry weight, total soluble solids, and colorimetric parameters (L, a* and b*) were analyzed and no significant differences were detected between treatments (Table 1). Additionally, control showed the lowest dry weight content and $Ca(NO_3)_2$ 2 kg.ha^{-1} treatment showed a higher dry weight content and a lower a* parameter. Regarding total soluble solids, L and b* parameter, $CaCl_2$ 6 kg.ha^{-1} treatment showed a higher values compared to the remain treatments.

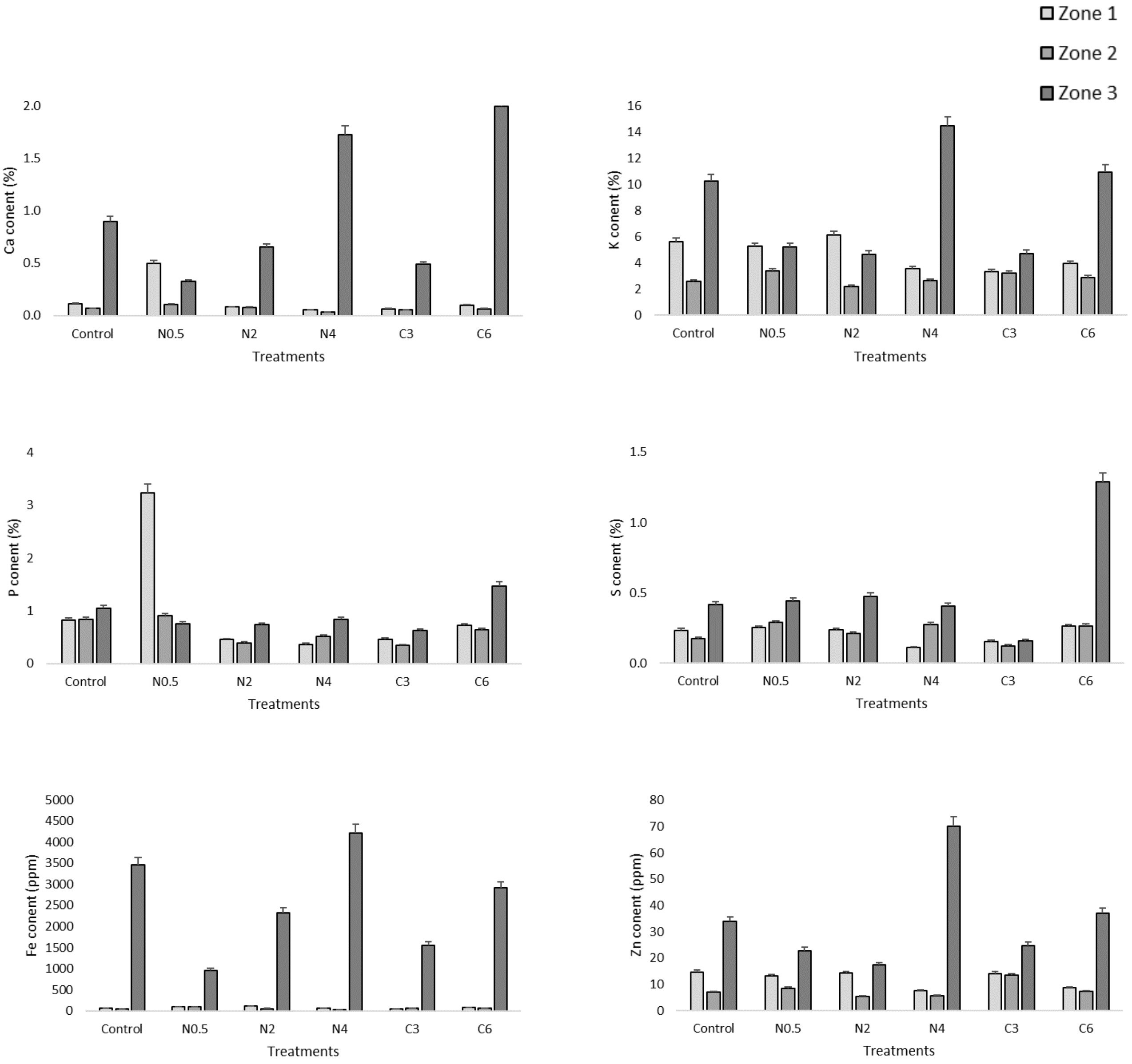

Figure 2. Average of Ca, K, P, S, Fe and Zn content of 3 replicates of three independent series (from center to epidermis, 1–3) in tubers of *Solanum tuberosum* L., cv. Agria, 3 months after harvest (under storage conditions). Foliar spray was carried out with three concentrations of $Ca(NO_3)_2$ (0.5 (corresponding to N0.5), 2 (corresponding to N2) and 4 (corresponding to N4) $kg.ha^{-1}$) and two concentrations of $CaCl_2$ (3 (corresponding to C3) and 6 (corresponding to C6) $kg.ha^{-1}$). Control was not sprayed.

Table 1. Mean values ± S.E. (n = 4) of dry weight, total soluble solids, and colorimetric parameters (L, a* and b*) in tubers of *Solanum tuberosum* L., cv. Agria, 3 months after harvest (under storage conditions). There were no significant differences, of each parameter, between treatments ($p \leq 0.05$). Foliar spray was carried out with three concentrations of $Ca(NO_3)_2$ (0.5, 2 and 4 $kg.ha^{-1}$) and two concentrations of $CaCl_2$ (3 and 6 $kg.ha^{-1}$). Control was not sprayed.

Treatments	Dry weight (%)	Total Soluble Solids (°Brix)	Colorimetric Parameters		
			L	a*	b*
Control	18.3 ± 0.75	5.17 ± 0.14	54.4 ± 1.00	−2.53 ± 0.19	20.5 ± 0.41
$Ca(NO_3)_2$ (0.5 $kg.ha^{-1}$)	19.8 ± 0.39	5.15 ± 0.12	55.7 ± 1.56	−2.74 ± 0.16	21.5 ± 0.89
$Ca(NO_3)_2$ (2 $kg.ha^{-1}$)	20.8 ± 0.60	5.17 ± 0.14	56.3 ± 1.34	−3.08 ± 0.24	20.9 ± 0.23
$Ca(NO_3)_2$ (4 $kg.ha^{-1}$)	19.8 ± 0.84	5.33 ± 0.27	54.8 ± 0.85	−2.51 ± 0.22	20.9 ± 0.24
$CaCl_2$ (3 $kg.ha^{-1}$)	20.6 ± 0.34	5.33 ± 0.14	54.2 ± 0.02	−2.54 ± 0.13	20.3 ± 0.21
$CaCl_2$ (6 $kg.ha^{-1}$)	20.3 ± 0.30	5.67 ± 0.36	56.8 ± 0.83	−3.07 ± 0.09	22.2 ± 0.27

4. Discussion

To allow the later use of potatoes, storage plays a vital role to ensure year-round supplies (both for fresh consumption and for the processing industry) [12]. Yet, not only good management during the post-harvest stage (cool temperatures or even refrigeration) are important, as well as the maintenance of the quality of the tubers, mainly in terms of nutrients—nutritive quality [7]. As such, after three months under storage conditions (under low temperatures), the mineral content and location of some mineral elements were carried out (Figure 2). In our previous research, carried out at harvest [10] we observed that for Agria variety, the highest contents of Ca were obtained close to the epidermis, concluding that Ca deposition in tubers tissues prevailed in the peel/epidermis region independently of the treatments applied (regardless control, $Ca(NO_3)_2$ 4 $kg.ha^{-1}$ and $CaCl_2$ 6 $kg.ha^{-1}$ treatments). After three months of storage (Figure 2), the data obtained suggest that Ca accumulation remained in the same regions of the tuber tissue verified at harvest [10]. Yet, compared to harvest data [10], Ca content (Figure 2) in control, $Ca(NO_3)_2$ 4 $kg.ha^{-1}$ and $CaCl_2$ 6 $kg.ha^{-1}$ treatments, showed an increase in the epidermis region of the tubers (zone 3). It was also verified in zone 2, equal values in control, and a decrease in the biofortification treatments and in center region (zone 1). Also, there was an increase in the Ca content in control and a decrease in the higher treatments applied with calcium nitrate and calcium chloride. Comparison of data obtained at harvest [10] and after three months of storage (Figure 2) suggest that there was a migration of Ca to the epidermis of the tubers, probably due to the beginning of sprouting in the tubers (that implies cellular growth) and consequentially, minerals stored/accumulated in the tuber can be transported to the sprout leading to decrease in the inner regions of the tuber (zone 1 and 2). In fact, with the onset of sprouting, tubers turn into a source organ for the growth of the developing sprout [13]. Additionally, it's important to denote that Ca plays a vital role in maintaining the structural integrity of cell walls and in intracellular adhesion [14] (being implicated in cell growth) and that sprouts, and Ca have a close relationship in tubers, being sub-apical necrosis on sprouts an indirect indicator of low calcium [15]. Also, this tendency verified in our data, of a greater concentration of Ca in the peel compared to other tissues, was already mentioned [16]. Regarding the remaining elements assessed (K, P, S, Fe, and Zn) with a greater concentration prevailing in epidermis/peel region than in flesh regions (zone 1 and 2) (Figure 2), as also reported by [17]. Yet, was also reported by [17] that the most phloem mobile elements (phosphorus, sulfur, and potassium) remain in greater concentration in the tuber flesh, assuming that was the reason why these elements showed similar distributions (despite some oscillations) in the three zones analyzed. However, in most treatments, the highest content (as seen in Ca) was obtained in zone 3, also suggesting that (after three months of storage) it's due to tubers turning into a source in the sprouting process [13]. Considering Ca, Fe, and Zn, they were found out in greater quantities in the epidermis region than in the middle and center tissues (quite lower contents), probably due to being less immobile [18], as such this preferential location can be associated with the fact that these elements are delivered (at least) by direct movement across the epidermis during the developing of the tuber [17].

Despite potato tubers being stored at low temperature (mainly to inhibit rapid sprouting and decay) [19] sprouting can occur (as occurred in our study). In fact, when the onset of sprout growth, can adversely affect not only the nutritional characteristics as the processing characteristics of the tubers [20], as such also some quality parameters were carried out (Table 1). Although there were no significant differences in dry weight, total soluble solids, and colorimetric parameters, overall, there was a decrease compared to harvest data [10,21]. Regarding dry weight content, only $Ca(NO_3)_2$ 2 $kg.ha^{-1}$, $CaCl_2$ 3 and 6 $kg.ha^{-1}$ treatments presented suitable for industrial processing (most be higher than 20%) [22], after 3 months under storage conditions and this is probably due to the fact that vegetables that have undergone treatments with Ca (usually calcium chloride) along with low temperatures in storage, have the potential to improve not only the nutritional quality of vegetables (considering that Ca can increase postharvest shelf life due to the role that as in maintaining cell wall stabilization and integrity), but also to reduce the respiration rate, which that has an effect in vegetable preservation/conservation [23,24].

Nevertheless, regarding most of the treatments, in soluble sugars (mostly, sucrose, glucose, and fructose) content there was a decrease compared to harvest data [10] (mainly in control tubers). Yet, regarding $Ca(NO_3)_2$ 4 $kg.ha^{-1}$, $CaCl_2$ 3 and 6 $kg.ha^{-1}$ treatments there was a higher content of total soluble sugars, being in accordance with [19], reporting that under low temperature storage soluble sugars content increase due to the function of granule-bound starch synthase 1, beta-amylase, invertase inhibitor and fructokinase [19]. Considering color (colorimetric paraments) is an important factor for consumers, affecting its acceptability [25]. Regarding L parameter, there was a decrease compared to harvest data [10], showing a less brighter tubers. Yet was possible to verify a mix of greenish (negative a* parameter) and yellowish tone (positive b* parameter).

5. Conclusions

Through the monitorization of mineral content and location of Ca, K, P, S, Fe, and Zn and the assessment of some quality parameters (color of the pulp, total soluble solid and dry weigh content) in *Solanum tuberosum* L. (Agria variety) after three months of storage, submitted to a Ca biofortification process with four foliar sprays with calcium nitrate or calcium chloride was possible to conclude that the deposition in tubers tissue of Ca, K, P, S, Fe and Zn prevailed close to the epidermis /peel region. Furthermore, there was a dry weigh content decrease in control and all the biofortified treatments (compared to harvest), concluding that only $Ca(NO_3)_2$ 2 $kg.ha^{-1}$, $CaCl_2$ 3 and 6 $kg.ha^{-1}$ treatments presented suitable for industrial processing after 3 months stored under low temperatures. Additionally, there wasn't a clear tendency regarding total soluble solids due to opposite behaviors (increase in half of the treatments and decrease in the other half).

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