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Micronutrient Foliar Fertilization for the Biofortification of Raw and Minimally Processed Early Potatoes

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Abstract: Agronomic fortification with microelement as well as macronutrients has been used in recent years with increasing frequency to improve the nutritional quality of plant products for human consumption. Here the influence of pre-harvest foliar micronutrients fertilization (Micro+) including B, Cu, Fe, Mn, Mo and Zn compared to control (Micro−) on mineral profiles of raw and minimally processed potatoes of cv. Bellini was investigated. The mineral profile was analyzed on raw tubers at harvest and on minimally processed potatoes after 0 and 12 days of storage at 4 ± 1 °C. Preliminary results showed that micronutrients fertilization improved mineral composition of raw potatoes, through an increase in tuber concentrations of Fe (+70%) and Zn (+27%), but also of N (+23%), and Mn (+18%). The increased concentrations of minerals in micro-fertilized raw potatoes led to a better concentration in micro-fertilized minimally processed potatoes, even if some minerals were lost in processing, presumably due to skin removal. The reduction was particularly evident in both Micro− and Micro+ samples for Fe (−29%) and Ca (−17%). However foliar micronutrient fertilization markedly improved the Fe and Zn contribution that a 200 g serving of potatoes can give to current recommended nutrient intakes (RNIs) both in raw and minimally processed potatoes. Storage for 12 days did not alter the mineral profile of the tubers. Observations of the mineral profiles of the studied samples suggest that the application of foliar microelement-containing solutions was able to fortify both raw and minimally processed potatoes.

Keywords: *Solanum tuberosum* L.; fortification; minerals; tubers; minimal processing

1. Introduction

Potato (*Solanum tuberosum* L.) is the third largest food crop in world, with an annual global tuber production of around 370 Mt [1]. In the Mediterranean basin, the million hectares dedicated to its production yields ~25 Mt of tubers [1], with most of the crop targeted at the "early" crop market [2,3]. According to the UNECE standard FFV-30/2001, early potatoes are those which are harvested prematurely, so that the skin can be removed without peeling. "Early" potato tubers are a proven source of vitamin C, vitamin B6 and essential minerals including mainly potassium, but also magnesium, phosphorus, manganese, zinc and iron to a lesser extent [4]. Essential mineral elements are a class of nutritionally important nutrients which play crucial roles in various biological processes for both plants [5] and human beings [6]. For humans, deficiencies in these elements can cause metabolic disorders and organ damage, leading to acute and chronic diseases and even death [7]; so an adequate dietary intake of mineral elements is necessary for human health and wellness.

Unfortunately, mineral malnutrition is still a common problem worldwide and considered one of the most important global challenges for human nutrition [8]. Notably, the micronutrient contents of several crops, including vegetables [9], have declined due to a number of factors, including the use of high yielding crop varieties [10], the continuous mining of soil micronutrients by crops and no replenishment by fertilization, and decreased use of farmyard manure compared to chemical fertilizers [11]. In particular in Mediterranean-type soils, there are worrying signs of the limited availability of indispensable micronutrients, attributable to their low organic matter [12], high pH and calcium carbonate content that can result in Fe, Mn and Zn-deficiency problems [13]. Given the nutritional importance of potato, it makes sense to consider biofortification as an important task for the potato valorization. Biofortification, in other words, the enrichment of the edible parts of plants with mineral elements, can be attained through either genetic (breeding), agronomic means, or both, (e.g., through the application of proper mineral fertilizers, complementary to the main fertilization programs) [14]. The considerable variation existing between genotypes in the concentration of mineral elements (copper, iron, manganese, zinc) in potato tubers [15–19], suggests that micronutrient content of potatoes can be improved through breeding, although genetic variation with tetraploid genotypes is more complex than with diploid ones [20]. To support ongoing efforts in genetic biofortification, agronomic fortification with micronutrients has been promoted in species such as wheat, rice, maize and sorghum as a cost-effective and fast approach to fight micronutrient malnutrition [11,21]. To date, only limited data are available on agronomic fortification of potatoes, for example, [22,23], most of all regarding Andean potato genotypes [24–26]. Information on agronomic fortification of potatoes in the Mediterranean area is lacking, particularly regarding novel products. Among them, minimally processed potatoes are increasingly preferred by consumers for their high added value and ease of use, both at home and in the food service industry [27]. Minimally processed potatoes are peeled and packed under vacuum or modified atmosphere, are ready-to-cook and have a limited shelf-life of 5–7 days at 4–5 °C, due to microbiological, sensory and nutritional deterioration [28]. In recent decades, consumer demand for convenient, ready-to-use or ready-to-eat potato products, with a safe and fresh-like quality, has increased. A balanced fortified mineral profile of minimally processed tubers could mean a good chance for the food industry to increase market sales with a product able to fully respond to the demand for healthy foods by modern consumers. For these reasons, we carried out this preliminary research with the aim to study the possibility of agronomic fortification (throughout pre-harvest micronutrient foliar fertilization) of raw and minimally processed "early" tubers from a Mediterranean potato crop.

2. Materials and Methods

2.1. Field Experimental Site, Climate and Soil

A field trial was carried out during 2015 on the coastal plain south of Siracusa (37°03′ N, 15°18′ E, 15 m a.s.l.), a typical area for early potato cultivation in Sicily. The climate is semi-arid Mediterranean, with mild winters and commonly rainless springs; this permits growing potato in a winter–spring cycle (from December–January to May). The rainfall and air temperature were recorded during the period of the trial on a CR10 data logger (Campbell Scientific Inc., Loughborough, UK) connected to a meteorological station sited 50 m away from the experimental field. Specific meteorological conditions during the field trials are listed in Table 1.

Compared to the 30-year average, higher maximum temperatures (+1.2 °C), lower minimum temperatures (−3.4 °C) and twice the rainfall (500 mm vs. 240 mm)—accounting for roughly 70% in February and March—were recorded during the field trial.

The soil, moderately deep, classified as Vertic Xerochrepts type [30] had a history of potato/globe artichoke, wheat, broad bean rotation of more than 10 years, and was analyzed before the start of the experiment (early October) according to procedures that were approved by the Italian Society of Soil Science [31]. Three soil samples per plot were collected, with a 4 cm (i.d.) core auger to a depth

of 30 cm, fractured into aggregates by hand pressure, air-dried and sieved (<2 mm). The soil with pH 7.5, had the following composition 12% sand (2–0.02 mm), 30% silt (0.02–0.002 mm), 58% clay (<0.002 mm) a moderate level of total N (0.13%), available P_2O_5 (28 mg kg^{-1}) and exchangeable K_2O (180 mg kg^{-1}) and low level of total $CaCO_3$ (3.3%). In addition, the soil had a moderate electrical conductivity (1.07 mS cm^{-1}) and a high cation exchange capacity (40.8 mequiv. 100 g^{-1}) and it was well endowed in organic matter (2.6%) and macro and micronutrients, K (352 mg kg^{-1}), Mg (610 mg kg^{-1}), Ca (6.660 mg kg^{-1}), Na (368 mg kg^{-1}), Fe (39.0 mg kg^{-1}), Mn (20.7 mg kg^{-1}), Cu (11.9 mg kg^{-1}), Zn (2.7 mg kg^{-1}), B (2 mg kg^{-1}) and Mo (0.2 mg kg^{-1}).

Table 1. Monthly maximum and minimum air temperatures and total rainfall during the potato growing season and long-term period 1977–2006 [29].

	Year	Dec	Jan	Feb	Mar	Apr	May
Max t (°C)	2015	18.4	16.8	14.8	17.9	21.9	28.7
	1977–2006	16.7	15.4	16.2	17.7	20.2	24.3
Min t (°C)	2015	6.2	3.7	4.5	5.7	6.5	11.3
	1977–2006	9.0	7.1	7.6	8.8	10.9	14.4
Rainfall (mm)	2015	59	51	239	118	1	5
	1977–2006	56	65	38	25	31	20

2.2. Experimental Design, Plant Material and Management Practices

The experiment was arranged in a randomized complete-block design with three replications, using a plot size of 4.2 m × 7.0 m with 140 plants and consisting of 10 rows. Whole disease-free seed tubers of cultivar Bellini were planted on December 13 at 0.3 m intervals in rows 0.70 m apart, corresponding to a planting density of 4.76 plants m^2. This cultivar was recently introduced for conventional production of early potato in the Mediterranean Basin, where it has shown a good adaptation to the pedoclimatic conditions. It has yellow skin and pulp, and is a B cooking type (i.e., multi-purpose cooking) according to the EAPR (European Association for Potato Research) cooking-type scale [32]. Micronutrient fertilization distributed by foliar spray application was applied (Micro+) or not (Micro−). The commercially formulated product Aximicro LSA (SCAM S.p.A., Modena, Italy), which contains B (0.9%), Cu (0.6%), Fe (13.6%), Mn (5.2%), Mo (0.2%) and Zn (2.2 %) was distributed by foliar spray application exclusively to plants of Micro+ plots. In the plants of Micro– plots the spray solution was replaced with deionized water. B and Mo are soluble in water; Fe, Mn, Cu and Zn were complexed with ammonium lignin sulfonate which is a water-soluble plant-based substance [33]. Aximicro LSA was applied 3 times: at 66 days after emergence (DAE) (50 % of tuber growth), at 78 DAE (75 % of tuber growth) and at 90 DAE (the end of tuber growth) on plant canopy at a dose of 1 g L^{-1}, using a volume of about 1000 L ha^{-1} of water. Foliar application was carried out at 10 a.m. on sunny days at each growth stage. Overall, considering the 3 applications, 0.3 (B), 5 (Fe), 1.8 (Mn), 0.07 (Mo), 0.2 (Cu) and 0.8 (Zn) kg ha^{-1}, were distributed to the plants of Micro+ plots. Standard crop management was followed, applying chlorpyrifos (30 kg ha^{-1}) and fertilization (130, 50 and 200 kg ha^{-1} of N, P_2O_5 and K_2O) corresponding to the crop uptake determined in a previous research [34]. Drip irrigation was provided once the accumulated daily evaporation rate (derived from measurements of an unscreened class A-Pan evaporimeter) (Siap+Micros, San Fior, Italy) had reached about 30 mm. Over the crop cycle 190 mm irrigation water was supplied by five irrigation applications. Weed and pest control followed standard commercial practice.

2.3. Tuber Harvest, Post-Harvest Treatments and Sampling

Tuber harvest was carried out when leaves (about 80%) were dry, at 110 DAE. The two external rows and two plants on each row-end were used as border to minimize contamination from adjacent micronutrient fertilization treatments. The six middle rows per plot were harvested to assess tuber yield and to collect tubers for analysis. Sixty plants from each plot and replicate were collected;

number and weight of both marketable and unmarketable tubers per plant were determined. Tubers which were greened, misshapen or displayed pathological damage were classed as unmarketable, as well as those with weight lower than 20 g. Marketable yields were higher in Micro+ than in Micro– (51.1 vs. 43.9 t ha^{-1}) attributable to a higher number of tubers per plant (9.1 vs. 8.7) and mean tuber weight (118 vs. 106 g). The yield of unmarketable tubers in Micro– and Micro+ was very low (below 2.0%).

At least 20 kg of marketable tubers (Ø 35–70 mm) for each micronutrient fertilization regime and replicate were selected for their uniform shape and lack of mechanical damage. Within 4 h of harvest, the samples were brought to the CNR-IBE laboratory in Catania and kept in the dark at 15 °C. The next day all tubers were washed with tap water to remove any soil and dried carefully with paper towels. Twenty tubers per microfertilization regime (Micro+ and Micro−) and replicate were utilized for analysis on raw potatoes. The remaining tubers for each micronutrient fertilization treatment were gathered together and used for minimally processed potatoes preparation. Potato slices were dipped in a freshly prepared solution containing ascorbic acid (20 g kg^{-1}) + citric acid (20 g kg^{-1}) which in previous tests had given the best results as anti-browning in early potatoes [35,36]. Then about 300 g of the potato slices were packaged in pouches (15 cm × 20 cm) of PAPE 85 µm of layer (65 µm of PE polyethylene and 20 µm of PA polyamide) with the following characteristics: water vapor transmission rate (WVTR): 6.70×10^{-29} mol d^{-1} m^2 Pa^{-1}; O_2TR: 1.67×10^{-28} mol d^{-1} m^2 Pa^{-1}; CO_2TR: 7.13×10^{-28} mol d^{-1} m^2 Pa^{-1} (System Packaging s.r.l., Siracusa, Italy). The film was selected since it is commonly used in the minimally processed potato industry. For each micronutrient fertilization treatment, were prepared 15 packages having passive modified atmosphere and hermetically sealed by a packaging machine (Cibra TIS 400 TG, Cibra nova, Cernusco sul Naviglio, Italy) and finally stored at 4.0 ± 1 °C, 95% RH for 12 day.

2.4. Mineral Profile of Raw and Minimally Processed Tubers

Twenty raw potatoes per micronutrient fertilization treatment and each replicate were selected and sliced into small cubes of 1 cm sides. Minimally processed tubers per micronutrient fertilization treatment were considered as three package replicates at both sampling times: 0 and 12 d of storage. Slices of each package were subjected to the analyses separately. Tuber dry matter (DM) content was determined, on a representative sample after drying at 65 °C in a thermo-ventilated oven (Binder, Tuttlingen, Germany) until constant weight was reached. The dehydrated material (slices of raw and minimally processed tubers) was finely ground through a mill (IKA, Labortechnick, Staufen, Germany) with a 1.0 mm sieve and used for the determination of macroelements (N, P, K, Ca, Mg and Na) and microelements (Fe, Zn, Mn, Cu and Mo). All analyses were performed in duplicate. N was determined by the Kjeldahl method (Kjeltec 2300 Auto Analyser; Foss-Tecator, Hillerød, Denmark) and the total N content in the samples was expressed as g kg^{-1} dry weight. Approximately 1 g of the oven-dried material was put in a muffle furnace at 550 ± 2 °C for 24 h. After cooling at room temperature in a desiccator, P was estimated according to the molybdovanadate colorimetric method 986.24 using a UV-Vis spectrophotometer mod. 7315 (Jenway, Stone, UK), and the absorbance was measured at 730 nm [37]. Other minerals (K, Ca, Mg, Na, Fe, Zn, Mn, Cu and Mo) were analyzed by atomic absorption spectrometry. Samples were digested using 2 mL concentrated nitric acid (HNO3, 65% *v/v*) on a hot plate. After drying, 10 mL of 3 mol L^{-1} hydrochloric acid (HCl) was added to each sample and allowed to flux for 2 h. Subsequently, the digest was filtered using Whatman #40 (Merck kGaA, Darmstadt, Germany) filter paper and the filtrate was diluted to a volume of 25 mL with 0.1 mol L^{-1} HCl [37]. Concentrations of Ca, Mg, K, Na, Fe, Zn, Mn, Cu and Mo in the solutions of the digested samples were determined using an AA-6200 flame atomic absorption spectrophotometer (Shimazdu, Kyoto, Japan). Each sample was analyzed in duplicate, and the results were expressed as mg kg^{-1} dry weight. All the reagents and solvents were obtained from Sigma-Aldrich (Milan, Italy) and were of analytical grade. Bi-distilled water was used throughout this research.

2.5. Statistical Analysis

All data were subjected to Bartlett's test for homogeneity of variance and then analyzed by ANOVA [38]. Data on raw potatoes were evaluated using one-way ANOVA; data on minimally processed potatoes were subjected to a two-way ANOVA, based on a factorial combination of micronutrient fertilization × storage time. Means were compared with Duncan's test, when the F-value was significant. CoStat Version 6.003 (CoHort Software, Monterey, CA, USA) was used. A 5% significance level was used for all statistical comparisons.

3. Results and Discussion

3.1. Effects of Foliar Micronutrient Fertilization on Mineral Composition of Raw Potatoes

Foliar micronutrient fertilization affected the mineral composition of raw potatoes for most of the mineral elements studied (Tables 2 and 3). Accordingly changing levels of macro and micro nutrients in potato tuber following foliar application of micronutrient fertilization suggested a direct association between the micronutrient fertilization during the vegetative growth of potatoes and the mineral element composition of tubers after harvest. Micronutrient fertilization caused a significant increase of N level (from 162 to 200 mg kg^{-1}) (Table 2).

Table 2. Macroelements content of raw potatoes as affected by micronutrient fertilization.

Microfertilization	N	P	K	Ca	Mg	Na
Micro−	162 ± 14 b	479 ± 26 a	4.682 ± 310 a	126 ± 10 a	169 ± 16 a	73 ± 12 b
Micro+	200 ± 17 a	465 ± 35 a	4.500 ± 260 a	69 ± 4 b	147 ± 18 a	90 ± 13 a

Note: the units of concentration of the studied mineral components are expressed as mg kg^{-1}. All data are expressed as mean ± standard deviation, $n = 6$; different letters within the same parameter indicate significant differences (LSD test, $p < 0.05$).

Table 3. Microelements content of raw potatoes as affected by micronutrient fertilization.

Microfertilization	Fe	Zn	Mn	Cu	Mo
Micro-	12.8 ± 1.0 b	5.2 ± 0.1 b	2.2 ± 0.06 b	2.0 ± 0.04 a	0.15 ± 0.001 b
Micro+	21.6 ± 2.0 a	6.6 ± 0.2 a	2.6 ± 0.08 a	1.0 ± 0.02 b	0.20 ± 0.001 a

Note: the units of concentration of the studied mineral components are expressed as mg kg^{-1}. All data are expressed as mean ± standard deviation, $n = 6$; different letters within the same parameter indicate significant differences (LSD test, $p < 0.05$).

This result is in consonance with other findings [39] in which a positive relationship was found between B supply and the concentration of N in wheat plants. As known, some micronutrients such as Fe, Mn, Zn, Cu, Ni, Mo and Cl all participate in the functioning of different enzymes, including DNA/RNA polymerases, N-metabolizing enzymes and numerous other enzymes involved in redox processes [40]. In sugar beet [41] it was found that the Zn treatments significantly affected total uptake of N; a significant positive linear relationship between tuber Zn concentration and tuber N concentration supported the hypothesis of co-transport of Zn and N-compounds in the phloem [23]. The concentrations of K, P and Mg were comparable with those reported for main crop potatoes [15,17,42] and showed no significant differences due to the effect of micronutrient fertilization; the latter, on the contrary, determined a Ca concentration decrease (69 vs. 126 mg kg^{-1}). It is increasingly being observed in many studies that the addition of specific micronutrients could also positively modulate the uptake of other micronutrients (primary and secondary nutrients) to improve the overall nutritional status of the crop beyond that of the added nutrient [43,44]. Na was the least effectively accumulated macro-mineral, as has been noted in the main crop tubers [15,42]. Na content of tubers significantly increased with microfertilization (73 vs. 90 mg kg^{-1}) (Table 2) and it was attributable to foliar micronutrient solution applied in this experiment, containing B and Mo as sodium

molybdate and sodium borate highly soluble in water. In carrot the supplement of either boron, calcium or both in the feeding solutions, during plant growth, influenced the accumulation of sodium in the storage roots [45]. Fe concentration in Micro– tubers (12.8 mg kg^{-1}), was in accordance with the values reported elsewhere [15], but rather low despite the good endowment of the soil, increased considerably due to the effect of microfertilization (+70%) (Table 3).

This result is extremely positive because in soils that are slightly calcareous, such as the one the trial was carried out in, the application of Fe fertilizer to the soil is usually less effective since its uptake is limited because in rhizosphere it is quickly converted into a plant-unavailable Fe^{3+} form. In addition Fe has low xylem mobility and translocation capacity in the potato plant and that limits the prospect of biofortifying potatoes with soil Fe fertilization [21,46]. This is confirmed by a recent study in Bolivia with two Andean potato cultivars receiving Fe sulfate (10 to 40 kg Fe ha^{-1}) applied to the soil before planting, which resulted in unsuccessful translocation of Fe to tubers [25]. In three trials on five Andean potato (*Solanum tuberosum* L., *andigenum* group) cultivars the effects of foliar Fe fertilization found no significant increased in the iron concentration of the tubers [26]. The authors attribute the unsuccessful effect of the Fe foliar applications to the Fe-EDTA compound used, which may have penetrated poorly through the leaf surface, because of low air humidity and high points of deliquescence known of chelates [47], but also due to the high rate of Fe-EDTA used that may not have been the optimal foliar Fe concentration. On the contrary, our results can successfully be attributed to the fact that in the foliar micronutrient solution applied in this experiment, iron was complexed with ammonium lignin sulfonate which is a water-soluble plant-based substance [33]. The concentration of Zn in Micro– tubers (5.2 mg kg^{-1}) was lower compared to values found in Tenerife (Spain) [15]. The low tuber Zn concentrations found in our trial may have been related to low (moderate) natural soil Zn availability in the soil enhanced P availability, high soil calcium concentrations and relatively high pH [48,49], but also to low phloem mobility of Zn and low functional xylem continuity to potato tubers from roots [21,23]. In a study done in the coastal area of Peru, in a high pH and calcareous soil, no effect of Zn sulfate applications (11 kg Zn ha^{-1} to soil plus two foliar Zn applications) on tuber Zn concentration in *chilotanum* group cultivars was found [24]. The concentration of Zn increased significantly (about 27%) due to the effect of foliar microfertilization according to that found in Iran [22]. However the tuber Zn increase due to foliar applications was markedly lower than 2.51-fold increases found in Andean potato (*Solanum tuberosum* L., *andigenum* group) in Ecuador [26] and considerably lower than the increases seen in studies with foliar applied Zn sulfate and Zn oxide in potato trials cultivar Maris Piper, a tetraploid European potato type in Scotland [23]. This can be attributed mainly to the lower doses used in our experiment (about 20 mg $plant^{-1}$) compared to aforementioned authors (up to 2.16 g $plant^{-1}$). The increase in Fe and Zn concentrations of tubers through foliar micronutrient fertilization is an interesting result since they are two of the most important essential microminerals in human nutrition [50]. Mn content shows a slight but significant increase (18%) due to microfertilizer application. Foliar application containing Mn, Fe and Zn caused an increase in grains' protein and Mn contents compared to control treatments [51]. In a study carried out in Iran [22] it was found that foliar Mn fertilization at 8 g L^{-1} increased (about 26%) the concentration of Mn in tubers compared to control. The potato Cu concentration, in accordance with the values found in potatoes harveseted in Tenerife (Spain) [15], was halved due to the effect of microfertilization (Micro+), presumably due to the competition that was triggered with the zinc present in the utilized foliar micronutrient solution both at the leaf surface level and in the transport in the xylem (zinc and copper are regarded as having very similar mobility in phloem) [52]. Mo increased significantly (33%) from Micro– to Micro+ (Table 3). The chief biochemical functions of Mo in plants include its role in N fixation in legumes and regulation of nitrate reduction and protein content, but the role of Mo in humans, in general, is less well understood [53].

3.2. Effects of Foliar Micronutrient Fertilization on Mineral Composition of Minimally Processed Potato

Tuber mineral composition of minimally processed potatoes was affected significantly by micronutrient fertilization, but not by storage time, nor from their interaction. Micronutrient fertilization in minimally processed potatoes determined a significant increase of N, Na, Fe, Zn, Mn, and Mo and a decrease in Ca and Cu (Tables 4 and 5).

Table 4. Macroelements content of minimally processed potatoes as affected by micronutrient fertilization and storage time.

	N	P	K	Ca	Mg	Na
Microfertilization						
Micro−	170 ± 14 b	460 ± 37 a	4.465 ± 320 a	108 ± 9 a	162 ± 7 a	66 ± 8 b
Micro+	205 ± 18 a	442 ± 40 a	4.272 ± 251 a	57 ± 4 b	143 ± 5 a	82 ± 7 a
Storage time (days)						
0	182 ± 15 a	453 ± 35 a	4.390 ± 272 a	85 ± 8 a	151 ± 6 a	75 ± 4 a
12	193 ± 16 a	449 ± 26 a	4.347 ± 352 a	80 ± 5 a	154 ± 8 a	73 ± 2 a

Note: the units of concentration of the studied mineral components are expressed as mg kg^{-1}. All data are expressed as mean ± standard deviation, $n = 12$, both for microfertilization and storage time; different letters within the same parameter and main effect indicate significant differences (LSD test, $p < 0.05$).

Table 5. Microelements content of minimally processed potatoes as affected by micronutrient fertilization and storage time.

	Fe	Zn	Mn	Cu	Mo
Microfertilization					
Micro−	9.0 ± 0.8 b	4.8 ± 0.16 b	2.0 ± 0.1 b	1.8 ± 0.06 a	0.14 ± 0.02 b
Micro+	15.5 ± 1.8 a	5.8 ± 0.18 a	2.3 ± 0.08 a	0.8 ± 0.02 b	0.18 ± 0.03 a
Storage time (days)					
0	11.5 ± 1.4 a	5.6 ± 0.14 a	2.1 ± 0.06 a	1.4 ± 0.08 a	0.15 ± 0.03 a
12	13.0 ± 1.6 a	5.0 ± 0.12 a	2.2 ± 0.04 a	1.2 ± 0.10 a	0.17 ± 0.04 a

Note: the units of concentration of the studied mineral components are expressed as mg kg^{-1}. All data are expressed as mean ± standard deviation, $n = 12$, both for microfertilization and storage time; different letters within the same parameter and main effect indicate significant differences (LSD test, $p < 0.05$).

Basically, the effects were very similar to those found in raw potatoes and this is quite obvious because the composition of the minimally processed potatoes depends on the starting material. However, minimally processed potatoes show a general lower concentration of elements compared to raw potatoes. Regardless of micronutrient fertilization, the decrease was 29% for Fe, 17% for Ca, about 12% for Zn and about 10% for Na, Mo and Mn. Concentrations of N, P, K, Mg and Cu in minimally processed potatoes were similar to the respective concentrations of raw tubers.

It is important to underline here that the reduction of sodium in minimally processed potatoes has not substantially changed the Na/K ratio, which, in this experiment, was equal to 0.015 in Micro− and 0.019 in Micro+ (data not shown). These values are very low and this is very important since a high value of this ratio is involved in increased blood pressure and cardiovascular diseases [54]. The observed decrease of several elements seems to be attributed on processing for minimally processed production, and in particular to elimination of the peel. A marked decrease in the total ash content in boiled peeled tubers compared to unpeeled tubers was found [55]. As is known, the concentrations of most minerals are higher in the skin than in the flesh of tubers [56,57]. The potato skin of cultivar Stirling contained about 17% of total tuber zinc, 34% of calcium and 55% of iron [58]. In our experiment the reductions of Fe, Ca and Zn from raw to minimally processed potatoes were not so high, probably due to the relatively large size of the cultivar's tubers used and very thin skin that characterizes early potatoes [59].

Mineral composition of minimally processed tubers at 12 days of storage was not significantly different compared to those at 0 days of storage for all studied elements (Tables 4 and 5). Studying the effects of preparation procedures, packaging and storage on nutrient retention in peeled potatoes it was found that ash content in packaged, pre-peeled potatoes has not undergone significant changes after a 7-day storage period [60]. This is expected since minerals are not metabolized and therefore their contents should not change. In addition, both our minimally processed Micro+ and Micro– potatoes have not developed microbial contamination up to T12 [35], which, as is known, can lead to variations of mineral content during storage of fruit and vegetables [61]. Based on the current recommended nutrient intakes (RNIs) values provided by FAO/WHO [50] and considering an average consumption of 200 g of fresh weight of potatoes per day, in regard to adult males 19–50 years old, was found that foliar micronutrient fertilization has markedly increased the contribution for Fe and Zn. Indeed the contribution to the RNIs increased in raw potatoes from 52% to 87% for Fe and from 41% to 52% for Zn whereas in minimally processed potatoes the contribution increased from 36% to 63% for Fe and from 38% to 46% for Zn (data not shown). These values need to be considered more as orientation values because they are based on the assumption of 100% absorptions of individual minerals. The absorptions of some minerals, however, in general can be reduced due to the presence of various antinutrients like phytic acid, fibers, certain tannins, oxalic acid and lectins. Fortunately, the bioavailability of minerals in potato tubers is potentially high, because they have high concentrations of promoter substances such as ascorbate, beta-carotene, protein cysteine and various organic and amino acids that enhance the absorption of essential micronutrients [17]. So, the agronomic fortification can be considered even more valid to maximize the intake of beneficial minerals in humans if the potatoes are destined for the processing industry where the peel is removed as in fresh minimally processed potatoes and in processed food products such as frozen potatoes, dehydrated potato flakes and potato flour. However, we also need to consider genotypic variation in uptake and accumulation of micronutrients [26]; therefore, in future research several potato genotypes characterized by different earliness and productivity in combination with proper agronomic management will be studied.

4. Conclusions

The observations about the mineral profiles of the studied samples suggests that the application of foliar micronutrient fertilizers was able to fortify raw potatoes by improving the content of iron and zinc which are important for a healthy diet. The better concentration of minerals in micro-fertilized raw potatoes also led to a better concentration of micro-fertilized minimally processed potatoes, even if some minerals were lost in processing, presumably due to the elimination of the peel. The agronomic approach via foliar microelements-containing solutions proved to be a sustainable, economical and fast strategy to increase micronutrients concentration in early potato tubers.

Author Contributions: A.I. conceived the experiments and proposed the experimental design; A.P. and R.P.M. carried out the experiments; A.P. and R.P.M. carried out chemical determinations; A.I. interpreted data and wrote the manuscript; C.L. critically revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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