Critical dilution curves for calcium, magnesium, and sulfur in potato (*Solanum tuberosum* L. Group Andigenum) cultivars Diacol Capiro and Pastusa Suprema

Curvas críticas de dilución de calcio, magnesio y azufre en cultivares de papa (*Solanum tuberosum* L. Grupo Andigenum) Diacol Capiro y Pastusa Suprema

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ABSTRACT

Diagnostic tools must be developed to optimize the management of calcium (Ca), magnesium (Mg), and sulfur (S) in potato crops. This research aimed to develop the critical dilution curves for Ca, Mg, and S in potato (*Solanum tuberosum* L. Group Andigenum), establishing harvest indices and characterizing the nutrient relationships. Four field experiments were established in two growth cycles in the localities of Facatativá (high fertility soils) and Chocontá (low fertility soils) in Colombia. Two cultivars (Diacol Capiro and Pastusa Suprema) and two levels of fertilization (0 and 100% of macro and micronutrients) were evaluated. The dry biomass and Ca, Mg, and S concentration in tubers and aerial parts were measured from the formation of main stems until tuber maturation; this information was used to calculate the critical concentrations (Cac, Mgc, Sc), harvest indices, and nutrient correlations. The critical curves established were for Capiro: Cac = $1.7326W^{-0.2956}$, Mgc = $0.7191W^{-0.2803}$, Sc = $0.6461W^{-0.3904}$ and for Suprema: Cac = $1.523W^{-0.2559}$, Mgc = $0.6507W^{-0.236}$, Sc = $0.7669W^{-0.3932}$. Critical levels were established for five phenological stages. Capiro had a higher accumulation of Ca, Mg, and S in the tubers independently of locality, while Suprema had better performance in Chocontá. The accumulation of mineral nutrients in the tubers followed the order Ca<Mg<S. Capiro was a genotype with greater Ca-Mg-S uptake and better adaptation to locations. The Cac, Mgc and Sc curves provided a tool to carry out the nutritional diagnoses at critical stages of development and they are the first ones reported for potato of Group Andigenum.

Key words: nutrient concentration, nutrient diagnostics, nutrient harvest index, secondary macronutrients.

RESUMEN

Herramientas de diagnóstico deben ser desarrolladas para optimizar el manejo de calcio (Ca), magnesio (Mg) y azufre (S) en cultivos de papa. La investigación tuvo como objetivos desarrollar las curvas críticas de dilución para Ca, Mg y S en papa (*Solanum tuberosum* L. Grupo Andigenum), establecer sus índices de cosecha y caracterizar la relación entre nutrientes. Se establecieron cuatro experimentos en campo en dos ciclos, en las localidades de Facatativá (suelos de alta fertilidad) y Chocontá (suelos de baja fertilidad) en Colombia. Se evaluaron dos cultivares (Diacol Capiro y Pastusa Suprema) y dos niveles de fertilización (0 y 100% de macro y micronutrientes). Se midió la biomasa seca y concentración de Ca, Mg y S en tubérculos y parte aérea, desde la formación de tallos principales hasta maduración del tubérculo y se calcularon las concentraciones críticas (Cac, Mgc, Sc), índices de cosecha y correlaciones entre nutrientes. Las curvas criticas establecidas para Capiro fueron: Cac = $1.7326W^{-0.2956}$, Mgc = $0.7191W^{-0.2803}$, Sc = $0.6461W^{-0.3904}$ y para Suprema: Cac = $1.523W^{-0.2559}$, Mgc = $0.6507W^{-0.236}$, Sc = $0.7669W^{-0.3932}$. Se establecieron niveles críticos para cinco etapas fenológicas del cultivo. Capiro presentó mayor acumulación de Ca, Mg y S en el tubérculo independiente de la localidad, mientras Suprema tuvo mejor desempeño en Chocontá. La acumulación de nutrientes minerales en los tubérculos siguió el orden Ca<Mg<S. Capiro mostró ser un genotipo de mayor consumo de Ca-Mg-S y de mejor adaptación a localidades con condiciones edafoclimáticas contrastantes. Las curvas de Cac, Mgc y Sc proporcionan una herramienta para realizar el diagnóstico nutricional en etapas críticas del desarrollo y son las primeras reportadas en cultivos de papa del Grupo Andigenum.

Palabras clave: concentración de nutrientes, diagnóstico nutricional, índice de cosecha de nutrientes, macronutrientes secundarios.

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Introduction

The potato (*Solanum tuberosum* L.), a species native to South America, has wide adaptability to different edaphoclimatic conditions and is cultivated in countries in temperate, tropical, and subtropical regions (Campos & Ortiz, 2020). Potato tubers are rich in carbohydrates, low in fat and have an adequate balance of vitamins and mineral nutrients (Handayani *et al*., 2019; Gaj *et al*., 2020). Due to its high nutritional quality and potential yield, the potato is a species of great importance for food security in the world (Raymundo *et al*., 2018). In recent years, there has been a progressive world increase in potato cultivation; currently 19 million ha are cultivated with an approximate production of 378 million t (Campos & Ortiz, 2020). In Colombia, the departments with the highest production are Cundinamarca with 37%, Boyacá with 27%, and Nariño with 20% (Minagricultura, 2019).

The cultivars Diacol Capiro and Pastusa Suprema from the Andigenum Group are among the most widely consumed in Colombia and are appreciated for their qualities for industrial processing (chips or cane) and fresh consumption (Barrientos & Ñústez, 2014; Gómez *et al*., 2019a). Both cultivars are tetraploid, produce tubers under short-day conditions, have good frying behavior, and potentially yield more than 40 t ha^{-1} (Guerrero-Guio *et al*., 2019; Campos & Ortiz, 2020).

The potato crop has a high demand for mineral nutrients compared to other short-cycle crops (Helal & AbdElhady, 2015); fertilization can represent about 24% of the total costs (Fedepapa, 2018). Nutritional research is extensive for nitrogen (N), phosphorus (P), and potassium (K) (Koch *et al*., 2020). However, the information on calcium (Ca), magnesium (Mg), and sulfur (S) necessary to obtain optimal tuber yield and quality is scarce (Hauer-Jákli & Tränkner, 2019; Koch *et al*., 2020; Naumann *et al*., 2020). These elements play fundamental roles, for example in cell walls and membranes, signaling, activation of enzymes, energy metabolism, formation of amino acids, sulfolipids, etc. (Koch *et al*., 2020).

The traditional management of crops with contributions focused on NPK in continuous production cycles, added to the natural processes of nutrient loss (leaching, erosion, fixation, among others), decreases the natural contents of secondary macronutrients in soil and generates imbalances that limit the availability of Ca, Mg, and S (Aula *et al*., 2019; Wang *et al*., 2020). The application of Ca-Mg-S is frequently carried out following general recommendations, with over- or under-dosage of nutrients (Koch *et al*., 2019). This problem is not necessarily detected during the production cycle; its negative effects on the yield and quality of the tuber are not evident until harvest. In this context, a diagnostic tool must be developed that allows the nutritional evaluation of Ca-Mg-S during the production cycle, to detect and correct excesses or deficits opportunely.

An adequate supply of Ca-Mg-S has positive effects on yield (Muthanna *et al*., 2017; Seifu & Deneke, 2017; Wang *et al*., 2020) and tuber quality (Singh *et al*., 2018; Koch, Naumann, *et al*., 2019; Assunção *et al*., 2020). A deficit of these nutrients leads to less translocation of photoassimilates to the tubers, low mechanical resistance, low specific gravity, and multiple physiological disorders, such as hollow heart (Koch *et al*., 2019; Schabow & Palta, 2019). In contrast, doses higher than the optimum can lead to negative effects due to excess of other nutrients, loss of fertilizer, and cost overruns (Wang *et al*., 2018; Barroso *et al*., 2021).

The critical dilution curve (CDC) of a mineral nutrient is an allometric relationship between its concentration in the plant and the biomass or leaf area (Lemaire *et al*., 2019). This tool is based on the principle of the existence of a minimum concentration required to achieve the maximum growth of the crop, which varies with the age of the plant and its biomass (Wang *et al*., 2018; Carciochi *et al*., 2019). The CDC is a useful tool for carrying out a quick nutrient diagnosis *in situ* at different stages of the crop, allowing timely corrections in nutrition to reach maximum development (Greenwood *et al*., 1990; Giletto & Echeverría, 2015; Lemaire *et al*., 2019). The CDC approach has been successfully used for the management of N in various crops in cereal research (Lemaire *et al*., 2019; Chen *et al*., 2021). Likewise, the CDC of P, K, and S has been calculated for crops such as corn, canola, and wheat (Carciochi *et al*., 2019; Lemaire *et al*., 2019). In the potato, the CDC has been established for N (Giletto & Echeverría, 2015), P (Zamuner *et al*., 2016; Gómez *et al*., 2019b) and K (Cogo *et al*., 2006; Gómez *et al*., 2019b), however, we found no reports for Ca-Mg-S.

In order to improve our knowledge of the nutrition of potato with Ca-Mg-S, it is of interest to establish what type of relationship exists between these nutrients as the crop develops and to understand the accumulation dynamics in the harvest organs (Duarte *et al*., 2019; Naumann *et al*., 2020). The objectives of this research were to develop the critical dilution curves and harvest indices of Ca, Mg, and S in the potato (*Solanum tuberosum* L. Group Andigenum) and to analyze the relationships among these nutrients. The results will provide a new tool, useful to potato producers, for the nutrient diagnosis and management of Ca-Mg-S during the productive cycle of two potato cultivars of importance in Colombia.

Materials and methods

Study site

The research was carried out at two localities in the Cundinamarca-Boyacá highlands (Colombia): Facatativá with Andic Eutrudepts (saturated bases, high fertility) and Chocontá with Humic Dystrudepts, (desaturated bases, acidic, low fertility) (Tab. 1). The localities were selected as representative of potato production in Colombia, showing high productive potential (> 50 t ha^{-1}) with contrasting edaphoclimatic conditions. Two production cycles were evaluated at each locality (2013-2016), each one with a total duration of 150-160 d after sowing (DAS). Soil analyses were carried out for each cycle and each locality for the arable layer (0-30 cm), prior to the establishment of the crop.

Experiment design and crop management

For each location and production cycle, an experiment was established in divided plots with four replicates distributed in completely random blocks. The main plot corresponded to the cultivars Capiro and Suprema and the subplots to the fertilization levels (0 and 100% of macro and micronutrients). Each experimental unit was 5 m x 10 m, with a distance between rows of 1 m and between plants of 0.37 m. As plant material, tubers of 70 g on average were used and sown manually. 135 plants were planted per plot with a density of 27,000 plants ha^{-1}. The fertilization doses (100% level) for each locality-cycle were established using the soil-plant balance method (Castro & Gómez, 2013) (Tab. 2). The 0% level corresponded to treatment without fertilization and represented the natural fertility conditions of the soil.

TABLE 1. Climatic variables and soil characteristics of the experiment locations.

Climatic variables * / Location	Facatativá		Chocontá	
	Cycle 1 (2013-I)	Cycle 2 (2015-I)	Cycle 1 (2013-II)	Cycle 2 (2016-I)
Altitude (m a.s.l.)	2597	2597	2780	2710
Latitude	4°49'26.9" N	4°49'39.9" N	5°5'30.37" N	5°6'23.94" N
Longitude	74°22'29.7" W	74°22'49.3" W	73°43'2.04" W	73°40'48.53" W
Annual precipitation (mm)	951	850	1295	1058
Annual precipitation/cycle (mm)	397	415	712	803
Evapotranspiration per cycle (mm)	454	382	640	603
Max air temperature (°C)	18.1	18.5	16.2	16.5
Min air temperature (°C)	7	7.2	4.4	10.1
Mean temperature (°C)	12.7	12.5	10.6	12.9
Soil properties**	Andic Eutrudepts		Humic Dystrudepts	
Texture	Loam	Loam	Clay loamy	Clay loamy
Soil fertility	High	High	Low	Low
pH	6.4	5.8	5.5	5.3
Al (cmolc kg^{-1})	0	<0.1	0.1	0.5
Organic matter (g kg^{-1})	166.7	127.1	67.7	85.9
CEC (cmolc kg^{-1})	31.95	19.14	9.52	7.90
N (g kg^{-1})	8.3	6.4	3.3	4.3
P (mg kg^{-1})	39.64	70.16	18.18	41.50
K (cmolc kg^{-1})	3.14	0.87	0.68	0.84
Ca (cmolc kg^{-1})	24.26	15.98	7.20	5.90
Mg (cmolc kg^{-1})	4.36	2.14	1.57	1.40
S (mg kg^{-1})	29.53	29.53	11.52	11.52

* Data on climatic variables obtained from IDEAM. ** The physical chemical analysis of the soil was carried out according to IGAC (2006). The methods used were as follows: Al: Yuan's method; Organic matter: Walkley-Black; P: Bray II-colorimetry; K, Ca, Mg: ammonium acetate-atomic absorption; S; monobasic phosphate-colorimetry. Soil classification was done according to the USDA (Soil Survey Staff, 2014).

TABLE 2. Nutrient contributions by location and growth cycle for 100% fertilization treatment.

Locality	Cycle	Fertilization dose* (kg ha^{-1})	Mineral nutrient dose (kg ha^{-1})										
			N	P	K	Ca	Mg	S	B	Zn	Mn	Fe	Cu
Facatativá	1	1582	171	113	149	23.2	70	74	3.4	5.6	7	2.8	0.56
	2	1900	164	126	195	34.1	80	150	2.3	4.6	5.6	2.2	0.45
Chocontá	1	2175	192	148	289	46.3	56	120	1.2	2.4	3	1.2	0.24
	2	2000	191	165	262	46.3	40	38	4.4	4.8	5.4	2.2	0.43

*The fertilizer sources were diammonium phosphate ($(NH_4)_2HPO_4$), potassium chloride (KCl), potassium sulfate (K_2SO_4), calcium nitrate ($Ca(NO_3)_2$), magnesium sulfate monohydrate ($MgSO_4H_2O$), and Nutricomplet® (Ingeplant, Colombia. Source of B, Zn, Mn, Fe, and Cu). Adapted by permission from Springer Nature: Nutrient Cycling in Agroecosystems. Nitrogen, phosphorus and potassium accumulation and partitioning by the potato group Andigenum in Colombia, Gómez MI *et al.* Copyright 2019.

Fractionation was carried out according to the historical management of the study sites (yield history per harvest > 50 t ha^{-1}) as follows: N 55% at sowing and 45% at 45 DAS; P 80% at sowing and 20% at 45 DAS; K 12% at sowing and 88% at 45 DAS; Ca, Mg, S and lower, 63% at sowing and 37% at 45 DAS. Phytosanitary management of the crop was carried out according to local practices.

Sampling and measurements

Five destructive samplings were carried for the five phenological stages (Roveda *et al.,* 2010): stage I, 50 to 55 DAS (formation of primary stems); stage II, 70 to 75 DAS (formation of secondary stems and beginning of tuberization); stage III, 90 to 100 DAS (flowering, maximum tuberization, and beginning of tuber filling); stage IV, 120 to 125 DAS (end of flowering, tuber filling); stage V, 150 to 160 DAS (leaf senescence, maximum filling, and tuber maturation). In each sampling, three (cycle 1 at both localities and cycle 2 in Facatativá) or four (cycle 2 in Chocontá) plants were harvested per experimental unit and their organs were sectioned (leaves, aerial + underground stems, and tubers). For quantification of mineral nutrients, the plant material was washed with deionized water, the same organs from the four plants were mixed and a 200 g subsample was oven-dried at 70°C until constant weight to determine the dry weight (Gómez *et al*., 2019a). The concentration of Ca, Mg, and S per organ was determined by chemical analysis according to IGAC (2006). The total contents of Ca, Mg, and S were estimated by multiplying the concentrations of nutrients in the organ (g 100 g^{-1} dry weight) by the amount of dry biomass accumulated in each stage (Abdallah *et al*., 2016).

Critical dilution curves

The critical dilution curve from dry matter (DW) for Ca (Cac), Mg (Mgc), and S (Sc) was calculated according to Equation 1, proposed by Greenwood *et al*. (1990),

$$Nut_c = aW^{-b} \quad (1)$$

where Nut_c corresponds to the critical concentration of the nutrient in the biomass (g 100 g^{-1}), W is the total dry weight of the biomass (t ha^{-1}), the coefficient a is the concentration of the nutrient when the biomass is ≤1 t ha^{-1}, and the coefficient b (dimensionless) is a dilution coefficient that describes the curvature or decrease of the nutrient as the total biomass increases (Giletto & Echeverría, 2015).

For the calibration of the critical curves, the identification and selection of data for which fertilization did not significantly limit the growth of the crop (total dry biomass) was carried out. The following steps were followed: i) the principles of normality and homoscedasticity were evaluated; ii) the analysis of variance (ANOVA) of the total biomass under the different fertilization levels was carried out for each combination of factors (cycle x locality x cultivar x phenological stage); iii) means were compared using the minimum test significant difference (LSD) (P<0.05); iv) the data of the fertilization level with the highest biomass production were selected. When there were no significant differences, the lowest dose was chosen (Abdallah *et al*., 2016; Wang *et al*., 2017). From the selected data, the dilution curve for each nutrient was constructed by calculating the coefficients a and b, their standard errors, and 95% confidence intervals using the PROC NLIN procedure (SAS Institute, 2017). The model's coefficients were compared based on the method of intervals of confidence described by Cumming *et al*. (2007). Based on total biomass measured and the critical dilution curves developed, critical dilution values for each phenological stage were calculated.

Harvest indexes

Harvest (150 DAS) indexes for Ca (CaHI), Mg (MgHI), and S (SHI) were calculated, dividing the amount of nutrients accumulated in the tuber (Nut_{tub}, kg ha^{-1}) by the total accumulation (leaves, aerial stems, stolons, tubers) in the plant (Nut_{tot}, kg ha^{-1}) as shown in Equation 2,

$$NHI = (Nut_{tub} / Nut_{tot}) \quad (2)$$

where NHI is the nutrient harvest index) (Giletto & Echeverría, 2015). Roots were not considered in the analysis. For the analysis, the PROC MIXED procedure (SAS Institute, 2017) was used, taking the repetitions as a random effect and the cultivar, location, cycle, and fertilization level as fixed effects. For each level of interaction between factors, the least square means were calculated; based on these means, comparisons were made with the adjusted Tukey statistic (P<0.05) for mixed models.

Correlation and linear regression

The correlations between variables were calculated from the Spearman correlation coefficient using the PROC CORR procedure (SAS Institute, 2017). A total of n=130 observations (measured plants: locality x cycle x cultivar x phenological stage x plants measured) were used for each cultivar and significance was established with a 95% confidence limit. Linear models of the form "y=bx+a " were established by linear regression, where a is the intercept on the y-axis and b is the slope of the line. For each model, the coefficient of determination (R^2) was calculated. The models were compared by their coefficients based on the method of intervals of confidence described by (Cumming *et al.*, 2007). The proportions of mineral nutrients in the plant were determined from the equations established for the linear model between the total contents of the nutrients, dividing 1 by the coefficient b (slope of the curve).

For all variables, the principles of normality and homoscedasticity were evaluated using PROC UNIVARIATE; an analysis of variance (ANOVA) was performed using PROC GLM in SAS 9.4 software (SAS Institute, 2017). The graphs were developed with ggplot2 (Wickham, 2016).

Results

Critical dilution curves

The dilution curves of Cac, Mgc, and Sc followed a potential negative model in relation to the increase in total dry biomass in the two cultivars (Fig. 1). The average dry biomass during the evaluation cycle was in the range of 1.7 to 22.6 t ha^{-1}. The coefficients a and b of the critical curves of the three nutrients did not show significant differences between cultivars (Tab. 3); however, a differential tendency was seen between the two Sc models. Capiro on average had 0.05 percentage unit lower concentration compared to Suprema throughout the growth cycle (Fig. 1C). For the biomass of 6 t ha^{-1}, the means averages of measured concentrations of Ca, Mg, and S in Capiro were 0.3, 0.2 and 0.1, higher than those established by the model (Fig. 1).

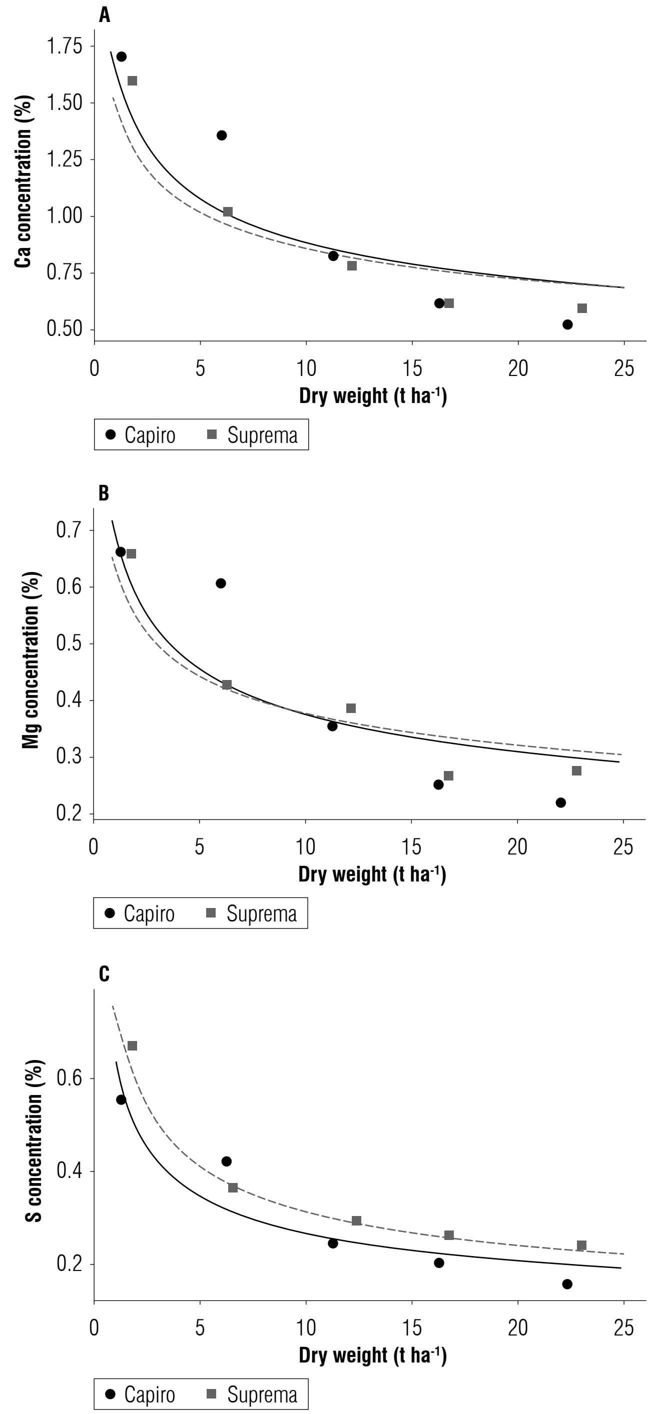

FIGURE 1. Critical dilution curves of A) Ca, B) Mg, and C) S for Diacol Capiro and Pastusa Suprema of *Solanum tuberosum* L. Andigenum Group under non-limiting nutrient conditions. The points constitute the data from which the critical curves were developed. Each point represents the average of 13 values taken per cultivar and phenological stage. The dotted and solid lines represent the CDC for each cultivar for a biomass greater than 1 t ha^{-1}.

TABLE 3. Coefficients of critical Ca, Mg and S dilution curves developed for Diacol Capiro and Pastusa Suprema from the total dry biomass (W) under non-limiting mineral nutrition conditions.

Nutrient	Cultivar	CDC ($N_c = aW^{-b}$)	RMSE	CI (*a*) 95%	CI (*b*) 95%	SE *a*	SE *b*
Calcium	Capiro	$1.7326W^{-0.2956}$	0.2133	1.3862- 2.0790 ns	0.1797- 0.4115 ns	0.1733	0.058
	Suprema	$1.523W^{-0.2559}$	0.1622	1.2172- 1.8288 ns	0.1508- 0.3610 ns	0.153	0.0526
Magnesium	Capiro	$0.7191W^{-0.2803}$	0.5493	0.5812 - 0.8570 ns	0.1731- 0.3875 ns	0.069	0.0536
	Suprema	$0.6507W^{-0.236}$	0.4199	0.5341- 0.7673 ns	0.1440- 0.3280 ns	0.0584	0.0460
Sulfur	Capiro	$0.6461W^{-0.3904}$	0.1480	0.5465- 0.7458 ns	0.2915- 0.4893 ns	0.0499	0.0495
	Suprema	$0.7669W^{-0.3932}$	0.2152	0.6090- 0.9249 ns	0.2660- 0.5204 ns	0.0791	0.0636

CDC: critical dilution curve; CI: confidence interval; SE: standard error; RMSE: root mean square error; ns: no significant differences found between the cultivars.

TABLE 4. Critical concentrations of Ca, Mg and S (%) by phenological stage under non-limiting conditions of mineral nutrition for Diacol Capiro and Pastusa Suprema.

Phenological stage	Capiro			Suprema		
	Ca_c	Mg_c	S_c	Ca_c	Mg_c	S_c
Vegetative growth	1.56	0.65	0.56	1.29	0.56	0.61
Initial tuberization	1.02	0.43	0.31	0.95	0.42	0.36
Flowering - maximum tuberization	0.85	0.36	0.25	0.80	0.36	0.28
End of flowering - tuber filling	0.76	0.33	0.22	0.74	0.33	0.25
Maximum filling - tuber maturation	0.69	0.30	0.19	0.68	0.31	0.22

The highest "dilution" of mineral nutrients was observed when the total dry biomass was between 1 and 6 t ha^{-1} (Fig. 1) in the tuberization initiation stage (Tab. 4). The average concentration of Ca in the plants decreased from a maximum of 1.6% (Capiro) and 1.3% (Suprema) in the vegetative growth stage to a minimum of 0.7% in the tuber maturation stage (Fig. 1A, Tab. 4). For Mg, the values were from 0.7% (Capiro) and 0.6% (Suprema) to 0.3% (Fig. 1B, Tab. 4) and for S the values varied from 0.6% to 0.2% (Fig. 1C, Tab. 4). The Cac and Sc curves had a greater fit with root mean square error (RMSE) values in the range of 0.1 to 0.2, while Mgc had an RMSE of 0.4 to 0.5 (Tab. 3). The Ca and Mg concentration of Capiro in the initial stage (stage I: vegetative growth) was 17% and 14% higher compared to Suprema, while that of S was 8% higher in Suprema (Tab. 4).

Harvest indexes

The CaHI values were in the range of 0.01-0.11 with a mean of 0.06. MgHI and SHI were in the range of 0.13-0.50 and 0.16-0.65 with means of 0.34 and 0.45, respectively (Fig. 2). The harvest indices showed differences among the localities, cycles, and cultivars (P<0.001). Capiro showed, on average, higher CaHI, MgHI and SHI values of 37%, 44%, and 57% compared to Suprema. The Mg and S indices of Suprema showed high variation between localities with a standard deviation (SD) of 0.14 and 0.20. The highest values were observed in Chocontá (CaHI: 0.05, MgHI: 0.39 and SHI: 0.50). Capiro had similar MgHI and SHI values in both locations with a SD of 0.08 and 0.06, respectively. Capiro had the highest CaHI value in Chocontá-1 and Suprema had the lowest value in Facatativá-1.

Relationship between Ca, Mg, and S in plant organs

The MgHI-SHI relationship showed the highest correlation (r=0.97) followed by CaHI-MgHI (r=0.94) and CaHI-SHI (r=0.91). The models established that MgHI and SHI increased by 4.38 and 4.92 units for each CaHI unit in Capiro and by 3.84 and 5.42 in Suprema. For each unit of MgHI, the SHI increased by 1.33 and 1.22 units in Capiro and Suprema, respectively. The determination coefficients (R^2) were greater than 0.7 except for the CaHI-SHI relationship. The values obtained for Capiro had lower dispersion and greater fit to the linear model with respect to Suprema. Between harvest indices these showed a positive linear behavior (Fig. 3, Tab. 6).

The correlations between the nutrient content in the aerial part of the plant and the tuber were 0.46, 0.41 and 0.29 for Ca, Mg, and S, respectively. Among the total nutrient contents, the highest correlation was between Ca-Mg (r=0.95), followed by Mg-S (r=0.88) and Ca-S (r=0.85).

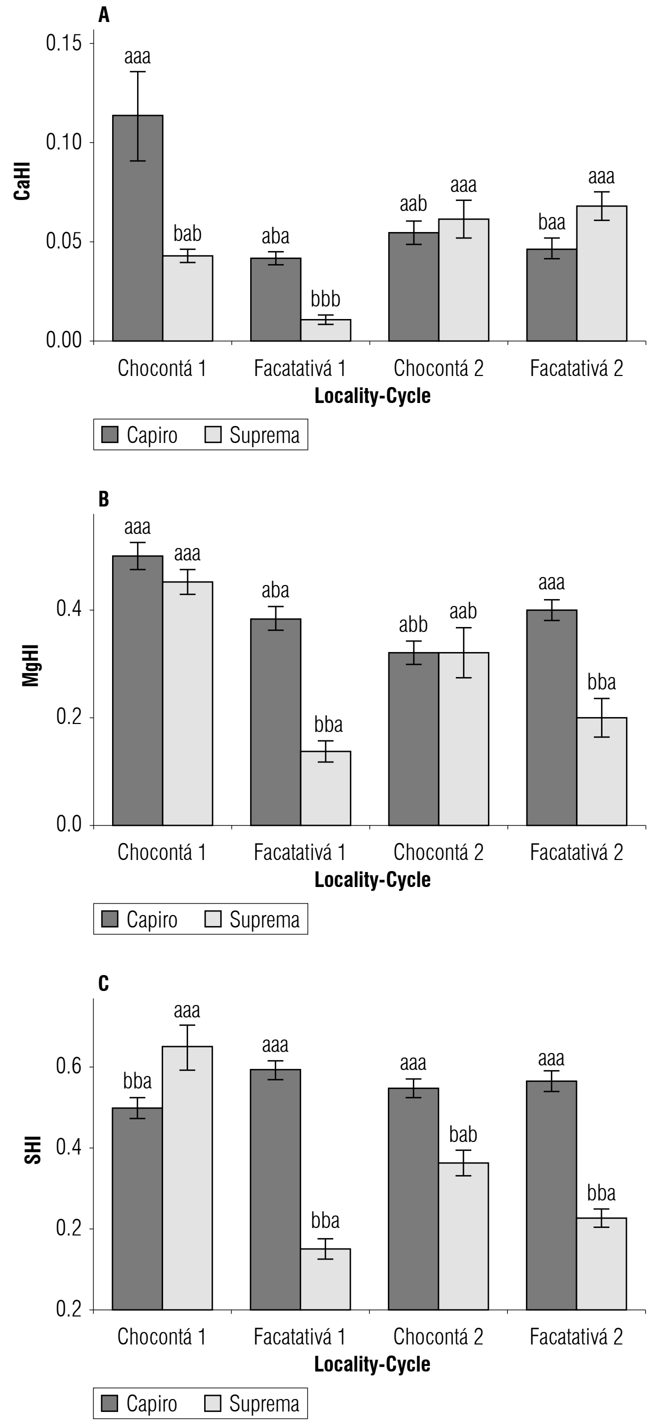

FIGURE 2. Harvest indexes (HI) for A) Ca, B) Mg, and C) S for Diacol Capiro and Pastusa Suprema in soils with low (Humic Dystrudepts, Chocontá) and high (Andic Eutrudepts, Facatativá) fertility, in two productive cycles (2013-2016). The first letter indicates significant differences between cultivars within the same cycle and locality; the second letter indicates significant differences between localities within the same cultivar and cycle; the third letter indicates significant differences between cycles within the same cultivar and locality. These were significant differences according to the Tukey's test (*P*<0.05). The error bars indicate the standard error.

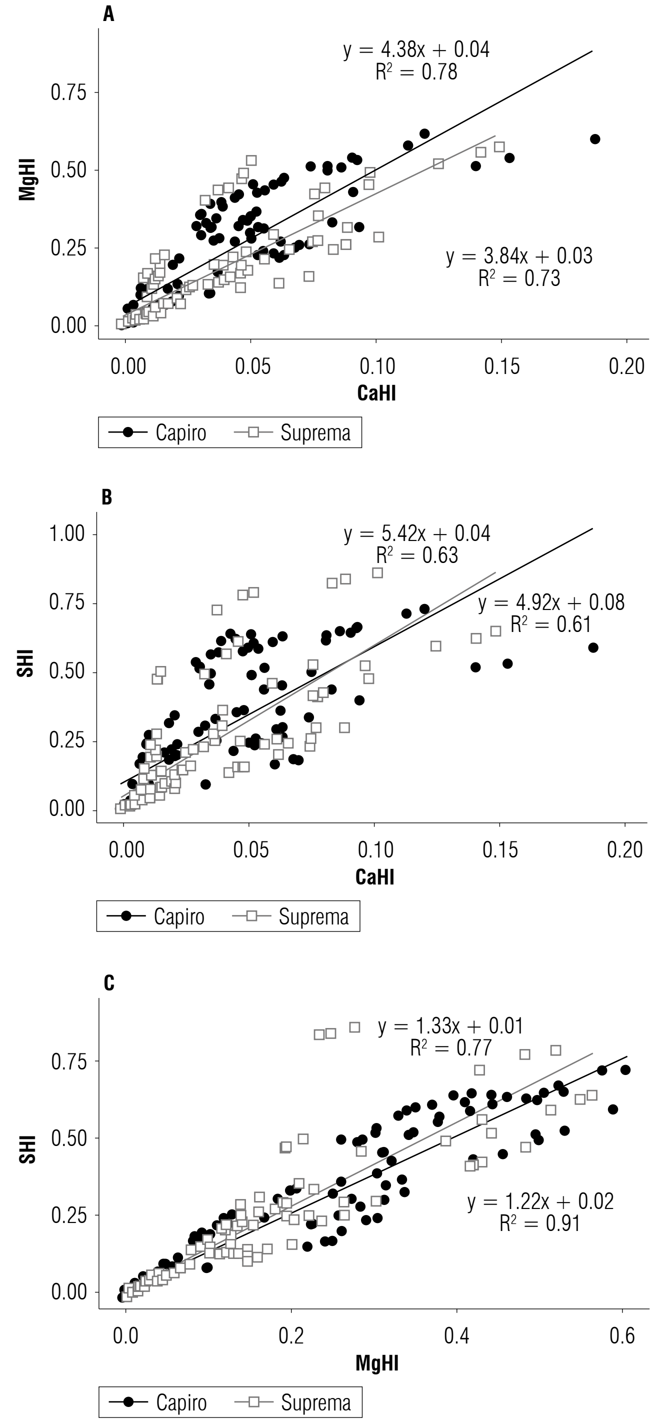

FIGURE 3. Relationships between the harvest indices of A) magnesium (MgHI) and calcium (CaHI), B) sulfur (SHI) and calcium (CaHI), and C) sulfur (SHI) and magnesium (MgHI) for Diacol Capiro and Pastusa Suprema (n = 130 for each cultivar). The lines represent the fitted model for each cv. R^2: coefficient of determination.

The models followed a positive linear behavior (Tab. 6) with an adjustment level greater than 0.7 (R^2) (Fig. 4). There were significant differences between cultivars for the total Ca-S and total Mg-S ratio. For each unit of Mg, there was an increase of 0.55 and 0.66 units of S in Capiro and Suprema, respectively. Each unit of Ca increased 0.40 and 0.36 units of Mg and of S 0.29 and 0.20 for Capiro and Suprema, respectively.

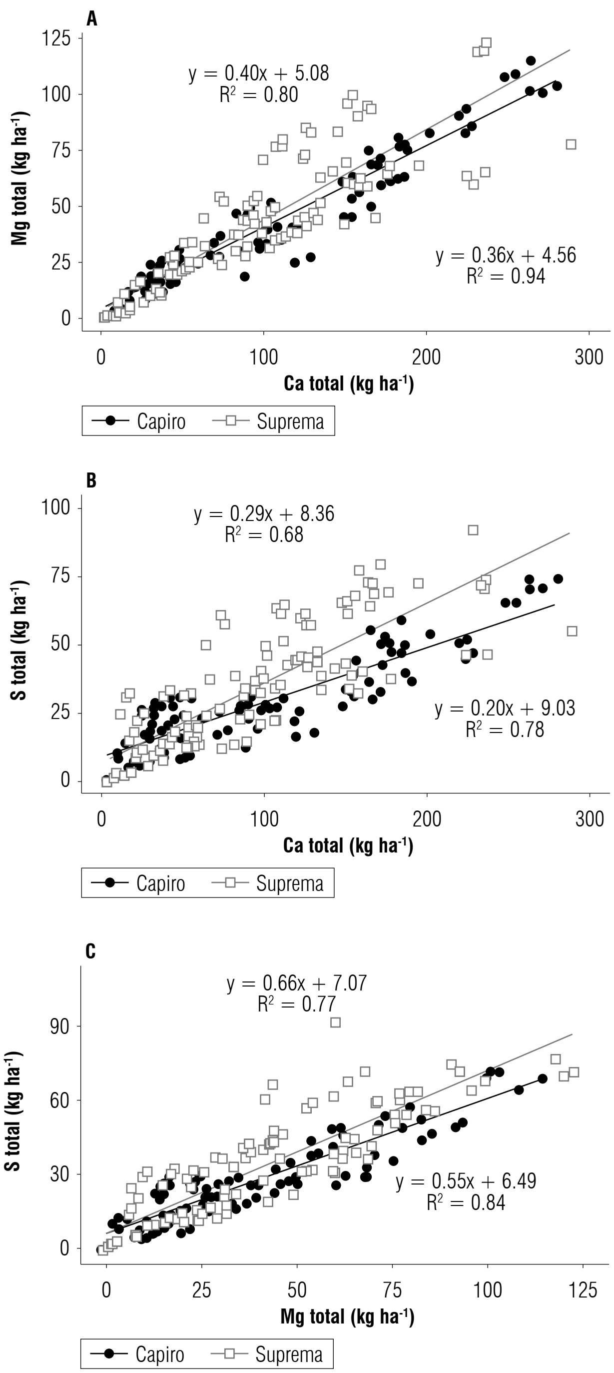

FIGURE 4. Relationship between the total content of A) Ca, B) Mg, and C) S for Diacol Capiro and Pastusa Suprema (n=130 for each cultivar). The lines represent the fitted model of each cv. R^2: coefficient of determination.

The Ca:S ratio was the highest one, followed by Ca:Mg and S:Mg, with Capiro having higher values than Suprema (Tab. 5). The correlation (r) between the yield (fresh weight of the tubers) and the content of Ca, Mg and S in the tubers was 0.94, 0.99 and 0.95, respectively (Tab. 6). The models had a positive linear behavior and an R^2 greater than 0.6. All the models showed significant differences between cultivars. For each t ha^{-1} increase in yield, Ca, Mg, and S increased 0.08, 0.28, and 0.27 kg ha^{-1} in the tubers for Capiro and 0.07, 0.25, and 0.29 kg ha^{-1} in the tubers for Suprema (Fig. 5, Tab. 6).

TABLE 5. Proportion between the total contents of Ca, Mg, and S in potato cultivars Diacol Capiro and Pastusa Suprema.

Relationship	Capiro	Suprema
Ca:Mg	2.8:1	2.5:1
Ca:S	5.0:1	3.4:1
Mg:S	1.8:1	1.5:1

TABLE 6. Confidence intervals for the linear models of the relationship between Ca, Mg, and S in cultivars Diacol Capiro and Pastusa Suprema.

Correlation	Cultivar	CI (m) 95%	CI (b) 95%
CaHI-MgHI	Capiro	3.98 - 4.78 ns	0.02 - 0.06 ns
	Suprema	3.43 - 4.25 ns	0.01 - 0.04 ns
CaHI-SHI	Capiro	4.22 - 5.61 ns	0.05 - 0.12 *
	Suprema	4.70 - 6.14 ns	0.01 - 0.07 *
MgHI-SHI	Capiro	1.15 – 1.28 ns	0.003 - 0.04 ns
	Suprema	1.21 – 1.46 ns	(-0.01) - 0.04 ns
Ca total-Mg total	Capiro	0.34 - 0.38 ns	2.68 - 6.44 ns
	Suprema	0.36 - 0.44 ns	0.81 - 9.35 ns
Ca total-S total	Capiro	0.18 - 0.22 **	6.90 - 11.16 ns
	Suprema	0.25 - 0.32 **	4.66 - 12.07 ns
Mg total-S total	Capiro	0.51 - 0.60 *	4.52 - 8.46 ns
	Suprema	0.59 - 0.72 *	3.87 - 10.28 ns
FTubW-Catub	Capiro	0.07-0.08 ns	(-0.34) – 0.12 **
	Suprema	0.06 - 0.08 ns	0.18 - 0.68 **
FTubW-Mgtub	Capiro	0.26 - 0.29 **	(-2.12) - (-0.73) **
	Suprema	0.24 - 0.26 **	(-0.66) - 0.001 **
FTubW-Stub	Capiro	0.27 - 0.30 ns	(-1.79) - (-0.53) *
	Suprema	0.24 - 0.31 ns	(-0.62) - 1.58 *

CI: confidence interval; CaHI: calcium harvest index; MgHI: magnesium harvest index; SHI: sulfur harvest index; FTubW: fresh weight of tubers; Catub: calcium content in the tubers; Mgtub: magnesium content in the tubers; Stub: sulfur content in the tubers.

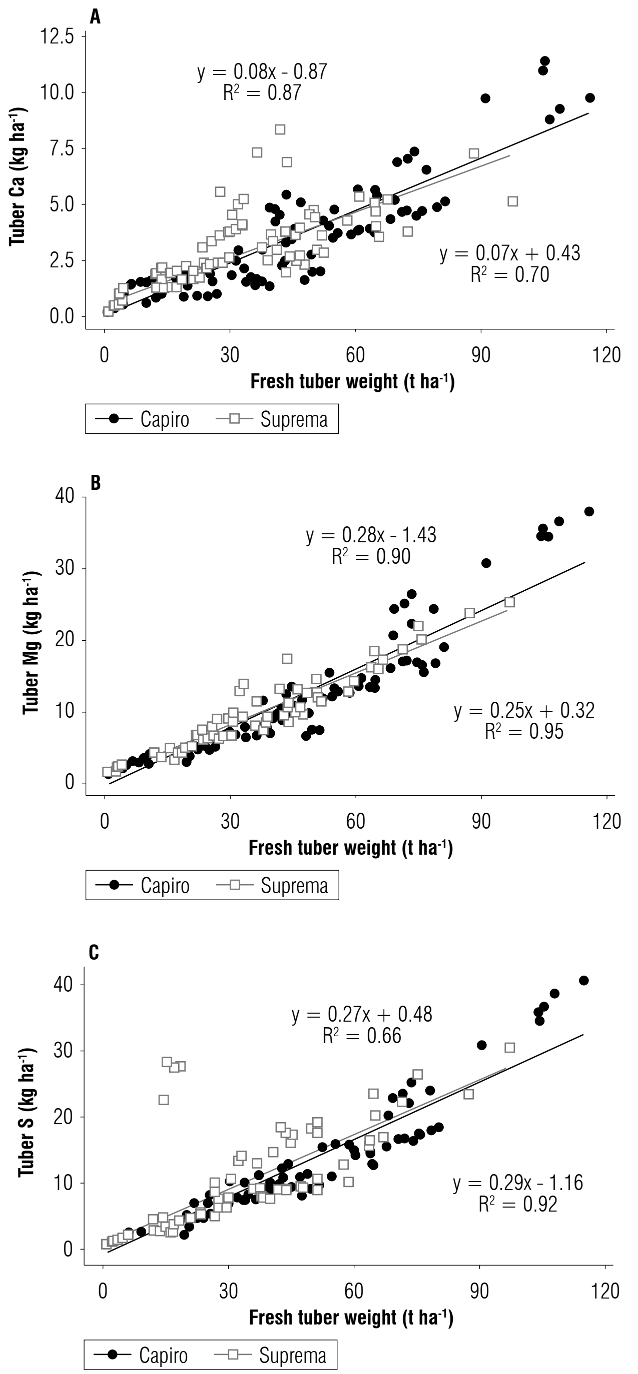

FIGURE 5. Relationship between the content of A) Ca, B) Mg, and C) S in the tubers with the fresh weight of the tubers (yield) for Diacol Capiro and Pastusa Suprema (n=130 for each cultivar). The lines represent the fitted model of each cultivar. R^2: coefficient of determination.

Discussion

The effect of "dilution" of Ca observed in potato agrees with Addiscott (1974), who reports a possible effect of dilution of a fixed amount of Ca in potato, contrasting with Walworth and Muniz (1993) who argue that the concentration of Ca tends to increase with age in the plants and to decrease in the tubers. The concentration of Ca required in the cytoplasm is less than 1 μM and the unused Ca stored in the vacuoles allows correct cellular activity (Koch *et al*., 2020). In this case, the Ca stored in the vacuole would not have a significant effect on the change in its concentration in the plant when considering a stable scenario for the availability of the nutrient. Although the concentration of Ca could be expected to increase as the plant grows due to its structural function, a greater and faster accumulation of other nutrients, proteins, carbohydrates, and other molecules explains the dilution effect (Koch *et al*., 2020).

The concentration of Ca in tubers during tuber maturation (0.68%) was lower than that reported by Jahanzad *et al*. (2017) for tubers of *S. tuberosum* "Dark Red Norland", (0.8%) and "Superior" (1.4%) at harvest time. The Mg concentration in tubers during the productive cycle (0.30-0.65%) was higher than that reported by Hauer-Jákli and Tränkner (2019) in leaves (0.14%) and by Walworth and Muniz (1993) in tubers (0.25%). This is because most studies do not establish the concentration in the whole plant and do not consider the variation of critical concentration during the development of the crop, instead proposing a single critical value. Likewise, the natural variation in nutrient consumption between cultivars must be considered. The concept of critical Mg concentration in plants has been poorly studied, so the establishment of values by phenological stage was a new proposal that complements what was previously published by Walworth and Muniz (1993).

The value of Sc for the flowering stage and maximum filling (0.25% and 0.28%) agrees with that reported by Walworth and Muniz (1993) in the potato. The Sc curve had a high dilution coefficient (b=0.39), higher than that established for other C3 crops such as wheat (b=0.17; Reussi *et al*., 2012), rape (b=0.18; Ferreira & Ernst, 2014), and soybean (b=0.11; Divito *et al*., 2016). The high coefficient *a* in potato (0.6-0.7) could indicate that the crop has a high requirement of S in the initial stages of development (<1 t ha^{-1}), explained by the rapid and high generation of foliage where the S is needed for the synthesis of proteins and sulfolipids.

The rapid decrease in the concentration of mineral nutrients observed for biomass of 1-6 t ha^{-1} is caused by the beginning of tuberization and filling of tubers. Where the total biomass in potato increases significantly, demand is high for photoassimilates and starch accumulates in harvestable organs (Gómez *et al*., 2019b), diluting the concentration of mineral nutrients. The nutrient with the highest dilution was S, possibly because the requirements of Ca and Mg remain higher during growth and development due to their structural functions in cell walls, chlorophylls, and energy metabolism (Maathuis, 2009) and during the end of the cycle due to its structural role and the filling of tubers. On the other hand, S is mainly found in amino acids, proteins, and as part of glutathione, whose need and synthesis rate may be lower than the growth rate (Moussa *et al*., 2018). The greater slope of Sc for Capiro may indicate that this variety is more efficient in the use of S than Suprema (Santana *et al*., 2020). The dilution in the Sc curve was similar to that previously established for N (Gómez *et al*., 2019b), confirming the interaction between the assimilation of S and N in relation to their function in protein formation (Kopriva & Rennenberg, 2004).

The higher Ca and Mg concentrations in Capiro throughout the cycle are consistent with its higher quality for industrial processing. The higher proportion and concentration of S in Suprema is related to its indeterminate growth habit which demands higher protein synthesis. The nutrient differences in the potato seed between cultivars that directly affect the concentration of nutrients in the early stages must also be considered. For future research, it would be of interest to establish the nutrient content of the potato seed.

The dilution curves of Cac, Mgc and Sc are a useful tool to carry out the diagnosis of these nutrients in critical stages of potato cultivation from a sample of plant tissue. Concentration values in the sampling of plants above or below the dilution curve (in the corresponding phenological stage) indicate that the plants are growing with an excess or deficiency of the nutrient. Concentration values close to or fitting the curve indicate sufficiency of the nutrient (Marouani *et al*., 2014; Carciochi *et al*., 2019).

The low harvest indexes of Ca-Mg-S show that their mobility to the tuber is low and is lower than what was previously reported for the N-P-K nutrients (CI greater than 0.6) (Gómez *et al*., 2019a). The higher indexes for Capiro and homogeneity between localities indicate that this cultivar has a better accumulation capacity and phenotypic plasticity in different environments, favoring its productive potential and agreeing with the results in yield previously published by Gómez *et al*. (2019a). The higher CaHI value of Capiro in the first Chocontá cycle could be related to the higher recorded evapotranspiration, which favors the movement of Ca. On the other hand, Suprema showed better adaptation to the conditions of Chocontá (acid soils and low fertility), possibly because the environmental conditions of higher precipitation and lower temperature favored the solubility of nutrients in the soil and decreased the respiration rate of the plants. In contrast, in Facatativá, with soils of high fertility and higher temperatures, Suprema had a high consumption of N (Gómez *et al*., 2019a), which affected tuberization, translocation, and accumulation of Ca-Mg-S.

The greater translocation of Mg and S from Capiro in Facatativá could have an indirect effect on their accumulation in the tubers by favoring a greater formation of roots on the tubers and stolons that participate in uptake of nutrients directly from the soil for their later accumulation in these organs (Kratzke & Palta, 1985; Palta, 1996), positively affecting the harvest indices in the cultivar. These results are related to the higher yield of this cultivar and its quality for industrial uses (Gómez *et al*., 2018), because these nutrients participate in the translocation of photoassimilates and protein synthesis. Additionally, the positive effect of the bearing of the Capiro plant must be considered, since its leaves have larger leaflets and are parallel to the ground, while Suprema has a more perpendicular arrangement. This characteristic favors the incidence of radiation and, therefore, the photosynthetic rate, yield, and nutrient translocation in Capiro.

For the nutrients evaluated, the accumulation in the tuber followed the order of Ca<Mg<S, a result consistent with their mobility in the phloem in potato (Subramanian *et al*., 2011). The mobility of Ca by transpiration stream affects its translocation to organs of low transpiration rate, such as tubers (Schabow & Palta, 2019). Compared to other crops, the CaHI in potato (0.05) was lower than that reported for wheat (0.09) (Shen *et al*., 2019) and similar for corn (0.05) (Szczepaniak, 2016). The high harvest rates of Mg and S (greater than 0.5 for S and 0.3-0.4 for Mg), confirm the high mobility and accumulation in the tuber proposed by Silva *et al*. (2020) and Subramanian *et al*. (2011). The high accumulation of S in the tubers is due to its role in the partition of photoassimilates towards the tubers and as a structural element in amino acids (methionine and cysteine) and proteins (Dhakad *et al*., 2019). On the other hand, the MgHI of potato was lower compared to cereal crops such as rice (0.52) (Sánchez *et al*., 2019) or wheat (0.46) (Shen *et al*., 2019).

From these models, the value of SHI can be estimated with a good level of reliability from the MgHI; it has greater predictive confidence than CaHI. Likewise, the S content in the entire plant can be established from the total Ca or Mg content. The higher proportion between nutrients (total contents) in Capiro could be related to the fact that its growth is determined with respect to Suprema; with

Capiro having a more rapid tuberization and accumulation of reserves. Likewise, the lower Ca:S ratio in Suprema may be related to a higher S requirement due to its indeterminate growth habit. Future research should establish the relationship between these results and qualities in terms of mechanical resistance, disease incidence, and occurrence of pathophysiologies in both cultivars. Differences between cultivars may indicate variation in the processes of accumulation or utilization, confirming that Capiro and Suprema present different requirements for Ca, Mg and S. The models established for the interaction between nutrients are valid for the experimental conditions evaluated for Diacol Capiro cultivars and Pastusa Suprema from the Andigenum Group.

The interaction between Ca, Mg, and S in their total content and Ca-Mg in the tuber is explained by the participation of these nutrients in linked processes during crop growth. Magnesium participates in photosynthesis, energy metabolism, synthesis of proteins, enzymatic activity, and the transport of photoassimilates. Calcium participates in signaling processes and structuring of cell membranes and walls, and S is part of sulfolipids, proteins, and participates in oxidation-reduction processes (Koch *et al*., 2020). The results of the Mg-S interaction agree and those of Ca-S and Ca-Mg contrast as reported by Subramanian *et al*. (2011). The results of this research should not be confused with nutrient interaction within the soil, where antagonism between Ca-Mg, synergism between S-Mg and lack of correlation between S-Ca can occur (Klikocka & Głowacka, 2013; Barczak & Nowak, 2015; Rietra *et al*., 2017; Rhodes *et al*., 2018).

The low correlation between the content of nutrients in the aerial part and in the tubers could indicate a low dependence on the accumulation of nutrients in the aerial parts with respect to the tuber growth, which agrees with what was proposed by Gómez *et al*. (2019a). On the other hand, the correlation between the fresh weight of the tubers and the content of Ca-Mg-S confirms the importance of these nutrients for crop yield (Hamdi *et al*., 2015; Helal & AbdElhady, 2015; Muthanna *et al*., 2017; Seifu & Deneke, 2017; Wang *et al*., 2020). The models proposed for this relationship are a first approach to estimating the content of Ca-Mg-S in the tubers, according to the tuber growth.

Conclusions

The critical dilution curves of calcium, magnesium, and sulfur established are the first reported for two potato cultivars of the Andigenum Group. These are a first approach and provide a guide to improved nutritional diagnosis and adjustments based on the growth and development of the crop. The tool is valid for the evaluated genotypes. The results in harvest indexes expand the information on the Ca-Mg-S accumulation dynamics of the tubers. The study confirms that Capiro has greater plasticity under contrasting edaphoclimatic conditions, while Suprema shows greater adaptation to low fertility soils. The Ca-Mg-S nutrients show a high correlation in the plant, making it possible to estimate the total content or the tuber content. The proposed linear models are a first step to make estimates; this should be expanded in future research. As well, it would be of interest to evaluate a range of fertilization doses ranging from moderate deficiency to excess of Ca-Mg-S.

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Conflict of interest statement

The authors declare that there is no conflict of interest regarding the publication of this article.

Author's contributions

KC developed the methodology, prepared, created, and presented the published work and oversaw its visualization, and wrote of the original draft; MIG developed the conceptualization, provided funding acquisition, and conducted the research process; LER carried out the supervision and validation. All authors reviewed the manuscript.

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