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Assessment of Agricultural Practices in Maize Crops (*Zea mays*) Based on Elemental Profile and Chemometrics Analysis

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Authors' contributions

This work was carried out in collaboration among all authors. Authors JZH and MS performed the elemental analysis and sample treatment. Author CAM wrote about the physiological effects of agronomic practices in results and discussion. Authors SMA and JMC performed the statistical analysis and built all the chemometrics models. Author RAG managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this work the effects produced by two treatments on maize crop samples have been studied. Analysis of maize grain based on two types of agronomical conditions was performed on: (a) lots treated with different fertilizers and (b) lots with different crop density. Analysis was carried out by microwave induced plasma with optical emission spectrometry (MIP OES) and included the quantification of 11 elements: Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb and Zn. With the purpose of

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understand the effect of agricultural practices on elemental profile, principal components analysis (PCA) and cluster analysis (CA) were used as chemometrics tools, finding a correct grouping of each crop based on the type of treatment. The obtained models can be useful to evaluate agricultural strategies, as well as for determining potential yields in maize crops.

Keywords: Maize; agricultural management; chemometrics; PCA; cluster analysis.

1. INTRODUCTION

The agricultural production is one of the most important activities around the world, not only from the point of view of economy, but also due the feeding interest [1]. Into this contribution, the evaluation of certain compounds that affect nutritional quality in crops becomes relevant; between them, multi-elemental profile comprises a key crop quality parameter because of its importance in biological systems and food product quality regarding with physiological effects on plants as well as human health.

Plants require at least 14 mineral elements as nutrients for its complete physiological activity. The concentration range of each element varies from >10,000 µg/g (e.g. calcium, nitrogen. potassium), to 0.001 µg/g (e.g. molybdenum, nickel). If mineral nutrients are out of the optimum range of content, the plant will show deficiency or toxicity symptoms that will affect the plant's health and survival [2]. The effect of metals on some crops has been studied focusing on contaminated soils where the influence of those metals is observed in the plant growing. In this way, a few studies of elemental determination on maize seeds in contaminated soils have been reported [3,4]. However, the information of elemental profile in maize seeds from crops under usual management practices to maximize the yields -as crop density or use of fertilizer- is scarce.

Adequate agricultural management can contribute to sustainability of production systems in the field, since their practice can determine both, the type of exploitation to carry out as the optimization crop production to allow high yields conserving soil fertility. In order to obtain the maximum yield under normal environmental conditions, crops should be able to benefit from sunlight during critical yielding periods. Maize plant development is associated with the capacity to capture sunlight. The most effective practice to improve sunlight capture is to optimize the crop density and row spacing. A suitable row spacing, or crop density increase the interception of incident light with a consequent increase of light capture by foliar area unit, increasing photosynthesis rates and improving the availability of water by canopy evaporation protection [5]. On the other hand, fertilization affect quality characteristics of maize seed as content of protein, nitrogen (N), phosphorus (P) and potassium (K) in grains [6,7].

The availability of soil nutrients limits maize production and yield; thus, it is important to know the plant's needs and the quality of the soil in which it will be developed. If those requirements are not provided in a natural way, different agricultural practices can be used to cover the deficiency. Fertilization is one of the main practices to improve the land yielding [8]. Even though fertilization with inorganic nitrogen alone or in variable combination with organic nitrogen (urea) does not affect the content of macronutrient as N, P and K in seeds, more proportion of organic N can decrease the uptake of micro-nutrients by plant [6]. As consequence, changes of mineral profile in plants organs and tissues -particularly in seeds- are expected.

The mineral profile of maize grains can help to infer about the environmental effects over the crop quality. This analysis is important for the assessment of essential and non-essential nutrients uptake by plants, whose dynamic in soil is complex [9]. On the other hand, the analysis of plant material can be used as diagnostic technique to determine nutritional status of crops, as well as to provide quality control and/or environmental pollution indexes. From the point of view of mineral analysis, emission atomic spectrometry is preferred for simultaneous multi-elemental analysis due to high sensitivity, wide range of linear response and low noise level compared to other methods, allowing the detection of a large number of elements, including a high number of metals and some non-metals. Currently, microwave induced plasma with optical emission spectrometry (MIP OES) is a challenging plasma technique used for numerous trace elements determination. The major advantages are related to the use of an inexpensive gas to generate plasma –purified atmospheric nitrogen instead argonsimultaneous multi-element detection, high sensitivity, wide range of linear response and low noise level. Also, multi-elemental analysis can provide important data about the nutritional quality of foods, because it can inform about major, trace and toxic elements, which can be present in seeds depending on the type of plant, geographical localization or environmental conditions. From the point of view of chemometrics, PCA is a tool which has been widely used to improve the analysis and interpretation of data. In this way, there are much works including PCA analysis to understand the presence of "hiden phenomena" which are presents in the data matrix and represent properties into the matrix that they can show, in some cases, classification properties which help to explain that phenomena. Then, cluster analysis is other chemometric tools which is used to confirm the information obtained by PCA, because in general, uses the same variables that selected to PCA model. According to our knowledge, there are not previous works that study agronomic practices on maize by chemomentrics. For the exposed, in the present work the mineral profile of maize seeds collected under different agricultural conditions such as seeding density and fertilization was studied with objective to determine differences between crop conditions by means of chemometrics analysis.

2. MATERIALS AND METHODS

2.1 Crop Conditions and Sampling

Sampling was conducted during harvest time, from September 2015 to March 2016 in La Pampa province (36° 37'S; 64° 17'W). The analysed samples were from *(a)* three lots with different crop density: six samples with a density of 25000 seeds/ha, three samples with a density of 35000 seeds/ha and six samples with a density of 45000 seeds/ha and *(b)* two lots treated with different fertilizers: twelve samples treated with ammonium phosphate (100 kg/ha) (PDA) and thirty-three samples treated with ammonium phosphate (100 kg/ha) combined with urea (140 kg/ha) (PDA-U). All samples were collected by triplicate.

2.2 Sample Preparation

Maize seeds were separated from kernels, cleaned, milled and stored in plastic bags until analysis. Before mineralization, the milled seeds were dried in an oven at 60°C for 24 hours. Mineralization was carried out accurately weighting 0.5 g of dry samples in a polyethylene tube, adding 5 ml of concentrated HNO_3, and placing into a thermostatic water bath at 100°C for 30 minutes. Then, the acid mixture of sample was placed into an ultrasound system for the same period, cooled at room temperature and diluted to 30 ml with deionized water [10].

2.3 Instrumentation and Sample Analysis

Elemental analysis was performed using an Agilent MP4100 (Santa Clara, USA) which includes a Czerny-Turner monochromator with a charge-coupled device (CCD) array detector, an inert One Neb nebulizer, a double-pass glass cyclonic spray chamber, and a SPS3 auto-sampler system Agilent. Eleven elements, including calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorus (P), lead (Pb) and zinc (Zn) were determined using the most sensible wavelengths for each one. Table 1 shows the figures of merit for multielemental determination in maize samples after mineralization. Limit of detection (LOD) and quantification (LOQ) were calculated considering 3.3 and 10 times the standard deviation of blanks, respectively [11].

2.4 Reagents

A Millipore (Darmstadt, Germany) ultra-purifier system was used to prepare all solutions, which produce ultra-pure deionized water (resistivity of 18.2 mΩ). To perform the mineralization of samples, concentrated nitric acid (HNO_3 - Merck, Darmstadt, Germany) was obtained by suboiling distillation into a Berghoff system (Eningen, Germany). For calibration step, SCP Science (Quebec, Canada) supplied multielement standards in 5% HNO_3. The glass material used throughout the study was washed with 10% HNO_3 for 24 hours before use and then rinsed with deionized water.

2.5 Data Analysis

Chemometrics model for crop density study was performed using the content of P, Mg, Zn, Fe, Ca, Mn, Cr, Cu and Ni as variables, while for fertilization study was conducted using the concentration of Fe, Mg, Zn, Ca, Mn, Cr, Cu and Ni. For cluster analysis, the criteria of amalgamation was Ward method and squared Euclidean distance for assessment of crop density, while Manhattan distance was used for N fertilization. All classification models (PCA and CA) were obtained using the chemometrics package Unscrambler X 10.5 software (CAMO AS, Trondheim, Norway).

3. RESULTS

3.1 Effect of Crop Density on Elemental Profile

Table 2 shows the results of multi-elemental analysis obtained for lots with different crop densities. The PCA model was performed using 2 principal components (PC's) which explained (according to the obtained percentage of explained variance) a 99% of the original information. Fig. 1 shows the PCA model in which three groups of samples can be observed according to number of seeds by hectare: A (25000 seeds/ha), B (35000 seeds/ha) and C (45000 seeds/ha). Also, the figure shows the influence of P on PC1, which is the main responsible to generate the groups, and in minor grade Mg. That mean, the content of P played a relevant role and showed a marked effect on the model, indicating that this element had significant differences according to crop density. However, if well Mg had also important influence on model, this element although of be an essential component of chlorophyll, not helped to obtain groups, but produced the scattering (ellipses) on ordinate axis. Fig. 2 shows the dendogram obtained by CA –using the same variables as PCA- for the classification of lots with different seed densities that confirm the results obtained by PCA, but also it can be observed that the highest density presents marked differences in comparison to the lowest densities, which are grouped together.

Table 1. Wavelengths and figures of merit for elementals analysis performed by MIP OES

Element	LOD[a]	LOQ[a]	Wavelength (nm)
Ca	0.13	0.39	422.673
Cd	0.47	1.42	228.802
Cr	0.09	0.26	324.433
Cu	0.51	1.55	324.754
Fe	1.34	4.05	259.940
Mg	0.23	0.68	383.829
Mn	0.08	0.25	403.076
Ni	0.28	0.86	352.454
P	0.24	0.72	214.915
Pb	1.70	5.20	283.305
Zn	1.67	5.06	481.053

[a]Concentration expressed in µg/g

3.2 Effect of Fertilizers on Elemental Profile

Table 3 shows the results of the multi-elemental analysis of lots treated with the different fertilizers (PDA and PDA-U) where most heavy metal contents increased under urea application (except for Ni). Among essential nutrients, Fe and Mg increased approximately 100% under PDA-U treatment while Mn and Zn increased in a minor proportion. Furthermore, toxic elements as Cd and Pb were under the limit of quantification (<LOQ) and Cr could be quantified in PDA-U but not in PDA treatment. On the other hand, Ca and Cu did not exhibit differences between PDA and PDA-U. The performed PCA model obtained for fertilizer allowed explaining 97% of the original information through four principal components. The 3D PCA score plot (Fig. 3) shows two groups: A) soil in which only one fertilizer (ammonium phosphate, PDA) was applied and

Table 2. Mineral contents of maize seeds at three seeding density

Analyte [a]	Crop density (seeds/h) 25 10[3 b]			35 10[3 b]			45 10[3 b]		
Ca	3.85	±	1.76	4.11	±	0.60	4.02	±	2.67
Cd		< LOQ			< LOQ			< LOQ	
Cr	0.59	±	0.20	0.55	±	0.01	0.53	±	0.08
Cu	2.38	±	0.32		< LOQ		2.13	±	0.85
Fe	24.75	±	7.42	32.86	±	19.79	34.58	±	9.10
Mg	1049.63	±	248.77	1378.38	±	108.54	1074.77	±	231.31
Mn	7.15	±	1.36	4.40	±	0.51	7.80	±	1.40
Ni	3.95	±	0.16	3.24	±	0.14	4.09	±	0.35
P	3338.86	±	275.58	4097.02	±	179.95	5051.37	±	305.63
Pb		< LOQ			< LOQ			< LOQ	
Zn	19.76	±	2.17	13.83	±	1.44	22.25	±	2.67

[a]Concentration expressed in µg/g; [b]Mean ± SD (n_A= 6; n_B = 3; n_C = 6)

Table 3. Mineral content of maize seeds according two fertilizers

	Fertilizer					
	PDA			PDA-U		
Ca	5.30	±	2.23	5.78	±	5.60
Cd		< LOQ			< LOQ	
Cr		< LOQ		0.53	±	0.09
Cu	2.00	±	0.86	1.87	±	0.76
Fe	13.79	±	4.28	28.79	±	11.84
Mg	450.72	±	55.97	1026.79	±	201.65
Mn	5.21	±	1.28	6.69	±	1.27
Ni	4.62	±	0.56	3.77	±	0.34
P	4306.23	±	525.68	4428.42	±	586.21
Pb		< LOQ			< LOQ	
Zn	15.89	±	5.21	19.71	±	3.01

[a]Concentration expressed in μg/g; [b]Mean ± SD (n_A= 12; n_B = 33)

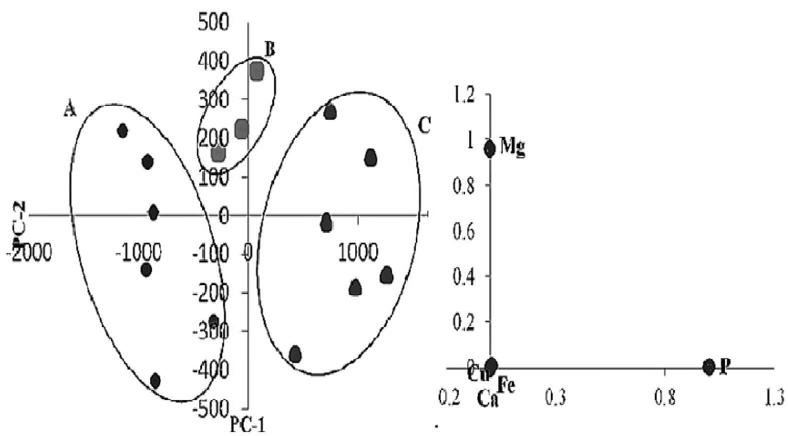

Fig. 1. PCA scores plot (left) for the classification of three density crops. A) 25,000; B) 35,000 and C) 45,000 seeds per hectare; PCA loading plot (right) showing the influence of original variables on the model

B) soil in which two combined fertilizers were applied (ammonium phosphate and urea, PDA-U). In this case, 8 elements were used to build the PCA model (Mg, Cu, Ni, Zn, Ca Fe, Cr and Mn, Fig. 3 right) from which, Cu and Ni had more influence on PDA treatment, while Mg, Fe, Cr followed to Zn, Mn and Ca were the more influent elements on PDA-U group. This model showed that minor elements –at difference to obtained in crop density- had strong influence on grouping, indicating a possible effect on enzymes composition, which are constituted by these elements. The dendogram in Fig. 4 obtained by cluster analysis (CA) also allowed the confirmation of clustering obtained by score plot. As mentioned, 3D PCA loading plot (Fig. 3, right) shows that Cr, Fe, Mg, Mn, Ca and Zn were the most influent variables for grouping of PDA-U samples, while Cu and Ni had influence in PDA grouping, which helps as qualitative criterion for distinguish both groups.

4. DISCUSSION

There is scarce information about mineral profile of seeds when crop density is the studied factor. Bisht et al. [7] reported a decrease of P contain in maize grains as crop density increase from 63000 plants/ha to 100000 plants/ha. However, crop densities evaluated in present work showed an increase content of P in maize seeds when crop densities are from 25000 plants/ha to 45000 plants/ha. This it seems to indicate that exist values of crop density in which accumulation of P in maize seeds achieve maximum levels (as in this work) but then decreasing as crop density increase. French et al. [12] established an optimum crop density for canola in various

Australian zones in function of grain yield, or grain oil as indicative parameters of yield. They report when those measured parameters achieved maximum values, they are stayed constant at higher crop density. This suggest that when crop density values overcome critical, although the yield may be did not be affected, the changes of mineral profile and quality in seeds could be compromised whit this type of management.

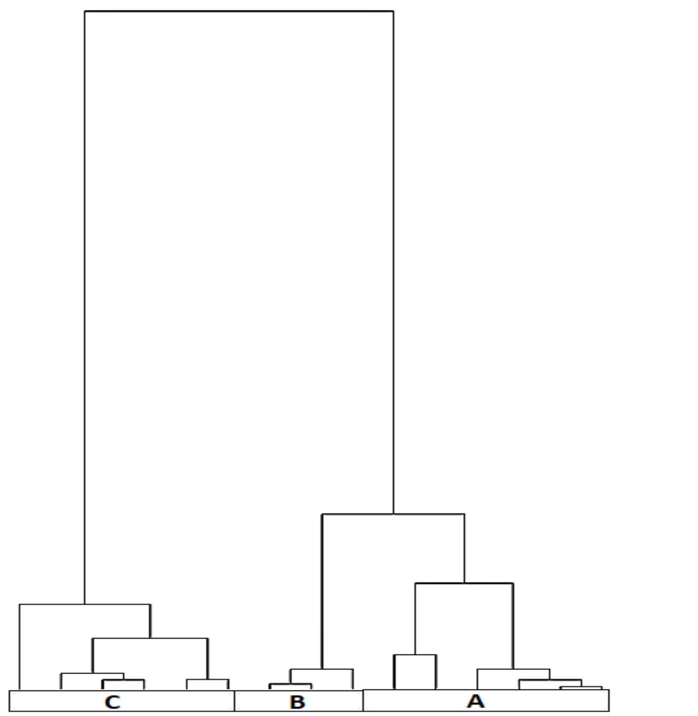

Fig. 2. Dendogram obtained by cluster analysis for density crops

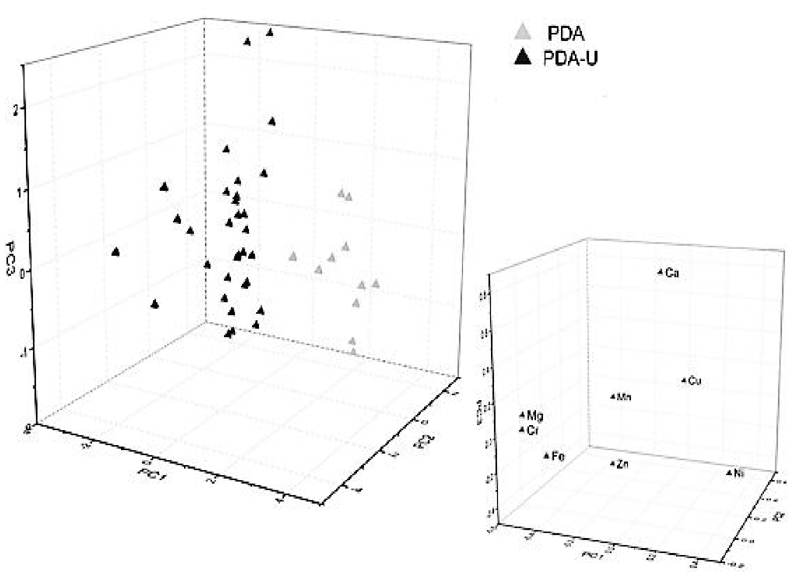

Fig. 3. PCA score plot for the classification of crops based on different fertilizers. A) ammonium phosphate (PDA); B) ammonium phosphate + urea (PDA-U); PCA loading plot shows the influence of variables on the fertilizers model

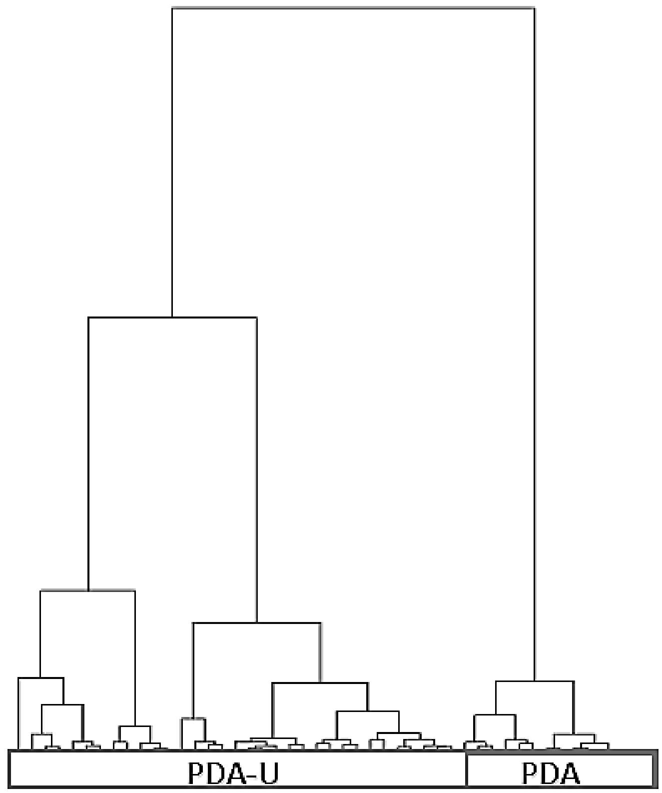

Fig. 4. Dendogram by cluster analysis according to fertilizers

The increasing of minerals showed in Table 3 according to type of fertilizers can be due bioavailability of heavy metals when soil pH decrease due urea application. Urea can acidify the soil resulting in the transformation of heavy metals and increasing their availability [13]. Although heavy metals are accumulated in roots, due pH the bioavailability of several minerals increase (including heavy metals), allowing its accumulation in cereal parts [14] and seeds as it is the case of Cr [15]. This fact can explain the increasing of Cr, Fe, Mg, Mn and Zn content in the analyzed samples; however it cannot explain the diminishing for Ni, whose soil bioavailability is also affected by pH. The analysis of results from PCA arises two issues to analyze: 1) the trend of heavy metal accumulation in seeds when urea is applied as fertilizer and 2) the decrease of Ni content in seeds by same reason. In the first case, there is several reports indicating the influence of urea in soil acidification [16,17], increasing in consequence the availability of heavy metal as was previously explained [14,18]. Nevertheless, the reduction of Ni in seeds can be explained by it inclusion as prosthetic group in urease enzymes of microbial community of soil [19] that in spite soil acidification by urea can make Ni more available, microbiological synthesis of urease in soil -which is activated by urea- could capture Ni reducing his availability for plant and in consequence diminish the Ni content in seed [20].

5. CONCLUSION

There is a close relationship between seed quality and nutrient content which influence in crop yield. This is because the nutrient reserves of the seed represent a key factor that affects germination and uniformity of seedlings in the field, and as consequence the yield. The positive effects of a greater quantity of reserve nutrients in the seed can be observed in the vigor of the crops in the field. This fact can see reflexed in this work, where principal components analysis as well as cluster analysis allowed the classification of each crop type in relation to type of fertilizer applied and the different density in crops based on mineral profile. Furthermore, integral analysis of mineral profile performed through multivariate analysis, allowed to determine differences among agricultural management practices and its possible effects on seed quality. The expected eco-physiological state of plants for more suitable and efficient maize production is fundamental to make decisions on crop practices to achieve higher yields. For this reason, a better understanding of effects of crop management over mineral profile of seeds contributes to a better expression of crops potential through the adequate adjustment of single agronomic practices. Combination of elemental analysis and chemometrics represents an important technological advance in crop science allowing improve yields based on statistical tools without lost of expense in soil or plant treatment.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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