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Characterization of the content of anions and metals in potatoes, tomatoes, and onions marketed in Cuenca, Ecuador to obtain a classification model

Caracterización del contenido de aniones y metales en papa, tomate y cebolla comercializados en Cuenca, Ecuador, para obtener un modelo de clasificación

Alvarez-Blacio Astrid^{1,2,*}, Alvitres-Medina Claudia^{1,2,*}, Castro Cynthia^{3,*}, Verdugo Josselyn^{3,*}, Pérez-González Andrés³, María Dolores Tonon¹, Pinos Verónica^{1,2**}, Tripaldi Piercossimo^{3**}

Abstract

Due to the accelerated growth of the world population, the need for food has increased. Due to the differentiated climatic factors that Ecuador has, the usage of pesticides and fertilizers has increased at an alarming rate, in search of increasing the productivity of crops, which results in an accumulation of residues in food and soil. In this study, the search for concentrations of metals and ions from fertilizers in four high-consumption products will be limited to INIAP Cecilia and Chaucha Amarilla potatoes, Kidney Tomato and Paiteña Onion found in markets and supermarkets. The metals were determined by using inductively coupled plasma spectrometry with a mass spectrometer (ICP-MS). For ions, through a UV-visible spectrophotometer. The values found were within the norm. Differences were found between the metal content of the potato between peel and pulp where the latter will appear at the highest concentrations. Multivariate statistics showed that the samples are grouped by the planting site and not the type of sample, which shows the importance of the soil and the cultivation process. The generation of a classification model for fed products with the analyzed parameters is discussed.

Keywords

Metals, Fertilizers, Nitrates, Potato, Tomato, Onion

Resumen

Debido al crecimiento acelerado de la población, el requerimiento de alimentos se ha incrementado. A esta demanda se suman los factores climáticos diferenciados que tiene Ecuador, los cuales inciden en que los agricultores utilicen pesticidas y fertilizantes de forma indiscriminada para incrementar la productividad de los cultivos. El resultado de esta práctica es una acumulación de residuos tanto en los alimentos como en el suelo.

En este estudio se determinó las concentraciones de metales e iones provenientes de los fertilizantes en cuatro productos de alto consumo: papa INIAP Cecilia, papa chaucha amarilla, tomate riñón y cebolla paiteña encontrados en los mercados y supermercados. Los metales fueron determinados por espectrometría de plasma acoplado inductivamente con espectrómetro de masas (ICP-MS) y los iones a través de un espectrofotómetro UV-visible. Los valores encontrados estuvieron dentro de la norma. Se detectó diferencias entre la concentración de metales de la papa entre cáscara y pulpa donde esta última mantenía las mayores concentraciones. La estadística multivariada permitió evidenciar que las muestras se agrupan por el sitio de siembra y no por el tipo de muestra, lo que revela la importancia del suelo y el proceso de cultivo. Se obtuvo un modelo de clasificación de productos con base en los parámetros analizados.

Palabras clave

Metales, fertilizantes, nitratos, papa, tomate, cebolla

1 IRCMA Investigation Group, Faculty of Chemistry, Victor Manuel Albornoz, EcoCampus Balzay. Cuenca-Ecuador.

2 Department of Water Resources and Environmental Sciences, University of Cuenca, Victor Manuel Albornoz, EcoCampus Balzay. Cuenca-Ecuador.

3 Investigation Group of Chemometry and QSAR, Faculty of Science and Technology, University of Azuay. Cuenca-Ecuador.

* These authors contributed equally, thus equal first authors

** [veronica.pinos@ucuenca.edu.ec; tripaldi@quazuay.edu.ec, <https://orcid.org/0000-0001-8278-5873>]

1. Introduction

The environmental contamination of toxic or eco-toxic inorganic compounds such as Lead, Cadmium, Mercury, Chromium, and Arsenic, among others, represents a danger to public health (McClintock et al., 2012; WHO, 1980). These metals are found diffused in different environmental matrices and come from natural and anthropogenic sources due to organometallic compounds that are illegally used in pest control products, as well as industrial and mining waste. Studies carried out to determine metals in soils have found considerable amounts of metals in soils destined for food production (Dziubanek et al., 2015). For example, the presence of high amounts of Arsenic and Cadmium in soils in Spain and Portugal and high levels of Zinc and Copper in arable soils in Greece and Macedonia has been found among others (Topalidis et al., 2017; Tóth et al., 2016). This fact is worrying because the consumption of food grown in environments contaminated with toxic metals has been detected as the greatest source of exposure for people to these (Khan et al., 2008). From the soils, the metals are mainly transferred to the foliar tissues of the plant. Confirming this fact, studies have found metals in foods (Dziubanek et al., 2015; Hu et al., 2017). For example, in China, a study of cultivated rice found high doses of Cadmium, Lead, Chromium, Copper, Zinc, and Nickel in the water and soil used to grow rice (Huang et al., 2019). Meanwhile, a study on the bioaccumulation of metals in pumpkin, carrot, and potato in several Polish cities found higher than allowed levels of Cadmium and Lead in these products (Dziubanek et al., 2015).

To the concern that foods contain toxic metals, compounds are added that are not toxic by themselves, but when they bioaccumulate or in large concentrations, they can be dangerous for man, such as nitrates. The availability of these compounds is varied (soil, plants, water) and occurs naturally from the nitrogen cycle: atmospheric and industrial fixation, mineralization of organic matter, and nitrification of released ammonium (Cabrera, 2007); but anthropogenic modifications (mining, industries, agricultural production) alter the normal concentrations of these in the different environmental matrices (Moreno C et al., 2015). For example, intensive greenhouse agriculture makes heavy use of nitrogenous fertilizers so vegetables and drinking water may contain higher nitrate concentrations than in the past. Nitrates are not considered toxic unlike nitrites; however, it should be considered that approximately 5% of nitrites are converted in the digestive tract during ingestion into nitrates (Santamaria, 2006). Nitrates from fertilizers remain in food as shown by studies in this regard. For instance, Leyva et al. (2005) determined concentrations in tomato fruits of up to 850 mg/kg using 454 kg of N/ha (Leyva et al., 2005).

According to the INEC (National Institute of Statistics and Censuses of Ecuador), potatoes, tomatoes and onions are high priority crops in Ecuador due to their high internal demand. The tomato is an annual, biannual herbaceous plant belonging to the Solanaceae family (*Solanum Lycopersicum*), in Ecuador, according to the Agricultural Public Information System (SIPA), there are productions of up to 38 thousand tons/year. Finally, the onion is a biennial herbaceous plant belonging to the Amaryllidaceae family (SIPA, 2020). According to MAGAP (2015), it is the second most-consumed vegetable (6 kg/year/capita) (MAGAP, 2015). The potato is a tuber belonging to the Solanaceae family (*Solanum tuberosum* L.) and according to the International Potato Center is the third most consumed crop worldwide. In Ecuador, figures from the Survey of Surface and Continuous Agricultural Production (ESPAC), estimate annual production of 523 thousand tons, with more than 400 varieties (MAG, 2020), it is also the main source of food in the highlands of the country, with an annual per capita consumption of 122 kg in Quito and 80 kg in Cuenca (Pumisacho & Sherwood, 2002). The Yellow Chaucha potato (*S. Phureja*), is one of the few native potato varieties of the high Andean communities, it is small, with an

approximate diameter of 4 cm, whose skin and pulp color is ocher or intense yellow, it has a high nutritional value, good flavor, and a short cycle, which means that they are harvested in less time. The INIAP Cecilia potato (*Solanum vertifolium* x *andígena* Var.), is one of the improved potato varieties by INIAP, it comes from the species *S. Vertifolia* and *S. Jabonilla* (INIAP, 2014). It has an elongated oval shape with a medium size, it is slightly flattened on the upper and lower faces, its skin is creamy-white and smooth, and it has eyes on the surface (Pumisacho & Sherwood, 2002). These crops are threatened throughout their cycle by different pests and diseases, such as *Globodera Pallida* and *Rostochiensis*, *Phytophthora infestans*, *Ralstonia solanacearum*, *Premnotrypes Vorax* Hustache in potatoes; *Tetranychus* spp., *Trialeurodes vaporariorum*, red spider mite in tomato and *Thrips tabaci*, *Lyriomyza huidrobensis* and *Sclerotium Cepivorum*, in onion (Chirinos et al., 2020; MIP, 2007). For this reason, various agrochemicals are used, sometimes unregulated or in overdose, which eliminate pests and beneficial insects for crops, causing secondary pests, without counting on the migration of organisms, which create new phytosanitary problems (Pumisacho & Sherwood, 2002). Despite the danger that the use of agrochemicals in crops could represent, tropical countries make tremendous use of them, justified by their functionality, being able to alter the natural chemical composition of crops and soil with toxic metals and nitrates. In Ecuador, the most widely used fungicides for potatoes are: Cymoxanil, Metalaxil, Propanocarb, Fosetil – Aluminum, Ofurace and Oxadixyl (Pumisacho & Sherwood, 2002). The pesticides most used are: Pythroids (cypermethrin, lambda cyhalothrin), Neonicotinoids (thiametoxan), Carbamates (carbofuran), Organophosphates (metamidophos, profenophos) (Chirinos et al, 2020); while potato fertilizers are based on nitrogen and those that contain the element phosphorus in their structure (Gaitán, González, Núñez, Saldaña & Cotes, 2013). In the case of onions, the most used insecticides are: Azocor (Profenofos), Cimox (Cymoxanil + Mancozeb), Fungloraz (Prochoraz) and the most used fertilizers are Sanacor (Mancozeb + Metalaxyl), Poncho de agua (Mancozeb + Cymoxanil) and Cypermethrin (Adama Andina, 2019; Agrocalidad 2020; Codex Alimentarius, 1999; Interoc Custer S.A., 2015; Grupo Andex S.A., 2015). For tomatoes, the most widely used pesticides are cypermethrin, Sanacor (Mancozeb + Metalaxyl), Poncho de agua (Mancozeb + cymoxanil) (Limin Chemical Co. Ltd, 2019; Codex Alimentarius, 2006; Codex Alimentarius, 2019; Interoc Custer S.A., 2015; JECFA, 2004).

In Cuenca, Ecuador, there are no studies on this subject, therefore, this work identifies and quantifies the absorption of toxic metals and anions in frequently consumed foods such as potatoes, tomatoes, and onions.

2. Methodology

2.1 Sampling

The content of metals and anions was taken in samples of potato Chaucha Amarilla (*S. Phureja*), INIAP Cecilia (*S. vertifolium* x *andígena* Var.), kidney tomato (*S. Lycopersicum*), and red onion (*Allium cepa*). Only in the case of potatoes, the analysis is carried out on the skin and pulp. For the collection of the samples, first, a list of supermarkets, markets, and organic fairs within the city was made. Later, a visit was made to each point, identifying, and classifying each of these, depending on whether there is a variety used for the study. Finally, 1 kg of each product was purchased, and a second sampling was carried out after one month. The selected outlets are shown in Table 1 and are found on the map in Fig.1.

Figure 1. Sampling points

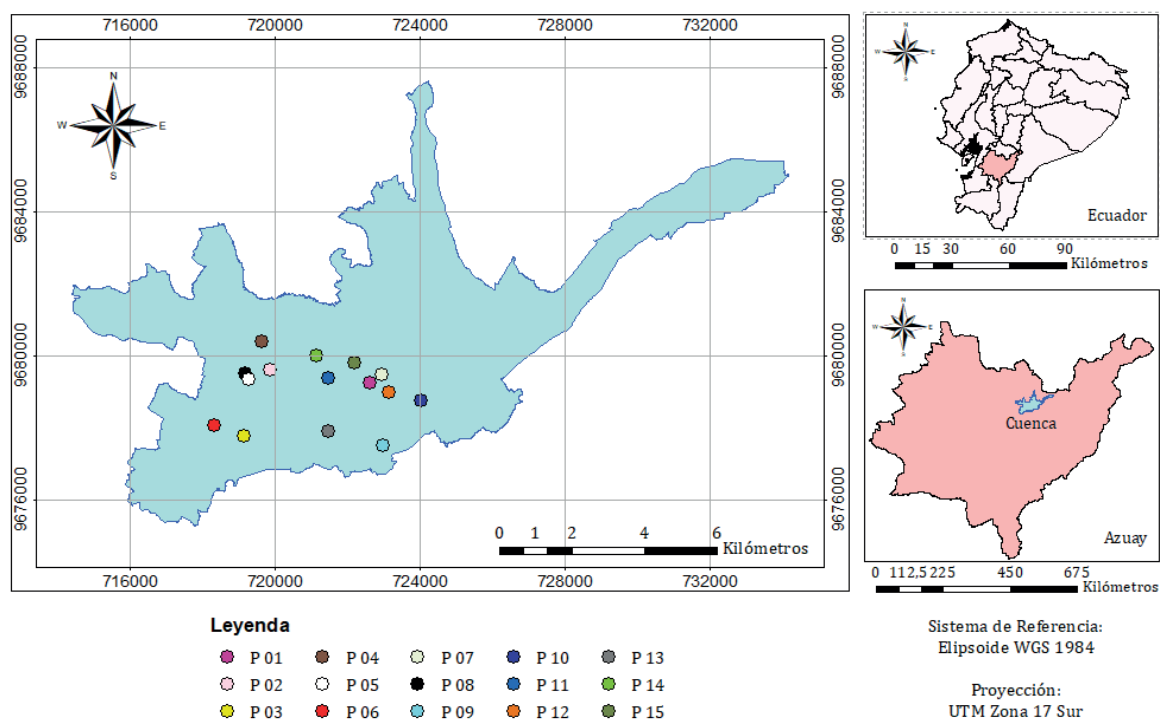


Table 1. Sampling sites

Local	Cod	Potato Chaucha Amarilla	Potato INIAP Cecilia	Tomato riñón	Red Onion
Coral supermercados: San Blas*	P01	0	0	2	2
Coral supermercados: El Batán*	P02	0	2	0	0
Coral supermercados: Don Bosco *	P03	0	0	2	2
Supermaxi: Las Américas*	P04	0	6	0	0
Tía supermercados: El Arenal*	P05	0	2	0	0
Mega Tienda del Sur: Las Américas*	P06	0	0	2	2
Gran Sol: González Suarez*	P07	0	0	2	2
Mercado Feria Libre	P08	2	0	2	2
Mercado El Vergel	P09	0	0	2	2
Mercado Empresa Eléctrica	P10	0	0	2	2
Mercado 10 de Agosto	P11	2	0	0	0
Mercado 12 de Abril	P12	2	0	2	2
Mercado 27 de Febrero	P13	2	0	2	2
Mercado 3 de Noviembre	P14	2	0	0	0
Mercado 9 de Octubre	P15	2	0	2	2

* The chosen point of sale represents a company, not the place of purchase. For mapping purposes, the locality is placed.

Note: The samples were taken according to market availability during the sampling date.

2.2 Pretreatment of Samples

The potatoes were washed with water for 1 minute, removing soil remains, then a bath in distilled water was made for 30 seconds to subsequently dry them. All the potatoes were peeled manually with a zirconium knife, removing up to 1 mm thickness of the skin. Peel and pulp were separated between them and between varieties. All samples were chopped into small pieces up to 2 cm and double quartered. Once the subsamples were obtained, they were ground in a porcelain mortar until obtaining a uniform texture and weighed on the analytical balance (KERN ABT 100-5M). The tomatoes were cut with a porcelain knife into pieces of approximately 1 mm, the same procedure was carried out on the onions, with a previous peeling. Then, a triple quartering was performed to obtain the sub-samples.

2.3 Determination of Nitrates

20 g of peel or pulp of each variety were weighed; maceration was carried out with 100 ml of distilled water. After 24 hours, the first filtering was carried out with cotton and a second with activated carbon where it was left to rest for 36 hours to remove color and colloids. Finally, it was filtered with filter paper to remove activated carbon. In the case of tomatoes and onions, the samples were placed in a muffle at 105 °C until a constant weight was obtained and then macerated with 25 ml of distilled water for 24 hours. The first filtering was done with cotton and later with activated carbon, it was left to rest for 3 days before making the last filtering; the filtered liquid was made up to 100 ml. Nitrates were determined through the absorbance measured in the Thermo SCIENTIFIC Evolution 60 UV-Visible spectrometer following the AOAC official method (1995). KNO_3 standards of 0.1, 0.25, 0.5, 1, and 2.5 ppm were prepared to obtain a calibration curve as ion nitrate (NO_3^-). Samples found to be outside the measurement range were diluted.

2.4 Metal determination

20 g of each potato sample were weighed and kept for 24 hours in an oven (Continental Equipment) at 105 °C. Subsequently, they were moistened with 1 ml of HNO_3 (SUPRAPUR at 65%) and dry calcination was carried out in the muffle (Nabertherm) at 550 °C until total calcination, ~ 6 h (Bianchini & Eyherabide, 1998). The onion and tomato samples were taken directly to the muffle at 550 °C for 10 hours, then 10 ml of 10% HNO_3 were added and left to calcine in the muffle for 10 hours. The ashes obtained were diluted with 3 drops of HNO_3 and made up to 50 ml with distilled water. The detection and quantification of metals were carried out through a multi-element analysis of trace elements, this technique allows elements to be quantified due to their high sensitivity, for which ICP-MS (NexION 350, Perkin Elmer) was used using EPA Method 200.8 (US EPA, 1994); to check reliability, two of the standards used in the calibration curve were read after having read every 20 samples. In total, 84 determinations of 43 metals were made.

2.5 Statistical analysis

Inferential statistical analyzes for potatoes were performed with the R statistical software and the RStudio version 1.2.5033 interface. To verify normality, histograms, and Q-Q (Quantile-Quantile) graphs were made, the statistical tests used were Shapiro Wilk, Jarque Bera, and Pearson. To verify homoscedasticity, the interquartile ranges were compared graphically through box and whisker plots, the statistical tests used were Bartlett, Levene, and Fligner Killeen, the latter

being a non-parametric test. In addition, the assumption of independence was verified with the Chi-Square test. Most cases did not meet the assumptions of normality and/or homoscedasticity, therefore, the non-parametric Kruskal Wallis test was used; if statistically significant differences were found, a non-parametric test was applied to determine differences between pairs, Wilcoxon (Pairwise Wilcoxon). In tomato and onion, no inferences were made because only one variety of each was studied.

For the multivariate analysis of the data, the Minitab 19 and MATLAB 2019 programs were used. As a first step, unsupervised analysis of the results was carried out using cluster analysis to obtain the greatest amount of information "hidden" behind the concentration values. The cluster analysis used was of the hierarchical agglomerative type in which at each step the two most similar elements are grouped to form a cluster; This process continues until you are left with a single large cluster that encompasses all the elements. For the creation of the groups, the Ward method was used in which the distance between two clusters is represented by the sum of the squares of the deviations of the elements from the centroid of the cluster, which allows for minimizing the distance between the elements in inside the cluster. The formula to calculate the distance is shown in equation 1. Where: d_{mj} is the distance between clusters m and j and N_j is the number of elements in cluster j

$$d_{mj} = \frac{(N_j + N_k)d_{kj} + (N_j + N_l)d_{lj} - N_j d_{kl}}{N_j + N_m}$$

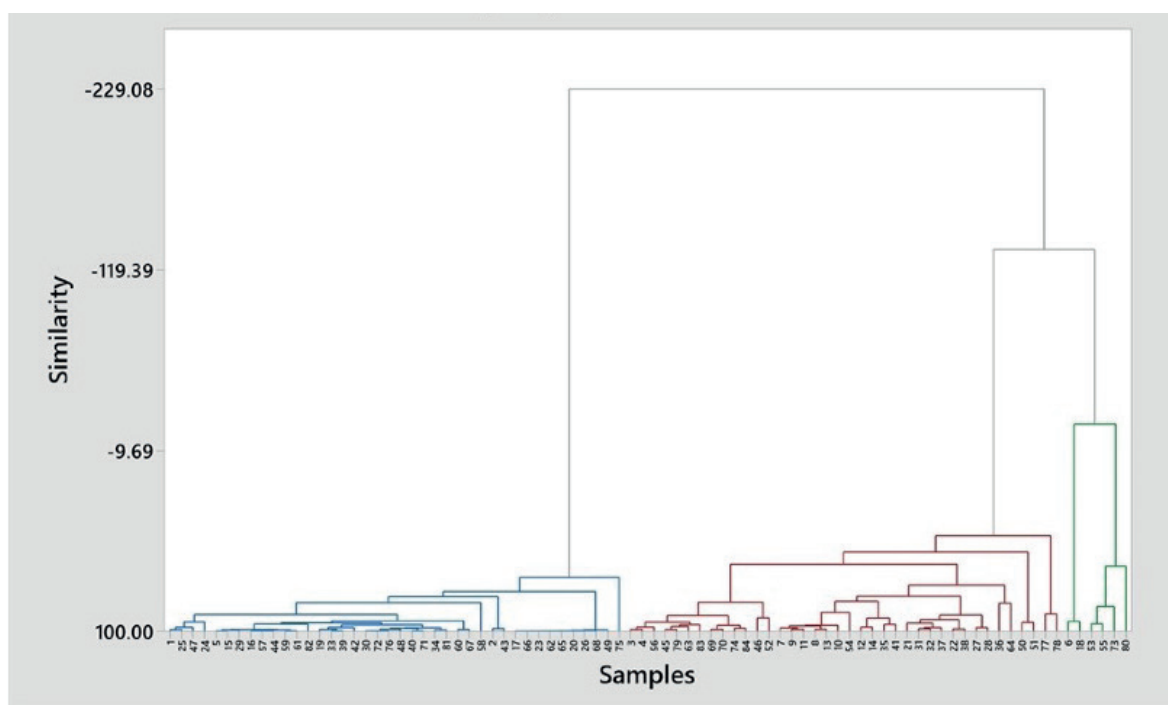
After exploring the data and grouping it into 4 clusters, a classification model was created to discriminate the composition of tomatoes, onions, and potatoes. For this purpose, the KNN (K-nearest-neighbors) algorithm coupled with a genetic selection of the most important metals in the classification was used. For this purpose, the data set was subdivided into two subsets: one for calibration (Training set 70 % of the samples) and one for the evaluation of the predictive capacity of the model (Test set 30 % of the samples). The assignment to each set was random, trying to maintain the numerosity of the three classes.

3. Results and Discussion

The concentrations found, both in fertilizers and metals, in the potato, tomato, and onion samples are reported in tables SI.1 and SI.2 of the annexes. The concentrations found, both in fertilizers and metals, are close to the concentrations found in other studies (Becker et al., 2011; Poberežny et al., 2015; Suárez et al., 2014). All the concentrations of metals and nitrates determined in the products studied were within the expected values, even though the samples chosen came from places where intensive crops are grown. For instance, potatoes are a great source of potassium, consuming 100 g of unpeeled potato or just its pulp of the Chaucha Amari-lla variety, 31.76 and 31.72 % of daily required K are obtained and 32.81 in the Cecilia variety. and 32.77 %, representing a slight problem when adding other products with large amounts of K in the daily intake. An elevated level of potassium in the blood can lead to blood arrhythmias, which in severe cases could be fatal (American Heart Association, 2017; Gabarra et al. 2017); the tomato is also a great source of potassium, however its daily consumption does not impose risk; on the other hand onions eaten raw as in salads have a not relevant contribution in minerals except from K (UCM, 2016). In addition, metals such as Chromium and Nickel that are susceptible to

being absorbed by these products were determined (Baghour et al., 2001; Chen et al., 2009) but not high concentrations were found in this study. This could be since a greater accumulation of toxic metals has been found in crops close to urban regions, where the soils are contaminated by industrialization (Gichner et al., 2006); and the cultivation areas of the country are distributed in the rural area. Other factors that influence the concentration of metals and ions are the use of residual water for irrigation (Khan et al., 2008), the mineral composition of the soil, and the application of fertilizers and pesticides, especially those not regulated indiscriminately.

Figure 2. dendrogram by Ward method

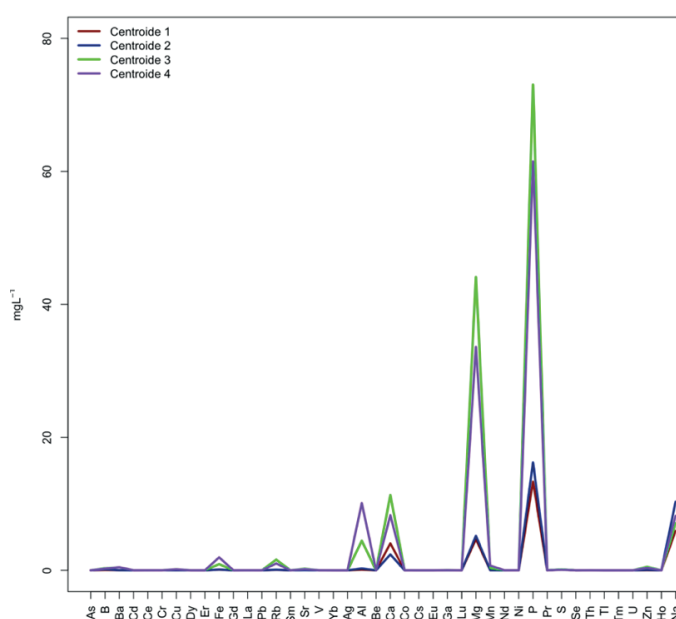


To determine if there are significant statistical differences between the two types of potato and between skin and pulp of the same variety, tests such as Wilcoxon and Kruskal Wallis were performed. Significant statistical differences were found between the peel and pulp of the yellow Chaucha potato in the content of metals V, Co, and Ni and in the INIAP Cecilia variety in the case of Ca, Sr, and V, being in both cases the peel where higher concentration was presented. Differences were found between the skin of both varieties in Co, Ni, Rb, and Mn, with the Chaucha Amarilla variety presenting a higher concentration. When comparing the pulps of the two varieties, significant differences were found in the P content, with a higher content in the INIAP Cecilia variety, and in the content of Co, Ni, Rb, and Cs, with a higher value in the Chaucha Amarilla variety. Comparing the concentrations of Chaucha Amarilla skin and pulp of INIAP Cecilia, significant differences were found in the concentrations of the elements Co, Ni, Rb, Zn, Ba, Sr, and V, where the concentration of Chaucha Amarilla skin was higher. Unlike P, the highest concentration was found in the pulp of INIAP Cecilia. Comparing the pulp of Chaucha Amarilla with the skin of INIAP Cecilia, the former presented a higher value in concentrations in the elements Co, Ni, Ca, Cs, Mn, and V, compared to the elements Ca and V whereas in the skin of INIAP Cecilia found the highest concentration. In general, the toxic metals where significant

differences were found, were found in higher concentrations in the Chaucha Amarilla variety, this could be since this variety has a very thin skin that allows the diffusion of metals in the tuber more easily.

The dendrogram in Figure 2 shows the presence of two large groups of samples. The first cluster is made up of 40 samples collected from many outlets: 18 tomato samples; 20 red onions; 2 potatoes (1 pulp and 1 peel). The second is made up of 2 tomato samples. The third group is made up of 38 potato samples, while the fourth cluster is made up of 4 potato samples collected at different points of sale. To know which metals, characterize the different clusters, the average concentration of each metal in each cluster has been calculated as shown in figure 3 and table SI.3.

Figure 3. A plot of the centroids of the four clusters

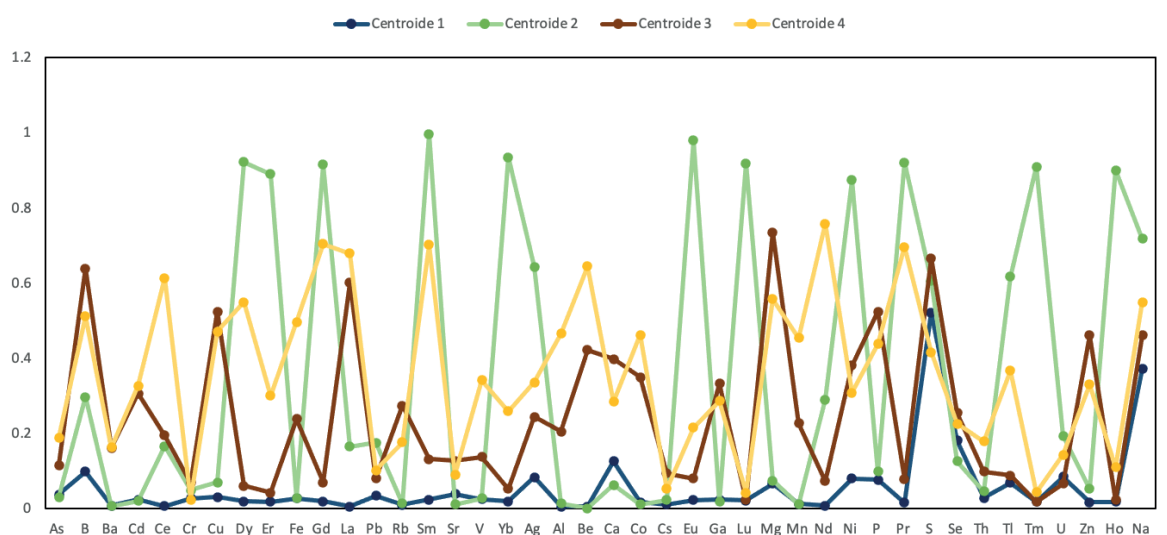


Clusters 3 and 4, which are made up of potatoes, have the highest concentrations in mgL^{-1} of Al, Ca, Mg, P and Na. Figure 4 shows the graph of the average values of the metals in the centroids of the clusters, where the maximums have been scaled to 1 and the minimums to zero.

The samples grouped in the first cluster (mainly tomato and red onion) present low relative values of almost all metals apart from Calcium, Magnesium, Nickel-phosphorus, Sulfur, Selenium, Titanium, and Uranium. Sodium is similar to the content of clusters 3 and 4. This could indicate that the marketing centers sell tomatoes and onions from the same area or that the two species concentrate metals in the same way. The samples grouped in cluster 2 present the highest relative values of all the other clusters in the following metals Dysprosium, Erbium, Gadolinium, Lead, Samarium, Ytterbium, Silver, Europium, Lutetium, Praseodymium, Sulphur, Thallium, Thulium, Uranium, Holmium, Sodium. While the values of Barium, Cadmium, Copper, Iron, Rubidium, Strontium, Vanadium, Aluminum, Beryllium, Calcium, Cobalt, Cesium, Gallium, Magnesium, Nickel, Phosphorus, Selenium, and Thorium are the lowest. The concentration of the other metals is comparable to that of the other clusters. The composition of these samples indicates that they are characterized by high values of metals from the Lanthanide family,

which, being quite rare, show that the two tomato samples come from the same area. Additionally, these two samples of tomatoes have been marketed by a supermarket and by a large store. The samples grouped in cluster 3 are all potatoes and present relatively high values of B, Ba, Cd, Cu, Rb, Ca, Ga, Mg, Ni, P, S, Se, and Zn; while the concentrations of Dy, Er, Gd, Pb, Yb, Cs, Eu, Lu, Nd, Pr, Th, Tm, U, Ho, are low. The other metals in this group have intermediate concentrations. The concentrations of lanthanides in this group are not high, so these samples come from different places than those of groups 2 and 1. The samples grouped in cluster 4 are potatoes and generally present relatively high values of B, Ba, Cd, Ce, Cu, Dy, Er, Fe, Gd, La, Rb, Sm, Sr, V, Yb, Ag, Al, Be, Ca, Co, Ga, Mg, Mn, Nd, Ni, P, Pr, Th, Te, Zn, Na; the greater presence of lanthanides in this cluster indicates that the origin of these samples is different from that of group 3 potatoes. Two samples have been collected in markets and two in supermarkets. The presence of a potato skin without the pulp is quite strange. In summary, the two potato clusters have very different compositions from those of tomato and onion.

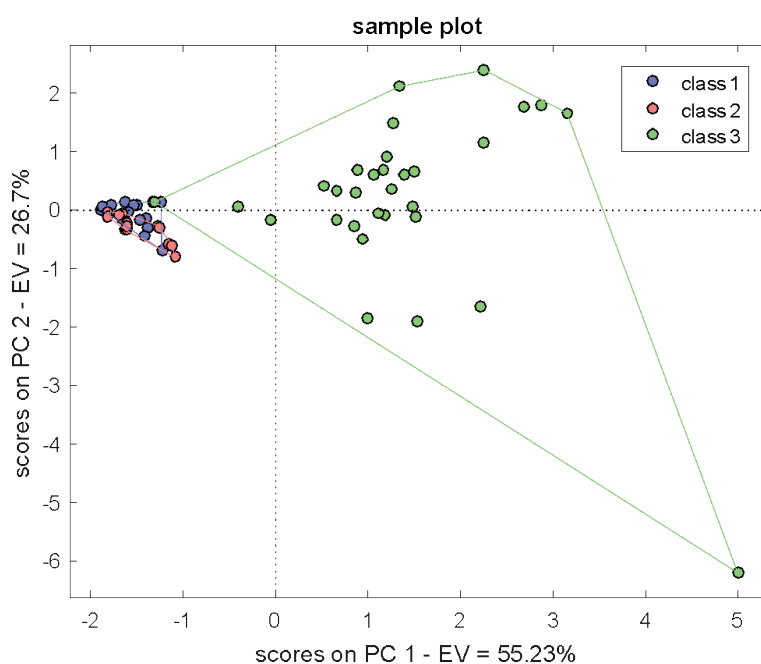
Figure 4. values of the average concentrations of the metals in the centroids of the 4 clusters



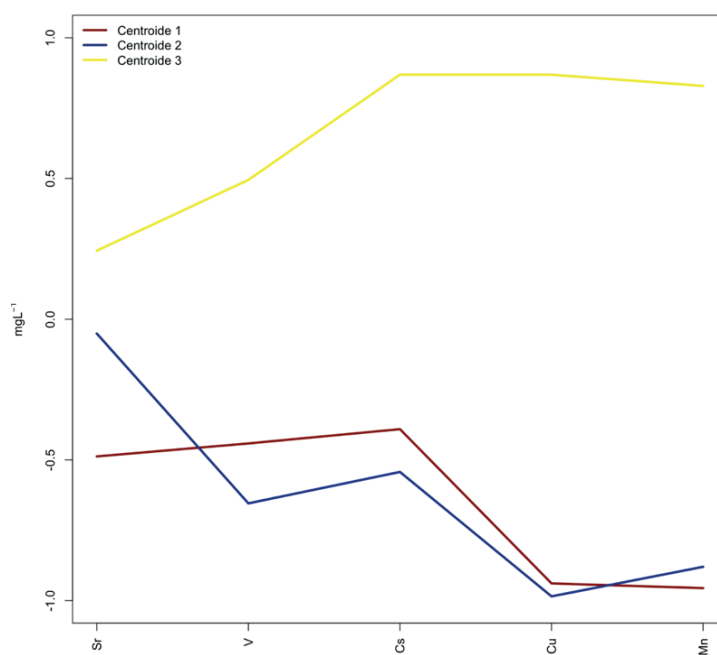
A model has been obtained to discriminate between the products studied with five metals: Sr, V, Cs, Cu, Mn. Whose quality parameters are presented below in Table 3.

Table 3. Quality parameters of the KNN classification models

	N.E.R	Parameters	Potato	Tomato	Onion
Calibration	0.96	Precision	1.000	0.929	0.933
		Sensibility	0.968	0.929	1.000
		Specificity	1.000	0.978	0.978
Prediction	0.89	Precision	1.000	0.830	0.830
		Sensibility	1.000	0.830	0.830
		Specificity	1.000	0.950	0.950

Figure 5. score plot

The tomato and onion samples are almost overlapping, as was also observed in the cluster analysis (cluster 1), however, the KNN manages to differentiate them. Potatoes form a class well separated from the previous two. The centroids of the auto-scaled data of the discriminant metals of the classes are presented in Table 4.

Figure 6. Centroids of the selected metals in each class

The analysis of figure 6 indicates that potatoes are richer in Sr, V, Cs, Cu, and Mn, while it is noted that the difference between tomato and onion is due to Strontium, which is higher for onions, vanadium, and cesium, which are higher for tomatoes, while for copper and manganese there is practically no difference between the two classes.

Tabla 4. Centroid values for each selected metal in each class in mgL^{-1}

Metal	Centroide 1	Centroide 2	Centroide 3
Sr	- 0.487702	- 0.051092	0.2433265
V	- 0.441522	- 0.654467	0.4949626
Cs	- 0.390787	- 0.542777	0.8687837
Cu	- 0.938824	- 0.984911	0.8687837
Mn	- 0.955663	- 0.879913	0.8289701

4. Conclusions and recommendations

None of the samples analyzed presented values outside the regulations for the concentrations of metals, and nitrates, this may be since they are planted in rural areas, far from factories and the use of wastewater for irrigation is not given. Therefore, we assume that there are no high concentrations of these compounds in the soil. The Chaucha potato presented higher metal contents compared to the Cecilia potato, this is explained because the Chaucha potato has a thinner skin, which makes it susceptible to the absorption of minerals by osmosis processes. When comparing each variety by skin and pulp, it was in the skin where the highest concentration of metals was found. Multivariate statistics allowed the grouping of by-products and origin, mainly due to their metal content. Being evident that depending on the amount of metals present, onions and tomatoes share the same cluster, except for 2 tomato samples that form a cluster, what they have in particular is that they do not share the same origin. The predictive model used four metals as classification variables, which indicates that these metals are those that are present in the three types of food and that their characteristic concentrations are influential for their characterization, being able to consider that these concentrations are due to selectivity processes specific to the absorption of each plant.

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References

- Adama Andina. (2019). *Ficha técnica Hammer*. Quito. <https://www.adama.com/ecuador/es/agroquimicos/fungicida/hammer>
- Agrocalidad - Agencia de Regulación y Control Fito y Zoonosanitario. (2020). Sanidad Vegetal: Gestión de manejo y control de plagas específicas. Quito. <https://www.agrocalidad.gob.ec>
- American Heart Association. (2017). *¿Qué es la hipercalcemia (potasio alto)?* <https://bit.ly/3PtSY3u>
- Association of Official Analytical Chemists (AOAC). (1995). *Official methods of analysis* (12th ed.).

- Baghour, M., Moreno, D. A., Villora, G., Hernández, J., Castilla, N., & Romero, L. (2001). Phytoextraction of Cd and Pb and physiological effects in potato plants (*Solanum Tuberosum* Var. Spunta): Importance of root temperature. *Journal of Agricultural and Food Chemistry*, 49(11), 5356–5363. <https://doi.org/10.1021/jf010428x>
- Becker, W., Jorhem, L., Sundström, B., & Grawé, K. P. (2011). Contents of mineral elements in Swedish market basket diets. *Journal of Food Composition and Analysis*, 24(2), 279–287. <https://doi.org/10.1016/j.jfca.2010.10.001>
- Bianchini, M. R., & Eyherabide, G. A. (1998). Técnicas de mineralización para la determinación de macronutrientes en muestras de raíz de zanahoria (*Daucus carota* L.). *Revista de la Facultad de Agronomía*, 103(2), 191–195. <http://sedici.unlp.edu.ar/handle/10915/15645>
- Cabrera, M. (2007). Mineralización y nitrificación: Procesos claves en el ciclo del nitrógeno. *Informaciones Agronómicas del Cono Sur*, 34, 1-9. [http://www.ipni.net/publication/ia-lacs.nsf/0/77FA8167A21708978525799500785679/\\$FILE/Cabrera-IA34.pdf](http://www.ipni.net/publication/ia-lacs.nsf/0/77FA8167A21708978525799500785679/$FILE/Cabrera-IA34.pdf)
- Chen, C., Huang, D., & Liu, J. (2009). Functions and toxicity of nickel in plants: Recent advances and future prospects. *CLEAN – Soil, Air, Water*, 37(4-5), 304–313. <https://doi.org/10.1002/clen.200800199>
- Chirinos, D. T., Castro, R., Cun, J., Castro, J., Peñarrieta Bravo, S., Solis, L., & Geraud-Pouey, F. (2020). Los insecticidas y el control de plagas agrícolas: La magnitud de su uso en cultivos de algunas provincias de Ecuador. *Ciencia & Tecnología Agropecuaria*, 21(1), 1–16. https://doi.org/10.21930/rcta.vol21_num1_art:1276
- Codex Alimentarius (1999). Métodos de muestreo recomendados para la determinación de residuos de plaguicidas a efectos del cumplimiento de los LMR. CAC/GL. <https://n9.cl/xxbmb>
- Codex Alimentarius. (2006). *Plaguicidas*. <http://www.fao.org/fao-who-codexalimentarius>
- Codex Alimentarius. (2019). *Metalaxyl*. <http://www.fao.org/fao-whocodexalimentarius>
- Dziubanek, G., Piekut, A., Rusin, M., Baranowska, R., & Hajok, I. (2015). Contamination of food crops grown on soils with elevated heavy metals content. *Ecotoxicology and Environmental Safety*, 118, 183–189. <https://doi.org/10.1016/j.ecoenv.2015.04.032>
- Gaitán Moreno, Á. P., González Mogollón, M. P. A., Núñez López, C. E., Saldaña Villota, T. M., & Cotes Torres, J. M. (2013). Análisis funcional de crecimiento y desarrollo de cuatro variedades de papa (*Solanum tuberosum* subsp. andigena). *Revista Facultad de Ciencias Básicas*, 9(2), 172–185. <https://doi.org/10.18359/rfcb.344>
- Gabarra, A., Soley, M., & Fernández, A. (2017). Ingestas de energía y nutrientes recomendadas en la Unión Europea: 2008-2016. *Nutrición Hospitalaria*, 34(2), 490–498. <https://doi.org/10.20960/nh.937>
- Gichner, T., Patková, Z., Száková, J., & Demnerová, K. (2006). Toxicity and DNA damage in tobacco and potato plants growing on soil polluted with heavy metals. *Ecotoxicology and Environmental Safety*, 65(3), 420–426. <https://doi.org/10.1016/j.ecoenv.2005.08.006>
- Grupo Andex (2015). *Primmex*. http://grupoandina.com.pe/media/uploads/ficha_tecnica/ft-primmex_25.ec.pdf
- Hu, W., Huang, B., Tian, K., Holm, P. E., & Zhang, Y. (2017). Heavy metals in intensive greenhouse vegetable production systems along Yellow Sea of China: Levels, transfer and health risk. *Chemosphere*, 167, 82–90. <https://doi.org/10.1016/j.chemosphere.2016.09.122>
- Huang, Y., Wang, L., Wang, W., Li, T., He, Z., & Yang, X. (2019). Current status of agricultural soil pollution by heavy metals in China: A meta-analysis. *Science of The Total Environment*, 651, 3034–3042. <https://doi.org/10.1016/j.scitotenv.2018.10.185>
- Instituto Nacional de Investigaciones Agropecuarias. (2014). *Papa*. <http://tecnologia.iniap.gob.ec/index.php/explore-2/mraiz/rpapa>
- Organización de las Naciones Unidas para la Alimentación y la Agricultura (FAO -Evaluación de los riesgos asociados con las sustancias químicas (JECFA). (2004). <https://www.fao.org/food/food-safety-quality/scientific-advice/jecfa/es/>
- Interoc Custer. (2015). *Metalaxyl*. <https://www.interoc.biz/producto/columbus/>

- Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z., & Zhu, Y. G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*, 152(3), 686–692. <https://doi.org/10.1016/j.envpol.2007.06.056>
- Guía del Manejo Integrado de Plagas (MIP) para técnicos y productores (2007). *Guía del manejo integrado de plagas (MIP) para técnicos y productores*. <https://bit.ly/3AksrkD>
- Leyva, G., Sánchez Zarza, P., Alcántar, G., Valenzuela, J. G., Gavi, F., & Martínez, A. (2005). Nitrates content in cellular extracts of tomato petioles and fruits. 28(2), 145–150. <https://docplayer.es/20965672-Contenido-de-nitratos-en-extractos-celulares-de-peciolos-y-frutos-de-tomate-nitrates-content-in-cellular-extracts-of-tomato-petioles-and-fruits.html>
- Ministerio de Agricultura y Ganadería. (2020). *Diagnóstico territorial: Resumen ejecutivo*. Ministerio de Agricultura y Ganadería. <https://bit.ly/3SR8ysP>
- Ministerio de Agricultura y Ganadería. (2015). *Manejo Agorcológico de plagas*. <https://www.agricultura.gob.ec/biblioteca/>
- McClintock, T. R., Chen, Y., Bundschuh, J., Oliver, J. T., Navoni, J., Olmos, V., Lepori, E. V., Ahsan, H., & Parvez, F. (2012). Arsenic exposure in Latin America: Biomarkers, risk assessments and related health effects. *The Science of the Total Environment*, 429, 76–91. <https://doi.org/10.1016/j.scitotenv.2011.08.051>
- Moreno C. B., Soto, O. K., & González, R. D. (2015). El consumo de nitrato y su potencial efecto benéfico sobre la salud cardiovascular. *Revista Chilena de Nutrición*, 42(2), 199–205. <https://doi.org/10.4067/S0717-75182015000200013>
- Limin Chemical. (2019). Mancozen y Cytoxanil <http://www.chinalimin.com>
- Poberežny, J., Wszelaczyńska, E., Wichrowska, D., & Jaskulski, D. (2015). Content of nitrates in potato tubers depending on the organic matter, soil fertilizer, cultivation simplifications applied and storage. *CHILEANJAR: Chilean Journal of Agricultural Research*, 75(1), 42–49. <https://bit.ly/3C1pJ4V>
- Pumisacho, M., & Sherwood, S. (2002). *El cultivo de la papa en el Ecuador*. Instituto Nacional de Investigaciones Agropecuarias; Centro Internacional de la Papa.
- Santamaria, P. (2006). Nitrate in vegetables: Toxicity, content, intake and EC regulation. *Journal of the Science of Food and Agriculture*, 86(1), 10–17. <https://doi.org/10.1002/jsfa.2351>
- Sistema de Información Pública Agropecuaria del Ecuador. (2020). *Cifras agroproductivas: Principales Cultivos-2020*. <http://sipa.agricultura.gob.ec/>
- Suárez, S., Ale, N., Trabucco, J., & Sanabria, O. (2014). Polifenoles, micronutrientes minerales y potencial antioxidante de papas nativas. *Revista de la Sociedad Química del Perú*, 80(2), 108–114. <https://doi.org/10.37761/rsqp.v80i2.155>
- Topalidis, V., Harris, A., Hardaway, C. J., Benipal, G., & Douvris, C. (2017). Investigation of selected metals in soil samples exposed to agricultural and automobile activities in Macedonia, Greece using inductively coupled plasma-optical emission spectrometry. *Microchemical Journal*, 130, 213–220. <https://doi.org/10.1016/j.microc.2016.09.004>
- Tóth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International*, 88, 299–309. <https://doi.org/10.1016/j.envint.2015.12.017>
- Universidad Complutense de Madrid. 2016. *La cebolla, una aliada para la salud*. <https://bit.ly/2wqu52U>
- United States Environmental Protection Agency. (1994). *EPA Method 200.8: Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry*. <https://bit.ly/3duCOUZ>
- WHO. (1980). Recommended health-based limits in occupational exposure to heavy metals : report of a WHO study group [meeting held in Geneva from 5 to 11 June 1979]. <https://apps.who.int/iris/handle/10665/41401>