LA GRANJA: Revista de Ciencias de la Vida

pISSN:1390-3799; eISSN:1390-8596

http://doi.org/10.17163/lgr.n32.2020.09

Scientific paper/ Artículo científico

SOIL SCIENCES



METAL CONTENT EVALUATION IN SOILS AND EDIBLE TISSUES OF Allium fistulosum L. ON CROPS NEAR THE TUNGURAHUA VOLCANO

Evaluación del contenido de metales en suelos y tejidos comestibles de *Allium fistulosum L.* cultivado en zonas cercanas al volcán Tungurahua

Jorge Briceño^{*1} ⁽ⁱ⁾, Evelyn Tonato¹ ⁽ⁱ⁾, Mónica Silva¹ ⁽ⁱ⁾, Mayra Paredes¹ ⁽ⁱ⁾ and Arnaldo Armado²

¹Laboratorry of functional foods. Faculty of Science, Food Engineering and Biotechnology. Universidad Técnica de Ambato. Campus Huachi, Av. Los Chasquis y Río Payamino, CP. 180206, Ambato, Ecuador.

² Environmental, chemistry, Biology Research Center. Scientific and Technological Faculty. Universidad de Carabobo, Naguanagua (2005), Carabobo, Venezuela.

*Corresponding author: jbriceno@uc.edu.ve

Article received on September 4th, 2019. Accepted, after review, on March 30th, 2020. Published on September 1st, 2020.

Abstract

The Tungurahua volcano, located in the eastern mountain range of Ecuador, since its reactivation in 1999 has had several phases of volcanic activity, which have produced gas, ash and lava emissions. These emissions release a large amount of metals to nearby soils that are currently used for agricultural purposes. Metal pollution can cause serious problems for human health; while other metals are necessary as nutrients in most agricultural crops. In this investigation, the metal content in agricultural soils of the Quero canton was evaluated, as well as its bioavailability and content in the culture of *Allium fistulosum L.*, in order to obtain information on the impact of potentially polluting metals (cadmium, lead, nickel, strontium, cobalt, copper and zinc) and nutrients (potassium, magnesium, iron and manganese) on crops. For the estimation of total metals in soil an acid digestion was performed; for bioavailabile metals an extractant mixture (EDTA-Triethanolamine-*CaCl*₂, pH 7) was used and for the branch onion a calcination followed by acid digestion was carried out. The quantification of the metals was carried out by flame atomic absorption spectroscopy or graphite furnace. The results showed that the metal content, both in the soil samples and in the branch onion, was below the maximum values allowed in the local regulations for all the metals studied. In addition, the intake of the metal by the branch onion was independent of the bioavailable fraction.

Keywords: Cadmium, copper, metal intake, bioavailable metal, branch onion.

Resumen

El volcán Tungurahua, ubicado en la cordillera oriental de Ecuador, desde su reactivación en 1999 ha entrado en varias fases de actividad volcánica, produciendo emisiones de gas, cenizas y lava. Estas emisiones liberan una gran cantidad de metales a suelos cercanos que, en la actualidad, se emplean con fines agrícolas. La contaminación por metales puede provocar graves problemas para la salud humana; mientras que otros metales son necesarios como nutrientes, en la mayoría de los cultivos agrícolas. En esta investigación, se evaluó el contenido de metales en suelos agrícolas del cantón Quero, su biodisponibilidad y el contenido en el cultivo de *Allium fistulosum L.*, con la finalidad de obtener información sobre el impacto de metales potencialmente contaminantes (cadmio, plomo, níquel, estroncio, cobalto, cobre y cinc) y nutrientes (potasio, magnesio, hierro y manganeso) sobre los cultivos. Para la estimación de metales totales en el suelo se realizó una digestión ácida; para metales biodisponibles se empleó una mezcla extractante (EDTA-Trietanolamina-*CaCl*₂, pH 7) y para la cebolla de rama se realizó una calcinación seguida de digestión ácida. La cuantificación de los metales se realizó mediante espectroscopia de absorción atómica (EAA) de llama o de horno de grafito. Los resultados mostraron que el contenido de metales, tanto en las muestras de suelo como en cebolla de rama, estaba por debajo de los valores máximos permitidos en las normas locales para todos los metales estudiados; además, la ingesta del metal por la cebolla de rama fue independiente de la fracción biodisponible.

Palabras clave: Cadmio, cobre, ingesta de metal, metal biodisponible, cebolla de rama.

Suggested citation:	Briceño, J., Tonato, E., Silva, M., Paredes, M. and Armado, A. (2020). Metal content evaluation in
	soils and edible tissues of Allium fistulosum L. on crops near the Tungurahua volcano. La Granja:
	Revista de Ciencias de la Vida. Vol. 32(2):112-123. http://doi.org/10.17163/lgr.n32.2020.09.

Orcid IDs:

Jorge Briceño: http://orcid.org/0000-0002-0692-1228 Evelyn Tonato: http://orcid.org/0000-0002-1707-4298 Mónica Silva: http://orcid.org/0000-0001-8887-1553 Mayra Paredes: http://orcid.org/0000-0001-9320-9177 Arnaldo Armado: http://orcid.org/0000-0003-4670-0339

1 Introduction

The Tungurahua volcano, located in the eastern mountain range of Ecuador, has been into different phases of volcanic activity since its activation in 1999, with gas, ash and lava emissions (Battaglia et al., 2019). These emissions release a large amount of metals to nearby soils that are currently used for agricultural purposes. Heavy metal contamination in agricultural soils can create serious human health problems, because many edible plant species can absorb large amounts of potentially toxic metals from the soil. The metal intake through the consumption of contaminated food can lead to malformations, neuronal dysfunctions and even death (Rai et al., 2019).

While heavy metals such as cadmium, lead, nickel, cobalt, copper and zinc are considered potentially toxic (Tóth et al., 2016), for plants, animals and even humans (Rai et al., 2019), other metals such as potassium, magnesium, iron and manganese, are necessary for the nutrition of plants and agricultural crops in general. It is important to evaluate the content of metals in soils and crops, since soil composition is one of the factors influencing the transfer of trace elements in the soil-plant chain as part of the biochemical cycle (Kabata-Pendias, 2004; Kabata-Pendias and Sadurski, 2004; Tóth et al., 2016). In addition, knowing the metal content makes it possible to show that the nutrient content is suitable for cultivation, and that potentially polluting heavy metals are below permissible limits, according to national and international environmental regulations.

Onion (*Allium fistulosum L.*) is grown in the Quero canton (Choumert-Nkolo and Phélinas, 2019), especially near Tungurahua Volcano. Therefore, there is the need to evaluate the content of metals that could have been expelled in the latest ash emissions in 2016 (Battaglia et al., 2019). In this investigation, the content of some metals in agricultural soils in the Quero canton, their bioavailability and content in the cultivation of *Allium fistulosum L.* were evaluated in order to obtain information on the possible impact of metals on crops, taking into account that metals such as cadmium, lead, nickel, strontium, cobalt, copper and zinc, may be potential pollutants; and metals such as macro and mi-

cronutrients for the crop.

2 Materials and methods

2.1 Soil sampling area and onion

The soil and onion samples were selected from a plot of $3\,884\,m^2$ located at $3\,185$ m.a.s.l in the Quero canton, 12 km from the Tungurahua volcano and 29 km from the Chimborazo volcano. Figure 1 shows its geographic location (A) and its subdivision into five similar transects for sampling (B).

2.2 Selection and preservation of samples

Soil and onion samples were collected in November 2018 near the ash catchment zone of the Tungurahua volcano. For the sampling, the zigzag method was used on a plot at approximately 5 meters of distance, and 10-30 cm of deep were dug, taking approximately 1-2 kg of soil. For the onion, a cluster in its final stage of growth was cut from the same places where the soil sample was obtained. The samples were moved in clean and properly labeled polyethylene bags. The entire sampling process was carried out within 5 months.

The soil sample underwent a drying process at room temperature, it was grounded and sifted with a mesh No. 14, and the onion was washed with distilled water to remove visible dirt and the edible portion was taken for analysis. Subsequently, it was subjected to a convection drying at 40 °*C* for 24h, it was grounded and sifted (Faithfull et al., 2005) and was properly stored until performing the analysis of the metals.

2.3 Physicochemical parameters

The moisture percentage for soil samples was determined by weight loss on a stove, using the method 93.06-37.1.10 (AOAC, 2006). Soil organic matter was determined in samples dried in a stove at 105 °*C*, by ignition loss at 450°*C* for 10 h using a flask NA-BERTHERM LT 15/12/B180 (Cargua Catagña et al., 2017). The pH and electrical conductivity were determined in distilled water (Kazlauskaitė-Jadzevičė et al., 2014), 1:2.5 w/v ratio by using a potentiometer METTER TOLEDO SEVENCOMPACT PH/ION and a THERMO SCIENTIFIC ORION VERSASTAR conductimeter, respectively. For the onion samples,

the moisture content was determined using an infrared balance METTER TOLEDO HX 2014 MOIS-TURE ANALYZER, using 3 g of sample with wor-

king condition of $150^{\circ}C$ and with drying criterion of 1 mg/50 seconds.



Figure 1. (A) Geographical location of the sampled plot. (B) Subdivision and sampling points. Source: Google Earth, 2019

2.4 Extraction of total and bioavailable metals in soil samples

For the estimate of the total fraction of each metal in the soil, digestion was performed with *agua regia* concentrated HNO₃ and concentrated HCl in 1:3 v/v ratio) (Sungur et al., 2014); 0.5 g of soil was weighted by triplicate on an analytical balance and agua regia was added in a ratio of 1:10 w/v to 90°*C* by 2 h with magnetic agitation, subsequently it was filtered and gauged at 25 mL with *HNO*₃ 0.14 M.

For the estimation of the bioavailable fraction of each metal, an extractant mixture prepared with EDTA 0.05M, triethanolamine 0.1 M and calcium chloride dihydrate 0.01M adjusted to pH was used: 7 (Khan et al., 2019). The extraction was performed in a ratio of 1:2 soil / extracting mixture, agitating it for 30 minutes, it was subsequently centrifuged at 4500 rpm for 10 min, the supernatant was filtered by gravity and graduated to 50 mL with HNO₃ 0.14 M (Golia et al., 2008).

2.5 Extraction of metals in onion samples

Onion samples were submitted to calcination at $450^{\circ}C$, followed by acid digestion. The ashes resulting from the determination of organic matter were taken and 0.50 mL of *HCl* and 0.25 mL of concentra-

ted HNO₃ were added, then were left to stand for 15 min and werefiltered with Nylon microfilters of 13 mm in diameter and with pore size of $0.45 \,\mu$ m, were gauged with 25 mL with HNO₃ 0.14 M.

2.6 Determination of metals using EAA

The determination of metals was carried out using an atomic absorption spectrophotometer with PG Intruments line source model AA500, using the electrical conditions recommended by the manufacturer for each metal. The instrument is equipped with flame atomizers and graphite furnace; a D2 deuterium lamp was used to correct nonspecific absorbance and an AUTO SAMPLER PG Intruments model AS500 was used for the introduction of liquid samples into the atomization system. Single-element standards (AccuStandart) were used to obtain daily calibration curves for each element. The concentration of cobalt, strontium, lead, nickel and cadmium was determined with the graphite furnace using argon 5.0 grade of 99.99% of purity (Linde Ecuador S.A.) during the pyrolysis stage and with stopped flow during atomization. Similarly, potassium, magnesium, manganese, copper, iron and zinc were determined with 2.5 grade of acetylene air flame and purity of 99.5% (Linde Ecuador S.A.). In all two cases, the determination of

the metal content was made by direct comparison of the signal of each element versus the calibration obtained for each metal. All samples were processed by triplicate, including a white interleaved between each sample. The quality of the data was verified by measuring a separately prepared calibration point with other certified reference material to determine the veracity of the method.

2.7 Bioavailability factor, β

The typical measurement of the total content of the metal in the soil is not always suitable for assessing its mobility or availability (Rieuwerts, 2007). In this sense, a bioavailability factor β , determined by Equation 1, was established to evaluate the bioavailable fraction and to verify that the metal content is independent from the total content of the same metal in the soil. With the value set, the metal absorbed

by the plant could be evaluated (Khan et al., 2015).

$$\beta = \frac{Metal_{bioavailable}}{Metal_{Total}} \tag{1}$$

3 Results and discussion

3.1 Physicochemical parameters of the soil

The soil samples were evaluated based on national reference values (Table 1) according to the Secretariat of Environment and Natural Resources (SE-MARNAT). The results obtained from the soil characterization are presented in Table 2. The pH was below 5, thus the sampling sector is strongly acid as specified in SEMARNAT (2003); these conditions favor the solubility of metallic elements, thus allowing better assimilation by plants (Kabata-Pendias and Sadurski, 2004; Tangahu et al., 2011).

Table 1. Reference values reported for the classification of soils. Values taken from SEMARNAT (2003).

Property	Classification	Value
pH	pH Stronly acid	
	Moderate acid	5.1 – 6.5
	Neutral	6.6 – 7.3
	Partly alkaline	7.4 - 8.5
	Stronly alkaline	> 8.5
Electric conductivity [dS/m]	Negligible salinity effects	< 1.0
	Slightly saline	1.1 - 2.0
	Moderate saline	2.1 - 4.0
	Saline soil	4.1 - 8.0
	Very saline	8.1 – 16.0
	Stronly saline	> 16.0
Organic matter [%]	Very low	< 4
	Low	4.1 - 6.0
	Medium	6.1 – 10.9
	High	11.0 – 16.0
	Very high	>16.1

As for the found values of electrical conductivity, the soils analyzed are considered to have negligible salinity effects and the values of the organic matter content were very low according to SEMAR-NAT (2003). However, these conditions have allowed an easy development of the plant, so it was

evident at the time of sampling, probably by the incorporation of rice shell residues into the soil by farmers as an attempt to improve the properties of the soil (Park et al., 2011).

The result of a low pH soil low in organic matter

Points	pН	EC [dS/m]	OM [%]	Humidity [%]
1	4.96 (0.06)	0.163(0.002)	2.9 (0.2)	20.4 (2.0)
2	4.88 (0.03)	0.160(0.002)	2.4 (0.1)	18.8 (0.3)
3	4.73 (0.06)	0.238(0.002)	2.6 (0.9)	17.4 (0.6)
4	4.36 (0.04)	0.525(0.003)	2.5 (0.2)	17.5 (1.2)
5	4.93 (0.04)	0.200(0.001)	3.0 (0.2)	20.4 (1.7)

 Table 2. Characterization of the soil studied.

pH: Hydrogen potential, EC: electrical conductivity, OM: organic matter. The average is displayed and the standard deviation for n = 3 is shown in parentheses.

increases the bioavailability of metals for the plant due to the lack of formation of organometallic complexes, making it impossible for metals to be absorbed by the root of the plant that is in direct contact with the soil (Tangahu et al., 2011; Bravo Realpe et al., 2014; Bornø et al., 2019). On the other hand, the humidity for the collected agricultural soil samples were between 17.4 and 20.4%, which is typical to the climate of the area and the conditions of the harvesting day.

3.2 Moisture and ash content in onion

In onion samples, the humidity and ash parameters were from 90.63 to 91.70% and 5.17 to 6.06%, respectively. In general, the moisture content is consistent with a review conducted by Mitra and Rao (2012) of 91.20%, while the ash content was similar to those obtained by Bello et al. (2013) who reported values up to 11.46%. However, these properties are of minimal control since they are influenced by climatic and soil conditions, conditions of transport and storage of the product during the post-harvest.

3.3 Metal content in the soil and onion

The metal content was compared to reference values according to national and international regulations. For the specific case of onion, no legislation regulating the metal content was found; however, the value corresponding to items similar to those analyzed was taken as a reference. Table 3 shows the values of various legislations for food and soils obtained from the MAE. The results obtained from the metal content in soil samples for soluble fractions in *agua regia* (totals), the soluble fraction in the extracting mixture (bioavailable) and onion samples are expressed as quantity of metal in fresh mass (Table 4). The discussion of the results was based on the total content, the bioavailable fraction and the value found in onion for each metal.

The cadmium content (total 0.09-0.13 mg/kg and bioavailable 0.0218-0.049 mg/kg) for soil samples was found within the environmental quality standards established for soils, according to the MAE (values below 0.5 mg/kg). The results obtained for cadmium are within the reported values (0.07–1.35 mg/kg) in New Zealand soils (Cavanagh et al., 2019); however, they are lower than those reported in soils of a petrochemical area (0.25-1.50 mg/kg) in Sardinia, Italy (Cortis et al., 2016) and in sediments of Texcoco Lake (0.64-2.28 mg/kg), located at the east of the Trans-Mexican Volcanic Belt (Sedeño-Díaz et al., 2020). In another sediment study of Caviahue Lake, Argentina, affected by Copahue volcano fluids, cadmium values were below the detection limit (Cabrera et al., 2015).

As for the Cd content in the edible portion of onion (0.0188-0.030 mg/kg) it was comparable to another variety of New Zealand onion with reported values of 0.007- 0.05 mg/kg (Cavanagh et al., 2019). In addition and according to the laws consulted, the samples were found in all cases below the established limits of the cadmium content (0.1 mg/kg for the European Union, Australia, Codex Alimentarius and 0.03 mg/kg for Russia).

Matal	Soil				Food products [mg	/kg]		
Metal	MAE [mg/Kg]	UE	Australian law	Brazilean law	Codex Alimentarius	Finland	Russia	Soth Africa
Cd	0.5	0.1	0.1	1	0.1		0.03	0.05
cu	0.5	Root vegetables, tubers and yound stems	Leaf/Root vegetables and tubers	Other food except juices, alcoholic drinks, and fishing products	Stem and root vegetables	-	Vegetables/ fruits	Fruits and vegetables
Co	10	-	-	-	-	-	-	-
Cu	30	-	-	5	-	10	-	5
				Fresh		Vegetables		Juices of vegetables, fruits and nectars
Ni	20	-	-	5 Other food except juices, alcoholic drinks and hidrogenated products	-	-	-	-
Pb	25	0.3	0.1	0.5	0.1	1 Potato,	0.5	0.1
		Vegetables	Vegetables (except Brassica)	Vegetables	Roots and tubers tubérculos	cucumber, natsudaidai (Pulp), peach, strawberry and grape.	Vegetables/ fruits	Fruits and other vegetables
Zn Fe, K,	60	-	-	-	-	-	-	5 Juices of vegetables, fruits and nectars
Mg, Mn, Sr		-	-	-	-	-	-	-

Table 3. Quality criteria of the soil and vegetables. Adapted from Diaz. (2014).

The lead content (total 0.64-1.28 mg/kg and bioavailable 0.25-0.29 mg/kg) for the soil did not exceed 25 mg/kg, remaining within the environmental quality standards established in accordance with the MAE, and below those found by Arnalds et al. (2007) for Italian volcanic soils that report values up to 3.420 mg/kg. In addition, the Pb content in onion (0.040-0.058 mg/kg) in all cases was lower than the limits established under the legislation consulted (0.3 mg/kg for the European Union, and 0.1 mg/kg for Australia, Codex Alimentarius and South Africa).

fable 4. Soil metal c	content and edible	tissue of Allium	fistulosum L.
-----------------------	--------------------	------------------	---------------

Metal	Soil con	tent (mg/kg)	Content in edible tissue of <i>Allium</i>
	Total	Bioavailable	fistulosum L. (mg/kg)
Cd	0.09 -0.13	0.0218 - 0.049	0.0188 - 0.030
Pb	0.64 - 1.28	0.25 - 0.29	0.040-0.058
Ni	13.9-18.6	0.9-1.8	5.1-6.9
Со	5.8-9.0	0.22-0.34	0.085-0.12
Sr	7.4-19.5	0.83-1.24	0.84-0.95
Cu	14.8-21.6	4.8-6.2	0.44-0.61
Zn	72.5-88.7	4.4-7.0	5.0-6.16
K	95-601	58-148	652-829
Mg	1217-3217	84-96	128-147
Fe	6462-7850	246-289	8.6-10.3
Mn	55-73	6.7-8.3	1.43-1.61

As for the nickel content (total 13.9-18.6 mg/kg and bioavailable 0.9-1.8 mg/kg) the soil did not exceed 20 mg/kg, remaining within the environmental quality standards established according to the MAE, being lower than those found by Arnalds et al. (2007) for Italian volcanic soils with values up to 101 mg/kg. Moreover, the values obtained (5.1 to 6.9 mg/kg) for the Ni content in the edible tissue of onion were above the established limits, in accordance with the legislation consulted (5 mg/kg for Brazil); however, it should be emphasized that the categorization is not specific to the onion.

The cobalt content (total 5.8-9.0 mg/kg and bioavailable 0.22-0.34 mg/kg) in soil did not exceed 10 mg/kg, remaining within the environmental quality standards established in accordance with the MAE, and it was consistent with the cobalt content reported for European volcanic soils with a maximum of 33 mg/kg (Arnalds et al., 2007) and agricultural soils on the São Miguel island, with average values from 1.66 to 13.9 mg/kg (Linhares et al., 2019). As for the content of Co in the edible portion of the onion, between 0.085 and 0.12 mg/kg was found (the legislation consulted does not indicate Co limit values).

In relation to the strontium content in soil (total 7.4-19.5 mg/kg and bioavailable 0.83-1.24 mg/kg) and in onion (0.84-0.95 mg/kg), no comparison was found with any legislation; however, higher values have been reported in other works, e.g. study of strontium accumulation by native plants grown on Gumuskoy mining soils, and values between 22.60 and 691.80 mg/kg were reported in soils and mean levels of Sr were 163.65 and 163.93 mg/kg for roots and shoots, respectively of the plants studied (Sasmaz and Sasmaz, 2017), and also, in Volcanic Minerals in Chaco Canyon, New Mexico with maximum values of 254 mg/kg (Tankersley et al., 2018).

The copper content (total 14.8-21.6 mg/kg and bioavailable 4.8-6.2 mg/kg) in soils did not exceed 30 mg/kg, being within environmental quality standards according to the MAE and below those reported for Italian volcanic soils with values up to 565 mg/kg (Arnalds et al., 2007); however, as a nutrient it was found at very high levels (>5 mg/kg). Moreover, the content of Cu in onion (0.44 to 0.61

mg/kg) was low, being below the established limits, in accordance with the legislation consulted (5 mg/kg for Brazil and South Africa, and 10 mg/kg for Finland).

The total zinc content obtained (72.5-88.7 mg/kg) exceeded 60 mg/kg, being outside the environmental quality standards according to the MAE; although the bioavailable fraction (4.4-7.0 mg/kg) is below that limit and below those reported for Italian volcanic soils with values of up to 2.550 mg/kg (Arnalds et al., 2007). As a nutrient, it is at very high levels (>20 mg/kg), and its bioavailability goes from average (2-5 mg/kg) to high (5-20 mg/kg). Moreover, the content of Zn in onion (5.0-6.16 mg/kg) was found above the reference value (5 mg/kg in accordance with South African legislation) for vegetable, fruit and nectar juices. No reference values of onion or some other vegetables were found.

Potassium content (total 95-601 mg/kg and bioavailable 58-148 mg/kg) in soils was very high as a nutrient; however, although there are no environmental rules regulating its content, it is below what is reported in other works; for example, there are values of up to 3,500 mg/kg of potassium in soils in an industrial location in Italy (Cortis et al., 2016). As for the content of onion, it resulted between 652 and 829 mg/kg. Importantly, the recommended potassium intake is between 90-120 mmol/day in adults to reduce blood pressure and the risk of cardiovascular disease, stroke and coronary heart disease in adults (WHO, 2012).

Magnesium content (total 1217-3217 mg/kg and bioavailable 84-96 mg/kg) in soils was high, resulting in very high bioavailability levels (>8 cmol/kg); although there are no regulations that restrict its content. Average Mg values of 29,052 mg/kg have been reported in Lake Texcoco sediments (Sedeño-Díaz et al., 2020). While the magnesium content in onion was between 128 and 147 mg/kg, the recommended daily intake for magnesium is varied, depending on age and sex with values between 30 and 420 mg to regulate muscle function, protein formation, bone growth, and others (NIH, 2016).



Figure 2. Metal absorption by onion based on the bioavailable fraction in the soil.

The iron content (total 6 462-7 850 mg/kg and bioavailable 246-289 mg/kg) in the soil as a nutrient was very high (>200 mg/kg), however, these high concentrations are common in most agricultural soils, without this representing negative effects. As an example, studies may be cited in sediments from a lake in Mexico (averages of 14 428 mg/kg) and in soils close to an industrial area in Italy with up to 3 200 mg/kg (Cortis et al., 2016). While the iron content in onion was found from 8.6 to 10.3 mg/kg, above reported values of 0.84 to 2.47 (Vilanova et al., 2008) and within those reported by Bello et al. (2013) up to 40 mg/kg in the estimated bulb with 90% of humidity. The manganese content (total 55-73 mg/kg and bioavailable 6.7-8.3 mg/kg) as a nutrient in the soil is considered high (50-100 mg/kg), although its bioavailability was low (2-10 mg/kg). These values are lower than those reported by Linhares et al. (2019) for agricultural soils in six volcanic areas of the island of São Miguel (1 782.50 \pm 108.98). While the manganese content in onion was found between 1.43 and 1.61 mg/kg. No legislation was found to regulate manganese content in soils or food. For most of the metals studied, it was observed that they were within the maximum values set out in the standards consulted, aligned with the results obtained in a study of metals in pineapple and pitahaya grown in the vicinity of the Masaya volcano in Ni-

caragua.

3.4 Bioavailability factor, β

Figure 2 shows the influence of the bioavailable fraction of the metal in the soil on the absorption of the metal by onion. The fine dashed line represents the average of the obtained metal values in onion and in the environment; the thick dashed lines represent the upper and lower limits determined as the average 1.96 (corresponding to the z value for 95% confidence) times the standard deviation.

The absorption of metal in the onion samples analyzed had an independent correlation of the bioavailable fraction in the soil, and in all cases it was lower than the total concentration of the same metal in the soil. This behavior observed in Figure 2 shows that onion is not a metal-accumulating plant since it exclusively absorbs necessary amounts of its nutrients from the soil. Unlike other plants such as Brassica napus that has been investigated its role in the recovery of soils contaminated with metals and Diesel by rhizoremediation (Lacalle et al., 2018) or vetiver (Vetiveria zizanioides) which is used for phytoremediation for its metal bioaccumulation properties (Chen et al., 2004; Almeida et al., 2019; Shabbir et al., 2019). Possibly these results could be because onion is short-cycle, which limits its exposure to metals for extended periods. It has been mentioned that plants absorb metals to varying degrees, depending on the plant species and metal exposure (Intawongse and Dean, 2006; Khan et al., 2015).

4 Conclusions

The studied soil collected in an area affected by the ashes of Tungurahua volcano was strongly acidic, with negligible salinity effect and low organic matter content. The content of potentially polluting metals (cadmium, lead, nickel, strontium and cobalt), in soil and onion of the Quero canton, is below the regulations consulted. The content of nutrient metals (potassium, manganese, magnesium, iron, copper and zinc) was found at adequate levels, in no case deficiency was found.

The bioavailability of metals in soils near the Tungurahua volcano allowed to determine that the

intake of metal by onion was independent of the bioavailable fraction of metal in the soil for all metals studied.

Acknowledgement

This work has been financed by the DIDE-UTA through the projects Bioavailability of metals in soils of the Quero canton of the province of Tungurahua HCU 0194-CU-P-2018 and Project Debt Exchange Ecuador-Spain HCU 0939-CU-P-2016, both from the Faculty of Science and Engineering in Food and Biotechnology.

References

- Almeida, A., Ribeiro, C., Carvalho, F., Durao, A., Bugajski, P., Kurek, K., Pochwatka, P., and Jóźwiakowski, K. (2019). Phytoremediation potential of vetiveria zizanioides and oryza sativa to nitrate and organic substance removal in vertical flow constructed wetland systems. *Ecological Engineering*, 138:19–27. Online:https://bit.ly/ 3gICrYg.
- AOAC (2006). Official methods of analysis proximate analysis and calculations moisture (m) fruits, vegetables, and their products - item 107. In *Association of Analytical Communities*, volume Reference data: Method 934.06 (37.1.10); NFNAP; WATER.
- Arnalds, Ó., Bartoli, F., Buurman, P., García-Rodeja, E., Óskarsson, H., and Stoops, G. (2007). Soils of volcanic regions in Europe.
- Battaglia, J., Hidalgo, S., Bernard, B., Steele, A., Arellano, S., and Acuña, K. (2019). Autopsy of an eruptive phase of tungurahua volcano (ecuador) through coupling of seismo-acoustic and so2 recordings with ash characteristics. *Earth and Planetary Science Letters*, 511:223–232. Online:https: //bit.ly/2W7wKLF.
- Bello, M., Olabanji, I., Abdul-Hammed, M., and Okunade, T. (2013). Characterization of domestic onion wastes and bulb (allium cepa l.): fatty acids and metal contents. *International Food Research Journal*, 20(5):2153–2158. Online:https:// bit.ly/3fhgwqJ.

- Bornø, M., Müller-Stöver, D., and Liu, F. (2019). Biochar properties and soil type drive the uptake of macro-and micronutrients in maize (zea mays l.). *Journal of Plant Nutrition and Soil Science*, 182(2):149–158. Online:https://bit.ly/2ZWJcPt.
- Bravo Realpe, I., Arboleda Pardo, C. A., and Martín Peinado, F. J. (2014). Efecto de la calidad de la materia orgánica asociada con el uso y manejo de suelos en la retención de cadmio en sistemas altoandinos de colombia. *Acta Agronómica*, 63(2):1– 14. Online:https://bit.ly/3gNvR2Q.
- Cabrera, J., Temporetti, P., and Pedrozo, F. (2015). Trace metal partitioning and potential mobility in th e naturally acidic sediment of lake caviahue, neuquén, argentina. *Revista Clínica Las Condes*, 26(2):217–222. Online:https://bit.ly/3g4YSpT.
- Cargua Catagña, F., Rodríguez Llerena, M., Damián Carrión, D., Recalde Moreno, C., and Santillán Lima, G. (2017). Analytical methods comparison for soil organic carbon determination in andean forest of sangay national park-ecuador. *Acta Agronómica*, 66(3):408–413. Online:https://bit.ly/ 321hjIN.
- Cavanagh, J. A. E., Yi, Z., Gray, C. W., Munir, K., Lehto, N., and Robinson, B. H. (2019). Cadmium uptake by onions, lettuce and spinach in new zealand: Implications for management to meet regulatory limits. *Science of the total Environment*, 668:780–789. Online:https://bit.ly/3iO1vip.
- Chen, Y., Shen, Z., and Li, X. (2004). The use of vetiver grass (vetiveria zizanioides) in the phytoremediation of soils contaminated with heavy metals. *Applied Geochemistry*, 19(10):1553–1565. Online:https://bit.ly/3fiLQpf.
- Choumert-Nkolo, J. and Phélinas, P. (2019). Natural disasters, land and labour. *European Review of Agricultural Economics*, 47(1):296–323. Online:https://bit.ly/2CnRiso.
- Cortis, P., Vannini, C., Cogoni, A., De Mattia, F., Bracale, M., Mezzasalma, V., and Labra, M. (2016). Chemical, molecular, and proteomic analyses of moss bag biomonitoring in a petrochemical area of sardinia (italy). *Environmental Science and Pollution Research*, 23(3):2288–2300. Online:https:// bit.ly/2W9MQUS.
- Diaz., A. (2014). Metales pesados. Technical report, Secretaria de Estado de Comercio, Valencia.

- Faithfull, N. T., T, N., and Ferrando Navarro, A. C. (2005). Métodos análisis quiímico agriícola: manual praáctico. acribia. Accessed: 19 August 2019.
- Golia, E. E., Dimirkou, A., and Mitsios, I. K. (2008). Influence of some soil parameters on heavy metals accumulation by vegetables grown in agricultural soils of different soil orders. *Bulletin of environmental contamination and toxicology*, 81(1):80– 84.
- Intawongse, M. and Dean, J. R. (2006). Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract. *Food additives and contaminants*, 23(1):36–48. Online:https://bit.ly/ 302bpnT.
- Kabata-Pendias, A. (2004). Soil-plant transfer of trace elements—an environmental issue. *Geoderma*, 122(2-4):143–149. Online:https://www.sciencedirect.com/science/ article/abs/pii/S0016706104000084.
- Kabata-Pendias, A. and Sadurski, W. (2004). Trace elements and compounds in soil. *Elements and their compounds in the environment: Occurrence, analysis and biological relevance,* pages 79–99. Online:https://bit.ly/3iRFZcB.
- Kazlauskaitė-Jadzevičė, A., Volungevičius, J., Gregorauskienė, V., and Marcinkonis, S. (2014). The role of ph in heavy metal contamination of urban soil. *Journal of Environmental Engineering* and Landscape Management, 22(4):311–318. Online:https://bit.ly/2DvLcXj.
- Khan, A., Khan, S., Khan, M., Aamir, M., Ullah, H., Nawab, J., Rehman, I., and Shah, J. (2019). Heavy metals effects on plant growth and dietary intake of trace metals in vegetables cultivated in contaminated soil. *International journal of Environmental Science and Technology*, 16(5):2295–2304. Online:https://bit.ly/38VdQgk.
- Khan, A., Khan, S., Khan, M. A., Qamar, Z., and Waqas, M. (2015). The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review. *Environmental Science and Pollution Research*, 22(18):13772–13799. Online:https://bit.ly/ 327Vmrx.

- Lacalle, R., Gómez-Sagasti, M. T., Artetxe, U., Garbisu, C., and Becerril, J. M. (2018). Brassica napus has a key role in the recovery of the health of soils contaminated with metals and diesel by rhizoremediation. *Science of The Total Environment*, 618:347–356. Online:https://bit.ly/2WrshUr.
- Linhares, D., Pimentel, A., Borges, C., Cruz, J., Garcia, P., and dos Santos Rodrigues, A. (2019). Cobalt distribution in the soils of são miguel island (azores): From volcanoes to health effects. *Science of The Total Environment*, 684:715–721. Online:https://bit.ly/2Zih2iP.
- Mitra, J.and Shrivastava, S. and Rao, P. S. (2012). Onion dehydration: a review. *Journal of food science and technology*, 49(3):267–277. Online:https://bit.ly/38Mbpwg.
- NIH (2016). ¿Qué es el magnesio? ¿Para qué sirve? Online: https://bit.ly/3ausdZH.
- Park, J., Choppala, G. k., Bolan, N., Chung, J. W., and Chuasavathi, T. (2011). Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and soil*, 348(1-2. Online:https://bit.ly/ 3fjXbVW):439.
- Rai, P.and Lee, S. S., Zhang, M., Tsang, Y. F., and Kim, K. (2019). Heavy metals in food crops: Health risks, fate, mechanisms, and management. *Environment International*, 125:365–385. Online:https://bit.ly/3iQAWcq.
- Rieuwerts, J. S. (2007). The mobility and bioavailability of trace metals in tropical soils: a review. *Chemical Speciation and Bioavailability*, 19(2):75–85. Online:https://bit.ly/3frUzWk.
- Sasmaz, M. and Sasmaz, A. (2017). The accumulation of strontium by native plants grown on gumuskoy mining soils. *Journal of Geochemical Exploration*, 181:236–242. Online:https://bit. ly/2ZkvYwP.
- Sedeño-Díaz, J. E., López-López, E., Mendoza-Martínez, E., Rodríguez-Romero, A. J., and Morales-García, S. S. (2020). Distribution coefficient and metal pollution index in water and sediments: Proposal of a new index for ecological risk assessment of metals. *Water*, 12(1):29. Online:https://bit.ly/3ei4Brr.

- SEMARNAT (2003). Acuerdo que establece las reglas de operación para el otorgamiento de pagos del programa de servicios ambientales hidrológicos. viernes, 3, 6-23. sgr. (2014). programa de prevención y mitigación para reducir el riesgo por diferentes amenazas. Technical report, Secretaría de Medio Ambiente y Recursos Naturales.
- Shabbir, A., Khan, M., Ahmad, B., Sadiq, Y., Jaleel, H., and Uddin, M. (2019). Vetiveria zizanioides (l.) nash: A magic bullet to attenuate the prevailing health hazards. In *Plant and Human Health, Volume 2*, pages 99–120. Online:https:// bit.ly/2ZUdlic. Springer.
- Sungur, A., Soylak, M., and Ozcan, H. (2014). Investigation of heavy metal mobility and availability by the bcr sequential extraction procedure: relationship between soil properties and heavy metals availability. *Chemical Speciation and Bioavailability*, 26(4):219–230. Online:https://bit.ly/3020RFp.
- Tangahu, B. V., Sheikh Abdullah, S. R., Basri, H., Idris, M., Anuar, N., and Mukhlisin, M. (2011). A review on heavy metals (as, pb, and hg) uptake by plants through phytoremediation. *International Journal of Chemical Engineering*, 2011. Online:https://bit.ly/3fqux5C.
- Tankersley, K. B., Huff, W. D., Dunning, N. P., Owen, L. A., and Scarborough, V. L. (2018). Volcanic minerals in chaco canyon, new mexico and their archaeological significance. *Journal of Archaeological Science: Reports*, 17:404–421. Online:https://bit.ly/2AP6RJ2. 17(November 2017).
- Tóth, G., Hermann, T., Da Silva, M. R., and Montanarella, L. (2016). Heavy metals in agricultural soils of the european union with implications for food safety. *Environment international*, 88:299–309. Online:https://bit.ly/3ekqQNE.
- Vilanova, M., Zamuz, S., Tardáguila, J., and Masa, A. (2008). Descriptive analysis of wines from vitis vinifera cv. albariño. *Journal of the Science of Food and Agriculture*, 88(5):819–823. Online:https: //bit.ly/3elNQfd.
- WHO (2012). Guideline: Potassium intake for adults and children. Technical report, World Health Organization.