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ASSESSMENT OF THE PRESENCE OF HEAVY METALS, AS FOR AN INVENTORY ON GARLIC, ONION AND IN SEMIURBAN SOILS OF AREQUIPA, PERU

EVALUACIÓN DE LA PRESENCIA DE METALES PESADOS, COMO PARA UN INVENTARIO EN AJO, CEBOLLA Y SUELOS SEMIURBANOS DE AREQUIPA, PERÚ

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Palabras clave: *Metales pesados, Ajo, Cebolla, Acumulación de suelos, ICP-MS*.

ABSTRACT

The objective of this study is the evaluation of the accumulation of heavy elements, namely Pb, Cr, Cd, Tl, Cu, Co in garlic, onion and soil of semi-rural soils and its potential effect on the health of the population of the city of Arequipa. The results showed concentrations below the permissible limits for all of them in garlic, onion and soils in accordance with international standards, showing that the accumulation of heavy metals in the soil does not exceed the limits according to international standards.

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RESUMEN

El objetivo de este estudio es la evaluación de la acumulación de elementos pesados, Pb, Cr, Cd, Tl, Cu, Co en ajo, cebolla y suelo de suelos semirurales y su efecto potencial en la salud de la población de la ciudad de Arequipa. Los resultados mostraron concentraciones por debajo de los límites permisibles para todos ellos en ajo, cebolla y suelos de acuerdo con los estándares internacionales demostrando que la acumulación de metales pesados en el suelo no supera los límites según los estándares internacionales.

INTRODUCTION

Contamination of agriculture soils by the long-term accumulation of different transitions element is considerate of the great importance around the world [1]. The ecotoxicity and persistence of heavy metals and metalloids through natural and anthropogenic contributions on agriculture soils is very important and has been attracted the attention of the global science community [2]. Heavy metals are defined as an inorganic chemical hazard, the most common are: lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni) [3,4]. Natural inventory of the heavy metals is inherited from parent rocks. Anthropogenic activities are sources that heavily influenced the nature inventory. These include coal combustion, traffic emissions, industrial activities, mining operations, and agriculture activities [1,5]. It is true that the anthropogenic contribution exceeds sometimes the natural contribution due to the crescent urban and industrial rising in the last decades.

Understanding the spatial distribution and accumulation of heavy elements is critical. It will help to evaluate the complex and different mechanism of transition of elements from soils to vegetals, their mobility and bioavailability, leaching losses, uptake for plants and their influence on human health by ingesting grazing livestock meat [2,3]. Quantify the number of heavy metals is essential. Their input and output on agriculture soils would provide information of the source apportionment and create an inventory about the source of heavy elements to agricultural soils, atmospheric depositions, fertilizer application, organic and inorganic waste disposal and the contribution of the industry and human activity, helping to diagnose the current situation of heavy metals on agriculture soils [6]. Worldwide concern about the crescent inventory of heavy metals have shown the importance to keep an update record it started in 1974 in Netherlands [7]. Since then, European nations have been performed periodical research, for example, France and Germany [8], in United States of America and lately China [9,10].

An inventory of the presence of the heavy elements is significant because it indicates the accumulation or depletion of the different elements in specific geographical areas, ecosystems, and provide a valuable knowledge base to improve the management and recommendation about norms and policies to regulate the anthropogenic sources [10]. Leclerc and Laurel published new global scale inventory for the period 2000-2014, indicating the accumulation of heavy metals on agricultural soils in 2017 [11]. However, the total release of the harmful heavy chemicals and their quantification result from the specific studies and for specific cases, and the data cannot be extrapolated for specific geographic locations because of several parameters that will affect the results of the analysis.

In this study, our team will aim to (1) Develop a framework to quantify the presence of heavy metals on livestock and agriculture soil in the urban region of Arequipa- Peru. (2) Contribute to creating a national inventory regionally and for the world. (3) Quantify the impact of heavy metals on livestock and their potential harm to human health.

EXPERIMENTAL

Data collection and materials

Our study evaluated the accumulation of heavy metals in livestock and soils in the urban region of Arequipa. The study was performed in the summer of 2016, the soil (onions and garlic) and livestock were collected from three places Tiabaya 71.631669 West; 16.426431 South Sachaca 71.562181 West; 16.424828 South and Uchumayo 71.631669 West; 16.426431 South. Soil samples were collected randomly and chemically analyzed by triplicate.

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Livestock samples were collected, carefully cleaned, cut, and dried using a lyophilization; the chemical analyzed was performed by triplicated as well.

Heavy metals concentration on the soil and livestock were measured digesting the samples in nitric acid and hydrogen peroxide at 150°C using digestor into a microwave oven. The samples with this treatment were diluted and measured with ICP-MS. For quality control, an internal control (Spinach NBS 1570 and Sea Lettuce BCR 279) were run in parallel to the livestock and soil samples.

The following seven heavy metals considerate as a priority pollutant element by the USEPA (United State Environmental Protection Agency) have been identified in this study as: chromium, copper, nickel, cobalt, lead, cadmium, and thallium.

RESULTS

Soils are an essential reservoir of chemical elements and a living matrix for compounds in their different states of the matter. Chemical analysis of the agriculture areas, plants, and soils show essential information about the inventory data for heavy metal in the Arequipa region.

Heavy metal concentration was determined using the weight of fresh vegetables and after drying. We used the following equation to calculate the concentration.

$$[C_{p.f.}] = \frac{(100-x-y)}{100}[C_{p.d.}] \qquad \text{equation 1}$$

Where:

X= Percentage loss of water after dry
Y= Percentage of residual water
$C_{p.d.}$ = Concentration mg/kg of the sample dry weight.
$C_{p.f.}$ = Concentration mg/kg of the sample fresh weight

***Table 1**: Summary of concentration of heavy metals concentrate on mg/kg for garlic, onion, and soils from the semi-urban area of Arequipa*

		Cr mg/kg	SD	Pb mg/kg	SD	Cd mg/kg	SD	Tl mg/kg	SD	Ni mg/kg	SD	Cu mg/kg	SD	Co mg/kg	SD
Sachaca	Onion	0.095	10.14	0.037	1.87	0.01	5.85	0.0001	0.06	0.034	1.58	0.302	15.56	0.008	0.06
Tiabaya	Onion	0.176	2.22	0.156	1.37	0.017	1.01	0.0008	0.02	0.013	0.52	0.432	19.82	0	0.00
Tiabaya	Garlic	0.484	12.93	0.189	7.86	0.014	1.07	0.00047	0.07	0.0028	0.50	1.259	35.47	0.0028	0.33
Uchumayo	Garlic	0.58	29.00	0.15	11.69	0.1	3.29	0.002	0.55	0.007	0.82	1.03	53.40	0.003	0.26
	Soil	39.41	6.85	10.99	1.26	<1	1.05	<1	0.00	11.38	1.52	34.5945	3.32	9.615	0.82
NBS 1570	Standard														
Measure				0,176±0.023		2,93±0.12				2.02±0.11		12.0±0.4		0.41±0.03	
Certified				[0,20]		2,84±0.07				2.14±0.10		12.2±0.6		0.39±0.05	
Sea lettuce BCR 279	Standard														
Measure				2.06±0.08		1.66±0.07				1.68±0.11				0.59±0.09	
Certified				1.99±0.06		1.52±0.04				1,59±0.02				0.57±0.02	

Statistical Analysis

The statistical analysis was performed evaluating the distribution t- Student, calculating the confidence intervals of the concentration average of the heavy metals with 98% of confidence. Results are shown in table 1 and 2 for the distribution of heavy metals on onion and garlic respectively on Tiabaya, Sachaca and Uchumayo semirural places of Arequipa Peru.

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Table 2. *Statistical results of concentration of heavy metals on onion.*

Pb in Onion (Sachaca)			Cr in Onion (Sachaca)		Cd in Onion (Sachaca)		Ni in Onion (Sachaca)	
Low limit		**High limit**	**Low limit**	**High limit**	**Low limit**	**High limit**	**Low limit**	**High limit**
IC(u;0.98)	0.02949358	0.04455268	0.05405020	0.13559697	0.01343154	0.03358234	0.02751816	0.04023940
t(0.99;2)	6.96456		6.96456		6.96456		6.96456	
Av dev	0.00108112		0.005854409		0.00337522		9.1328E-04	
Est error	0.00752955		0.040773385		0.02350694		0.00636062	

Tl in Onion (Sachaca)			Cu in Onion (Sachaca)		Co in Onion (Sachaca)	
Low limit		**High limit**	**Low Limit**	**High limit**	**Low Limit**	**High limit**
IC(u;0.98)	-0.00009317	0.00038338	0.23973107	0.36486933	0.00053110	0.00100813
t(0.99;2)	6.96456		6.96456		6.96456	
Av dev	3.4213E-05		8.9839E-03		3.4247E-05	
Est error	0.00023828		0.06256913		0.00023851	

Pb in Onion (Tiabaya)			Cr in Onion (Tiabaya)		Cd in Onion (Tibaya)		Ni in Onion (Tiabaya)	
Low limit		**High limit**	**Low limit**	**High limit**	**Low limit**	**High limit**	**Low limit**	**High limit**
IC(u;0.98)	0.15075141	0.16176005	0.16700422	0.18488458	0.01258763	0.02069264	0.01078956	0.01496291
t(0.99;2)	6.96456		6.96456		6.96456		6.96456	
Av dev	0.00079033		0.001283668		0.00058187		2.9961E-04	
Est error	0.00550432		0.00894018		0.0040525		0.002086673	

Tl in Onion (Tiabaya)			Cu in Onion (Tiabaya)		Co in Onion (Tiabaya)	
Low limit		High limit	Low limit	High limit	Low limit	High limit
IC(u;0.98)	0.00000867	0.00014418	0.35233739	0.51171031	0.00000000	0.00000000
t(0.99;2)	6.96456		6.96456		6.96456	
Av dev	9.7285E-06		1.1442E-02		0.0000E+00	
Est error	6.77548E-05		0.079686456		0	

DISCUSSION

Trace elements in livestock and soil

Chromium

The mean content of chromium in onion for Sachaca and Tiabaya was 0.095 mg/kg and 0.176 mg/kg respectively, in the case of garlic for Tiabaya was 0.484 mg/kg and Uchumayo 0.58 mg/kg. The content of chromium in soil was 39.41 mg/kg on average; this result is between the average value for the background concentration of chromium on Europe'soils report that signals limits of 5 to 65 mg/kg [12,13]. The presence of Cr(VI) reported in Plants (*Alyssum obovatum, Cochlearia arctica (Brassicaceae), Armeria scabra (Limoniaceae), Salix arctica (Salicaceae*) showed values from 0.09–0.59 mg/kg [14]. Our research didw not target the presence of different ionic species of chromium, the samples essayed indicated that onion from Sachaca had values between the limits reported by Panichev et al [14]. However, samples from Tiabaya onion and garlic and Uchumayo garlic showed the highest value compared with onion from Sachaca. The highest value found in the garlic sample in Tiabaya had close values found in the same species reported by Sakizadeh et al. 2018 [15]. The daily amount of chromium intake per day in our diet according to the European Food Safety Authority (EFSA) is 57.3–83.8 ug/kg and for the World Health Organization (WHO) is 47 ug/kg [1,16].

Lead

The concentration of lead in onion samples shown values of 0.037 mg/kg and 0.156 mg/kg for Sachaca and Tiabaya, whilst garlic showed 0.189 mg/kg for Tiabaya and 0.15 for Uchumayo. The determined content of lead on the soil

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was 10.99 mg/kg. The limit permissible for lead in soils according to the World Health Organization (WHO) is 50 mg/kg. The amount on the lead registered on garlic was 0.21 mg/kg reported for Sakizadeh et al. 2018 [15]. Our data show that the concentration of lead is low, besides onion sample from Sachaca that show the lowest content on lead, the other samples show very close values. Cai Li et al [17], report that vegetable on China depending on its kind allows between 0.3 to 0.1 mg/kg. According to the FAO/WHO the maximum intake for lead is 25 ug/kg body weight per week [18].

Table 3. *Statistical results of concentration of heavy metals on garlic.*

Pb in Garlic (Tiabaya)			**Cr in Garlic (Tiabayaa)**		**Cd in Garlic (Tiabaya)**		**Ni in Garlic (Sachaca)**	
Low limit		High limit	Low limit	High limit	Low limit	High limit	Low limit	High limit
IC(u;0.98)	0.15776423	0.22098166	0.43209324	0.53611145	0.00958078	0.01816291	0.00077297	0.00478184
t(0.99;2)	6.96456		6.96456		6.96456		6.96456	
Av dev	0.00453851		0.00746768		0.00061613		2.8780E-04	
Est error	0.03160871		0.052009108		0.00429107		0.002004432	

Tl in Garlic (Tiabaya)			**Cu in Garlic (Tiabaya)**		**Co in Garlic (Tiabaya)**	
Low limit	**High limit**		**Low limit**	**High limit**	**Low limit**	**High limit**
IC(u;0.98)	0.00021031	0.00074039	1.11619461	1.40141010	0.00145688	0.00408328
t(0.99;2)	6.96456		6.96456		6.96456	
Av dev	3.8056E-05		2.0476E-02		1.8856E-04	
Est error	0.00026504		0.142607744		0.0013132	

Pb in Garlic (Uchumayo)			**Cr in Garlic (Uchumayo)**		**Cd in Garlic (Uchumayo)**		**Ni in Garlic (Uchumayo)**	
Low limit		**High limit**	**Low limit**	**High limit**	**Low limit**	**High limit**	**Low limit**	**High limit**
IC(u;0.98)	0.10303576	0.19706734	0.46402363	0.69724771	0.08714731	0.11358056	0.00331994	0.00990781
t(0.99;2)	6.96456		6.96456		6.96456		6.96456	
Av dev	0.00675072		0.016743634		0.0018977		4.7296E-04	
Est error	0.047015789		0.116612041		0.01321663		0.003293933	

Tl in Garlic (Uchumayo)			**Cu in Garlic (Uchumayo)**		**Co in Gralic (Uchumayo)**	
Low limit	**High limit**		**Low limit**	**High limit**	**Low limit**	**High limit**
IC(u;0.98)	0.00030555	0.00468898	0.81268662	1.24210686	0.00159131	0.00367445
t(0.99;2)	6.96456		6.96456		6.96456	
Av dev	3.1470E-04		3.0829E-02		1.4955E-04	
Est error	0.00219171		0.214710122		0.00104157	

Cadmium

Similarly, the concentration of cadmium ranged from 0.014 to 0.1 mg/kg in garlic and onion, in comparison, Sakizadet et al., 2018 [15] reported cadmium in fresh vegetables with an average value of 0.01mg/kg and Xinyu Li et al 2018 [19] reported 0.21 mg/kg on the edible part of vegetables cultivated on contaminated areas but 0.05 mg/kg on vegetable cultivated on controlled soils. The values of Sachaca, Tiabaya for onion showed very close values, 0.01 and 0.014 mg/kg respectively. The value of the amount of cadmium of garlic from Tiabaya was similar to the content in onions. However, the average value on Uchumayo had shown one magnitude higher on Garlic 0.1 mg/kg. The mean concentration of cadmium on soil was determined as less than 1 mg/kg and it’s below to the value recommended for the WHO/ FAO that is 3mg/kg. The daily amount of cadmium consumed recommended by the USEPA 2009 is 1ug/kg/day [18].

Thallium

The average content of thallium in onions from Tiabaya and Sachaca is 0.0008 and 0.0001 mg/k, respectively. The content in Garlic showed differences between samples from Tiabaya 0.00047 mg /kg and Uchumayo with 0.002 mg/kg. Huang Yun Yu et al. 2018 [20], reported the average content of thallium as 0.051 mg/kg and for cabbage from 0.01 to 0.06 mg/kg. These values corresponded to samples coming from farmlands close to mining and

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industrial activities. Our data indicated that there is no contamination in onion and garlic with thallium, in accordance to the German and Chinese guide food for thallium that indicated the permissible limit as 0.05mg/kg. The content of thallium on soils according to the Canadian and Swiss regulations [21] is 1mg/kg; our data showed that the concentration of thallium is less than 1 mg/kg. The daily amount recommended for consumption is 0.00001 mg/kg/per day [18].

Nickel

The content of nickel in onions in Tiabaya and Sachaca showed values of 0.034 and 0.011 mg/kg respectively. Values found on garlic were 0.0028 and 0.007 mg/kg for Tiabaya and Uchumayo, respectively. The concentration of nickel in plant cells was reported to be in the rank 0.5 to 5 mg/kg [22], the concentration in onions and garlic showed that the concentration is below the limits for nickel with values from 0.007 and 0.034 mg/kg. The permissible limit for Nickel on soils according to WHO is 50mg/kg. The average content of nickel in the soil in the present study was 11.38 mg/kg. The recommended daily amount of consumption of nickel is 0.02mg/kg/per day [18].

Copper

The average concentration of copper in onions from Tiabaya en Sachaca were 0.302 and 0.432 mg/kg, the concentration of copper in garlic was higher, samples from Tiabaya en Uchumayo showed 1.259 and 1.03 mg/kg. Copper concentration on livestock has been reported with ranges between 1.75 to 9.26 mg/kg [23,24], the maximum permissible amount of copper in vegetable is 50 mg/kg [25]. The content of copper in onion and garlic are below the permitted limits. In the case of the soil, the maximum amount of copper is 100mg/kg according to the WHO [18]. Our sample had a value of 34.5945 mg/kg, indicating that there is no contamination with copper. The amount of copper for human ingestion is 0.04 mg/kg/per day [18].

Cobalt

The concentration of cobalt in onions ranged from 0.008 mg/k to no detected for samples of Sachaca and Tiabaya. In the case of garlic, the values varied from 0.0028 and 0.003 mg/kg for Tiabaya and Uchumayo. Amin et al. 2013 [26], reported that the concentration of cobalt in onion and garlic in contaminated areas were of 0.03 to 0.06 mg/kg and 0.01 to 1mg/kg. Khan et al. 2008 [27] and Chekri et al. 2019 [28] reported the presence of cobalt in toddler food with values between 0.7 to 8.6 ug/kg similar to the values of Melo et al., 2008 [29]. The concentration of the analyzed soil sample fall between the results reported by the literature. The content of cobalt in the examined soil was 9.3 mg/kg which is below the maximum amount according to USEPA or 80mg/kg. The daily intake of cobalt is 0.0003 mg/kg per day [18].

CONCLUSIONS

The presence of seven heavy inorganic elements Pb, Cr, Cd, Tl, Ni, Cu, and Co was assessed on garlic, onion and soils from semiurban areas of Arequipa city. The concentration of these elements were all between the limits for vegetables and soils according to the international standards. The concentration of the heavy elements in the vegetables does not show potential harm to the health of the population, and the same condition can be expressed for the evaluated soils samples. The results indicated that the presence of heavy metals in vegetables and soils are low. However, the accumulation, physical and chemical behavior of the soils, and the identification of the sources still remains a pending task.

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