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Determination of Potentially Toxic Elements in Quinoa Crops Located in the Huacaybamba–Huanuco-Peru Area

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Abstracts: Soil contamination by heavy metals is a global environmental problem, which has attracted public attention due to the consumption of various agricultural products. When heavy metals are mentioned, they refer mainly to metals and metalloids that have biological toxicity such as cadmium, lead, mercury and arsenic, which have the capacity to bioaccumulate in the kidneys and liver, causing carcinogenic renal and brain tumors. These elements are mobilized in soils through natural processes such as mineral deposits, groundwater, hot springs, volcanic rocks, and also through anthropogenic activities related to mining activity in the area. Consequently, heavy metal contamination poses a great threat to human health, due to the potential risk of bioaccumulation of these heavy metals through the food chain. Quinoa is a plant grown in the Andean highlands of Peru and Bolivia and is becoming increasingly popular due to its high nutritional value and protein content. In particular, the cultivation of quinoa has grown substantially in recent years, and is in great demand in the national and international markets, due to the fact that the free trade agreement for imports of quinoa in the US does not pay tariffs, thus Peruvian exports could be favored. However, despite the interest that quinoa has generated in terms of its nutritional properties, little is known about the environmental profile of its production and processing. Therefore, the main objective of this study is to determine the presence of some potentially toxic elements (PTE) such as As, Pb, Cd, Zn and Cu that can be found in quinoa production. Currently, there is no information on the contents of these elements in the crops located in Huacaybamba-Huánuco. That is why in the present work we will use a methodology for taking soil samples from the areas, then through instrumental analysis by atomic absorption spectrophotometry, the concentrations of PTE present in the study area will be determined. As a result, according to the quality standard for agricultural soils in Peru and the European standard, it was found that in the case of Arsenic, Copper and Zinc all the concentration data obtained were below the permissible limits, while for Lead, the 46 % of the data obtained exceeded the standard and in the case of Cadmium, 100 % of the data obtained exceeded the environmental quality standard in the soil. Based on this information, the distribution of these elements will be characterized using geochemical maps of the area.

Keywords: Heavy Metals, Soils, Quinoa, Arsenic, Lead, Cadmium, Copper, Zinc

1. INTRODUCTION

Heavy metal pollution is one of the negative consequences of industrialization, and heavy metals are quite widespread pollutants [1,2]. In the work of [3], it is mentioned that heavy metals can be released into the environment through different anthropogenic activities such as phosphate fertilizers, sewage sludge, Ni–Cd batteries, plating, use of lead–based solders or lead pipes, or from sources of contaminated water. Where anthropogenic activities such as mining and smelting [4], combustion of fossil fuels [3], municipal waste disposal [5] pesticide application [6], wastewater irrigation [7], and fertilizer application [8] contribute to increase the concentration of heavy metals in agricultural soil. According to [9], the disturbance of the heavy metal geochemical cycle that occurs slowly in nature by anthropogenic processes results in the accumulation of one or more heavy metals in the soil. Recent advances in the agricultural sector, industrialization and urbanization have substantially contributed to increasing heavy metal contamination in the soil.

According to [10], it is mentioned that some elements due to pollution impacts should be called potentially toxic elements (PTE). In [11], it is mentioned that potentially toxic elements (PTEs) are not susceptible to biodegradation, they are persistent in the environment and plants can absorb them from the soil and accumulate them in edible parts.

Currently, there is great worldwide interest in quinoa for its beneficial effects on people's health, due to the high amount of protein and vitamins it presents. According to [12], quinoa seeds have been an important source of protein for indigenous communities in the highlands of the Andes in Peru, Bolivia and Ecuador for centuries. But it has become popular in other parts of the world in recent decades, due to its interesting nutritional properties. According to [13] the origins of arsenic in the altiplano–puna plateau are diverse and are mainly of natural origin. Of the natural sources, the most important correspond to mineral deposits, brines, hot springs and volcanic rocks, while anthropogenic sources are related to mining activities and the release of acid mine drainage.

Then in the harvest and production of quinoa in places close to mining areas and in the highlands, there are some problems such as:

According to [13], elevated concentrations of Arsenic in water supplies represent a global health problem. In at least 14 South American countries, high levels have been detected in relation to international standards and guidelines. Within these countries, the high plateau called “Altiplano–Puna”, which covers areas of Argentina, Bolivia, Chile and Peru, exhibits high concentrations of arsenic that could be affecting 3 million inhabitants. In [14], it is mentioned that the consumption of vegetables grown in soils contaminated with arsenic (As) is an important route of exposure to the element for humans. The present study focuses on locally grown and frequently consumed vegetables, such as carrots (Daucus carota), beets (Beta vulgaris), and quinoa (Chenopodium) from the As–contaminated area of Chiu Chiu in northern Chile. This latter region is affected by both, As discharge from copper mining activity and natural As contamination, leading to high As content in local food and water. For the selected vegetables, the total content of As, Cu, Pb, Cr, Cd and Mn was investigated.

According to [15], it is mentioned that quinoa is a plant that is cultivated in the Andean highlands of Peru and Bolivia. It is becoming increasingly popular due to its high nutritional value and protein content. Independently, in [16], it is mentioned that heavy metals in crops and processed foods are a cause for concern and represent a serious potential health hazard. In their study, the authors investigated the possible presence of heavy metals in grains and processed products in the Arequipa Region of Peru. Concentrations of Cd, As, Sn, Pb and Hg were determined for commonly consumed grains in 18 districts of the region and processed products from 3 popular markets in the city of Arequipa. Heavy metal concentrations were found above the limits of the Codex standard for As and Cd in grain and high concentrations of Pb were found for quinoa, corn and rice products.

In particular, the cultivation of organic quinoa has grown substantially in recent years, since it is the most demanded type of quinoa in the foreign market. However, despite the interest that quinoa has generated in terms of its nutritional properties, little is known about the environmental profile of its production and processing. Therefore, the main objective of our study was to analyze the environmental impacts that are linked to the production and distribution of organic quinoa to the main export destinations. In our study, we analyzed the distribution of the elements that present quality standards in the soil in Peru, such as As, Pb and Cd in quinoa cultivation soils in the Huacaybamba area. Independently, the Cu, Zn, and Fe analyzes were also carried out in the study area, from which the distribution of these elements in the area was generated by means of geochemical maps.

2. MATERIALS AND METHODS

2.1. Study area location

The study area is located in Peru, in the Department of Huánuco, adjacent to the western border that limits with the department of Ancash, belonging to the Quichirragra Huacaybamba Population Center. It is characterized by being planting land for agricultural crops, such as potatoes, wheat, barley and especially quinoa. A representative area was chosen for the taking of 50 sampling points of agricultural soil producing quinoa. The area comprises approximately 4 hectares, the samples taken considered the criterion of spatial homogeneity for the efficient representation of field data. Figure 1 shows the location of the sampling points and the study area.

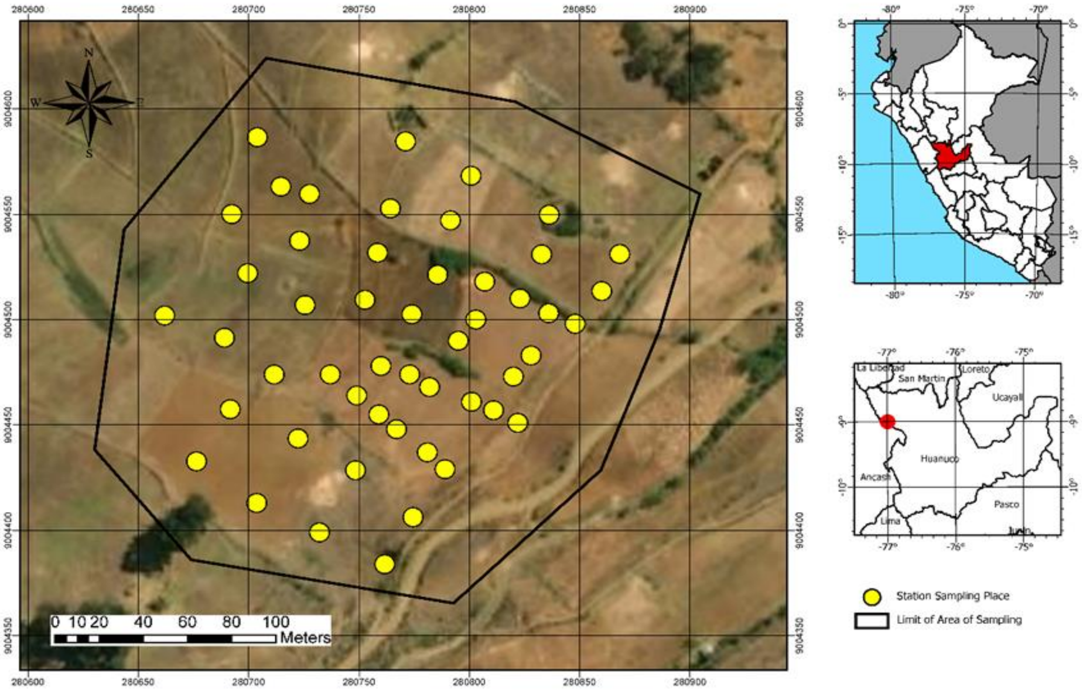

Figure 1. Delimitation of work area

2.2. Regional and Local Geological Context

The study region is located in the Peruvian Andes in rocks altered by pressure and temperature known as meta–sedimentary that date from the Paleozoic era between the Ordovician and Silurian–Devonian periods. In the Marañón valley, an igneous granite–type rock emerges from the depths of the earth's crust, altered by pressure and temperature, having a recrystallization of the minerals that compose it, undergoing a gneiss effect. It is mainly made up of quartz (SiO2), orthose ($KAlSi_3O_8$) and biotite (K(Mg, Fe, Mn)3[(OH, F)2(AlSi3O10)]) as the main minerals that compose it [17]. In the study area, the polymetamorphic rocks of the Marañón Complex present cheap gold mineralizations in quartz veins, rich in sulfides [17].

Regional multi-elemental studies according to INGEMMET [18] indicate that the surrounding areas could contain metallic minerals of Cu, Ag, Au in the rocks (schist and gneiss) in contact with granitic igneous rocks, as well as Ni, Co, Ti, Pt, among others, within rocks of deep origin with a high content of ferromagnesians. Galena (PbS), chalcopyrite (CuFeS2), azurite (2CuCo3Cu(OH)), sphalerite (Zn,Cd)S with hydrothermal alterations of silification, sericitization, propylitization and argilitization are present in the study area, and also important heavy metal resources such as Pb, Cd, Fe, Zn and Cu, as well as As in the study area.

2.3. Collection and Processing of Soils

2.3.1. Soil Sampling

For soil sampling, a grid was made with a separation of 20 m x 20 m as shown in Figure 1, where a sample is taken for analysis for each point generated. The soil samples used for our study were collected at 30 cm on the side of pits 50 cm deep, as indicated in the soil sampling guide, for agricultural soil [19]. In our work, 50 soil samples of approximately 1 kg each were collected. The samples were packed in Ziploc bags and sent to the FIGMM–UNI analysis laboratory. Care was taken not to contaminate the sample with the instrument used or any debris or surface garbage (branches, stones, garbage, among others), and then take the sample from the soil wall (fresh sample) and free of contaminants added during sample collection. Generally, when this waste exists, it is suggested to remove the first centimeters of surface outcrop in a circular area of 15 cm radius [19]. From the test pit, a portion of soil is separated from a wall of the same test pit, considering that the sample must be a portion of soil that has not been in contact with the tool that was used to extract this sample.

2.3.2. Sample Processing

When the soil samples arrive at the laboratory, they are inspected, homogenized and dried, in this way it is possible to rule out analysis inconveniences that can influence the analysis results. Once the sample has been inspected and homogenized, it is placed in coded trays, placed in a drying oven, set at a temperature of 105°C +/- 5°C. The samples are passed through 10 mesh to separate coarse particles such as stones and roots. The grinding is carried out with a Cole-Parmer brand jar mill, which contains burundum grinding media. The product of this grinding is a homogeneous material with a granulometry of 75 microns.

2.3.3. Chemical Analysis of Samples

The elements to be quantified are determined by atomic absorption spectrophotometry after disintegrating the sample with common acids, in order to bring the analyte to a state that can be quantified by the selected method. The method used to quantify the As, Pb and Cd present in the soil samples was the one provided by the Environmental Protection Agency (EPA 3050 – B) [20].

2.3.4. Atomic Absorption Analysis

The identification of the elements to be quantified was carried out using the flame atomic absorption spectrophotometer (AAS), GBC Scientific Equipment brand, XplorAA model. For the reading of Arsenic, a wavelength of 193,7 nm was used. For the reading of Cadmium and for the determination of Lead, a wavelength of 228,8 nm and a wavelength of 217,0 nm were used respectively. In the case of Copper, a wavelength of 324,7 nm was used. For the reading of Zinc, a wavelength of 213,9 nm was used. Finally, for the reading of Iron, a wavelength of 248,3 nm was used. Subsequently, the calibration curves for the other elements to be measured were evaluated, observing linearity in the responses and high coefficients of determination (99 %). To check the reliability of the analysis in terms of precision and accuracy, control measures were applied, placing a duplicate every 10 samples, and every 25 samples a blank and an internal standard were analyzed.

3. RESULTS

The results of the concentration of metallic elements in the soil such as As, Cu, Zn, Pb, Cd and Fe in ppm are shown in Table 1. With these results obtained, the statistical treatment of the data was carried out.

Table 1. Average concentration in soils (mg/kg) of: As, Cu, Zn, Pb, Cd, Pb,and Fe.

X_{east}	Y_{north}	As_{soil}	Cu_{soil}	Zn_{soil}	Pb_{soil}	Cd_{soil}	Fe_{soil}
280860.1	9004513	1.38	53.78	126.39	52.73	2.39	57434.55
280868.2	9004531	2.38	62.63	149.47	53.85	2.33	61783.30
280832.8	9004531	1.50	50.10	117.37	62.24	1.81	44509.10
280836.2	9004550	1.89	59.62	129.34	44.70	1.90	49284.61
280791.5	9004547	1.65	68.79	156.26	51.91	2.15	55052.31
280800.8	9004568	1.96	77.55	151.29	56.26	2.32	66501.98
280764.3	9004553	1.57	65.74	134.23	45.38	1.59	49914.74
280771.1	9004585	1.67	63.75	135.68	52.23	2.50	60502.65
280785.7	9004521	1.99	73.17	143.58	79.87	1.96	55806.29
280758.5	9004532	1.76	92.61	161.93	64.67	2.13	68568.65
280774.0	9004503	2.17	75.59	138.20	88.30	1.66	54346.04
280752.7	9004509	1.75	76.28	141.63	192.79	1.72	62667.13
280725.6	9004507	1.77	75.61	135.81	324.00	2.17	63459.98
280699.6	9004522	1.63	71.55	127.57	high	1.95	61826.83
280723.1	9004537	1.85	88.34	171.54	85.98	2.19	76834.36
280727.6	9004560	2.15	85.34	152.77	301.03	1.95	67895.19
280714.6	9004563	2.01	72.01	163.93	55.82	2.26	77284.30

280692.4	9004550	1.54	57.94	157.26	63.04	2.02	74388.55
280703.9	9004587	1.75	48.16	143.24	62.45	1.83	62187.56
280711.6	9004474	1.52	67.10	117.04	high	1.47	53711.14
280689.1	9004491	2.96	68.28	126.84	64.84	2.26	47511.12
280661.9	9004502	1.75	65.51	127.14	65.85	2.35	46484.58
280691.7	9004457	1.83	85.77	115.90	197.83	2.32	74701.33
280722.4	9004444	1.64	85.32	121.54	223.78	2.38	74933.17
280748.5	9004428	1.62	85.56	129.25	379.42	2.74	63310.19
280774.5	9004406	1.70	77.35	130.92	154.75	2.67	58689.74
280676.4	9004433	2.56	46.18	111.03	51.66	4.49	62534.44
280703.7	9004413	1.71	50.36	114.47	60.90	2.01	51174.94
280732.1	9004399	1.27	64.21	124.45	142.83	2.55	55635.57
280761.7	9004384	1.39	61.54	109.85	90.82	2.09	67060.51
280848.0	9004498	1.98	59.76	66.30	28.14	2.43	35190.22
280836.0	9004503	2.20	52.07	82.45	38.34	2.25	47369.98
280823.0	9004510	2.30	32.17	66.73	36.88	2.28	45094.67
280807.0	9004518	2.96	35.55	73.67	31.57	2.77	57087.35
280828.0	9004483	2.52	58.41	62.05	41.48	3.36	71817.45
280803.0	9004500	3.93	41.27	61.24	36.56	2.54	50984.61
280820.0	9004473	3.51	82.92	93.67	47.54	3.66	85646.01
280795.0	9004490	3.04	60.37	83.12	49.84	2.67	67933.46
280822.0	9004451	1.95	60.44	73.73	40.46	2.81	73910.81
280811.0	9004457	1.98	77.49	78.81	80.57	3.67	85932.38
280801.0	9004461	2.07	69.91	75.11	116.79	3.15	76703.35
280782.0	9004468	1.99	66.83	72.04	135.48	2.89	69326.95
280773.0	9004474	1.96	56.83	62.60	129.99	2.49	60401.25
280760.0	9004478	1.97	50.84	70.57	190.01	1.62	61092.65
280789.0	9004429	2.06	51.63	89.03	69.76	2.53	67719.77
280781.0	9004437	2.16	55.11	79.73	39.72	2.03	65448.95
280767.0	9004448	2.13	51.62	70.90	134.14	2.18	64357.25
280759.0	9004455	2.03	52.79	63.50	211.04	2.54	70538.26
280749.0	9004464	1.83	57.15	76.00	234.83	2.53	69442.40
280737.0	9004474	1.83	65.89	83.81	232.77	2.24	71266.50

3.1. Statistics of Multielemental Analysis

The samples were subjected to univariate statistical analysis to determine the measures of central tendency, dispersion and asymmetry to understand the behavior of the data in the study area. The elements considered are As, Cu, Zn, Pb, Cd, Fe. To carry out the analysis, the R software [21] was used and following the basic criteria of [22,23,24], for the univariate exploratory analysis of the data. From the univariate analysis, for Arsenic (As) in Table 2, it has a minimum value of 1,27 mg/kg and a maximum of 3,93 mg/kg with a variation from the mean of 2,01 ± 0,52 mg/kg and from the median of 1,95 ± 0,31 mg/Kg.

Figure 2 shows the histogram, it shows us a distribution of values with a tendency towards the first quartile (1,70 mg/kg) where the data is concentrated, the boxplot shows us the existence of outlier values that are points of high concentration detected in the area of study, finally the density curve shows a concentration trend towards the 2,0 mg/kg value and small mounds to the right in the curve that represent the high values and outliers.

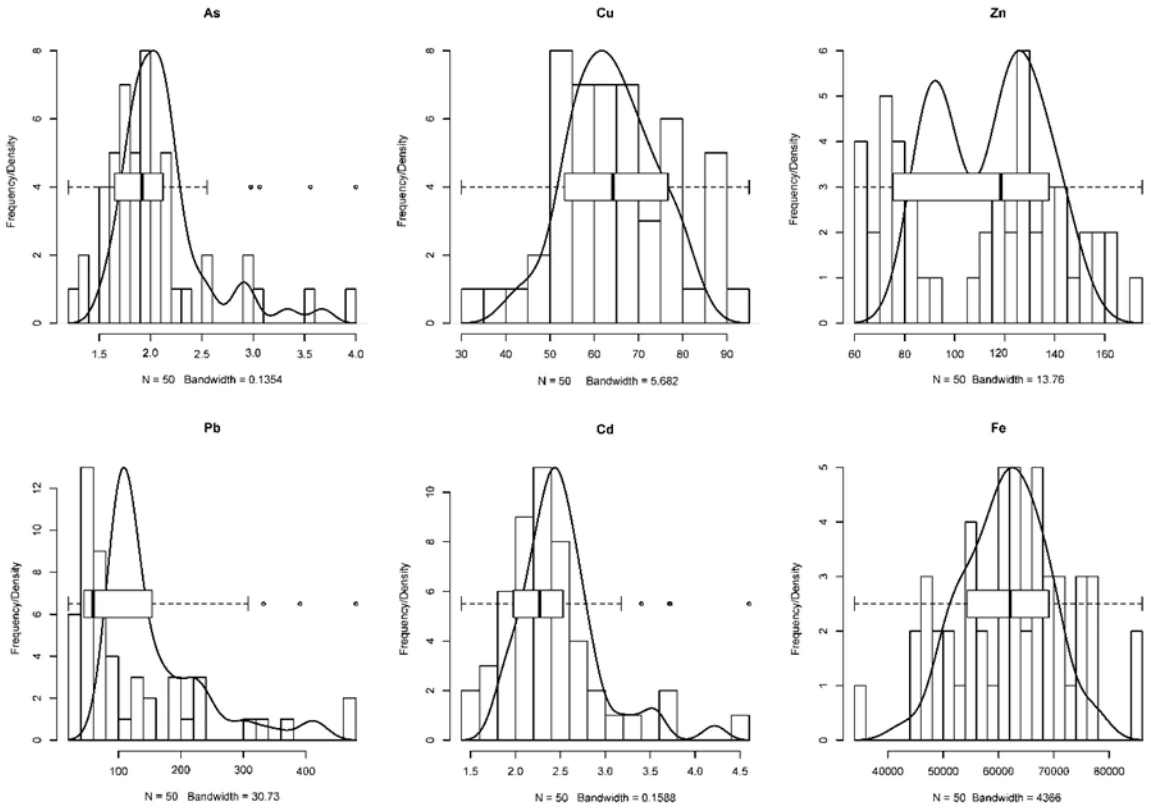

Figure 2. Histograms, boxplots and density curves

For Copper (Cu) in Table 2, it has a minimum value of 32,17 mg/kg and a maximum of 92,61 mg/kg with a variation from the mean of 64,27 ±13,81 mg/kg and from the median of 63,98 ±15,86 mg/kg. Figure 2 shows the histogram that presents us with a distribution of values with a centered trend although slightly inclined towards high values, the central 50 % of the data range from 54,11 mg/kg to 92,61 mg/kg, which indicates data centered with respect to the average, the boxplot shows an equal distribution of the concentration values obtained, finally the density curve shows a trend of data normality.

From the univariate analysis, for Zinc (Zn) in Table 2, it has a minimum value of 61,24 mg/kg and a maximum of 171,54 mg/kg with a variation from the mean of 111,02 ± 33,45 mg/kg and from the median of 117,20 ± 48,68 mg/kg. Figure 2 shows the histogram, it presents us with a distribution of values cut with a division value of 100 mg/kg where the data is divided, the boxplot gives us concentration of values between 80 and 140 mg/kg where approximately 50 % of the data is found, finally the density curve corroborates the bimodal trend of the information, detecting two concentration groups for Zn.

For Lead (Pb) in Table 2, it has a minimum value of 28,14 mg/kg and a maximum of 464,04 mg/kg with a variation from the mean of 120,29 ±109,05 mg/kg and the median of 65,34 ±37,33 mg/ kg. Figure 2 shows the histogram; it shows us a distribution of values with a tendency towards the first quartile (51,72 mg/kg) where the data is concentrated. The boxplot shows us the existence of outlier values that are points of high concentration detected in the area of study, finally the density curve shows a concentration trend towards the 100 mg/kg value and small mounds on the curve to the right that represent the high values and outliers.

For Cadmium (Cd) in Table 2, it has a minimum value of 1,47 mg/kg and a maximum of 4,49 mg/kg with a variation from the mean of 2,37 ±0,56 mg/kg and from the median of 2,29 ± 0,39 mg/kg. Figure 2 shows the histogram; it shows us a distribution of values with a tendency towards the first quartile (2,02 mg/kg) where the data is concentrated. The boxplot shows us the existence of outlier values that are points of high concentration detected in the area of study, finally the density curve shows a concentration trend towards the 2,4 mg/kg value and small mounds on the curve to the right that represent the high values and outliers.

For Iron (Fe) in Table 2, it has a minimum value of 35190,22 mg/kg and a maximum of 85932,38 mg/kg with a variation from the mean of 62465,18 ± 10908,10 mg/kg and the median of 62600,78 ± 10759,00 mg/kg. Figure 2 shows the histogram; it presents us with a distribution of values with a centered trend although slightly inclined towards high values. The central 50 \% of the data range from 55198,13 mg/kg to 64414,00 mg/kg, which indicates very centered data with respect to the average, however there are values that are very high and very low that two solitary bars are displayed, the boxplot shows an equitable distribution of the concentration values obtained, finally the density curve shows a trend of data normality.

Table 2. Univariate analysis of: As, Cu, Zn, Pb, Cd, Pb,and Fe.

Element	As_{soil}	Cu_{soil}	Zn_{soil}	Pb_{soil}	Cd_{soil}	Fe_{soil}
n	50	50	50	50	50	50
Min	1.272	32.170	61.240	28.140	1.474	35190.22
LL	1.041	22.805	-11.907	-98.346	1.247	33875.011
Q1	1.702	54.113	76.703	51.724	2.022	55198.125
Median	1.952	63.984	117.204	65.348	2.297	62600.783
Mean	2.014	64.276	111.02	120.298	2.376	62465.182
Trimmed Med	1.990	64.354	110.796	115.057	2.351	62544.51
Q3	2.143	74.984	135.776	151.771	2.539	69413.535
Max	3.930	92.613	171.538	464.04	4.491	85932.375
UL	2.364	85.42	165.312	201.794	2.798	76521.24
IQR	0.441	20.872	59.073	100.047	0.517	14215.41
MAD	0.312	15.862	48.676	37.335	0.386	10758.993
Sd	0.520	13.805	33.427	109.049	0.562	10908.103
As	1.668	-0.023	-0.042	1.678	1.387	-0.107
k	3.097	-0.522	-1.413	2.175	2.826	-0.375
CV	25.823	21.478	30.109	90.648	23.672	17.463
QSL	50	None	None	70	1.4	None
S-UQSL	0	0	0	23	50	No Limit

The values of positive asymmetry (As) from highest to lowest are Pb, As and Cd having a distribution with a tendency to high values, while Cu, Zn and Fe have a tendency towards 0, indicating a symmetrical distribution. Regarding kurtosis (k), the positive values range from 3,10, 2,83 and 2,18 for As, Cd and Pb, and present leptokurtic curves, while the values of –0,522 and 0,375 for Cu and Pb respectively indicate mesokurtic (normal tendency). In the case of Zn, its value is –1,41 platicurtic, indicating a difference with respect to the others due to its bimodality. Regarding the coefficient of variation (CV), Lead is considered a variable with a heterogeneous distribution because it has a 90,65 % coefficient of variation, however, the other variables have a value of less than 31 %.

Finally, there are the Quality Standard Limit (QSL) statistics for As, Cd and Pb with values of 50, 70 and 1,4 mg/kg according to Peruvian standards, of which 23 and 50 points for Pb and Cd are exceeded, called S-Upper Quality Standard Limit (S-UQSL) statistic. Additionally, the study carried out by [25], was considered, where the limits with a threshold value of 100 mg/kg for Cu and 200 mg/kg for Zn are considered as referential values for metals in the study of agricultural soils that can affect both the ecosystem and human health. These threshold values of the European Union are not exceeded by any of the values of the samples analyzed in the study area of Huacaybamba.

3.2. Quality Standards of Soil

The quality standard for agricultural soils in Peru is determined by MINAM [26]. In this part, the points that exceed the value of the environmental quality standard were identified. Below that value, it is considered that there are no problems in the metal concentration values in soils from the information collected in the field for purposes of agricultural use.

Among the elements studied, such as: As, Cu, Zn, Pb, Cd and Fe, there are only values established by [26] for As, Pb and Cd with limits of 50, 70 and 1,4 mg/kg in soil. Then from Table 2, it is observed that no point is above the quality standards. In Figure 3, for the concentration of Lead in soil, 23 points in the study area exceed the environmental quality standard for soils, while for Cadmium, all the points analyzed (50) exceed the environmental quality standard for soils, as can be seen in Figure 4.

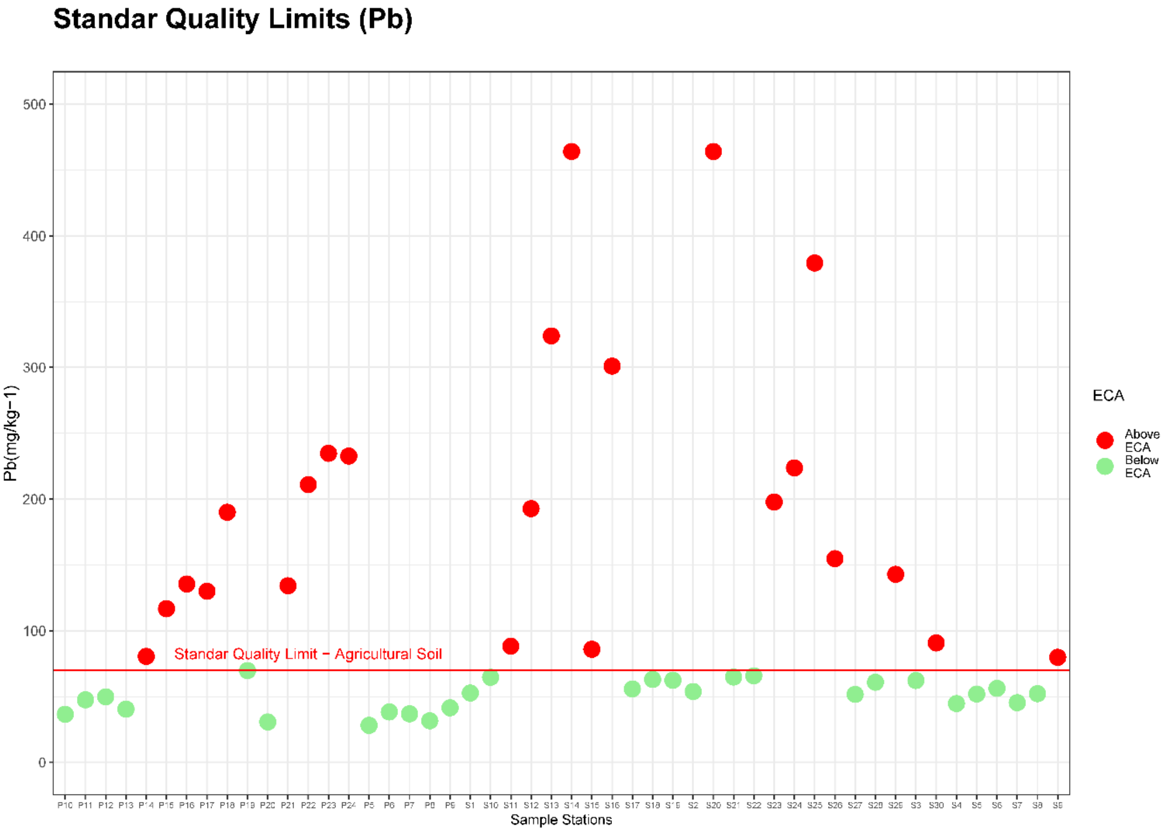

Figure 3. Points above quality standard of Pb

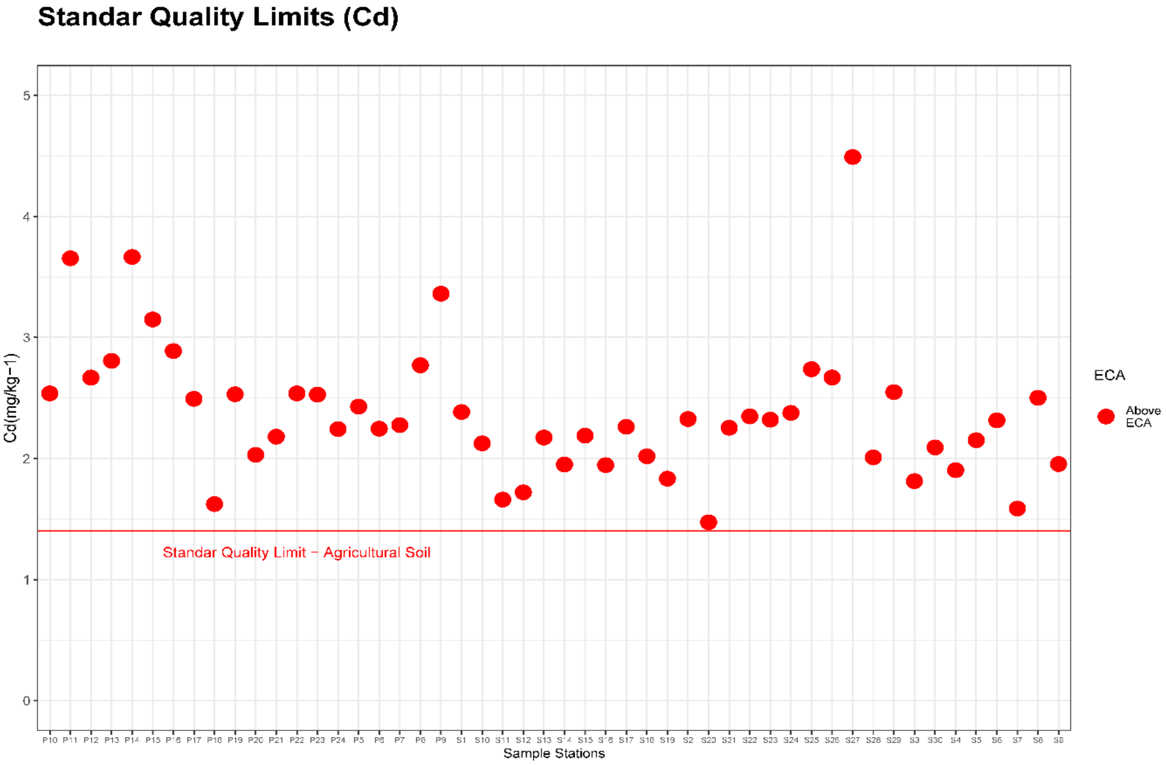

Figure 4. Points above quality standard of Cd

In the case of the elements Zn and Cu, we will use the standards established by the European community whose thresholds are 100, 200 mg/kg. All the values obtained in our study for these elements are below what was established according to [25].

3.3. Univariate Geostatistics

To complete the analysis carried out (non-spatial), the geostatistical analysis was carried out following the spline interpolation method [27,28]. Based on the measurements carried out in Huacaybamba, multi–elemental geochemical maps were made for the elements Pb, As, Cd, Zn, Cu and Fe, using the ArcGis software [29]. It should be noted that several methods are feasible for this area due to the high density (1/800 m2) of points collected for the analyzed area.

The geostatistical maps show data distribution patterns following different trends as shown in Figure 5. For lead, the high values (red area) are concentrated in the central–southern part of the study zone, considering an area of Pb accumulations in the study zone. For As, the behavior is associated with higher values towards the southeast of the study area where higher accumulations are observed. On the other hand, cadmium is relegated to the external south-west, south and south–east areas of the study zone, presenting a behavior contrary to Pb, where the area of spatial accumulation tends to minimum values of Cd. For Zn, presents accumulations in the north–west zone, which is the direction of the slope, because the zone's altitude decreases from southeast to northwest, that is, Zn accumulates at lower points following the topographic trend. For Cu, has a certain spatial relationship with Pb, however it has two concentration zones defined in the north-west central part and in the south–west central part. For Fe, has an irregular behavior that is not clearly defined. These trends give us the spatial univariate distribution of the metallic elements housed in the soil, and with them a guide to understand the most important accumulation zones in the study area.

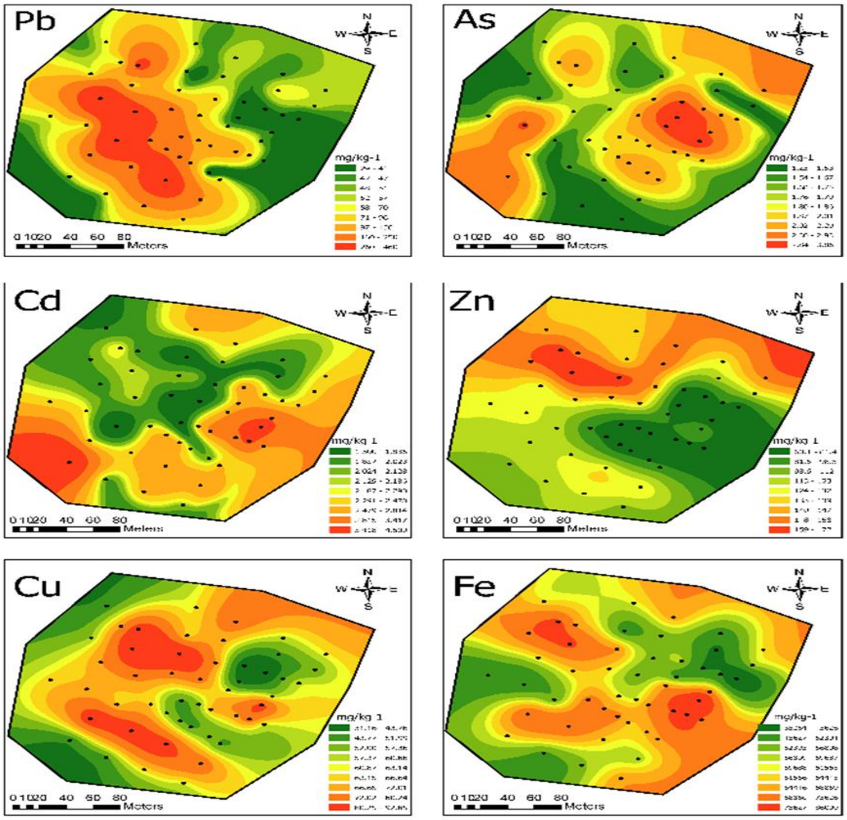

Figure 5. Univariant Geochemical Maps of Pb, As, Cd, Zn, Cu y Fe

3.4. Principal Component Analysis

Principal component analysis (PCA) allows us to understand the multivariable association of the elements [30]. PCA is used to find hidden patterns in the data of numerical variables, reduce their dimensionality by removing noise and redundancy, and identify correlated variables [31]. Due to the difference in scale in the concentration values of metallic elements in the soil, scaling (standardization) of the variables was planned to make them comparable. The first thing to analyze will be the eigenvalues obtained by applying the PCA algorithm. The variance explained by the first calculated eigenvalue is 37,45 % and the second is 27,08 %. These values will be taken for the analysis of the principal components, which represents 64,52 % of the total variance of the multi–element information, as observed in Figure 6.

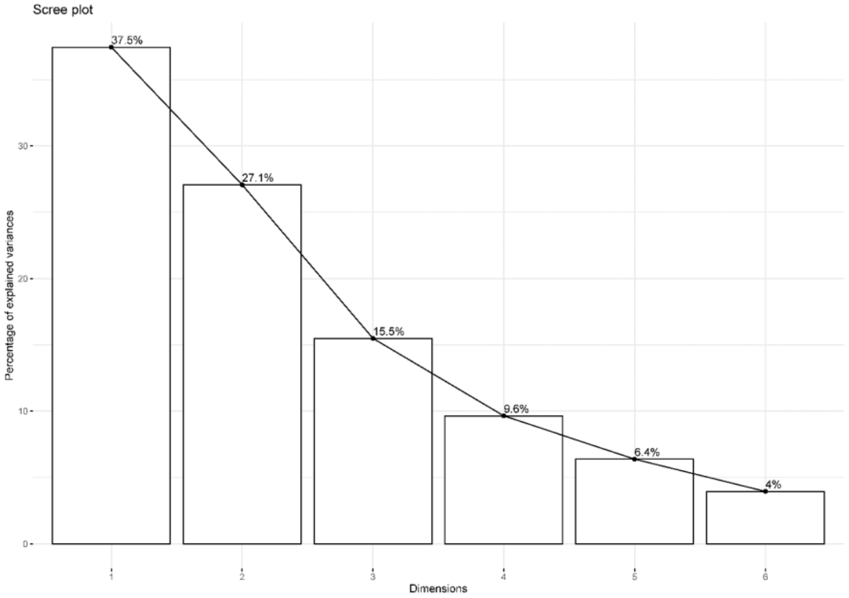

Figure 6. Percentage of explained variance by Dimensions.

The percentage of explained variance of the variables is measured with the representation quality of Cos2, with which it is determined that the variables Cu, Fe, Cd, Zn, As and Pb are well represented, as shown in Figure 7

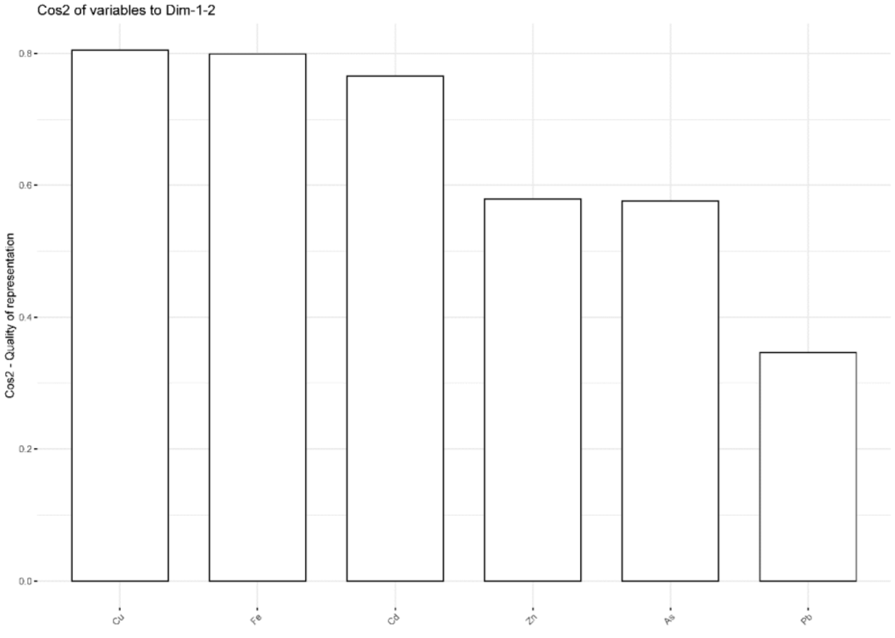

Figure 7. Representation quality of variables

This is complemented with the correlation plot, which indicates that the variables Cu, Pb and Zn are positively correlated (grouped). Zn and As are negatively correlated. Fe–Zn, Fe–As, Cu–Cd do not present a direct or indirect relationship, as shown in Figure 8.

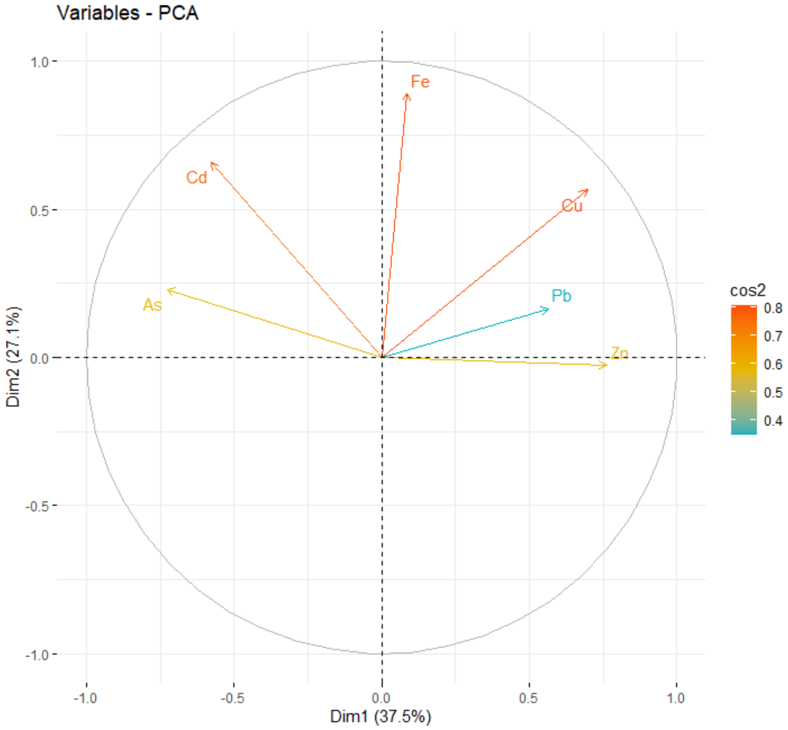

Figure 8. PCA – Biplot

To finish with the interpretation, we will use the biplot, which will use the address of the variable as the main part, but not its absolute position. Furthermore, it serves to consider that the individuals who are on the same side of a given variable have a high value for this variable, while the individuals on the opposite side have a low value for this variable. The PCA biplot for this case represents the associations that have the concentrations of metallic elements in which we consider all the variables. However, in the analysis only those considered representative for eigenvalues 1 and 2 should be taken, as shown in Figure 9.

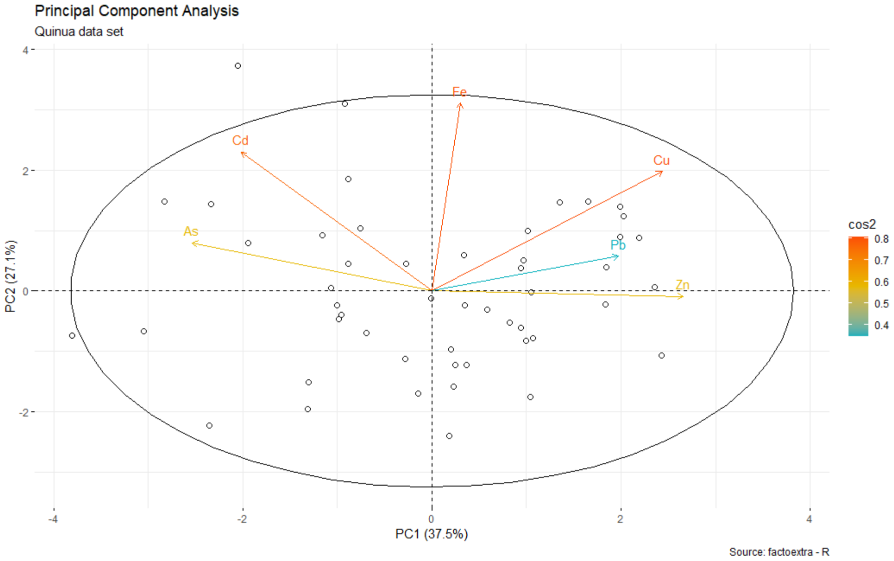

Figure 9. PCA - Biplot with points

4. DISCUSSION OF RESULTS

There are certain works that relate to Cd and Pb in soils. In the works of [32], they mention that potentially toxic elements (PTE) are not susceptible to biodegradation. They are persistent in the environment, and plants can absorb them from the soil and accumulate them in edible parts. Consequently, PTE can enter the food chain, creating a risk to human health.

According to [33], it mentions that Cd and Pb are not necessary for the normal metabolic functions of plants, and, therefore, both are considered non–essential elements. However, in doses higher than the standards, they can cause various health disorders.

In [34], it finds that the cocoa crops in the area where the study was carried out presented a high average concentration of Cadmium equal to 1,63 mg/kg. These data obtained confirmed that, in the case of soils, the average concentration is above the Environmental Quality Standards (ECA) established by MINAM, whose value is 1,4 mg/kg [26].

In [35,36], it indicates that quinoa has shown good tolerance and potential for metal stabilization in soils contaminated with a single metal. Then in [33], it mentions that the combined effects of Cd and Pb on the morphophysiological and metal absorption responses of quinoa have not been investigated until now. Then in their experiments, they analyze the combined effects of these metals on the growth and physiological characteristics of quinoa.

As can be seen, there are few works developed on the contamination of quinoa crops by PTE, based on this in the study area, the analysis of various potentially toxic elements in the Huacaybamba–Huánuco area was determined. For the determination of potentially toxic elements, we will use the standards established by MINAM [26] and the European Community [25]. In the case of As, Cu and Zn, according to the aforementioned standards, they are below the permissible limits, while in the case of Pb and Cd, these exceed the established standards, for which it can be concluded that the area presents contamination of Pb and Cd.

These studies obtained agree with [13] in the high–Andean area of study, who found that the prominence of these heavy metals is mainly of natural origin. In the regional studies carried out by INGEMMET, the geological context determines that it is related to mineral deposits with the presence of hydrothermal deposits and the presence of minerals of metallic value with an important content of lead and silver that are found within a radius of up to 23 km in the area, with sectors in which Gold occurs, with Arsenic being a guide for this type of deposits, that is, where Gold exists there is As. In addition, the area presents a greater exposure to mineralization events and erosion deposition of the upper units, which could have been enriched with the chemical elements studied in the work area.

Additionally, the values found determine that the accumulation of toxic metals presents a pattern not only dependent on the geochemical characteristics of the area but also dependent on the water sources and the slope of the land, as it is the case of Arsenic. These factors need to be analyzed for more surrounding areas in order to obtain a correct interpretation of the geospatial variation of these toxic metals in quinoa.

5. CONCLUSION

According to the analysis and study of the area, we expect the presence of the elements Pb, As, Cd, Zn, Cu and Fe. This was corroborated in our analyzes by determining the concentrations of these elements, so it can be said that the area presents a pollution of the natural type.

Regarding the regulations of our country, there are no standards for soils that present Zn and Cu, that is why in our study, we based ourselves on the European Union standard. In the case of Arsenic, Copper and Zinc, the soils are free of contamination from these elements because they do not exceed the contamination thresholds established by MINAM and the European Community.

In the case of Cadmium and Lead, the concentrations of soils studied present values that exceed the environmental quality standards established by MINAM [26] and also by the European Community [25]. Then it can be concluded that the area presents natural contamination of Cd and Pb in the soils, due to the presence of sphalerite (Zn, Cd)S as shown by the INGEMMET studies [18].

In the PCA analysis according to Figure 9, a positive correlation between Pb–Zn, and an inverse trend for As–Cd is found respectively. Cadmium and Zinc are closely related as chemical elements in the composition of sphalerite, a mineral that occurs as part of the aforementioned deposits, cadmium being an element that replaces zinc in the mineral, acting as a contaminant. These elements have a natural origin in the study area due to the type of mineralization that occurs close to the study area.

As future work, the mobility of PTE in the area should be analyzed in order to carry out soil remediation.

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REFERENCES

[1] Dwivedi, S., Mishra, A., & Saini, D. (2012). Removal of heavy metals in liquid media through fungi isolated from waste water. Int J Sci Res, 1(3), 181-185

[2] Pushkar, B. K., Sevak, P. I., & Singh, A. (2015). Isolation and characterization of potential microbe for bio-remediating heavy metal from Mithi river. Ann Appl Bio-Sciences, 2, 20-27.

[3] Muradoglu, F., Gundogdu, M., Ercisli, S., Encu, T., Balta, F., Jaafar, H. Z., & Zia-Ul-Haq, M. (2015). Cadmium toxicity affects chlorophyll a and b content, antioxidant enzyme activities and mineral nutrient accumulation in strawberry. Biological research, 48(1), 1-7.

[4] Chen, Z., Zhao, Y., Fan, L., Xing, L., & Yang, Y. (2015). Cadmium (Cd) localization in tissues of cotton (Gossypium hirsutum L.), and its phytoremediation potential for Cd-contaminated soils. Bulletin of environmental contamination and toxicology, 95, 784-789.

[5] Khan, I., Ghani, A., Rehman, A. U., Awan, S. A., Noreen, A., & Khalid, I. (2016). Comparative analysis of heavy metal profile of Brassica campestris (L.) and Raphanus sativus (L.) irrigated with municipal waste water of sargodha city. J Clin Toxicol, 6(307), 2161-0495.

[6] Ogunlade, M. O., & Agbeniyi, S. O. (2011). Impact of pesticides use on heavy metals pollution in cocoa soils of Cross-River State, Nigeria. African Journal of Agricultural Research, 6(16), 3725-3728.

[7] Sun, W. H., Jiang, Y. X., & Li, X. (2013). Research of the evaluation on heavy-metal pollution in rice by sewage irrigation. In Applied Mechanics and Materials (Vol. 295, pp. 1594-1599). Trans Tech Publications Ltd.

[8] Atafar, Z., Mesdaghinia, A., Nouri, J., Homaee, M., Yunesian, M., Ahmadimoghaddam, M., & Mahvi, A. H. (2010). Effect of fertilizer application on soil heavy metal concentration. Environmental monitoring and assessment, 160, 83-89.

[9] Dixit, R., Malaviya, D., Pandiyan, K., Singh, U. B., Sahu, A., Shukla, R., ... & Paul, D. (2015). Bioremediation of heavy metals from soil and aquatic environment: an overview of principles and criteria of fundamental processes. Sustainability, 7(2), 2189-2212.

[10] Pourret, O., & Hursthouse, A. (2019). It’s time to replace the term “heavy metals” with “potentially toxic elements” when reporting environmental research. International journal of environmental research and public health, 16(22), 4446.

[11] Radovanovic, V., Djekic, I., & Zarkovic, B. (2020). Characteristics of cadmium and lead accumulation and transfer by Chenopodium quinoa Will. Sustainability, 12(9), 3789.

[12] Jacobsen, S. E. (2003). The worldwide potential for quinoa (Chenopodium quinoa Willd.). Food reviews international, 19(1-2), 167-177.

[13] Tapia, J., Murray, J., Ormachea, M., Tirado, N., & Nordstrom, D. K. (2019). Origin, distribution, and geochemistry of arsenic in the Altiplano-Puna plateau of Argentina, Bolivia, Chile, and Perú. Science of the Total Environment, 678, 309-325.

[14] Pizarro, I., Gómez-Gómez, M., León, J., Román, D., & Palacios, M. A. (2016). Bioaccessibility and arsenic speciation in carrots, beets and quinoa from a contaminated area of Chile. Science of the Total Environment, 565, 557-563.

[15] Cancino-Espinoza, E., Vázquez-Rowe, I., & Quispe, I. (2018). Organic quinoa (Chenopodium quinoa L.) production in Peru: Environmental hotspots and food security considerations using Life Cycle Assessment. Science of the Total Environment, 637, 221-232.

[16] Román-Ochoa, Y., Delgado, G. T. C., Tejada, T. R., Yucra, H. R., Durand, A. E., & Hamaker, B. R. (2021). Heavy metal contamination and health risk assessment in grains and grain-based processed food in Arequipa region of Peru. Chemosphere, 274, 129792.

[17] Prospeccion Geoquimica regional de sedimentos. https://repositorio.ingemmet.gob.pe/handle/20.500.12544/219 accessed Jan 3, 2023

[18] INGEMMET. (Marzo de 2006). INVENTARIO DE LOS RECURSOS MINERALES DE LA REGIÓN HUÁNUCO. Obtenido de, Reterived From: https://repositorio.ingemmet.gob.pe/bitstream/20.500.12544/2442/1/Ingemmet-Inventario_recursos_minerales_Huánuco.pdf

[19] MINAM. Available online: http://www.minam.gob.pe/calidadambiental/wp-content/uploads/sites/22/ 2013/10/GUIA-PARA-EL-MUESTREO-DE-SUELOS-final.pdf (accessed on 3 February 2020).

[20] USEPA, U. (1996). Method 3050B: acid digestion of sediments, sludges, and soils. Test methods for evaluating solid wastes: physical/chemical methods. EPA SW-846, 1, 3050B-1.

[21] R Software. Available online: https://www.r-project.org/, accessed Jan 3, 2023

[22] Tukey, J. W. (1962). The future of data analysis. The annals of mathematical statistics, 33(1), 1-67.

[23] Morgenthaler, S. (2009). Exploratory data analysis. Wiley Interdisciplinary Reviews: Computational Statistics, 1(1), 33-44.

[24] Härdle, W. K., Simar, L., Härdle, W. K., & Simar, L. (2015). Canonical correlation analysis. Applied multivariate statistical analysis, 443-454.

[25] Tóth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. J. E. I. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. Environment international, 88, 299-309.

[26] Decreto Supremo 002-2013 MINAM. Available online: https://fonamperu.org.pe/un-fondo-ambientalpara-el-peru/download/decreto-supremo-n-002-2013-minam/ (accessed on 3 February 2023).

[27] Awanou, G., Lai, M. J., & Wenston, P. (2005). The multivariate spline method for scattered data fitting and numerical solutions of partial differential equations. Wavelets and splines: Athens, 24-74.

[28] Huang, H. C., & Chen, C. S. (2007). Optimal geostatistical model selection. Journal of the American Statistical Association, 102(479), 1009-1024.

[29] ArcGIS Pro, Software. Available online: https://www.esri.com/es-es/arcgis/products/arcgis-pro/overview (accessed on 30 June 2022).

[30] Härdle, W. K., Klinke, S., & Rönz, B. (2015). Introduction to statistics: using interactive MM* Stat elements. Springer.

[31] Kassambara, A. (2017). Practical guide to cluster analysis in R: Unsupervised machine learning (Vol. 1). Sthda.

[32] Gall, J. E., Boyd, R. S., & Rajakaruna, N. (2015). Transfer of heavy metals through terrestrial food webs: a review. Environmental monitoring and assessment, 187, 1-21.

[33] Bamagoos, A. A., Alharby, H. F., & Abbas, G. (2022). Differential uptake and translocation of cadmium and lead by Quinoa: A multivariate comparison of physiological and oxidative stress responses. Toxics, 10(2), 68.

[34] Rosales-Huamani, J. A., Breña-Ore, J. L., Sespedes-Varkarsel, S., Huamanchumo de la Cuba, L., Centeno-Rojas, L., Otiniano-Zavala, A., ... & Castillo-Sequera, J. L. (2020). Study to determine levels of cadmium in cocoa crops applied to inland areas of Peru:“The case of the Campo Verde-Honoria Tournavista corridor”. Agronomy, 10(10), 1576.

[35] Elarab, M., Ticlavilca, A. M., Torres-Rua, A. F., Maslova, I., & McKee, M. (2015). Estimating chlorophyll with thermal and broadband multispectral high resolution imagery from an unmanned aerial system using relevance vector machines for precision agriculture. International Journal of Applied Earth Observation and Geoinformation, 43, 32-42.

[36] Iftikhar, A., Abbas, G., Saqib, M., Shabbir, A., Amjad, M., Shahid, M., ... & Qaisrani, S. A. (2022). Salinity modulates lead (Pb) tolerance and phytoremediation potential of quinoa: A multivariate comparison of physiological and biochemical attributes. Environmental Geochemistry and Health, 44(1), 257-272.

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