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Assessment of the variation of heavy metals and pesticide residues in native and modern potato (*Solanum tuberosum* L.) cultivars grown at different altitudes in a typical mining region in Peru

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A R T I C L E   I N F O

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A B S T R A C T

This research paper presents the preliminary outcomes of an investigation conducted on the levels of heavy metals (such as As, Cd, Pb, Al, Mn, Cu, Ba, Cr, and Ni) and pesticide residues found in both traditional and modern potato cultivars grown in Moquegua, one of the principal copper-producing departments of Peru. A total of 160 samples of potatoes and soil were collected at altitudes between 58 and 3934 m above sea level (m.a.s.l.), and measured by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES), respectively. Determinations of pesticide residues were conducted by using the QuEChERS method. Metal concentrations in potato samples varied from 0.006 to 0.215 mg/kg for Pb; 0.01–0.25 mg/kg for As; 0.001–0.048 mg/kg for Cd; 0.4–47.9 mg/kg for Al; 0.008–0.802 mg/kg for Cr; 0.505–2.729 mg/kg for Cu; 0.022–29.894 mg/kg for Mn; 0.03–2.76 mg/kg for Ba; to 0.006–0.419 mg/kg for Ni. Among the principal findings of the study were that (i) potatoes grown at lower altitude (Chala and Yunga regions) accumulated more As, Cr, Ni and Al than those grown at higher altitudes (Suni region); (ii) modern potatoes in most cases show a higher concentration of metals than native ones; (iii) the principal positive correlation found between soil and potatoes was for As; (iv) 90% of the samples analyzed were free from pesticide residues.

1. Introduction

In areas where farming and mining coexist, controversies concerning food safety are commonplace. On the one hand, mining is a man-made source of contamination of farm land and irrigation water by heavy metals that can be absorbed by crops [1]. Consequently, it is possible that food produced in mining areas could accumulate worrying levels of toxic metals [2–4]. On the other hand, farming is also a source of man-made pollution by heavy metals, due among others factors to excessive use of agrochemicals [1,5] and organic fertilizers [6].

For that reason, the determination of levels of heavy metals and pesticides in soil, ground water and crops remains a subject of interest, both for mitigating transfer into the food chain and for achieving sustainable agriculture. Human exposure to these pollutants can cause adverse health consequences [5,7–9], which can be exacerbated by the interaction between the two, causing combined toxicity of the soil and plants [1,10,11].

Very few studies have addressed the presence of chemical pollutants in agricultural areas of South America influenced by mining. This is especially true in regions with major copper ore deposits and significant unexploited potential, such as Peru, the world́s second largest producer of copper [12]. Because future global copper demand is expected to grow, as are the environmental impacts [13,14], issues threatening food safety and agricultural production around areas close to mining sites need to be addressed.

In such a context, this is the first investigation to analyze heavy metals and pesticide residues in one of Peru's principal copper-producing department: Moquegua. We focused our analysis on potato (*Solanum tuberosum* L.) because of its importance in the local diet, whose consumption of potatoes per capita amounts to 92 kg/year, and also

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because there is a precedent for the contribution of potato to dietary intakes of heavy metals of population living near a gold mine in the Peruvian Andes [4]. Since potato is considered a crop of the future and a vital element in global food security [15], it is essential to understand how heavy metal accumulation is influenced by land use patterns.

Knowing the level of heavy metals in potatoes grown in Moquegua is especially interesting because, although it is the second smallest department in Peru, farming is carried on from sea level up to at least 4000 m. Thus, farms can be found in four agroecological zones or natural regions, using the geographic guidelines for land use described by Javier Pulgar Vidal [16] and agroecological zoning regulations [17]: (i) Chala (0 – 500 m.a.s.l.), (ii) Yunga (500 – 2300 m.a.s.l.), (iii) Quechua (2300 – 3500 m.a.s.l.) and (iv) Suni (3500 – 4000 m.a.s.l.). Each region has its own particular characteristics regarding land use, farming practices and -principally- crops and their varieties [18].

The potato is a versatile crop that adapts to different conditions from sea level up to the Andean highlands [19]. Indeed, it is reported to be able to adapt to soils contaminated by heavy metals [20] and that its ability to absorb them is less than that of leafy vegetables [21–23]. Nevertheless, the absorption level varies from one place to another, as it depends on various factors such as metal concentration in the soil, soil pH and altitude [24].

This investigation therefore has more than one aim. The first is to evaluate whether the concentration of heavy metals in potatoes varies with the altitude at which they are grown. The second is whether the cultivar influences the accumulation of heavy metals. The third is whether there is a relationship between heavy metal concentration and the soil in which they are grown. The fourth is whether there is a difference in heavy metal concentration between potatoes grown in different agricultural zones. That is why the metals analyzed are the same as used in studies of areas impacted affected by mining [22,25,26]: arsenic (As), cadmium (Cd), lead (Pb), aluminum (Al), manganese (Mn), copper (Cu), barium (Ba), chromium (Cr) and nickel (Ni). The final aim of the study is to determine concentrations of pesticide residues in potatoes.

Peruvian regulation establishes maximum limits for 72 pesticide residues in potatoes [27], but it does not set regulatory limits for heavy metals in foods. Currently, the permissible limits established by FAO/WHO [28] and the European Union [29] are considered. Specifically for potatoes, limit values for Cd and Pb are provided at 0.1 mg/kg. However, since there are no reference values available for other heavy metals, the results of this study can be utilized by policymakers for addressing regulatory references.

2. Materials and methods

2.1. Description of the study area

The department of Moquegua is in southern Peru, between 15°17′ and 17°23′ latitude south; it covers 1.2% of Peruvian territory (15,733.97 km^2). Moquegua includes coastal and highland zones with altitudes that vary from sea level up to more than 6000 m [30]. The region holds important ore bodies and contains the largest reserves of copper in Peru.

In 2021 the potato was the most important crop grown in the department after the avocado, with 7101.24 t harvested from 581 ha [31]. Peru's Ministry of Agriculture and Irrigation classifies potato varieties according to their origin, as modern (improved or hybrid) and native (commercial and non-commercial) [32]. Native potatoes have a late vegetative growth, whilst modern potatoes have an early or intermediate vegetative growth.

As explained by De Haan et al. (2010) [33], one characteristic that distinguishes native varieties from modern ones is that the former are of superior quality from a culinary point of view because they contain more dry material, and are usually only boiled for direct consumption. Improved cultivars are the product of formal improvement programs combining native Andean potatoes with modern European or North American varieties and certain wild varieties. In general, they give a high yield and are resistant to disease.

The distribution of samples by variety (native and modern) is shown in Table 1.

In Peru, agroecological regions are classified on the basis of altitude [16–18], as shown in Table 1, for the samples collected between 58 and 3934 m.a.s.l. Due to variations in potato land use across different agroecological regions, the sampling sites are not evenly distributed. Potato growing (such as the choice of genotype and farming practices) depends on the specific agroecological conditions in the growing area [19].

In the Chala agroecological region, the area given over to potato growing is minimal because the traditional crop is olives. In the period 2015–2018 there were between 1 and 4 ha growing potatoes, but from 2019 this area was reduced to a few rows in all, for own consumption. In this region and in Yunga, it is difficult to grow native varieties due to their late growing season, which makes them vulnerable to damage by pests and diseases influenced by the climate. That is why modern varieties predominate. Potato is the main staple crop in the Quechua and Suni regions, where it is common to find both varieties being grown together [34], although native varieties dominate, especially above 3000 m.a.s.l.

2.2. Potato tubers and soil sampling

Fig. 1 shows the sample points grouped in nine agricultural zones, taking into account geographic proximity and local farm zoning. The locations making up each zone are shown in Table S1. The map also distinguishes between agroecological regions by altitude: Chala (0–500 m.a.s.l.), Yunga (500–2300 m.a.s.l.), Quechua (2300–3500 m.a.s.l.) and Suni (3500–4000 m.a.s.l). No potato crops were found above 4000 m.a.s.l., where the landscape consists of volcanoes and snow-capped mountains. In total, 160 potato samples (fully mature) with their respective soils, were collected at altitudes between 58 and 3934 m.a.s.l.

Samples were collected during the 2021 growing season. Potato fields were chosen for convenience, with participation by local farmers and technicians from the Moquegua Regional Agricultural Department (DRA-Moquegua). Field sizes varied from 10 m^2 to 1000 m^2. Potato plants were selected at random from each field, to obtain the most representative sample possible of the land in question. Potato samples were removed with approximately 100 g of the soil in which the plant was growing. Soil samples were taken at random from the upper horizon (0–25 cm) and materials such as stone fragments, thick roots, organic residue and insects removed. Both the potato and soil samples were mixed to obtain compound samples of 1 kg (one sample for heavy metals analysis and another for pesticide residue analysis). The samples were placed in airtight polyethylene bags, which were labelled and taken to the laboratory.

2.3. Analytical procedure

2.3.1. Heavy metals in potato tubers and in soil used for potato cultivation

The samples were analyzed for the following heavy metals: As, Cd, Pb, Al, Mn, Cu, Ba, Cr, and Ni. The edible portion of the potato samples was used, including the skin and pulp, because both are usually eaten in the local area. Metals were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using the EPA 200.3/EPA 6010B method (validated in 2016) [35,36]. In addition, during the preliminary stage As, Cd and Pb in 14 samples were analyzed using method NOM-117-SSA1–1994 [37]. Heavy metals in the soil samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), using the EPA 3050 B method, Rev. 2 / EPA 6010 D Rev. 5 [38,39]. In order for the results to be officially valid, the chemical analyses were carried out in a laboratory accredited by the Instituto Nacional de Calidad del Peru - INACAL (Peru's National Quality

Table 1
Agroecological regions where potatoes are grown in the department of Moquegua.

Agroecological region	Altitude at which samples were collected (m.a.s.l)	Climate[b]	District	Number of samples	Potato variety	
					Native	Modern
Chala[a]	58–191	Cool, humid, scarce precipitation, seasonal sun.	El Algarrobal	3	0	3
Yunga[a]	1030–2275	Hot, dry, scarce seasonal precipitation.	Moquegua, Samegua, Torata, La Capilla, Coalaque.	34	2	32
Quechua	2322–3494	Temperate, moderate diurnal temperature variation, seasonal precipitation.	Puquina, Matalaque, Ubinas, Coalaque, La Capilla, Lloque. Chojata, San Cristóbal, Cuchumbaya, Carumas, Torata.	77	25	52
Suni	3516–3934	Cold, dry, strong diurnal temperature variation, seasonal precipitation.	Ubinas, Ichuña, Lloque, Yunga, Chojata, Carumas, Cuchumbaya, San Cristóbal.	46	34	12
Total samples				160		

[a] The Chala and Yunga agroecological regions are analyzed together in this study because of the sample size.
[b] Descriptions of weather and characteristics for each region can be seen in Zimmerer and Bell (2013) [18].

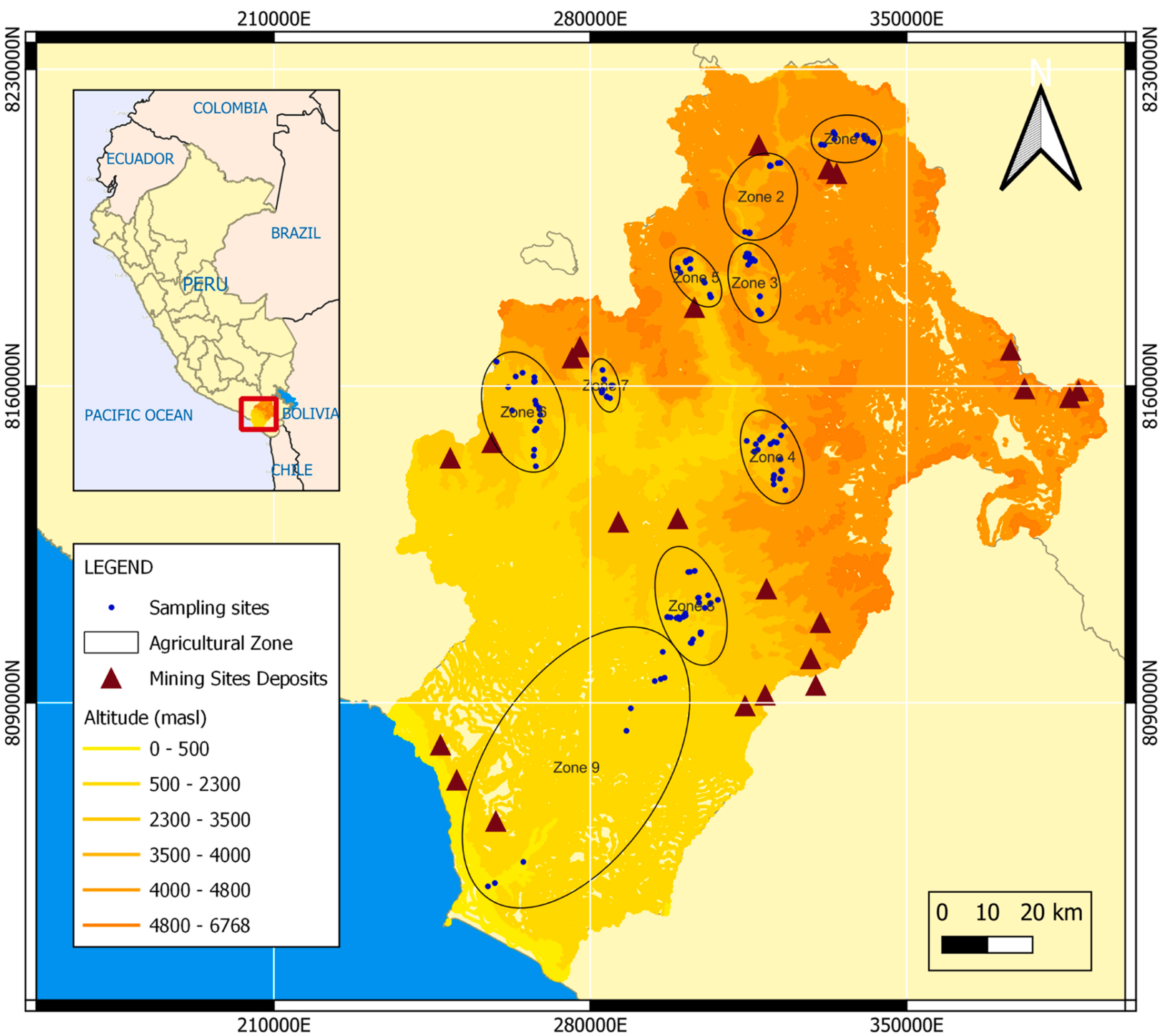

Fig. 1. Location map of study area, Moquegua department, Peru. The map shows the sampling points grouped in nine agricultural zones. The locations making up each zone are shown in Table S1.

Institution) in accordance with Peruvian Technical Standard NTP-ISO/IEC 17025. The limits of detection and quantification of measured elements in potato and soil samples are presented in Table S2.

2.3.2. Soil pH and electrical conductivity

Electrical conductivity (EC), total dissolved solids (TDS) and pH of the soil samples were measured using Hanna multiparameter meter (model HI991300, USA). The determinations were done in 1:2 dried soil / distilled water mixtures using 20 g of sieved soil sample in 40 ml of distilled water. The suspension of water and soil particles was stirred for 30 min, then allowed to settle for 2 h after which the pH and electrical conductivity of the supernatant were measured.

2.3.3. Determination of pesticides residues

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was used for the extraction of pesticide residues from potato samples. Pesticide residues were extracted from a homogenized sample using the EN QuEChERS procedure, with acetonitrile, magnesium sulfate and citrate salts. The extract was analyzed by liquid chromatography with MS/MS detection (LCMS/MS) and gas chromatography with MS/MS detection (GC-MS/MS). The procedure was developed based on EN-15662:2008 Foods of plant origin – Determination of Pesticide Residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE –QuEChERS method. The calibrated range of the method was 0.005–0.2 μg/ml which equates 0.005–0.2 mg/kg in the sample (0.01–0.4 mg/kg in dry and rehydrated samples). Samples containing a higher concentration than 0.2 mg/kg (0.4 mg/kg in dry and rehydrated samples) required dilution. The reporting limit was 0.01 mg/kg for all compounds. A total of 606 active ingredients were screened.

Both skin and pulp were analyzed. The chemical analyses were carried out in a laboratory accredited by the Instituto Nacional de Calidad del Peru - INACAL in accordance with Peruvian Technical Standard NTP-ISO/IEC 17025.

2.3.4. Regulation limits

Pesticide residues were compared using the Peruvian standard establishing the maximum residue levels (MRL) for farm pesticides used on potato crops [27]. As Peru has no specific standard for heavy metals in foodstuffs, heavy metals found in the potato samples were compared with limit and critical values according to FAO/WHO (2019) [28] and the MERCOSUR Technical Regulation on maximum limits for inorganic pollutants in food [40]. Soil comparisons used the Environmental Quality Standards (ECA) for agricultural soils in Peru [41].

2.3.5. Data processing and statistical analysis

The data consist of a collection of information related to heavy metal concentrations in potatoes and soil at different altitudes, classified as Chala & Yunga, Quechua, and Suni, and potato varieties (modern and native). To investigate the influence of altitude and variety on the concentration of heavy metals in potatoes, the strategy is to conduct an ANOVA analysis to determine the required influences as differences in mean responses.

Due to methodological limitations, concentrations smaller than a certain threshold could not be detected and were registered as "$< \chi$" where the value for χ depends on the sampled metal. This implies that the data from certain variables is left censored, requiring specialized techniques to perform the intended analysis.

Typically, for uncensored data, the first step of an ANOVA analysis is applying a normality test to determine whether the responses can be considered normally distributed. Upon applying Shapiro-Francia's normality test [42], none of the variables were considered normally distributed. To overcome this limitation, we used the non-parametric Kruskal-Wallis test for comparison among two or more groups and Mann-Whitney's test to determine which differences are significant. All tests in this section were conducted at a 5% confidence level.

For censored data, we used a similar approach but with specialized tools. We tested whether there was a significant difference in the logarithm of the means of the metal concentrations by assuming that the censored observations are lognormally distributed and two-by-two comparisons (where necessary) were made using Tukey's contrasts. We applied Shapiro-Francia's normality test to each variable's residual logarithm to determine whether the censored observations are lognormally distributed. To perform the tests, we employed packages NADA [43] and NADA2 [44], which have functions that perform ANOVA and t-test-like routines for censored data.

To summarize, for each variable, if the data is censured, we first apply a Shapiro-Francia normality test in the residuals. If the null hypothesis is not rejected, then we proceed by testing whether the log concentrations present the same mean, by using maximum likelihood estimators based on the log-normal distribution and Tukey's contrasts. If the null hypothesis is rejected, then we apply the Kruskal-Wallis test to determine whether there are differences in the distribution and if that's the case, we apply Mann-Whitney's test to determine which pairs differ.

The Pearson's correlation was used to analyze the correlation between the content of heavy metals in the potatoes and soil, soil pH, TDS and EC. All statistical analyses were conducted using the free software R version 4.21.

3. Results

3.1. Comparison between altitude and heavy metal accumulation in native and modern potatoes

Tables S3 and S4 show the heavy metals content of potato tubers and soil, respectively. In this section we present a comparison between the concentration of metals in potatoes stratified by altitude and variety. There are two main cases: metals for which there were no censured observations, but the Shapiro-Francia's test rejected the null hypothesis, and the case where the data presented censored observations, but normally distributed residuals. The results are presented in Table 2, where different letters in the same column indicate significant differences between groups ($p < 0.05$).

Comparing concentration of metals by altitude, significant differences were found for Al, Ba, As, Cd, Cr, Mn, and Ni ($p < 0.05$). No differences were observed for Cu and Pb. The Chala & Yunga altitude was found to have among the highest concentrations in all cases, Quechua was among the highest for Al and Ni and Suni was among the highest for Ba, Cd, and Mn. Among potato varieties, significant differences were found for Al, As, Cd, Cr, and Mn, in all cases ($p < 0.05$). We also found that modern potatoes in most cases present higher metal concentrations than native ones. Comparing metal concentrations in potatoes by altitude or among potato varieties, no differences were observed for Pb and Cu ($p < 0.05$).

3.2. Correlation between the concentrations of heavy metals in soil and potato tubers

In this section we present a correlation analysis relative to the concentration of metals in the potatoes and in the soil and also pH, TDS and EC. The correlation matrix is depicted in Fig. 2.

From the matrix, we observe that there is a strong positive correlation between some metals in the soil, especially between Ni and Cr (0.73), Al and Mn (0.57) and Al and Ba (0.54), so the higher the concentration of one of these metals, the higher the concentration of the other. There is also a positive correlation between As found in the soil and in the potatoes (0.55). Also interesting to note is that there is no negative correlation with an absolute value greater than -0.32. Regarding variable EC, this correlates highly (0.71) with the concentration of Cr in potatoes. pH doesn't seem to affect substantially any other variable. As expected, we observe an almost perfect positive correlation between EC and TDS (0.99), as the magnitudes of these

Table 2
Comparison among heavy metals grouped by altitude and variety.

Factors	Levels	Heavy metal concentration in potato samples (mg/kg)								
		Al[a]	**Ba**[a]	**Cu**[a]	**Mn**[a]	**Pb**[a]	**As**[b]	**Cd**[b]	**Cr**[b]	**Ni**[b]
Altitude	Chala & Yunga	14.504^{a}	0.833^{a}	1.338^{a}	3.012^{a}	0.037^{a}	0.065^{a}	0.008^{a}	0.067^{a}	0.043^{a}
	Quechua	4.096^{a}	0.336^{b}	1.466^{a}	1.302^{b}	0.044^{a}	0.037^{b}	0.007^{b}	0.015^{b}	0.044^{a}
	Suni	3.657^{b}	0.418^{a}	1.408^{a}	10.179^{a}	0.038^{a}	0.012^{c}	0.011^{a}	0.010^{c}	0.043^{b}
Variety	Modern	7.261^{a}	0.542^{a}	1.391^{a}	2.902^{b}	0.036^{a}	0.050^{a}	0.007^{a}	0.032^{a}	0.044^{a}
	Native	4.012^{b}	0.335^{a}	1.469^{a}	7.891^{a}	0.049^{a}	0.014^{b}	0.010^{b}	0.011^{b}	0.043^{a}

Different letters in the same column indicate significant differences between groups, $p < 0.05$.
[a] Comparison among metals not normally distributed grouped by altitude and variety.
[b] Comparison among metals presenting censored observations and normally distributed residuals, grouped by altitude and variety.

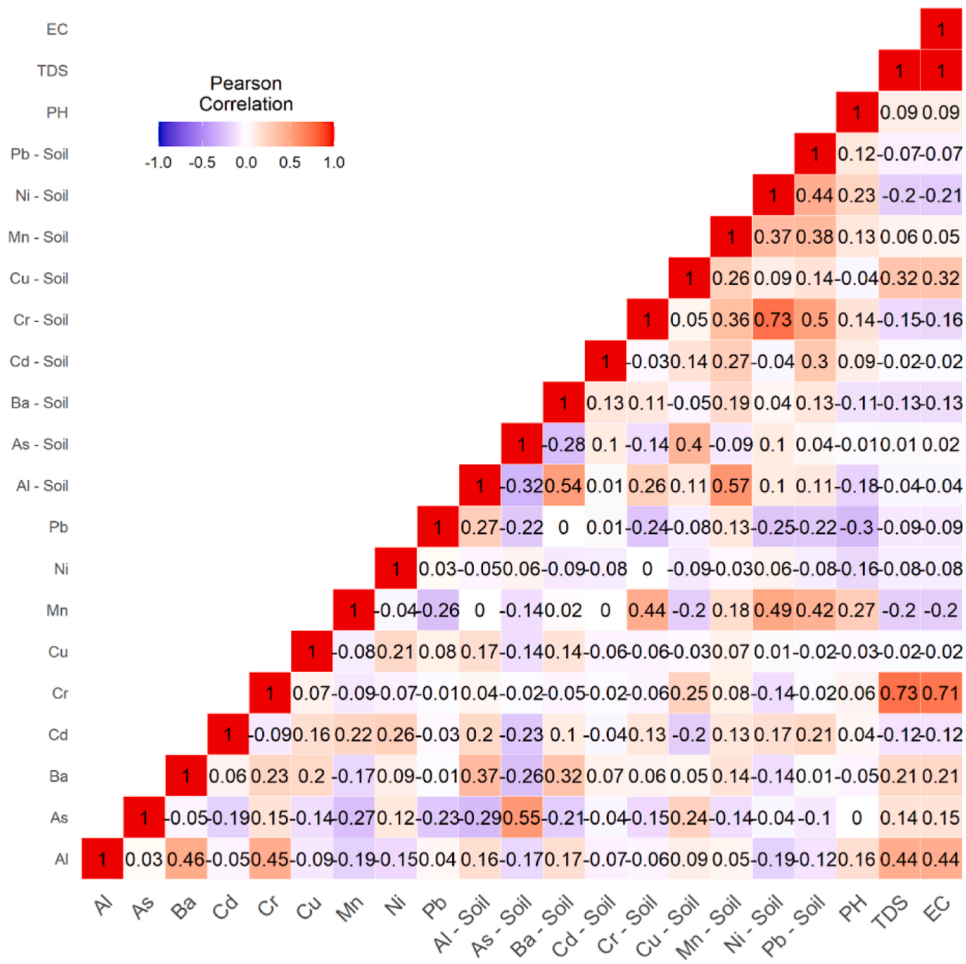

Fig. 2. Pearson correlation between the heavy metal content in potatoes and soil parameters.

parameters are directly proportional.

3.3. *Comparison of heavy metals content in potatoes grown in different agricultural zones*

Fig. 3 shows the spatial distribution of heavy metals in potatoes and soils in the study area. For further details, Tables S3 and S4 give descriptive statistics for the concentration of heavy metals in potatoes and soil, respectively.

Heavy metal concentrations in soils and the order in which they are found vary from one place to another because the heavy metal content of the soil depends on a wide range of factors relating to lithogenic and anthropogenic sources [45]. For example, in mining areas in Weining County in China, the soil in which potatoes are grown contains the heavy metals considered in our study, concentrated in the following order: Cr (119 mg/kg) > Pb (59.3 mg/kg) > Ni (50.8 mg/kg) > Cu (47.8 mg/kg) > As (25.8 mg/kg) [24] > Cd (2.60 mg/kg) [46]. In our study, as can be seen from Table S4, the concentration order of heavy metals in the potato-growing soil was Al (13,127.84 mg/kg) > Mn (509.248 mg/kg) > Ba (187 mg/kg) > Cu (51.38 mg/kg) > As (23.607 mg/kg) > Pb (16.861 mg/kg) > Ni (10.199 mg/kg) > Cr (9.798 mg/kg) > Cd (0.352 mg/kg).

Table S3 shows that the potatoes grown in these soils accumulated heavy metals in the following ranges: 0.4–47.9 mg/kg for Al; 0.01–0.25 mg/kg for As; 0.03–2.76 mg/kg for Ba; 0.001–0.048 mg/kg for Cd; 0.008–0.802 mg/kg for Cr; 0.505–2.729 mg/kg for Cu; 0.022–29.894 mg/kg for Mn; 0.006–0.419 mg/kg for Ni; and 0.006–0.215 mg/kg for Pb.

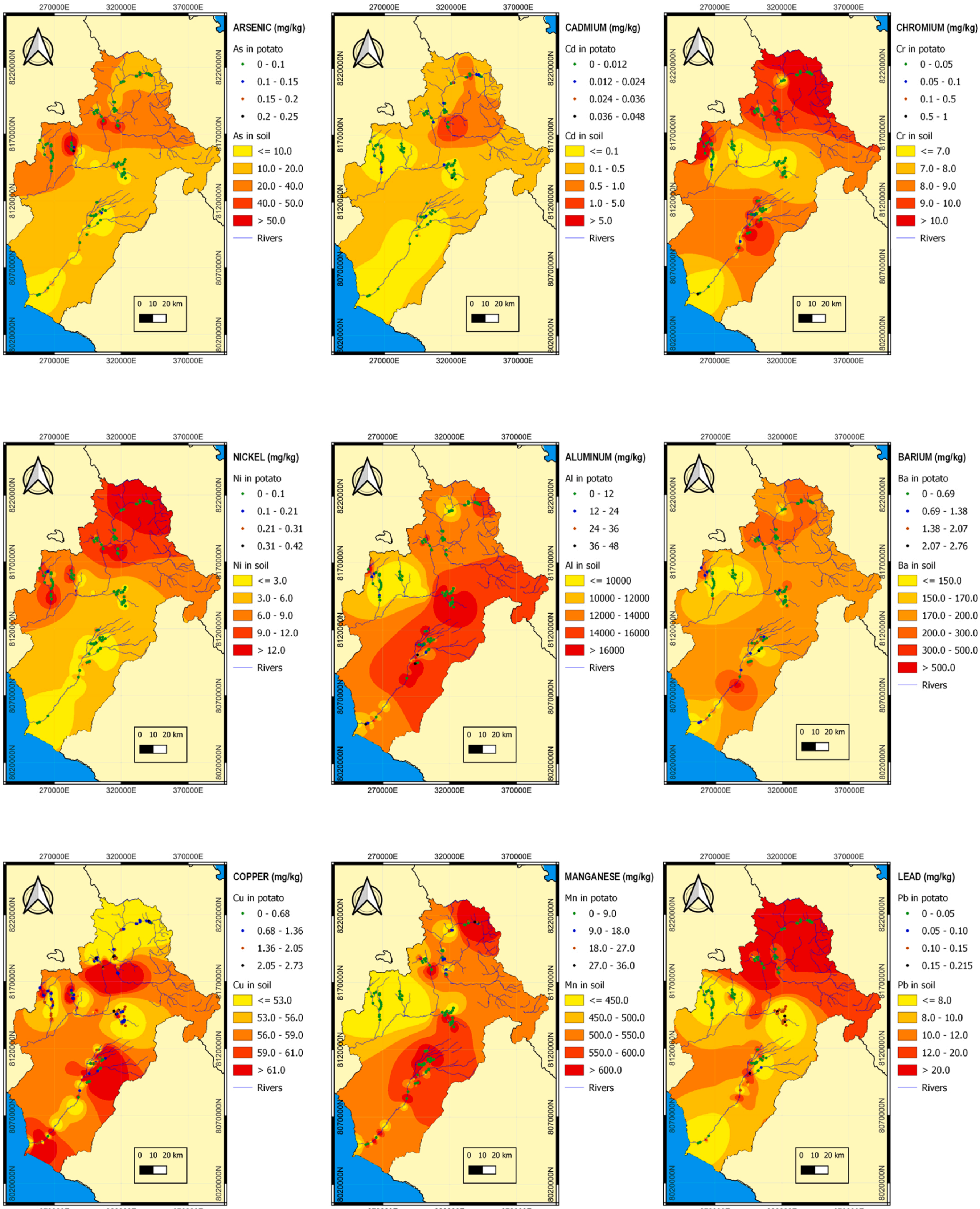

Fig. 3. Maps of heavy metals distribution in Moquegua department. The base map was generated with QGIS (3.28 Firenze version), a free and open-source Geographic Information System (https:// www. qgis. org/).

Mean comparison tests were performed to analyze the concentration of each of the metals in the nine agricultural zones studied (Fig. 1), made up of the places detailed in Table S1. The results are shown in Table 3, with information on the average of each metal per zone and whether this average was considered statistically different from the other zones ($p < 0.05$), by using letters to indicate grouping.

Although it is not possible to conclude that there is a zone with a higher concentration of each of the metals, it can be seen that zones 1 and 2 had higher concentrations of Cd, while zones 8 and 9 had higher concentrations of As, and Cr. Zones 1, 2, and 3 can be considered the most homogeneous since for almost all metals, except Cd and Ni, the metal concentrations in these zones cannot be considered statistically different. Zone 9 stands out as having the lowest concentration of Ni.

For variables without censoring or for which the normality of the residuals was rejected, results are presented in Table 4.

We can see that zones 9, 8, 6 and 5 (in this order) present the highest concentrations of Al and zone 7 the lowest concentrations of Ba while zones 4 and 7 have the lowest concentrations of Al. No significant differences were found between the concentration of Cu in the agricultural zones studied. Zone 4 presented the highest concentration of Pb, twice as high as in zone 9. Despite this difference, it was not considered statistically different ($p < 0.05$) from the concentration of Pb in the properties in zone 9. Regarding Mn, there is a difference of magnitude in the concentrations observed in zones 1, 2 and 3 compared to the others, although the concentration of Mn presented by zone 2 is not statistically different from that presented by zones 5 and 6.

3.4. Pesticide residues in potato tubers

Pesticide residues in potato samples from the nine agricultural zones are given in Table 5. These values are for analytes that exceeded the quantification limit (0.01 mg/kg).

In 10% of the samples analyzed, pesticide residues were quantified in the following order of incidence, according to the altitude at which they were grown: 15% in Chala & Yunga (lower altitude), 10% in Quechua (intermediate altitude) and 7% in Suni (higher altitude). Chlorpyrifos was the most commonly found analyte, but in no case did it exceed the MRL contained in Peruvian standards (less than 2.00 mg/kg) [27]. Concentrations of Permethrin, Cypermethrin and Metalaxyl and metalaxyl-M were lower than the MRL contained in Peruvian standards (less than 0.05 mg/kg), as was Tebuconazole (less than 0.02 mg/kg) [27].

Table 3
Comparison among heavy metals presenting censored observations and normally distributed residuals, grouped by agricultural zones.

Agricultural zone[a]	Heavy metal concentration in potato samples (mg/kg)			
	As	Cd	Cr	Ni
	mean	mean	mean	mean
Zone 1	0.010^{acd}	0.011^{ab}	0.009^{c}	0.039^{ac}
Zone 2	0.010^{acd}	0.016^{a}	0.011^{bc}	0.062^{ab}
Zone 3	0.011^{d}	0.008^{bc}	0.012^{c}	0.034^{bc}
Zone 4	0.011^{d}	0.008^{bc}	0.011^{c}	0.045^{ac}
Zone 5	0.027^{cd}	0.009^{ac}	0.015^{ac}	0.034^{bc}
Zone 6	0.022^{c}	0.007^{bc}	0.016^{bc}	0.038^{ac}
Zone 7	0.111^{a}	0.004^{c}	0.021^{ab}	0.063^{a}
Zone 8	0.072^{ab}	0.009^{c}	0.047^{a}	0.058^{c}
Zone 9	0.055^{bc}	0.007^{c}	0.161^{a}	0.009^{d}

[a] The locations making up each agricultural zone are shown in Table S1. Different letters in the same column indicate significant differences between groups, $p < 0.05$.

Table 4
Comparison among heavy metals grouped by agricultural zones.

Agricultural zone[a]	Heavy metal concentration in potato samples (mg/kg)				
	Al	Ba	Cu	Mn	Pb
Zone 1	2.794^{bde}	0.458^{ab}	1.264^{a}	15.145^{a}	0.016^{ce}
Zone 2	2.778^{bcdf}	0.342^{ab}	1.408^{a}	12.638^{ab}	0.018^{be}
Zone 3	2.485^{ef}	0.207^{b}	1.521^{a}	10.502^{a}	0.016^{de}
Zone 4	0.871^{g}	0.297^{b}	1.534^{a}	1.479^{c}	0.135^{a}
Zone 5	8.380^{ad}	0.389^{ab}	1.604^{a}	1.465^{bc}	0.023^{b}
Zone 6	8.596^{ac}	0.474^{ab}	1.366^{a}	1.598^{bc}	0.022^{bd}
Zone 7	1.814^{efg}	0.070^{c}	1.222^{a}	1.086^{c}	0.009^{e}
Zone 8	10.869^{ab}	1.350^{a}	1.572^{a}	1.217^{c}	0.033^{b}
Zone 9	30.800^{a}	0.693^{ab}	0.970^{a}	1.195^{c}	0.065^{abc}

[a] The locations making up each agricultural zone are shown in Table S1. Different letters in the same column indicate significant differences between groups, $p < 0.05$.

4. Discussion

4.1. Comparison between altitude and heavy metal accumulation in native and modern potatoes

Few studies include altitude as a factor in the analysis of heavy metal content in potatoes, and even fewer in mining areas. In an area of abundant ore deposits in Weining County, China, altitude was found not to have a significant influence ($p < 0.05$) on the Pb, Cr, Ni and As concentrations in potatoes grown between 2151 and 2744 m.a.s.l., but lower altitudes favored the accumulation of Cd and Cu [24,46].

Our study covered a greater altitude range, from 58 to 3934 m.a.s.l., and shows that altitude has a significant influence ($p < 0.05$) on the accumulation of As, Cd, Al, Mn, Ba, Cr, and Ni in potatoes, but not Cu or Pb. Potatoes grown at higher altitude (Suni agroecological region) accumulate less As, Cr, Ni and Al than potatoes grown at lower altitude (Chala & Yunga agroecological region).

In Suni, the concentration of heavy metals in potatoes was as follows: Mn (10.179 mg/kg) > Al (3.657 mg/kg) > Cu (1.469 mg/kg) > Ba (0.418 mg/kg) > Pb (0.049 mg/kg) > Ni (0.043 mg/kg) > As (0.012 mg/kg) > Cd (0.011 mg/kg) > Cr (0.010 mg/kg). This is a different order to that found in Chala & Yunga: Al (14.504 mg/kg) > Mn (3.012 mg/kg) > Cu (1.338 mg/kg) > Ba (0.833 mg/kg) > Cr (0.067 mg/kg) > As (0.065 mg/kg) > Ni (0.043 mg/kg) > Pb (0.037 mg/kg) > Cd (0.008 mg/kg).

As far as the variety of potato was concerned, we also found that in the majority of cases the modern variety accumulated more heavy metals than the native variety. Statistically ($p < 0.05$), the modern variety accumulated more As, Cr, and Al, while the native variety accumulated more Cd and Mn. Various studies have shown that the capacity of plants to absorb and accumulate metals can vary considerably between cultivars of the same species. In the potato, differences in Cd levels were found from one cultivar to another and also from one part to another of the same plant. For example, some cultivars accumulate less Cd in the tuber but more in the stem and leaves [47]. Other plants have also shown differences in the accumulation of heavy metals between different cultivars; for example rice [48], sunflower [49] and quinoa [50].

The highest and statistically equal ($p < 0.05$) concentrations of Cd are found in the Suni region (higher altitude) and Chala & Yunga region (lower altitude), averaging 0.011 and 0.008 mg/kg, respectively. The cause may be the repeated use of agro-chemicals in Chala & Yunga and organic fertilizer in Suni, as other studies have shown that both products favor the accumulation of Cd in potatoes [6,51].

Table 1 shows that the two regions have totally different climates. The Chala & Yunga region, where modern potato varieties predominate, is characterized by a climate favorable to pests and therefore pesticides must be used on a regular basis. On the other hand, the Suni region, where most potatoes grown are native varieties, the climate is cold and

Table 5
Pesticide residues in potato tubers.

Potato sample[a]	Analyte	Concentration (mg/kg)	Variety	District	Altitude (m.a.s.l.)	Location by agricultural zone
1	Chlorpyrifos	0.0340**	Native	Ichuña	3842	Zone 1
	Tebuconazole	0.0110				
2	Cypermethrin	0.0200**	Modern	Ichuña	3825	Zone 1
3	Sum of carbofuran & 3-OH carbofuran	0.0020**	Native	Chojata	3608	Zone 3
4	Piperonyl Butoxide	0.2700**	Native	Chojata	3494	Zone 3
5	Metalaxyl and metalaxyl-M	0.0110	Native	San Cristóbal	3144	Zone 4
6	Metalaxyl and metalaxyl-M	0.0100	Modern	San Cristóbal	3144	Zone 4
7	Chlorpyrifos	0.2100**	Native	Ubinas	3414	Zone 5
8	Sum of carbofuran & 3-OH carbofuran	0.0010**	Modern	Puquina	3350	Zone 6
9	Chlorpyrifos	0.0280	Modern	Puquina	3061	Zone 6
10	Chlorpyrifos	0.0200	Modern	Torata	2605	Zone 8
11	Permethrin	0.0130**	Modern	Samegua	1777	Zone 8
12	Chlorpyrifos	0.0100**	Modern	Samegua	1759	Zone 8
	Permethrin	0.0160**				
13	Chlorpyrifos	0.0110**	Modern	El Algarrobal	91	Zone 9
	Permethrin	0.0110**				
14	Chlorpyrifos	0.0100**	Modern	El Algarrobal	58	Zone 9
	Permethrin	0.0160**				

** Above international MRLs.
[a] Samples containing pesticide residues above the quantification limit (0.01 mg/kg), equivalent to 10% of the samples analyzed (n = 144).

dry and agroecological soil management practices are frequently used. One of these is the use of animal manure. It is worth noting that 92% of the native potatoes were collected above 3000 m.a.s.l.

Nevertheless, as explained in Section 4.3, although the native varieties accumulated more Cd than the modern varieties (0.010 mg/kg and 0.007 mg/kg, respectively) ($p < 0.05$), it did not exceed the MRL. This is important because native varieties are preferred by those living in the high Andes [33]. In areas between 3800 and 4200 m.a.s.l. in the department of Junín, Peru, the Cd concentration found in native potatoes was almost four times higher (0.042 mg/kg) [52].

As with Cd, the highest concentration of Mn was found in the Suni region (higher altitude), and the native varieties also accumulated more Mn than modern varieties (7.891 and 2.902 mg/kg, respectively) ($p < 0.05$). As the average concentration deriving from vegetable sources is estimated to vary between 0.42 and 6.64 mg/kg [53], it is possible that the high concentrations of Mn are the result of an excess of Mn in irrigation water, a condition that has been reported in various parts of this region [54].

4.2. Correlation between the concentrations of heavy metals in soil and potato tubers

Correlation coefficients show the limited absorption of most heavy metals by potatoes from the soil and that the pH does not appear to have a substantial effect on any other variable. This may be because the majority of land used to grow potatoes are alkaline (pH no more than 8.717). Only 28% of soils were at all acidic (pH not less than 5.067). Various studies have shown that pH is one of the factors that affect heavy metal absorption by plants. It is known that a reduction in pH leads to an increase in mobility of heavy metals and, therefore, greater accumulation in plants [55,56]. Even so, this depends on the soil type, use of fertilizers, changes in sources of contamination and other factors [57,58].

Other studies show similar results, without finding any correlation between Cu, Pb, Cr, Ni, As [24], Cd [59] in the soil or in the potatoes. Nevertheless, our study emphasizes that there is a positive correlation between As found in the soil and in the potatoes (0.55), which suggests that this metal is absorbed from the soil by the potatoes. The strong positive correlation between Ni and Cr (0.73) and Pb (0.44) is not unusual, given that synergistic interactions have been identified by NiPb and NiCr in agricultural soils [60].

EC, which is a very important parameter for estimating soil salinity, varies between 0.075 and 4.297 dS/M. Salinity increases the mobility of heavy metals [61], but our study did not find such a relationship because 94% of the soil used for potato growing is free from salts (EC less than 1 dS/M), according to soil classification by salinity [62]. In contrast, in areas where soil salinity was significant (EC of up to 4.297 dS/m), potato samples were found to contain higher concentrations of Cr, Al and Ba (for example in El Algarrobal, Moquegua, Samegua and Torata). This explains why there is only a positive correlation between the EC and these metals (coefficients of 0.71, 0.44 and 0.21, respectively). In the following section we analyze the content of each heavy metal individually.

4.3. Comparison of heavy metals content in potatoes grown in different agricultural zones

4.3.1. Arsenic content

As discussed in Section 4.1, altitude influenced the As concentration of potatoes ($p < 0.05$), which was higher at lower altitude. The lowest agroecological region (Chala & Yunga) contains agricultural zones 7 (district of Coalaque) and 8 (districts of Torata and Samegua), where the highest concentrations of As in potatoes were found (0.111 and 0.072 mg/kg, respectively). In these zones 28% of land used to grow potatoes exceeded the maximum levels of As permitted by Peruvian standards (50 mg/kg), but this figure rises to 81% if Ecuadorian or Canadian standards are used (12 mg/kg).

In these zones modern potato varieties predominate, which absorb more As than the native potatoes ($p < 0.05$). As there a positive correlation between As found in the soil and in the potatoes (0.55), our study suggests that it is important to evaluate the farm land in these zones and other crops as well, although it is believed that As poisoning caused by plants is very rare [25].

Nevertheless, the As concentrations in potatoes in all the agricultural zones were lower than the MRL, though they were greater than the As range found in potatoes from other countries (0.01–0.02 mg/kg) [25]. Similar results were found in the Andean highland zones of Junín, Peru (at altitudes from 3000 to 4200 m.a.s.l.), where the average As content of native potatoes was 0.1556 mg/kg [52].

4.3.2. Cadmium content

The highest agroecological region (Suni) contains agricultural zones 1 and 2, in which potatoes with the highest Cd concentrations were found (0.011 and 0.016 mg/kg, respectively). In these zones, the Cd concentrations in the soils used to grow potatoes are within acceptable limits (less than 1.4 mg/kg). Indeed 95% of soil samples taken for this study have Cd concentrations lower than 0.3 mg/kg (quantification limit) and are alkaline to a certain degree (values up to 8.72). Therefore, our results are similar to the findings of Mench (1998) [63], who reported that the highest Cd concentration in tubers was found in neutral or alkaline soils which had relatively low Cd concentrations.

Even so, all Cd concentrations in potato tubers were lower than the MRL (0.1 mg/kg), if not lower than the Cd range found in potatoes from various other countries (0.016–0.3 mg/kg) [25]. Other studies in areas influenced by mining activity in Slovakia [56,64], Kosovo [59] and China [24] also report Cd concentrations in potatoes that were lower than the MRL, even when grown in soils contaminated by Cd or other heavy metals. Similarly, in areas influenced by mining activity in the central region of Peru it was found that there was very little bioaccumulated Cd in the living tissue of the Andean tuber maca *Lepidium meyenii* [65].

4.3.3. Lead content

Although none of the soil samples used for growing potatoes exceeded the MRL for Pb (70 mg/kg), agricultural zones 4 and 9 produced the highest concentrations of Pb in potatoes (0.135 and 0.065 mg/kg, respectively). Zone 4 in particular exceeded the MRL (0.1 mg/kg). In this zone, 83% of soil used to grow potatoes had Pb concentrations lower than 3 mg/kg (the quantification limit). It has therefore been suggested that other sources of contamination be evaluated, such as the water used for irrigation as it has been shown that watering vegetables with river water contaminated by Pb causes accumulations of this metal above the MRL [66].

Despite the fact that zone 4 (made up of the districts of Carumas, Cuchumbaya and San Cristóbal) provided the highest concentration of Pb, twice as high as the properties in zone 9 (the districts of Moquegua and El Algarrobal), it was not considered statistically different ($p < 0.05$). These zones use water from the Pasto Grande reservoir, which faces considerable challenges in improving the quality of its water in terms of heavy metal content [67]. Our results are lower than the Pb concentrations in potatoes grown in various countries (between 0.5 and 3.0 mg/kg) [25] and the average in areas influenced by mining activity (0.230 mg/kg) [64].

4.3.4. Chromium content

As we discuss in Section 4.1, altitude influences the concentration of Cr in potatoes ($p < 0.05$), which is higher in the lowest agroecological region (Chala & Yunga) and the intermediate region (Quechua). These regions made up of zones 9 and 8, where the highest concentrations of Cr in potatoes were found (0.161 and 0.047 mg/kg, respectively). These concentrations exceed the average reported by several countries (0.04 mg/kg) [25]. Nevertheless, the soils used for growing potatoes contained Cr concentrations within the permissible limits allowed by Canadian or Ecuadorian legislation (64 and 65 mg/kg, respectively). The greatest accumulation of Cr in potatoes from these zones could be caused by the influence of soil salinity on the mobility of heavy metals [61], as soils with an EC of up to 4.297 dS/m have been found. Although it is also important to take into account that the potatoes could be contaminated by Cr in the irrigation water, even when grown in unpolluted soil [68].

4.3.5. Nickel content

No soil sample used for growing potatoes exceeded the MRL for Ni contained in Canadian or Ecuadoran legislation (50 mg/kg). Neither was any relation found between Ni concentration in the soil and in potatoes, similar to the results of a study from China [24]. As with As, the highest concentration of Ni in potatoes (0.063 mg/kg) was found in agricultural zone 7 (district of Coalaque) but this figure was lower than Ni concentrations in potatoes grown in various countries (between 0.29 and 1.0 mg/kg) [25]. Other studies in areas contaminated by mining reported values of 0.055 mg/kg in China [24] and 0.243 mg/kg in Slovakia [56].

4.3.6. Copper content

Comparing concentration of metals in potatoes by altitude or variety no differences were observed for Cu ($p < 0.05$). Similarly, no significant differences were found between Cu concentrations in the agricultural zones studied ($p < 0.05$). This may be because there are copper deposits everywhere in the study area (Fig. 1). 20% of the soils used to grow potatoes exceed Ecuadorian or Canadian standards for Cu (63 mg/kg) and the Cu concentration in potatoes varies between 0.505 and 2.729 mg/kg. This range is below the average for various countries (4.4 mg/kg) [25].

Other studies have reported an absence of Cu in potatoes, in spite of the soil in which they grow being contaminated [59]. However, the excess Cu in the soil induces stress in the plants, delays their growth and causes chlorosis of the leaves [69]. The soils containing the highest concentrations of Cu (above 100 mg/kg) are found in different sectors of the districts of Moquegua, Chojata, Coalaque, Torata, Samegua, El Algarrobal, Matalaque and Cuchumbaya.

4.3.7. Aluminum content

Agricultural zones 9, 8, 6 and 5 contained the highest concentrations of Al in potatoes (30.8, 10.869, 8.596 and 8.38 mg/kg, respectively), but these figures are below the average reported for various countries (76 mg/kg) [25]. Al concentrations in the soils used for growing potatoes in these zones varied from 7335–2,4715 mg/kg (in zones 8 and 9) and 3961–2,9765 mg/kg (in zones 5 and 6). These values are above the level of contamination that can damage the plants and cause soil erosion in Hungary (18,221 mg/kg) [70]. The difference in the levels of Al concentration in zones 9 and 8 may be because in these zones contained all the saline soils encountered during the study (up to 4.297 dS/m), which is what increases heavy metal mobility [61].

Very little is known about the tolerance and physiological consequences of Al stress in *Solanaceae* plants [71], but we do know that the toxicity of Al is a factor that limits the productivity of the potato in acid soils [72]. This should be taken into account in soils with a pH lower than 6, which includes 8% of the soils used for potato cultivation (in sectors of the districts of San Cristobal, Carumas, Coalaque, La Capilla and Torata).

4.3.8. Manganese content

The highest concentration of Mn in potatoes (15.145, 12.638 and 10.502 mg/kg, respectively) were found in agricultural zones 1, 2 and 3. These zones are part of the highest agroecological region (Suni) and the intermediate region (Quechua). As there are other natural sources of dietary Mn, such as vegetables, cereals, animal products, water, etc., it is important to remember that the World Health Organization [73] calculates that an adequate daily intake of Mn varies between 0.003 mg/day (for infants from birth to 6 months) and 1.8 or 2.3 mg/day (for adult women and men respectively).

83% of soils used to grow potatoes in these zones are alkaline, and the Mn concentration in soils oscillates between 209.2 and 1025 mg/kg, respectively. Although Peruvian legislation does not establish levels for Mn, other studies carried out in areas affected by mining can be used as a baseline. Thus 57% of soils exceed the reference concentration used in Mexico (542 mg/kg) [74], which is similar to the Mn concentration found in mine tailings in India (578 mg/kg) [75]. In contrast, alkaline farm soils in Spain, though not contaminated, contain Mn concentrations between 124 and 483 mg/kg [76].

The results obtained coincide with local technical reports, which indicate that parts of agricultural zones 1 and 3 contain an excess of Mn in water used for irrigation [54]. It is important to note that Mn concentration tends to vary with the environmental conditions (temperature, season, humidity, etc.) [77] and that toxicity due to excess Mn can damage potato plant growth, especially when the pH level is low [78].

4.3.9. Barium content

The lowest agroecological region (Chala & Yunga) contains agricultural zones 8 (districts of Torata and Samegua) and 9 (districts of Moquegua and El Algarrobal), where the highest levels of Ba in potatoes were found (1.35 and 0.693 mg/kg), which were nevertheless lower than the average reported for several other countries (5 mg/kg) [25]. No soil sample used for growing potatoes exceeded the MRL for Ba contained in Peruvian legislation (750 mg/kg). But as for Al and Ba, the soils in these zones were alkaline (EC up to 4.297 dS/m), which favours heavy metal mobility [61].

4.4. Pesticide residues in potato tubers

Ninety percent of the samples analyzed were free from pesticide residues, leading to the conclusion that the majority of small potato farmers in Moquegua department do not use pesticides indiscriminately. Chlorpyrifos, Permethrin, sum of carbofuran & 3-OH carbofuran, Metalaxyl and metalaxyl-M, Cypermethrin, Piperonyl Butoxide, and Tebuconazole were the residues found one or more times out of a total of 18 observations.

Peruvian legislation has no MRL for Piperonyl Butoxide or for sum of carbofuran & 3-OH carbofuran. But they are higher compared to international MRL levels, which accept 0.25 mg/kg [79]–0.5 mg/kg [80] and 0.001 mg/kg [81], respectively. Although the other analytes do not exceed the MRL contained in Peruvian legislation, it is important to note that Chlorpyrifos [81] and Cypermethrin [80] do exceed the MRL used in international standards, which establish 0.01 mg/kg as the safe limit. Furthermore, Carbofuran and Permethrin are banned from use in agriculture by international conventions due to their high toxicity [82]. Based on international standards, therefore, 15 of the 18 observations in our study are outside the safe limits. Other studies have also reported the presence of Carbofuran (1.40 mg/kg) [83], Chlorpyrifos and Cypermethrin (up to 0.11 and 0.50 mg/kg, respectively) [84] in potatoes.

The results also show a lower incidence of pesticide residues in native potatoes and in those grown at higher altitude. This is an important finding, given that native varieties are preferred by the people of the high Andes, who keep their crops free from pests using little or no conventional pesticides. The climate is also a favorable factor: in these zones it is cold and dry, with a large temperature variation between day and night and seasonal rainfall (Table 1). In contrast a higher incidence of pesticide residues was found in modern varieties, which are grown mainly at lower altitude.

In this study the samples evaluated included potato skins, because they are usually eaten. It is therefore advisable to reduce pesticide residues in potatoes by techniques such as washing, peeling and boiling [85,86].

5. Conclusions

This study shows that altitude, between 58 and 3934 m.a.s.l. influences the accumulation of As, Cd, Al, Mn, Ba, Cr, and Ni in potato tubers ($p < 0.05$), but not Cu or Pb. Another important discovery is that there is a significant difference ($p < 0.05$) in heavy metal concentrations between modern and native potato varieties: the modern variety accumulates more As, Cr and Al, while the native variety accumulates more Cd and Mn. There is a notable positive correlation between As found in the soil and in the potatoes. There is also a notable positive correlation between EC and Cr, Al and Ba only, in potatoes, which may be associated with soil salinity in certain agricultural zones (EC up to 4.297 dS/m). As far as pesticides are concerned, seven residues were found in 10% of potato samples in a total of 18 observations, of which 15 exceeded the MRL contained in international standards but not those in Peruvian standards. Chlorpyrifos was the most commonly-found pesticide (between 0.01 and 0.21 mg/kg).

The results of this research will serve as a baseline for future investigations or monitoring of heavy metal levels in foodstuffs produced in the department of Moquegua, with a view to improving food safety and achieving sustainable local production of potatoes. Thus, the evaluation of Pb in agricultural zone 4 (consisting of the districts of Carumas, Cuchumbaya and San Cristóbal) stands out, because although the soils in which potatoes are grown do not exceed the levels permitted by Peruvian legislation, the potatoes themselves do exceed the MRL for Pb set by the Codex Alimentarius. The evaluations of As in agricultural zones 7 (District of Coalaque) and 8 (districts of Torata and Samegua) are also noteworthy, because although potato samples did not exceed the MRL, 28% of soil samples used to grow potatoes did exceed the levels permitted in Peruvian legislation and 81% according to international standards.

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CRediT authorship contribution statement

Noelia S. Bedoya-Perales: Funding acquisition, Writing – original draft preparation, Overall supervision. **Noelia S. Bedoya-Perales, Diogo Maus**: Conceptualization, Investigation. **Elias Escobedo-Pacheco, Diogo Maus**: Methodology. **Noelia S. Bedoya-Perales, Elias Escobedo-Pacheco**: Validation, Project administration. **Guilherme Pumi, Alisson Neimaier**: Formal analysis, Data curation, Software. **Diogo Maus, Alisson Neimaier, Guilherme Pumi:** Writing – review & editing. **Guilherme Pumi**: Supervision. **Elias Escobedo-Pacheco:** Visualization, Resources, Project administration. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.toxrep.2023.06.005.

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