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Patterns of accumulation and baseline values for metals in agricultural soils from a copper mining region in southern Peru

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A B S T R A C T

As global copper demand surges, it's vital to conduct a thorough analysis of metal concentrations in the agricultural soils of mining districts. This is especially pertinent for the Andean region, where, in the face of clear soil degradation, there's a notable lack of in-depth research. This study is the first attempt to characterize variations in the concentration of 17 metals in the agricultural soils of Moquegua – a region with a long history of mining activity that contributes significantly to Peru's position as the world's second-largest producer of copper. The surface horizons of 336 agricultural soils under vegetable crops were sampled between 9 and 3,934 m above sea level (m.a.s.l.) to determine the total content of metal nutrients (MNs) (Ca, Mg, K, Na, Fe, Cu, Mn, Zn) and heavy metals (HMs) (Cd, Cr, Ni, Pb, As, Co, Ba, V, Al) by inductively coupled plasma-optical emission spectrometry (ICP-OES). The accumulation of metals was found to increase with altitude. The study identified hotspots with a high concentration of metals and spatial patterns in their geographic distribution. The observed median values for As (70.9 mg/kg), Cd (7.1 mg/kg), and Pb (89.7 mg/kg) represent the highest metal concentrations among the identified clusters. Notably, these values surpass the Environmental Quality Standards (ECA) set for agricultural soils in Peru. As there are no local standards for all the metals studied, our results can serve as reference values for guiding land management practices, particularly in the context of copper mining.

1. Introduction

There is a consensus on the importance of soil health in improving food security (Pozza and Field, 2020). However, its ability to provide its many ecosystem services is threatened by contamination, among other factors, thus compromising global food security (Kopittke et al., 2019; Evangelista et al., 2023). Contamination can trigger significant alterations in the physical, chemical and biological properties of the soil, generating imbalances in nutrient cycles and affecting its ability to maintain normal plant production or the quality of food produced for animals or humans in terms of health and nutrition (He et al., 2005).

Despite a large number of studies on land management and land use, their geographical coverage is quite limited, and the need for more local knowledge is acute (Jian et al., 2020; Beillouin et al., 2022). This is clearly evident in the Andean countries, where soil degradation is getting worse (Hassani et al., 2021), but has still not been sufficiently investigated. As a region with great potential for copper exploitation, with Chile and Peru being the main producers worldwide, it is essential to understand the possible influence that this activity may have on levels of soil contamination and its relationship to food safety. The relevance of the topic is accentuated if we consider the growth forecast for global copper demand (Valenta et al., 2019) and the increase in land use for mining (Maus et al., 2022).

Recent scientific evidence from these regions has reported significant metal concentrations in dust, farmland, and river sediments in localities in northern Chile (Zanetta-Colombo et al., 2022) and southern Peru (Valladares et al., 2022; Bedoya-Perales et al., 2023a), which emphasizes the importance of obtaining more information on this subject in order to guide data-based policies, develop management plans (Omuto et al., 2013), and establish reference values as a basis for defining environmental quality standards for agricultural land (Van-Camp et al., 2004; Brevik et al., 2016; Li et al., 2022).

A major concern associated with soil contamination is the presence of metals and metalloids, whether they are of natural or anthropogenic

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origin. Arsenic (As), cadmium (Cd), lead (Pb), barium (Ba), aluminium (Al), chromium (Cr), cobalt (Co), nickel (Ni), and vanadium (V) are some of the toxic elements which, when accumulated in high concentrations, can cause damage to the soil structure, alter its fertility and contaminate crops, representing a risk to human health (Yadav et al., 2021; Haidar et al., 2023). On the other hand, some elements are essential for the healthy growth of plants; such as calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn). However, when unbalanced their levels can interfere with plants' metabolic processes and cause phytotoxicity, which can compromise soil health and farm production (Kabata-Pendias, 2010; Morgan and Connolly, 2013; Gong et al., 2020; Yadav et al., 2021).

Several studies have shown that agricultural soils in areas close to mines exhibit significantly higher levels of contamination compared to areas distant from such activities (Armienta et al., 2020; Darko et al., 2022; Chen et al., 2022). However, variabilities in soil composition and properties are influenced by land use patterns (including soil management, agricultural practices, crops cultivated, etc.) (Tang et al., 2012; Xu el al., 2022), altitude (Bai et al., 2011) and pedogenic processes (Niu et al., 2019), among other factors.

As a contribution to our knowledge of this topic, this study is the first attempt to characterize variations in the concentration of 17 metals in the agricultural soils of Moquegua, a traditional mining region that contributes significantly to Peru's position as the world's second-largest copper producer (Reichl et al., 2022). It has different altitude-dependant agroecological regions from the coast to the highlands. Each one has unique climate and geographic conditions that influence food production (Zimmerer and Bell, 2013), as can be verified in the region's statistical yearbooks (DRA, 2023). In general, olives are grown between 0 and 500 m above sea level (m.a.s.l.), while between 500 and 2,300 m.a.s.l., vegetables, fruit and to a lesser extent tubers are the principal crops. Between 2,300 and 3,500 m.a.s.l., high-altitude crops such as tubers, corn and some vegetables are the main crops, and between 3,500 and 4,000 m.a.s.l., hardy food crops are grown, mainly tubers.

In this relatively unexplored region, the specific factors contributing to the concentration of metals in the soil remain poorly understood. Moquegua's unique environmental conditions, influenced by a history of mining activities and agriculture, raise concerns about the unknown levels of metals in the area. Recent research conducted by Valladares et al. (2022) identified the presence of naturally occurring arsenic minerals in the sediments of the Moquegua River, which may also be influenced by anthropogenic activity. Additionally, research focused on potato crops at different altitudes has revealed variations in the distribution of metals across diverse agroecological regions, shedding light on the complexities of metal concentration (Bedoya-Perales et al., 2023b).

With this in mind, this study aimed to investigate the total content of nutrient metals (MNs), including macronutrients (Ca, Mg, K, Na) and micronutrients (Fe, Cu, Mn, Zn), as well as heavy metal (HM) levels (Cd, Cr, Ni, Pb, As, Co, Ba, V, Al) in agricultural soils using inductively coupled plasma-optical emission spectrometry (ICP-OES), which is recognized for its effectiveness in agricultural soil analysis when assessing metal contamination (Shaheen et al., 2023). The variation and spatial distribution characteristics of these metals at a regional scale were also analyzed. Furthermore, the relationships between metals and some soil properties were established, and the study evaluated the influence of altitude on the concentration of metals in agricultural soils. Finally, it identified groups and spatial patterns of similarity in the concentrations of metals in the soils.

The information acquired in this study could set a precedent in this specific territory, as well as being useful for studies in other regions where agriculture and mining coexist.

2. Materials and methods

2.1. Description of soil sampling region and site selection

The department of Moquegua is located in southern Peru, between 15°17′ and 17°23′ latitude south, and it accounts for 1.2 % of the area of the country (15,733.9 km^2) (DGP, 2019); it has a population of 174,863 inhabitants (INEI, 2017). Moquegua has important ore deposits and contributes significantly to Peru's position as the world's second-largest copper producer (Reichl et al., 2022). The department of Moquegua is divided into three large provinces: Ilo, Mariscal Nieto and General Sánchez Cerro. In addition, four agroecological regions can be identified, which are classified by altitude: (i) Chala (0–500 m.a.s.l.), (ii) Yunga (500–2,300 m.a.s.l.), (iii) Quechua (2,300–3,500 m.a.s.l.), and (iv) Suni (3,500–4,000 m.a.s.l.) (Pulgar Vidal, 1996; Tapia, 1996). Each of them has particular characteristics relating to land use, agricultural practices and crop management (Zimmerer and Bell, 2013).

Table 1 shows the agricultural zones (AZs) where soil samples were collected, their respective agroecological regions and altitude ranges. The smallest number of samples was collected in Chala, around 3 % of the total, since this region represents only 2.5 % of the agricultural area of the department of Moquegua (DRA, 2022).

Fig. 1 shows the location of the sampling points in the altitude range 9 to 3,934 m.a.s.l. Only 7 % of the soil samples collected were from areas destined for permanent cultivation of olives (zone AZ-18), avocado and sweet lime (zones AZ-13 and AZ-14). The rest of the soil samples were obtained from areas destined for transient crops. The crops grown in each zone are shown in the Supplementary Information (Table S1).

Given the absence of earlier information regarding metal levels in the soils of the department of Moquegua, a convenience sampling approach was employed for the selection of sampling sites. This approach involved active collaboration with local farmers and technicians from the Dirección Regional de Agricultura de Moquegua (Regional Agriculture Office of Moquegua) to identify suitable sampling locations. Soil samples were exclusively collected from areas designated for agricultural use, with a particular focus on areas with significant food production. This ensured that the selected soils were directly associated with areas where food crops play a pivotal role in the local economy and diet. The soil samples were collected when the crops in these specific soils were ready for harvest, providing valuable insights into metal presence in soils that could potentially affect food crop safety. Additionally, input from local farmers, who expressed concerns about potential heavy metal contamination of irrigation water, played a significant role in guiding the site selection process. Furthermore, permission was obtained from landowners to facilitate sample collection.

2.2. Collecting soil samples

A total of 336 samples of agricultural soils were collected for this study in 2021. Sampling points were randomly selected from each plot to obtain a soil sample that was as representative as possible of the land in question, taking into account Peru's national guide for soil sampling (MINAM, 2014), which outlines recommended sampling patterns based on the area's size. 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 were removed. The number of samples taken to create the composite sample varied based on the size of the cultivated area in accordance with the guidelines. The samples were mixed to form a 1 kg composite sample. They were then placed in airtight polyethylene bags, labeled, and taken to the laboratory for analysis.

2.3. Analytical methods

2.3.1. Total metal content and validation of the analytical method

All elements were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES). This analysis was conducted using the

Table 1
Agricultural zones where soil samples were collected, by agroecological region.

Agroecological region	Altitude (m.a.s.l.)	Agricultural zone (AZ) (a)	Crops by agroecological region	Number of samples
Chala	9—357	El Algarrobal, Pacocha.	Olive, potato.	11
Yunga	964—2,275	Moquegua, Samegua, Torata, La Capilla, Coalaque, Omate, Quinistaquillas.	Potato, arracacha, strawberry, spinach, celery, carrot, lettuce, tomato, beetroot, chard, avocado, lime.	100
Quechua	2,308—3,494	Puquina, Matalaque, Ubinas, Coalaque, La Capilla, Lloque. Chojata, Pachas, San Cristóbal, Cuchumbaya, Carumas, Torata.	Potato, arracacha, Andean tubers (oca, olluco, mashua), corn, alfalfa, celery, carrot, spinach, lettuce, chard, broad bean.	158
Suni	3,502—3,934	Ubinas, Ichuña, Lloque, Yunga, Chojata, Carumas, Cuchumbaya, San Cristóbal.	Potato, Andean tubers (oca, mashua, olluco).	67
Total samples				336

(a) The crops grown in each agricultural zone are shown in the supplementary information (Table S1).

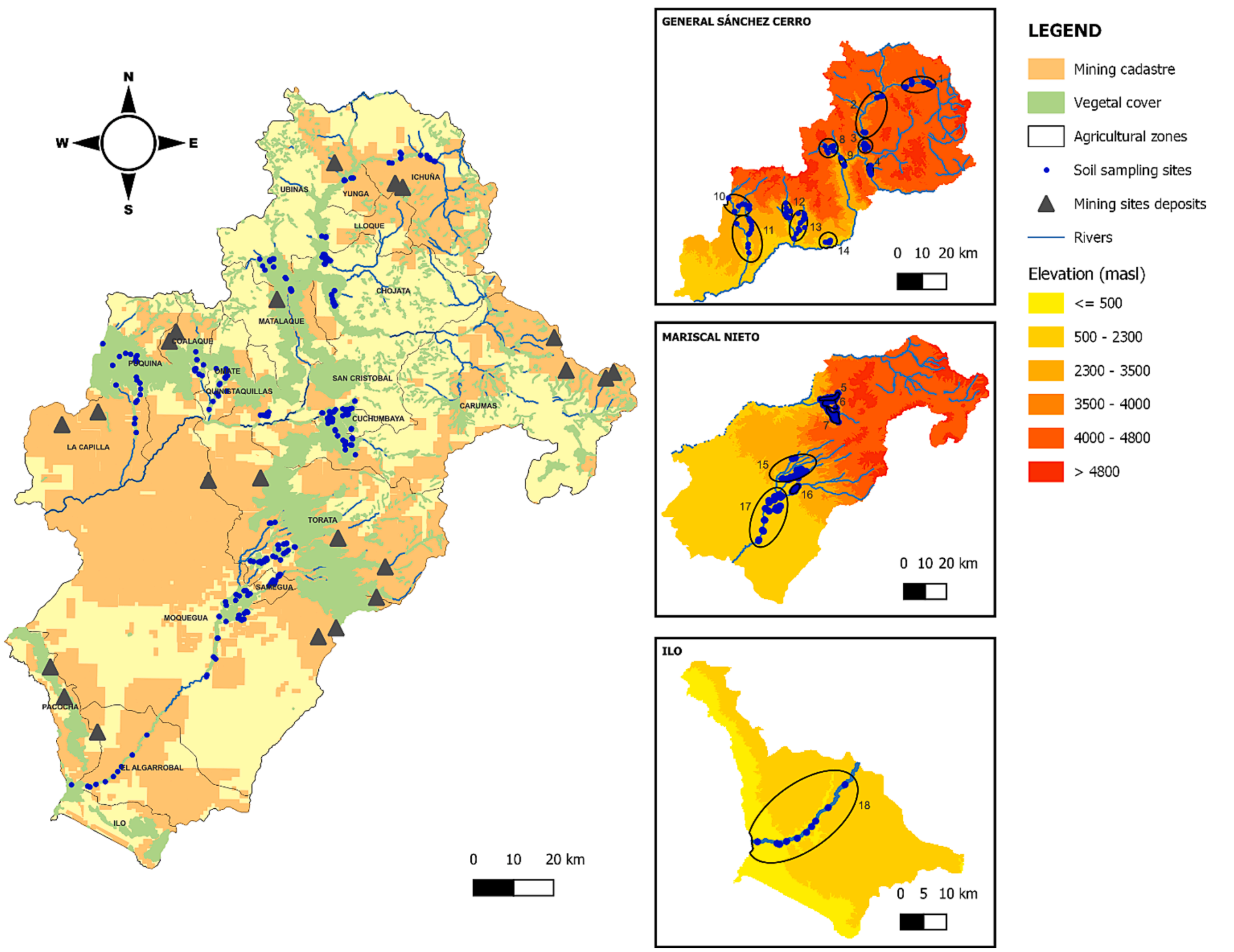


Fig. 1. Study area and sampling points. The map shows the department of Moquegua divided into three provinces: General Sánchez Cerro, Mariscal Nieto and Ilo. It also distinguishes between the following agroecological regions by altitude: Chala (0–500 m.a.s.l.), Yunga (500–2,300 m.a.s.l.), Quechua (2,300–3,500 m.a.s.l.) and Suni (3,500–4,000 m.a.s.l). The map also identifies 18 specific agricultural zones (AZs): (1) Ichuña, (2) Yunga & Lloque, (3) Chojata, (4) Pachas, (5) San Cristóbal, (6) Cuchumbaya, (7) Carumas, (8) Ubinas, (9) Matalaque, (10) Puquina, (11) La Capilla, (12) Coalaque, (13) Omate, (14) Quinistaquillas, (15) Torata, (16) Samegua, (17) Moquegua, (18) El Algarrobal & Pacocha. The crops grown in each AZ are provided in the supplementary information (Table S1).

accredited method EPA 3050B (rev. 2) / EPA 6010 D (rev. 5), July 2018, for acid digestion of sediments, sludges and soils (US/EPA, 1996, 2014). Table 2 shows the elements analyzed and their respective limits of detection (LOD) and limits of quantification (LOQ).

In order to obtain officially valid results, the chemical analyses were carried out by ALS LS laboratory in Lima, Peru. Both the laboratory and the method are accredited by the Instituto Nacional de Calidad del Perú - INACAL (National Quality Institute of Peru), in accordance with Peruvian Technical Standard NTP-ISO/IEC 17025, which establishes general requirements for testing and calibration. Quality assurance and control were conducted following the quality control protocol established by ALS Laboratories, encompassing instruments and reagents, sample processing, standard curve configuration, quantitative analysis of samples, determination of method detection limit and lower limit, method

Table 2
Limits of detection (LOD) and limits of quantification (LOQ) for the elements analyzed.

	Element	LOD (mg/kg)	LOQ (mg/kg)
Macronutrients	Calcium (Ca)	1.5	2.5
	Magnesium (Mg)	3.0	17.0
	Potassium (K)	3.5	10.0
	Sodium (Na)	12.0	20.0
Micronutrients	Iron (Fe)	2.5	6.0
	Copper (Cu)	0.8	2.5
	Manganese (Mn)	2.0	10.0
	Zinc (Zn)	0.6	2.0
Heavy metals	Arsenic (As)	3.6	5.5
	Barium (Ba)	0.3	1.0
	Cadmium (Cd)	0.3	0.5
	Aluminum (Al)	3.0	10.0
	Chromium (Cr)	1.0	2.0
	Cobalt (Co)	1.0	2.0
	Lead (Pb)	3.0	5.0
	Nickel (Ni)	1.0	2.0
	Vanadium (V)	0.7	2.0

precision, and method accuracy (ALS, 2021).

2.3.2. Soil parameter analysis

Electrical conductivity (EC), total dissolved solids (TDS) and pH of the soil samples were measured using a Hanna multi-parameter meter (model HI991300, USA). The determinations were performed 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 allowed to settle for two hours after which the pH, EC, and TDS of the supernatant were measured.

2.4. Regulation limits

For comparative purposes, we used the Environmental Quality Standards (ECA) for inorganic compounds in agricultural soils of Peru. The ECAs constitute a mandatory reference for the design and application of environmental management instruments. If the ECAs are exceeded, farmers and farming companies must carry out evaluations and, if applicable, take action to remedy contaminated sites in order to protect human and environmental health (MINAM, 2017). As the ECAs include only As, Cd, Pb and Ba, the standard reference values for agricultural soils in Ecuador and Canada were used to assess the other metals.

2.5. Statistical analysis

The strategy is to conduct an ANOVA analysis to determine the required influences as differences in mean responses to investigate the influence of altitude on the concentration of metals in soils. Descriptive statistics, encompassing measures such as the mean, maximum, minimum, and median, were computed for the samples. The Shapiro-Francia test (Shapiro and Francia, 1972) was employed, to assess the normality of the variables.

Due to methodological limitations, concentrations smaller than a certain threshold could not be detected and were registered as "$< s$" where the value for s 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. However, the Shapiro-Francia test rejected normality for all variables.

To overcome the lack of normality in the case of non-censored data, we used the non-parametric Kruskal-Wallis test (Hollander and Wolfe, 1973) for comparison among two or more groups and Wilcoxon's rank sum test with continuity correction (Bauer, 1972) to determine which differences are significant.

For censored data, we used a similar approach but with specific methods capable of handling censored data, as described in what follows. 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. To verify the lognormal distribution hypothesis, we applied Shapiro-Francia's normality test to each variable's residual logarithm.

For those variables for which normality holds, that is, the Shapiro-Francia test did not reject the null hypothesis of normality; subsequent pairwise comparisons were carried out using Tukey's contrasts (Steel et al., 1997; Hsu, 1996), whenever necessary. To actually perform the tests, we employed packages NADA (Lee, 2020) and NADA2 (Julian and Helsel, 2022), which have functions that perform ANOVA and *t*-test-like routines for censored data.

For those variables for which normality was rejected by the Shapiro-Francia test, 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 were conducted at a 5 % confidence level.

The Pearson correlation coefficient was employed to examine the associations among the concentrations of heavy metals, macronutrients, micronutrients, pH, TDS, and EC. K-medians clustering (Clarke et al., 2009) was employed to identify patterns within the concentrations of heavy metals, macronutrients, and micronutrients. The use of the median was chosen due to substantial data variability, as it is a statistic less sensitive to extreme values.

All statistical analyses were conducted using the free software R (R Core Team, 2023) version 4.3.0.

3. Results and discussion

3.1. Descriptive statistics

This section gives a general description of the concentrations of 17 metals in agricultural soils in the department of Moquegua, including their pH and EC properties.

Descriptive statistics of soil properties are shown in Table 3. Approximately 80 % of the soil samples had a pH of $\geq$ 6.6, oscillating between neutral and strongly alkaline, according to the land classification in Peru (SERFOR, 2009). In 20 % of samples with a pH of $<$ 6.6, soils were found to vary between slightly acid and extremely acidic. Additionally, it was found that in 94 % of the samples, the EC was less than 1 dS/m, which suggests that the salinity levels of most of the soils in the department of Moquegua are not such as to limit crop growth (Castellanos, 2010).

Table 3 also provides descriptive statistics for MNs and HMs in the soil. The mean concentrations of MNs in soil decrease in the following order: Fe > Ca > Mg > K > Na > Mn > Zn > Cu. A similar pattern was reported in mining-impacted agricultural fields in Zamfara State, Nigeria, albeit at lower concentrations: Fe (16,678.6 mg/kg) > Mg (1,759.4 mg/kg) > Ca (1,458.5 mg/kg) > K (1,400.3 mg/kg) > Mn (184.1 mg/kg) > Na (27.1 mg/kg) > Zn (11.4 mg/kg) > Cu (10.7 mg/kg) (Mandal et al., 2022). Since Ca is the predominant macronutrient and is found in high concentrations, it is to be expected that the soils of the department of Moquegua would be mostly alkaline (Fageria and Nascente, 2014). None of the MNs are covered by ECAs in Peru. However, if we consider the permitted limits of Cu (63 mg/kg) and Zn (200 mg/kg) in agricultural soils in countries like Ecuador and Canada, an excess of 28.3 % and 4.2 %, respectively, is evident. As far as Mn is concerned, although this metal is not commonly considered in environmental regulations, it is important to note that 42 % of the soils exceeded the geochemical background level used as a reference in the evaluation of agricultural soils in central Sonora, Mexico (542 mg/kg)

Table 3
Summary of the descriptive statistics of soil properties, metal nutrients and heavy metals (mg/kg) in soil from the study area (n = 336).

		Mean (mg/kg)	Median (mg/kg)	Range (mg/kg)
Soil properties	**pH**	7.4	7.4	4.4–9.0
	EC (dS/m)	0.4	0.2	0.1—6.8
	TDS (mg/L)	244.5	139.3	34.0–3,820.0
Macronutrient concentrations (mg/kg)	**Ca**	9,280.1	6,374.0	1,417.0–89,583.0
	Mg	5,018.8	4,224.5	1,527.0–37,838.0
	K	2,583.1	2,358.0	878.1–7,893.0
	Na	611.0	433.0	132.7–4,918.0
Micronutrient concentrations (mg/kg)	**Fe**	18,995.9	18,528.0	6,556.0–37,865.0
	Cu	57.1	49.7	11.1–233.5
	Mn	512.3	514.4	114.8–1,383.0
	Zn	78.3	60.1	18.3–537.0
Heavy metal concentrations (mg/kg)	**As**	20.7	13.8	n.d.-182.9
	Ba	181.9	168.5	64.2–1,292.0
	Cd	0.6	0.3	n.d.-7.9
	Al	13,511.2	12,566.5	2,974.0–49,883.0
	Cr	8.9	8.0	n.d.-39.8
	Co	10.4	10.0	n.d.-26.6
	Pb	16.6	10.4	n.d.-145.8
	Ni	7.6	8.0	n.d.-46.6
	V	49.9	48.4	14.0–116.6

n.d.: non-detectable, less than the limits of detection (LOD).

(Morales-Perez et al., 2021).

Regarding HMs, it was observed that their mean concentrations in soil decrease in the following order: Al > Ba > V > As > Pb > Co > Cr > Ni > Cd. In Peru, ECAs include some of these metals, such as As (50 mg/kg), Ba (750 mg/kg), Cd (1.4 mg/kg) and Pb (70 mg/kg). Thus, we find that 12 % of the samples exceeded the ECA for As. However, if Ecuadoran and Canadian reference values (12 mg/kg) are considered, this percentage rises to 57.4 %. On the other hand, it was found that 4.5 % of the samples exceeded the established ECA for Cd, and 7 % exceeded the ECA for Pb.

Table 4 provides average metal concentrations reported in studies of agricultural soil near mines across various regions worldwide. Notably, these concentrations exhibit substantial variation, both by metal type and geographic area.

Our study reveals interesting data. For instance, we observed relatively high concentrations of As and Cd when compared to certain areas in China (Wang et al., 2022; Liu et al., 2022). Similar As levels were also found in other South American regions (Ulloa et al., 2018; Romero-Crespo et al., 2023), including Junín, Peru (Orellana et al., 2021). In contrast, concentrations of Cr, Co, Pb, Ni, and V in the Moquegua department tended to be lower when compared to numerous locations listed in Table 4.

The concentrations of Zn and Fe moderately resemble those reported in mining-impacted regions of central Peru (Orellana et al., 2021). Nevertheless, Zn concentrations were lower than in several other global regions. Meanwhile, Mn concentrations were similar to those in zinc mine tailings in Udaipur, India (Misra et al., 2009), and Shanxi, China (Yang et al., 2022).

In terms of Cu concentrations, our study reported higher values than certain mining-impacted agricultural areas in China, Mexico, Colombia, and Tanzania. However, it is worth noting that our Cu concentrations were found to be lower than the average values observed in agricultural regions across Latin America, which included locations in Chile, Panama, Mexico, as well as more distant regions in India, China, and Cameroon.

These findings underscore the substantial variability in metal concentrations among various mining-affected regions worldwide. The absence of a consistent pattern in metal concentrations is evident, as certain areas exhibit elevated levels of specific metals alongside lower levels of others. These variations highlight the complexity of the interplay between geological, environmental, and anthropogenic factors in shaping metal distributions unique to each region. The complex nature of these variations emphasizes the importance of considering local disparities and area-specific conditions when evaluating metal concentrations in agricultural soils, emphasizing the need for tailored approaches to land use management.

In the following section, the variation and distribution of MNs and HMs in different areas of the department of Moquegua are discussed in detail.

3.2. Total concentrations and spatial distribution characteristics of metals in soil

In this section, the variation and distribution of metals at the regional level are analyzed, taking into account the 18 zones shown in Fig. 1. Fig. 2 and Fig. 3 show the variability in levels of MNs and HMs in these zones, respectively. Additionally, for each zone, Table S2 provides a statistical description of the pH, EC, and TDS variables, while Table S3 presents descriptive statistics of MNs and HMs.

As far as macronutrients (Ca, Mg, K and Na) are concerned, AZ-17 (Moquegua) stands out for ranking among the highest concentrations, while the lowest concentrations were primarily found in AZ-10 (Puquina) and AZ-12 (Coalaque). Particularly noteworthy is the level of Ca in AZ-17 (Moquegua) (22,144.0 mg/kg), more than ten times higher than in AZ-10 (Puquina), where the lowest concentration was recorded. Na is another notable macronutrient in AZ-17 (Moquegua), as well as in AZ-18 (El Algarrobal & Pacocha) and AZ-9 (Matalaque), where the highest concentrations were recorded (1,106.0, 887.8 and 975.2 mg/kg, respectively). These same areas also provided some of the highest pH (8.1, 8.1 and 7.7, respectively) and EC values (0.7, 0.8 and 0.4 dS/m, respectively) (Table S2). K stands out in AZ-9 (Matalaque) and AZ-8 (Ubinas) for the opposite extreme values (3,970.0 and 1,439.0 mg/kg, respectively).

Regarding micronutrients, AZ-9 (Matalaque) is distinguished by having the highest values of Fe, Zn and Cu (26,310.5, 171.3 and 97.1 mg/kg, respectively), with ranges that exceed the permissible limits in countries such as Ecuador and Canada in the case of Zn (200 mg/kg) and Cu (63 mg/kg). Other areas that exceed the concentration of Cu after AZ-9 (Matalaque), are AZ-4 (Pachas) (71.6 mg/kg), AZ-16 (Samegua) (68.7 mg/kg), AZ-18 (Ilo and Pacocha) (65.3 mg/kg) and AZ-12 (Coalaque) (62.6 mg/kg).

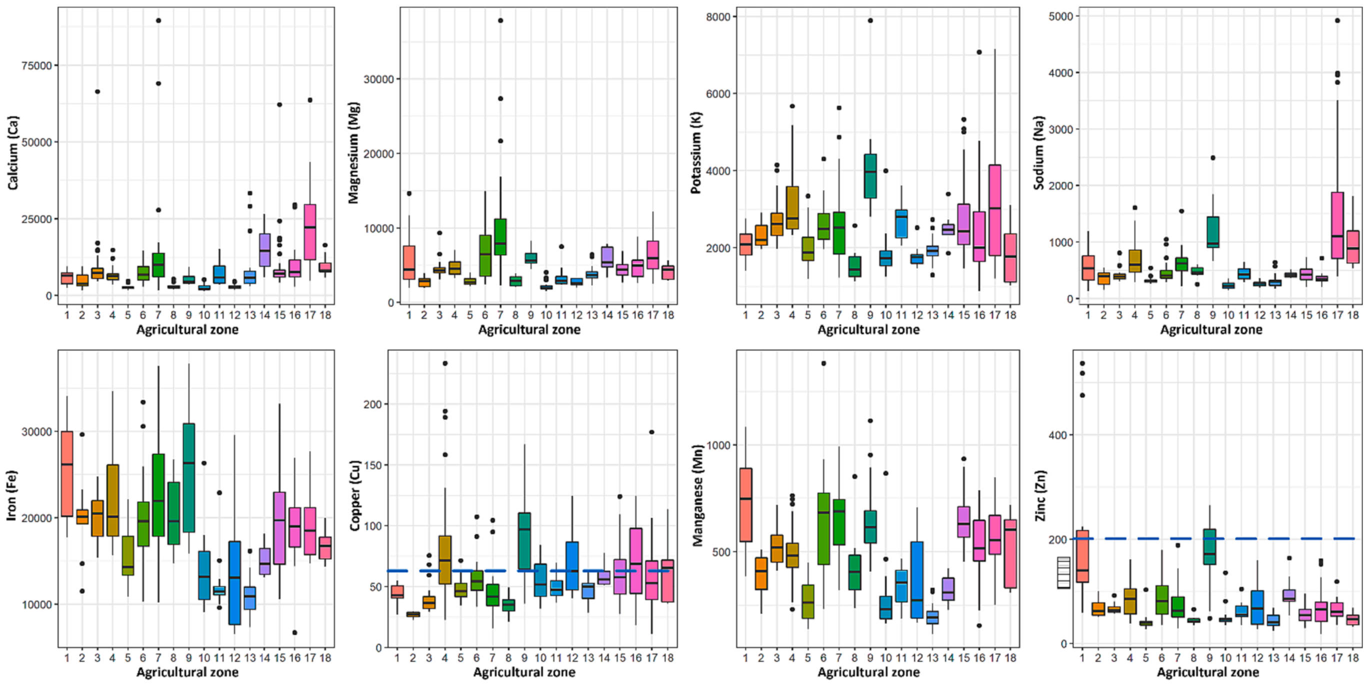
Table 4 shows that these concentrations are higher than in several agricultural areas impacted by mining in China (Wang et al., 2022; Liu et al., 2022), Mexico (Jha et al., 2021), Colombia (Marrugo-Negrete et al., 2019), and Tanzania (Mng'ong'o et al., 2021). They are also lower than concentrations found in Valparaíso, Chile (Ulloa et al., 2018); Daye, China (Zhou et al., 2023); and Goa, India (Daripa et al., 2022). As far as Zn is concerned, concentrations more than eight times higher than those found in our study have been reported in Zimapán and Zacatecas, Mexico (Castro-Larragoitia et al., 2013; Armienta et al., 2020) and Udaipur, India (Misra et al., 2009). With regard to Mn, although zone AZ-1 (Ichuña) has the highest concentration (747.3 mg/kg), it is noteworthy that the most striking outliers are observed in AZ-6 (Cuchumbaya) and AZ-9 (Matalaque), indicating even higher values.

For HMs (Fig. 3), it's worth noting that all the samples collected in AZ-12 (Coalaque), AZ-9 (Matalaque) and AZ-4 (Pachas) had As concentrations above 12 mg/kg, which is the limit allowed in agricultural soils in Ecuador and Canada. Notably, these locations also exhibited the highest medians (76.2, 59.3 and 51.5 mg/kg, respectively). However, if the ECA (50 mg/kg) is taken into account, 64.2 % of samples from these

Table 4
Concentrations of metals in agricultural soils from other studies compared to current work.

Region and country	Fe	Cu	Mn	Zn	As	Ba	Cd	Al	Cr	Co	Pb	Ni	V	References
Moquegua, Peru	18,995.9	57.1	512.3	78.3	20.7	181.9	0.6	13,511.2	8.9	10.4	16.6	7.5	49.9	Present study (mean)
Moquegua, Peru	6,556.0–37,865.0	11.1-233.5	114.8–1,383.0	18.3-537.0	3.6-182.9	64.2–1,292.0	0.3-7.9	2,974.0–49,883.0	1.0-39.8	1.0-26.6	3.0-145.8	1.0-46.6	14.0-116.6	Present study (range)
Daye, China	NA	355.7	NA	NA	43.2	NA	1.4	NA	90.5	NA	102.3	32.3	NA	(Zhou et al., 2023)
Zhejiang, China	NA	27.9	NA	NA	14.2	NA	0.1	NA	49.0	NA	40.2	26.9	NA	(Wang et al., 2022)
Guizhou, China	36.7	26.3	641.5	115.6	8.3	NA	0.4	NA	45.4	NA	29.9	3.2	NA	(Liu et al., 2022)
Shanxi, China	NA	24.3	564.0	88.7	14.2	NA	0.3	NA	46.7	NA	19.6	30.7	NA	(Yang et al., 2022)
Suxian, China	NA	37.9	NA	202.7	78.7	NA	NA	NA	NA	NA	160.1	NA	NA	(Chen et al., 2018)
Mbeya, Tanzania	7,371.1	3.3	NA	18.2	NA	NA	0.0	NA	15.3	2.9	5.6	4.1	NA	(Mng'ong'o et al., 2021)
Pawara, Cameroon	57.5	122.2	NA	128.7	NA	NA	9.0	NA	633.6	NA	4,265.0	NA	NA	(Fodoué et al., 2022)
Zamfara, Nigeria	16,678.6	10.7	184.1	11.4	NA	NA	NA	NA	15.7	4.3	NA	NA	20.5	(Mandal et al., 2022)
Iberian, Spain	NA	NA	NA	367.4	NA	NA	NA	NA	95.4	27.9	254.6	66.3	NA	(González-Morales et al., 2022)
Goa, India	162,638.0	125.6	2,091.0	75.6	NA	NA	25.7	NA	69.3	21.2	96.4	51.2	NA	(Daripa et al., 2022)
Udaipur, India	NA	186.2	577.6	720.5	NA	NA	NA	NA	NA	NA	637.5	NA	NA	(Misra et al., 2009)
Kurdistán, Iran	NA	NA	NA	145.4	NA	NA	NA	NA	95.7	13.9	163.1	55.0	103.2	(Rafiei and Bakhtiari-Nejad, 2022)
San Juan, Mexico	NA	20.0	NA	NA	5.4	NA	NA	NA	28.3	NA	47.5	NA	NA	(Jha et al., 2021)
Zimapán, Mexico	31,500.0	NA	NA	937.5	641.3	NA	7.0	NA	NA	NA	610.0	NA	NA	(Armienta et al., 2020)
Zacatecas, Mexico	NA	860.0	NA	592.0	145.0	NA	5.0	NA	NA	NA	261.0	NA	NA	Castro-Larragoitia et al. (2013)
Veraguas, Republic of Panama	NA	70.3	NA	54.4	110.0	NA	NA	NA	NA	NA	NA	NA	NA	(González-Valoys et al., 2023)
Junín, Peru	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	212.3	NA	NA	(Castro-Bedriñana et al., 2021)
Junín, Peru	16,528.4	NA	NA	90.9	17.9	NA	0.6	NA	NA	NA	59.9	NA	NA	(Orellana et al., 2021)
La Mojana, Colombia	NA	48.5	NA	81.2	NA	NA	NA	NA	NA	NA	3.3	58.5	NA	(Marrugo-Negrete et al., 2019)
Valparaiso, Chile	NA	492.4	NA	184.5	21.1	NA	NA	NA	NA	NA	50.7	NA	NA	(Ulloa et al., 2018)
Azuay, Ecuador	NA	100.9–225.5	NA	150.5–220.0	23.5-421.7	NA	1.0-1.9	NA	77.2-101.0	NA	8.6-15.1	50.2-67.5	NA	(Romero-Crespo et al., 2023)

*NA, not applicable.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Ichuña	Yunga/Lloque	Chojata	Pachas	San Cristóbal	Cuchumbaya	Carumas	Ubinas	Matalaque	Puquina	La Capilla	Coalaque	Omate	Quinistaquillas	Torata	Samegua	Moquegua	Algarrobal/ Pacocha

Fig. 2. Boxplots of metal nutrients in agricultural soils in the department of Moquegua, Peru. The blue dotted line represents the permissible standards in Canada or Ecuador. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

areas contained excess concentrations. AZ-4 (Pachas) also stands out because in soils intended for corn and alfalfa crops concentrations of Cd up to 7.9 mg/kg were found, six times more than the ECA (1.4 mg/kg). For Pb, AZ-9 (Matalaque) and AZ-1 (Ichuña) are significant because 59.5 % of the samples exceed the ECA (70 mg/kg), reaching concentrations of up to 145.8 and 134.8 mg/kg, respectively.

The agricultural soil limits established in Ecuador and Canada for Cr (65 mg/kg), Ni (50 mg/kg), V (130 mg/kg) and Co (40 mg/kg) were not exceeded in any of the areas studied, nor by the maximum values. However, as far as Al was concerned, it should be noted that in AZ-7 (Carumas) (20,579.0 mg/kg), approximately 62 % of samples had concentrations higher than 18,221.0 mg/kg, up to three times more. According to the study carried out by Rasulov et al. (2020) in Hungary, this concentration can be detrimental both for plants and for the soil, since it can cause erosion.

Spatial visualization maps were created to offer a visual representation of areas with high MNs (Fig. 4) and HMs (Fig. 5) concentration values in soils, including areas where samples were not collected. This GIS-based approach has been utilized in prior studies for assessing various soil variables, including metals, and their impact on crops (Marchetti et al., 2012; Wani et al., 2013; Ahmadi et al., 2019; Sun et al., 2019; Xu et al., 2022). In order to exercise caution when evaluating areas without sampled data, Figs. S2 and S3 depict metal concentration values exclusively at the sampling locations. These maps help pinpoint geographic hotspots with significant metal concentrations, providing valuable insights into their distribution for researchers and decision-makers.

Both Fig. 2 and Fig. 3 reveal high concentrations of specific HMs in certain agricultural areas, which have been statistically identified as outliers. This trend is evident in Fig. 4 and Fig. 5, illustrating that areas with elevated metal concentrations often adjoin regions with lower metal levels. These variations may be related to factors that have already been reported in the literature, for instance agricultural practices, including land management by farmers, the use of livestock manures, fertilizers, and agrochemicals (Luo et al., 2009). Moreover, the source of water for irrigation and water quality could potentially be influenced, to some extent, by mining activities (Liu et al., 2021).

According to the Moquegua agricultural statistics yearbook (DRA, 2023), the widespread use of fertilizers across the entire department aligns with findings reported in existing literature that demonstrate increased soil concentrations of Cu, Zn, Fe, and Mn due to fertilizer usage (He et al., 2005). Similarly, a prior study on sediments in the Moquegua River, which supplies water to AZ-15 (Torata) and downstream areas, found elevated levels of Ca, Fe, K, and Al. These increases were primarily attributed to anthropogenic factors, notably the significant use of fertilizers by local farmers (Valladares et al., 2022).

In the case of HMs, as depicted in Fig. 5, it's noteworthy that As, Cd and Ba exhibit distinct concentration patterns compared to other metals in the department. Specifically, these three metals show localized high concentrations in specific areas. For instance, the highest levels of As are concentrated in AZ-12 (Coalaque) and AZ-9 (Matalaque), while Cd reaches its peak concentration in AZ-4 (Pachas). One potential explanation for these localized hotspots could be related to reported water pollution incidents in these areas (GORE, 2020). This is reminiscent of situations observed in other parts of the world, such as the Tongling mining area in China, where contamination of agricultural soils by Cd was attributed to river pollution near cultivated regions (Xu et al., 2022). Considering that these zones were growing corn, it is important to note that other studies have revealed that an excess of As and Cd in the soil can adversely affect corn plants, leading to stunted growth, reduced height, and physiological cob immaturity (Armienta et al., 2020). This underscores the potential ecological and agricultural implications of the elevated metal concentrations in these specific areas.

The map of Ba shows an area of high concentration in the south of the department (1,292.0 mg/kg), seven times higher than the regional average and 1.7 times higher than the ECA (750 mg/kg). This relates to the outlier found in AZ-17 (Moquegua) (Fig. 3). On the other hand, Co, V and Al follow a similar pattern in terms of their distribution, as do Ni, Pb

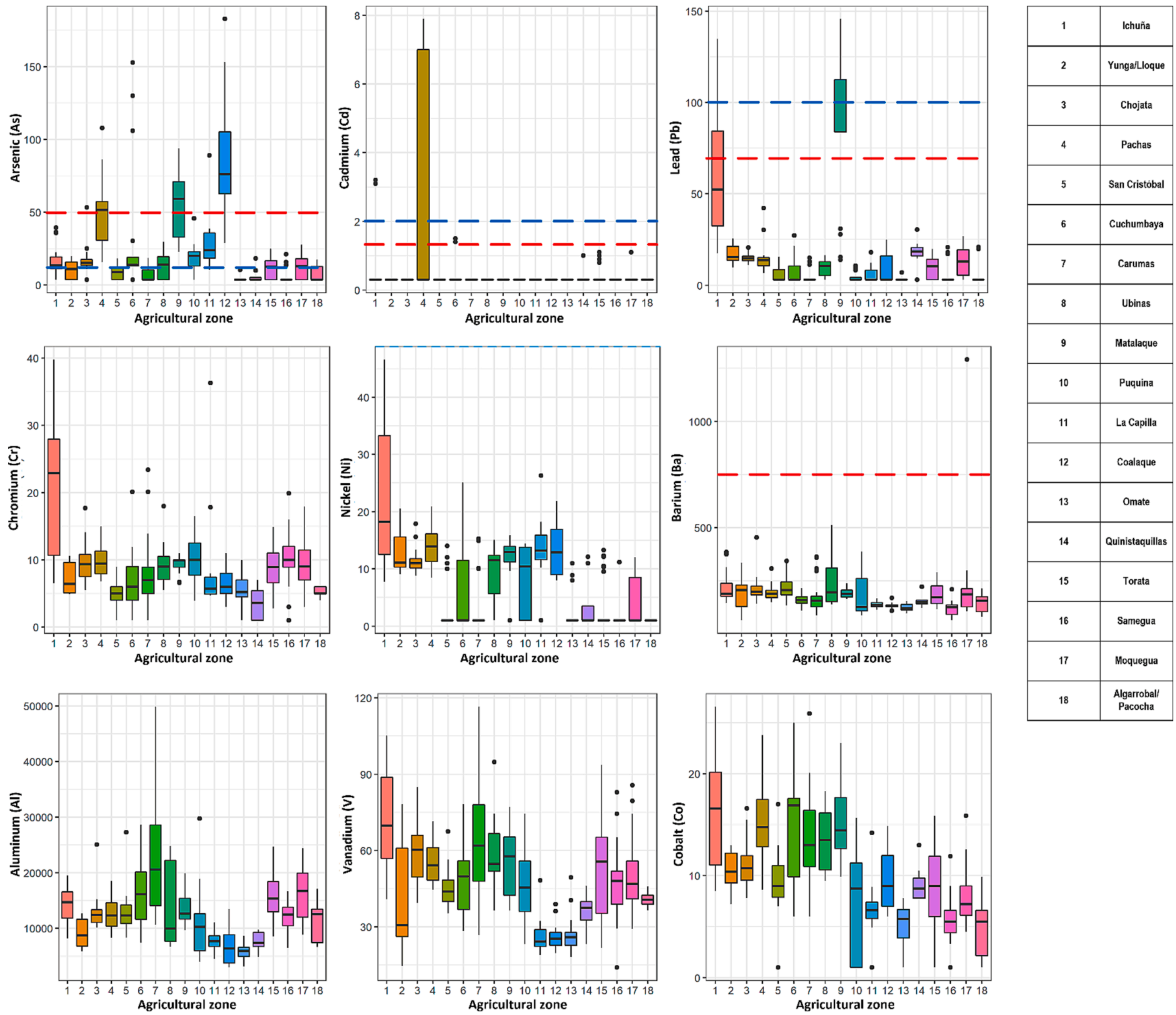


Fig. 3. Boxplots of heavy metals in agricultural soils of the department of Moquegua, Peru. The red dotted line represents the permissible standards in Peru, while the blue dotted line represents the permissible standards in Canada or Ecuador. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and Cr. Radomirović et al. (2020) also observed analogous spatial distribution patterns for Ni and Cr in soil in Belgrade.

Fig. S1 shows the spatial distribution of pH and EC in agricultural soils, highlighting where soils with the highest EC (up to 6.8 ds/m, AZ-17) and lowest pH (up to 4.4; AZ-10) are concentrated. The lowest median pH values were found in AZ-5 (San Cristóbal), AZ-7 (Carumas), AZ-8 (Ubinas) and AZ-10 (Puquina), with values of 6.3, 6.6, 6.4 and 6.7, respectively (Table S2). Increased acidification in the soils of these areas may be the consequence of various factors such as mineralization of organic matter, intensive crop cultivation, or the use of fertilizers (ammonium-based and nitrogen-based fertilizers) (Fageria and Nascente, 2014). Figs. 3 and 4 show that the highest levels of Co, V, Pb, Al, Cr, Ni, Mg, Fe and Zn are found in these same zones. Although a reduction in pH can increase the mobility of HMs, potentially leading to further accumulation in plants (Zeng et al., 2011; Musilova et al., 2016), it is important to remember that this effect can vary depending on the soil type, fertilizer use, sources of contamination and other factors (Lu et al., 2012; Zhou et al., 2014).

The variability in the spatial distribution patterns of MNs and HMs in agricultural soils in the department of Moquegua reinforces the importance of introducing monitoring and management strategies adapted to the unique characteristics of each zone.

The following section analyses the correlation between the metals studied and soil parameters (pH and EC).

3.3. Correlation matrix of studied metal nutrients and heavy metals in agricultural soils of Moquegua department, Peru

The Pearson correlation coefficients matrix for metals and other soil parameters from the study area are presented in Fig. 6.

Positive correlations were found between the contents of all MNs, as well as between these and most of the HMs. Notably, Fe stands out, potentially linked to its status as the major soil element in the department of Moquegua. Strong correlations were found between the element pairs Fe and V ($r = 0.85$) and Fe and Co ($r = 0.76$). This result deserves special attention given the geographical coverage of this metal (Fig. 4)

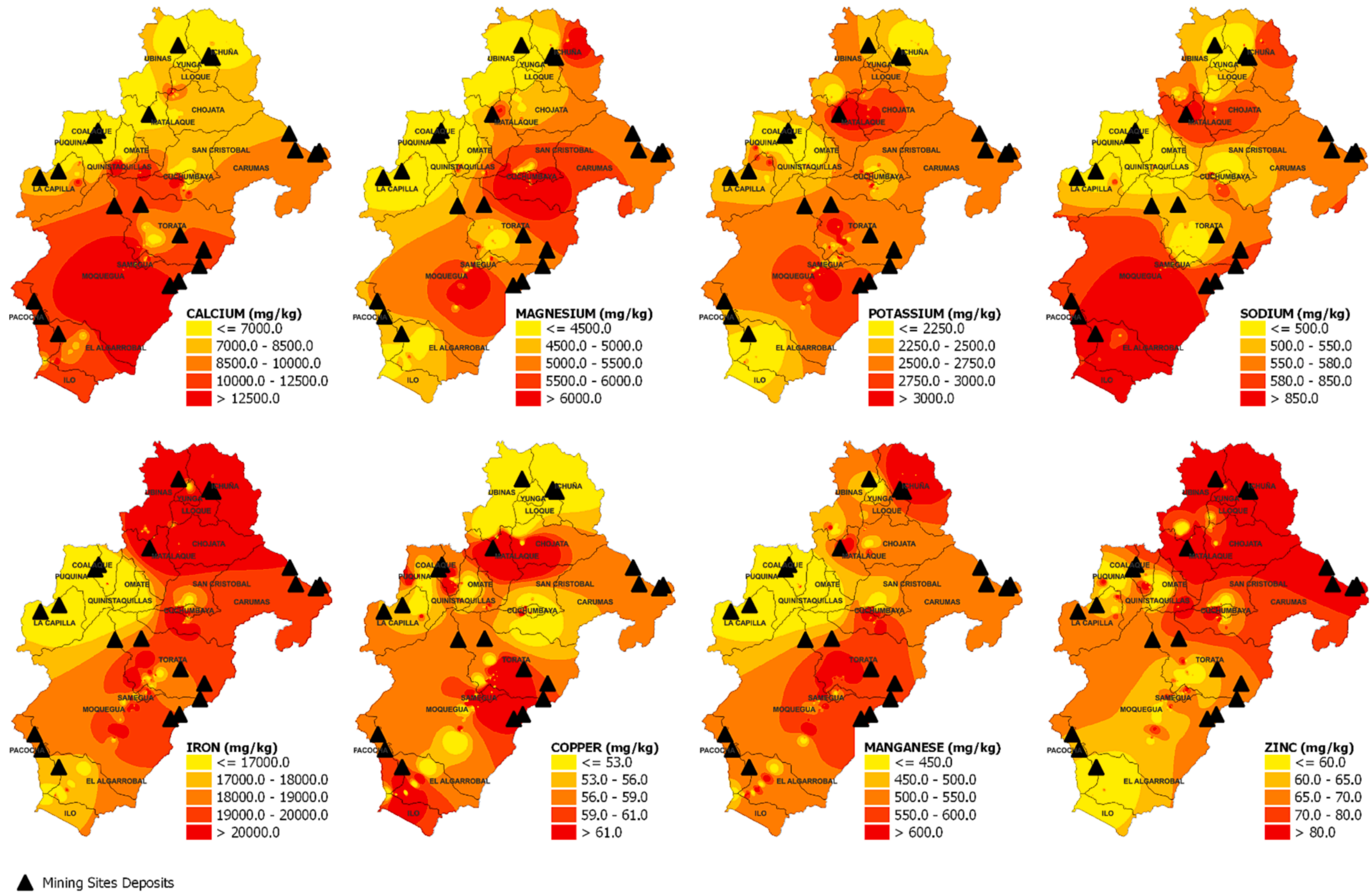


Fig. 4. Spatial distribution of metal nutrients in agricultural soils of the department of Moquegua, Peru. The base map was generated with QGIS (3.28 Firenze version), a free and open-source Geographic Information System (https:// www. qgis. org/).

and because it is the metal found in the highest concentration (Table 3). It should be noted that in agricultural soils of the Guanzhong Plain in China, Fe has been shown to be the most significant factor in the distribution of HMs and metalloids in the soil (Deng et al., 2023).

Other strong correlations were found between the element pairs Zn and Pb ($r = 0.71$), Mg and Al ($r = 0.70$), and V and Co. ($r = 0.71$). Figs. 4 and 5 confirm that these metals follow similar spatial distribution patterns. On the other hand, the MNs with negative correlations with some HMs were Mg (with Cd, Ba and As), Ca (with Cr, Ni, Pb, Cd and As) and Cu (with Ba).

In relation to the soil parameters, strong correlations are observed only between the EC, TDS and Na ($r = 0.70$). These results are consistent with other soil studies that reported similar correlations between pH, EC and the metals analyzed (Radomirović et al., 2020; Ahmadi et al., 2017). According to Lu et al. (2012) and Zhou et al. (2014), the lack of significant correlation between pH and HMs could be attributed to different causes of contamination, soil type and the use of fertilizers in the area evaluated.

3.4. Influence of altitude on the concentration of metals in the soil

This section shows how altitude between 9 and 3,934 m.a.s.l., influences the concentration of metals in agricultural soils in the department of Moquegua. Mean comparison tests were performed to analyze the concentration of each of the metals in the Chala, Yunga, Quechua and Suni agroecological regions (as shown in Table 1 and Fig. 1).

There are two main cases: elements for which there were no censured observations, but 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 5 and Table 6, respectively, with information on the average of each metal per region and whether this average was considered statistically different from the other zones ($p < 0.05$), by using letters to indicate grouping.

For the HMs with uncensored data, Al concentration was not found to vary with altitude. However, higher concentrations of Ba and V were found in the higher altitude regions (Quechua and Suni), where Andean tubers, alfalfa, corn and some vegetables are grown (Table 1). As far as MNs were concerned, the concentration of Mn was not found to vary with altitude. The Chala and Yunga regions (9–2,275 m.a.s.l.) had the same concentrations of Fe, Cu, Mg and Ca. The lowest concentrations of Fe and highest concentrations of Ca, Na and Mg were found at these lower altitudes. However, Suni had a higher concentration of Fe and Zn, and a lower concentration of Cu compared with the other regions, which indicates a reduction in Cu concentration at altitudes equal to or higher than 3,500 m.a.s.l.

Yunga (964–2,275 m.a.s.l.) revealed significant concentrations of Ca and Mg, which probably favors different crops. The greatest diversification was found in this altitude range, with crops such as potato, arracacha, strawberry, spinach, celery, carrot, lettuce, tomato, beetroot, chard, avocado and aromatic lime being grown (Table 1).

Statistical analysis using censored values of the relationship between altitude and heavy metal concentration (Table 6) indicates that Suni (3,502–3,934 m.a.s.l.) has the highest concentrations of Pb, Co, Ni and Cr. Similarly, the highest concentrations of As and Cd were found at the altitude of Quechua (2,308–3,494 m.a.s.l.), while Chala (9–357 m.a.s.l.) had the lowest concentrations of all the HMs analyzed. Thus, an increasing trend in the concentration of HMs can be seen in the higher altitude regions. This same behavior was observed in a study of heavy metal deposition in the European Alps (Zechmeister, 1995), with a notable increase in the concentrations of Pb and Cd as altitude increases.

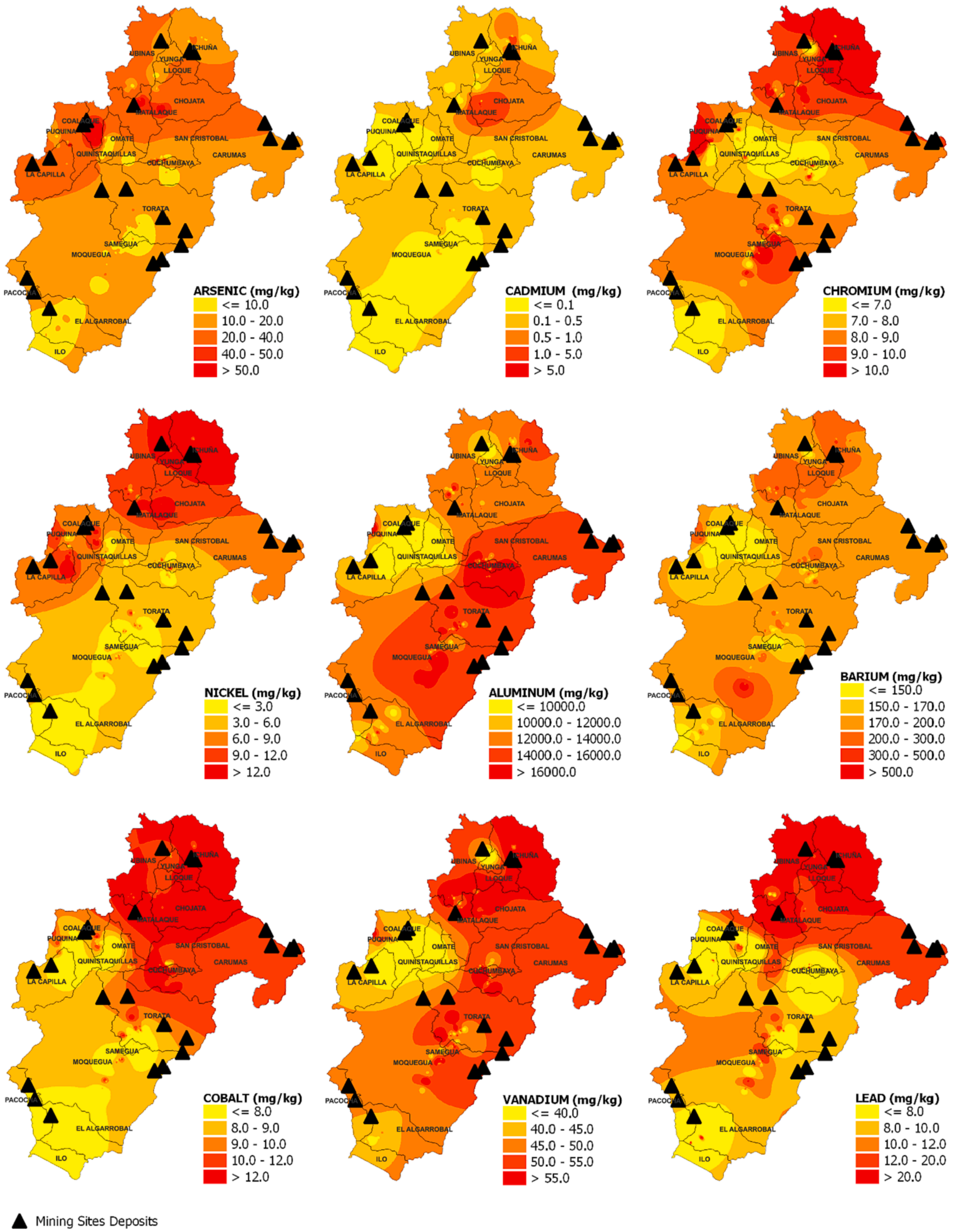


Fig. 5. Spatial distribution of heavy metals in agricultural soils of the department of Moquegua, Peru. The base map was generated with QGIS (3.28 Firenze version), a free and open-source Geographic Information System (https:// www. qgis. org/).

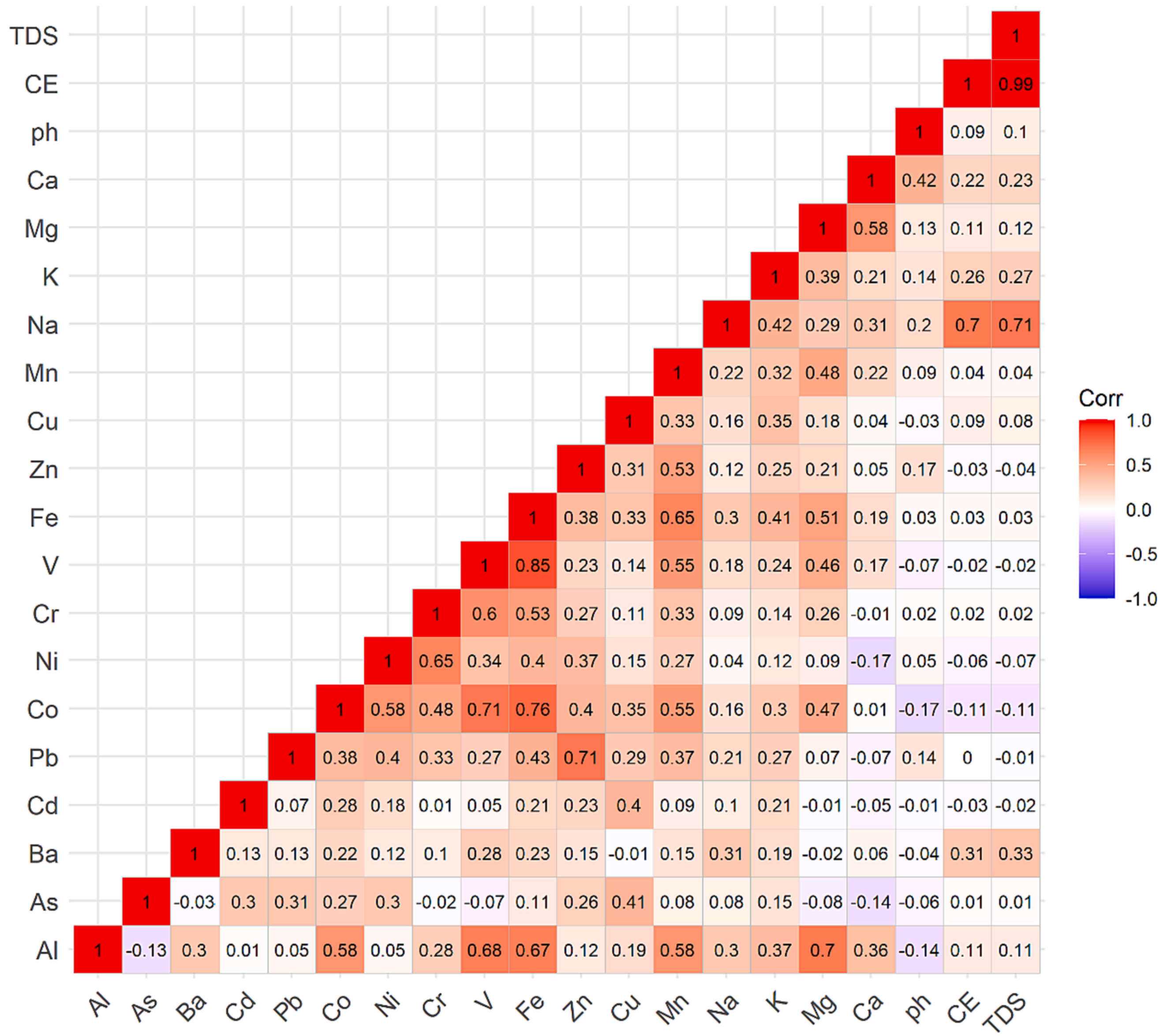


Fig. 6. Pearson correlation coefficient matrix for metals and other soil parameters (n = 336).

Table 5
Comparison among metals grouped by altitude using uncensored observations.

Agroecological Region	Metal concentrations (mg/kg)										
	Al	Ba	V	Fe	Zn	Cu	Mn	Na	K	Mg	Ca
Chala (9 – 357 m.a.s.l.)	11,101.1 ^{a}	142.6 ^{ab}	40.8 ^{a}	16,678.1 ^{a}	46.4 ^{a}	61.3 ^{ab}	509.5 ^{a}	971.2 ^{a}	1,759.6 ^{a}	4,108.4 ^{ab}	9,451.2 ^{a}
Yunga (964–2,275 m.a.s.l.)	12,837.3 ^{a}	167.0^{b}	44.7 ^{a}	17,625.0 ^{a}	65.8^{b}	59.2 ^{a}	510.1 ^{a}	793.5^{c}	2,664.4 ^{bc}	5,167.2^{b}	14,986.7 ^{a}
Quechua (2,308–3,494 m.a.s.l.)	13,820.3 ^{a}	178.0 ^{a}	49.8^{b}	18,933.4 ^{a}	80.0^{b}	62.5 ^{a}	493.4 ^{a}	541.9^{b}	2,740.2^{b}	5,208.4 ^{ab}	6,963.5^{b}
Suni (3,502–3,934 m.a.s.l.)	14,183.9 ^{a}	220.0^{c}	59.7^{c}	21,569.7^{b}	98.1^{b}	40.6^{b}	560.6 ^{a}	442.3^{b}	2,226.3 ^{ac}	4,499.3 ^{a}	6,197.6^{b}

Different letters in the same column indicate significant differences between groups, $p < 0.05$.

It is also important to note that most mines are found at the highest altitudes (Quechua and Suni) (Fig. 1), which may contribute to the increase in the concentration of HMs in this altitude range.

Different letters in the same column indicate significant differences between groups, $p < 0.05$.

3.5. Cluster analysis

This section seeks to identify groups and patterns of similarity in the geographic distribution of metals based on their concentration levels. Thus, the cluster analysis results for MNs and HMs in soils in the study area are shown in Fig. 7. In addition, Figs. S4–S6 show the variations in metal concentrations in the different groups identified.

As we can see from Fig. 2 and Fig. 3, in some agricultural areas high metal contents that were statistically identified as outliers were found, these were excluded from the clusters in order to establish more precise reference values, following the approach used by Micó et al. (2007) in their study of HMs in agricultural soils in Alicante, Spain.

Table 6
Comparison among metals grouped by altitude using censored observations.

Agroecological Region	Metal concentrations (mg/kg)					
	As	Cd	Pb	Co	Ni	Cr
Chala (9 – 357 m.a.s.l.)	7.5 ^{ab}	0.3^{b}	6.2 ^{ab}	4.7 ^{a}	1.0 ^{a}	5.3 ^{a}
Yunga (964–2,275 m.a.s.l.)	14.2^{b}	0.3^{b}	10.3^{b}	7.2 ^{a}	4.2 ^{a}	8.0^{b}
Quechua (2,308–3,494 m.a.s.l.)	28.6 ^{a}	0.8 ^{a}	17.3 ^{ab}	11.7^{b}	7.8 ^{a}	8.5^{b}
Suni (3,502–3,934 m.a.s.l.)	13.8^{b}	0.4 ^{ab}	26.1 ^{a}	12.9^{b}	13.2 ^{a}	11.9^{c}

The cluster analysis identified a different number of groups for MNs and HMs, whose correlations are given in Fig. S7. As far as macronutrients are concerned, five groups were identified. In Fig. S4 we can see that cluster 1 (64.3 % of the samples) is characterized by grouping the samples with the lowest concentrations of Na, K, Mg and Ca. This suggests a greater uniformity in the distribution of macronutrient levels. On the other hand, cluster 5 (1.2 % of the samples) groups those samples with the highest concentrations of Ca and Mg. In fact, a strong positive correlation was found between this pair of metals ($r = 0.99$) (Fig. S7). Furthermore, cluster 4 (2.1 % of the samples) is characterized by the samples grouped with the highest concentrations of Na, while cluster 3 (17 % of the samples) groups the highest concentrations of K.

Five groups were also identified that share similar characteristics in terms of the concentrations of micronutrients Fe, Zn, Cu and Mn. However, no cluster is dominant, suggesting a more unequal distribution of the levels of these metals in the soil compared to macronutrients. Cluster 1 (17.3 % of samples) stands out as it groups the samples with the highest concentrations of Fe, Zn, Cu and Mn. The strongest correlation was found between Fe and Mn ($r = 0.98$), and important correlations were also observed between Zn and Fe ($r = 0.85$), Cu ($r = 0.84$) and Mn ($r = 0.76$) (Fig. S7). Fig. S5 shows that cluster 1 (17.3 % of the samples) has the highest concentrations of Fe, Zn and Mn. Cluster 2 (23.5 % of the samples) is shown below, followed by cluster 5 (17.9 % of the samples), cluster 3 (21.4 % of the samples) and finally cluster 4 (19.9 % of the samples). In the case of Cu, clusters 1, 4 and 5 account for 55 % of the samples.

With regard to HMs, the cluster analysis revealed the existence of seven groups, with clusters 1, 4 and 6 being the most representative because they included 75.6 % of the samples (Fig. S7). Cluster 7 (7.4 % of the samples) accounts for the samples with the highest concentrations of As and Pb, while cluster 3 (2.97 % of the samples) contains the highest concentrations of Cd. Cluster 2 (4.17 % of the samples) stands out as containing the highest concentrations of Cr and Ni, while cluster 5 (9.8 % of the samples) accounts for the highest concentrations of Ba and Al. It should be noted that Cr and Ni, and Ba and Al are the heavy metal pairs for which there is the strongest correlation ($r = 0.91$ and $r = 0.90$, respectively). In contrast, cluster 1 (23.2 % of samples) groups the samples with the lowest concentrations of all metals. Important correlation was also found between Ba and Co ($r = 0.76$); Co and Ni ($r = 0.87$); V and Al ($r = 0.76$), Cr, Ni, Co ($r = 0.8$). In Fig. S6 we can see that these metal pairs follow a similar dynamic in their cluster distribution.

Table 7 displays the concentrations of metals that characterize each identified cluster. Due to the lack of information available for the study area, it was not possible to compare our results with other reference values. However, the median values revealed significant diversity in the concentration of metals, which are important as reference values to guide soil prevention, protection and recovery work.

The complexity of the soil analysis is revealed in this study, which has multiple interrelated factors because the soils are exclusively used for farming, with particular characteristics in each agroecological region typical of the Andean countries, varying with altitude, geographic location, agricultural practices, etc. Each section of this study helps to complement our understanding of the variability of metal concentrations in soils of the department of Moquegua. The results, in the form of reference values, can be used to develop indicators or to establish local standards. This acquires even greater importance as it contributes to closing the gap in our knowledge of metal levels in agricultural areas influenced by copper mining, beyond the As, Cd, Pb and Ba covered by ECAs in Peru.

4. Conclusion

The study's spatial analysis indicated a consistent distribution of macronutrients (Ca, Mg, K, Na) in contrast to the marked variability seen in micronutrients (Fe, Cu, Mn, Zn) and heavy metals (Cd, Cr, Ni, Pb, As, Co, Ba, V, Al). Distribution maps were generated for each metal, pinpointing hotspots of elevated metal concentrations across agricultural zones. This data is instrumental for targeting soil management

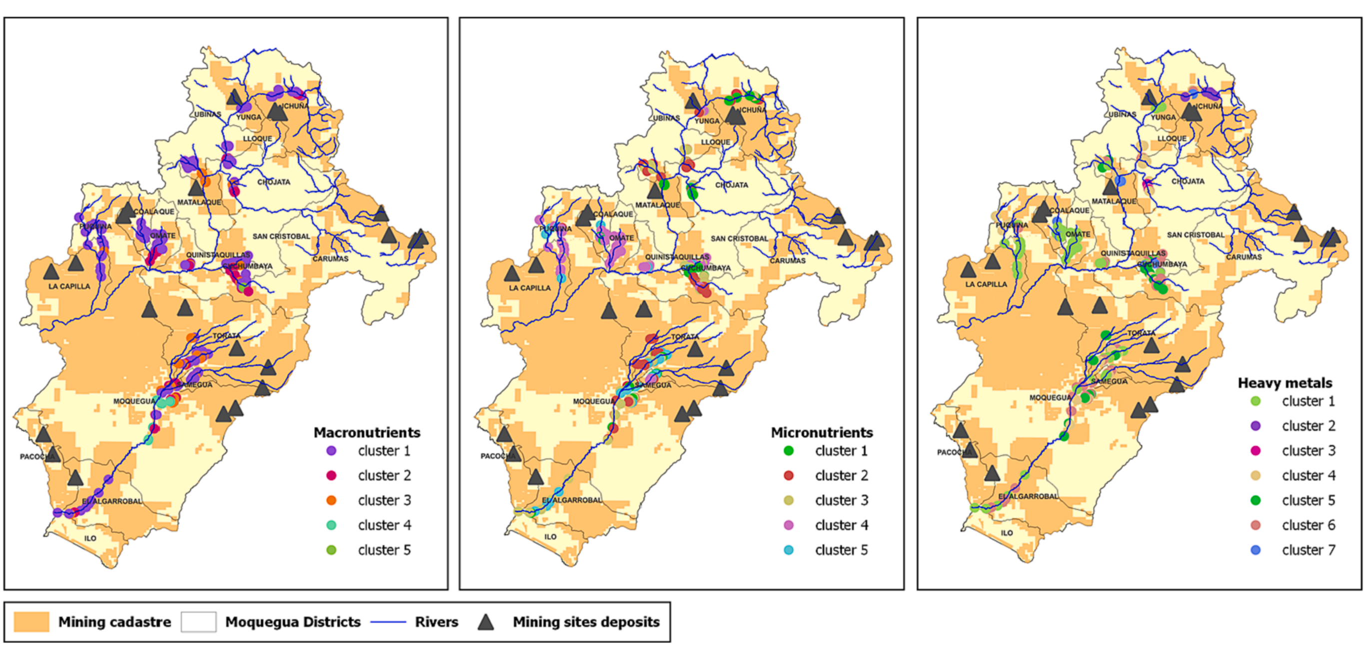


Fig. 7. Visualization of clusters of metals in the agricultural soils of Moquegua department.

Table 7
Reference values of metal concentration in agricultural soils of the department of Moquegua, obtained through cluster analysis.

Cluster group	Median concentration (mg/kg)																
	Macronutrients				Micronutrients				Heavy Metals								
	Ca	Mg	K	Na	Fe	Cu	Mn	Zn	Al	As	Ba	Cd	Cr	Co	Pb	Ni	V
Cluster 1	5,017.0	3,400.5	2,066.5	369.6	26,243.5	89.5	737.4	143.7	7,070.0	10.6	124.6	0.3	5.0	5.9	3.0	1.0	28.2
Cluster 2	15,908.5	7,437.0	2,382.5	612.8	22,306.0	42.9	646.3	64.9	15,363.0	13.8	180.2	0.3	25.8	18.1	50.2	28.1	85.3
Cluster 3	6,667.0	5,684.0	4,239.0	802.8	16,440.0	35.2	446.5	48.7	14,033.5	55.4	214.1	7.1	9.0	18.0	14.8	15.6	54.5
Cluster 4	24,187.0	8,657.0	3,459.0	3,824.0	11,437.0	46.3	221.8	44.0	13,701.0	15.2	187.2	0.3	10.0	11.9	12.6	10.9	57.7
Cluster 5	67,739.0	24,513.0	3,403.0	527.3	17,869.0	70.9	526.0	60.6	24,804.0	12.3	243.2	0.3	9.9	15.9	11.3	10.3	74.5
Cluster 6									12,630.0	8.9	163.9	0.3	6.6	8.0	3.0	1.0	43.5
Cluster 7									11,962.0	70.9	176.3	0.3	9.9	13.9	89.7	13.0	45.2

initiatives to diminish potential health hazards from crop contamination.

Additionally, the study underscored altitude's role in metal accumulation in soils spanning 9 to 3,934 m.a.s.l. Notably, clusters comprising 10.4 % of the samples surpassed the established Peruvian standard for As (50 mg/kg). However, when aligned with standards from countries like Ecuador and Canada (12 mg/kg), this fraction jumps to 50.3 %. Clusters that cross the Peruvian thresholds for Cd and Pb represent 3 % and 7.4 % of the samples, respectively. The cluster findings offer benchmark values for 17 metals, bolstering agricultural soil management at the local level. These benchmarks gain added significance given that current Peruvian guidelines set environmental quality standards for merely four metals in agricultural soils (As, Cd, Pb, and Ba).

Given the identified variability and potential risks, it is crucial to instigate proactive soil management practices in regions highlighted by the study, especially in those exceeding international standards. Regular monitoring, promoting awareness among farmers, and implementing sustainable agricultural techniques should be employed to safeguard both environmental health and food quality.

CRediT authorship contribution statement

Noelia S. Bedoya-Perales: Funding acquisition, Conceptualization, Investigation, Project administration, Writing – original draft, Writing – review & editing. **Alisson Neimaier:** Formal analysis, Data curation, Visualization, Software. **Diogo Maus:** Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Elias Escobedo-Pacheco:** Methodology, Investigation, Validation, Visualization, Project administration. **Karina Eduardo:** Investigation, Writing – review & editing. **Guilherme Pumi:** Formal analysis, Supervision, Data curation, Writing – original draft.

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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enmm.2023.100896.

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