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METAL CONTAMINATION IN SOILS OF THE JUNIN NATIONAL RESERVE - PERU

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ABSTRACT

Improper dumping of tailings from nearby mining companies into the rivers that flow into Lake Junín as well as improper management and discharge of the Upamayo hydroelectric dam can cause soil contamination. The aim of the study was to analyze metal pollution in the soils of the Junín National Reserve in Peru. Samples were taken at 10 points within the study area at 2 depths (0-15 and 15-30 cm) to assess the impact of metals on the soil. Concentrations of As, Cd, Cu, Hg, Pb, and Zn have exceeded the thresholds of the soil quality guidelines for the protection of the environment and human health according to Canadian regulations. Similarly, the ecological risk index revealed that the risk level for Cd, Cu, Hg, and Pb is severe and/or serious at both depths. The geoaccumulation index indicates that an accumulation of Cu, Zn, Pb, and Hg in the soils of the study area, indicating they are persistent pollutants. Furthermore, spatial distribution shows that the nearest sites to the pollutant sources were the most contaminated. Likewise, pH, texture and EC are factors influencing metal concentrations in soil. In conclusion, mining activity and other human actions have contaminated the soils near Lake Junín, impacting the environment and local communities. Although metal concentrations vary, the uniformity in their vertical distribution highlights the complexity of pollution.

Keywords: ecological risk index; geoaccumulation index; spatial distribution.

CONTAMINACIÓN CON METALES EN LOS SUELOS DE LA RESERVA NACIONAL DE JUNÍN – PERÚ

RESUMEN

El objetivo del estudio fue analizar la contaminación por metales en los suelos de la Reserva Nacional de Junín, Perú. Esta contaminación se debe a la descarga de relaves de empresas nacionales mineras en los ríos que desembocan en el Lago Junín, así como a la gestión inadecuada del embalse y las descargas en la represa Upamayo, que opera con fines energéticos. Se tomaron muestras en 10 puntos a diferentes profundidades (0-15 y 15-30 cm) para evaluar el impacto de los metales en el suelo. Se encontró que los niveles de As, Cd, Cu, Hg, Pb y Zn superan las normas de "Soil quality guidelines for the protection of the environment and human health" de la regulación canadiense. El índice de riesgo ecológico indicó que los niveles de Cd, Cu, Hg y Pb representan un riesgo severo y/o grave en las dos profundidades. El índice de geoacumulación sugiere que Cu, Zn, Pb y Hg se están acumulando en los suelos, indicándose como contaminantes persis-

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tentes. La distribución espacial muestra que los primeros puntos fueron los más contaminados. Asimismo, el pH, la textura y la conductividad eléctrica son factores que influyen en las concentraciones de metales en el suelo. En conclusión, la actividad minera y otras acciones humanas han contaminado los suelos cercanos al Lago Junín, afectando al medio ambiente y a las comunidades locales.

Palabras clave: índice de riesgo ecológico; índice de geoacumulación; distribución espacial.

INTRODUCTION

Lake Junin, also known as Chinchaycocha, is part of the Junín National Reserve (JNR) in Peru which hosts numerous endemic species and some endangered ones. According to the Organismo de Evaluación y Fiscalización Ambiental (OEFA, 2015), this lake has been subjected to a series of anthropogenic activities, including the construction of hydroelectric dams, railway lines, extraction of natural resources, discharge of mining tailings and sewage, and accumulation of garbage from adjacent towns. In this regard, it is important to recapitulate the historical events that have led to the contamination of Lake Junín and the surrounding soils.

In 2011, the Mayor of the Junín province denounced four mining companies (Volcán, Aurex, El Brocal, Doe Run) and public entities (Lira, 2023) since they were dumping their tailings into the San Juan, Blanco, and Colorado rivers, leading to metal deposition on the lake bottom, altering water quality, and affecting flora and fauna as specified by the Comisión de Pueblos Andinos, Amazónicos y Afroperuanos, Ambiente y Ecología (CPAAAAE, 2008). This ecological disaster contaminated the lake and affected the communities of Ondores, San Pedro, Carhuamayo, Ninacaca, Cochamarca, Churo, and Santa Clara, home to an estimated 20,000 to 30,000 residents (Castro et al., 2022). It resulted in the infertility of five thousand hectares of agricultural land and mass death of livestock, which negatively affected meat and wool business (CPAAAAE, 2008). Additionally, the Organismo Supervisor de la Inversión en Energía y Minería (OSINERGMIN) reported that the lake's water flow is managed by Electroandes and Electroperú which operates the hydroelectric Upamayo dam (CPAAAAE, 2008), without considering the environmental impact. Inadequate monitoring of these operations led to floodings and sediment accumulation in soils (Servicio Nacional de Áreas Naturales Protegidas por el Estado, 2011).

In 2015, an environmental assessment of the San Juan River basin was conducted (García et al., 2015), where concentrations of free cyanide, Cr, As, Cd, Hg, and Pb in soils were analyzed. In all sampling points, their concentrations exceeded the Environmental Quality Standards of Peru (Ministerio del Ambiente, 2017), and the presence of metals was associated with mining tailings from Pasco. As evidenced, Lake Junín and the surrounding soils are heavily contaminated with metals, prompting the need to analyze the presence of these contaminants in the soils adjacent to the lake, in order to ensure the quality of the receiving body. This survey will enrich and contribute new information to the existing knowledge of metal contamination in the soils surrounding Lake Junín.

MATERIALS AND METHODS

Study area

The study area is located on the shores of the northwest zone of Lake Junín (Figure 1). The selection of the 10 sampling points was made based on the "Inventory of mining-related environmental liabilities in the Junín National Reserve" (Ministerio del Ambiente, 2023), a study that identifies various areas affected by tailings. Five points (P1-P5) were taken from this inventory. The remaining sampling sites (P6-10) were determined based on the lake course (northwest-southeast) to assess contaminant dispersion. Table 1 shows the geographical location of each sampling site. Additionally, background level samples were taken at 3 sites that are far from the other sites, for calculating the ecological risk index; Table 2 indicates their geographical location.

Table 1. *Coordinates of the 10 sampling sites*
Tabla 1. *Coordenadas de los 10 puntos de muestreo*

Point	X Coordinate (m)	Y Coordinate (m)
P1	360372 E	8792646 N
P2	361036 E	8792395 N
P3	361557 E	8792434 N
P4	361892 E	8792485 N
P5	362444 E	8792364 N
P6	363558 E	8791177 N
P7	363870 E	8789969 N
P8	365048 E	8788514 N
P9	366090 E	8786690 N
P10	366959 E	8785552 N

Table 2. *Coordinates of the 3 background level points*
Tabla 2. *Coordenadas de los 3 puntos de nivel de fondo*

Point	X Coordinate (m)	Y Coordinate (m)
P11	386879 E	8765982 N
P12	386902 E	8766008 N
P13	386918 E	8765946 N

Figure 1 shows the map of the study area (red outline), as well as the 10 sampling sites.

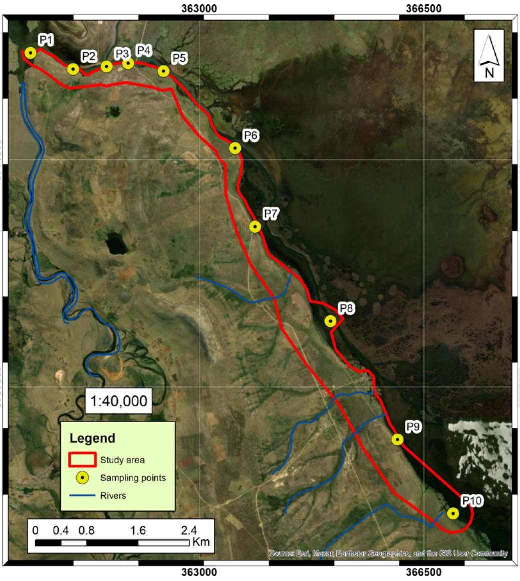

Figure 1. *Map with the location of the sampling sites within the study area*
Figura 1. *Mapa de la ubicación de los puntos de muestreo dentro del área de estudio*

Soil sampling

A soil auger was used for sample collection; soil samples were taken at 2 depths (0-15 cm, and 15-30 cm) at 10 points, with soil auger. Additionally, based on the guide for soil sampling (Ministerio del Ambiente, 2014) composite samples of both depths were collected at each sampling site. Similarly, composite samples were collected from the 3 background level sites. Samples were placed in ziplock bags and stored until analysis.

Soil physicochemical parameters

The pH and electrical conductivity (EC) of each soil sample were measured using a multiparameter device HANNA HI991301. Conductimetry was measured in three soil suspension dilutions ($EC_{1:1}$, $EC_{1:2}$, $EC_{1:5}$) using 10 mg of soil and 0.01 M KCl, as appropriate, in each dilution (10 mL, 20 mL, and 50 mL, respectively) (Carter & Gregorich, 2008).

Soil texture

Soil texture was determined using the Bouyoucos method. Composite samples from the 0-30 cm layer from all sites were used to determine the content of sand, clay, and silt. Fifty grams of soil sample and 100 mL of distilled water were added to a dispersion cup and mixed with 5 mL of sodium oxalate solution and 5 mL of sodium hydroxide solution. After that, distilled water was added to fill two-thirds of the cup's capacity. Next, the suspension was transferred to a sedimentation cylinder, and distilled water was added to reach 1000 mL. The suspension was then stirred for 5 minutes with a circular base wooden rod with holes. Subsequently, two readings were taken using a hydrometer and a thermometer, the first after 40 seconds and the second after 2 hours. With the collected data, the sand, clay, and silt content were determined using the following formulas (Beretta et al., 2014):

thermometer correction factor (FC): $FC = (LT - 20) * 0.2$ (1)

hydrometer correction factor (LHC): $LHC = LH + FC$ (2)

calculation of % sand, silt, and clay: $\%sand = 100 - (LHC1 * 2)$ (3)

$\%clay = LHC2 * 2$ (4)

$\%silt = 100 - (\%Sand + \%Clay)$ (5)

where LCH1 is the hydrometer correction factor at 40 seconds, and LCH2 is the soil texture was determined hydrometer correction factor at 2 hours. Finally, soil texture was determined with the soil texture triangle (Beretta et al., 2014).

Metal concentration analysis

The samples were sent to the laboratory of Servicios Analíticos Generales S.A.C., to determine the total concentrations of Al, As, Ba, Be, Cd, Ce, Co, Cr, Cu, Mn, Ni, Pb, Sb, Ti, V, and Zn at 0-15 cm and 15-30 cm soil depths. Method 200.7 Rev. 4.4 EMMC Version (1994) of EPA 3050-B (1996) was used, employing the Acid Digestion of Sediments, Sludges, and Soils technique for the Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. In the case of Hg, the Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique) 2007, EPA Method 7571B, was used. The results were compared with the guidelines established by the Canadian Environmental Quality Guidelines (Canadian Council of Ministers of the Environment, 2024), whose reference values (all expressed in mg kg^{-1}) for agricultural soils as those of this study are as follows: As = 12, Ba = 750, Be = 4, Cd = 1.4, Co = 40, Cr = 64, Cu = 63, Hg = 6.6, Ni = 45, Pb = 70, Sb = 20, V = 130, and Zn = 250.

Statistical analysis

The data were statistically analyzed using the IBM SPSS Statistics 25 software. Descriptive statistics were calculated, and the correlation between metal concentrations and both pH and EC was investigated.

Normality test: In order to perform the data analysis, it is first necessary to determine whether the data has a symmetric distribution; this is to decide whether to use parametric or non-parametric tests. Therefore, the Shapiro-Wilk test was used for each metal at the 2 considered depths, with a p-value = 0.05.

Correlation tests: A linear correlation analysis was performed between the concentrations of metals at the both sampling depths and the parameters pH and EC to determine the linear relationship and proportionality that exists between these variables. The Pearson correlation test (parametric data) and the Spearman correlation test (non-parametric data) were used for the 0-15 cm and 15-30 cm soil depths, respectively. Analyses of EC were performed with the Spearman test. For the present study, the following ranges will be considered: $R < 0.3$ indicates no correlation, $0.3 < R < 0.5$ indicates low correlation, $0.5 < R < 0.7$ indicates medium correlation, and $0.7 < R < 1$ indicates strong correlation.

Indexes

Ecological Risk Index: It is a tool used to measure the level of danger or threat faced by an ecosystem or a particular region due to various human influences and environmental factors. Its purpose is to provide a deeper understanding of how human activities, such as urban expansion, intensive agriculture, deforestation, pollution, and climate change, impact the health and stability of ecosystems (Canadian Council of Ministers of the Environment, 2024). The calculation formula is as follows:

$$E_r^i = T_r^i \frac{C_i}{S_i} \tag{6}$$

where E_r^i is the parameter for heavy metal contamination; C_i is the measured value and S_i is the reference value (in general, background values are taken as reference values); T_r^i is the toxicity coefficient of the heavy metal. Previous studies have determined the toxicity coefficients of various metals, indicating values as follows: Zn = 1, Ce = 1, Ti = 1, Mn = 1.5, V = 2, Cr = 2, Cu = 5, Co = 5, Pb = 5, Ni = 5, As = 10, Sb = 19, Cd = 30, Hg = 40 (Chen et al., 2023; Suseela et al., 2023; Wang et al., 2018; Zhou et al., 2020; Chen et al., 2020). The ecological risk index is classified into 5 grades: $E_r^i < 30$ it is low grade, $30 \leq E_r^i < 60$ it is mild grade, $60 \leq E_r^i < 120$ it is moderate grade, $120 \leq E_r^i < 240$ it is moderate severe grade and $E_r^i \geq 240$ is a severe grade (Yang et al., 2022).

Geoaccumulation Index: It is a tool that has been developed and employed by the scientific community specializing in environmental geochemistry and soil and sediment quality assessment. Its purpose is to identify the accumulation of chemical elements and assess their potential influence on the environmental surroundings (Hui et al., 2021). The basic formula for the Geoaccumulation Index (Igeo) is as follows:

$$I_{geo} = log_2\left(\frac{C_n}{1.5 * B_n}\right) \tag{7}$$

where C_n it is the measured concentration of the contaminant metal n (mg kg^{-1}) in the soil, B_n the background geochemical value (mg kg^{-1}) of the element. The geoaccumulation index is classified into 7 grades: $I_{geo} \leq 0$ (class 0) indicates an uncontaminated grade, $0 < I_{geo} \leq 1$ (class 1) indicates uncontaminated to moderately contaminated grade, $1 < I_{geo} \leq 2$ (class 2) indicates moderately contaminated grade, $2 < I_{geo} \leq 3$ (class 3) it is from moderately to highly contaminated grade, $3 < Igeo \leq 4$ (class 4) indicates highly contaminated grade, $4 < I_{geo} \leq 5$ (class 5) indicates highly to extremely contaminated grade, and $I_{geo} > 5$ (class 6) indicates an extremely contaminated grade (Hui et al., 2021).

Spatial distribution of the dispersion of pollutants

For the spatial distribution and dispersion of contaminants, the kriging tool available in the ArcMap 10.8 application of the ARCGIS Desktop software, was used.

RESULTS

Metal concentrations and compliance with Canadian regulations

Table 3 shows the metal concentrations that exceed Canadian regulations, listed for each sampling site and soil depth.

Table 3. *Metal concentrations exceeding regulations*
Tabla 3. *Concentraciones de metales que exceden las regulaciones*

Sampling site	Soil depth	
	0-15 cm	15-30 cm
P1	As, Cd, Cu, Hg, Pb and Zn	As, Cd, Cu, Hg, Pb and Zn
P2	As, Cd, Cu, Hg, Pb and Zn	As, Cd, Cu, Hg, Pb and Zn
P3	As, Cd, Cu, Hg, Pb and Zn	As, Cd, Cu, Pb and Zn
P4	As, Cd, Cu, Hg, Pb and Zn	As, Cd, Cu, Hg, Pb and Zn
P5	As, Cd, Cu, Hg, Pb and Zn	As, Cd, Cu, Hg, Pb, Sb and Zn
P6	As, Cd, Cu, Hg, Pb and Zn	As, Cd, Cu, Hg, Pb, Sb and Zn
P7	As, Cd, Cu, Pb and Zn	As, Cd, Cu, Pb and Zn
P8	As, Cd and Zn	As, Cd and Zn
P9	As, Cd, Cu, Pb and Zn	As and Cd
P10	As, Cd, Pb and Zn	-

At 0-15 cm soil depth, metals such as As, Cd, and Zn exceed soil quality guidelines at all sites, while Hg only exceedes from the first to the sixth point. Copper is evident in 8 out of 10 sites, and Pb in 9 out of 10. On the other hand, at 15-30 cm soil depth, As and Cd exceede up to the 9th site, Zn up to the 8th site, while Cu and Pb exceede up to the 7th site, and Hg up to the 6th site. It is worth mentioning that Sb was also identified in excess at 15-30 cm only at sites 5 and 6.

Soil texture

The texture of each sampling site was determined, and the results are shown in Table 4.

Table 4. *Soil texture at each sampling site*
Tabla 4. *Textura del suelo de los puntos de muestreo*

Sampling point	% Sand	% Clay	% Silt	Soil Texture Classes
P1	59.04	19.52	21.44	Sandy Loam
P2	44.36	27.64	28.00	Loam
P3	58.16	3.64	38.20	Sandy Loam
P4	74.36	13.52	12.12	Sandy Loam
P5	57.36	19.76	22.88	Sandy Loam
P6	52.56	21.52	25.92	Sandy Clay Loam
P7	60.76	25.52	13.72	Sandy Clay Loam
P8	68.48	23.60	7.92	Sandy Clay Loam
P9	80.92	15.48	3.60	Sandy Loam
P10	60.16	25.52	14.32	Sandy Clay Loam

Sand is the predominant particle size at all sites, reaching up to 80% at P9. Clay had a maximum value of 27%, while silt reached a maximum content of 38%. Thus, soils are “Sandy Loam” (5 sites), “Silty Clay Loam” (4 sites), and “Loam” (1 site). This implies that the soil in the study area has large particles and exhibits macropores, leading to greater drainage and aeration capacity.

Statistical analysis

Table 5 presents descriptive mean, standard deviation and the results of the Shapiro-Wilk test.

Normality test: The results of the Shapiro-Wilk test indicated that the concentrations of metals Al, Ba, Be, Cd, Ce, Co, Cr, Mn, Ni, Pb, Ti, and V at both depths follow a symmetric distribution. On the other hand, for metals As, Cu, Hg, Sb, and Zn, the values did not exhibit a symmetric distribution.

Table 5. *Normality test results*
Tabla 5. *Resultados de la prueba de normalidad*

Metal	Soil Depth (cm)	Mean	Standard deviation	Shapiro - Wilk test	
				W	p value
Al	0-15	12525.20	5447.52	0.95	0.63
	15-30	14035.66	6841.20	0.89	0.16
As	0-15	166.98	89.91	0.95	0.64
	15-30	308.81	305.75	0.89	0.16
Ba	0-15	239.34	45.86	0.93	0.44
	15-30	307.33	89.26	0.86	0.07
Be	0-15	0.59	0.31	1.00	0.97
	15-30	0.57	0.36	0.91	0.27
Cd	0-15	17.78	12.74	0.90	0.23
	15-30	17.42	12.98	0.94	0.52
Ce	0-15	32.75	12.14	0.93	0.48
	15-30	31.98	15.84	0.93	0.46
Co	0-15	7.46	3.71	0.95	0.70
	15-30	5.25	3.83	0.96	0.73
Cr	0-15	8.56	4.02	0.98	0.98
	15-30	17.19	12.55	0.86	0.07
Cu	0-15	581.44	370.38	0.88	0.13
	15-30	850.50	753.70	0.90	0.19
Hg	0-15	15.53	15.81	0.90	0.20
	15-30	16.53	22.79	0.77	0.01
Mn	0-15	1726.40	469.85	0.97	0.88
	15-30	1144.79	851.49	0.94	0.50
Ni	0-15	14.66	7.08	0.98	0.95
	15-30	10.13	6.61	0.95	0.71
Pb	0-15	824.11	696.2	0.91	0.30
	15-30	1677.85	1801.19	0.85	0.05
Sb	0-15	5.80	5.29	0.84	0.04
	15-30	9.45	10.45	0.86	0.09
Ti	0-15	28.00	12.00	0.95	0.62
	15-30	30.06	11.92	0.92	0.37
V	0-15	34.75	11.34	0.96	0.76
	15-30	44.25	19.68	0.92	0.36
Zn	0-15	3516.33	1774.28	0.83	0.03
	15-30	2663.72	2296.52	0.82	0.03

Correlation tests: Results of the Pearson and Spearman normality tests are presented in Tables 6, 7, and 8; negative signs indicate an inverse relationship. A low inverse correlation was observed between pH and Cu, Sb, and V, while a moderate inverse correlation was found between pH and Cd, Mn, Pb, and Zn at 0-15 cm soil depth. At 15-30 cm soil depth, Ba, Cd, Cr, Cu, Sb, Co, and Mn showed a low correlation with pH, while As, Pb, V, Be, and Ce have a moderate correlation. A strong correlation was observed between pH and Ni.

Regarding EC, it was found that at the depth of 0-15 cm, metals As, Cu, Hg, Mn, Ti, V, Co, Cr, and Ni have a low correlation, while metals Cd, Pb, Sb, and Zn showed a moderate correlation. For the depth of 15-30 cm, metals Cr, Sb, Zn, and Ce had a low correlation; metals As, Cd, Cu, Pb, and Ni had a moderate correlation, and V was the only metal one showing a strong correlation with this parameter.

Table 6. *Correlation results for the metals Al, As, Ba, Be, Cd, and Ce*
Tabla 6. *Resultados de correlación para los metales Al, As, Ba, Be, Cd y Ce*

Soil parameter	Soil Depth (cm)	Metals					
		Al	As	Ba	Be	Cd	Ce
pH	0-15	0.01	-0.25	-0.01	-0.05	-0.65	0.15
	15-30	0.14	-0.52	-0.31	0.52	-0.39	0.53
EC	0-15	0.11	0.43	-0.21	-0.23	0.67	-0.16
	15-30	0.24	0.60	0.14	-0.18	0.56	-0.39

Table 7. *Correlation results for the metals Co, Cr, Cu, Hg, Mn and Ni*
Tabla 7. *Resultados de correlación para los metales Co, Cr, Cu, Hg, Mn y Ni*

Soil parameter	Soil Depth (cm)	Metals					
		Co	Cr	Cu	Hg	Mn	Ni
pH	0-15	-0.07	0.20	-0.33	-0.26	-0.50	-0.07
	15-30	0.30	-0.46	-0.43	-0.20	0.38	0.72
EC	0-15	-0.33	-0.35	0.45	0.46	0.43	-0.36
	15-30	-0.15	0.49	0.68	0.17	0.09	-0.62

Table 8. *Correlation results for the metals Pb, Sb, Ti, V and Zn*
Tabla 8. *Resultados de correlación para los metales Pb, Sb, Ti, V y Zn*

Soil parameter	Soil Depth (cm)	Metals				
		Pb	Sb	Ti	V	Zn
pH	0-15	-0.70	-0.48	-0.12	-0.30	-0.50
	15-30	-0.67	-0.43	-0.15	-0.50	-0.27
EC	0-15	0.62	0.62	0.43	0.47	0.57
	15-30	0.62	0.41	0.12	0.87	0.35

Ecological Risk Index

Tables 9 and 10 indicate the distribution of the ecological risk index of metals at the two soil depths, also showing the average risk level and its degree at each sampling site.

Table 9. *Statistics of the ecological risk index of metals (0-15 cm)*
Tabla 9. *Estadísticas del índice de riesgo ecológico de metales (0-15 cm)*

Metal	Distribution of ecological risk levels					Medium risk level	
	Low	Mild	Moderate	Serious	Severe		
As	10	-	-	-	-	16.19	Low
Cd	-	-	2	3	5	288.28	Severe
Ce	10	-	-	-	-	9.63	Low
Co	6	4	-	-	-	24.21	Low
Cr	10	-	-	-	-	2.83	Low
Cu	2	1	-	7	-	127.56	Serious
Hg	-	2	1	-	7	6212	Severe
Mn	10	-	-	-	-	11.95	Low
Ni	10	-	-	-	-	10.11	Low
Pb	8	1	1	-	-	22.08	Low
Sb	10	-	-	-	-	5.95	Low
Ti	10	-	-	-	-	2.5	Low
V	10	-	-	-	-	1.28	Low
Zn	4	6	-	-	-	38.34	Mild

At the depth of 0-15 cm, Cu presented a severe level of risk, while Cd and Hg were the most concerning metals as they pose a severe risk. Similarly, each metal identifies carries a certain risk level, with the least concerning being As, Ce, Co, Cr, Mn, Ni, Pb, Sb, Ti, and V. This implies that minor ecological risk exists at the depth of 0-15 cm as most metals are at a low-risk level.

Table 10. *Statistics of the ecological risk index of metals (15-30 cm)*
Tabla 10. *Estadísticas del índice de riesgo ecológico de metales (15-30 cm)*

Metal	Distribution of ecological risk levels					Medium risk level	
	Low	Mild	Moderate	Serious	Severe		
As	4	3	3	-	-	44.47	Mild
Cd	-	1	-	2	7	533.39	Severe
Ce	6	4	-	-	-	5.33	Low
Co	7	3	-	-	-	21.99	Low
Cr	10	-	-	-	-	5.45	Low
Cu	3	-	1	-	6	432.17	Severe
Hg	-	2	1	-	7	8264.50	Severe
Mn	9	1	-	-	-	16.45	Low
Ni	10	-	-	-	-	4.99	Low
Pb	3	1	-	-	6	732.68	Severe

Sb	5	3	2	-	-	31.82	Mild
Ti	10	-	-	-	-	1.29	Low
V	10	-	-	-	-	2.69	Low
Zn	3	2	-	5	-	88.41	Moderate

At the depth of 15-30 cm, metals Cd, Cu, Hg, and Pb pose the greatest danger to ecosystems, as they present severe risk levels. Zn is considered moderate, while Cd is categorized as mild. The other metals do not have significant values that could pose ecological risk; these include Ce, Co, Cr, Mn, Ni, Ti, and V. Therefore, at the depth of 15-30 cm, there is a considerable ecological risk, raising environmental concerns.

Geoaccumulation Index

Tables 11, and 12 display the geoaccumulation index of metals at both soil depths, also indicating the average risk level and its degree at each sampling point.

Table 11. *Statistics of the geoaccumulation index of metals (0-15 cm)*
Tabla 11. *Estadísticas del índice de geoacumulación de metales (0-15 cm)*

Metal	Distribution of geoaccumulation level							Average geoaccumulation índex	
	Class 0	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6		
As	4	6	-	-	-	-	-	-0.17	Unpolluted
Cd	-	2	1	4	3	-	-	2.32	Moderately to heavily polluted
Ce	-	-	2	7	1	-	-	2.58	Moderately to heavily polluted
Co	1	1	4	4	-	-	-	1.49	Moderately polluted
Cr	6	4	-	-	-	-	-	0.33	Unpolluted
Cu	-	2	-	1	-	7	-	3.49	Heavily polluted
Hg	2	1	-	-	1	-	6	4.73	Heavily to extremely polluted
Mn	-	-	1	9	-	-	-	2.36	Moderately to heavily polluted
Ni	3	5	2	-	-	-	-	0.24	Unpolluted to moderately polluted
Pb	3	-	5	1	1	-	-	0.81	Unpolluted to moderately polluted
Sb	10	-	-	-	-	-	-	-2.95	Unpolluted
Ti	3	4	3	-	-	-	-	0.60	Unpolluted to moderately polluted
V	10	-	-	-	-	-	-	-1.29	Unpolluted
Zn	-	-	-	1	2	2	5	4.43	Heavily to extremely polluted

As shown in Table 11, values of geoaccumulation range from uncontaminated to extremely contaminated. Metals with the highest contamination range are Cu, Zn, and Hg, while Ce and Mn are moderately contaminated, and the rest of the metals show minimal geoaccumulation. This depth is less concerning due to the low amount of geoaccumulation.

Table 12. *Statistics of the geoaccumulation index of metals (15-30 cm)*
Tabla 12. *Estadísticas del índice de geoacumulación de metales (15-30 cm)*

Metal	Distribution of geoaccumulation level							Average geoaccumulation índex	
	Class 0	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6		
As	4	-	3	2	1	-	-	0.22	Unpolluted to moderately polluted
Cd	1	-	2	1	2	4	-	2.98	Moderately to heavily polluted
Ce	1	1	4	4	-	-	-	1.60	Moderately polluted
Co	2	1	4	3	-	-	-	0.61	Unpolluted to moderately polluted
Cr	4	3	2	1	-	-	-	0.51	Unpolluted to moderately polluted
Cu	-	2	1	-	1	-	6	4.45	Heavily to extremely polluted
Hg	2	1	-	-	1	-	6	4.57	Heavily to extremely polluted
Mn	2	1	-	1	5	1	-	2.08	Moderately to heavily polluted
Ni	8	2	-	-	-	-	-	-1.51	Unpolluted
Pb	1	1	1	1	-	-	6	4.72	Heavily to extremely polluted
Sb	5	3	2	-	-	-	-	-1.60	Unpolluted
Ti	8	2	-	-	-	-	-	-0.31	Unpolluted
V	6	4	-	-	-	-	-	-0.28	Unpolluted
Zn	1	-	1	-	1	2	6	4.74	Heavily to extremely polluted

Table 12 shows four metals that are present in extremely contaminated soils, or have the highest geoaccumulation, namely Cu, Hg, Pb, and Zn. There is also geoaccumulation of other soils classified as “moderately contaminated” or “uncontaminated”. Therefore, at this depth 15 cm to 30 cm, there is already a metal geoaccumulation.

Spatial distribution

The analysis of the spatial distribution of metals presenting a severe or high ecological risk index was conducted. This was done to gain a deeper understanding of the contaminants distributed in the study area, which in turn allows the identification of zones with higher contamination levels, thereby facilitating the development of efficient remediation strategies. Firstly, Figure 2 illustrates the spatial distribution of metals Cd, Hg, and Cu at the soil depth of 0-15 cm.

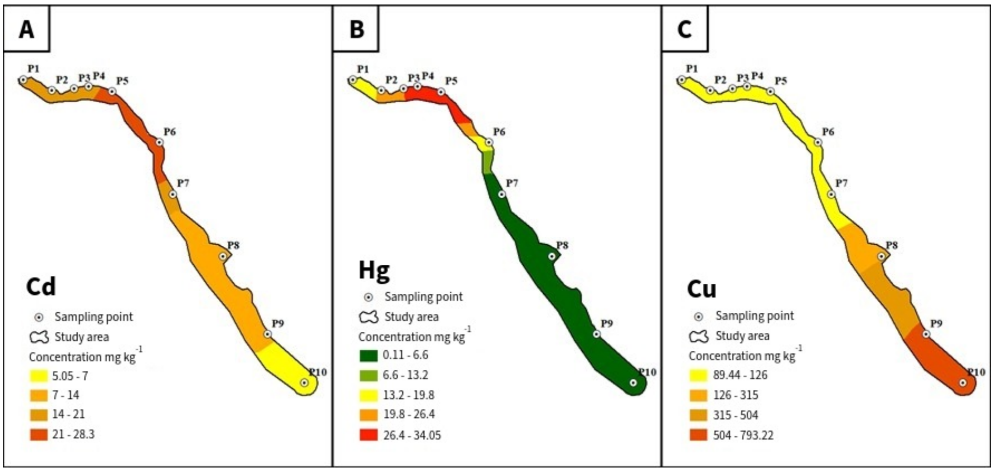

Figure 2. *Spatial distribution of (A) Cd, (B) Hg, and (C) Cu, at a sampling depth of 0-15 cm.*
Figura 2. *Distribución espacial de (A) Cd, (B) Hg y (C) Cu, a una profundidad de muestreo de 0-15 cm*

The concentration of Cd in the first four sites exceeds Canadian soil quality standards by fifteen times, reaching up to 20 times in sites 5 and 6. In the latter sites, there is a reduction, but still not in compliance with the regulations, as in site 10 it is five times higher than the established limit according to Figure 2A. On the other hand, Hg exceeds the maximum allowed concentration by up to five times, but only in the first five sites. From site 7 onwards, the concentrations of Hg do not exceed the maximum levels, as shown in Figure 2B. As for Cu, it exceeds Canadian guidelines by two times in the first seven sites, reaching up to twelve times the allowed limit in the last point, as shown in Figure 2C. Secondly, Figure 3 shows the distribution of metals Cd, Hg, Pb, and Cu in the soil depth of 15-30 cm.

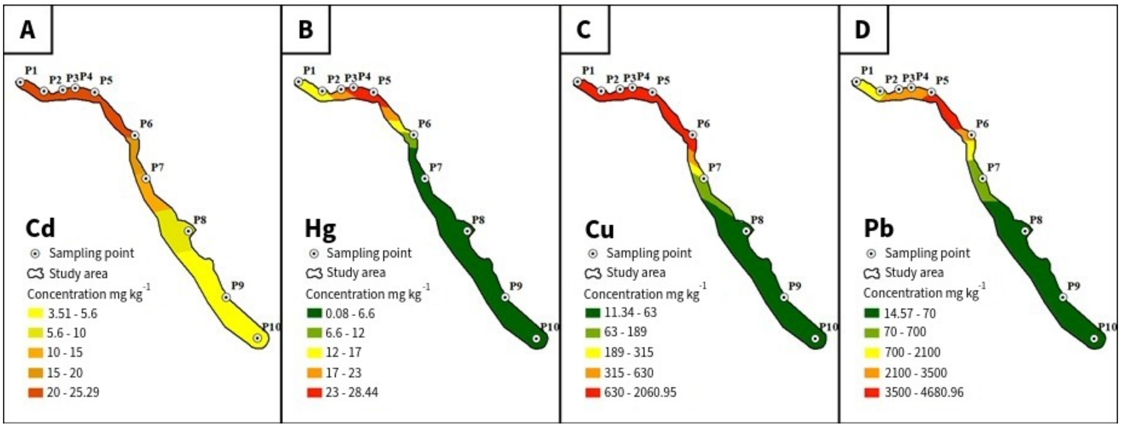

Figure 3. *Spatial distribution of (A) Cd, (B) Hg, (C) Cu, and (D) Pb, at a sampling depth of 15-30 cm.*
Figura 3. *Distribución espacial de (A) Cd, (B) Hg, (C) Cu y (D) Pb, a una profundidad de muestreo de 15-30 cm.*

In the second sampling depth, Cd concentration continues to exceed the standards by eighteen times in the first six sites, surpassing by seven times at site 8, and reaching four times in the last two sites, as shown in

Figure 3A. As for Hg, it exceeds four times in the first five sites, and similarly to the first depth, the soil quality guidelines are met from point 7 onwards, as depicted in Figure 3B. For Cu, there is a significant variation because the exceedance is 33 times in the first six sites, and only from site 8 onwards values found are below the maximum allowed, as reflected in Figure 3C. Regarding Pb, as shown in Figure 3D, it exceeds 50 times in the first four sites, reaching 67 times at site 5, and similar to Cu, the standards are met from site 8 onwards.

DISCUSSION

Compliance with regulations and relationship with previous studies

Metals such as Ba, Be, Co, Cr, Ni, and V were not detected at significant concentrations in the present study, likely because mine tailings do not contain these contaminants at concerning levels. Similarly, an investigation conducted by OEFA in 2015 (García et al., 2015) found that metals such as Ba, Be, Co, Cr, Ni, and V did not exceed the standards of the Canadian Environmental Quality Guidelines (CEQG) for soils, further supporting the conclusion that the soil in the study area does not exhibit significant contamination by these metals. In contrast, both this study and the OEFA investigation observed that metals such as As, Cd, Cu, Hg, Pb, and Zn exceeded environmental quality standards, indicating substantial soil contamination by these elements. Likewise, a study conducted in China found that soils adjacent to mining facilities exhibited elevated concentrations of As, Cd, and Pb (Di et al., 2023). These findings suggest that mining activity could be a major source of heavy metal contamination, and the Peruvian case may be no exception. It is possible that metal contamination has impacted soils near Lake Junín, potentially damaging local environment.

In the depth of 15-30 cm, the results are related to the soil composition in those areas, given that the first seven sites show a proportion of between 40 and 50% of clay and silt, indicating that metals were absorbed in the surface layers of the soil. In the deeper layers of the soil, in some places concentrations exceeding the limits established by the regulations were found. This suggests that the soil's finer particles, such as clay and silt, play a significant role in metal retention near the surface, while coarser particles at deeper levels may limit the migration of contaminants. However, metal concentrations exceeding regulatory limits at certain points in deeper layers highlights localized contamination events, possibly linked to historical mining activities or fluctuating groundwater levels, which can mobilize metals and transport them to lower soil strata. These findings indicate a complex interaction between soil composition and metal mobility, which deserve further investigation on the potential pathways of contamination in these deeper layers.

Correlation

At the depth of 0-15 cm, pH had a negligible influence on most metal concentrations, with only Cd, Mn, Pb, and Zn showing a moderate impact. EC had a low influence on several metals but exerted a moderate influence on Cd, Pb, Sb, and Zn. At the depth of 15-30 cm, pH showed a moderate influence on metals such as As, Pb, V, Be, and Ce, but a strong influence on Ni concentrations in the soil. Similarly, EC exhibited a moderate influence on concentrations of As, Cd, Cu, Pb, and Ni, with a strong influence on V. These findings suggest that the relationship between pH and EC and metal concentrations is complex and varies with depth and site. Generally, pH tends to increase slightly with depth, likely due to the leaching of organic acids in the surface layers, while EC often decreases as soluble salts accumulate near the surface.

Such fluctuations may indeed impact the mobility of these elements. For instance, acidic conditions can enhance the solubility of metals, particularly Cd and Pb, while a shift to more neutral pH levels may facilitate the mobility of As. Differences in metal concentrations observed at each sampling depth indicate the necessity to explore correlations between soil texture and metal retention; finer soils rich in clay typically exhibit higher metal adsorption capacity, thereby potentially reducing the mobility of metals compared to coarser soils.

Moreover, the redox status of the soil is crucial in this context. The mobility of elements such as Cr can vary significantly based on their oxidation state — as Cr(III) is less mobile and Cr(VI) is highly soluble and capable of redistributing in deeper soil layers. This highlights the importance of considering the interactions between pH, EC, texture, and redox potential in future studies to fully understand the factors influencing metal availability and contamination in the soil. As the findings align with previous research by Das et al. (2023) and Smedley and Kinniburgh (2002), there is a clear need to further investigate how these parameters collectively influence the ecological risks associated with heavy metal contamination, particularly in areas impacted by mining activities.

Some authors found a strong correlation between pH and Ni, Cd, and Ag, with salinity showing a moderate inverse correlation with Mn and Cu and strong inverse correlations with Cd and Ag (Hui et al., 2021). Similarly, Wang et al. (2017) found a significant inverse correlation between pH and metals Cd, As, Hg, Zn, Cu, and Cr (Wang et al., 2017). No correlation was found between pH and the analyzed metals (Cu, As, Pb and Cr) at a depth of 0 to 20 cm, while strong inverse correlations with the four metals were found at a depth of 20 to 40 cm (Wang et al., 2017).

Ecological Risk Index

According to the results obtained from the ecological risk index, it is evident that the potential contamination is higher due to metals such as Cd, Hg, Pb, and Cr. These metals have become a significant threat to humanity and the environment (Hoque et al., 2023). First, both Cd and Hg show significantly high concentration values, at 0-15 cm and 15-30 cm soil depths, resulting in a severe risk level in both of them. Additionally, other metals like Cu and Pb also pose severe risks at 15-30 cm soil depth. Following this analysis, soil with high concentrations of both metals could lead to environmental problems (Puga et al, 2006). These results indicate that the presence of Cd and Hg both studied soil depths represents a serious ecological risk in these areas, as mentioned by the Canadian Council of Ministers of the Environment (2018) and Chen et al. (2020).

The high concentration of these metals generates numerous negative effects on ecosystems and humans through damage to the food chain, food quality, and agricultural production (Sheng et al, 2023). In general, metals such as As, Co, Cu, Mn, Ni, Sb, Ti, and V exhibit moderate or low risk levels at the soil depths analyzed in this study. This suggests that although they are present, their concentration does not pose a severe risk to the environment in these specific areas (Hoque et al, 2023). It is important to highlight that the risk levels vary according to the depth of the soil. Overall, it is observed that the risk levels tend to increase as the soil depth increases, suggesting that contamination is more severe in deeper layers (Iyama et al., 2021). This raises an important question as to why contamination appears to be more pronounced at greater depths. One potential explanation is the mobility of these elements. Certain combinations of pH and salinity conditions can promote the mobility of specific metals, particularly in sandy soils, which typically have high infiltration rates and low cation exchange capacity (CEC). The dominant sandy texture may facilitate the downward movement of contaminants, allowing metals to leach deeper into the soil profile. Under these conditions, elements such as As, Cd, and Pb can remain soluble and mobile, further exacerbating contamination at deeper soil layers.

Geoaccumulation Index

At deeper soil layers, the levels of Cu, Hg, Pb, and Zn are particularly concerning due to their extreme contamination (Hui et al., 2021). Results from this study show moderately high levels of Cd, Ce, and Mn accumulation at different sites which indicates a concerning presence of these metals and underscores the need for immediate action to address their contamination. The rest of the metals represent a low degree of contamination that is not alarming. Therefore, the diversity in metal contamination highlights the complexity of pollution in the area and underscores the need for specific management approaches for each metal (Binici & Pulatsü, 2022).

Spatial distribution

Regarding the spatial distribution of metals at of 0-15 cm, in the case of Cd, an area of 768,800 m² exceeded the Canadian soil quality standard by fifteen times, with this concentration occurring in the first four sites, and an area of 716,900 m^2 exceeds the standard by twenty times (at sites 5 and 6). However, for the last site covering 878,200 m^2, it is five times higher than the standard; these results reflect that the entire study area is contaminated by Cd, which can alter the microbiological soil processes, and affect nearby. A similar pattern was identified for Hg, with metal presence exceeding five times the allowed concentration at sites 3 to 5, covering an area of 470,600 m^2. However, from site 7 onwards, covering 3,342,300 m^2, Hg concentrations do not exceed the standard; this represents an area greater than 70% which is free of Hg contamination. Regarding Cu, one-third of the total area under study, corresponding to 1,639,600 m^2, doubles the maximum Cu concentrations, and the remaining area is contaminated by up to twelve times, generating toxicity in flora and negatively altering soil microbial activity.

On the other hand, as for the spatial distribution of metals at 15-30 cm soil depth, the contamination with Cd was found throughout the whole study area, with an area of 1,011,300 m^2 exceeding the standard by 20 times, being the area of greatest environmental concern. Besides, the contamination with Cd is also present in an area of 1,975,700 m^2 in which the values exceeded the standard by five times. As for Hg, Cu, and Pb, although much of the area under study no longer shows contamination by these metals (3 422 500 m^2, 2 859 200 m^2, and 2 954 700 m^2 for each metal, respectively), small areas were identified where soil quality guidelines are not met; variations are explained due to factors such as rainfall, geography, soil, organic matter, and soil density.

CONCLUSIONS

In summary, various studies suggest that mining activity, along with other human activities such as the construction of hydroelectric dams and natural resource extraction, may have significantly contributed to the presence of metals in the soils near Lake Junín. However, further research is needed to conclusively confirm the impact of such activities on the contamination in this area, which not only affects the environment but also the local communities that depend on the land for their livelihoods. Despite the variability in metal concentrations between depths, there is uniformity in the vertical distribution of metals in the soil. This suggests that pollution processes have homogeneously affected different soil layers, which could have important implications for pollution management and remediation. The influence of pH, texture, E.C., and other edaphological and geochemical factors on metal concentrations in the soil is highlighted. These results emphasize the importance of considering the interaction of multiple factors in the distribution and availability of metals in the soil, which can complicate remediation processes. The assessment of ecological risk and the geoaccumulation index confirm the presence of Cd, Hg, Pb, and Zn as the most concerning metals for the environment in the study area. These metals present contamination levels that pose a significant risk to human health and local ecosystems. The spatial distribution reveals areas of high metal concentration, especially in the surface layers of the soil, indicating a greater influence of human activities in these regions. On the other hand, areas where contamination is less pronounced are identified, which can be attributed to factors such as local geography, soil-water interaction, physicochemical properties of the soil, and contaminant dynamics. Given the evidence of metal contamination in soils surrounding Lake Junín, it is imperative to implement remediation measures to reduce metal concentrations and mitigate associated environmental and social impacts. These measures must be specific and tailored to the characteristics of the study area, considering factors such as the depth of contamination and the spatial distribution of metals.

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