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Heavy Metal Pollution Assessment in Lake Rinconada in the Southern Andes, Peru

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ABSTRACT

The study was conducted in Lake Rinconada, a glacial lake affected by artisanal and small-scale gold mining activities in the southern Andes in Peru. The objectives of the study were to investigate the spatial distribution of heavy metals (As, Cu, Hg, Pb and Zn) in water and sediments and to assess the degree of metal pollution and ecological risk using the geoaccumulation and potential ecological risk indexes. The concentrations of As and Hg in sediments from Lake Rinconada exceeded the Canadian sediment quality regulations, whereas the concentrations of As, Hg and Pb in water and sediments from the mining-affected tributary, Lunar de Oro River exceeded the Peruvian and Canadian guidelines for water and sediments quality respectively. According to the geoaccumulation and potential ecological risk indexes, Lake Rinconada is extremely polluted by As and Hg, and the pollution is mostly concentrated in the northern part of the lake, where the mining-affected Lunar de Oro River flows into the lake. Concentrations of Pb are also high in the northern part of the lake, suggesting that the nearby gold mining town is a source of pollution. The results of this study allows to report that Lake Rinconada is completely deteriorated.

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INTRODUCTION

Fresh water is one of the most important resources in the world given that 0.01% of this vital resource exists on the *earth's* surface (Weekley and Li, 2019) and it is mostly stored in lakes and lagoons (Karlovi and Markovi, 2022). Some lakes such as glacial lakes are very important as they store considerable amounts of fresh water from glaciers (Wilson et al., 2018) and are usually located as headwaters of important basins (Drenkhan et al., 2019). The waters that flow from these lakes supply its populations, contributing to the development of their agricultural and domestic activities (Lintern et al., 2016).

The activities commonly developed in areas near the glacial lakes are livestock, tourism and mining (Arroyo Aliaga, 2014; Ehrbar et al., 2018; Schoolmeester et al., 2018). Mining includes the processes of extraction and recovery of valuable metals, being gold the main mineral which indirectly generates the release of heavy metals such as As, Cu, Hg, Pb and Zn

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(Kayembe et al., 2018; Rahim et al., 2019; Tapia et al., 2019; Toledo Orozco & Veiga, 2018). When their concentrations increase, they affect species, the health of populations and the balance of the surrounding ecosystems (Eghbal et al., 2019; Lintern et al., 2016). Once heavy metals enter aquatic ecosystems, they are transported long distances and transformed through biogeochemical processes, affecting the quality of water and sediments (Custodio et al., 2020).

Given that metals precipitate in water, the highest concentration accumulates in sediments (Pejman et al., 2015) at the bottom waterbodies (Konhauser et al., 1997). These elements can be reincorporated into the water column by internal hydrodynamic processes such as resuspension (Schoolmeester et al., 2018), which could cause these elements to enter the food chain due to their accumulation in living organisms (Karbassi et al., 2014), generating a risk to human health and wildlife. Consequently, it is important to identify the sources of contamination, and to determine the mechanisms involved in the origin of these metals from each source (Lintern et al., 2016).

According to Dai et al. (2018), an appropriate identification of sources of pollution includes the assessment of metal concentrations in sediments using validated indices, to later apply a combination of statistical and geostatistical methods to demonstrate their distribution and how they are transported.

Other studies, such as the one by Wang et al. (2014) suggest applying geo-accumulation (Igeo) and potential ecological risk index (RI) in sediments to determine the degree of heavy metal contamination and to identify the elements responsible for the ecological deterioration of a lake. Furthermore, Tendaupenyu et al. (2018) suggest using the ordinary kriging interpolation method to determine dominant sources of pollution using spatial distribution maps because it has little bias. The combination of these methods would increase the likelihood of a good evaluation of the concentrations of heavy metals. International standard regulations (CCME, 1998) were used to evaluate the quality of sediments because in Peru such standards do not exist.

Named after the highest settlement in the world (Willer & Takahashi, 2018), la Rinconada is one of the most important non-industrial mining centers located in the Southern Peruvian Andes. Mining has been carried out in that town since the Inca times (Regal, 1995). However, the small-scale mining center are located upstream of lake Rinconada have caused society problems due to the pollution of the water sources since this lake is the headwaters of a basin. The problems are the result of the many illegal mining concessions and their rudimentary processes for extraction and recovery processes (Cuentas and Velarde, 2017).

The contamination could be the result of large amounts of neglected rocky material from within the mines, residuals from the gold recovering process using mercury, and the lack of sewage infrastructure. Therefore, it is important to know the degree of pollution of potentially toxic metals and to identify the sources of contamination. Previous investigations carried out in the area focused in characterizing concentrations of some metals, mainly mercury, in the tributaries and effluents of Lake Rinconada. The results were only compared with regulations (Brousett-Minaya et al., 2021; Gammons et al., 2006; Loza and Ccancapa, 2019), suggesting that there is an incomplete understanding of pollution levels of the area (Salas-Ávila et al., 2021).

The objectives of the study were to: (1) determine the degree of contamination; and to (2) assess the spatial distribution of heavy metals in Lake Rinconada by applying geo-accumulation and potential ecological risk indices, as well as geostatistical methods.

METHODS AND MATERIALS

Description of Study Area

The study was in Lake Rinconada (-14° 38 'S, -69° 29 'W), a glacial lake formed by the retreat of the Ananea glacier in the region of Puno in southern Peru (ANA, 2011). The lake is located at 4636 m above sea level, has a surface area of 516 ha (ANA, 2014; Loiza and Galloso, 2008), and gives origin to the Ramis River basin, one of the most important basins that feeds Lake

Titicaca, the highest lake in the world. Lake Rinconada is fed by two tributaries: the first one is the Lunar de Oro River (A, B, C), whose water originates from the Ananea glacier and drains the goldmining area La Rinconada. The second river (D), comes from the Casablanca lagoon, a natural reservoir that is used for livestock activities. The single effluent (E) is the Ramis River, which flows out the southern part of the lake. One of the main economic activities in the area, primarily in the southern part of the lake, is raising livestock. The natural pasture lands and water sources such as wetlands (Fidel and Rodriguez, 2008) support the breeding of camelids and sheep (Loiza and Galloso, 2008). Also, mining and metallurgical activities have been carried out since the Inca times (Regal, 1995). In this area, there are two settlements that were developed without proper planning, they are Lunar de Oro and La Rinconada (Wieland, 2020) and near these settlements, activities such as underground mining and the recovery of gold-bearing material by amalgamation are common.

La Rinconada, at 5100 m above sea level, is the highest settlement in the world with 5000 inhabitants (Mallet et al., 2021). Mining activities in the area increased in 2009 (Goyzueta and Trigos, 2009) causing people to move there and start the settlement. This town does not have sewage and drainage infrastructure thus the discharges flow to Lake Rinconada (Goyzueta and Trigos, 2009). The micro-basin, where the lake is located, is divided into four lithostratigraphic units (Gobierno Regional de Puno (GRP), 2015), where moraines deposits predominate with 43.39% of the basin´s area, followed by the Ananea and Sandia formations with 32% and 16% respectively, coming from the ages of the Upper Quaternary Ordovician (Antenor et al., 1996).

Sample Collection

Sediment and water samples were collected from five locations, were selected in, the tributaries and effluents. Following the guidelines of Peruvian national protocols to monitor quality of water resources (PMRH) (ANA, 2016), sample site A was designated in the tributaries and effluents of lake Rinconada. Sites B and C were at the beginning and middle area of the Lunar de Oro River. Finally, also following specific PMRH guidelines, sites D and E were located, one 50 m before the origin of the lake and the other one 50m after the end of the lake.

Samples were collected during the 2021 rainy season. At each sample site, 50 ml of water was collected and subsequently filtered using Whatman paper (0.45 μm). They were stored in falcon-type centrifuge tubes previously washed with MiliQ water; after that1% of HNO3 was added for conservation. Similarly, 250g of surface sediments (0 – 5 cm) from tributaries and effluents, were collected at each sampling point using a plastic spoon and stored in WhirlPAK bags.

As shown in Fig. 1., 22 additional sampling sites were established in order to cover the entire lake. This was done using the systematic transect method used in other studies such as the one by Tendaupenyu et al. (2018). In addition, the PMRH recommendations were considered, which suggest taking samples at a distance of 25 m from tributaries/effluents. Therefore, three points were considered in each transect with points at 250 m within both shores of the lake and at the center of these. Sediment samples from the bottom of the lake were collected with an Eckman dredge and stored in WhirlPAK bags. All samples were kept at 4°C, transferred in a cooler, and stored in the dark until laboratory analysis was performed.

Sample treatment and heavy metal analysis

The level of concentrations of the heavy metals: Arsenic (As), Copper (Cu), Mercury (Hg), Lead (Pb) and Zinc (Zn) were determined in a commercial laboratory (ALS Global, Arequipa, Peru; ISO/IEC 17025 and ISO 9001:2000.3). Water samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using method 6020B (EPA, 2014). The sediments from each sample site were analyzed with the natural Graulometric composition of each site in order to determine the measure pollution (Salas-Mercado et al., 2022). In addition, the sediment samples were analyzed by atomic emission spectroscopy with inductively coupled plasma (ICP-

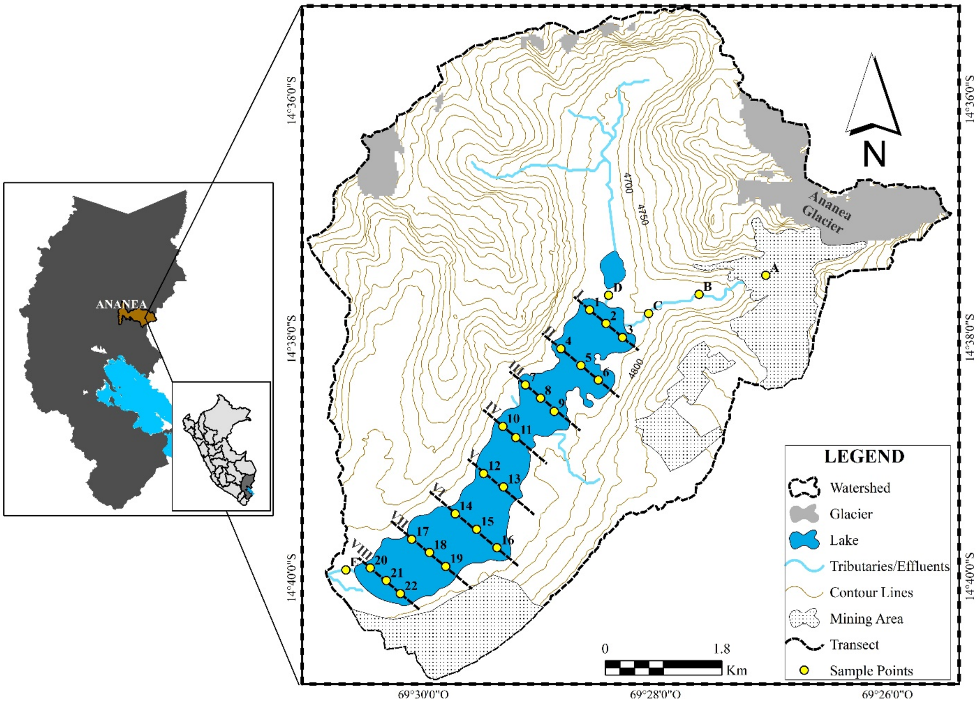

Fig. 1. Micro-basin of Lake Rinconada, distribution of sample sites in tributaries (A, B, C, D), effluent (E) and inside Lake Rinconada (from 1 to 22); Transects (I to VIII)

OES) with methods 3050B (EPA, 1996) and 7471B (EPA, 2007). The analytical range for each element is reported in the supplementary material.

Assessment of heavy metals pollution in water and sediment samples

Pollution in water samples was assessed according to the Environmental Quality Standards (ECA) used to protect rivers in the coast and highlands of Peru (MINAM, 2017). In the case of sediment, because Peru does not have sediment quality regulations, pollution was assessed according to the Canadian regulations (CCME, 1998). These guidelines provide concentration limits for elements that are likely to cause biological effects. There are two thresholds: the first one is the probable effect levels (PELs), which indicate the degree to which adverse effects are continuous on the aquatic ecosystems, and the second one is the threshold effect levels (ISQG o TELs), which refers to the degree to which adverse effect may occasionally occur.

Determination of Pollution levels

In this research, the geo-accumulation (I_{geo}) index proposed by Forstner and Muller (1974) was used to determine the level of metal contamination in sediments. This index consists of comparing the concentrations found with the background geochemical values. Based on the type of slate rock predominant in the study area (Antenor et al., 1996; GRP, 2015), the geochemical values suggested by Turekian et al. (1961) were used. The values were calculated using the following equation:

$$I_{geo} = log_2 \left[\frac{C_{metal}}{1.5\, x\, B_{metal}} \right]$$

Where, C_{metal} is the concentration of explored element (mg kg-1), B_{metal} is the background geochemical value of the explored element (mg kg-1) and 1.5 is the correction factor of the background geochemical value, which is used to reduce the effects of possible lithogenic variations. The values of I_{geo} are evaluated through seven classes that are shown in Table 1 (Forstner & Muller, 1974).

In addition, the potential ecological risk index (RI) developed by Hakanson (1980) was used. This is a tool that helps identify the areas that need control actions against contamination and classify the metals that are causing it. RI is calculated using the following equations:

$$E_r^i = T_r^i \, x \frac{C_n^i}{B_n^i}$$

$$RI = \sum_{i=1}^{n} E_r^i$$

Where, E_r^i represents the ecological risk factor and T_r^i describes the toxic response factor of each metal. For this study we use the following values: As =10, Cu =5, Hg = 40, Pb =5, and Zn = 1 (Ahamad et al., 2020; Mendoza et al., 2020; Yang et al., 2020). Finally, C_n^i and B_n^i denote the concentrations and the background geochemical values of each metal respectively. The values of E_r^i and RI are classified in ranges that indicate the degree of ecosystem risk as shown in Table 2 (Hakanson, 1980).

Spatial Analysis

The ordinary interpolation kriging method (Bhattacharjee et al., 2019; Wu and Li, 2013) was used to analyze the sediments of Lake Rinconada in order to determine the spatial distribution of heavy metal concentrations, and to suggest their sources. The heavy metal concentration and the RI values were imported with their respective coordinates into ArcGis V 10.8.1 software under license No. 1585448458. Subsequently, the data were transformed into a logarithmic scale and trends were verified for better interpolation results. Finally, the octant search method was

Table 1. Classification of Geo-accumulation index values and environmental conditions.

Class	Value I_{geo}	Condition
0	$I_{geo} < 0$	Unpolluted
1	$0 \leq I_{geo} < 1$	Unpolluted to moderately polluted
2	$1 \leq I_{geo} < 2$	Moderately polluted
3	$2 \leq I_{geo} < 3$	Moderately to heavily polluted
4	$3 \leq I_{geo} < 4$	Heavily polluted
5	$4 \leq I_{geo} < 5$	Heavily to extremely polluted
6	$I_{geo} \geq 5$	Extremely polluted

Table 2. Ecological risk factor (Er) and potential ecological risk index (RI) classification.

Er		RI	
Values	Risk Factor	Values	Ecological Risk
Er < 40	Low	RI < 110	Low
40 ≤ Er < 80	Moderate	110 ≤ RI < 200	Moderate
80 ≤ Er < 160	Considerable	200 ≤ RI < 400	Considerable
160 ≤ Er < 320	High	RI ≥ 400	Very high
Er ≥ 320	Very high		

applied for each sampling site to obtain the interpolation of the concentrations of heavy metals in order to delineate/outline the concentration limits throughout the extension of the lake.

Statistical analysis

The descriptive statistics of the concentrations of each heavy metal of water and sediment samples of all water sources described above were determined. In addition, Spearman´s correlation analysis was applied to determine the relationship between heavy metals. Prior to this, the normality of the concentrations was verified with the Shapiro-Wilk analysis, and the data were standardized under the z scale in order to avoid the large differences of the concentrations of the metals. Spearman's correlation coefficient is represented by ρ which takes values between ± 1; and the significance is represented by p. All statistical analyses were performed with R software version 4.0.2.

RESULTS AND DISCUSSION

Concentrations of heavy metals in water simples Table 3 shows the average concentrations of heavy metals present in the water samples of the tributaries (A, B, C, D) and the effluent (E) of lake Rinconada. The concentrations of toxic metals listed in a descending order for Site A are: Zn > As > Cu > Pb > Hg. This sample site is located within the mining area and its concentration levels exceed the ECA values for water. The results suggest that the metals come from mining and metallurgy residuals, and from wastewater. For sites B and C the concentration values in descending order are: Zn, As, Pb, Cu and Hg exceeding national regulations. This could be connected to the residuals transported downstream to Lunar de Oro River since sites B and C are inside the river but before lake Rinconada.

The results are consistent with other investigations conducted in Lunar de Oro River where metals Hg, Pb and Zn exceeded the ECA recommendations for water (Gammons et al., 2006; Loza and Ccancapa, 2020). Hg, Pb and Zn exceed the national regulations in tributary D, which is the Casablanca lagoon. It should be noted that, at this site, livestock farming is common but it is progressively declining. In effluent E, Hg is the metal that exceeds the limit recommendations. This would suggest that the presence of Hg at sites D and E may be the result of burning gold and mercury amalgams, thus its volatilization would be brought downstream (Veiga, 1997) and deposited in water sources and soils in the form of Hg^{+2}.

Table 3. Concentration of heavy metals in water samples from the tributaries and the effluent of Lake Rinconada.

Sampling Sites (river)	As (ug/L)	Cu (ug/L)	Hg (ug/L)	Pb (ug/L)	Zn (ug/L)
A (Lunar de Oro)	243.1±1	114.9±7	6.4±0.6	51.2±3	3986±240
B (Lunar de Oro)	237.9±1	12.7±2	2.4±0.2	20.3±1	1613±100
C (Lunar de Oro)	150.3±7	13.4±2	2.6±0.2	21.7±1	1402±89
D (Casa Blanca)	1.0±0.6	13.9±2	1.2±0.2	7.6±0.7	562±37
E (effluent)	4.3±0.7	2.6±1	1.3±0.2	1.1±0.4	33±20
Min	1.0	2.6	1.2	1.1	33
Max	243.1	114.9	6.2	51.2	3986
Average	127.3	31.5	2.8	20.4	1519.2
Wáter ECA*	150	100	0.1	2.5	120

* *Peruvian government recommended limits.*

Concentration of heavy metals in sediment samples

Tributaries and effluents

The average concentrations of metals from the tributaries and effluent sediments are presented in Table 4 where the concentrations of heavy metals from sample site A (within the mining area) in descending order are: As > Zn > Pb > Hg > Cu. While the descending order from site B is: As > Zn > Pb > Cu > Hg, and from site C is: As > Pb > Zn > Hg > Cu. This suggests that the metals might have been transported downstream from the mining areas because the concentrations at sites B and C located within Lunar de Oro River increase their values drastically being the main element As which has the highest value at site C.

As values, in all the sampling sites, exceed the PEL threshold for sediments given by the Canadian guidelines. The presence of As may be related to the weathering of the large volumes of mineral waste (rocks) left and neglected in the open, since this material derived from the interior of the Andean mountains contains minerals such as arsenopyrite (Herail et al., 1989; INGEMMET, 1980).

In addition, Hg values of the sampling sites of Lunar de Oro River were above the PEL levels. These results could indicate that Hg comes mainly from the metallurgy activities because the recovery of gold-bearing material happens through the formation of gold amalgamation with Hg (Wade, 2013). This process is accomplished using rudimentary equipment such as the quimbalete (a grindstone) and the mill (Cuentas and Velarde, 2017) where mercury is dispersed in the water and remains in the tailings (fine material). Another source of Hg would come from the gold traders (amalgam burners) (ISAT, 2002) who work in the towns of Lunar de Oro and La Rinconada.

Pb only exceeds PEL value at sites B and C, sites that are located downstream of the town; and the concentrations might be due to the leaching of urban waste and domestic wastewater (Nasrabadi et al., 2010) . Because these towns do not have municipal waste deposits or a sewage network (Goyzueta and Trigos, 2009), the channels of the streets are used for the disposal of waste, which then flow into the stream, This concurs with Drozdova et al. (2019), who mentions that Pb is one of the metals present in domestic wastewater. The ISQG is surpassed by Cu and Zn at sites B and C; the cause for this values might be because of the erosion in the slopes

Table 4. Concentration of heavy metals in surface sediments of the tributaries and the effluent of Lake Rinconada.

Sample sites		**As (mg/kg)**	**Cu (mg/kg)**	**Hg (mg/kg)**	**Pb (mg/kg)**	**Zn (mg/kg)**
A (Lunar de Oro)		4199	15.1	20.3	42.4	70.5
B (Lunar de Oro)		3898	45.4	27.1	120	127.9
C (Lunar de Oro)		22342	41.6	51.1	283.7	140.7
D (Casa Blanca)		49.7	13	0.15	11.2	113.7
E (effluent)		78.4	15.3	0.08	18.1	91.8
Min		49.7	13.0	0.08	11.2	70.5
Max		22342	45.4	51.1	283.7	140.7
Average		6113	26.1	19.7	95.1	108.9
CCME*	PEL	17.0	197	0.49	91.3	315.0
	ISQG	5.9	35.7	0.17	35.0	123.0
Background values**		13.0	45.0	0.4	20.0	95.0

**Threshlods recommended by the Canadian Guidelines for the sediment quality*

***Background values suggested by Turekian et al. (1961)*

that channel the stream, since minerals such as chalcopyrite and sphalerite can be found in its superficial geology (Gammons et al., 2006; INGEMMET, 1980).

Lake Rinconada

The metal concentrations of the 22 surface sediments samples collected from Lake Rinconada are shown in Table 5, where the average values in descending order are: As > Zn > Cu > Pb > Hg. 100% of the sampling sites analyzed from Lake Rinconada exceeded PEL values of As, while 91% and 81% of them surpassed the values of Hg and Zn, respectively. Cu concentrations exceed the ISQG level in 91% of the sample sites and Pb in 86% of them. The results agree with what was determined by Brousett-Minaya et al. (2021), who mention that the surface sediments of the northern part of the lake are potentially contaminated by As, Cu, Hg, Pb and Zn in a natural and anthropogenic way. The results of Spearman correlation indicate that As has a strong association

Table 5. Concentration of Heavy Metals in surface sediments from Lake Rinconada

Sample Sites		**As (mg/kg)**	**Cu (mg/kg)**	**Hg (mg/kg)**	**Pb (mg/kg)**	**Zn (mg/kg)**
1		1511	60.5	41.5	66.2	726.0
2		719.6	22.3	8.1	46.2	76.6
3		719.7	20.3	40.8	28.9	74.3
4		2360	68.1	33.9	73.7	658.9
5		2883	56.8	38.8	59.8	552.2
6		2206	116.1	14.8	85.8	1372
7		685.7	113.3	22.1	62.8	1042
8		2275	86.7	20.8	67.6	763.1
9		5355	88.8	4.7	69.6	443
10		388.8	85.8	3.4	43.5	772.3
11		183.5	63.2	0.8	54.6	509.6
12		565.2	52.3	0.5	44.7	349.5
13		305.3	96.9	11.9	40.1	676.3
14		542.8	91.2	1.9	42.8	1031
15		954.4	84.3	1.8	48.8	676.4
16		353.8	70.7	1.2	35.5	677.1
17		448.5	73.0	1.6	47.9	140.2
18		434.8	84.4	1.2	48.6	765.6
19		436.1	80.6	0.9	45.9	744.8
20		208.3	59.5	1.1	25.6	589.8
21		312	97.0	1.9	37.6	934.5
22		166	38.1	0.47	21.5	204.2
Average		1091.6	73.2	11.6	49.9	626.3
Max		5355	116.1	41.5	85.8	1372
Min		166	20.3	0.5	21.5	74.3
CCME	PEL	17	197	0.49	91.3	315
	ISQG	5.9	35.7	0.17	35	123
Background Values (Turekian et al., 1961)		13.0	45.0	0.4.0	20.0	95.0

with Hg and Pb (r>0.77 - 0.79; p<0.01), which suggest that these metals come from the mining gold exploitation and recovery residuals, as well as from the wastewater and other domestic waste. Furthermore, the relationship between Cu and Zn (r>0.87; p<0.01), suggests that they derive from natural sources such as soil erosion, since it is within the metallogenic area where Lake Rinconada is located (Acosta et al., 2009; GRP, 2015; Mendoza et al., 2020). This study´s findings report that the concentrations of heavy metals in sediments of Lake Rinconada are among the highest of those reported for lakes adjacent to mining activities in South America (Table 6).

Determination of the contamination levels

Geo-accumulation Index

Fig. 2 shows the classification of the contamination level of each heavy metal, in the sediments sampled in tributaries and in the effluent. The average values of the tributaries are presented in decreasing order as follows: As (6.9±3.5) > Hg (3.5±4.3) > Pb (1.3±1.7) > Zn (-0.5±0.5) >

Table 6. Ranges of heavy metal concentrations in Lake Rinconada compared to other Latin American Lakes considered very polluted.

Lake	Country	As (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	References
Macanillal	Venezuela	-	33 – 62	-	20 – 71	-	(Narayan et al., 2020)
Cardonales	Venezuela	-	32 – 55	-	21 – 40	-	
Junín	Peru	0.9 - 119	6.2 – 372	-	4.9 – 65	16.3 – 203.6	(Custodio et al., 2019)
Mallorquin	Colombia	-	18.9 – 45.9	0.1 – 0.2	1.3 – 1.7	50.3 - 95	(Fuentes-Gandara et al., 2021)
Rinconada	Peru	166-5355	20.3 – 116.1	0.5 – 41.5	21.5 – 85.8	74.3 - 1372	This study

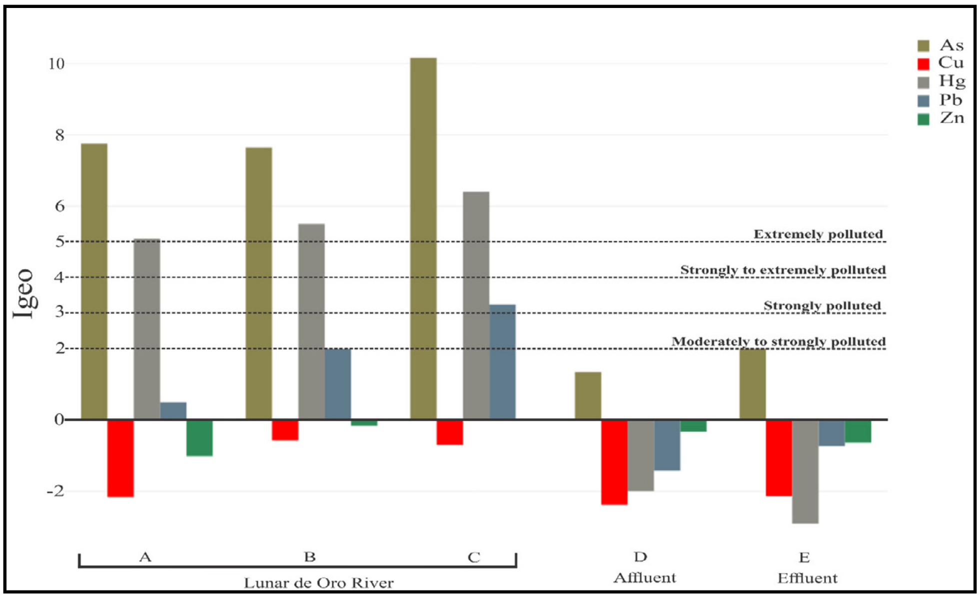

Fig. 2. Geo-accumulation index of metals in sediments from the tributaries and the effluent.

Cu (-1.4±0.9). These denote that all the sample sites of the Lunar de Oro River are extremely contaminated by As and Hg, suggesting that there is anthropogenic contamination coming from mining and nearby towns (Gammons et al., 2006). Pb levels are in the moderate to heavily polluted range at sites B and C of the Lunar de Oro river, which would confirm that this element could come from residuals related to mining.

On the other hand, the contamination levels of metal at sampling site D (tributary) is caused by As. This site is moderately polluted, which would suggest that this element is predominant in the southern Andes and that its origins are natural (Dalmiro A. et al., 2014) because this is an area located far from mining facilities. Also, site E (effluent) falls in the range of moderately to heavily polluted, which suggests that surface sediments are being transported downstream and increasing their concentration values at this point. This finding would concur with (Gammons et al., 2006), who mention that heavy metal contamination comes from Lake Rinconada since it stores tons of sediment. In contrast, element values to less than zero or negative would indicate that there is no increase in concentration due to anthropogenic contribution (Salas-Mercado et al., 2022).

Fig. 3. shows the I_{geo} values of metals of the surface sediments taken from Lake Rinconada, where the results, in descending order are: As (5.1±1.4) > Hg (2.8±2.2) > Zn (1.8±1.2) >Pb (0.7±0.5) >Cu (0.0±0.66). The highest I_{geo} values are found in the northern part of the lake, which indicate that it is through the Lunar de Oro River that As and Hg are transported into the lake. Also, we can infer that this part of the lake is in an extremely polluted condition and moderately contaminated by Zn. It is worth noting that starting at site 9 these metals would be accumulating, due to the morphology of the bottom of the lake that prevents sediments from being transported downstream along with their high concentrations. On the other hand, Pb is in the range from uncontaminated to moderately contaminated, except at point 9, where it seems to be accumulating just as As and Hg are.

The results of the geo-accumulation index revealed that As exceeds the base values of the slate sedimentary rock with a value of 13 mg/kg, due to its high concentrations in sediments found in the three hydraulic sections (tributaries, effluents and lake). These results agree with Santos-Frances et al. (2017) who mention that the Peruvian Andes have high concentrations of heavy metals in soils compared to other parts of the world. This is because the geological age of the area dates back to the Late Ordovician to the Silurian periods before the formation of the Andes (Ramos, 2008). In this area volcanic activity was strong, and important deposits of

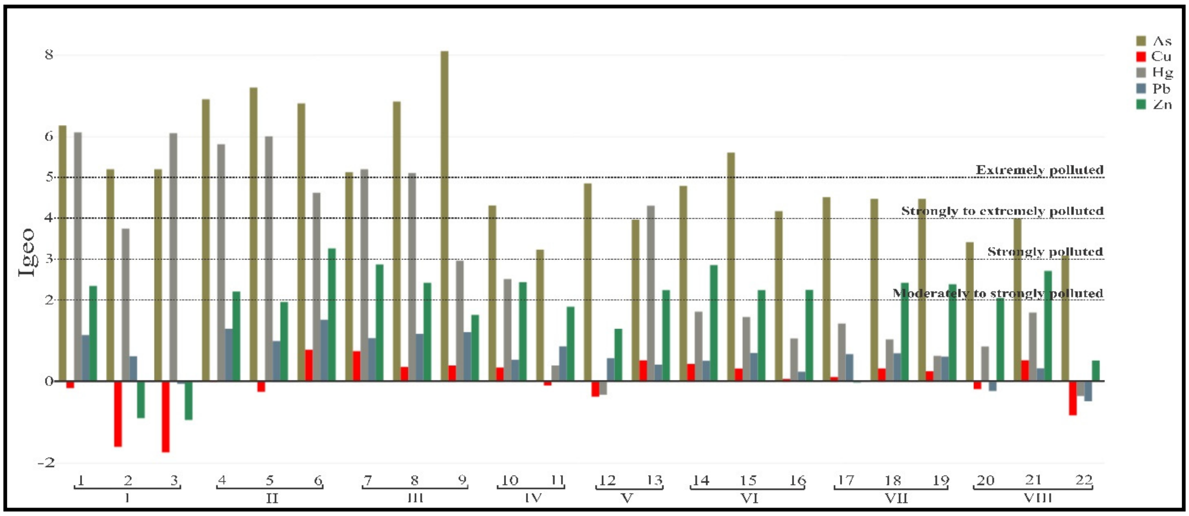

Fig. 3. Geo-accumulation index of metals in sediments from Lake Rinconada.

arsenic sulfide minerals were formed (ATSDR, 2013; Herail et al., 1989).

The presence of As in water sources would come from two sources: the natural erosion of Andean soils, and the disintegration of clearings and tailings from mining (Zuzolo et al., 2017). Likewise, the degree of contamination could be due to the fact that over the years metallurgical activities were carried out near the river and the lake. The major supply for these rudimentary and traditional techniques is mercury, and it is used to recover the gold-bearing material where a percentage of the mercury volatilizes and the other recovers the gold from the rock (Gammons et al., 2006). On the other hand, the values of Zn, Cu and Pb represent a low degree of pollution that could be due to the lithology of that area, which is rich in these elements (Acosta et al., 2009; Quispe-Zuniga et al., 2019). All this would suggest that the increase in concentrations that influence the I_{geo} is the product of soil erosion generated by anthropogenic activities and domestic wastewater discharges (Brousett-Minaya et al., 2021).

Potential ecological risk index

The values obtained from the calculation of the ecological risk factor (Er), which identifies the heavy metals that could cause a risk of ecological contamination for each sample site, are shown in Fig. 4. The results suggest that the Lunar de Oro River is at a very high risk of contamination due to the presence of As and Hg. Likewise, the effluent from Lake Rinconada (E), which is also the water source of the Ramis River, has a moderate level ecological risk due to As though this may increase over time. Contamination by Cu, Pb and Zn represent a low risk level, which suggests that the lake receives these metals but the aquatic fauna would not have problems and could coexist. The potential ecological risk, which indicates the level of risk caused by the set of elements at each sampling site, would show and confirm that the Lunar de Oro River has a very high ecological risk. This would result in the inexistence of and the inappropriate development of aquatic life, with the likelihood of adverse effects from the consumption of water from this source.

When calculating the ecological risk factors of Lake Rinconada sample sites (Fig. 5.), these revealed that 54.5% and 45.5% of the sampling sites have very high degrees of As and Hg, respectively. The degree of ecological risk is between low and moderate when evaluating Cu,

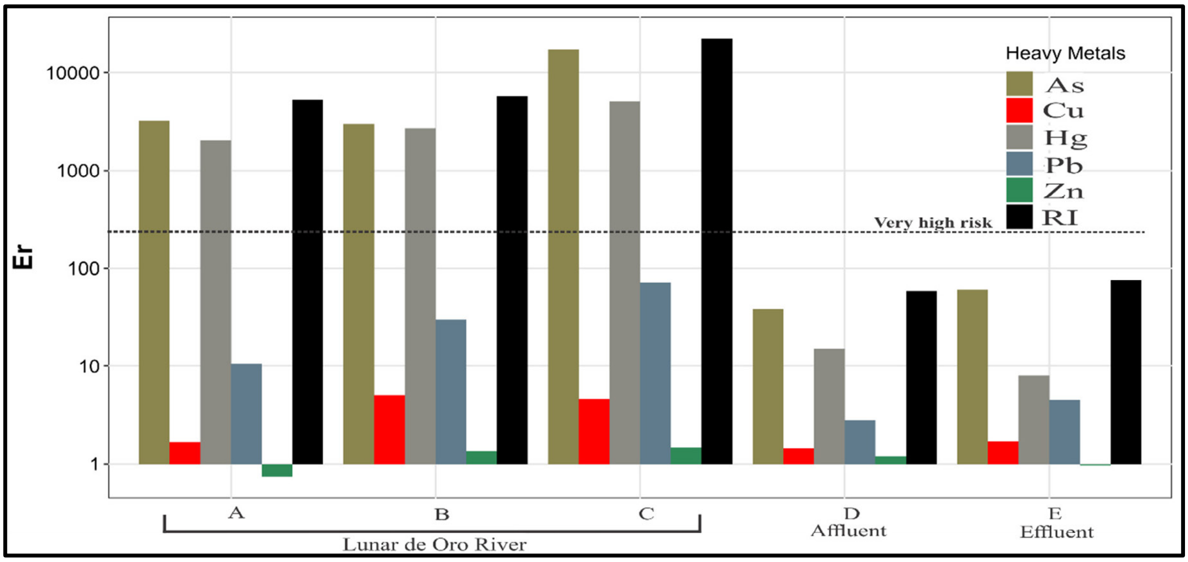

Fig. 4. Values of the Ecological Risk Factor and the Potential Ecological Risk of the tributaries and effluent sediments.

Pb and Zn. The grouping of heavy metals (RI) suggests that 86.4% of the entire lake is at a very high-risk level (RI≥400) which suggests that heavy metals could enter the food chain through bioaccumulation in grasslands and through fish found in the area.

The results of the ecological risk factor corroborate the results of the I_{geo}, where it is evident that contamination by heavy metals is produced mainly by the presence of As and Hg. These metals are generated by the development of mining activities, which are responsible for the negative biological effects that occur in the bodies of water. Because of that, Okonkwo et al. (2021) and Tan & Aslan (2020) recommend evaluating sediments with this index to consider appropriate monitoring strategies and subsequently propose technological, social and political action plans in order to reduce pollution. These metals represent a latent risk to health and the ecosystems, since the concentrations of metals in the sediments could increase through the continuous landslides and the accelerated melting of the Ananea glacier. The increase in flow and the effects of sediment transport, such as resuspension, could cause the incorporation of these elements into the lake's water column. Once there, the elements would be transported downstream, possibly entering the food chain, and affecting the inhabitants in their socioeconomic activities (Fazeli et al., 2019).

Spatial Analysis

Fig. 6. shows the spatial distribution of the content of As, Cu, Hg, Pb, Zn and the potential ecological risk (RI) found in the sediment samples of Lake Rinconada. The highest concentrations of Cu and Zn are distributed in the middle of the lake, which would be the result of the erosion in the steep slopes that channel the lake (Vilca et al., 2021). This in turn, confirms that the contribution of these metals is of natural origin due to the erosion of the lithology present the area (GRP, 2015). The concentrations of As, Hg and Pb were higher in the samples taken from the upper end of the lake than the ones taken from lower end which could be the result of the mining activities in that side of the lake. High RI levels of As, Hg and Pb have been found in the samples and being these the main elements for pollution and bioaccumulation (Rodriguez et al., 2018), there is an imminent risk of these elements entering the food chain since these are transported downstream from the lake to the nearby towns.

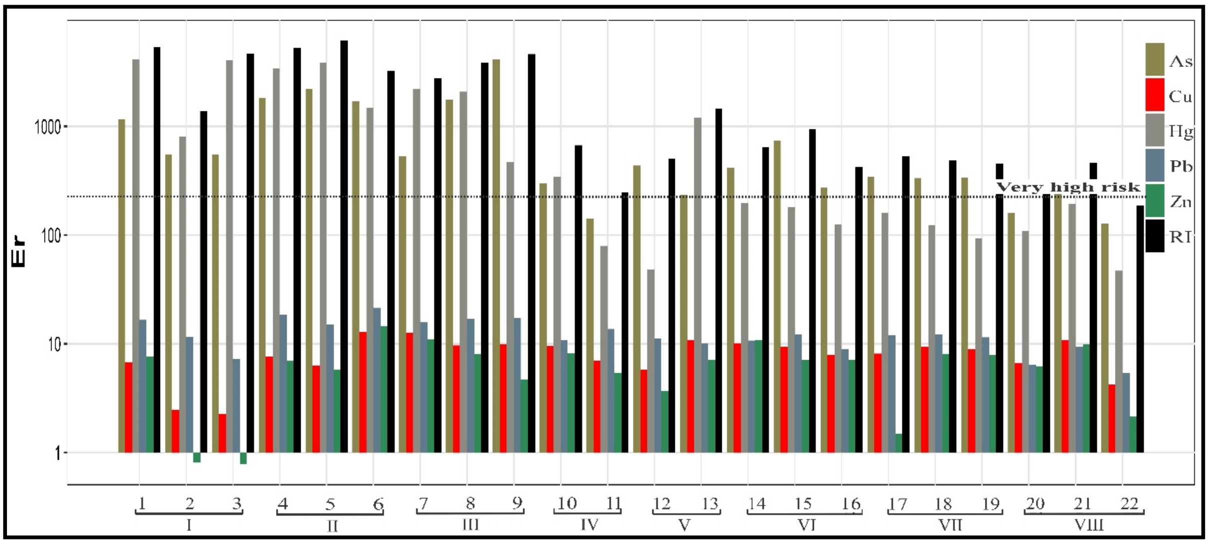

Fig. 5. Values of the Ecological Risk Factor and the Potential Ecological Risk of Lake Rinconada.

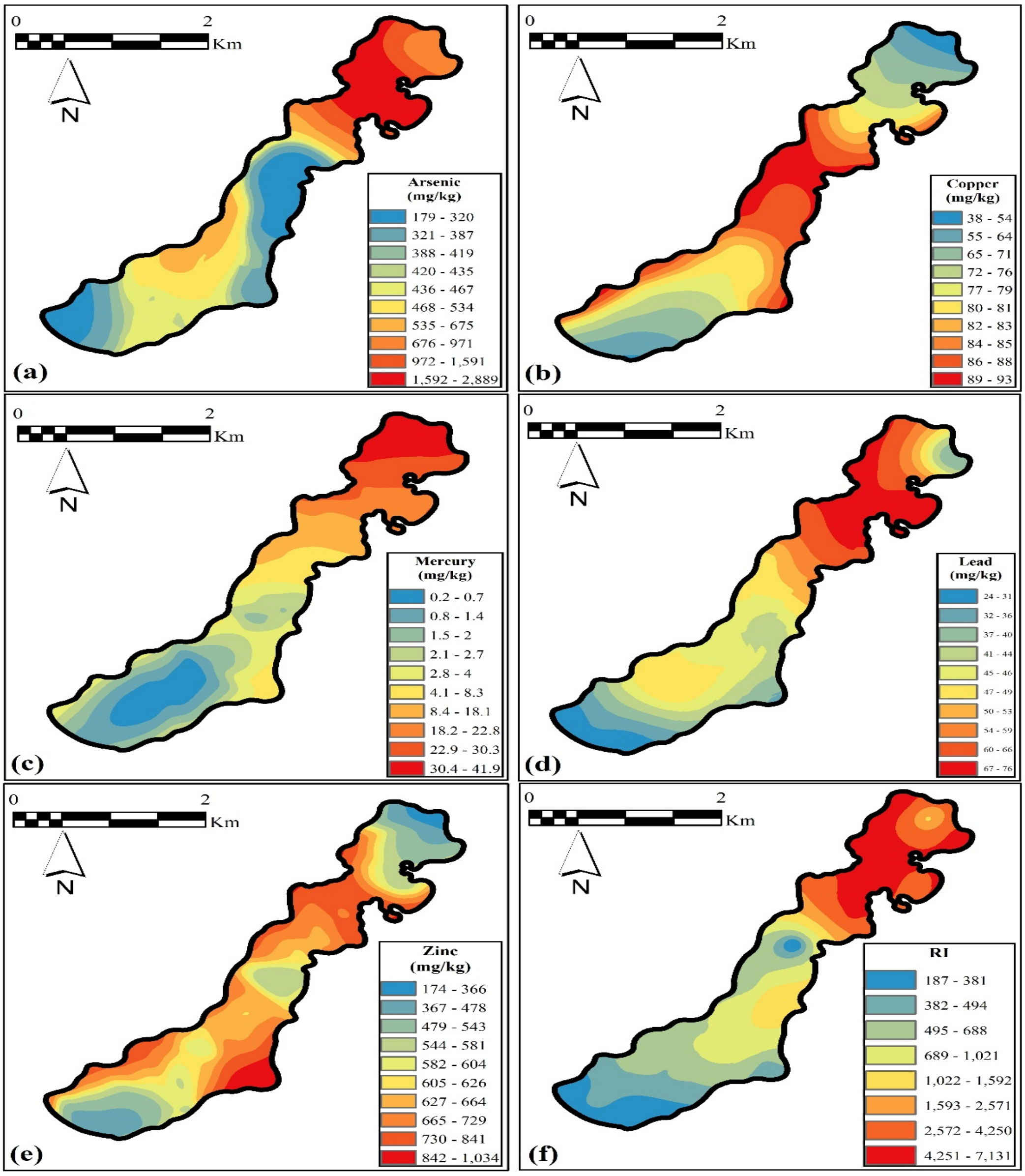

Fig. 6. Spatial Distribution of As (a), Cu (b), Hg (c), Pb (d), Zn (e) and RI (f) of the superficial sediments of Lake Rinconada.

CONCLUSION

The pollution assessment revealed that both the tributaries and the effluent of Lake Rinconada have high concentrations of As in their sediments. In addition, the Lunar de Oro River has high concentrations of Hg and Pb, suggesting that the of mining activities and the development of urban areas are affecting the quality of the sediments and the quality of the water indirectly.

According to the geo-accumulation index in sediments from the tributaries and the effluent suggest that the Lunar de Oro stream is extremely polluted and that it represents a very high ecological risk; hence, the use of its water for domestic tasks and for human consumption is not suitable. The results of the geo-accumulation index in sediments of the tributaries and the effluent suggest that the Lunar de Oro stream is extremely polluted and that it represents a very high ecological risk; hence, the use of water for domestic tasks and for human consumption is not possible.

Lake Rinconada is contaminated by As, Hg and Zn which exceed the PEL level of international regulations and, when compared to other lakes in Peru and Latin America, it is one of the most polluted lakes. In addition, the northern part of the lake has the highest contamination level and potential ecological risk, for which environmental remediation actions must be taken before the contaminants move to the southern part and thus to the mouth of the Ramis River.

Finally, we conclude that the assessment of pollution using the methods described allowed us to identify which metals are deteriorating the glacial lake and, complemented with the geostatistical method, allowed us to predict the extent of the contaminated areas and confirm their cause.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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