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Research article

Ecological risk of metals in Andean water resources: A framework for early environmental assessment of mining projects in Peru

Simón B. Moreno-Aguirre [a,*], Jacinto J. Vértiz-Osores [b], Christian E. Paredes-Espinal [c], Enrique Meseth [d,e], Guillermo L. Vílchez-Ochoa [b], Jessica A. Espino-Ciudad [c], Lisveth Flores del Pino [f]

[a] Master's Program in Water Resources, Universidad Nacional Agraria La Molina, UNALM, Lima, Peru
[b] Faculty of Engineering and Management, Universidad Nacional Tecnológica de Lima Sur, Villa El Salvador, 15834, Lima, Peru
[c] Technical Operations Functional Unit (OTEC), Organismo de Evaluación y Fiscalización Ambiental (OEFA), Lima, Peru
[d] Doctoral Program in Water Resources, Universidad Nacional Agraria La Molina, UNALM, Lima, Peru
[e] Research Office in Geosciences, Environment and Climate, Asociación Ingenieros para el Desarrollo - Engineers for Development INDEFOD, Paita, Piura, Peru
[f] Center for Research in Environmental Chemistry, Toxicology, and Biotechnology, Universidad Nacional Agraria La Molina, Lima, 15024, Peru

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ABSTRACT

Metallic contaminants in Andean water resources influenced by mining activities poses risks to aquatic ecosystems and a challenge to regulatory agencies responsible for environmental compliance. In this study, the Ecological Risk Assessment (ERA) framework was adapted to assess dissolved heavy metal concentrations at 283 surface water monitoring stations near to six mining projects during the dry and wet seasons. Reports from OEFA-Peru on Early Environmental Assessment (EEA) were used to apply various criteria and non-parametric statistical tests. They included ecological, ecotoxicological, chemical, and regulatory factors. The main goal of this research was to identify, analyze, characterize, and compare the risks present at different trophic levels. These levels were categorized as T1 (Microalgae), T2 (Zooplankton and Benthic invertebrates), and T3 (Fish). Individual risk (IR) was estimated using the quotient model, while total risk (TR) was assessed using the additive probability rule. Rainbow trout (*Oncorhynchus mykiss*), representing trophic level T3, showed the highest sensitivity to Fe and Cu. Statistical tests ranked the IR as Fe > Cu > Zn > Mn > Pb ($p < 0.01$). The TR was more prevalent during the wet season compared to the dry season ($p < 0.01$). Notably, around 50 % of the monitoring stations ($n = 142$) were classified as high risk, and 9 % ($n = 13$) showed extremely high-risk values for Cu and Fe. The adapted ERA framework demonstrated great effectiveness in identifying critical points of metal contamination in high Andean aquatic ecosystems under mining influence. However, specialized studies are suggested that allow the sources of pollution to be associated with specific regulatory actions.

1. Introduction

The importance of preserving water resources is particularly critical in high mountain regions such as the Andes [1]. Water

* Corresponding author.
E-mail address: smorenoa@unitru.edu.pe (S.B. Moreno-Aguirre).

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resources in the Andes constitute fragile and critical ecosystems that harbor rich biodiversity, playing an essential role in regulating the water cycle and supporting the communities inhabiting these areas [2,3]. However, in recent decades, the mining industry, both globally and especially in Peru, has experienced significant growth driven by the demand for minerals and metals in various economic sectors [4–6]. This activity poses significant environmental risks to aquatic ecosystems; including lakes, rivers, and streams near mining operations; such as open-pit mines, waste deposits, excavation sites, and landfills [7,8]. In 2021, around 6902 sites contaminated by mining waste were reported by the Peruvian Ministry of Energy and Mines [9]. These mining liabilities release heavy metals and other toxic compounds into the water, causing disruptions to natural ecosystems and local populations [10,11]. Heavy metals; such as lead, cadmium, and mercury; are common pollutants associated with mining activities, posing a threat to aquatic ecosystems [12].

In high Andean mining areas of Peru and South America, as well as in other latitudes of the world, rural communities use water from rivers and streams for agricultural and animal drinking [13]. For example, some studies from Africa show that metals are usually in dissolved form or formed complexes in sediments [14]. They can be absorbed by vegetables or ingested by animals, representing a risk to health and food safety [15,16].

The environmental assessment and monitoring of these contaminants are essential to ensure the preservation of these fragile environments and prevent potential adverse effects on biodiversity and human health. In this context, the Ecological Risk Assessment (ERA) emerges as a crucial interdisciplinary tool to evaluate and manage the potential impacts of contaminants on natural systems, by assessing the exposure of aquatic organisms to metals and their potential toxicity [17]. The ERA allows the integration of information on metal concentrations in water (exposure) and the biological response of organisms (effect), to effectively identify vulnerable areas and species, while establishing safe limits for contaminants to protect aquatic ecosystems [18,19].

In Peru, Early Environmental Assessments (EEAs) are conducted by the Agency for Environmental Assessment and Enforcement (OEFA, by its initials in Spanish), an entity operating under the Ministry of the Environment [20]. Its primary objective is to collect surveillance information complementary to the environmental management instruments (IGA) for audited units that have not yet started operations. In environmental regulation, this process is a fundamental step in the broader environmental application procedure and aims to document the quality of the natural environment before a given project begins [21]. However, these assessments have limitations when it comes to adequately addressing the ecological risks associated with metals [22].

While EEAs collect data on physical, chemical, and biological parameters in major environmental matrices (air, water, sediment, soil, flora, etc.), they do not specifically address ecological risks linked to metal contaminants. As a result, there is a lack of clarity in terms of criteria and a specific framework for assessing and managing the ecological risks of metals in bodies of water affected by mining [23–25]. This lack of focus can lead to poorly informed decisions and the implementation of inadequate mitigation measures to protect these ecosystems [26]. Including ecological risk related to metals as a criterion for determining environmental quality in EEAs would enable more efficient, informed, and sustainable decision-making [27]. This would establish a strong foundation for the implementation of preventive and corrective measures and the development of strategies for mitigating and restoring the Andean stream and river ecosystems affected by mining activities [28].

Globally, comparable studies focusing on ERA have been conducted for metals in aquatic systems impacted by mining, such as those conducted in Asia, Europe, Africa, and North America [24,29–34]. These studies reveal the adverse effects on aquatic biodiversity and emphasize the urgency of implementing appropriate mitigation measures. Nevertheless, there are still shortcomings and

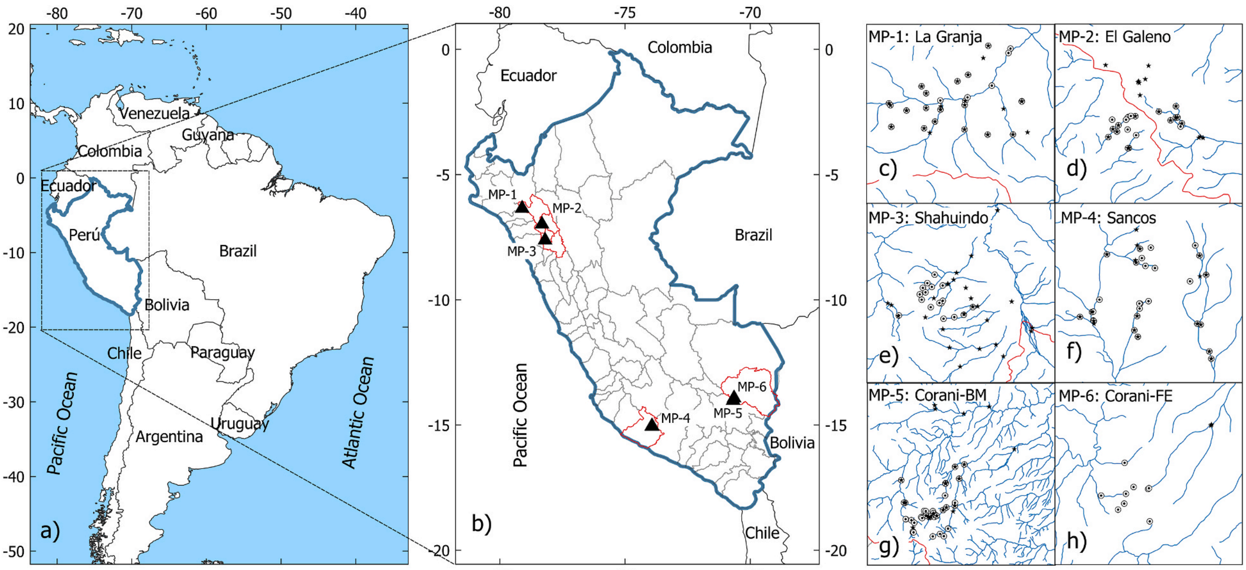

Fig. 1. Location map of the water quality monitoring stations of rivers and streams under the influence of the six MP in the study. The edges in red represent the area of influence of the basin. The black dots are the main water monitoring stations.

gaps in contemporary research at the Latin American and national levels [22,23]. One such limitation arises from the absence of a comprehensive evaluation of metal exposure and toxicity within these systems. Furthermore, specific information concerning the long-term impacts of metal pollution on Andean stream aquatic biodiversity remains elusive [28]. These deficiencies impede informed decision-making and the implementation of efficient preventive and corrective measures required to safeguard and conserve these invaluable ecosystems.

It is crucial to address current limitations and establish a specific framework for assessing the ecological risk of metals in surface water bodies affected by mining activities in the Peruvian Andean Region. The primary objective of this research was to incorporate an ERA approach into the EEA of mining projects, using a multi-criteria approach. It is necessary to mention that this methodological proposal is limited to the ecotoxicological information available as a key criterion to simplify environmental control actions. This endeavor aims to enhance monitoring procedures within OEFA's environmental assessments while bridging gaps in scientific and technical knowledge. Ultimately, this approach seeks to provide a scientifically sound assessment for the more effective management of metal contamination risks over both spatial and temporal dimensions, promoting sustainable practices and informed decision-making aimed at conserving Andean aquatic ecosystems.

2. Materials and methods

2.1. Study area

This study was located in the mountainous areas of the Andes of Peru in the South American region (Fig. 1a–h). The research area included monitoring stations that were used to evaluate the condition of surface water near rivers and streams. These stations were strategically placed in areas that were impacted by six major mining projects (MP), which were identified as analytical units. The monitoring stations were established as part of activities carried out within the framework of EEA during the dry (DS) and wet seasons (WS), conducted by OEFA in 2017 and 2018, respectively. The MP are located in the departments of Cajamarca, Ayacucho, and Puno, situated within the upper basins of seven Local Water Authorities (ALA) at altitudes ranging from 2500 to 4800 m above sea level (Table 1).

For a more comprehensive spatial risk assessment, the six analytical units were assigned unique codes and positioned under their respective ALAs, as illustrated in Fig. 1.

2.2. Data collection

Data of total and dissolved heavy metal concentrations were collected from 283 monitoring stations. These stations were active during the dry season months (May, July, and September 2017, n = 122) and the wet season months (February and March 2018, n = 161). The data were sourced from reports produced during the EEA of six mining projects, namely, MP-1, MP-2, MP-3, MP-4, MP-5, and MP-6 [35]. To compare these findings, a review of hydrobiological monitoring reports was carried out to identify representative aquatic biota in high Andean rivers and streams. Acute ecotoxicological concentrations of dissolved heavy metals were then used, from the ECOTOX database [36].

2.3. Data evaluation

A review of laboratory test reports from the ALS Limited® accredited laboratory was performed. These reports contained results obtained from water samples collected at the monitoring stations exposed to the six mining projects during the EEA carried out by the OEFA. Only results about inorganic parameters for total and dissolved metals analyzed through ICP-MS were taken into consideration. In the case of the most concerning heavy metals, concentrations that fell below the Limit of Detection (LOD) and were not detected were adjusted to proxy values. This adjustment involved calculating half of the Limit of Quantitation (LOQ) used by the analytical method [37]. This criterion was employed due to the assumption of a potential risk related to metal contamination in the water matrix, following US EPA's Risk Assessment Guidance for Superfund. Representative concentrations used for metals of concern with values below the LOD were presented in Table 2.

A list of ecological criteria was designed to identify and group representative aquatic biota within the study area due to the limited availability of local ecotoxicological data. This selection was based on the organisms tested and documented in the ECOTOX database [36]. The lowest values for acute effect concentrations were used for risk assessment.

Table 1
Main characteristics of the mining projects included in this study.

Mining Project	District - Region	Products	Basin/Altitude (m.a.s.l.)	Extension (km^2)/Stage
MP1-La Granja	Querocoto – Cajamarca	Cu	Chotano -LLaucano ALA/2500 -2800	39.0/Exploration
MP2-El Galeno	Sorochuco – Cajamarca	Cu, Au, Mo	Cajamarca and Las Yangas-Suite ALA/3800–4200	5.5/Exploration
MP3-Shahuindo	Cachachi – Cajamarca	Au, Ag	Crisnejas and Huamachuco ALA/2200–3500	2.9/Operation
MP4-Sancos	Chaviña – Ayacucho	Au	Cháchparra - Acarí ALA/3500 -4000	15.9/Operation
MP5-Corani BM	Carabaya – Puno	Zn, Pb, Ag	Tambopata-Inambari ALA/4200–4800	2.1/Operation
MP6-Corani FE	Carabaya – Puno	U	Tambopata-Inambari ALA/4200–4800	4.0/Exploration

Table 2
Proxy concentrations (LOQ/2) used for metals of concern.

Metal	LOD (mg L^{-1})	LOQ (mg L^{-1})	LOQ/2 (mg L^{-1})
Cu	0.00003	0.00010	0.00005
Fe	0.0004	0.0020	0.0010
Mn	0.00003	0.0002	0.0001
Pb	0.0002	0.0004	0.0002
Zn	0.010	0.020	0.010

Source: Metal testing reports from OEFA Early Environmental Assessments (EEA).

2.4. *Risk assessment framework*

The main steps of the methodological approach used in this study are shown in Fig. 2. This framework adapted from the US EPA Ecological Risk Assessment is composed of four main phases and a set of ecological, ecotoxicological, chemical and regulatory criteria. They allowed the identification of contamination by dangerous metals in high Andean aquatic ecosystems influenced by mining projects in any of their stages of development and subsequent management actions by environmental regulatory organizations such as the OEFA.

2.4.1. *Hazard identification*

The logical process of the ERA framework was used to identify, analyze and characterize the risk associated with hazardous metals

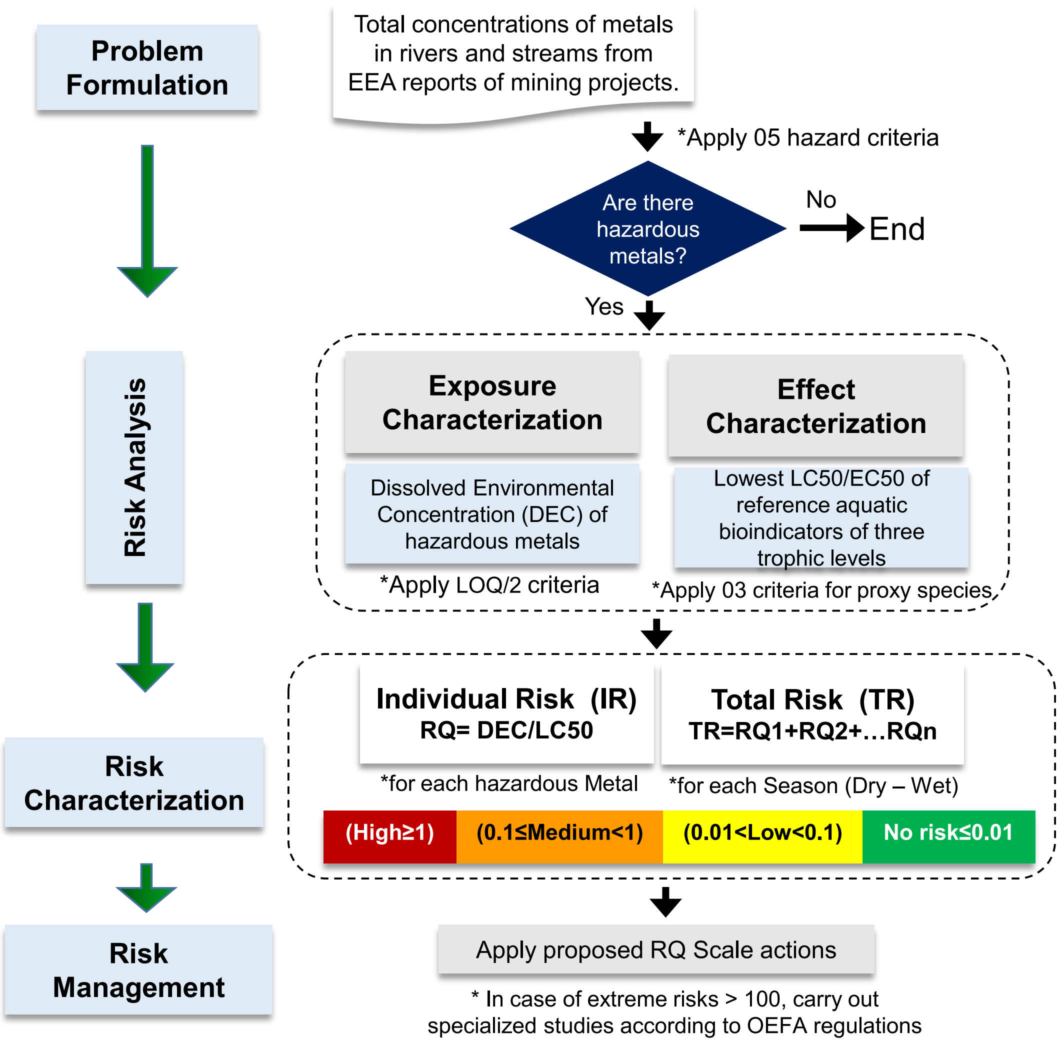

Fig. 2. Adaptation of the ERA Framework proposed in this study for EEA in mining projects.

[38]. The problem identification focused on the detection and selection of metals with the highest potential for ecotoxicological risk at water monitoring stations within the six mining projects. Five risk criteria were designed based on an adaptation of the US EPA metal risk assessment framework [17]. These criteria were used to detect the hazardous metals for the study as detailed in Table 3, these are (1) Metals and/or metalloids regulated by the Environmental Quality Standards (EQS) for Water Category III and IV, following current Peruvian regulations, specifically Supreme Decree D.S. No. 004-2017-MINAM [39]; (2) Metals and/or metalloids regulated by the EQS with high atomic density due to their chemical nature [40]; (3) Metals and/or metalloids that, due to their chemical nature, are essential trace elements and toxic in quantities exceeding metabolic requirements [41]; (4) Total metals and/or metalloids exceeding the EQS for water in Category III: D1 Vegetation Risk and Category IV: E1-E2 Aquatic Environment Conservation, in more than 5 % of the monitoring stations during both seasons [42], (5) Metals and/or metalloids with acute ecotoxicological scientific information in the ECOTOX database for indicative and representative aquatic organisms of the study area [36]. The metals selected up to the fifth criterion do not exclude those of the fourth level. Five were chosen only due to the availability of ecotoxicological data for risk analysis.

2.4.2. Risk analysis

For risk analysis, exposure and effect assessment criteria were applied, which were based on the dose-response relationship [38]. The lowest acute effect concentration values were selected from ECOTOX (Table 4), which served as the most sensitive ecotoxicological reference level for risk estimation. Exposure assessment was carried out by identifying and selecting the dissolved concentrations of the metals of concern (Cu, Fe, Mn, Pb, and Zn). This particular selection was based on the presumption of metal contamination due to mining activity in the study area [37].

Additionally, ecotoxicological criteria were considered due to the dissolved fraction's tendency to be bioavailable and absorbed by aquatic biota [34]. The assessment of the effects was conducted by identifying and selecting acute endpoints for the reference representative aquatic biota in the study area. Four criteria were applied to choose indicator hydrobiological organisms: (1) Being species or families reported in the EEA of OEFA, (2) Being endemic or naturalized species in the high-altitude rivers and streams of the study areas [43], (3) Serving as indicators of water [44]– [45] (4) Having available ecotoxicological information for the hazardous metals [36,46,47]. Following these criteria, EC_{50} and LC_{50} values at 96 h for Cu, Fe, Mn, Pb, and Zn were identified in six aquatic organisms from different taxonomic groups: *Chlorella vulgaris*, *Chironomus* sp., *Hyalella* sp., *Daphnia* sp., *Argia* sp., and *Oncorhynchus mykiss*. These organisms were grouped into trophic levels T1, T2, and T3, as recommended by the US EPA for exposure pathways in food webs [48].

2.4.3. Risk characterization

Individual Risk (IR): The deterministic risk quotient model was used to estimate the individual proportion (n_1) of dissolved environmental concentrations (DEC) of heavy metals relation to ecotoxicological endpoints in reference biota (EC_{50}, LC_{50}) [38]. Risk quotients were calculated for Cu, Fe, Mn, Pb, and Zn at T1, T2, and T3 trophic levels for each monitoring station in the six mining projects. Concentration units in mg L^{-1} were used to apply the risk quotient equation. The highest quotient obtained for each trophic level was chosen as the representative value for the IR of each metal. The quotient equation is described as follows in Eq. (1):

$$IR_{n1} = \frac{DEC_{n1}}{EC_{50}\ \text{ó}\ LC_{50}\ n1} \tag{1}$$

Total Risk (TR): The maximum quotient values for each metal were used to calculate the Total Risk (TR) at each monitoring station for each mining project (MP). The criteria of additive and multiplicative probability were applied to establish the total and representative ecological risk of the metals of concern (Cu, Fe, Mn, Pb, and Zn) as a mixture [49]. Two criteria based on general probability rules were assumed [50]: (1) if within the set of concern metals there are 1 or 2 quotients with extreme values ($IR > 1$) above the others, the addition rule (Eq. (2)) is applied because it is very likely that the extreme IR values of one metal exclude the other metals; (2) if within the set of concern metals, the IR quotients values are close and between 0 and 1, the multiplication rule (Eq. (3)) is applied because it is very likely that the risks of all metals will occur.

Addition rule:

$$TR_{nMetales} = (IR_{n1} + IR_{n2} + \ldots + IR_n) \tag{2}$$

Multiplication Rule:

$$TR_{nMetales} = (IR_{n1} + IR_{n2} + \ldots + IR_n) - (IR_{n1} * IR_{n2} * \ldots * IR_n) \tag{3}$$

Table 3
Five criteria for the selection of hazardous metals in the study area.

Criteria	N	Metals
Total Metals	33	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, U, V, Zn
Criterium (1)	19	As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Li, Mg, Mn, Ni, Pb, Sb, Se, Ta, Zn
Criterium (2)	17	As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Ta, Zn
Criterium (3)	16	As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Ta, Zn
Criterium (4)	13	As, Ba, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ta, Zn
Criterium (5)	5	Cu, Fe, Mn, Pb, Zn

Table 4
Ecotoxicological concentrations used to estimate the risk quotient.

Trophic level	Category	Indicator Organism	En[a]dpoint	Metal concentration (mg L^{-1})				
				Cu	Fe	Mn	Pb	Zn
T1	Microalgae	*Chlorella vulgaris*	$EC_{50–96h}$	0.062	10.00	1.750	1.94[a]	1.200
T2	Zooplankton and Benthic invertebrates	*Chironomus* sp., *Hyalella* sp., *Daphnia* sp., *Argia* sp.	$LC_{50–96h}$	0.030	0.620	5.270	0.100	0.430
T3	Fish	*Oncorhynchus mykiss*	$LC_{50–96h}$	0.003	0.150	3.320	0.098	1.719

Abbreviations: EC_{50}, Median effective concentration; LC_{50}, Median lethal concentration.
Note.
[a] All endpoint data are at 96 h except for Fe and Pb for *Chlorella vulgaris,* which were 9 and 12 days respectively.

Risk scale: Similar criteria to US EPA ecological risk concern levels were applied, but with a distinct scale for metallic contaminants following the suggestions of other authors [27,51,52]. A qualitative risk scale was developed based on bounded intervals with the following categories (Fig. 3): High-Red (IR or TR ≥ 1, indicating high metallic contamination with acute effects on aquatic biota), Medium-Orange ($0.1 \leq$ IR < 1 or $0.1 \leq$ TR < 1, reflecting moderate metallic contamination with potential acute effects on aquatic biota), Low-Yellow ($0.01 <$ IR < 0.1 or $0.01 <$ TR < 0.1, representing low metallic contamination with possible chronic effects on aquatic biota), and No risk - Green (IR or TR ≤ 0.01, indicating very low metallic contamination with no observable effects on aquatic biota). For this study, values with IR or TR > 100 have been classified as an "extreme risk" level.

Risk Map: The criterion of employing maps allowed for the precise identification of potential sources generating effluents, discharges, waste, or liabilities in proximity to monitoring stations with high levels of risk [53]. Maps were created based on Geographic Information Systems (GIS) to provide a spatial visualization of risk at each monitoring station. Shapefiles of the watersheds from the ALA were used to pinpoint streams exposed to the six mining projects under study [54]. A compliance action list was developed in line with the proposed risk scale and aligned with OEFA regulations, with the following characteristics: (1) High-Red: Immediate special environmental monitoring actions with a potential initiation of administrative penalty proceedings, (2) Medium-Orange: Regular environmental assessment and monitoring actions and the implementation of preventive measures, (3) Low-Yellow: Regular guidance-based monitoring actions or specific mandates, and (4) Green - No Risk: Regular guidance-based monitoring actions (Table 5).

2.5. Statistical analysis

The IBM® SPSS® Statistics program was used for statistical analysis, preparation and management of the data. The calculated risk level data were organized into two-way matrices for each MP and each season (dry, wet). Monitoring stations were placed in rows and the risk levels (IR and TR) were in columns. Subsequently, submatrices were created to conduct comparative statistical tests aiming to identify the most sensitive trophic level, compare the IR for each metal, and TR during the dry and wet seasons. The most sensitive trophic level was determined by counting the highest observed frequencies of the maximum risk quotient for each metal in relation to each trophic level used (T1, T2, and T3). Kolmogorov-Smirnov ($N > 50$) and Shapiro-Wilk ($N < 50$) normality tests were applied to assess the "Goodness of fit" of risk data to a normal distribution. As the statistics indicated significances below the p-value (sig. < 0.05), non-parametric tests, including Kruskal-Wallis and Mann-Whitney U for different samples were utilized [55,56]. The Kruskal-Wallis test was employed to ascertain if significant differences existed in the IR levels of the metals Cu, Fe, Mn, Pb, and Zn. Subsequently, paired comparisons with the Bonferroni correction proposed by Dunn [57] were carried out to identify pairs of metals with the most significant differences (maximum-minimum) and to estimate a ranking of risk for each metal. The Mann-Whitney *U* test for two independent samples was used to determine differences in total risk (TR) between wet and dry seasons.

3. Results

3.1. Most sensitive trophic level

Fig. 4 represents the average frequencies of the maximum individual risk level (IR) for each trophic level considering the monitoring points of the six MPs in both seasons. These frequencies were obtained by counting the times that the trophic level of the most sensitive organism gave a high-risk level. It is important to indicate that a conservative criterion was applied, which consisted of selecting the highest IR values for each metal. Trophic level T3, represented by rainbow trout (*Oncorhynchus mykiss*), presented the highest frequencies of high-risk levels, particularly for Cu and Fe (50 %). Trophic level T2: Zooplankton and benthic invertebrates, followed with moderate risk for Zn (18 %), and trophic level T1 (Microalgae) showed low risk for Mn (17 %). For cases in which no

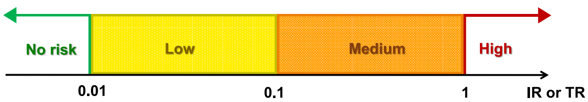

Fig. 3. Bounded intervals for low (yellow) and medium (orange) risk categories.

Table 5
Proposed risk scale for ecological risk assessment due to metals.

Risk level	Scale	Description	Management action
High	IR or TR ≥ 1	High level of metal contamination; acute effects on aquatic biota.	Immediate environmental monitoring actions; specialized studies, initiation of procedures for possible administrative sanctions.
Medium	0.1 ≤ IR < 1 or 0.1 ≤ TR < 1	Moderate level of metal contamination; possible acute effects on aquatic biota.	Regular environmental assessment and monitoring; implementation of preventive measures.
Low	0.01 < IR < 0.1 or 0.01 < TR < 0.1	Low level of metal contamination; possible chronic effects on aquatic biota.	Guiding regular monitoring actions or specific mandates.
No risk	IR or TR ≤ 0.01	Very low level of metal contamination; no observable effects on aquatic biota.	Guiding regular monitoring actions.

Note: Management actions are based on environmental control activities that could be applied by the OEFA agency.

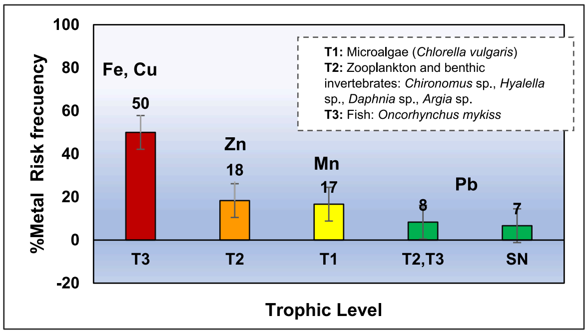

Fig. 4. Average frequencies of the trophic level used that showed the maximum level of individual risk (IR) in all the monitoring points of the six MPs in the dry and wet seasons. The acronym SN stands for No Specific Trophic Level. That is, the trophic level used showed no risk levels.

specific trophic level showed a risk level for a given metal, the category No Specific Trophic Level (SN) was specified, which represents 7 % of the cases.

Trophic Levels T2 (Zooplankton and Benthic Invertebrates) and T1 (Microalgae) exhibited no significant differences in their usage frequencies, yet they were specifically applied for assessing the risk of metals Zn and Mn, respectively. Supplementary trophic levels "T2, T3″ and "SN" had low utilization frequencies, particularly concerning the metal Pb. Based on this analysis, the sensitivity order for the detected metals was established as follows: T3 (Cu, Fe) > T2 (Zn) > T1 (Mn), with trophic level T3 (fish) representing the highest risk and, therefore, the most sensitive.

3.2. *Higher-risk metals*

The Kolmogorov-Smirnov and Shapiro-Wilk tests confirmed that the risk quotient observations for each metal (N = 1415) across all

Table 6
Results of Normality for IR during DS and WS in the six MP. Note the difference in average ranks.

MP	Season	Normality				Kruskal-Wallis H (K–W)								
		N	K–S	Sh-W	p	Average Range IR					H	df	p	BC
						Cu	Fe	Mn	Pb	Zn				Pair Max > min (*p*<*0,01*)
MP-1: La Granja	DS	125	0.49		<0.01	69	89	59	16	82	65	4	<0.01	Fe>Pb
	WS	150	0.47		<0.01	123	108	44	25	77	110	4	<0.01	Cu>Pb
MP-2: El Galeno	DS	115	0.39		<0.01	83	88	31	19	68	81	4	<0.01	Fe>Pb
	WS	105	0.45		<0.01	87	80	29	16	52	88	4	<0.01	Cu>Pb
MP-3: Shahuindo	DS	130	0.45		<0.01	90	93	62	16	65	71	4	<0.01	Fe>Pb
	WS	90	0.51		<0.01	69	62	41	14	41	49	4	<0.01	Cu>Pb
MP-4: Sancos	DS	100	0.41		<0.01	57	72	58	14	52	47	4	<0.01	Fe>Pb
	WS	175	0.40		<0.01	124	124	92	22	78	98	4	<0.01	Cu>Pb
MP-5: Corani-BM	DS	125	0.40		<0.01	68	90	46	41	70	31	4	<0.01	Fe>Pb
	WS	240	0.38		<0.01	152	174	71	79	127	80	4	<0.01	Fe>Mn
MP-6: Corani-FE	DS	15		0.67	<0.01	13	12	3	5	8	12	4	0.02	Cu > Mn
	WS	45		0.51	<0.01	30	38	10	9	28	39	4	<0.01	Fe>Pb

a. K–S: Kolmogorov-Smirnov, Sh-W: Shapiro-Wilk. DS: Dry season, WS: Wet season, N: Total number of observations.
b. H: K–W statistic. *df*: degrees of freedom. *p*: assign. sig. (bilateral) < 0,05. BC: Bonferroni correction of Dunn for pairwise differences.

monitoring stations ($n = 283$) in the six mining projects followed non-parametric distributions ($p < 0.01$). The Kruskal-Wallis test revealed significant differences in the median risk levels for each metal, with a significance level of $p < 0.01$ in most monitoring stations, except for MP-6: Corani-FE, which showed a significance level of $p = 0.02$ (Table 6). Bonferroni correction indicated significant differences between the pairs Fe–Pb and Cu–Pb in most cases ($p < 0.01$). When comparing the average ranks of the five metals, a clear pattern of risk levels emerged, with the highest values for Fe and Cu, followed by Zn, Mn, and finally Pb (Fe > Cu > Zn > Mn > Pb). Furthermore, another pattern becomes evident, depicting an alternating behavior during the monitoring period. In the dry season, the highest risk frequencies are associated with Fe, while in the wet season, they shift to Cu, specifically in the case of analytical units MP-1: La Granja, MP-2: El Galeno, MP-3: Shahuindo, and MP-4: Sancos. This observation holds except for MP-5: Corani-BM and MP-6: Corani-FE, where opposite patterns are observed.

Although the average ranges in Table 6 displayed noteworthy differences in the IR values for Cu and Fe, the Kruskal-Wallis box plots in Fig. 5a and b, which compare average ranges for independent samples of IR, unveiled outliers in the risk levels. These outliers were considered extreme, as they indicated values significantly deviating from the norm. Certain monitoring stations exhibited substantially elevated risk values, surpassing the maximum value of the risk scale used ($IR \geq 1$) by tens, hundreds, and even thousands of times, both during the DS and the WS. Notably, mining projects MP-3: Shahuindo and MP-1: La Granja were remarkable for having monitoring stations with risk values exceeding a thousand times the maximum. In the cases of mining projects MP-2: El Galeno, MP-4: Sancos, and MP-6: Corani-FE, some stations recorded values that exceeded the maximum risk scale by tens or hundreds of times. Interestingly, mining project MP-6: Corani-FE did not yield any extreme values (Table 6).

3.3. Total risk analysis

The outcomes of the TR analysis revealed that the most prevalent risk levels were High-Red ($TR \geq 1$), signifying a high degree of metal contamination in the water resources with acute impacts on aquatic biota, and Medium-Orange ($0.1 \leq IR < 1$), which indicated a moderate level of metal contamination with potential acute effects on aquatic biota. In contrast, the Low-Yellow level ($0.01 < TR < 0.1$) indicated a low degree of metal contamination that might lead to chronic effects on aquatic biota. Notably, there were no instances of risk-free ecological conditions. These results showed that the frequencies of TR were lower during the DS and higher in the WS (Fig. 6a and b). Particularly noteworthy were the monitoring stations in the water resource areas (rivers and streams) within the influence zones of the El Galeno and Shahuindo mining projects, which exhibited High-Risk levels exceeding 50 % during the dry season. In the WS, the El Galeno, La Granja, Corani-BM, and Sancos mining projects demonstrated High-Risk frequencies ranging from 49 % to 90 %. On the other hand, the Corani-FE mining project displayed a limited number of stations, but they consistently exhibited High and Medium Risk levels in both seasons.

3.3.1. Season of highest risk

The normality test revealed that the data for TR during the DS and WS in the mining projects did not follow a normal distribution ($p < 0.01$) (Table 7). The average rank ranges from the Mann-Whitney test indicated that, in most of the monitoring stations within the mining projects, the frequency of high levels of TR due to metals tended to be higher during the WS. This phenomenon was particularly noticeable in the cases of MP: La Granja, Shahuindo, Sancos, and Corani-MB ($p < 0.05$). However, in the case of MP-2: El Galeno, it was observed that TR was the same in both seasons ($p = 0.45$). For the MP-6: Corani-FE project, an inconsistency in the statistic value was noted, as it yielded a result of $U = 0$, making it impossible to draw a clear statistical conclusion about the seasonal risk behavior in that mining project.

3.3.2. Risk Map

The majority of monitoring stations displayed a high or medium level of TR. However, a total of 13 monitoring stations with

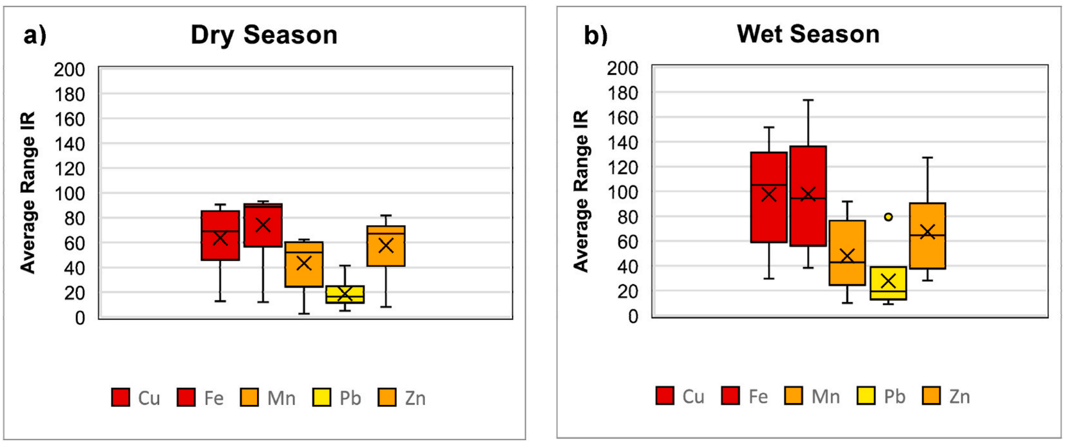

Fig. 5. Boxplots of average range IR during the dry (a) and wet (b) seasons at the six MP. The "x" position represents the average.

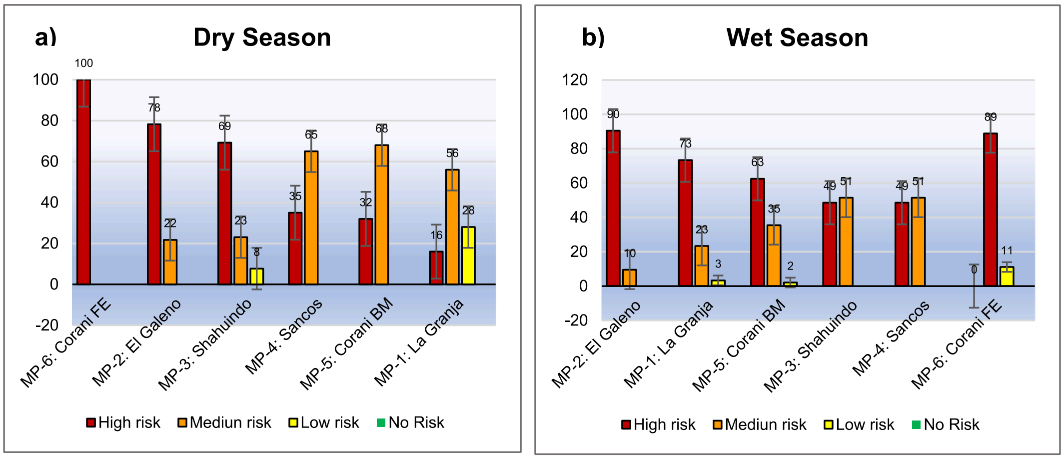

Fig. 6. Frequencies of TR at the monitoring stations of the six mining projects for dry (a) and wet (b) season.

Table 7
Normality tests and Mann-Whitney *U* test for TR during DS and WS in the six MP.

MP	Season	Normality				Mann-Whitney (M − W)						
		N	K–S	Sh-W	p	N	Average Range TR	U	W	Z	p[a]	P75
MP-1: La Granja	DS	55	0.47		<0.01	25	17	101	426	−4.63	<0.01	WS>DS
	WS					30	37					
MP-2: El Galeno	DS	44		0.48	<0.01	23	21	209	485	−0.76	0.45	WS = DS
	WS					21	24					
MP-3: Shahuindo	DS	44		0.22	<0.01	26	19	133	484	−2.41	0.02	WS > DS
	WS					18	28					
MP-4: Sancos	DS	55	0.31		<0.01	20	22	221	431	−2.26	0.02	WS > DS
	WS					35	32					
MP-5: Corani-BM	DS	73	0.40		<0.01	25	29	403	728	−2.29	0.02	WS > DS
	WS					48	41					
MP-6: Corani-FE	DS	12		0.66	<0.01	3	11	0	45	−2.50	0.01	DS, WS*
	WS					9	5					

Note: The amount of data from the MP6-Corani-FE monitoring stations gave a U = 0, so it could not be determined in which station the risk was highest (DS, WS*).
Abbreviations; K-Kolmogorov-Smirnov; Sh-Shapiro-Wilk; DS, Dry Season; WS, Wet Season; N, Total number of observations.
U, W, z: M − W test statistics.
[a] p: sig. like this (2-sided) <0.05. P75: 75 % percentile.

extreme levels of TR were identified (Fig. 7). During the wet season, the MP-03: Shahuindo and MP-01: La Granja projects exhibited the three most critical extreme values among all the monitoring stations in the study area, surpassing the ecological risk scale by thousands of times. These stations included Qshi1b (TR: 4 4111.18) and QShi1c (TR: 3 4237.77), both located in the Shingomate stream, approximately 300 m and 560 m upstream from the confluence with the El Grajo stream, respectively. They fall under the water management of ALA Crisnejas and ALA Huamachuco (Cajamarca). Additionally, station QSald1 (TR: 1260.86) is situated in a spring near the Nuevo Amanecer hamlet, Paraguay village, which serves as a source of water supply for the local population and is managed by ALA Chotano-LLaucano (Cajamarca). The other 13 monitoring stations (Table 8) displayed values hundreds of times above the scale limit, with examples including station RCañ2 (TR: 600.37), situated in the Cañarís River, approximately 450 m downstream from the confluence with Caipuro stream, and station Qsald1 (TR: 133.24), which falls under the influence of MP-1.

MP-06: Corani-FE did not exhibit extreme values. According to the characterization of the risk scale used (Table 5), it was observed that the water monitoring stations of almost all mining projects, with the exception of MP-06: Corani-FE (wet season) have an ecological high risk for the trophic level T3 (*Oncorhynchus mykiss*), considered the most sensitive for Cu and Fe, so they were located within the following actions (1) High-Red: Immediate special environmental supervision actions with possible initiation of administrative sanctioning procedure, (2) Medium-Orange: Regular environmental evaluation and supervision actions and application of preventive measures.

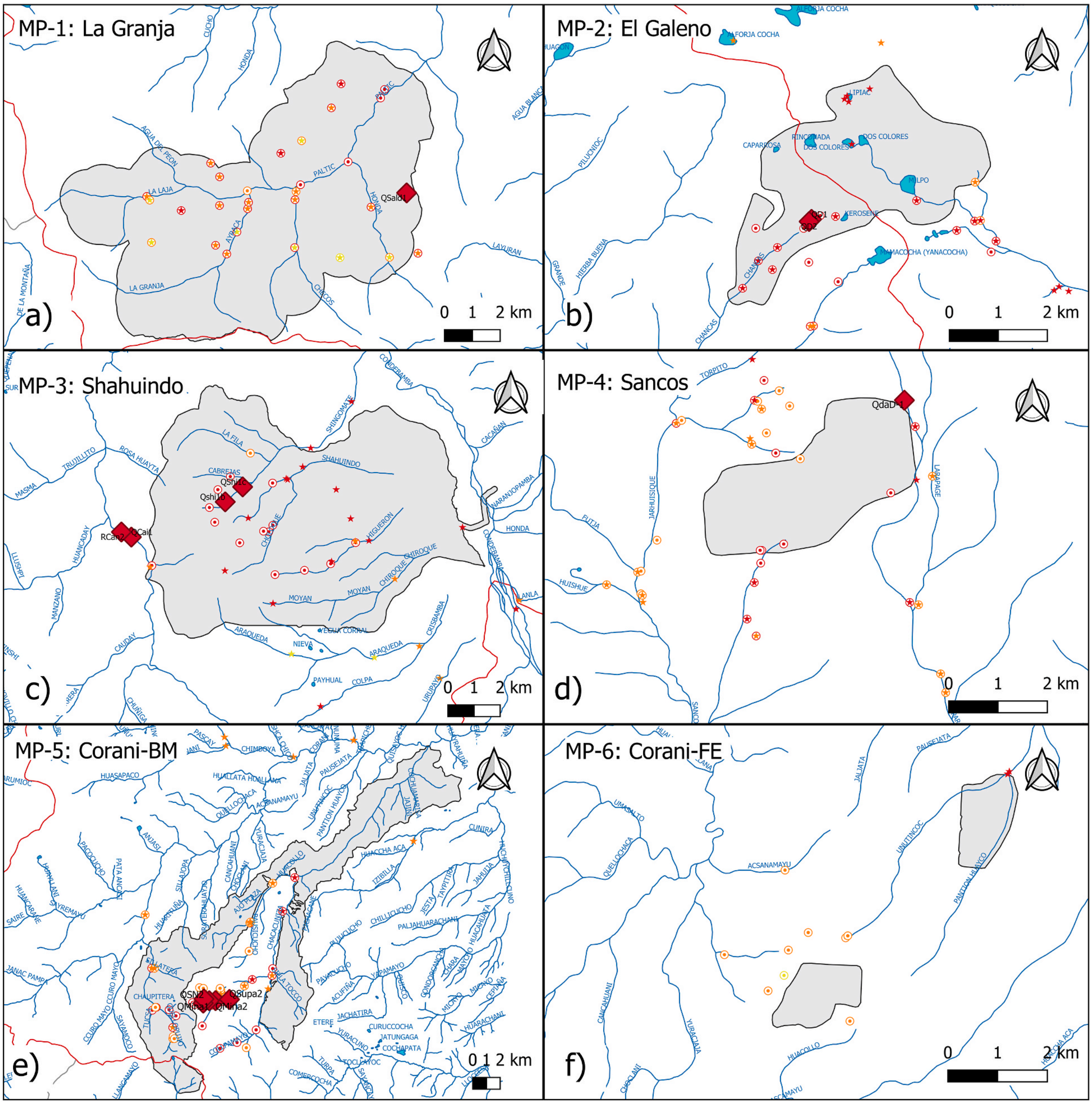

Fig. 7. TR Map of metals in monitoring stations in Andean rivers and streams under EEA of the six mining projects under study. Note the red boxes indicating 13 monitoring stations with extremely high risk. (a) Station QSald1 in the influence area of Project La Granja, Cajamarca (2557 masl). (b) Stations QD1 and QD2 in the influence area of Project El Galeno, Cajamarca (3800 masl), noting the presence of high Andean lakes. (c) Stations RCañ2, Qshi1b, and QShi1c in the influence area of Project Shahuindo, Cajamarca (2600–2900 masl). (d) Station QdaD-1 in the influence area of Project Sancos, Ayacucho (3770 masl). (e) Stations QMina2, QSN2, QSupa2, QMina1, QSala2, QSN2 in the influence area of Project Corani-BM, Puno (4700–4900 masl). (f) Stations from Project Corani-FE, Puno. Star symbols represent the stations in the dry season, while circles with dots represent the wet season. The gray-shaded area represents the indirect influence area of the mining project. In Table 8, the drainage basin and surrounding water bodies are described.

4. Discussion

4.1. The most sensitive trophic level

It was observed that trophic level T3 (*Oncorhynchus mykiss*) exhibited the highest risk levels for metals Cu and Fe, with a risk percentage of 50 % (Fig. 4). This suggests that cold-water fish like trout in this ecosystem might face exposure to metal concentrations

Table 8
Hydrographic and location characteristics of the 13 EEA monitoring stations with extreme levels of TR > 100.

MP	Season	Code	Extreme TR	Description	Altitude	ALA (Basin)
MP-1: La Granja	DS	QSald1	133.24	Spring of the hamlet Nuevo Amanecer, Paraguay village, the water supply of the local population.	2557	ALA Chotano-LLaucano (Cajamarca)
	WS	QSald1	1260.86	Spring of the hamlet Nuevo Amanecer, Paraguay village, the water supply of the local population.	2557	
MP-2: El Galeno	WS	QD1	156.35	Unnamed stream, located approx. 10 m south of the checkpoint (Bravo 4), El Galeno mining project.	3806	ALA, Cajamarca and ALA Las Yangas-Suite (Cajamarca)
		QD2	173.81	Unnamed stream, located approx. 70 m SW of the checkpoint (Bravo 4), El Galeno mining project.	3803	
MP-3: Shahuindo	DS	RCañ2	600.37	Cañarís River, located approx. 450 m downstream from the confluence with Caipuro stream.	2615	ALA Crisnejas and ALA Huamachuco (Cajamarca)
	WS	Qshi1b	44 111.18	Shingomate stream, located approx. 300 m upstream from the confluence with El Grajo stream.	2910	
		QShi1c	34 237.77	Shingomate stream, located approx. 560 m upstream from the confluence with El Grajo stream.	2644	
MP-4: Sancos	WS	QdaD-1	120.21	Site located upstream of D (Lambre) stream.	3770	ALA Cháparra-Acarí (Ayacucho)
MP-5: Corani-BM	DS	QMina2	167.58	Supayhuasi stream, located 20 m downstream from the confluence with Piruacarca and Minaspata streams.	4851	ALA, Tambopata-Inambari (Puno)
		QSN2	317.41	Unnamed stream, located upstream of the confluence with Minaspata stream	4873	
		QSupa2	123.83	Supayhuasi stream, located 3 km southeast of the Chacaconiza peasant community	4781	
	WS	QMina1	122.16	Minaspata stream, located 50 m upstream from the confluence with Piruacarca and Supayhuasi streams.	4851	
		QSala2	126.16	Sala Sala stream, located downstream from adits 8 and 9 (environmental liabilities)	4913	
		QSN2	115.42	Unnamed stream, located upstream of the confluence with Minaspata stream	4873	

[a]MP-6: Corani-FE did not have extreme TR exceeding 100.

that could be ecologically concerning [58]. Trophic level T2, which includes Zooplankton and Benthic invertebrates, showed a moderate risk for Zn, with a risk percentage of 18 % (Fig. 4). This implies that this trophic level might encounter moderate levels of Zn in their environment, potentially impacting their sensitivity and ecological balance [59]. Trophic level T1, corresponding to microalgae, exhibited a low risk for the metal Mn (manganese), with a risk percentage of 17 %. This indicates that microalgae are exposed to relatively low levels of Mn in the environment, suggesting a lower ecological risk associated with this metal compared to other trophic levels [60]. As for lead (Pb), it is worth noting that the environmental concentrations of this metal did not indicate risk for trophic levels T2 and T3. Consequently, its infrequent use in assessing ecological risk may be may be due to the fact that environmental lead concentrations do not reach levels of concern for aquatic organisms in the ecosystem [40,61]. These findings highlight that fish (trophic level T3) pose the highest risk for metals Cu and Fe, followed by zooplankton and Benthic invertebrates (T2 level) for Zn, and microalgae (T1 level) for Mn.

4.2. High-risk metals

The statistical analyses conducted in the study provide essential insights into the risk levels associated with metals at the monitoring stations of mining projects (Table 6). The Kolmogorov-Smirnov and Shapiro-Wilk tests demonstrated that the risk ratio data did not adhere to a parametric distribution, highlighting the necessity of employing non-parametric methods in the analysis [57]. The Kruskal-Wallis test revealed significant differences in the median risk levels for each metal in most of the monitoring stations [62]. This suggests notable variations in the risk levels among the different studied metals. It's worth noting that slightly higher significance was found in the monitoring stations of MP-6: Corani-FE compared to the others. The well-defined pattern of risk levels, where iron (Fe) and copper (Cu) show the highest values followed by zinc (Zn), manganese (Mn), and lead (Pb), indicates that Fe and Cu are the most concerning metals in terms of environmental risk in the studied ecosystem. This could be attributed to the specific characteristics of the mining projects and how these metals are released into the aquatic environment [63]. The observation of an alternating behavior during the monitoring period, with higher risk frequencies occurring for Fe in the DS and Cu in the WS, emphasizes the importance of considering seasonal variations in the assessment of ecological risk from metals [61]. These results reveal that changing environmental conditions can influence the mobility and availability of metals, which, in turn, can affect the risk levels for aquatic organisms [64,65]. The identification of extreme risk values in some monitoring stations is concerning, as it indicates the presence of exceptionally high metal concentrations, exceeding the maximum value on the scale several times. This suggests areas with higher contamination and underscores the need to address and mitigate these risks in those specific locations.

4.3. Total risk (TR)

The results of the Mann-Whitney test indicate that, in most of the monitoring stations of mining projects, the frequency of high levels of TR tends to be higher during the wet season compared to the dry season. This suggests that the rainy season is associated with a greater risk of metallic contamination in water resources. The seasonal variation in the total high-level risk in most of the sites that are primarily exploration projects, such as MP1, MP2, MP4, and MP5, may be due to the formation of acid drainage that solubilizes metals from the mineralogical characteristics of the area and other climatic factors. For example, the MP-2 mining project: El Galeno showed consistent risk levels in both seasons, indicating consistency in metallic contamination levels throughout the year. This could be due to specific project factors, such as the type of mining operations, implemented environmental management practices, or specific area characteristics, such as rock geochemistry that might be exposed and generate acid mine drainage [52]. Additionally, in cases of abrupt variations such as in MP-1: La Granja, it may be due to the presence of environmental liabilities or waste from closed or abandoned mines near the project's area of influence that can also generate drainage with metals such as Zn, Fe, As, Cd, Mn, and Pb, with potential toxic effects on aquatic biota [66].

This process occurs when in mineralized mountainous areas, climate conditions such as precipitation generate the production of acidic drainage with a high concentration of metals, which tend to be transported or diluted downstream [65,67]. In other words, rain can contribute to the transport of metals from mining areas to water bodies, increasing metal concentrations and risks to aquatic biota [19,68]. Regarding sites that presented a slight opposite variation, i.e., lower levels of high risk in the wet season compared to the dry season, such as in the case of MP-3: Shahuindo, it may be due to certain drainage management or remediation actions implemented by the company, as the project is in operation. These management actions usually improve the chemical quality of nearby rivers and streams [69]. This seasonal variation in risk underscores the importance of considering fluctuations in environmental conditions when assessing and managing metallic contamination in water resources. Moreover, it is noteworthy that the mining project MP-6: Corani-FE showed a low number of monitoring stations but with high risk in both seasons despite the limited station quantity, making it difficult to draw clear conclusions about the seasonal risk behavior in that area. This peculiarity could be attributed to various factors, such as natural variability in metallic contamination levels or site-specific characteristics [70,71].

In summary, the frequent presence of high and medium levels of TR indicates significant metallic contamination in the water, with possible acute effects on aquatic biota. Therefore, the identification of specific areas with high-risk frequencies at monitoring stations, particularly in areas influenced by mining projects, emphasizes the need to thoroughly analyze the specificities of each mining project when assessing seasonal risks and designing appropriate mitigation strategies.

4.4. Risk Map

Specifically, the mining projects MP-03: Shahuindo and MP-01: La Granja displayed the most critical values during the wet season.

These monitoring stations exhibited risk levels that exceeded the scale used by thousands of times, indicating an extremely high ecological risk and severe metal contamination at these specific locations. This could potentially be associated with the presence of mining liabilities in the Alto Marañón basin [72,73]. Furthermore, other monitoring stations in various mining projects were identified with risk levels hundreds of times above the scale's limit. While these stations also indicated significant metal contamination, it was of a lesser magnitude compared to those with extreme levels. Nonetheless, this should not be underestimated, as it still represents a noteworthy risk to aquatic biota and the ecological equilibrium. The assessment of trophic level T3 (*Oncorhynchus mykiss)*, known as the most sensitive to metals Cu and Fe, revealed a high ecological risk in most monitoring stations of mining projects, except for MP-06: Corani-FE during the wet season. This implies that fish, such as *Oncorhynchus mykiss*, are exposed to hazardous levels of metal contamination, potentially leading to adverse effects on their health and the ecological balance of the aquatic ecosystem [31,74–76]. The results indicated that the majority of monitoring stations in the study area displayed high and moderate levels of TR, suggesting a widespread presence of metal contamination in the assessed water resources. However, it is a cause for concern to identify a total of 13 monitoring stations with extreme levels of TR, indicating significantly elevated metal contamination in these areas [77]. These stations were under the administration of different ALA, underscoring the need for effective coordination among stakeholders to address and control pollution in these critical areas [25]. These entities are responsible for the management and control of water resources within their respective areas of influence. Their primary role is to ensure water quality and availability and to safeguard aquatic ecosystems [11,28]. The presence of critical stations with extreme levels of TR, as identified in the mining projects MP-03: Shahuindo and MP-01: La Granja, emphasizes the significance of effective management by the Local Water Authorities (ALA). These organizations must collaborate closely with mining projects and other stakeholders to implement control and mitigation measures for metal contamination.

Although this study is useful for decision makers and officials of environmental enforcement agencies, some limitations were found related to the availability of ecotoxicological data for reference organisms in these high Andean areas of Peru and South America. In our country, the generation of research on ecotoxicological tests with metals in aquatic organisms is still deficient and there is no platform where it can be used to evaluate ecological risks due to metals or other contaminants. However, for this study we were able to use proxy organism endpoints from the ECOTOX database in order to carry out the methodological framework. Another limitation was the low number of water quality monitoring stations in some rivers and streams such as MP-6 project: Corani FE. Some recommendations include promoting greater research in ecotoxicological tests with local aquatic species or representatives of high Andean areas, expanding the number of monitoring stations in water bodies close to mining projects and ensuring the continuity of measurements. In addition, it is essential to update and expand the ECOTOX database to include parameters for highly toxic metals such as As, Cd, and Hg. These metals pose significant risks even at trace concentrations, and their inclusion in the database would enable Peruvian agencies to conduct more comprehensive environmental studies to assess contamination levels and associated risks accurately. The need to improve species identification, not only up to the genus level, particularly in invertebrate groups, is also emphasized. Likewise, it is proposed to establish a new level of extreme risk for ratios that exceed values of 50 or 100, which should imply immediate environmental control actions.

5. Conclusion

This study revealed the significant presence of metals and thus high levels of ecological risk. The vulnerability of rainbow trout at trophic level T3 to Fe and Cu underscores the complex interactions between contaminants and aquatic species. Furthermore, statistical analyses revealed that ecological risk follows the order: Fe > Cu > Zn > Mn > Pb, indicating variability in risk levels depending on the metal. Additionally, the identification of monitoring stations with atypical extreme risks, especially during the wet season, highlights the importance of considering both the timing and spatial location when assessing risk, for more effective identification of critical points of metallic contamination and its potential impact on Andean aquatic biota. The connection between precipitation and metallic contamination during the wet season (WS) also underscores the need for a deeper understanding of hydrological and chemical interactions in these regions. Moreover, this emphasizes the significance of collaboration between local water management units (ALA), mining projects (MP), Environmental Assessment and Enforcement Agency (OEFA) and key stakeholders to address metallic contamination risks and preserve the integrity of aquatic ecosystems. In this context, the findings suggest the importance of adopting the ERA approach in EEA of mining projects under OEFA supervision as a fundamental tool to justify specialized studies and improve environmental regulation in the country's mining industry.

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Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Simon B. Moreno-Aguirre: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jacinto J. Vértiz-Osores:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Christian E. Paredes-Espinal:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Enrique Meseth:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Guillermo L. Vílchez-Ochoa:** Writing – review & editing, Investigation, Data curation. **Jessica A. Espino-Ciudad:** Writing – review & editing, Investigation. **Lisveth Flores del Pino:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Investigation, Formal analysis, Data curation, Conceptualization.

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.

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