



Assessment of toxic metal contamination, distribution and risk in the sediments from lagoons used for fish farming in the central region of Peru

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ABSTRACT

Toxic metal contamination, distribution and risk were evaluated in the sediments of three lagoons used for fish farming in the central region of Peru. The distribution of toxic metals in the sediment was in the following descending order of $Zn > V > Ni > Cu > Pb > As > Cr > Co > Cd > Sb$. Contamination factor (CF) and geo-accumulation index (I_{geo}) values for Co, Cr, Cu, Ni, Pb, Sb, V and Zn indicated low contamination and for Cd moderate contamination. The pollution load index (PLI) ranged from 0.3856 to 0.5622; indicating no appreciable contamination and the modified degree of contamination (mCd) corroborated this result. The potential ecological risk (R_i) in the Tranca Grande and Pomacocha lagoons revealed a low potential ecological risk and in Tipicocha a moderate potential ecological risk. HI values < 1 indicated that non-carcinogenic adverse effects were negligible. In adults, the Total carcinogenic risk (TCR) values for As, Cd, Cr, Ni and Pb were less than $1.00E-04$, indicating no significant carcinogenic risk. In children, TCR values showed similar behavior with the exception of As. Therefore, considering that fish production for domestic consumption and export is carried out in these lagoons, it is important to continue monitoring toxic metals to protect the health of these ecosystems and human health.

1. Introduction

Toxic metal contamination is an issue of increasing global concern as a function of urban growth, industrialization and population density [6]. The presence of toxic metals in the environment is due to natural and/or anthropogenic sources. Natural sources include geological weathering, volcanoes, atmospheric deposition, erosion and hydrodynamic processes. Anthropogenic sources are influenced by mining, industrial or agricultural activity [16,51]. In addition, the continuous accumulation of pollutants in the environment seriously deteriorates the quality of the environment and affects the structure and functioning of ecosystems [59]. Freshwater ecosystems are being affected by the high potential for anthropogenic pollution [40]. The chemical composition and sediment quality of different water bodies are influenced by high pollutant loads. In many regions of the world, the intensification of water resources shows a significant correlation between water pollution and human health [35].

Most studies related to aquatic ecosystems have focused primarily on

heavy metal contamination, monitoring the physicochemical state of water, assessing disturbances in biological components, using feasible methods to reflect changes in aquatic ecosystems and estimating pollution rates, and assessing the impact of water pollution on aquatic ecosystems [66]. Toxic metals with low solubility, once released into the aquatic environment tend to deposit in the bottom sediment [13], constituting a potential source of toxic metals to the water column. Toxic metals that are incorporated into the food chain by accumulation and biomagnification in tissues [25], affect aquatic organisms [50] and humans exposed to these environments [48]. Although the potential risk to human health from the presence of toxic metals in bottom sediments is not fully known, it is not yet fully understood [65]. Therefore, sediment quality must be monitored to maintain water quality and ensure safe water for its various uses [2,33].

In recent decades, ecological risk assessment of toxic metals in sediments has gained more attention in many countries globally [8]. However, in some regions (especially in developing countries), research focused on assessing the ecological and human risk of sediments from

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environments contaminated with toxic metals using integrated methods is still scarce (N. [64]). Although sediment is an important part of aquatic systems that provides the necessary environmental information and is considered the final precipitating medium for toxic metals, it is also an important source of information about the environment [21]. In the evaluation of sediment and water quality, different simple indices have been applied, such as the geoaccumulation index (I_{geo}), contamination factor (Cf) or the enrichment factor (EF), and complex indices, such as the pollution load index (PLI), modified pollution degree (mCd) and the potential ecological risk (R_i) [3,4,54].

In the evaluation of human health risks from toxic metals, the Hazard Quotient (HQ) and Hazard Index (HI) are constantly used for the estimation of non-carcinogenic effects, while the carcinogenic risk (CR) and total carcinogenic risk (TCR) are usually used for the estimation of carcinogenic effects [9]; K. [33], [23]. Other research has successfully integrated the potential ecological risk of an ecosystem with human health risk assessment [5]; N. [64,65]. The objective of this research was to evaluate the contamination, distribution and risk of toxic metals in the sediments of three lagoons used for fish farming in the central region of Peru.

2. Materials and methods

2.1. Description of the study area

The lagoons considered in the study are located in the Central Andes of Peru, between latitudes: $11^{\circ} 43' 45''$ S - $12^{\circ} 08' 19''$ S and longitudes: $75^{\circ} 13' 40''$ W - $75^{\circ} 38' 01''$ W between 4300 and 4700 masl (Fig. 1). The climate presents seasonal variations, from May to September corresponds to the dry season and from October to April to the rainy season. The area and depth of the lagoons vary from 90 to 164 ha and from 9 to 25 m, respectively [36]. Two of the lagoons are dominated by sandy sediments and one by clayey sediments. These lagoons have been used for intensive aquaculture of *Oncorhynchus mykiss* in long floating cages since 1990. To date, the three lagoons are in a mesotrophic-eutrophic

state [15].

2.2. Sampling and pretreatment

Surface sediment samples (0–10 cm depth) were collected from the three intensively cultured ponds of *Oncorhynchus mykiss* in November 2019, according to the standard protocol [56]. Nine sampling stations or zones were established in each lagoon, covering the northern, central and southern parts of the lagoon. At each sampling station, three sampling sites were selected for sediment collection. Sediment samples from each lagoon were collected using a stainless steel auger device. Samples from each station were mixed to obtain two 250 g composite samples. Sediment samples were placed in acid rinsed, airtight polyethylene plastic bags. The sediment composite samples were kept at 4°C while being transferred to the laboratory for analysis. Sediment samples were dried at 40°C , disaggregated and ground. They were then sieved through a $100\ \mu\text{m}$ mesh sieve to obtain uniformly mixed samples and extract metals efficiently. The resulting sediment was stored in glass bottles until further analysis.

2.3. Analytical procedures

Toxic metals were extracted according to the standard method of environmental quality validated by INACAL-Peru (abbreviation of the National Institute of Quality). A concentrated mixture of HF, HNO_3 and HClO_4 (5:2:1) was used for the digestion of sediment samples for 10 h. The digested samples were filtered ($0.45\ \mu\text{m}$ membrane filter) and adjusted to an appropriate volume. Total concentrations of Ni, Co, Cd, Cr, Cu, Zn, Pb, V, Sb and As were analyzed with an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer NexION 1000).

2.4. Quality control and assurance

Quality control and quality assurance was performed using standard laboratory methods, including replication and determination of

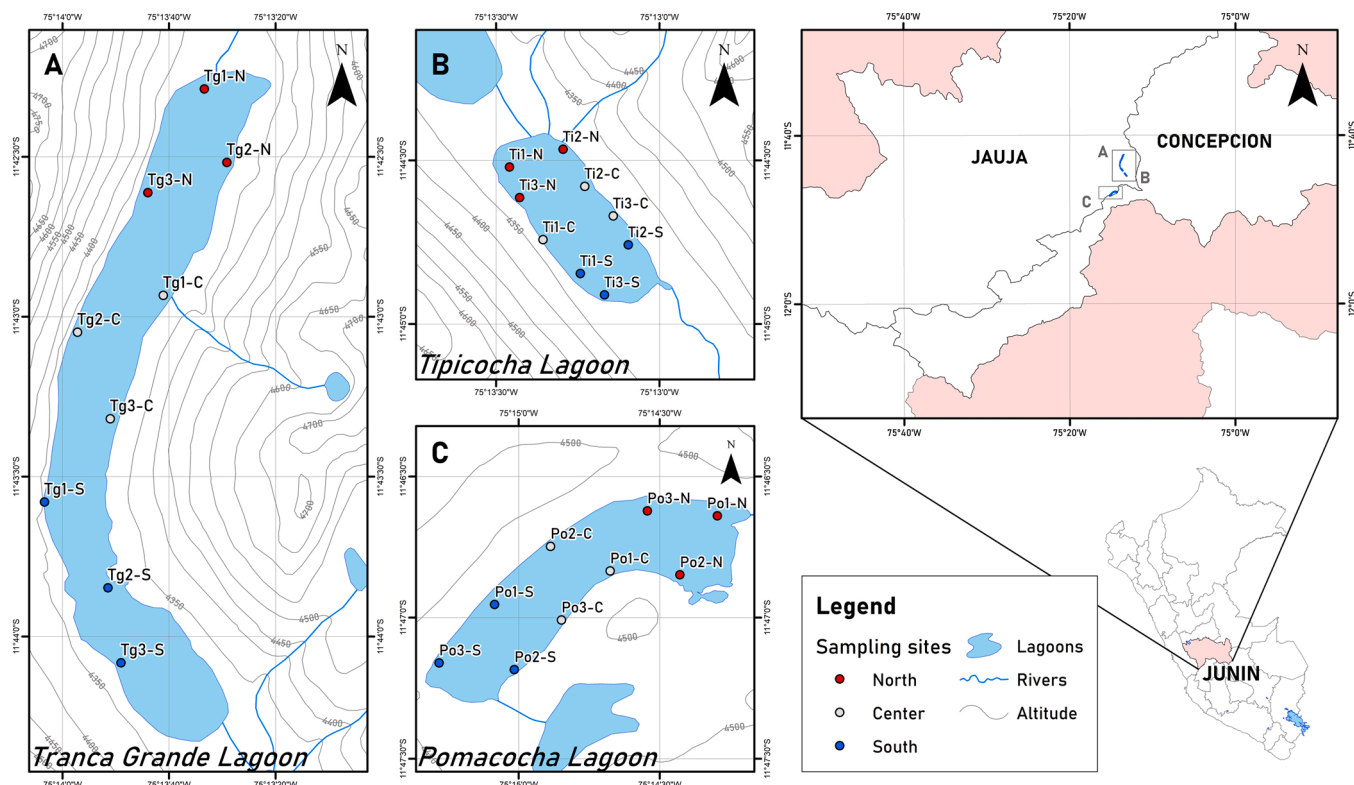


Fig. 1. Map of the location of sediment sampling sites in fish farming lagoons in the central region of Peru.

instrument accuracy (APHA, 2012). The determination of toxic metals was performed in triplicate and the blank experiments followed the same procedure applied for the samples. The total content of each metal was expressed as the mean concentration of the replicates. The reagents were of superior quality and analytical grade, and the solutions were prepared with ultrapure water. The glassware was cleaned with HNO₃ (10 %) for 48 h and then rinsed repeatedly with ultrapure water.

2.5. Risk assessment methods

2.5.1. Contamination factor (Cf)

The Cf measures the ratio between the concentration of each metal in the sediment and the background value, considered as the average concentration of the metal in the upper continental crust raised by Taylor and McLennan [53]. Cf quantifies the sediment contamination status for each metal evaluated [17,24], and is calculated by Eq. (1).

$$Cf = \frac{C_{m\text{ sample}}}{C_{m\text{ background}}} \quad (1)$$

Where, Cf is the contamination factor, $C_{m\text{ sample}}$ is the concentration of metal in the sediment, $C_{m\text{ background}}$ is the metal concentration in the upper continental crust. The categories are described as low contamination factors ($Cf < 1$), moderate contamination ($1 < Cf < 3$), considerable contamination ($3 < Cf < 6$) and very high contamination ($Cf \geq 6$) [17].

2.5.2. Geoaccumulation index (I_{geo})

The I_{geo} is used to establish the difference in metal concentrations between samples and naturally occurring background values in the upper continental crust [43,53]. This index evaluates the levels of contamination in the sediment for each metal [28,49]. The I_{geo} is calculated by Eq. (2).

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n} \quad (2)$$

Where, C_n is the metal concentration in the sediments, B_n is the metal concentration in the upper continental crust, and 1.5 is a factor applied to minimize the effect of possible variations in background values [46]. I_{geo} is classified into categories according to level, not polluted (level 0; $I_{geo} \leq 0$), not polluted to moderately polluted (level 1; $0 < I_{geo} < 1$), moderately polluted (level 2; $1 < I_{geo} < 2$), moderately to heavily polluted (level 3; $2 < I_{geo} < 3$), heavily polluted (level 4; $3 < I_{geo} < 4$), heavily to extremely polluted (level 5; $4 < I_{geo} < 5$) and extremely polluted (level 6; $I_{geo} > 5$) [43].

2.5.3. Pollution load index (PLI)

The PLI is used for the total assessment of the degree of sediment contamination by toxic metals [41,55]. The PLI is calculated as a geometric average of Cf using Eq. (3).

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 \times \dots \times Cf_n)^{1/n} \quad (3)$$

Where, Cf_n is the contamination factor for each metal, and n is the number of metals evaluated. A value of $PLI = 0$ indicates the state of perfection of the evaluated ecosystem, $PLI = 1$ indicates the presence of only basic levels of contaminants, and $PLI > 1$ indicates progressive deterioration of the quality of the site and the ecosystem [55].

2.5.4. Modified degree of contamination (mCd)

The mCd is a global contamination index that evaluates the degree of contamination of sediments, integrating all the toxic metals evaluated in the ecosystem [1,46]. The mCd is calculated using the Eq. (4).

$$mCd = \frac{\sum_{i=1}^{i=n} Cf_i}{n} \quad (4)$$

Where, Cf is the contamination factor, i represents the "ith" metal, and n is the number of metals evaluated. The mCd is classified into contamination grades: uncontaminated to very low contamination grade ($mCd \leq 1.5$), low contamination grade ($1.5 < mCd \leq 2$), moderate contamination grade ($2 < mCd \leq 4$), high contamination grade ($4 < mCd \leq 8$), very high contamination grade ($8 < mCd \leq 16$), extremely high contamination grade ($16 < mCd \leq 32$), and ultra-high contamination grade ($mCd > 32$).

2.6. Potential ecological risk (R_i)

The R_i is calculated from the sum of the ecological risk factors (E_r) calculated for each toxic metal evaluated. It is an index applicable for the evaluation of the overall degree of ecological risk caused by toxic metal concentrations in sediment samples [24]. R_i is calculated by Eq. (5).

$$E_r^i = T_r^i \times CF_r^i; R_i = \sum_{i=1}^n E_r^i \quad (5)$$

Where, T_r is the biological toxic factor of each metal, and i represents the "ith" metal. R_i is classified as low potential ecological risk ($R_i \leq 95$), moderate potential ecological risk ($95 < R_i \leq 190$), considerable potential ecological risk ($190 < R_i \leq 380$) and very high potential ecological risk ($R_i > 380$) [49].

2.7. Site rank index (SRI)

The SRI allows a better understanding of the state of contamination of the sediments with respect to the studied environment and compares the level of contamination of the sampling sites with respect to the concentrations of elements analyzed under the same metric avoiding the comparison in different classifications of each contamination index (Cf and I_{geo}) [46,68]. The SRI is calculated using Eq. (6).

$$W = \frac{\sum n_i}{\sum i}; SRI = \frac{W}{S} \times 100 \quad (6)$$

Where, S is the number of sampling stations, n is the site contamination rank in ascending order (at each value used: Cf and I_{geo}), and i represents the "ith" metal. The uniformity of the categories is calculated for each index, expressed as: low contamination ($SRI < \text{median} - SD$), moderate contamination ($\text{median} - SD < SRI < \text{median}$), high contamination ($\text{median} < SRI < \text{median} + SD$) and severe contamination ($\text{median} + SD < SRI$).

2.8. Evaluación del riesgo para la salud humana

Health risk assessment is generally used to estimate the risk of human exposure to certain contaminants. Human exposure to toxic metal impacts can occur through three main pathways, such as ingestion, inhalation and dermal contact. The chronic daily dose (CDD, mg/kg/day) proposed by EPA [20] was used to estimate these types of exposure. The methods for each CDD are shown in Eqs. (7–9).

$$CDD_{\text{ingestion}} = \frac{CM}{ABW} \times \frac{IR}{AET} \times \frac{ED}{AET} \times \frac{EF}{AET} \times CF \quad (7)$$

$$CDD_{\text{inhalation}} = \frac{CM}{ABW} \times \frac{IHR}{AET} \times \frac{ED}{AET} \times \frac{EF}{PEF} \quad (8)$$

$$CDD_{\text{dermal}} = \frac{CM}{ABW} \times \frac{SA}{AET} \times \frac{SAF}{AET} \times \frac{DAF}{AET} \times \frac{ED}{AET} \times \frac{EF}{AET} \times CF \quad (9)$$

The chronic daily dose was estimated taking into consideration the age of the individuals (adults or children). The description and values for

each of the equations used can be found in the Table S1. For health risk assessment, the indices proposed by the Environmental Protection Agency [19] were considered. These indices are divided into two categories, the first focuses on the risk of non-carcinogenic effects, and were determined through the hazard quotient (HQ) and the hazard index (HI). The second category focuses on the evaluation of the risk of carcinogenic effects through the measurement of carcinogenic risk (CR) and total carcinogenic risk (TCR).

2.8.1. Non-carcinogenic risk assessment

The non-carcinogenic risk was evaluated based on the HQ (Eq. 10), this index is calculated by dividing the CDD by the reference dose (Reference Dose Slope, RfD, mg/kg/day), according to each metal and route of exposure considered in the investigation. The HI (Eq. 11) was used for the integration of the HQ values obtained for the ingestion, inhalation and dermal route estimates. It is worth mentioning that if $HI < 1$, it is assumed that the non-carcinogenic adverse effect due to a given route of exposure is negligible, whereas the potential for chronic effects may be of concern when $HI > 1$.

$$HQ_{\text{ingestion}} = \frac{CDD_{\text{ing}} / \frac{\text{inh}}{\text{der}}}{RfD_{\text{ing}} / \frac{\text{inh}}{\text{der}}} \quad (10)$$

$$HI = \sum_{\text{ing}} HQ_{\text{ing}} / \frac{\text{inh}}{\text{der}} \quad (11)$$

2.8.2. Carcinogenic risk assessment

The carcinogenic risk was evaluated on the basis of the CR (Eq. 12). This index is calculated using the CDD and the factor corresponding to each exposure route considered in the investigation (Slope factor (SF) for $CDD_{\text{ingestion}}$, inhalation unit risk (IUR) for $CDD_{\text{inhalation}}$ and gastrointestinal absorption factor (G) for CDD_{dermal}). In addition, TCR (Eq. 13) was used for the integration of CR values. If $TCR > 1.00E-04$ is

considered an unacceptable risk; $1.00E-06 < TCR < 1.00E-04$ is considered an acceptable range of risk depending on the exposure conditions; $TCR < 1.00E-06$ is considered no significant risk for health effects.

$$CR_{\text{ing}} = CDD_{\text{ing}} \times SF; CR_{\text{inh}} = CDD_{\text{inh}} \times IUR; CR_{\text{der}} = CDD_{\text{der}} \times \frac{SF}{G} \quad (12)$$

$$TCR = \sum_{\text{ing}} CR_{\text{ing}} / \frac{\text{inh}}{\text{der}} \quad (13)$$

The RfD, SF, IUR and G values considered for each metal are summarized in Table S2.

2.9. Data analysis for identification of potential contamination sources

In order to evaluate the clustering patterns of the data and identify potential sources of contaminants in the sediments, cluster analysis and principal component analysis (PCA) of the selected toxic metals in the research were performed. The cluster analysis was developed using the Euclidean distance method, Ward's linkage and standardization was done using Z-scores. PCA was developed taking into account the KMO value and Bartlett's test of sphericity. All data were analyzed and plotted using PAST V4.08 software and R and RStudio software (Version 4.1.0).

3. Results and discussion

3.1. Analysis and distribution of toxic metals in sediments

Table 1 shows the mean concentration and standard deviation of toxic metals recorded in composite samples of sediments extracted from the north, center and south of Pomacocha, Tipicocha and Tranca Grande lagoons. The distribution of the mean concentration of toxic metals in

Table 1

Descriptive statistics (DS) of toxic metal concentrations in sediment of lagoons used for fish farming and international reference values - upper continental crust, threshold effect levels and probable effect levels of the interim sediment quality guidelines.

Toxic metals	DS	Lagoons			UCC	TEL	PEL
		Tranca Grande	Tipicocha	Pomacocha			
As	Mean	4.62	6.953	3.267	1.5	7.24	41.6
	SD	0.242	0.566	0.45			
	Max	4.90	7.56	3.78			
Cd	Mean	0.176	0.18	0.169	0.098	0.7	4.2
	SD	0.011	0.007	0.002			
	Max	0.188	0.187	0.172			
Cu	Mean	10.828	8.428	5.365	25	18.7	108
	SD	1.095	1.272	1.035			
	Max	11.869	9.807	6.447			
Cr	Mean	3.447	4.413	3.253	35	52.3	160
	SD	0.214	0.201	0.214			
	Max	3.68	4.6	3.44			
Pb	Mean	6.658	6.877	6.874	20	30.2	112
	SD	0.423	0.186	0.609			
	Max	7.125	7.03	7.395			
Zn	Mean	36.303	36.141	30.241	71	124	271
	SD	0.844	0.947	1.293			
	Max	37.21	37.016	31.34			
Co	Mean	1.678	2.123	1.673	10	–	–
	SD	0.032	0.132	0.135			
	Max	1.713	2.21	1.81			
Ni	Mean	11.16	10.34	5.16	20	–	–
	SD	0.501	0.816	0.232			
	Max	11.61	11.076	5.42			
V	Mean	31.03	28.127	18.745	60	–	–
	SD	1.528	1.677	0.438			
	Max	32.43	30.05	19.025			
Sb	Mean	0.16	0.17	0.147	0.2	–	–
	SD	0.01	0.01	0.006			
	Max	0.17	0.18	0.15			

the fish-use lagoons was in the descending order of $Zn > V > Ni > Cu > Pb > As > Cr > Co > Cd > Sb$. The mean concentration of As (Tranca Grande: 4.62 ± 0.24 , Tipicocha: 6.95 ± 0.57 , Pomacocha: 3.27 ± 0.45 $mg\ kg^{-1}$) and Cd (Tranca Grande: 0.18 ± 0.01 , Tipicocha: 0.18 ± 0.01 , Pomacocha: 0.17 ± 0.01 $mg\ kg^{-1}$) exceeded upper continental crustal reference values (UCC) (As: 1.5 and Cd: $0.098\ mg\ kg^{-1}$). These results are similar to those obtained by [45] who reported As and Cd concentrations in sediments higher than the interim sediment quality guidelines. The high concentration of As in lake sediments could be attributed to anthropogenic activities such as intensive fish farming and agriculture that misuse arsenic fertilizers and pesticides [7] and Cd could be due to low input from streams to lagoons causing precipitation of Cd in the sediments, increasing its concentration [34]. The mean concentrations of the other metals were lower than the UCC reference values [53], threshold effect levels (TEL) and probable effect levels (PEL) [14]. The behavior of the maximum concentrations of toxic metals recorded in the sediments of each lagoon showed a marked variability. In the Tranca Grande lagoon, the highest concentrations of As ($4.90\ mg\ kg^{-1}$), Zn ($37.21\ mg\ kg^{-1}$) and V ($32.43\ mg\ kg^{-1}$) were found in the northern zone; Cu ($11.87\ mg\ kg^{-1}$) and Ni ($11.61\ mg\ kg^{-1}$) were found in the central zone; while Cd ($0.19\ mg\ kg^{-1}$), Cr ($3.68\ mg\ kg^{-1}$), Pb ($7.13\ mg\ kg^{-1}$), Co ($1.71\ mg\ kg^{-1}$) and Sb ($0.17\ mg\ kg^{-1}$) were found in the southern zone. In the Tipicocha lagoon, the highest concentrations of As ($7.56\ mg\ kg^{-1}$) and Zn ($37.2\ mg\ kg^{-1}$) were found in the northern zone; Pb ($7.03\ mg\ kg^{-1}$), Co ($2.21\ mg\ kg^{-1}$) and Sb ($0.18\ mg\ kg^{-1}$) were found in the central zone; while, Cd ($0.19\ mg\ kg^{-1}$), Cu ($9.81\ mg\ kg^{-1}$), Cr ($4.60\ mg\ kg^{-1}$), Ni ($11.08\ mg\ kg^{-1}$) and V ($30.05\ mg\ kg^{-1}$) were found in the southern zone. In the Pomacocha lagoon, the highest concentrations of Pb ($7.40\ mg\ kg^{-1}$) was found in the north zone, Cr ($3.44\ mg\ kg^{-1}$), Ni ($5.42\ mg\ kg^{-1}$), V ($19.03\ mg\ kg^{-1}$) and Sb ($0.15\ mg\ kg^{-1}$) were found in the central zone; while, As ($3.78\ mg\ kg^{-1}$), Cd ($0.17\ mg\ kg^{-1}$), Cu ($6.45\ mg\ kg^{-1}$), Zn ($31.34\ mg\ kg^{-1}$), Co ($1.81\ mg\ kg^{-1}$) and Sb ($0.15\ mg\ kg^{-1}$) were found in the southern zone. Compared to other national studies, the concentrations of toxic metals recorded in the sediments of the three lagoons were lower than those recorded in Lake Titicaca [42]. Compared to studies in other regions of the world, the values found in this research were lower than those recorded in the Batticaloa lagoons [3] and Bizerte [18]. From these results, it can be observed that most of the toxic metals evaluated were found in the southern zone of each lagoon. While, the northern and central zones have between one to four metals in their maximum concentration.

3.2. Cluster analysis

Cluster analysis (CA) has been applied in numerous studies to group sampling sites with similar characteristics, process and sources [10,11,37,44]. This analysis was conducted to group similar sediment samples in fish production use ponds based on toxic metal concentrations. Fig. 2 shows that Tipicocha and Tranca Grande lagoons presented similar concentrations of V, Ni, Zn and Cu. The CA shows sets of clusters with elements in the clusters similar to each other, but dissimilar to those in different groups. The Tipicocha lagoon presented higher concentrations of Sb, As, Co and Cr, which were grouped in a cluster. The analysis shows that the concentrations of V, Ni, Zn and Cu tend to correlate positively. This behavior is due to the fact that these elements are part of the fuels and lubricants [39] used in the fish farms. The combustion of fuels and the use of inputs for fish production would provide a flux of toxic elements into the aquatic environment. The close association between Co and Cr would indicate that terrigenous aluminosilicate minerals are the main metal-bearing minerals in this area [27]. The association between As and Co, reveals that in the study area cobalt ferrites are attracted to As (III) [38]. In the cluster of sediment samples from the Pomacocha lagoon, there is a tendency to be significantly separated from the zone of the other lagoons, as they have lower concentrations of toxic metals, except for Pb.

3.3. Identification of the potential source of pollutants through principal component analysis

A principal component analysis (PCA) was performed to explore the origin of toxic metals and reduce the data set to a few influential factors avoiding some insignificant data [63,67]. Fig. 3 shows a significant difference between the lagoons studied with respect to the concentration of metals evaluated. The PCA shows that Pomacocha lagoon has lower concentrations of toxic metals than Tipicocha and Tranca Grande lagoons. Components 1 and 2 covered 81.25 % of the total variance (PC1: 59.06 % and PC2: 22.18 %; Table S3). Principal components (PC) helped to classify the contribution of each metal. In PC1 As, Zn, Ni and V showed the highest eigenvalues (0.37, 0.38, 0.37 and 0.36). In PC2 Cu, Pb and Co showed the highest eigenvalues (−0.45, 0.45 and 0.46) (Table S4). This distribution could be explained by the proximity of the lagoons and the receptivity of water from the Tranca Grande lagoon to the Tipicocha lagoon, which acts as a reservoir for the former. Both lagoons have the highest concentrations of As, Sb, Zn, Ni and V; the difference between them is significantly given by the concentrations of Co and As in the Tipicocha lagoon, with a positive association [38] and Cu with higher concentration in the Pomacocha lagoon. This distribution

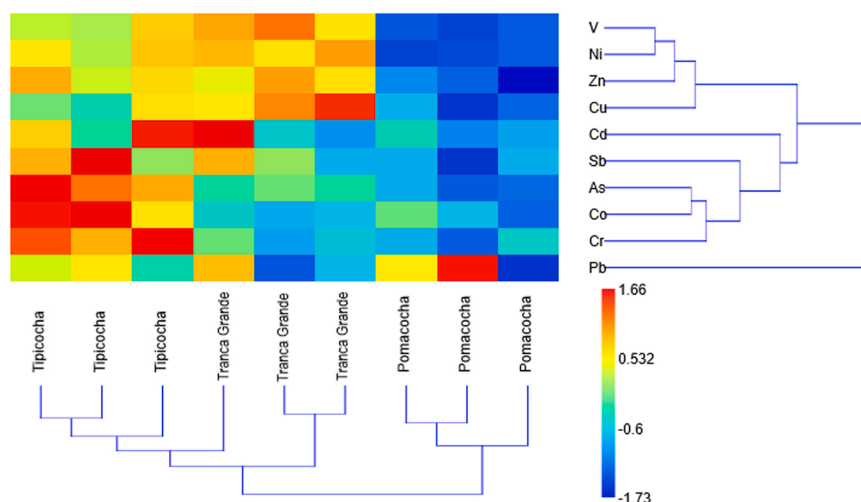


Fig. 2. Dendrogram showing the clustering of sampling sites according to the concentration of toxic metals in sediments of lagoons used for fish farming.

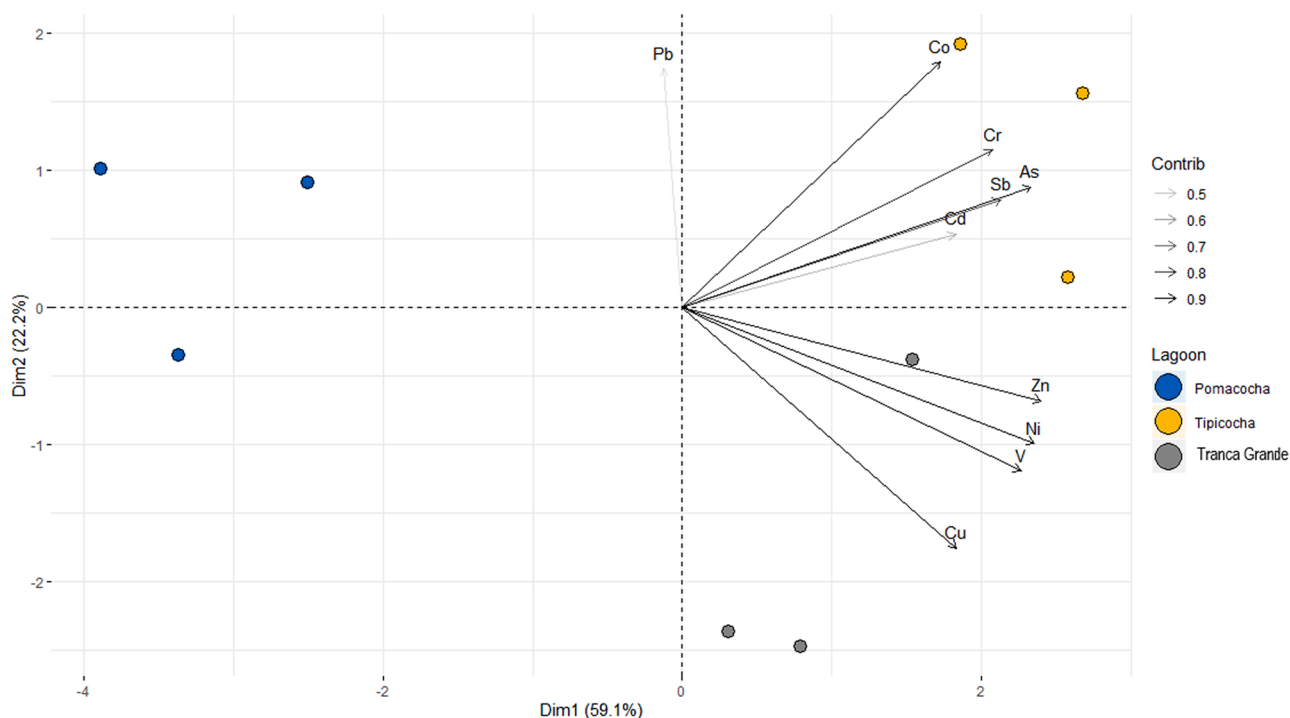


Fig. 3. Principal component analysis based on the concentrations of toxic metals in sediment of lagoons used for fish farming.

shows that Co and As do not tend to stabilize in the sediment when there is a possibility to move due to the effect of water dynamics. PC1 also shows the great impact of fish farming activity in the lagoons, especially for As [27,52] and could generate considerable levels of contamination and risk.

3.4. Assessment of sediment contamination by toxic metals

The Tranca Grande, Tipicocha and Pomacocha lagoons presented Cf values of Co, Cr, Cu, Ni, Pb, Sb, V and Zn, lower or close to 1, qualifying as low contamination factors ($Cf < 1$). In the case of As, the behavior of Cf values was different in each lagoon. In the Tranca Grande lagoon, in the northern zone, As presented a considerable Cf ($Cf: 3.27$) and in the central and southern zones moderate Cf with a tendency to reach a considerable Cf ($Cf: 2.99$). In Pomacocha and Tipicocha lagoons, in the three sampling zones, As presented moderate ($1 < Cf < 3$) and considerable ($3 < Cf < 6$) Cf respectively. In Pomacocha lagoon in the central and southern zones ($Cf: 2.05$ and 2.52 , respectively) and Tipicocha lagoon, the maximum Cf values of As were recorded in the northern and central sampling zones ($Cf: 5.04$ and 4.57 , respectively). The Cd Cf values recorded in the three lagoons were higher than one and lower than three ($1 > Cf < 3$), qualifying as a moderate Cf. In the Tranca Grande and Tipicocha lagoons, the maximum Cf values for Cd were

recorded in the northern and southern sampling zones, while in the Pomacocha lagoon, the maximum Cf values were recorded in the central and southern zones. The PLI in the Pomacocha, Tipicocha and Tranca Grande lagoons ranged from 0.3856 to 0.5622, indicating no appreciable contamination by these metals (Table 2). The PLI provides sediment quality information that is essential for decision makers on the contamination status of the study area [32].

The three lagoons in this study presented I_{geo} values of Co, Cr, Cu, Ni, Pb, Sb, V and Zn lower than zero, indicating that the sampling sites of the evaluated lagoons are not contaminated by these metals. The sediments of Tipicocha and Pomacocha lagoons were found to be enriched by As. In Pomacocha lagoon, the As I_{geo} values showed an increasing trend, $0 < I_{geo} < 1$ (class 1), revealing indications of As contamination. In the Tipicocha lagoon, the As I_{geo} values were higher than one and lower than two ($1 < I_{geo} < 2$), revealing that they are moderately contaminated, corresponding to class 2. The maximum As I_{geo} values in this lagoon were recorded in the northern and central zones ($I_{geo}: 1.75$ and 1.61 respectively). In the Tranca Grande lagoon, As I_{geo} values indicating signs of contamination and moderate contamination were recorded. In the three lagoons, the Cd I_{geo} values were $0 < I_{geo} < 1$, revealing signs of contamination (Table S5).

The mCd corroborated this result, indicating that these lagoons have a very low degree of contamination (Table S6). In order to eliminate

Table 2

Contamination factor (Cf) and Pollution load index (PLI) of toxic metals in sediment of lagoons used for fish farming, according to sampling site.

Lagoon	Sampling zone	Contamination factor - CF										PLI
		As	Cd	Cu	Cr	Pb	Zn	Co	Ni	V	Sb	
Pomacocha	Northern	1.96	1.70	0.18	0.09	0.37	0.43	0.17	0.25	0.30	0.70	0.3856
	Central	2.05	1.72	0.21	0.10	0.31	0.41	0.15	0.27	0.32	0.75	0.3945
	Southern	2.52	1.75	0.26	0.09	0.35	0.44	0.18	0.25	0.32	0.75	0.4216
Tipicocha	Northern	5.04	1.85	0.33	0.13	0.35	0.52	0.22	0.52	0.46	0.85	0.5612
	Central	4.57	1.77	0.29	0.12	0.35	0.49	0.22	0.47	0.45	0.90	0.5393
	Southern	4.29	1.91	0.39	0.13	0.33	0.51	0.20	0.55	0.50	0.80	0.5622
Tranca Grande	Northern	3.27	1.74	0.44	0.09	0.32	0.52	0.17	0.53	0.54	0.80	0.5202
	Central	2.99	1.71	0.47	0.10	0.33	0.51	0.17	0.58	0.49	0.75	0.5185
	Southern	2.99	1.92	0.39	0.11	0.36	0.50	0.17	0.56	0.52	0.85	0.5309

arbitrary and different classifications of each individual index, the SRI was used. This index allows comparing the level of contamination of the sampling sites (Cf and I_{geo}) with the concentrations of the analyzed metals [46,68]. In addition, the SRI provides a better understanding of the sediment contamination status of each lagoon. The SRI values obtained for Cf and I_{geo} were identical and varied by lagoon. In Pomacocha lagoon the SRI ranged from moderate to high (from 60 to 83.33), in Tipicocha lagoon the SRI ranged from low to high (from 56.67 to 73.33) and in Tranca Grande lagoon it ranged from low to severe (from 50 to 83.33) (Table S7).

In general, the present results reveal the pressure from fish farming, the input of toxic metals through rivers running through areas with mining activity and runoff from agricultural areas. Other studies support our results and report that fish farming and environmental conditions around fish cages influence the sedimentation of the metals studied [26]. As and Cd were the main toxic metals in the sediments of the three lagoons in this study. These findings reveal the influence of mining, agricultural activities, including livestock and poultry farming, as well as pesticide and fertilizer application in increasing the content of As and Cd. Although the sediment serves as a trap for toxic metals, it is also an important source of these metals to the water column [22].

3.5. Evaluation of the potential ecological risk from toxic metals

The values of Ri were obtained from the concentrations of As, Cd, Cu, Cr, Pb and Zn in the sediments, since these are the elements that have their biological toxic factor (Tr) for the calculation of the ecological risk factor (Er) of each metal [46]. These results show that Tranca Grande Lagoon (Ri-North: 74.04, Ri-Center: 75.38, Ri-South: 81.45) and Pomacocha Lagoon (Ri-North: 89.45, Ri-Center: 85.96, Ri-South: 91.93) have a low potential ecological risk, while Tipicocha Lagoon has a moderate potential ecological risk (Ri-North: 109.95, Ri-Center: 102.65, Ri-South: 104.70). Our results agree with other studies that report similar trends in potential ecological risk. However, this comparison reflects the variability in the concentrations of toxic metals and the anthropogenic pressure that aquatic systems have been experiencing in different regions of the world [47,61,8].

Fig. 4 shows the degree of contamination and the potential ecological

risk of each lagoon obtained from the SRI-Cf and Ri. The Tranca Grande and Pomacocha lagoons presented a low potential ecological risk. However, the central and northern zones of Tranca Grande had moderate contamination and the southern zone had high contamination. The central and southern zones of Pomacocha lagoon showed high and severe contamination due to the presence of the toxic metals evaluated. As and Cd were the metals that presented the greatest ecological risk in the sediments, revealing that the release and bioavailability of these metals can be affected by natural and anthropogenic pressures [62]. The Tipicocha lagoon presented a moderate ecological risk potential, i.e., there is a potential effect of the metals evaluated on the organisms of this ecosystem [49]. Likewise, the southern and northern zones of Tipicocha lagoon are highly contaminated by toxic metals and represent the areas of greatest ecological risk. Finally, the toxic metal risk assessment in this study maintained some uncertainties, which are inherent in quantitative risk assessment.

3.6. Risk to human health from exposure to sediments contaminated with toxic metals

HI values for toxic metals were found to be in the order of $As > V > Pb > Cr > Ni > Sb > Cu > Cd > Zn$ in the three ponds in this study (Fig. 5). The HI values in adults and children were < 1 , suggesting that non-carcinogenic adverse effects are negligible or unlikely to develop in adults and children coming into contact with sediments from the three ponds in this study. As HI values for children ranged from $1.29E-02$ in Pomacocha lagoon to $3.33E-02$ in Tipicocha, while As HI values for adults ranged from $5.95E-03$ to $1.53E-02$ in these lagoons. These results revealed a non-carcinogenic risk caused by the metals studied for children and adults, although the HI values for children were an order of magnitude higher than for adults. The order of the hazard quotients that determined the HI values were ingestion $>$ dermal $>$ inhalation; which is an important point to consider due to the trout production practices that occur in these ponds. The present results coincide with other studies that refer to ingestion as the main route of exposure, followed by dermal contact. It also shows that it is the route of greatest contribution to health risks originating in sediments contaminated with potentially toxic elements ([57]; K. [31,47]).

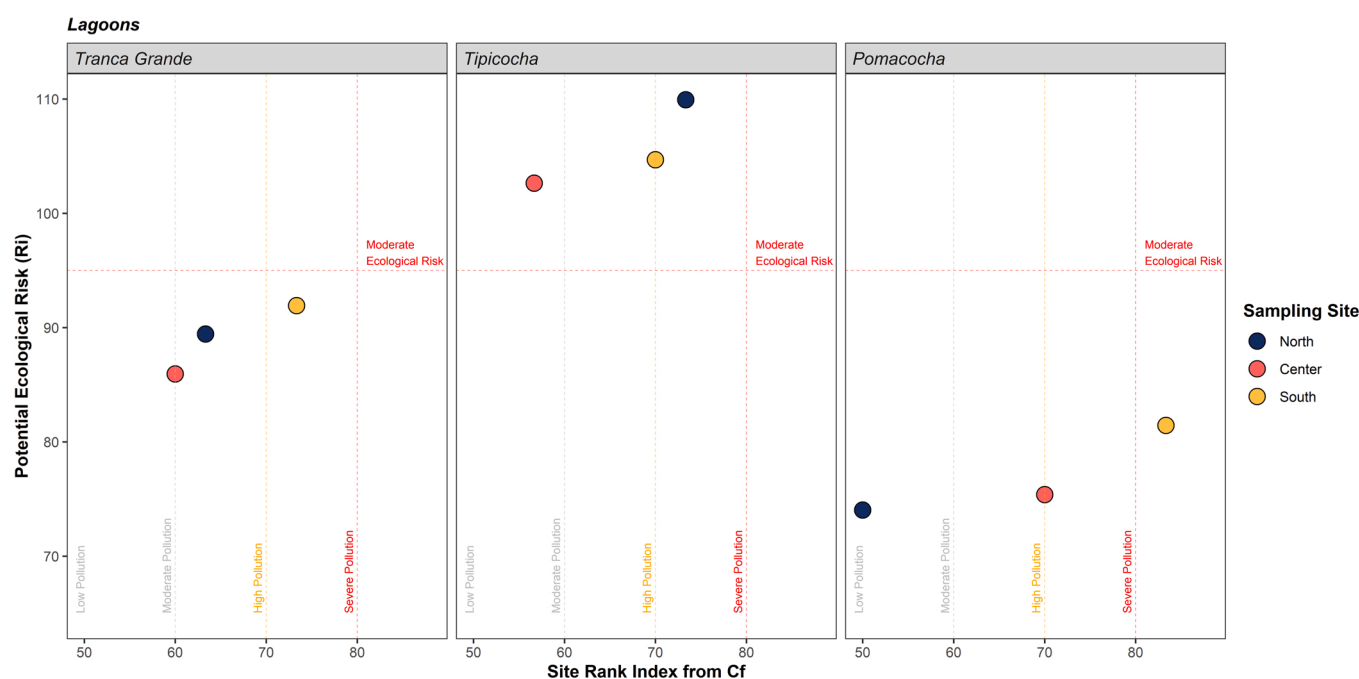


Fig. 4. Behavior of the site rank index (SRI-Cf) versus the potential ecological risk (Ri) from toxic metals in sediment of lagoons used for fish farming, according to sampling area.

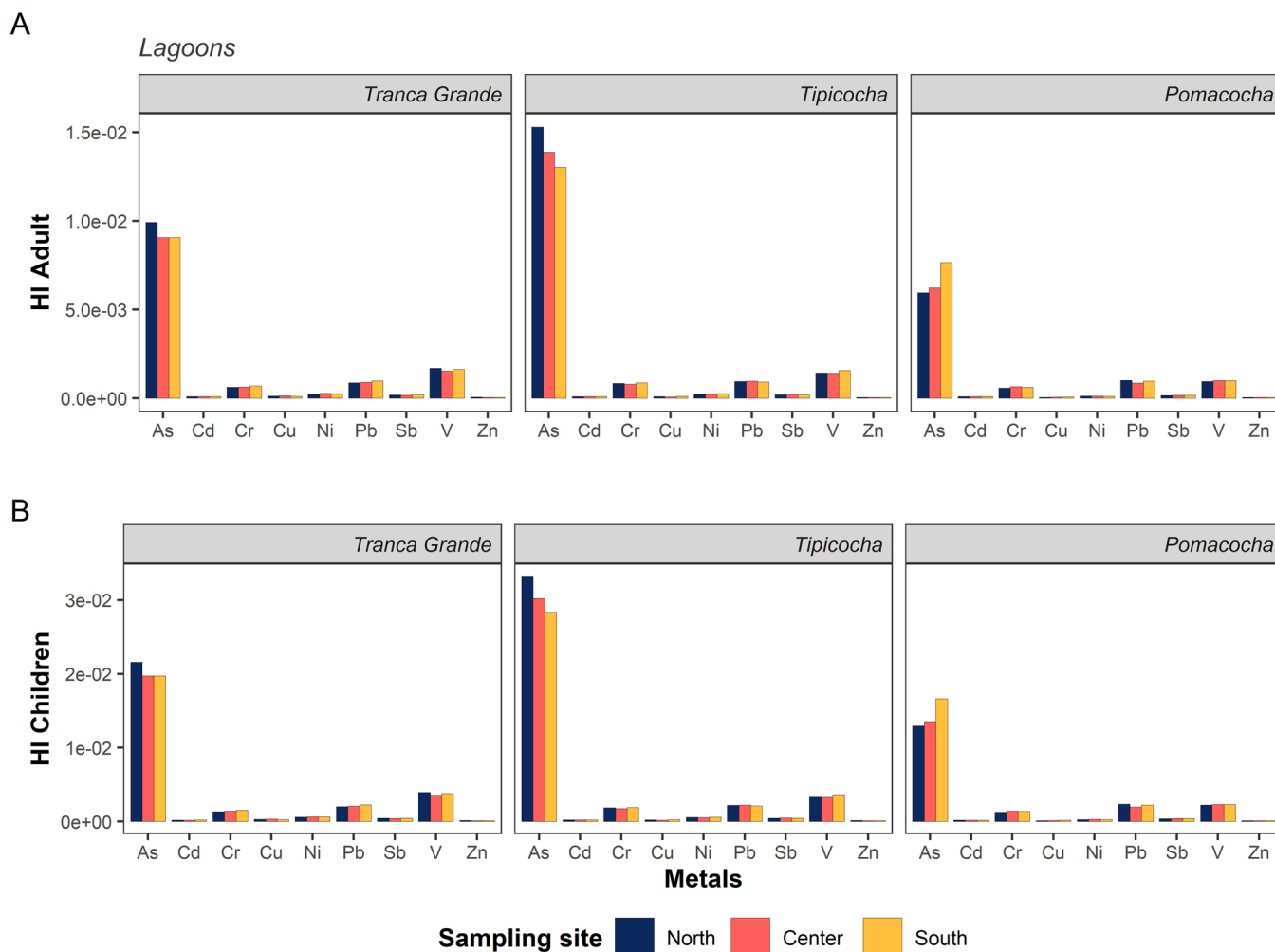


Fig. 5. Hazard index (HI) for children and adults for exposure to toxic metals in sediment of lagoons used for fish farming.

The TCR values (i.e., lifetime cancer risk, LCR) of As and Cr were the highest compared to the other metals evaluated (Fig. 6). In adults, the TCR values of As ranged from $1.30\text{E}-05$ to $8.70\text{E}-06$, Cr from $2.40\text{E}-06$ to $3.53\text{E}-06$, Ni from $6.29\text{E}-07$ to $1.47\text{E}-06$, Cd from $1.70\text{E}-07$ to $1.91\text{E}-07$ y Pb from $7.25\text{E}-08$ to $8.22\text{E}-08$. The TCR values for As, Cr and most Ni were greater than $1.00\text{E}-06$ and less than $1.00\text{E}-04$, indicating that they are in an acceptable range of carcinogenic risk. However, it should be re-evaluated based on the conditions to which adults mainly engaged in fish farming are exposed. In children, the TCR values of As ranged from $6.11\text{E}-05$ to $1.57\text{E}-04$, Cr from $2.15\text{E}-05$ to $3.27\text{E}-05$, Ni from $5.71\text{E}-06$ to $1.33\text{E}-05$, Cd from $1.52\text{E}-06$ to $1.71\text{E}-05$ and Pb from $6.76\text{E}-07$ to $8.06\text{E}-07$ (Table S8). TCR values for these metals were found to be below $1.00\text{E}-04$ in all three lagoons, indicating no significant carcinogenic risk. Similarly, carcinogenic risk values for these toxic metals have been found in other settings to be lower than the range $1.00\text{E}-06$ – $1.00\text{E}-04$ recommended by the USEPA [58]. The TCR values for As in the three zones of the Tipicocha lagoon and in the northern zone of the Tranca Grande lagoon were greater than $1.00\text{E}-04$, revealing a possible cancer risk in children associated with exposure to this toxic metal. These results are similar to those reported in other studies that report As as the main potentially toxic element of carcinogenic risk [30, 60]. As toxicity involves multiple systems; cardiovascular system, central nervous system and hematopoietic system, etc. However, the highest concentration of As is observed in the kidneys and liver [12,29].

The routes of exposure with the greatest influence on the TCR calculation were in the order of ingestion > dermal > inhalation. According to this study, oral ingestion of toxic metals is the most important

route of exposure, so it is necessary to evaluate dietary exposure, since trout production is carried out in these ponds. Therefore, the enrichment and amplification of toxic metals would affect human health along the food web.

4. Conclusions

The evaluation of toxic metal contamination, distribution and risk in the sediments of Pomacocha, Tipicocha and Tranca Grande lagoons used for fish farming is of great importance to ensure the supply of water suitable for trout production and other uses. Mean As and Cd concentrations were observed to exceed upper continental crustal reference values and interim sediment quality guideline values. Cf values for Cd and As indicated moderate and considerable contamination. The I_{geo} for Cd indicated indications of contamination and for As moderate contamination. However, the PLI indicated no appreciable contamination by these toxic metals, being corroborated by the modified degree of contamination. The potential ecological risk ranged from low to moderate. The health risk assessment showed that exposure to sediments contaminated with toxic metals through ingestion or dermal contact presents a low risk. However, trout are an important source of nutrients grown in these ponds and the release of toxic metals from the sediment into the water column may compromise safe fish and pose a threat to human health. TCR values for these metals were found to be below $1.00\text{E}-04$ in all three lagoons, indicating no significant carcinogenic risk. The TCR values for As in the three zones of Tipicocha lagoon and in the northern zone of Tranca Grande lagoon are revealed a possible

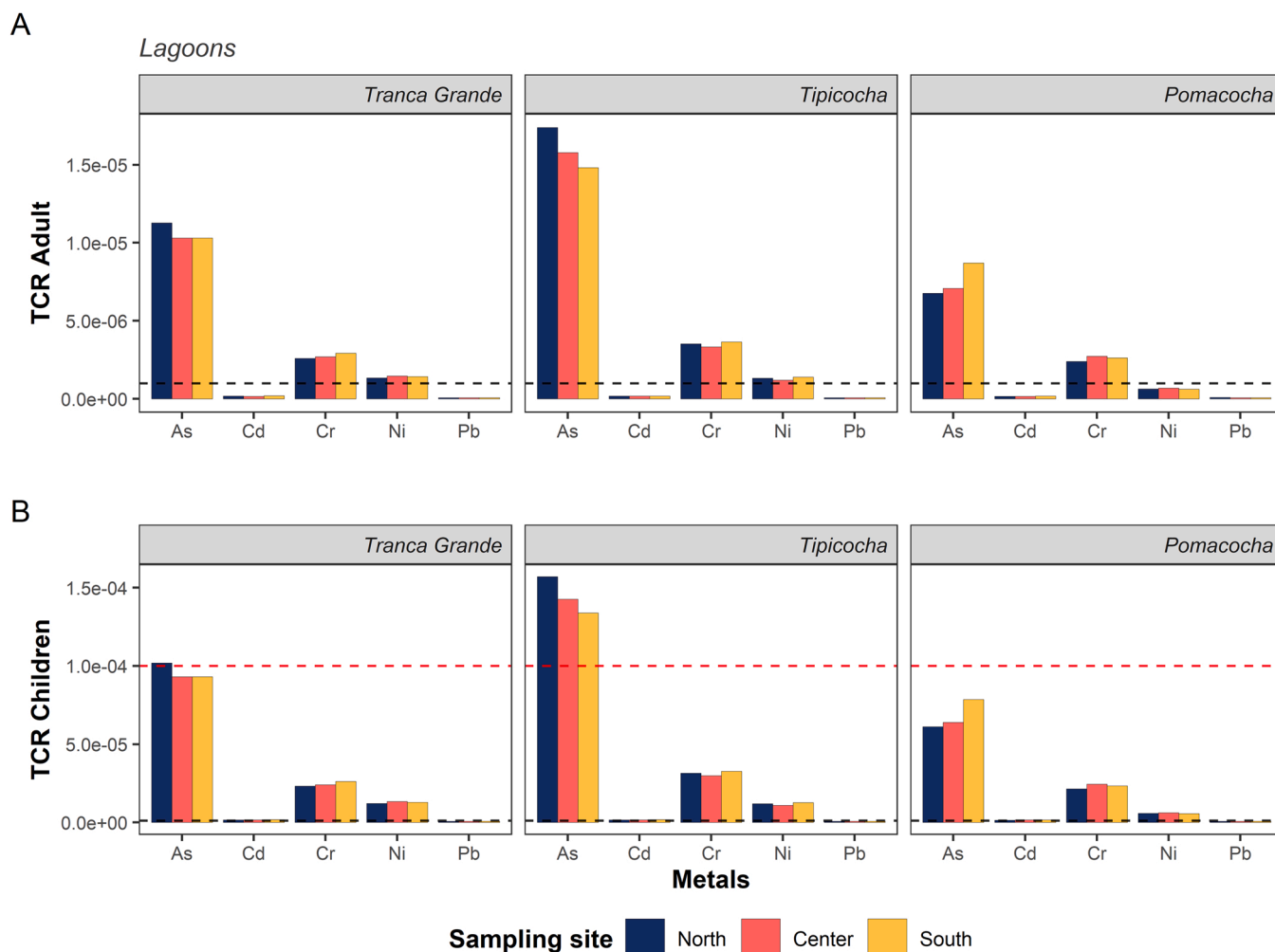


Fig. 6. Total carcinogenic risk (TCR) for adults and children for exposure to toxic metals in sediment of lagoons used for fish farming.

cancer risk in children associated with exposure to this toxic metal. Therefore, considering that these lagoons are used for fish production for domestic consumption and export, it is important to continue monitoring for toxic metals to protect the health of these ecosystems and human health.

CRediT authorship contribution statement

M. Custodio: Investigation, Conceptualization, Methodology, Writing – original draft, Project administration, Funding acquisition. **C. Espinoza:** Investigation, Methodology, Supervision. **E. Orellana:** Investigation, Methodology. **F. Chanamé:** Investigation, Methodology. **A. Fow:** Performed the data analysis and wrote the first draft of the manuscript. **Richard Peñaloza:** Data curation, Visualization.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.toxrep.2022.07.016](https://doi.org/10.1016/j.toxrep.2022.07.016).

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