Potential ecological risk from heavy metals in surface sediment of lotic systems in central region Peru

María Custodio[1]*, Anthony Fow[2], Heidi De la Cruz[3], Fernán Chanamé[4] and Javier Huarcaya[1]

[1]Environmental Science and Health Research Group, Facultad de Medicina Humana, Universidad Nacional del Centro del Perú, Huancayo, Peru, [2]Facultad de Ingeniería Ambiental y de Recursos Naturales, Universidad Nacional del Callao, Callao, Peru, [3]Facultad de Ingeniería Química, Universidad Nacional del Centro del Perú, Huancayo, Peru, [4]Facultad de Zootecnia, Universidad Nacional del Centro del Perú, Huancayo, Peru

High Andean rivers are fragile ecosystems in the face of various threats, including heavy metal contamination. The objective of this study was to evaluate the potential ecological risk of heavy metals in surface sediment of lotic systems in the central region of Peru. Composite samples of surface sediments were collected from the Chía and Miraflores rivers and the concentrations of heavy metals were determined. The ecological risk analysis was carried out based on the contamination indexes and confirmed by the modified degree of contamination (mCd). The concentration of heavy metals in the sediment of the Chía river was in the following descending order: Fe > Mn > Zn > V > Pb > Cr > Ni > Cu > Mo > Hg, y en el río Miraflores fue: Fe > Mn > Zn > Ni > V > Cr > Cu > Pb > Hg > Mo. The mean concentration of Cu, Cr, Fe, Mn, Mo, Ni, Pb, and V in the sediment samples in both rivers did not exceed the threshold values of the continental crust concentration, nor the interim sediment quality guidelines of the Canadian Council of Ministers of the Environment. However, the mean concentration of Hg exceeded the guideline values in the Miraflores river and the likely effect ($0.7 \, \text{mg.kg}^{-1}$) adverse effects. The values of the enrichment factor (EF), contamination factor (CF), geoaccumulation index (I_{geo}), and pollution load index (PLI) indicated low contamination in the sediments of the rivers studied, being confirmed by the modified degree of contamination (mCd). Finally, the risk assessment showed that heavy metals in the sediments presented a low potential ecological risk.

KEYWORDS

contamination, ecological risk, heavy metals, surface sediment, lotic systems, aquatic environment

1 Introduction

Water quality is high on the global sustainability agenda, especially in rivers, as it is directly related to human wellbeing (Töre et al., 2021; Uddin et al., 2021; Nayak et al., 2023). The conditions of these aquatic ecosystems have deteriorated over time due to heavy metal inputs from anthropogenic and natural sources (Zhang et al., 2022; Heikkinen et al., 2023). Metallic elements released into rivers by human activities such as urban wastewater discharges, mining and industrial emissions, intensive agriculture and livestock farming alter the balance of aquatic ecosystems (Redwan and Elhaddad, 2017; Luo et al., 2019; Ali et al., 2022; Zhang et al., 2023). Natural sources also contribute significant concentrations of heavy metals to water bodies (Duncan et al., 2018; Dendievel et al., 2022). For example, in areas with volcanic activity, it is possible to find high concentrations of boron and

arsenic in water bodies (Ali and Khan, 2018). Heavy metals accumulated in sediments can mobilize to the water column and increase their bioavailability in both matrices and influence their bioaccumulation and biomagnification in aquatic flora and fauna (Ustaoglu and Tepe, 2019; Algül and Beyhan, 2020; Ambrosino et al., 2023). Several factors influence the accumulation and spatial distribution of heavy metals in sediments (Wei and Wen, 2012), such as solubility, mobility, adsorption, bioavailability, precipitation, and cation dynamics (Bakshe and Jugade, 2021). However, the degree of risk from heavy metals will vary depending on concentration levels and source (Sojka et al., 2023).

Heavy metals can enter the human body through a wide range of food chains and reach toxic amounts (Jaishankar et al., 2014; Isroni and Maulida, 2022; Peñaloza et al., 2023). Prolonged exposure to heavy metals can alter biochemical processes, lead to their accumulation in the liver and kidneys and induce toxicity in many organs of the body with carcinogenic, teratogenic, and cardiovascular consequences (Algül and Beyhan, 2020; Bakshe and Jugade, 2021; Alam et al., 2023). Over the past decades, many studies have reported on sediment contamination by heavy metals, source identification, distribution pattern, degree of contamination, and health risks (Saiful et al., 2015; Engin et al., 2017; Yi et al., 2017; Ibrahim et al., 2019); however, few have attempted to establish a link between them. The degree of sediment contamination by heavy metals and the risks they pose can be assessed using individual and complex indices such as contamination factor (CF), enrichment factor (EF), modified contamination index (mCd), and potential ecological risk (Ri; Bian et al., 2016; Jia et al., 2017; Libralato et al., 2018; Li et al., 2020; Wieringa et al., 2022), as they allow associating pollution patterns to their potential sources (Wang et al., 2017).

In Peru, heavy metal contamination of rivers is a major concern not only because it degrades these ecosystems and restricts their use, but also because it threatens human health. Specifically, specific research experiences oriented to evaluate the ecological risk of heavy metals in Andean aquatic ecosystems are scarce (Custodio et al., 2021b). The Chía and Miraflores rivers, located in the central region of Peru, are of vital importance for the various ecosystem services they provide. The predominant activities dependent on these water bodies are mainly fish farming, water for human consumption and water for irrigation and recreation. Currently, there is no known research on the level of contamination and ecological risks of heavy metals in sediments of these rivers. Therefore, it is of utmost importance to generate relevant information on river sediment quality conditions for water quality protection and control. In this study, the degree of contamination and the potential ecological risk of sediment by heavy metals have been evaluated to obtain a comprehensive understanding of the pressure that these ecosystems are experiencing. In addition, the results will allow decision makers to propose and implement action measures to protect and conserve these ecosystems and reduce information gaps aligned with Sustainable Development Goal 6 (Clean Water and Sanitation). In this sense, the objective of this study is to evaluate the potential ecological risk of heavy metals in surface sediment of lotic systems in the central region of Peru.

2 Materials and methods

2.1 Study area

The Chía and Miraflores rivers are located in the Mantaro river watershed in Peru between parallels $10°34'30''$ and $13°35'30''$ south latitude, and meridians $73°55'00''$ and $76°40'30''$ west longitude (Figure 1). Both rivers are characterized by fish farming activities, but downstream they are strongly influenced by agricultural and urban activities. The Mantaro basin has a climate that varies according to altitude. In the study area of the Chía and Miraflores rivers, the climate is temperate and cold, with low humidity. The average air temperature is lowest in July and highest in November. In areas above 4,000 masl the temperature is around $4.3°C$, in areas between 3,000 and 4,000 masl the temperature varies between 8.1 and $10.4°C$ and in areas between 2,000 and 3,000 masl the temperature varies between 14.6 and $17.4°C$ (Custodio et al., 2021a). Rainfall occurs gradually from September onwards, intensifies in February and March and decreases in April to reach minimum values in June (Ministry of Agriculture, 2010). The sampling sites were established according to the existing sources of contamination, such as wastewater discharges from fish farms, runoff from agricultural areas and urban wastewater. In both rivers, three sampling sites were established with three sampling sub-sites in each sector.

2.2 Sample collection and laboratory analysis

Surface sediment samples (0–10 cm depth) from the Chia and Miraflores rivers were collected using a stainless steel device, according to standard protocol (USEPA, 2001) in June 2022. Samples from each zone were mixed following the protocol of Condor et al. (2021) to obtain composite samples; these were transferred to the laboratory in cold chain for analysis (APHA, 2012). Sediment samples were dried at $40°C$, ground and sieved with an $85\,\mu m$ mesh sieve to obtain uniform samples. Heavy metal extraction was performed according to the protocol of Custodio et al. (2022) from 1 g of sediment per sample. Finally, the 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). Quality control and quality assurance was performed by applying standard laboratory methods (APHA, 2012).

2.3 Heavy metal contamination and ecological risk assessment methods

The ecological risk due to heavy metals was evaluated based on contamination indices, such as the enrichment factor (EF), contamination factor (CF), geoaccumulation index (Igeo), pollution load index (PLI), modified degree of contamination (mCd), and potential ecological risk (Ri). In addition, the site rank index (SRI) was applied to integrate the EF, Cf, and I_{geo} results obtained for each metal evaluated. This integrated value was

FIGURE 1
Location map of sediments sampling sites. **(A)** Chía and **(B)** Miraflores rivers.
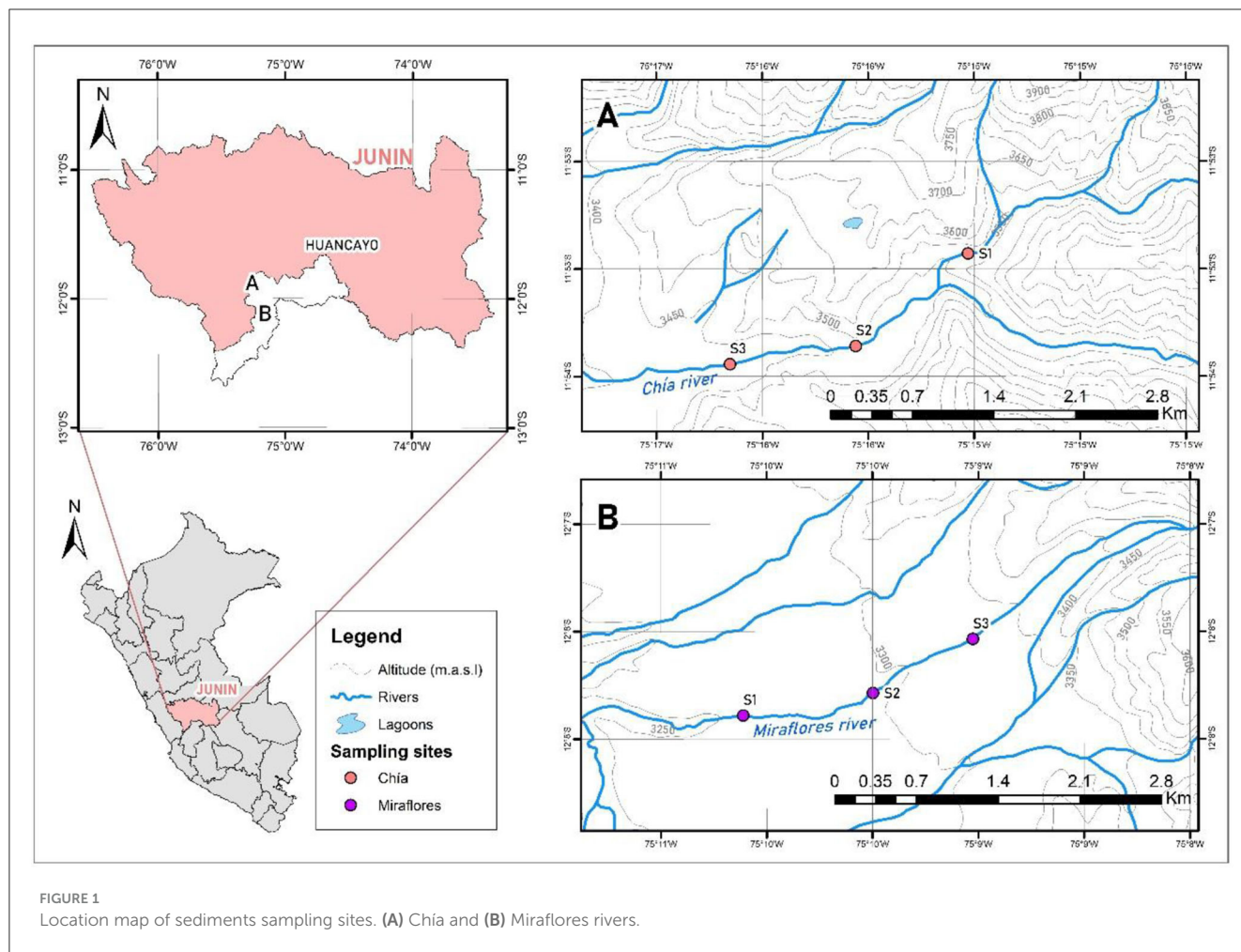
then compared with the complex indices, such as PLI, mCd, and Ri (Omwene et al., 2018). In the calculation of these indicators, the upper continental crust values were considered because they provide a reference value for the Hg (Turekian and Wedepohl, 1961).

2.3.1 Enrichment factor

The FE estimates the anthropogenic impact of metals on sediments. It usually uses iron as a marker to differentiate or normalize the natural and anthropogenic components in the collected sample (Abrahim and Parker, 2008; Fernández et al., 2018). The EF is calculated using Equation 1.

$$EF = \frac{(C_m \text{ sample } \times C_{Fe} \text{ background})}{(C_m \text{ background } \times C_{Fe} \text{ sample})} \quad (1)$$

Donde, sample es la concentración de metal en el sedimento, C_m background es la concentración del metal en la corteza continental, sample es la concentración de hierro en el sedimento y C_{Fe} background es la concentración de hierro en la corteza superior continental.

Where, C_m sample is the concentration of metal in the sediment, C_m background is the concentration of metal in the continental crust, C_{Fe} sample is the concentration of iron in the

sediment and C_{Fe} background is the concentration of iron in the continental upper crust. An EF <1 qualifies as not enriched, 1 < EF < 3 low enrichment, 3 < EF < 5 moderate enrichment, 5 < EF < 10 moderately severe enrichment, 10 < EF < 25 severe enrichment, 25 < EF < 50 very severe enrichment and EF > 50 extremely severe enrichment (El-amier et al., 2017; Omwene et al., 2018).

2.3.2 Contamination factor

Cf is the ratio of the concentration of each metal in the sediment to the background value (Turekian and Wedepohl, 1961). This index was used to quantify the metal contamination status of the sediment for each metal evaluated (Hakanson, 1980; El-amier et al., 2017) and is calculated by the Equation 2.

$$CF = \frac{C_m \text{ sample}}{C_m \text{ background}} \quad (2)$$

Where, C_m sample is the metal concentration in the sediment, and C_m background is the metal concentration in the upper continental crust. A CF < 1 indicates a low contamination factor, 1 < CF < 3 moderate contamination factor, 3 < CF < 6 considerable contamination factor, and CF ≥ 6 very high contamination factor (El-amier et al., 2017).

2.3.3 Geoaccumulation index

I_{geo} determines the difference of metal content in the samples and background values that exist naturally in the continental crust (Turekian and Wedepohl, 1961). This index establishes the sediment contamination levels for each metal evaluated (Kowalska et al., 2018; Ranjbar et al., 2020) which is calculated by Equation 3.

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n} \qquad (3)$$

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. I_{geo} is classified into seven levels: Igeo ≤ 0, level 0 (not contaminated); 0 < Igeo < 1, level 1 (not contaminated to moderately contaminated); 1 < Igeo < 2, level 2 (moderately contaminated); 2 < Igeo < 3, level 3 (moderately to heavily contaminated); 3 < Igeo < 4, level 4 (heavily contaminated); 4 < Igeo < 5 level 5 (heavily to extremely contaminated); Igeo > 5, level 6 (extremely contaminated; Müller, 1979).

2.3.4 Pollution load index

The PLI determines the degree of sediment contamination by heavy metals and the degree of impairment in the environment (Tomlinson et al., 1980; Mohiuddin et al., 2011). The PLI is calculated using the Equation 4.

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots CFn)^{1/n} \qquad (4)$$

Where, CF_n is the contamination factor for each metal, and n is the number of metals evaluated. A value of PLI = 0 indicates good ecosystem condition, PLI = 1 indicates baseline levels of contaminants in the ecosystem, and PLI > 1 indicates progressive deterioration of ecosystem quality (Tomlinson et al., 1980).

2.3.5 Modified degree of contamination (mCd)

The mCd evaluates the degree of global contamination of sediments, integrating all the heavy metals evaluated in the ecosystem (Abrahim and Parker, 2008). The mCd is calculated using the Equation 5.

$$mCd = \frac{\sum_{i=1}^{i=n} C_F^i}{n} \qquad (5)$$

Where, CF is the contamination factor, i is the "ith" metal, and n is the number of metals evaluated. mCd is classified in the ranges: mCd ≤ 1.5, from uncontaminated to very low degree of contamination; 1.5 < mCd ≤ 2, low degree of contamination; 2 < mCd ≤ 4, moderate degree of contamination; 4 < mCd ≤ 8, high degree of contamination; 8 < mCd ≤ 16, very high degree of contamination; 16 < mCd ≤ 32, extremely high degree of contamination; mCd > 32, ultra-high degree of contamination.

2.3.6 Potential ecological risk (Ri)

The Ri results from the sum of the ecological risk factors (Er) calculated for each heavy metal evaluated. This index determines the overall degree of ecological risk of heavy metals in sediment samples (Hakanson, 1980). Ri is calculated using the Equation 6.

$$E_r^i = T_r^i \times CF_r^i \ ; \ Ri = \sum_{i=1}^{n} E_r^i \qquad (6)$$

Where, T_r is the biological toxic factor for each metal, and i is the "ith" metal. Ri is classified in the ranges: Ri ≤ 95 low potential ecological risk; 95 < Ri ≤ 190 moderate potential ecological risk; 190 < Ri ≤ 380 considerable potential ecological risk and Ri > 380 very high potential ecological risk (Ranjbar et al., 2020).

2.3.7 Site rank index (SRI)

The SRI indicates the state of sediment contamination by comparing the level of metal contamination of the sampling sites under the same metric avoiding the comparison in different classifications of each contamination index (CF and Igeo; Omwene et al., 2018; Zhang et al., 2020). The SRI is calculated using Equation 7.

$$W = \frac{\sum n_i}{\sum i} \ ; \ SRI = \frac{W}{S} \times 100 \qquad (7)$$

Where, S is the number of sampling sites, n is the site contamination rank in ascending order (at each value used: CF and Igeo), and i is the "ith" metal. An SRI < median - SD indicates low contamination; median - DS < SRI < median, moderate contamination; median < SRI < median + DS, high contamination; median + DS < SRI < SRI, severe contamination (Omwene et al., 2018).

2.4 Statistical analysis

Data analysis and processing were performed using R software and R-Studio (Version 4.1.3). The Shapiro-Wilk test was used to assess whether the data have a normal distribution. A cluster analysis was performed using the Euclidean distancing method, Ward's linkage and a standardization of values using Z-scores. A principal component analysis (PCA) was performed to identify possible sources of metal contamination in the sediments of both rivers.

3 Results

3.1 Analysis and distribution of metals in sediments

Descriptive statistics for metals in sediment from the Chía and Miraflores rivers, continental crust (CC) reference values (Turekian and Wedepohl, 1961) and Canadian Council of Ministers of the Environment (ISQG-CCME) interim sediment quality guidelines (Canadian Council of Ministers of the Environment, 2001) values are presented in Table 1. The mean concentration of Cu, Cr, Fe, Mn, Mo, Ni, Pb, and V in sediment samples in the Chía and Miraflores rivers did not exceed the threshold values of the continental crust concentration, nor the ISQG-CCME values. The mean Hg concentration in the Chía river (0.16 ± 0.01 mg.kg^{-1})

TABLE 1 Descriptive statistics (DS) of metals concentrations (mg/kg) in sediments of rivers and international reference values [Continental crust (Turekian and Wedepohl, 1961), threshold effect level (TEL), and probable effect level (PEL) of the interim sediment Quality guidelines (Canadian Council of Ministers of the Environment, 2001)].

Metals	DS	River		Continental crust	TEL	PEL
		Chía	Miraflores			
Cu	Mean	8.8	6.95	45	18.7	108
	SD	0.04	0.32			
	Max	8.83	7.3			
Cr	Mean	11.57	9.27	90	52.3	160
	SD	0.53	0.2			
	Max	11.9	9.45			
Fe	Mean	8,922.33	15,845.33	47,200	-	-
	SD	114.61	33.08			
	Max	8,989	15,877			
Mn	Mean	145.41	301.13	850	-	-
	SD	0.55	1.65			
	Max	146.04	302.98			
Hg	Mean	0.16	1.01	0.4	0.13	0.7
	SD	0.01	0.03			
	Max	0.17	1.05			
Mo	Mean	0.39	0.94	2.6	-	-
	SD	0.03	0			
	Max	0.41	0.94			
Ni	Mean	9.39	13.5	68	-	-
	SD	0.55	0.43			
	Max	10.02	13.87			
Pb	Mean	13.31	5.05	20	30.2	112
	SD	0.05	0.3			
	Max	13.36	5.35			
V	Mean	15.94	10.32	130	-	-
	SD	0.04	1.03			
	Max	15.98	11			
Zn	Mean	120.12	48.21	95	124	271
	SD	1.86	1.74			
	Max	122.04	50.03			

did not exceed the threshold value of the continental crust concentration (0.4 mg.kg^{-1}), but it was between the TEL and PEL values of the ISQG-CCME, being located in the range of possibility where adverse effects occasionally occur. Regarding the mean Hg concentration in the Miraflores river (1.01 ± 0.03 mg.kg^{-1}), this exceeded the threshold value of the continental crust, in addition to exceeding the PEL value (0.7 mg.kg^{-1}) of the ISQG-CCME, which means that it is above the range of possibility where adverse effects occur frequently. The mean Zn concentration in the Miraflores river did not exceed any of the comparison standards. While in the Chía river, the mean Zn concentration

(120.12 ± 1.86 mg.kg^{-1}) only exceeded the threshold value of the continental crust.

The decreasing order of heavy metal concentration in the sediments of the Chía river was: Fe > Mn > Zn > V > Pb > Cr > Ni > Cu > Mo > Hg, and in the Miraflores river it was: Fe > Mn > Zn > Ni > V > Cr > Cu > Pb > Hg > Mo (Supplementary Table 1). With respect to the metals that exceeded any of the comparison standards, the highest concentration of Hg (1.05 mg.kg^{-1}) was recorded in the middle zone of the Miraflores river. While the highest concentration of Zn (122.04 mg.kg^{-1}) was recorded in the highest zone of the Chía river. In the specific case of

Hg, it is observed that it has exceeded at least one of the standards in each of the rivers, revealing the ease of adsorption on surfaces. These results are supported by Ullrich et al. (2010) who report that in aquatic environments Hg is mostly bound to sediments. In addition, it is the metal that occupies the last places in terms of concentration levels in the sediments of the rivers studied. This behavior of Hg is due to the fact that its occurrence in nature is not common and its complex dynamics in ecosystems does not allow it to be easily detected by common analytical techniques (Velásquez et al., 2021; Cheng et al., 2023). In addition, the chemical speciation of Hg determines its mobility and toxicity in sediments where microbial methylation can occur (Beckers and Rinklebe, 2017; Pavithra et al., 2023).

3.2 Cluster analysis and identification of potential source of contamination

The dendrogram obtained by the Ward method shows the clustering of metal concentrations in the sediments (Figure 2). Cluster analysis shows the clustering of heavy metals in each of the rivers studied (Figure 2). The clustering procedure highlighted clusters in which the sampling sites have similar characteristics. The first cluster groups sampling sites in the upper and middle part of each river and the second cluster groups sampling sites in the lower part. In addition, it allows the metals with the highest concentrations in the Chía river (V, Cr, Cu, Pb, and Zn) to be separated from those found in the Miraflores river (Ni, Mo, Hg, Fe, and Mn). On the other hand, the principal component analysis (PCA) was performed to identify the potential source of contamination, through the grouping and behavior of the metals evaluated. The data were analyzed taking into account the sample adequacy measure KMO (0.55) and Bartlett's test of sphericity (p-value $= 0.01$). Components 1 and 2 covered 99.3% of the total variance (PC1: 98.1% and PC2: 1.2%; Supplementary Table 2). According to the contribution of each metal in the principal components, all are above 0.94 in PC1, where Fe, Pb, Mn, and Hg have the highest contribution values (0.99), while Cr and V show the highest contributions in PC2 (0.036 and 0.037, respectively; Supplementary Table 3). The high contributions found in PC1 and the high degree of variability shown by this PCA may be due to the high degree of association shown by certain groups of metals and the clear distinction between the two rivers studied. This situation is also observed in Figure 3, where there is a clear differentiation between the Chía and Miraflores rivers with respect to the heavy metals evaluated. The distribution of these metals in each river would reveal the possible specific anthropogenic contribution in each body of water, which could be due to the main activities practiced in these ecosystems.
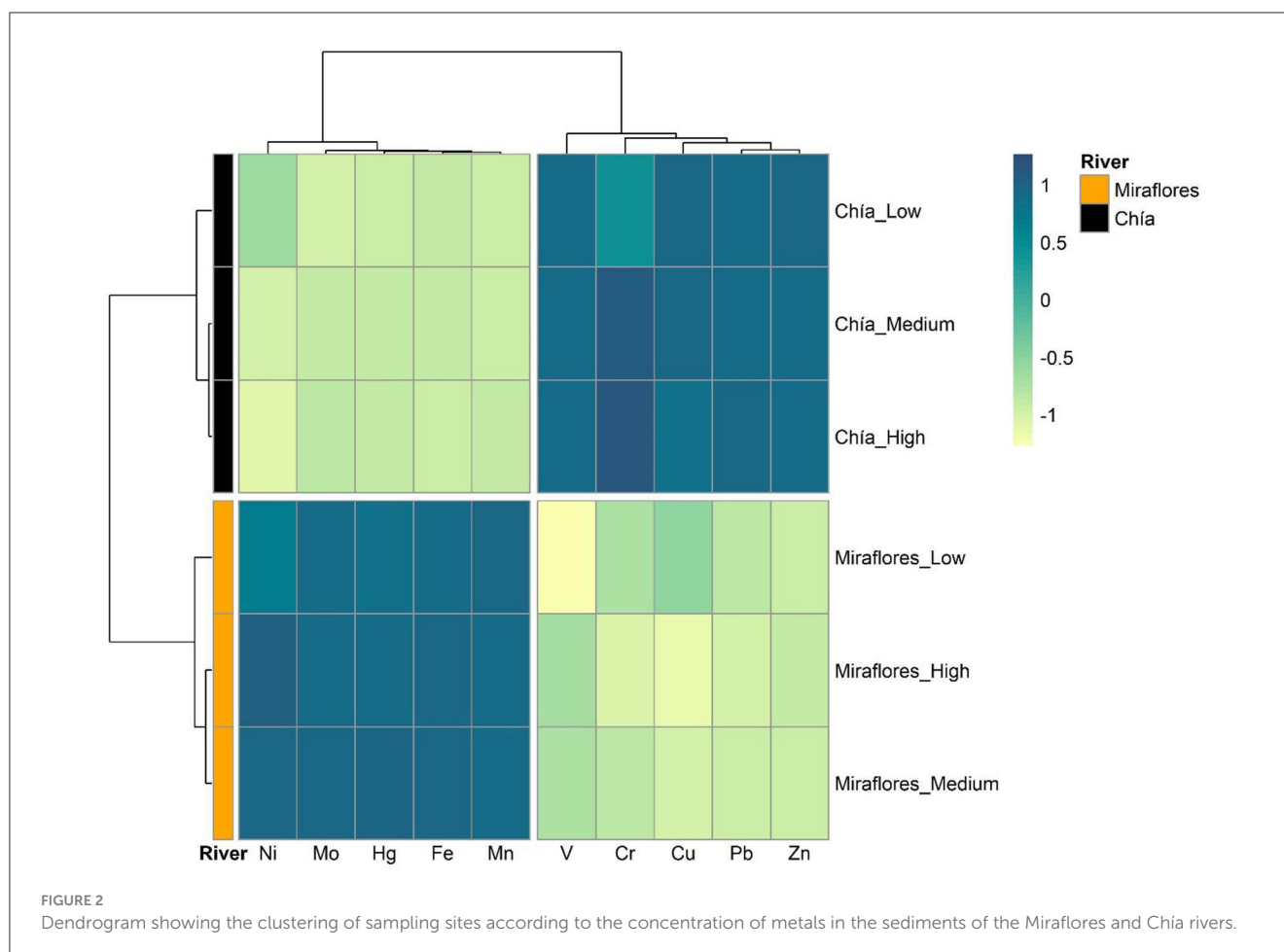
3.3 Assessment of contamination and potential ecological risk by metals in sediments

Table 2 shows the results obtained from the individual contamination indexes obtained for each metal, according to river.

The highest EF values were found for Hg, Pb, and Zn, both in the Chía and Miraflores rivers. However, when categorizing these values qualitatively, we can note that for the Chía river, minor enrichment ($1 <$ EF < 3) of Cu and Hg, moderate enrichment ($3 <$ EF < 5) of Pb and moderately severe enrichment ($5 <$ EF < 10) of Zn have been found. While the other metals have presented values categorized as absence of enrichment ($1 <$ EF). On the other hand, in the Miraflores river, minor enrichment has been observed due to the presence of Mn and Mo and moderately severe enrichment due to the presence of Hg.

In the case of CF values, the highest levels were found for Hg and Zn (CF-Hg> 2, CF-Zn > 1). When categorizing these values, moderate contamination levels ($1 <$ CF < 3) of Hg and Zn were determined for the Miraflores and Chia rivers, respectively; while for the rest of the metals evaluated, contamination levels categorized as low were found. In the case of the Igeo values, only positive values were found for Hg levels in the Miraflores river. However, these were <1, categorized as not contaminated to moderately contaminated. For the rest of the metals, the Igeo category corresponded to not contaminated. It should be noted that these results found by the individual indices are in agreement with those found in Table 1, where Hg and Zn were determined to have exceeded at least one of the standards considered. However, the individual analysis of each metal allows us to observe certain anomalies in the levels of Cu and Pb for the Chía river, which added to the levels of Zn contamination could be part of a mix of metals anthropogenically contributed to this body of water.

Table 3 shows the complex contamination indexes evaluated by river, such as PLI, mCd, and Ri and the Site Rank Index (SRI) generated from EF and Cf. Regarding the complex indexes such as PLI and mCd, these have shown values below 0.5 for both rivers; qualifying as sediments without contamination and very low degree of contamination, respectively. In the same sense, the values of ecological risk and potential ecological risk are categorized as low ecological risk (Er < 40) and low potential ecological risk (Ri < 95). These results are due to the fact that all these complex indices consider the contribution of all the metals evaluated, and probably, the low contribution of contamination observed in metals such as Cu, Cr, Fe, Mn, Mo, Ni, and V, which means that the global index does not present considerable contamination categories. Likewise, when calculating the SRI for the most representative individual indices (EF and CF), values above 50 are observed, which after being categorized (Supplementary Tables 4, 5) show moderate ($50 <$ SRI-EF < 63) and high ($63 <$ SRI-EF < 77) enrichment levels for the Miraflores river and moderate and severe enrichment (SRI-EF > 77) for the Chía river; as well as moderate ($59 <$ SRI-CF < 65) and severe (SRI-CF > 71) contamination levels, because both indices, in their individual calculation, have categorized Hg and Zn at their highest impact levels. These results also reveal the need to implement action measures to protect and conserve these dynamic systems (Matta et al., 2022) so that, in the intervention area, the diversity of uses (in fish farming, irrigation, and human consumption) of these ecosystems is not restricted and does not affect the economy of local residents.

FIGURE 2
Dendrogram showing the clustering of sampling sites according to the concentration of metals in the sediments of the Miraflores and Chía rivers.

4 Discussion

4.1 Analysis and distribution of metals in sediments

Heavy metal contamination is a widespread concern due to the adverse impacts on ecosystems and human health (Ting et al., 2020; Fisher et al., 2021; Liu et al., 2023). The results show that contamination of lotic systems varies by downstream sector, and could increase due to the transport of pollutants through runoff from agricultural areas and those with mining operations. Heavy metals entering these aquatic systems tend to adsorb on suspended particles and deposit in sediments, which could cause long-term effects on local benthic organisms and other species (Zeng et al., 2018; Liu et al., 2022). In this study, the concentration of heavy metals in sediment samples from the Chía and Miraflores rivers, determined based on upper continental crust reference values (Taylor and Mclennan, 1995) and the Interim Sediment Quality Guidelines at their Threshold Effect Levels and Probable Effect Levels (Canadian Council of Ministers of the Environment, 2004) did not exceed the threshold values, except for Hg and Zn. In comparison to the heavy metal content of the Mantaro river basin, the metal contents found in the present study are lower due to the different industrial structure and economic development (Custodio et al., 2021b).

Most of the mean heavy metal concentrations in the sediments of the Chia and Miraflores rivers did not exceed the threshold values of the continental crust concentration, nor the ISQG-CCME values. However, the mean Hg concentration in both rivers revealed the possibility of adverse effects. The impact of relatively intense human activities in the area downstream of both rivers may be the main reason for the distribution of heavy metals. For example, the mean concentration of Zn and Hg exceeded the threshold value of the interim sediment quality guidelines. These results are in agreement with other studies reporting that sediments are the main sink for heavy metals in the aquatic environment (Wei et al., 2023), where sediment quality could reflect the degree of environmental contamination status on a longer time scale (Qian et al., 2021). In addition, unlike other pollutants, metals do not biodegrade and are toxic and bioaccumulative (Zeng and Wu, 2013; Ranjbar et al., 2017; Sojka et al., 2022). However, the metals that exceeded some of the comparison standards were Hg in the Miraflores river and Zn in the Chía river. Hg is the metal with the lowest concentration level in sediments, because its occurrence in nature is not common and its complex dynamics in ecosystems does not allow it to be easily detected by common analysis techniques (Velásquez et al., 2021; Cheng et al., 2023).

The pattern of heavy metal concentrations found in the rivers of this study differs from that reported by Monroy et al. (2014) in water bodies with similar characteristics. The concentrations of

FIGURE 3
Principal component analysis based on the concentration of metals in sediment of Chía and Miraflores rivers.
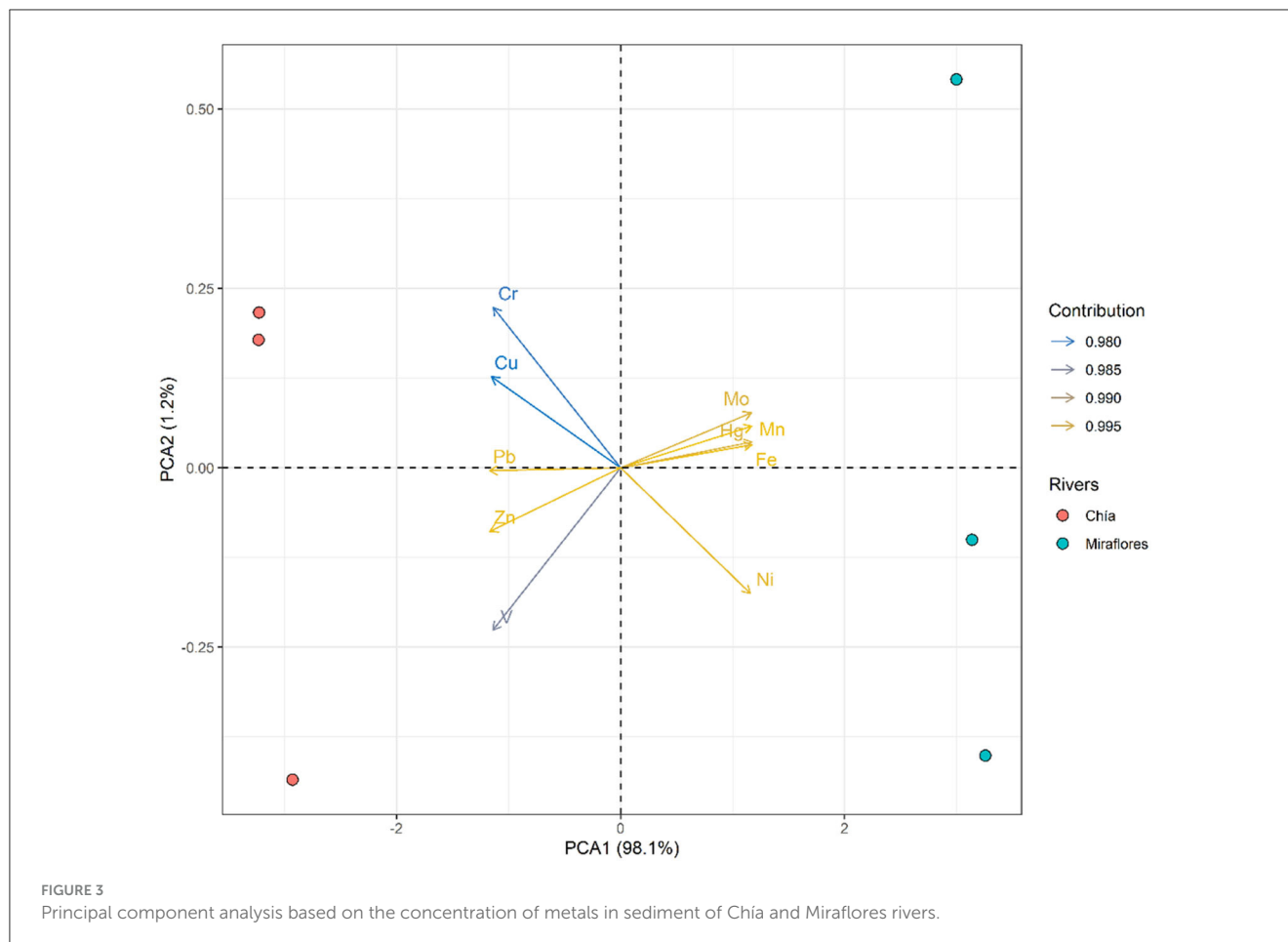
metals in the sediments of the Chía and Miraflores rivers were lower; however, wastewater discharges significantly affect the water column, sediments and fish. Therefore, source and risk assessments of sediment contamination in aquatic ecosystems are essential for effective management. Rainbow trout farming is one of the main activities in the central highlands of Peru. However, several studies have reported that in aquaculture, the use of feed additives containing metals or antibiotics can cause adverse environmental impacts in receiving water bodies (Seiler and Berendonk, 2012; Jaishankar et al., 2014; Wang et al., 2019). Metal ions can be released from these feed additives or antibiotics and adsorbed on suspended particles, subsequently deposited and accumulated in sediments, and from there, distributed to other compartments such as the water column and aquatic fauna.

Spatial variation in heavy metal levels was revealed through cluster analysis. River sectors with similar characteristics were grouped together, while those with different characteristics had distant links. This behavior allowed disaggregating the metals with higher concentrations found in the Chia river in relation to those found in the Miraflores river. Principal component analysis was used to explore the possible sources of sediment contamination by heavy metals. PCA generated a vector matrix plotted on a two-dimensional axis. The high contributions found in PC1 and the high degree of variability shown by this PCA may be due to the high degree of association presented by some groups of metals and the clear difference between the two rivers studied. The distribution

of these metals in each river would reveal the possible specific anthropogenic contribution in each water body, which could be due to the main activities practiced in these ecosystems. These results coincide with other studies of similar environments that report that Zn, Cr, Ni, Hg, and Cu contamination is mainly related to industrial activities (Chen et al., 2016; Meng et al., 2021). In general, Hg is an important component of agrochemicals, pesticides and herbicides (Wang et al., 2023), Cu and Zn mainly come from animal excrement, as they are micronutrients added to animal feed as growth promoters (Yang et al., 2020). Cr and Pb come from the electroplating and transportation industries (Chen et al., 2016; Jin et al., 2022) as a result of wear and tear on vehicle parts, use of lubricants and gasoline, and from automobile manufacturing (as additives for airbag detonators), and as a feed additive (Zhang et al., 2022). Natural sources are another important source of metal contaminants in sediments when the pH is low (Luo et al., 2019). Low pH can increase metal solubility and influence metal concentrations in river sediments (Bai et al., 2016).

4.2 Assessment of contamination and potential ecological risk by metals in sediments

The individual contamination indices obtained for each metal in the Chía and Miraflores rivers showed different levels of

TABLE 2 Enrichment factor, contamination factor, geoaccumulation index, and ecological risk of metals in sediment of Chía and Miraflores rivers.

River	Altitude	Metals									
		Cu	Cr	Fe	Mn	Hg	Mo	Ni	Pb	V	Zn
		Enrichment factor									
Chía	High	1.03	0.64	-	0.90	2.03	0.73	0.77	3.49	0.64	6.75
	Medium	1.03	0.69	-	0.90	2.21	0.79	0.71	3.49	0.64	6.63
	Low	1.04	0.71	-	0.92	2.28	0.85	0.71	3.59	0.66	6.69
Miraflores	High	0.48	0.31	-	1.06	7.37	1.08	0.57	0.80	0.21	1.46
	Medium	0.46	0.31	-	1.05	7.82	1.08	0.60	0.75	0.25	1.51
	Low	0.44	0.30	-	1.05	7.43	1.07	0.61	0.71	0.25	1.57
		Contamination factor									
Chía	High	0.20	0.12	0.19	0.17	0.39	0.14	0.15	0.66	0.12	1.28
	Medium	0.20	0.13	0.19	0.17	0.42	0.15	0.13	0.66	0.12	1.26
	Low	0.19	0.13	0.19	0.17	0.43	0.16	0.13	0.67	0.12	1.25
Miraflores	High	0.16	0.10	0.33	0.36	2.47	0.36	0.19	0.27	0.07	0.49
	Medium	0.15	0.10	0.34	0.35	2.63	0.36	0.20	0.25	0.08	0.51
	Low	0.15	0.10	0.34	0.35	2.50	0.36	0.20	0.24	0.08	0.53
		Geoaccumulation index									
Chía	High	−2.93	−3.62	−2.98	−3.14	−1.95	−3.43	−3.35	−1.18	−3.62	−0.22
	Medium	−2.94	−3.51	−2.98	−3.13	−1.84	−3.33	−3.48	−1.18	−3.61	−0.25
	Low	−2.95	−3.50	−3.01	−3.13	−1.82	−3.25	−3.50	−1.17	−3.61	−0.27
Miraflores	High	−3.21	−3.84	−2.16	−2.07	0.72	−2.05	−2.97	−2.49	−4.42	−1.61
	Medium	−3.29	−3.86	−2.16	−2.08	0.81	−2.05	−2.91	−2.58	−4.17	−1.57
	Low	−3.34	−3.90	−2.16	−2.09	0.74	−2.05	−2.88	−2.66	−4.15	−1.51
		Ecological risk									
Chía	High	0.98	0.24	-	-	7.62	-	-	0.85	-	0.39
	Medium	0.98	0.26	-	-	7.62	-	-	0.85	-	0.42
	Low	0.97	0.26	-	-	7.45	-	-	0.86	-	0.43
Miraflores	High	0.81	0.21	-	-	13.40	-	-	1.78	-	2.47
	Medium	0.76	0.21	-	-	13.43	-	-	1.77	-	2.63
	Low	0.74	0.20	-	-	13.46	-	-	1.76	-	2.50

TABLE 3 Pollution load index (PLI), modified contamination degree (mCd), potential ecological risk (Ri), site rank index (SRI) for enrichment factor (EF), and contamination factor (Cf) of metals in sediment of Chía and Miraflores rivers.

River	Altitude	PLI	mCd	Ri ($\sum$Er)	SRI-EF	SRI-CF
Chía	High	0.26	0.34	10.08	53.33	60.00
	Medium	0.27	0.34	10.14	56.67	63.33
	Low	0.27	0.34	9.97	90.00	73.33
Miraflores	High	0.26	0.48	18.67	66.67	60.00
	Medium	0.26	0.50	18.79	73.33	73.33
	Low	0.26	0.49	18.66	60.00	66.67

contamination. The enrichment indexes of Hg, Pb, and Zn in both rivers were the highest. However, when categorizing these values, minor enrichment of Cu and Hg, moderate enrichment of Pb and moderately severe enrichment of Zn were found in the Chía river. In the Miraflores river, minor enrichment of Mn and Mo and moderately severe enrichment due to the presence of Hg were found, indicating that the study area of both rivers is impacted by human activities (agriculture, industry, urbanization,

etc.). In contrast, other heavy metals evaluated were in a safe state. The CF showed that Hg and Zn presented the highest levels of contamination. By categorizing these values, moderate levels of Hg and Zn contamination were determined for the Miraflores and Chía rivers, respectively; while for the rest of the heavy metals, low levels of contamination were determined for the Miraflores and Chía rivers, respectively; while for the rest of the heavy metals, low levels of contamination were determined for the Miraflores and Chía rivers, respectively.

The I$_{geo}$ values for Hg in the Miraflores River showed values <1, categorized as not contaminated to moderately contaminated. The I$_{geo}$ of the rest of the metals qualified as uncontaminated. However, the individual analysis of each metal allows us to observe certain important levels of Cu and Pb contamination for the Chía river, which, added to the levels of Zn contamination, could be part of a mix of metals anthropogenically contributed to the water body. For instance, Hahn et al. (2018) indicates that sediments become contaminated due to the release of metals from soils by leaching and soil erosion processes. The results found are supported by other studies that refer that Cu, Pb, and Zn tend to be rapidly diluted and transported long distances once they are released into the water body and finally deposited in the sediment (Zhuang et al., 2021; Nagarajan et al., 2023). These findings also indicate that Hg is the main contributor to heavy metal pollution in the Miraflores river (Zahra et al., 2014; Ke et al., 2017; Li et al., 2022).

Complex contamination indices such as PLI and mCd, showed values below 0.5 for both rivers, qualifying as sediments with no contamination and very low degree of contamination, respectively. In general, the PLI index reflects the non-negligible integrated contamination of the studied heavy metals in the river sediments. These results are supported by Ali et al. (2016) who refer that PLI can provide some insight to populations about sediment quality. As well as, information for decision makers about the pollution status of the study area. In the same sense, the values of ecological risk and potential ecological risk are categorized as low ecological risk and low ecological risk potential. The results also indicate that the contribution of all the heavy metals evaluated determines the degree of contamination of the sediments (Omwene et al., 2018; Zhang et al., 2020), and a potential effect on organisms (Ranjbar et al., 2020). However, heavy metal contamination of both rivers is related to the human activities that take place in them (Liu et al., 2022). These results suggest that the ecological risk from metals in the sediments of the Miraflores river comes mainly from Hg, as it is the main contributor.

5 Conclusion

The constant population growth and development around the Chía and Miraflores rivers goes hand in hand with the strong pressure experienced by these ecosystems and the demand for good quality water. This study revealed that the concentrations of heavy metals in the sediments of both rivers did not exceed the reference values and thresholds of the upper continental crust and the provisional guidelines on sediment quality, respectively; with the exception of Hg in the Miraflores river and Zn in the Chía river. The application of statistical ordination methods revealed a clear partition in the importance of certain metals

for each river, where the difference in metallic elements was determined by Hg, Pb, and Zn. The EF and Cf values showed that the most important metals were Hg, Pb, and Zn with moderate to moderately severe enrichment and moderate contamination. However, applying complex indices such as PLI, mCd, and Ri, very low levels of contamination and/or low ecological risk were found, which shows the importance of the contribution of the other metals that were not relevant in the analyses, since these are global indices. The SRI revealed that the Miraflores river has moderate to high enrichment levels and the Chía river has moderate to severe levels, mainly influenced by Hg and Zn concentrations. Finally, this study revealed that the main contributions of metallic elements come from various anthropogenic activities. Therefore, it is recommended that stricter control and monitoring measures be directed to point sources of heavy metals in order to reduce the pressure of these sources of contamination on Andean aquatic ecosystems.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

MC: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Visualization, Writing—original draft, Writing—review & editing. AF: Data curation, Formal analysis, Investigation, Writing—review & editing. HD: Investigation, Methodology, Visualization, Writing—review & editing. FC: Investigation, Writing—review & editing. JH: Investigation, Methodology, Writing—review & editing.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/frwa.2023.1295712/full#supplementary-material

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