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Ingeniería en Biotecnología

ENVIRONMENTAL RISK ASSESSMENT OF METAL CONTAMINATION BY MINING IN THE AMAZON BASIN

Naomi Carolina Yacelga Villavicencio

28 de abril de 2021, Ciudad de Tena, Napo, Ecuador

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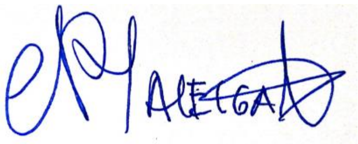

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PhD. Mariana Vellosa Capparelli
C.I: 1758616898

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Dedicatoria

A mi familia, Rocío, Ivan, Mela y Chiwie,
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mis sueños y objetivos.

ÍNDICE GENERAL

Artículo desarrollado bajo las directrices de la revista Science of the Total Environment

Environmental risk assessment of metal contamination by mining in the Amazon Basin

Naomi Yacelga[1], Andreu Rico[2,3], Gabriel M. Moulatlet[4], Mariana V. Capparelli[4]

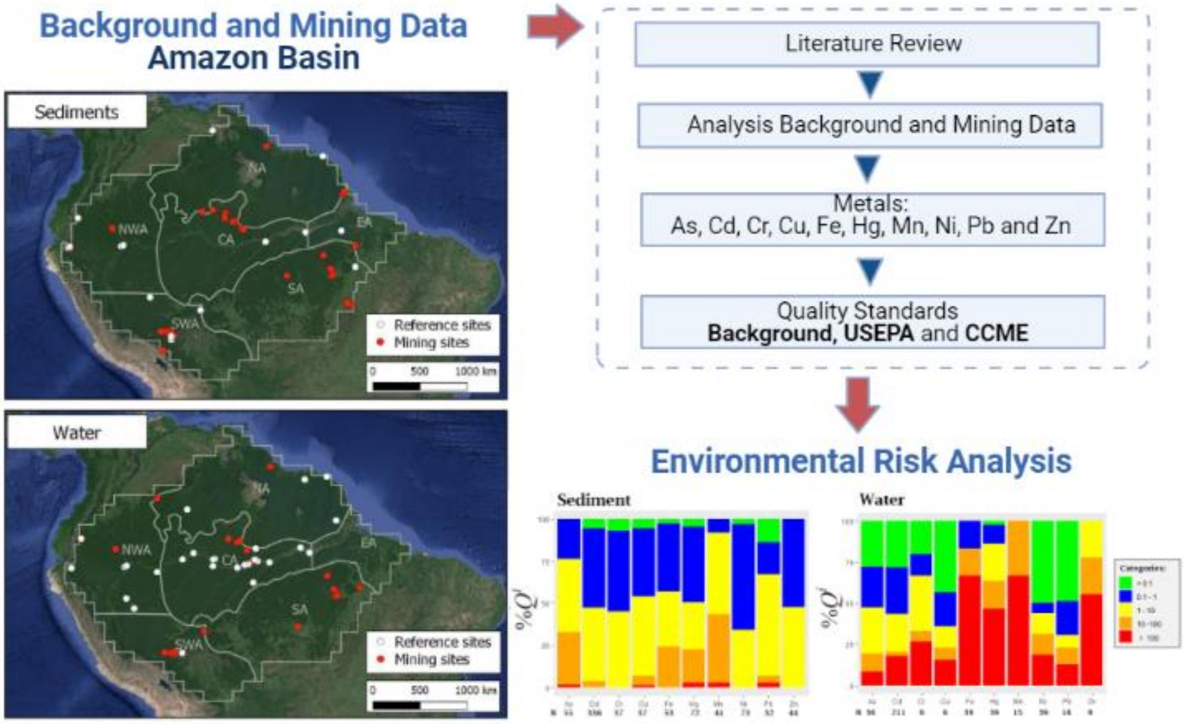
[1] Facultad de Ciencias de la Vida, Universidad Regional Amazónica Ikiam, Tena, Napo, Ecuador
[2] IMDEA Water Institute, Science and Technology Campus of the University of Alcalá, Av. Punto Com 2, Alcalá de Henares 28805, Madrid, Spain
[3] Cavanilles Institute of Biodiversity and Evolutionary Biology, University of Valencia, c/ Catedrático José Beltrán 2, 46980, Paterna, Valencia, Spain
[4] Facultad de Ciencias de la Tierra y Agua, Universidad Regional Amazónica Ikiam, Tena, Napo, Ecuador

Highlights:

- The background data are below the thresholds allowed for the protection of aquatic life
- The southern peripheral area has the highest levels of background metal concentration in the entire basin for Cd, Cu, Hg, Mn, and Zn.
- Pb, As, and Mn have the highest percentage of the environmental risk in sediment, and Fe, Hg, Mn, and Zn in water
- For mining areas, in sediment As, Cu, Fe, Hg, Mn, and Pb exceed the mean background data, and Cd the threshold TEL.
- In mined areas in water Cd, Cr, Fe, Hg, Mn and, Zn exceeds the background data, Fe, and Hg the short-term threshold, and Zn the long-term threshold.

Keywords: Amazon, mining, freshwater contamination, metals, sediment, water

Graphical Abstract



Abstract

Several anthropogenic pressures contribute to the modification of ecosystems and hydrological regimes in the Amazon basin. Among them, mining is of great concern due to the remobilization and emission of potentially toxic elements, such as metals, which have detrimental consequences for the ecosystem and human health. Our study aimed to establish the background metal concentrations for water and sediments and the increase of metal exposure caused by mining in four geochemical regions of the Amazon basin: 1) Western; 2) Central; 3) Northern and 4) Southern. Furthermore, we evaluated the environmental risk of mining activities to the aquatic ecosystem and the ecological risk assessment in fish populations. A total of 53 studies spanning mined and non-mined areas reporting metal concentrations for As, Hg, Mn, Fe, Cd, Cu, Cr, Pb, Ni, and Zn were reviewed. The mean background metal concentration values were compared with the environmental quality standards thresholds for the protection of aquatic life in sediment (CCME) and water (CCME and USEPA). Overall, for non-mined areas, all metals are below the established thresholds allowed for the protection of aquatic life in sediments and water, namely, our metal concentration data for reference sites are within international quality standards. The southern peripheral area has the highest levels of background metal concentration in the entire basin for Cd, Cu, Hg, Mn, and Zn. For mining areas, As, Cu, Fe, Hg, Mn, and Pb exceed the mean background metal concentration, and Cd exceeds the threshold TEL in sediment samples, and for water Cd, Cr, Fe, Hg, Mn and, Zn exceed the mean background value, and Fe and Hg exceed the short-term threshold and Zn exceeds the long-term threshold. Metals with the highest percentages of environmental risk for the basin in the sediment were Pb (67,12 %), As (76,36%), Mn (91,89%), and in water were Fe (83,33 %), Hg (86,26 %), Mn (100 %) and Zn (100 %), since these metals have an increase in the concentration of 10 to 100 times higher concerning the mean background values. Finally, according to the ecological assessment As,

Cd, Cu, Hg and Pb show a high risk of metal concentration in Amazonian fish populations.

1. Introduction

The Amazon basin is the largest drainage on Earth with an area of about 6 million km2 (Frederico et al., 2021). The river basin discharges approximately 16% to 18% of the planet's freshwater flow and shelter of 25% of the world's freshwater biodiversity (Sioli, 1984; Latrubesse et al., 2017) and plays a crucial role in the regulation of global climate, the provision of ecosystem services, and exceptional biodiversity and endemism (Flores et al., 2010; WWF, 2015; Josse et al., 2013). The modifications of ecosystems and hydrological regimes in the Amazon basin have been driven by different anthropogenic pressures (Charity et al., 2016). Among them, mining is of great importance due to the deforestation and pollution derived from this activity, which includes the environmental cumulative impacts by fragmenting native forests, hydrology, and loss of biodiversity, due to the release of mining waste that contains high concentrations of metals (Miserendino et al., 2013; GIATOC, 2016; Sonter et al., 2017; Dezécache et al., 2017; Crespo-López et al., 2021).

Mining is considered a relevant economic activity, both in industrialized and developing countries (Mol and Ouboter, 2004; Moreno-Brush et al., 2016; Teixeira et al., 2018). Together, the countries of Latin America and the Caribbean produce the highest proportion of minerals consumed in the world: gold, silver, copper, manganese, nickel, cassiterite, iron, and tin which are equivalent to 20% of the revenues of the governments of the region (Lobo et al., 2018). The mining sector in Latin America represented 24% of total investment between 2009-2014, being: Peru (25%), Brazil (11%), and Colombia (6%), the countries with the highest investments in mineral exploration (Vio Gorget and Walter, 2016). Metals like gold, silver, copper, and manganese though all these materials have their specific properties and applications, have unique environmental impacts on air, soil, water, and the environment (Rios, 2018; Farjana et al., 2019). Silver is of particular interest because of its value, its relative scarcity, and its toxicity (Eckelman and Graedel, 2007). Approximately 57% of silver in discarded products worldwide is recycled but much is lost in various emissions to the environment (Johnson et al., 2005). Gold and silver mining is estimated to have released approximately 250,000 Mg of Hg into the environment between 1580 and 1900 causing the formation of sinkholes, soil and environmental pollution, or even can cause loss of biodiversity (Nriagu, 1994; Farjana et al., 2018). Most Cu deposits are mined in open pits. These operations generate huge amounts of mine waste and tailings each day, more than mining any other metal, so that is a threatening element for the aquatic environment and species and also causes deforestation (Dudka and Adriano, 1997; Farjana et al., 2019).

In the Amazon, 64% of the total mining area is related to small-scale gold mining (Lobo et al., 2018). Artisanal and small-scale gold mining (ASGM) is the informal mining technique that has been practiced since the 1950s in a few sites called Garimpos in Brazil and is one of the most common in the basin (Harada et al., 2001; Lobo et al., 2016; Teixeira et al., 2018; Weinhouse et al., 2020). Although some actions were taken against ASGM in the late 1990s, illegal gold mining has not stopped in that area (Vega et al., 2018). Despite being totally prohibited, the ASGM has the potential to increase 305.73% for the next few years within indigenous lands (IL) (Rorato et al., 2020). The constant and growing mining activity, combined with the lack of politics, makes them one of the human activities with the greatest socioeconomic impacts worldwide, and tragic environmental impacts (Vintró et al., 2014; Carvalho, 2017).

Although the mining activities increase the concentration of metals in the aquatic ecosystem, the natural concentration of metals in various environmental systems depends on the geographical area, the variability in the composition of the earth's crust, the type of soil and the geochemical processes (McClain and Naiman, 2008; Grill et al., 2019). The sediment regimes and geochemistry of Amazon tributaries differ according to the dominant geotectonic regions that they drain (Park and Latrubesse, 2015). The geological diversity of the Amazon basin is surrounded to the west and southwest by the Andean mountains and foreland rivers, in the north, as well as in the south, the tributaries rise in the geologically very ancient massifs of the Guianas and central Brazil, where they are divided in large river systems. Between these massifs and the Andes Mountains, there are flat areas and low altitudes with enormous geochemical diversity (Schreider and Schreider, 1970; Sioli, 2012; Latrubesse et al., 2017). The division of the Amazon into fourth large geochemical provinces by Fittkau (1971) was basically based on the differences in the electrolyte content of the running waters of the region showing decreasing ionic concentrations from the west, through the north to the central geochemical provinces. This division in water is reflected in the differences in background metal concentrations (Sioli, 1984). The fact that the natural concentrations of metals are dissimilar, to date, has not been considered in most environmental studies performed in the Amazon basin, which may lead to misleading metal risk assessment (Di Toro, 1991; Ankley, 1996).

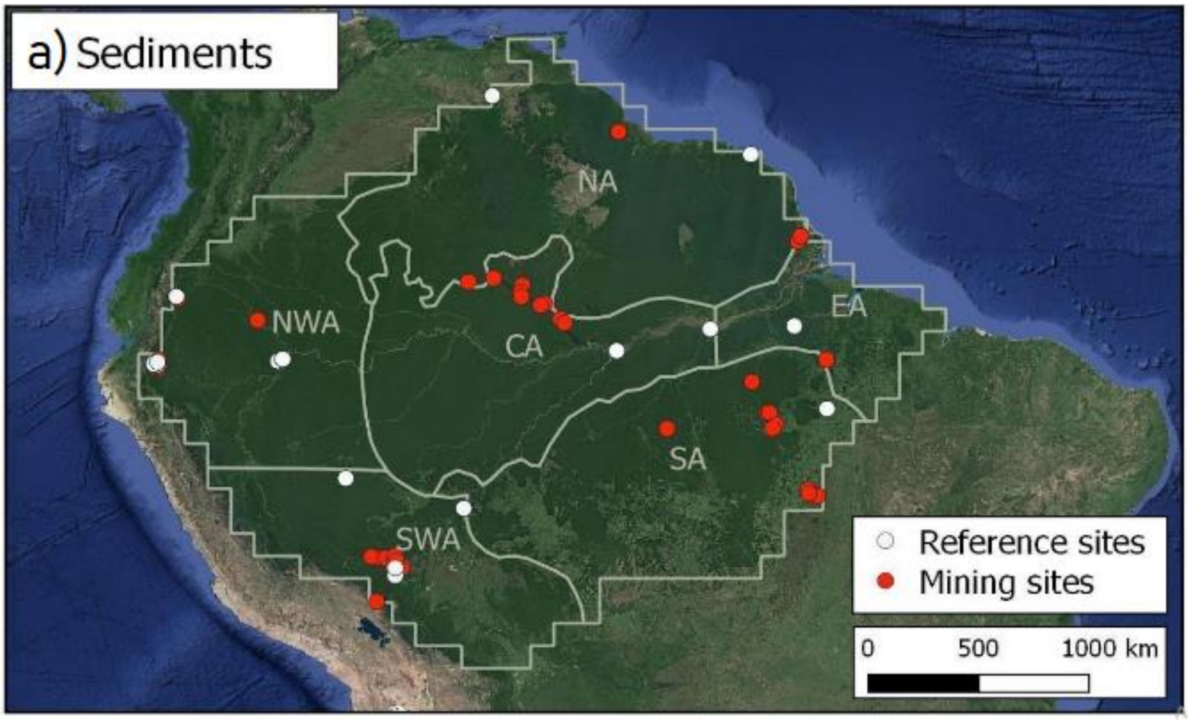
Several water and sediment quality standards have been published by the United States Environmental Protection Agency (USEPA) and Canadian Environmental Quality Guidelines standards (CCME) to assess the environmental risks of metal contamination (Garcia et al., 2011; Weber et al., 2013). These standards are used to determine if the concentration of metals present in the environment may involve risks for aquatic organisms (Birch, 2017; Mikkonen et al., 2018). Even though these thresholds are internationally agreed that should be considered for new studies, specific thresholds of the reference levels for each country, and even sometimes each region (Baird et al., 2016). The high concentration of metals generated by mining can exert a high toxicity potential and pose environmental risks to both ecological security and human well-being (Xu et al., 2017; Demková et al., 2017). The environmental risk assessment has been recognized and has resulted in the ongoing development of various types of models for assessing risks of chemicals to populations, communities, and ecosystems (Bartell et al. 2003; Galic et al., 2010; Sana et al., 2017). However, several obstacles hindering the science-based assessment of the potential impact of metals on aquatic environments have been identified (Janssen et al., 2003). The quality and the relevance of the data are often too low to derive ecologically meaningful standards, especially in the Amazon region (Cromey and Black, 2005). To better understand where and how background metal enrichment occurs, it is important to incorporate aspects of ecological relevance, focusing on scenarios representative of each region (De Laender et al., 2014; Lombardo et al., 2015).

In Latin America, although studies used quality standards, these are based on the rivers of North America, with different characteristics from those of the Amazon (Silvert and Sowles, 1996; Henderson et al., 2001; Cromey and Black, 2005). Furthermore, there have been few investigations that have evaluated background environmental concentration controls in sediments, soils, water, and organisms (Mikkonen et al., 2018). Consequently, the metal concentrations measured in environments suspected of contamination must be compared with data from local background samples, to take into account, the concentration of metals expected to occur naturally (Adamo et al., 2005; CCME, 1995; Santos-Francés, et al., 2017). Therefore, the aim of our study was to determine background metal concentrations in water and sediments in areas not impacted by mining of different Amazonian geochemical regions and to assess the risk of metal enrichment in different areas impacted by mining based on available studies. Furthermore, we assessed the exceedance of international environmental quality standards and calculated the environmental risk and the ecological assessment in freshwater aquatic organisms, that should be considered in future conservation and ecosystem management plans.

2. Materials and methods

2.1. Study Area

We use the limits of the Amazon lato sensu, which covers an area of 8,121,313 (km^2) (Eva et al., 2005). Sioli (1984) classified the Amazon basin into the main geochemical regions: 1) Western peripheral area (Northwest Area (NWA) and Southwest Area (SWA)); 2) Central Amazon (Central Amazon (CA) and Eastern Area (EA)); 3) Northern Peripheral Area (NA); and 4) Southern Peripheral Area (SA), which we use in the article, see Figure 1. The countries that make up the western area of the basin are: Ecuador, Colombia, Peru, Bolivia and Brazil, the central Amazon and the southern region is composed only by Brazil and finally within the northern region are the countries: Brazil, Venezuela, Suriname, Guyana and French Guiana.



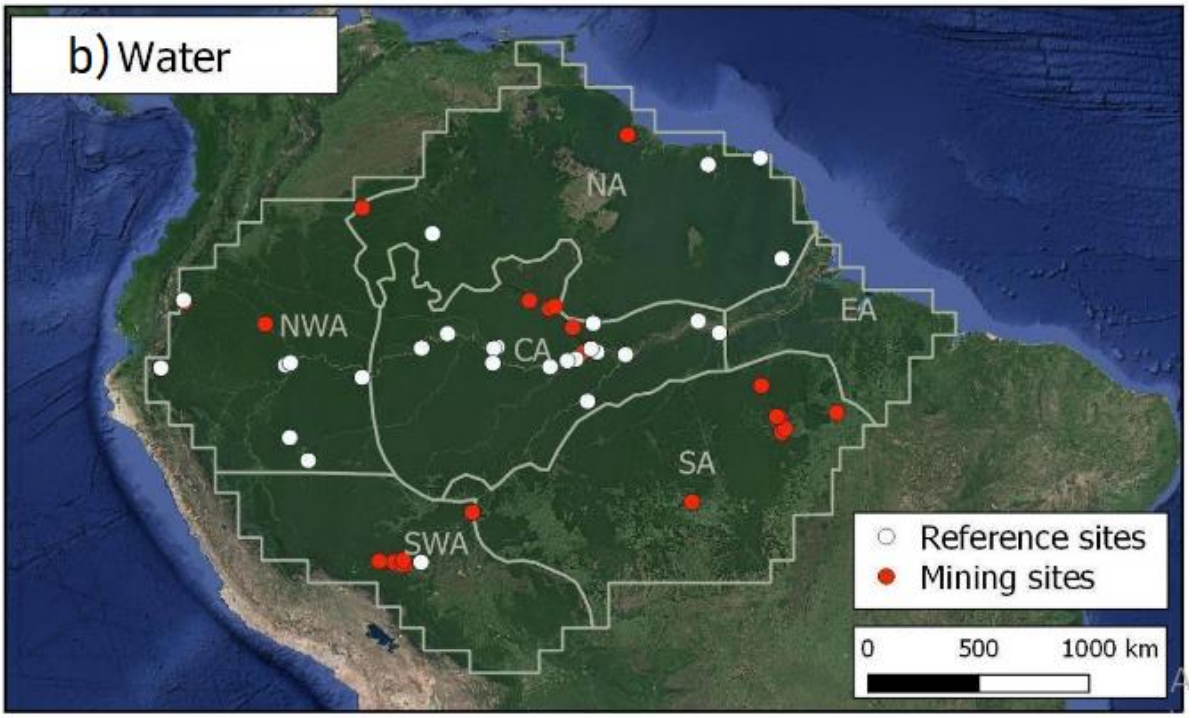


Figure 1. Data from articles published between 1989-2020 related to the analysis of metal contamination risks in mining areas of the Amazon basin. **a)** Data from sediment samples in mining sites and background metal concentration (reference sites); **b)** Data from water samples in mining sites and background metal concentration (reference sites). The gray lines indicate the limits of the 4 geochemical regions of the Amazon Basin: *1) Western peripheral area* (Northwest Area (NWA) and Southwest Area (SWA)); *2) Central Amazon* (Central Amazon (CA) and Eastern Area (EA)); *3) Northern Peripheral Area* (NA); and *4) Southern Peripheral Area* (SA).

2.2. Literature review

We reviewed 53 articles published between 1989 and 2020 that assess environmental exposure to metals in mining areas of the Amazon basin. The bibliographic search was carried out systematically using Google Scholar and using the keywords: "Amazon", "mining", "environmental analysis", "sediments", "water" "metal contamination". From these documents, the concentrations of metals in the water and sediments at reference sites and mining sites are collected. The mining types studied were: gold (86.78%), silver (5.66%), cassiterite (1.89%), diamond (1.89%), manganese (1.89%), and copper (1.89%). To establish the reference sites, information on the concentration of background metals in the water and sediments was collected from the literature, based on the reference sites of the 53 articles. The metals evaluated: As, Hg, Mn, Fe, Cd, Cu, Cr, Pb, Ni, and Zn were chosen because they have been commonly reported and because most of them are highly toxic to freshwater and/or terrestrial ecosystems (do Nascimento et al., 2018).

2.3. Analysis of metal concentration data

We classified the metal concentration data from mining sites and reference (background) sites in the four geochemical regions of the Amazon basin. We calculate the following parameters: the number of samples (N °), the geometric mean (Mean), the maximum (Max) and the minimum (Min) for sediment and water samples in background sites (see Table 1) and for mining sites (see Table 2) for the entire Amazon basin. The standard deviation (s.d.) was not calculated for this study due to the high variability of the results, being the data mainly reported from different studies of several journals. Background sites reflect the natural concentration of metals in water and sediments that provide the basis for evaluating their quality and monitoring areas suspected of contamination (Teng et al., 2009; Preston et al., 2014). Similarly, we calculate the same parameters for the four regions of the basin (see table S1 and table S2).

2.4. Comparison with quality standards and Environmental risk analysis

The mean background metal concentration of water and sediments was compared to environmental quality standards provided by the United States Environmental Protection Agency (USEPA) and the Canadian Environmental Quality Guidelines (CCME) (USEPA, 1994; CCME, 2002), to establish reference specific values for the Amazon basin. The concentrations of metals in water and sediments reported in the mining sites were compared with the mean background metal concentrations and with the environmental quality standards provided by the USEPA and the CCME, to evaluate the increase in the concentrations of each metal with respect to the reference values (USEPA, 1994; CCME, 2002). The Water Quality Criteria for the Protection of Aquatic Life established by USEPA, 1994 consider the thresholds of acute (any poisonous effect produced in a short period of time after an exposure, usually 24 to 96 hours) and chronic (ability of a substance to cause adverse effects to human health due to repeated or prolonged exposures). CCME, 2002 considers monitoring thresholds in the short term (effects resulting from short-term intermittent or transient exposures) and long-term (chronic effects resulting from long-term exposures). Thresholds are set by the CCME in the Canadian Sediment Quality Guidelines, may pose a threat to aquatic life, and are assessed using various sets of sediment quality guidelines, such as TEL (Threshold Effect Level) and PEL (Probable Effect Level) (Long, et al., 1995; MacDonald, 2003). Table 3 shows the number of samples in percent (% excess) of metal concentration at mine sites that exceed the mean background metal concentration and the CCME and USEPA environmental quality standards. The excess percentage was calculated by dividing the mean concentration of each metal at the mining sites by the mean concentration of background metal and the environmental quality thresholds TEL and PEL in sediment and short-term, long-term, acute and chronic thresholds in water.

Environmental risk analysis was calculated by the Q^i, which is the relationship obtained by dividing the dataset of concentration of each metal in Q^i_{Metals} mining sites by the mean background value $Mean^i_{background}$, where (*i*) represents the 10 metals evaluated in the study, as presented in Eq. (1) (Demková et al., 2017).

$$Q^i = \frac{Q^i_{Metals}}{Mean^i_{background}} \quad \text{Eq. (1)}$$

From the set of values obtained for each metal Q^i, the percentage that represented of the total samples of the same metal N^i was determined and classified into 5 categories, as presented in Eq. (2).

$$\%Q^i = \frac{Q^i}{N^i} \times 100 \quad \text{Eq. (2)}$$

The categories are: 1. does not exceed mean background; 2. equal to the mean background; 3. exceeds the mean background 10 times; 4. exceeds mean background 100 times and, 5. exceeds mean background more than 100 times. Category 1 is the one that does not represent a risk of contamination for the ecosystem, and category 5 represents a high risk of contamination (see Figure 2).

2.5. Toxicity and bioaccumulation data in aquatic organisms and Ecological Risk Assessment

For the ecological risk assessment, we evaluated the toxicity and bioaccumulation data in aquatic organisms. We take toxicity data from laboratory tests for different trophic levels: algae, daphnids, and fish (*Pseudokirchneriella subcapitata*, *Oncorhynchus mykiss*, *Chlorella pyrenoidosa* and Daphnia) and calculated the geometric mean when more than one toxicity value. The toxicity test considered for this study were; EC50 is the median effective concentration at which 50 percent of the organisms displayed the effect to the 48, 72 and 96h. The LC50 is the dilution of the medium at which 50 percent of the organisms died to the 96h, and the No Observed Effect Concentration (NOEC) to the 21d (Update, 1994). All the toxicity data was compared with acute and chronic quality standards according to the toxicity database US-EPA, 1992 (see Table 4).

The bioaccumulation data was collected from 24 articles published between 1990 and 2018 that evaluate the impact of the concentration of metals in aquatic organisms in mining areas of the Amazon basin. All documents used evaluate metal concentrations in fish samples (ug g-1 wet weight), so we focus only on these organisms for the risk assessment. The metals evaluated: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. For Fe and Mn no articles were found that report contamination in any aquatic organism. Finally, we compared with acute limits (Criterion of Maximum Concentration) and chronic limits (Criterion of Continuous concentration.) of the Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1995) thresholds, and with the mean metal concentration of mining sites in the Amazon basin previously calculated in the table 2 (see Figure 3).

3. Results and discussion

3.1 Background metal concentrations

The mean background concentrations for the metals evaluated were found below the established thresholds allowed for the protection of aquatic life in sediment (CCME) and water (CCME and USEPA) samples of the Amazon basin (see Table 1). The maximum background values for Hg (0,94 ug g -1) and Cr (104 ug g -1) exceed the thresholds in sediment samples, and Cd (3,10 ug L -1) and Cu (11,15 ug L -1) exceed the quality standards in water samples (Table 1).

Based on our results in the sediment samples, the background metal concentration of Cr, Cu, Hg, Ni, and Zn has the lowest concentration levels compared to the other regions. Likewise, in the water samples, the western region presented the lowest concentration levels of the entire basin, showing a behavior similar to that of Seyler and Boaventura, (2003) where Andean rivers (Western Peripheral Area) tend to have low levels of Cu, Cd, Cr and Zn concentrations compared to the Central Amazon and the peripheral areas of the North and South. On the other hand, in the water samples from the southern peripheral zone, Cd, Cu, Hg, Mn and Zn showed the highest levels of background metal concentration of the entire basin. Although concentration levels did not exceed environmental quality standards, in this region the scarce number of studies limits the comparison (see Table S1).

Table 1. Background metal concentrations in sediment (ug g $^{-1}$) and water (ug L $^{-1}$) samples from the Amazon basin. Values compared with the environmental quality standards: Canadian Environmental Quality Guidelines (CCME, 2002) for sediment and water and the Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1994) thresholds.

	Sediment						Water							
	N°	Mean	Max	Min	CCME		N°	Mean	Max	Min	CCME		EPA	
					TEL	PEL					Short Term	Long Term	Acute	Chronic
As	6	0,47	5,51	0,049	-	-	2	0,09	0,09	0,090	-	-	-	-
Cd	6	0,98	3,10	0,107	0,6	3,5	54	0,02	3,10	0,001	1	0,100	1,800	0,7
Cr	14	8,85	104	0,049	37,3	90	35	0,44	0,88	0,050	-	-	-	-
Cu	12	17,87	107,85	2,500	35,7	197	85	0,43	11,15	0,002	2	-	-	-
Fe	12	1204	67400	0,650	-	-	86	5,53	297	0,100	300	-	-	1000
Hg	92	0,09	0,94	< 0.001	0,17	0,49	58	0,002	0,24	< 0.001	0,030	-	1,4	0,8
Mn	15	54,10	3460	0,080	-	-	154	2,28	992	0,008	-	-	-	-
Ni	8	9,14	55,85	0,900	-	-	35	0,42	1,34	0,090	-	25	470	52
Pb	15	7,30	75,10	1,000	35,0	91,3	17	0,15	45,90	0,005	-	-	82	3,2
Zn	12	53,35	223	21	123	315	66	0,52	31,20	0,029	37	7	120	120

Background data: number of samples (N°), geometric mean (Mean), maximum (Max), minimum (Min) of background metal concentrations in sediment, and water samples. Thresholds: Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1996), showing acute and chronic thresholds; Canadian Environmental Quality Guidelines (CCME, 2002), with short term and long-term thresholds. TEL (threshold effect level) and PEL (probable effect level) values originate from Canadian Environmental Quality Guidelines (CCME, 2002).

3.2. Metal concentration in mining areas

Comparing the concentrations of metals in sediment (ug g -1) and water (ug g -1) samples from mining sites with environmental quality standards (CCME and USEPA). In sediment samples, the mean concentration values of As (1,679 ug g -1), Cu (22,1 ug g -1), Fe (1957 ug g -1), Hg (0,116 ug g -1), Mn (383 ug g -1) and Pb (7,542 ug g -1) of the mining sites exceed the mean background metal concentration, and only Cd (0,752 ug g -1) exceeds the threshold TEL (see Table 2). Also, in 6 of the 10 metals evaluated, at least 45% of their samples exceed the mean background value: As (76,4%), Cu (54,2%), Fe (54,7%), Mn (91,9%), Hg (49,7%) and Pb (67,1%) and 47,2% of Cd samples exceed the threshold TEL (see Table 3).

In the case of the water samples, when we compared the mean background concentration with the metal concentration values in the mining areas (Table 1 and 2), 6 metals de un exceeded the concentration levels of the background mean samples: Cd (0,021 ug L -1), Cr (0,677 ug L -1), Fe (933 ug L -1), Hg (0,134 ug L -1), Mn (793 ug L -1) and Zn (47,9 ug L -1), also Fe, Hg exceed the short-term threshold and Zn exceed the long-term standard. Therefore, when evaluating the number of samples that exceed the background values, these 6 metals at least 40% of their samples exceed the mean background value: Cd (43,6%), Cr (66,7 %), Fe (83,3%), Hg (86,3%), Mn (100%) and Zn (100%), also Fe and Hg exceeds 83,3% and 66,1% to the short-term threshold and Zn 77,8% to long-term threshold (see Table 3).

Table 2. Metal concentrations in sediment (ug g $^{-1}$) and water (ug L $^{-1}$) samples from the Amazon basin at mining sites. Values compared with the environmental quality standards: Canadian Environmental Quality Guidelines (CCME, 2002) for sediments and water and the Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1994) thresholds.

	Sediment						Water							
					CCME						CCME		EPA	
	Nº	Mean	Max	Min	TEL	PEL	Nº	Mean	Max	Min	Short Term	Long Term	Acute	Chronic
As	55	1,679	1860	0,049	-	-	36	0,087	50	0,002	-	-	-	-
Cd	53	0,752	48,100	0,019	0,6	3,5	38	0,021	46	< 0.001	1	0,100	1,800	0,7
Cr	41	5,90	81,3	0,049	37,3	90	14	0,677	238	< 0.001	-	-	-	-
Cu	72	22,1	5360	0,500	35,7	197	38	0,198	500	0,002	2	-	-	-
Fe	37	1957	39701	110	-	-	6	933	28700	5,2	300	-	-	1000
Hg	336	0,116	151	< 0,001	0,17	0,49	210	0,134	32,50	< 0.001	0,030	-	1,4	0,8
Mn	37	383	16000	40	-	-	5	793	3250	75	-	-	-	-
Ni	32	4,910	51,7	< 0,001	-	-	15	0,025	155	< 0.001	-	25	470	52
Pb	73	7,542	4470	0,019	35,0	91,3	38	0,039	133	< 0.001	-	-	82	3,2
Zn	44	47,144	517,7	6,500	123	315	8	47,9	712	3,000	37	7	120	120

Mining data: number of samples (N°), geometric mean (Mean), maximum (Max), minimum (Min) of mining metal concentrations in sediment, and water samples. Thresholds: Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1996), showing acute and chronic thresholds; Canadian Environmental Quality Guidelines (CCME, 2002), with short term and long-term thresholds. TEL (threshold effect level) and PEL (probable effect level) values originate from Canadian Environmental Quality Guidelines (CCME, 2002).

Table 3. Percentage excess (%) from the mining sites that exceed the background metal concentration, and the thresholds of the Canadian Environmental Quality Guidelines (CCME, 2002) for sediments and water and the Water Quality Criteria for the Protection of Aquatic Life for the entire Amazon basin (USEPA, 1994).

	Sediment			Water				
		CCME			CCME		EPA	
	Background	TEL	PEL	Background	Short Term	Long Term	Acute	Chronic
As	76,4	-	-	47,2	-	-	-	-
Cd	47,2	47,2	24,5	43,6	17,9	28,2	17,9	17,9
Cr	46,3	9,8	0,0	66,7	-	-	-	-
Cu	54,2	36,1	6,9	35,9	30,8	-	-	-
Fe	54,7	-	-	83,3	83,3	-	-	66,7
Hg	49,7	35,7	25,0	86,3	61,1	-	31,8	35,1
Mn	91,9	-	-	100,0	-	-	-	-
Ni	34,4	-	-	43,8	-	25,0	0,0	12,5
Pb	67,1	19,2	5,5	30,8	-	-	5,1	20,5
Zn	47,7	15,9	2,3	100,0	55,6	77,8	44,4	44,4

Fe (1957 ug g $^{-1}$- 933 ug L $^{-1}$) and Mn (383 ug g $^{-1}$ - 793 ug L $^{-1}$) were the elements with the highest concentration in sediment and water in mining areas (mean), compared to other metals (Table 2). The macroelements are abundant in the earth's crust and are found in many rocks and minerals (Bernoux et al., 2001). Furthermore, the soils of the Amazon basin correspond mainly to the family of red ferralitic soils. Its mineralogy is dominated by quartz, Al and Fe oxides and kaolinite, with some minerals such as anatase and zircon (Seyler and Boaventura, 2003). In the same way, it is known that Mn is concentrated in lateral soils (ferricrete) that represent 80% in the Amazon basin. Furthermore, this element can be stored in the surrounding floodplain areas (varzea) (Richey et al., 1989). There is a direct exchange of suspended sediments between the varzea and the main river through the processes of entrainment and deposition. The exchange rate between the floodplain and the main channel can control, at least partially, the temporal concentration of Mn (Dunne et al., 1998).

Approximately half (49.7 %) of the data for the mean Hg concentration (0,116 ug g^{-1}) in sediment samples at mining sites exceeds the mean background concentration (0,09 ug g^{-1}) (see, table 1-3). On the other hand, in the water samples, the Hg with a mean value of 0,134 (ug L^{-1}) in the mining sites exceeded the mean background concentration (0,002 ug L^{-1}), and the threshold Short Term (0,03 ug L^{-1}), 86,3% and 66,7% of the Hg samples exceeded the quality standards, respectively (see, table 1-3). Hg pollution can be due to natural sources such as volcanoes, soil and ocean erosion, or anthropogenic sources such as fossil fuels, chlor-alkali plants, metal production, and gold mining. But, mercury-dependent artisanal and small-scale mining (ASM) is the largest source of mercury pollution on Earth (Esdaile and Chalker, 2018; Afrifa et al., 2019). The high concentration of Hg in mining sites is due to the fact that in artisanal small-scale mining the extensive burning of biomass and deforestation is extremely high, and the indiscriminate use of Hg in the amalgam process, results in an release of this metal to the environment without a legal ambiental control. (Maurice-Bourgoin et al., 2000; Esdaile and Chalker, 2018; Crespo-lopez et al., 2021). In efficient amalgam processes, approximately 1 kg of Hg is used for every kg of gold. However, ASM often uses inefficient processes that can consume up to 50 kg of Hg for every kg of gold (WHO, 2016). Mining in South and Central America is estimated to have released approximately 196,000 t of Hg into the environment between 1570 and 1900 (Strode et al., 2009). Due to the use of Hg to concentrate and extract gold and silver from low-grade minerals (Lacerda, 1997; Veiga and Hinton, 2002). These mining types may partly be responsible for the high fluxes of Hg in many parts of South America and the high background levels of mercury in the global environment (Nriagu, 1993). Since this metal can be transported hundreds of kilometers by rain or wind, it can be easily concentrated until it is transformed into different chemical forms, which manage to enter the environment and the food chain (Crespo-lopez et al., 2021).

According to the results, only in the sediment samples the mean concentration value of mining sites the As (1,679 ug g^{-1}) exceeded the mean background value (0,47 ug g^{-1}), 76,4% of these samples exceeding the control (Table 1-3). The source material that most contributes to the occurrence of As in soils of the Amazon is the presence of arsenopyrite (FeAsS), present in metamorphic rocks and in different geological formations in the basin (Tallarico et al., 2017). Recent studies have argued that much of Hg is directly related to As concentrations (Barats et al., 2020). The high correlation between these metals suggests that they are derived from the same source. Mining companies do not use arsenic in the Hg amalgam process, but both As and Hg are commonly enriched in gold deposits. Therefore, the three elements Au, Hg, and As are present together, either by the erosion of alluvial terrace deposits or transported to the gold-rich region of mineralization in the Andes (Lechler et al., 2000).

Certain metals such as Cd, Cr, Cu and Pb are considered highly dangerous pollutants, as the increased trophic transfer of these elements in the aquatic and terrestrial food chains / webs has important implications for wildlife and human health (Ali et al., 2019). Our results show that in sediment samples, the mean concentration of Cu (22,1 ug g $^{-1}$) and Pb (7,542 ug g $^{-1}$) in mine sites exceed the background mean values (17,87 ug g $^{-1}$) and (7,3 ug g $^{-1}$), respectively. While the mean concentration of Cd (0,752 ug g $^{-1}$) of the mining sites exceeds the threshold of TEL 0.6 ug g^{-1} (Table 1 and 2). Da Silva, (2002) reported that Cd was mostly associated with the bioavailable fraction of the sediment, and that its origin is anthropic, and its presence in the environment is closely linked to the activities carried out in the river, such as mining activities. On other hand, in water samples, Cd (0,021 ug L $^{-1}$) and Cr (0,677 ug L $^{-1}$) exceeded the mean background value 0,02 ug L $^{-1}$ and 0,44 ug L $^{-1}$, respectively (table 1 and 2). Metals such as Cr, Pb and Ni tend to accumulate preferentially in sediments and soil than in water, this may be due especially to the extraction of cassiterite, which mobilizes many metals from rocks and soils, and the rain contributes to the metals reaching the river sediment (Ribeiro et al., 2017). However, there are other metals such as Ni and Zn that can also be toxic if they exceed certain concentration levels (Laino-Guanes et al., 2015). The data shows that Ni levels are below the mean background value and quality standards in water and sediment samples. The mean concentration of Zn in water samples from the mining sites (47,9 ug L $^{-1}$) was higher than the mean background value (0,52 ug L $^{-1}$), and both Short-term (37 ug L $^{-1}$) and Long-term (7 ug L $^{-1}$) thresholds, exceeding up to 100 %, 55,6% and 77,8% the quality standards used, respectively (Table 1-3). Certain metals such as Pb, Cu and Zn are good indicators of anthropogenic contamination, due to limited closeness to the areas of origin of the contamination the high concentration in the environment, it can reflect the great activity of human and industrial origin like mining industries (Gonzáles and Ramírez, 1995; Márquez et al., 2016).

3.2. Environmental risk

According to the risk analysis in the sediment samples, the following are the percentages of each that are within categories 1 and 2 (green and blue): As (23,64%), Cd (45,83%), Cr (54,76%), Cu (52,83%), Fe (43,24%), Hg (49,40%), Mn (8,11%), Ni (65,63%), Pb (32,88%) and Zn (52,27%) that is, they do not exceed or are equal to the mean background concentration. On the other hand, the percentages of each metal that are within category 5 (red) are: As (1,80%), Cu (1,39%), Hg (2,68%), Mn (2,70%), Pb (2,74%), present the highest risk of contamination compared with the sediment samples. The remaining percentage of the samples of each metal are distributed between categories 3 and 4 (yellow and orange) (see, figure 2A). In the case of water samples, the increase in the concentration levels of mining sites with respect to the mean background concentration are higher, more evident. Because they present a much higher level of contamination risk than in sediment samples. Well, the percentage of metals that are in category 5 (red) are quite high: As (8,33%), Cd (15,39%), Cr (26,67%), Cu (17,95%), Fe (66,67%), Hg (46,45%), Mn (66,67%), Ni (18,75%), Pb (69,23%) and Zn (55,56%). On the other hand, the metals that are within categories 1 and 2, which do not present risks of contamination are quite low and even null as in the case of Mn and Zn: As (52,78%), Cd (64,10 %), Cr (33,33%), Cu (56,41%), Fe (16,67%), Hg (13,74%), Mn (0,00%), Ni (56,25%) , Pb (69,23%) and Zn (0,00%) (see Figure 2B). The metals with the highest percentages of contamination risk in the sediment are Pb (67,12 %), As (76,36%), Mn (91,89%), and in water are Fe (83,33 %), Hg (86,26 %), Mn (100 %) and Zn (100 %), since most of their samples are distributed in categories 3, 4 and 5. That is, they present an increase in concentration of 10 to 100 times higher with respect to the mean background values.

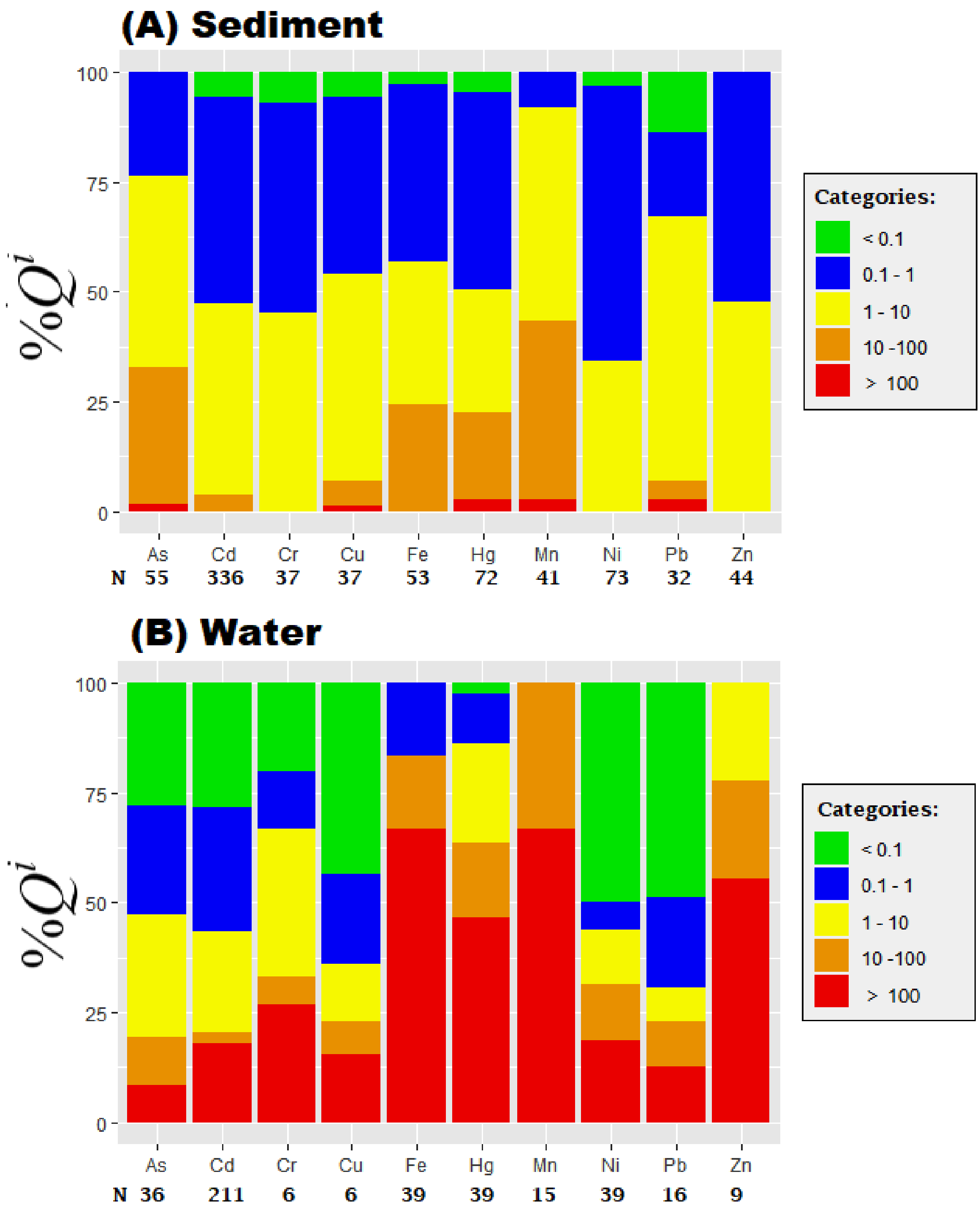


Figure 2. Risk analysis in sediment **(A)** and water **(B)** is the percentage classified into 5 categories of the relationship obtained by dividing the dataset of concentration of each metal in mining sites by the mean background value. The categories are: 1. does not exceed mean background (green); 2. equal to the mean background (blue); 3. exceeds the mean background 10 times (yellow); 4. exceeds mean background 100 times (orange) and 5. exceeds mean background more than 100 times (red).

3.3. Metal concentration data in aquatic organisms and Ecological Risk Assessment

Mining has caused environmental alterations such as extensive ecological degradation, a decrease in the distribution and structure of aquatic biodiversity, and the extinction of species (Affandi and Ishak, 2019). Water discharged from mining processes contributes to the release of high concentrations of metals in river water and sediments (Taiwo and Awomeso, 2017). Until it affects aquatic organisms through bioaccumulation and biomagnification effects, and metal toxicity (Reis, 2013; Okpala et al., 2018). Many studies have reported the presence of toxic metals such as Hg, As, Pb, Cr, Cd, Ni, and Mn in various organisms that exceed allowable levels (Tarras-Wahlberg et al., 2001; Gusso-Choueri et al., 2018). Therefore, the use of aquatic organisms have been widely used as biological indicators for risk assessment because their health and abundance represent the health of aquatic environments (Tarras-Wahlberg et al., 2001; Affandi and Ishak, 2019). According to our ecological risk assessment based on toxicity data in aquatic organisms, it shows that for Cd and Fe the toxicity data exceed the quality standards for the three trophic levels (algae, fish and daphnia) in the three toxicity tests (EC50 , NOEC and LC50). Followed by Hg and Ni which exceed the EC50 in algae and daphnia, and the LC50 in fish. For Pb and Zn only the toxicity data on Daphnia do not exceed quality standards (see Table 4).On the other hand, the bioaccumulation in riverian amazonian fish results show that Cu (4,085 ug g $^{-1}$ ww) and Pb (3,831 ug g $^{-1}$ ww) exceed the mean concentration of metals in the mining areas and the acute and chronic limits. As (230 ug g $^{-1}$ ww) exceed the chronic limits and the mean mineral concentration, and Cd (0,594 ug g $^{-1}$ ww) and Hg (0,485 ug L $^{-1}$ ww) exceed the mean concentration of metals of the mining areas (see Figure 3). Since these 5 metals exceed the acute and chronic limits of the Water Quality Criteria for the Protection of Aquatic Life, the metal concentrations evaluated in this article may adversely affect Amazonian riverian fish populations. The magnitude of the impact of heavy metals in fish depends on multiple factors like natural background levels, the contamination levels in their immediate environment (water and metal contamination from sediments) and the exposure time (acute versus chronic), bioaccumulation, etc (Ungherese et al., 2010; Kemp et al. 2011; Suedel et al. 2017). Studies revealed that exposure to Hg, Pb and Cu can enter to aquatic organisms through direct consumption of water or biota, and by absorption through gills, skin, and digestive tract and can alter the neurotransmitter and neuromuscular functions of fish (Rahman et al., 2012; Hayat et al., 2016). Furthermore, it can cause fish kills from metal toxicity, gill damage, reduced growth and survival and reduced reproductive success, hormonal, neurological and metabolic damage (Ricciardi et al. 2009; Nelson et al., 2015; Affandi and Ishak, 2019). According to our results, the remaining metals Cr, Ni and Zn do not exceed any of them, and do not pose any risk to the fish populations of the Amazon basin (see Figure 3).

Table 4. Toxicity data in aquatic organisms and Quality Standards for Ecological Risk Assessment.

	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
algae 72h EC50	2000[1]	**20,7**[5]	550[1]	53[1]	**2400**[4]	**9**[8]	11500[1]	**290**[5]	**2200**[8]	53[1]
algae 72h NOEC	-	**2,4**[5]	62[1]	23[1]	**2000**[1]	0,2[8]	-	74[5]	**500-1000**[8]	23[1]
daphnia 48hEC50	5600[2]	**32,6**[6]	290[2]	38[2]	**3500**[2]	**3-5,2**[6]	19500[2]	**500-7600**[6]	82[6]	**1280**[2]
daphnia 21d NOEC	1080[2]	0,2 - 0,8[6]	15[2]	26[2]	1000[2]	0,7[6]	1100[2]	4,2-26[6]	1-64[6]	**255**[2]
fish 96h LC50	32900[3]	**2,6-2748**[7]	22300[3]	91[3]	**71000**[3]	**4-193**[7]	15000[3]	**2500- 46000**[7]	**113-1470**[7]	**527**[3]
fish chronic NOEC	<500[3]	**1 - 22**[7]	10200[3]	18[3]	**50000**	0,3-1[7]	830[3]	27-414[7]	**4,3-230**[7]	**128**[3]
Acute-QS	-	1,8	-	-	-	1,4	-	470	82	120
Chronic-QS	-	0,7	-	-	1000	0,8	-	52	3,2	120

From European WQS Sheet
From US EPA ECOTOX
Used for Risk assessment

[1] Geometric mean EC50 and NOEC 72h *Pseudokirchneriella subcapitata;* [2] Geometric mean EC50 48h and Range of 21 d Daphnia reproduction NOEC; [3] Geometric mean EC50 96h and chronic NOEC *Oncorhynchus mykiss;* [4] Available data EC50 72h on algae (*Chlorella pyrenoidosa*); [5] EC50 and NOEC 96h *Pseudokirchneriella subcapitata;* [6] Selected EC50 48h and Range of 21 d Daphnia reproduction NOEC; [7] Range of fish LC50 96h and NOEC data; [8] Range of selected NOECs algae. The quality standards (QS) used for risk assessment were acute and chronic limits (USEPA, 1992). **Note:** Numbers in bold exceed the QS.

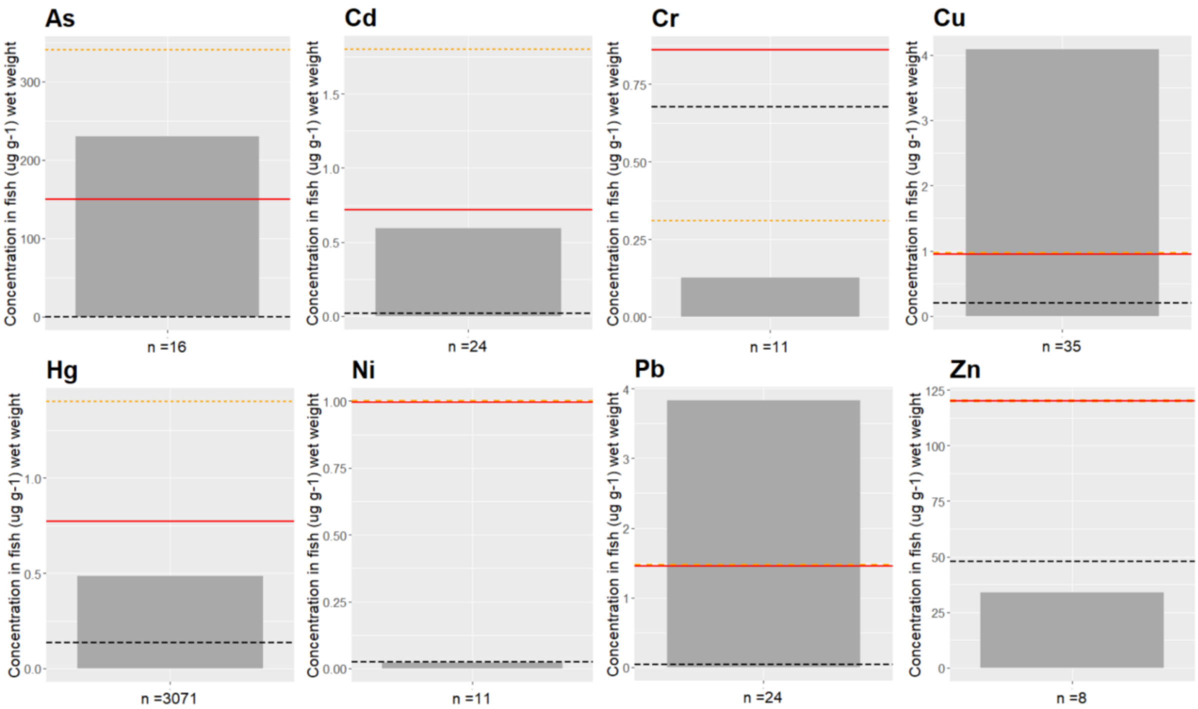


Figure 3. Metal concentrations (µg g^{-1} wet weight) in fish samples from the Amazon basin. The red lines indicate the acute limits (*CCM*) and the dashed orange lines the chronic limits (*CCC*) of the Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1995) thresholds. The black dotted lines indicate the mean concentration of mining sites in the Amazon basin (see Table 2). n represents the number of specimens reported in the articles. *CCM: Criterion of maximum concentration* and *CCC: Criterion of continuous concentration*.

Although there are currently more studies on risk assessment for contamination of metals in mining areas in the Amazon Basin, these investigations are restricted to certain regions. The Brazilian region, where there is the largest number of studies except the central Amazon, focuses mainly on the impact of Hg, since ASGM is the most explored in this region. In the Amazon, the ASM is responsible for emitting more than 200 metric tons of mercury annually, which means that approximately 27% of global ASM emissions and 80% of total emissions in South America originate from the Amazon (Siqueira et al., 2018). For the rest of the countries that make up the basin, the information is more extensive in terms of the metals they consider for risk assessment, but the number of studies is much lower, especially in the northern and southern peripheral area. However, it is known that mining and especially artisanal small-scale gold mining ASGM have had a high increase in the entire Amazon basin (Teixeira et al., 2018). The Amazon Georeferenced Social and Environmental Information Network (AISG) reports that there are currently more than 119 illegal mining sites in the State of Pará (the second largest state in the Brazilian Amazon) and approx. 300 illegal mining sites throughout the Amazon (AISG, 2020; Crespo-López et al., 2021). Therefore, this type of study is of vital importance since a complete compilation of information on mining activity in the entire basin has not been carried out.

Conclusions

According to our results, the mean background concentration value of all metals is below the established thresholds allowed for the protection of aquatic life in sediments (CCME) and water (CCME and USEPA). In other words, our metal concentration data for reference sites are within international quality standards. Although it is important to mention that the metal concentration of these standards used is based on the rivers of North America, with different characteristics from those of the Amazon basin, it is important to consider for future studies the development of specific regulations for the study area. In water samples from the southern peripheral zone, Cd, Cu, Hg, Mn and Zn showed the highest levels of background metal concentration in the entire basin. Although concentration levels did not exceed environmental quality standards, that region has a limited number of studies, thus comparing with the rest of the regions is difficult. On the other hand, although in the Amazon region of Brazil, the number of investigations on the effects of mining is quite high, these articles focus mainly and only on the levels of Hg concentration and its effects on the ecosystem, despite the concentration of the rest of the metals also tend to increase due to mining. In the sediment samples, the mean concentration values of As, Cu, Fe, Hg, Mn and Pb of the mining sites exceed the mean background metal concentration, and only Cd exceeds the threshold TEL. In water samples the mining concentration of Cd, Cr, Fe, Hg, Mn and, Zn exceed the mean background value, and Fe, Hg exceed the short-term threshold and Zn exceed the long-term standard. According to our environmental risk analysis, Pb, As and Mn in sediments, and Fe, Hg, Mn, and, Zn in water samples, are the metals that represent a high risk of contamination in the mining sites of the basin. Finally, according to the ecological assessment As, Cd, Cu, Hg and Pb exceed the acute and chronic limits of the Water Quality Criteria for the Protection of Aquatic Life, and can present adverse impacts on Amazonian fish populations.

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Supporting Information

Table S1. Background metal concentrations in sediment (ug g^{-1}) and water (ug L^{-1}) samples from the 4 regions of the Amazon basin. Values compared with the Canadian Environmental Quality Guidelines (CCME, 2002) for sediment and water and the Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1994) thresholds.

Sediment (ug g -1)

	CCME		Western Peripherial Area				Central Amazon				Northern Peripherial Area				Southern Peripherial Area			
	TEL	PEL	N°	Mean	Max	Min	N°	Mean	Max	Min	N°	Mean	Max	Min	N°	Mean	Max	Min
As	-	-	4	1,358	5,51	0,049	2	0,055	0,060	0,050	-	-	-	-	-	-	-	-
Cd	0,60	3,50	6	0,977	3,10	0,107	-	-	-	-	-	-	-	-	-	-	-	-
Cr	37,30	90,00	13	7,41	104	0,049	-	-	-	-	1	88,25	88,25	88,25	-	-	-	-
Cu	35,70	197,00	11	15,18	66,70	2,50	-	-	-	-	1	108	108	108	-	-	-	-
Fe	-	-	7	16786	67400	2748	2	0,707	0,770	0,650	1	7745	7745	7745	2	80,00	80,00	80,00
Hg	0,17	0,49	26	0,036	0,942	< 0.001	24	0,204	0,400	0,012	31	0,090	0,308	0,050	12	0,115	0,346	0,020
Mn	-	-	10	556	3460	231	2	0,080	0,080	0,080	1	128	128	128	2	0,207	0,330	0,130
Ni	-	-	7	7,06	44,90	0,900	-	-	-	-	1	55,85	55,85	55,85	-	-	-	-
Pb	35,00	91,30	14	6,18	37,70	1,00	-	-	-	-	1	75,10	75,10	75,10	-	-	-	-
Zn	123,00	315,00	11	50,98	223	21,00	-	-	-	-	1	87,95	87,95	87,95	-	-	-	-

Water (ug L -1)

	CCME		EPA		Western Peripherial Area				Central Amazon				Northern Peripherial Area				Southern Peripherial Area			
	Short Term	Long Term	Acute	Chronic	N°	Mean	Max	Min	N°	Mean	Max	Min	N°	Mean	Max	Min	N°	Mean	Max	Min
As	-	-	-	-	2	0,090	0,090	0,090	-	-	-	-	-	-	-	-	-	-	-	-
Cd	1	0,1	1,8	0,700	33	0,015	3,10	0,001	17	0,035	0,179	0,002	2	0,059	0,251	0,014	2	0,064	0,215	0,019
Cr	-	-	-	-	16	0,399	0,874	0,050	15	0,474	0,747	0,146	2	0,668	0,884	0,504	2	0,433	0,815	0,230
Cu	2	-	-	-	52	0,442	11,15	0,002	24	0,503	1,60	0,090	7	0,160	1,80	0,020	2	1,27	1,90	0,845
Fe	300	-	-	1000	34	3,21	123	0,100	34	9,30	297	0,820	18	5,80	178	2,14	-	-	-	-
Hg	0,026	-	1,4	0,800	13	0,001	0,024	< 0.001	22	0,001	0,003	< 0.001	20	0,003	0,110	< 0.001	3	0,221	0,241	0,202
Mn	-	-	-	-	69	1,94	102	0,008	63	3,67	992	0,060	20	0,764	155	0,100	2	11,41	19,79	6,58
Ni	-	25	470	52,000	17	0,401	1,28	0,090	14	0,463	1,34	0,116	2	0,416	1,12	0,154	2	0,318	0,893	0,113
Pb	-	-	82	3,200	17	0,148	45,90	0,005	-	-	-	-	-	-	-	-	-	-	-	-
Zn	37	7	120	120,000	40	0,410	31,20	0,029	17	0,792	5,52	0,040	7	0,458	4,10	0,060	2	3,44	9,73	1,22

The geochemical regions of the Amazon basin: 1) *Western peripheral area* (Northwest Area (NWA) and Southwest Area (SWA)); 2) *Central Amazon* (Central Amazon (CA) and Eastem Area (EA)); 3) *Northern Peripheral Area* (NA); and 4) *Southern Peripheral Area* (SA).

Table S2. Metal concentrations in sediment (ug g -1) and water (ug L -1) samples from the 4 regions of the Amazon basin at mining sites. Values compared to the percentage (%) that exceeds the background metal concentration and the thresholds of the Canadian Environmental Quality Guidelines (CCME, 2002) for sediments and water and the Water Quality Criteria for the Protection of Aquatic Life (USEPA, 1994).

Sediment (ug g -1)																
	Western peripheral area				Central Amazon				Northern peripheral area				Southern peripheral area			
	Nº	Mean	Max	Min	Nº	Mean	Max	Min	Nº	Mean	Max	Min	Nº	Mean	Max	Min
As	41	2,60	1860	0,049	-	-	-	-	0	-	-	-	14	0,464	5,38	0,060
Cd	42	0,946	47,80	0,019	-	-	-	-	11	0,312	48,10	0,100	-	-	-	-
Cr	23	4,92	27,20	0,049	-	-	-	-	10	2,94	81,30	1,25	8	23,82	61,91	5,22
Cu	53	38,70	5360	4,40	-	-	-	-	11	2,59	107	0,500	8	10,33	18,65	2,22
Fe	20	5650	39701	858	-	-	-	-	11	537	7991	365	6	612,5	1670	110
Hg	120	0,548	34,00	< 0.001	28	0,078	3,40	0,008	45	0,012	0,425	< 0.001	143	0,070	151	0,010
Mn	20	869	16000	229	-	-	-	-	11	57,67	112	40,00	6	804	1840	380
Ni	13	9,97	25,90	4,20	-	-	-	-	11	3,59	51,70	1,75	8	2,39	26,62	< 0.001
Pb	59	11,04	4470	0,019	-	-	-	-	6	0,32	70,61	0,050	8	4,80	11,46	0,900
Zn	33	76,98	518	21,30	-	-	-	-	11	10,8	87,60	6,50	-	-	-	-

Water (ug L -1)																
	Western peripheral area				Central Amazon				Northern peripheral area				Southern peripheral area			
	Nº	Mean	Max	Min	Nº	Mean	Max	Min	Nº	Mean	Max	Min	Nº	Mean	Max	Min
As	27	0,063	50,00	0,002	-	-	-	-	-	-	-	-	9	0,292	0,430	0,120
Cd	30	0,016	46,00	< 0.001	-	-	-	-	-	-	-	-	9	0,052	0,220	0,010
Cr	6	15,07	238	0,250	-	-	-	-	-	-	-	-	9	0,099	1,32	< 0.001
Cu	30	0,168	500	0,002	-	-	-	-	-	-	-	-	9	0,411	16,60	0,110
Fe	2	41,68	334	5,20	-	-	-	-	4	4417	28700	1560	-	-	-	-
Hg	74	0,192	32,50	< 0.001	26	0,124	1,14	< 0.001	75	0,201	20,000	< 0.001	36	0,031	9,97	< 0.001
Mn	6	509	3250	55,00	-	-	-	-	-	-	-	-	-	-	-	-
Ni	7	6,81	156	0,075	-	-	-	-	-	-	-	-	9	0,001	3,90	< 0.001
Pb	30	0,078	133	0,003	-	-	-	-	-	-	-	-	9	0,006	9,90	< 0.001
Zn	8	38,17	712	2,000	-	-	-	-	-	-	-	-	1	12,40	12,40	12,40

The geochemical regions of the Amazon basin: 1) *Western peripheral area* (Northwest Area (NWA) and Southwest Area (SWA)); 2) *Central Amazon* (Central Amazon (CA) and Eastern Area (EA)); 3) *Northern Peripheral Area* (NA); and 4) *Southern Peripheral Area* (SA).