A systematic review on metal contamination due to mining activities in the Amazon basin and associated environmental hazards.

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Abstract

Metal contamination associated with mining activities has been considered one of the main environmental pollution problems in the Amazon region. Understanding the levels of metal contamination from mining activities requires a good understanding of background metal concentrations, which may vary notably according to the geology/lithology characteristics of the region, soil type, and predominant biogeochemical processes. This review assessed 50 papers and reports published between 1989 and 2020 describing environmental concentrations of different metals and metalloids (As, Hg, Mn, Fe, Cd, Cu, Cr, Pb, Ni, and Zn) in water and sediments of mining and non-mining areas in five geographic regions of the Amazon basin. Metal enrichment caused by mining activities was calculated and exposure concentrations were compared with sediment and water quality standards set for the protection of aquatic life. Significant enrichments of Cd, Cu, Cr, Fe, Hg, Mn, Ni and Zn were observed in mining areas in both sediment and water. Regarding background levels in the different geographic regions, the highest prevalence of metal enrichment (i.e., concentrations 10 to 100-fold higher than mean background values) in sediment samples was found for Fe (100% of samples), Ni (90%), and Mn (69%). For water, high prevalence of metal enrichment occurred for Zn, Mn, and Fe (100% of samples), and for Hg (86%). Hg, Fe, Pb, Cu, Cd, Ni and Zn exceeded water and/or sediment quality standards in a significant number of samples in the proximity of mining areas. This study indicates that mining activities significantly contribute to water and sediment contamination across the Amazon basin, posing hazards for freshwater ecosystems and potentially having human health implications.

Keywords: Amazon River, freshwater contamination, environmental quality standards, mining, metals.

Introduction

The Amazon is one of the most biodiverse regions on Earth and plays a crucial role in global climate regulation (Strand et al., 2018). The increasing anthropogenic pressures in the Amazon have significantly contributed to the alteration of ecosystem dynamics, a reduction of the forest area, and increased carbon emissions (Caballero Espejo et al., 2018; Csillik and Asner, 2020; Gatti et al., 2021). Water contamination in Amazonia has also increased, as pollution emission sources have multiplied due to the increasing demographic pressure, industrialization and agricultural expansion and intensification (Rico et al., 2021, 2022, 2023; Cabrera et al. 2023; Rizzi et al. 2023). Metal mining has been classified as one of the most detrimental pollution sources in the Amazon (Capparelli et al., 2020). This activity does not only contaminate aquatic and terrestrial ecosystems by metal mobilization and/or release, but also causes direct environmental impacts, such as deforestation and hydromorphological alteration of rivers (Adler Miserendino et al., 2013; Crespo-Lopez et al., 2021; Dezécache et al., 2017; Sonter et al., 2017), which can cause severe social conflicts (Mancini and Sala, 2018; Mestanza-Ramón et al., 2022). Metal mining operations, including illegal mining, have increased in the last few years, expanding to protected areas and indigenous territories due to the limited governmental control and careless environmental management plans (Abessa et al., 2019; Guayasamin et al., 2021; Rorato et al., 2020; Tollefson, 2021).

Overall, three types of mining operate in the Amazon basin: underground mining, alluvial mining, and open-pit mining (Hammond et al 2007). The former consists of extracting minerals and rocks below ground surface through the digging of tunnels or shafts. Alluvial mining is typically performed on riverbeds and riverbanks and consists of removing alluvial material to uncover valuable minerals. Finally, open-pit mining is the most abundant in the Amazon, and it is used when valuable minerals/metals are found in surface deposits. It consists of deforesting rich-mineral deposit zones and pumping water against the pit walls to break off the mineral-rich sediments, and then separate the valuable materials (usually gold) from sediments (Asner and Tupayachi 2016).

Metal pollution due to mining activities can result in significant toxicity to freshwater organisms next to mining areas, as well as downstream from the contamination source, where metals can be transported and deposited (Capparelli et al., 2020; Mora et al., 2019). Moreover, when metals reach inundated areas, they may be transported into river terraces and can lead to plant growth impairment in riverine systems and soils (Capparelli et al., 2021). Several studies have demonstrated that organometallic ions formed by anaerobic bacteria can be accumulated in fish and other edible organisms, posing a potential hazard for local human populations that rely on these food sources (Gusso-Choueri et al., 2018; Jiménez-Oyola et al., 2021; Olivero-Verbel et al., 2016; Pinzón-Bedoya et al., 2020; Galarza et al., 2023). Thus, it is evident that metal contamination problems associated to mining activities are not restricted to the mining areas themselves but can result in direct and indirect impacts on ecosystems at a regional scale, affecting different socioeconomic activities (da Silva Montes et al., 2022).

Assessing metal enrichment (*i.e.*, concentrations above local background levels) due to mining activities requires an adequate understanding of background metal concentrations (Santos-Francés et al., 2017). In Amazonia, background metal concentrations vary notably according to the geology/lithology characteristics of the region, soil type, and predominant biogeochemical processes (McClain and Naiman, 2008; Park and Latrubesse, 2015). The west and southwest Amazonian landscape are formed by the orogenic mountains of the Andes and foreland river basins. In the north and south, rivers drain the ancient intensively eroded massifs of the Guianas and central Brazil, respectively, while the Central Amazon region is formed by sedimentary low-elevated flat areas, displaying enormous geochemical diversity compared to other regions (Fittkau et al., 1975; Hoorn et al., 2010; Rossetti et al., 2005). The location of river headwaters and drainage areas in this heterogeneous landscape result in electrolyte differences in running waters, with increasing ion concentrations noted from the west through the north to the central area (Junk, 1997; Sioli, 1984). To date, information on background metal concentrations naturally occurring in the different regions of the Amazon basin is limited (but see Adamo et al., 2005; do Nascimento et al., 2018; Santos-Francés et al., 2017). Considering the global importance of this region, an assessment of background metal concentrations and potential enrichment due to mining activities can provide valuable information for a better environmental management of these activities.

Environmental hazards associated with metals due to mining in sediments are estimated based on established threshold values, which include the Threshold Effect Level (TEL) and the Probable Effect Level (PEL). The TEL is established as the threshold above which metals can cause rare adverse biological effects, while the PEL is the threshold above which metals are expected to result in clear adverse biological effects. For the aquatic compartment, short- and long-term exposure thresholds have been established to indicate unacceptable ecological effects by the United States Environmental Protection Agency (US EPA, 1994) and the Canadian Environmental Quality Guidelines (CCME, 2002). Although some studies have assessed local biological impacts caused by increasing metal exposure concentrations in the Amazon, often beyond such quality standards (Capparelli et al., 2020; Carrillo et al., 2022; Silva et al., 2018), regional assessments are still incipient.

Therefore, this study aimed (1) to assess metal background concentrations in water and sediments in different regions of the Amazon basin based on a literature review, (2) to calculate the net metal enrichment caused by mining activities in these regions, and (3) to assess the environmental hazards posed by metal contamination. Metal enrichment due to mining activities was assessed by calculating differences between mining and non-mining areas, while environmental hazards were determined based on comparisons between measured exposure concentrations and international water and sediment quality standards. Our systematic review provides the first large-scale assessment of metal contamination in the Amazon basin and assists in defining knowledge gaps that may motivate future studies in the region.

Materials and methods

Literature review

Peer-reviewed papers and reports published between 1989 and 2020 (Supplementary Information 1) describing metal concentrations in water and sediments of mining and no-mining areas of the Amazon River basin were compiled. The literature search was constrained to the limits of the Amazon *lato sensu* (~8,000,000 km^2), as established by Eva and Huber (2005). The search was carried out systematically using the Google Scholar and Scopus databases employing the following keywords: "Amazon", "mining", "environmental analysis", "sediments", "water", "metal contamination". The Portuguese and Spanish translation of those keywords were also used as to retrieve literature published in these languages. First, the titles and abstracts of all retrieved articles were screened for adequacy. Then, all studies were read in full and those that provided data either on the freshwater and sediment metal contamination or on background metal concentrations (*i.e.,* reports of metal concentrations not necessarily from mining areas) were selected irrespective of the sampling design or analytical metal determination approach. Initially, data on all possible metals released or enriched by mining activities were retrieved, but our final database included only Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn, as well as the metalloid As (hereafter “metals”), as these were the most commonly assessed elements and the ones having the largest toxicity potential to aquatic organisms. When GPS coordinates were not provided in the reviewed articles, available Google Earth maps were used to assign the nearest GPS coordinates based on the described localities. Our review employed relevant sources of available information that could be combined regarding analytical metal determination methods. By doing so, we chose to include in our analysis all possible data without any data dispersion treatment.

Studies were classified into each of the main geographic regions suggested by Feldpausch et al. (2011): Southern Amazon (SA), Southwestern Amazon (SWA), Northwestern Amazon (NWA), Northern Amazon (NA), Central Amazon (CA), and Eastern Amazon (EA) (Figure 1). Water and sediment samples reported by the different studies were classified into non-mining areas (for the determination of background levels) and mining areas. Background levels reflect the natural metal concentration in water and sediments, providing the basis for environmental quality assessments (Preston et al., 2014; Teng et al., 2009).

The soil classes of the study area were categorized according to the Soil and Terrain Database (SOTER) for Latin America and the Caribbean (SOTERLAC), version 2.0 (Dijkshoorn et al., 2005) to obtain the dominant soil taxonomy defined by the World Reference Base Soil Groups (FAO, 2006). The dominant soil class for each sample was extracted through geographical coordinates using the QGIS software v3.03.

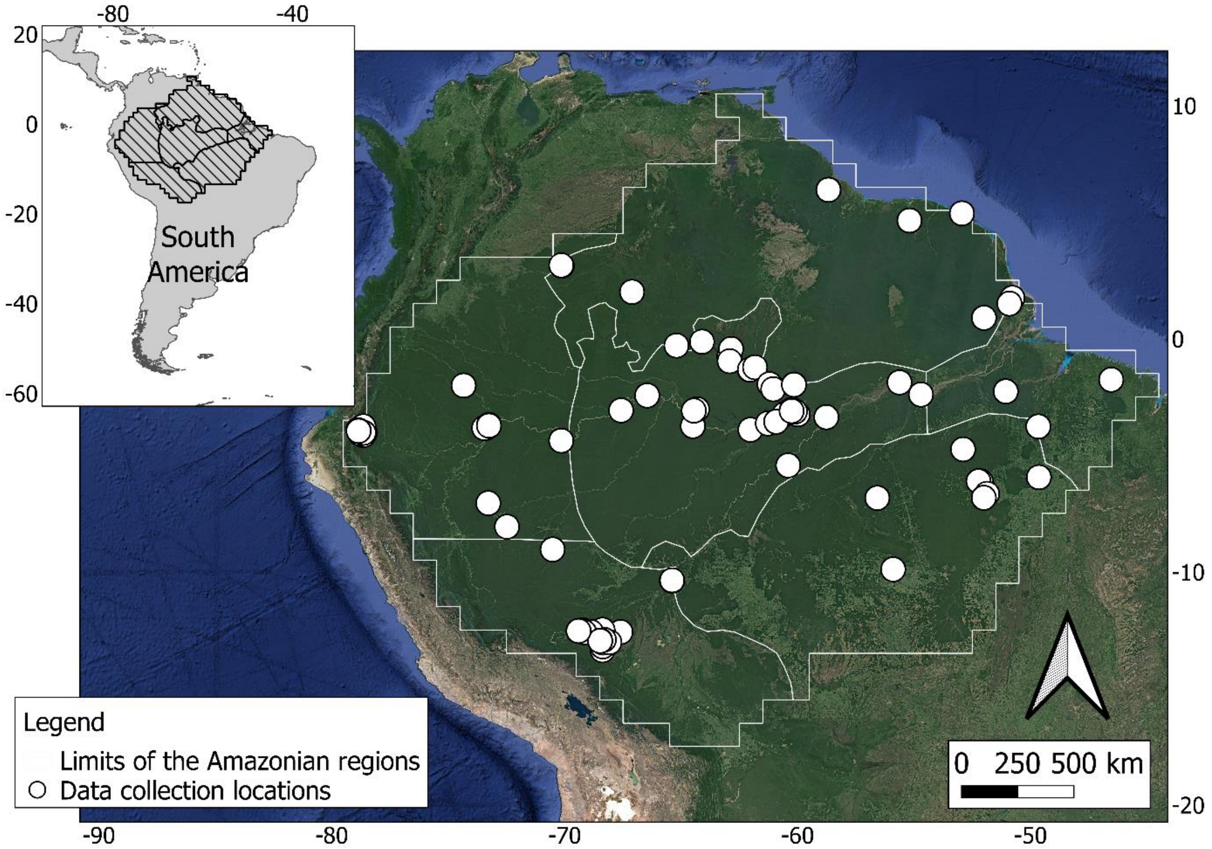

Figure 1. Amazon water and sediment sampling locations (white dots). The gray lines indicate the limits of the six geographic regions, namely Southern Amazon (SA), Southwestern Amazon (SWA), Northwestern Amazon (NWA), Northern Amazon (NA), Central Amazon (CA), and Eastern Amazon (EA). The map in the upper left corner depicts the location of the study area (the Amazon basin) in South America.

Data analysis

Metal water and sediment concentrations reported by the different studies were stored in a database (Supplementary Tables S1 to S4). The following parameters were calculated for each metal: number of samples reporting metal concentrations above the limit of detection, geometric mean of the reported exposure concentrations, and maximum and the minimum water and sediment concentrations in mining and non-mining areas in each geographic region. For each study the analytical method employed, together with the limit of detection and quantification (when available), was recorded to note differences regarding analytical capabilities of the groups involved in the different investigations.

Metal enrichment in mining areas was assessed by calculating the Q^i, which is the ratio obtained by dividing the measured metal concentrations (Q^{i}_{Metals}) by the mean background concentration $(Mean^{i}_{background})$ in non-mining areas of each geographical region for each metal (i), according to Demková et al. (2017). The Q^{i} values were used to calculate: (i) the percentage of samples in which the measured metal concentrations were more than 10-fold lower than the mean background concentration; ii) the percentage of samples that were between 10-fold lower and the mean background concentration; iii) the percentage of samples that were between the mean background concentration and 10-fold the background concentration; iv) the percentage of samples whose concentration was 10- to 100-fold higher than the mean background concentration and; v) the percentage of samples that were over 100-fold the mean background concentration. Only metals with at least five samples to calculate the background information in each of the six geographic regions were evaluated, so enrichment was only calculated for Hg, Mn, Fe, Cd, Cu, Cr, Pb, Ni and Zn.

To assess environmental hazards, the water and sediment metal concentrations reported in mining and no-mining areas were compared with environmental quality standards. For water, these standards include the environmental thresholds for short term exposure (effects resulting from short-term intermittent or transient exposures) and long-term exposure (chronic effects resulting from long-term exposures) proposed by the Canadian Environmental Quality Guidelines (CCME, 2002), and the acute and chronic standards set by the United States Environmental Protection Agency (US EPA, 1994). Sediment concentrations were compared with the available Threshold Effect Level (TEL) and Probable Effect Level (PEL) established by the Canadian Environmental Quality Guidelines (Long et al., 1995). Measured environmental concentrations were divided by the corresponding water and sediment quality standards. Then the percentage of samples exceeding the standard and the magnitude of exceedance was assessed. Similar to the classification performed for the metal enrichment assessment, environmental samples were classified as posing no hazard when the ratio between the measured concentration and the standard was <0.1; a potential hazard when the ratio was 0.1-1; a moderate hazard when the ratio was 1-10; a high hazard when the ratio was 10-100, and a very high hazard when the ratio was >100.

Results

Data availability

Our database contained a total of 50 studies, 14 reporting background metal concentrations in water, 17 reporting background metal concentrations in sediment, 24 reporting water contamination in mining areas, and 30 containing sediment contamination in mining areas (Figure 2). The main mining type studied in the reviewed articles was gold mining (87%). Silver mining was reported in only 6% of the articles. Cassiterite, diamond, manganese, and copper mining were investigated in only one study each.

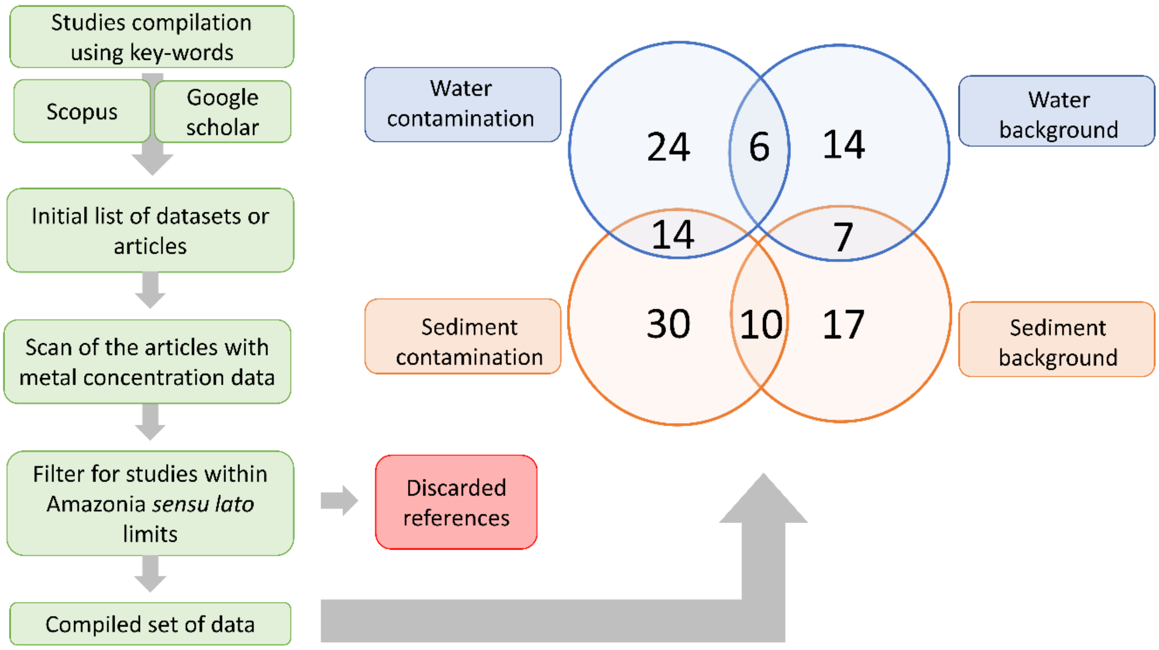

Figure 2. Flowchart diagram of the applied literature search employed to obtain the data used in this study. The Venn diagram on the right-hand side depicts the number of studies in each category, comprising water and sediment background levels from non-mining areas and water and sediment samples collected in mining areas. The complete list of studies used to draw the datasets can be found in the supplementary material Table S5.

Background metal concentrations

A total of 838 samples (251 for sediments and 587 for water) were classified to determine background metal concentrations (Table 1). Mercury was detected in 40 % of the sediment samples, while Mn was the most prevalent metal in water samples (26%), followed by Fe and Cu (ca. 14% each). Fe and Mn presented the widest concentration variation (as represented by the 95% confidence interval of the geometric mean) in sediment, while Mn presented the widest variation in water samples (Table 1).

Table 1. Background metal concentrations in the Amazon according to the literature search carried out in this study. Data is displayed as the number of samples (N), minimum and maximum values and the geometric mean and confidence intervals (CI) at 95%. Values for sediment samples were expressed as µg g $^{-1}$, and for water samples as µg L $^{-1}$. <LOD: lower than the limit of detection.

	Sediment					Water				
Metal	N	Mean	CI (95%)	Min	Max	N	Mean	CI (95%)	Min	Max
As	8	0.27	(0.04 - 1.7)	0.04	5.5	2	0.09	(0.09 - 0.09)	0.09	0.09
Hg	102	0.12	(0.08 - 0.1)	<LOD	4.0	57	0.002	(0.001 - 0.004)	<LOD	2.4
Mn	14	94.1	(15.7 - 564)	0.08	1103	153	2.27	(1.49 - 3.47)	0.008	992
Fe	20	3377	(1946 - 5859)	650	26350	85	5.34	(3.58 - 7.97)	0.1	297
Cd	18	0.53	(0.24 - 1.17)	0.107	52.4	54	0.02	(0.01 - 0.04)	0.001	3.1
Cu	22	25.9	(16.9 - 39.7)	2.5	107.8	84	0.42	(0.26 - 0.69)	0.002	11.1
Cr	13	7.32	(2.4 - 22.1)	0.049	103	35	0.44	(0.36 - 0.54)	0.05	0.8
Pb	25	15.6	(8.85 - 27.6)	1	76.4	17	0.14	(0.04 - 0.52)	0.005	45.9
Ni	7	7.28	(2.31 - 22.8)	0.9	55.8	35	0.42	(0.31 - 0.56)	0.09	1.34
Zn	22	53.2	(43.7 - 64.9)	21	114.1	65	0.50	(0.32 - 0.80)	0.029	31.2

Concerning mining areas, data for 1067 samples were available: 661 for sediments and 406 for water (Table 2). Hg was the most studied metal, and the most prevalent one, with 41% and 50% of sediment and water samples showing values above the limit of detection, respectively. The second most detected metal in sediment samples was Pb (present in ca. 10% of samples). As, Cd, Cu and Pb, were present in ca. 10% of water samples above the limit of detection.

Table 2. Metal concentrations in Amazon mining areas according to the literature search carried out in this study. Data is displayed as the number of samples (N), minimum and maximum values and the geometric mean and confidence intervals (CI) at 95%. Values for sediment samples were expressed as µg g $^{-1}$, and for water samples as µg L $^{-1}$. <LOD: lower than the limit of detection.

	Sediment					Water				
Metal	N	Mean	CI (95%)	Min	Max	N	Mean	CI (95%)	Min	Max
As	As	55	1.679	(0.96 - 2.92)	0.049	36	0.106	(0.04 - 0.28)	0.002	100
Hg	Hg	272	0.145	(0.11 - 0.19)	0	201	0.14	(0.08 - 0.23)	<LOD	100
Mn	Mn	37	383	(229 - 640)	40	6	1096	(156 - 7708)	75	5500
Fe	Fe	26	1455	(619 - 3418)	10.46	6	933	(42.85 - 20330)	5.2	28700

Cd	Cd	42	1.002	(0.56 - 1.81)	0.019	39	0.019	(0.01 - 0.06)	<LOD	46
Cu	Cu	61	19.912	(12.95 - 30.62)	0.5	39	0.25	(0.07 - 0.92)	0.002	1000
Cr	Cr	41	5.903	(3.39 - 10.27)	0.049	15	0.861	(0.07 - 10.36)	<LOD	250
Pb	Pb	62	5.432	(2.87 - 10.27)	0.019	39	0.039	(0.01 - 0.16)	<LOD	325
Ni	Ni	32	4.569	(1.83 - 11.41)	0	16	0.016	(0 - 0.76)	<LOD	250
Zn	Zn	33	49.852	(28.73 - 86.49)	6.5	9	72.6	(12.6 - 418)	3	2000

The concentration of each metal was variable within each geographic region (Figure 1, Supplementary Information Tables S1 to S4). Regarding background data, sediment samples were reported for all six Amazonian regions, while water samples were not reported for the EA and SA regions. Regarding sediment samples, Hg was reported in all regions and Fe presented the widest variations within the same region (Figure 3A). Concerning water samples, Hg was reported in all regions, and Fe and Mn presented the widest variations within the same region (Figure 3C).

Regarding mining areas, water and sediment samples were available for all regions (Figure 3B, D). Regarding sediment samples, Hg was reported for all regions and, alongside Fe and Mn (both not reported for the EA and CA regions), presented the widest variations. Regarding water samples, Hg was reported in all regions. Data was particularly variable for Cu, Pb, Ni and Zn within the SA region (Supplementary material, Figures S1 to S4).

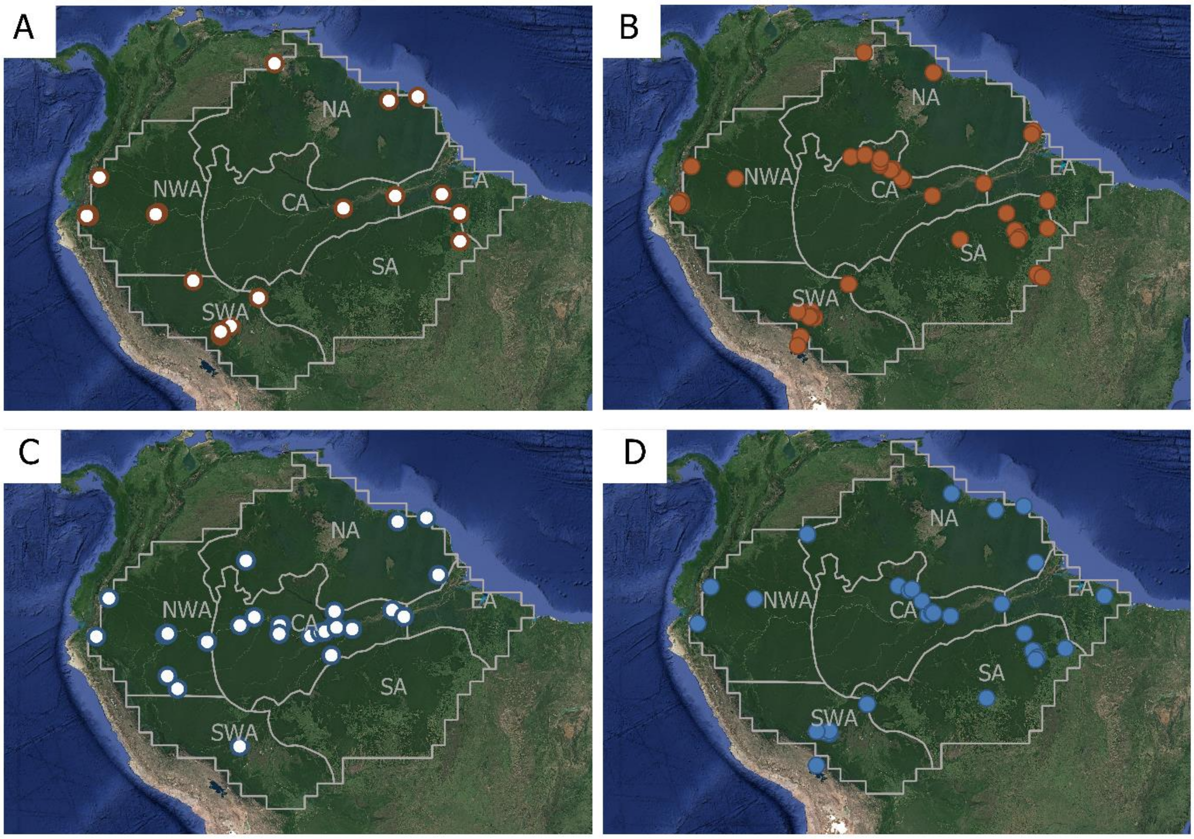

Figure 3. Geographical distribution of available studies describing sediment (A, B) and water (C, D) metal concentrations in reference (white center dots) and mining areas (colored dots) in the Amazon basin. Geographic region abbreviations: Southern Amazon (SA), Southwestern Amazon (SWA), Northwestern Amazon (NWA), Northern Amazon (NA), Central Amazon (CA), and Eastern Amazon (EA).

Concerning all sediment samples taken from areas not impacted by mining activities, almost half were taken in areas where the predominant soil types were Dystric Cambisols and Eutric Gleysols (Figure 4A). These are common tropical soils, characteristic of waterlogged areas. The prevalent soil types in the areas without mining activities where the water samples were taken were Dytric Plinthosol (Figure 4B). As the Eutric Gleysols, Dytric Plinthosol is also a common soil type in waterlogged areas but presents a higher clay content. The samplings were variable in each geographic region. For example, in the NWA almost half of the sediment samples were collected from areas dominated by Dystric Cambisols, whereas the same proportion represented Dystric Leptosols soils in the NA and Haplic Ferralsols in the SWA regions. For water, most of the samples were collected in areas where the dominant soil type was Eutric Gleysols in CA and NWA, and Gleyic Arenosols in NA.

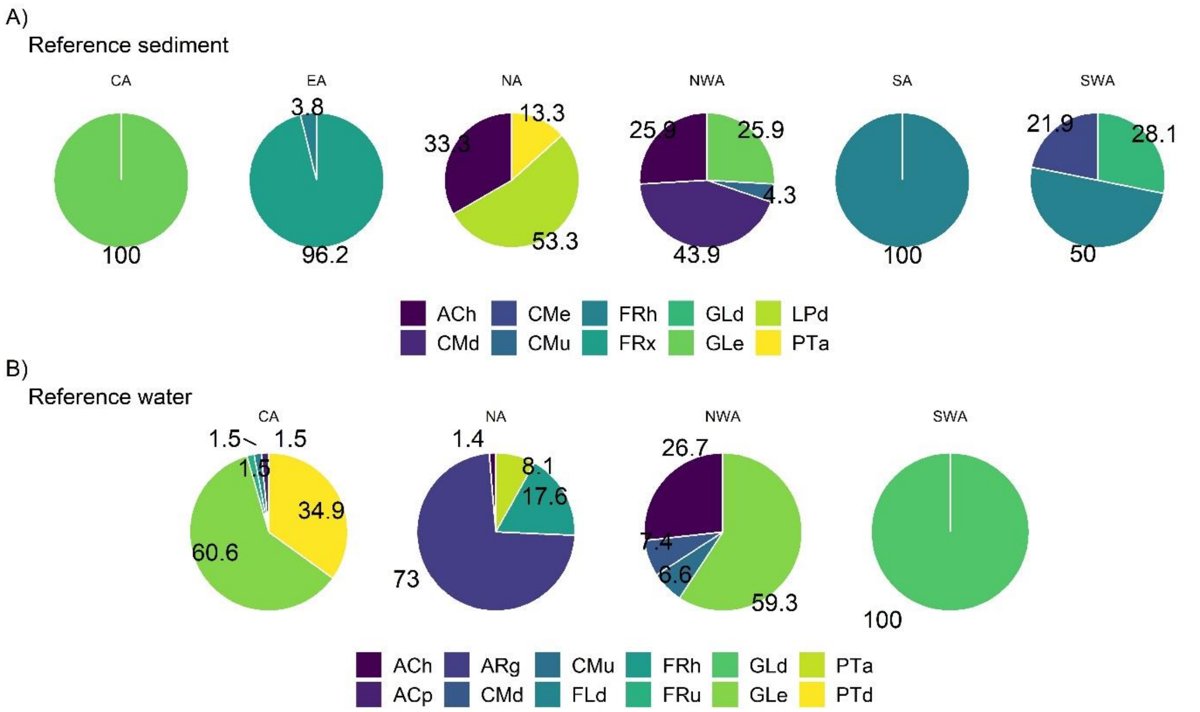

Figure 4. Dominant soil types in the areas were background sediment and water samples had been collected per geographic region. Ach = Haplic Acrisols, ACp = Plinthic Acrisols, Arg = Gleyic Arenosols, CMd = Dystric Cambisols, CMe = Eutric Cambisols, CMu = Humic Cambisols, FLd = Eutric Fluvisols, FRh = Haplic Ferralsols, FRu = Humic Ferralsols, FRx = Xanthic Ferralsols, GLd = Dystric Gleysols, GLe = Eutric Gleysols, LPd = Dystric Leptosols, PTa = Albic Plinthosols, PTd = Dystric Plinthosols. Region abbreviations: Southern Amazon (SA), Southwestern Amazon (SWA), Northwestern Amazon (NWA), Northern Amazon (NA), Central Amazon (CA), and Eastern Amazon (EA). Values are shown in percentages.

Metal enrichment in mining areas

For most metals, the differences between the calculated geometric mean and the maximum value in our database were approximately 1-fold. Given such high data variability, we considered as clear metal enrichment by mining activities only those samples whose exceedance to the geometric mean was 100 times or larger. Regarding sediments, NWA was the geographic region where more metal species were found to exceed background levels by more than 100 times (Figure 5A). As such, in this region, 100% of Fe samples, 67% of Cd samples, 18% of Pb samples, 13% of Zn samples, 11% of Cu and 3 % of Hg samples were considered to be enriched due to mining activities. Hg exceeded background levels in the SWA (5% of samples) and the CA (7% of samples) regions as well, while the other metals could not be evaluated in this region according to the established criteria (i.e., concentration evaluated in more than 5 samples).

Concerning water contamination (Figure 5B), the only regions that had sufficient number of samples to allow robust comparisons (i.e., more than 5 samples) were NA, NWA and CA. For those, Hg exceeded the median background concentration by more than 100 times in 30% of samples in CA, 60% of samples in NA and 85% of samples in NWA. In the NWA region, Fe, Mn and Zn exceeded the median background concentration by more than 100 times in all samples. The other metals (Cd, Cr, Cu, Ni, Pb and Zn) exceeded the background levels by more than 100 times in over 65% of the samples in the NWA region.

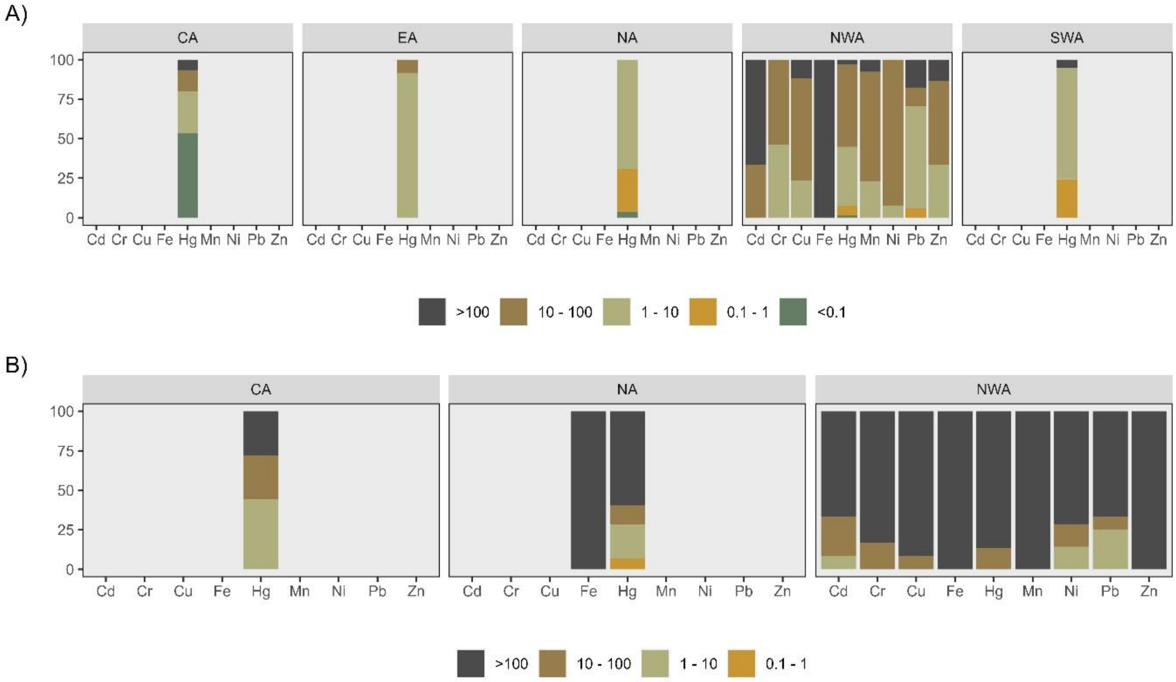

Figure 5. Metal enrichment assessment in sediment (A) and water (B) in Amazonia, categorized as 1) does not exceed mean background levels (<0.1); 2) similar or lower than background levels (0.1 - 1); 3) exceeds mean background levels by up to 10-fold (1 - 10); 4) exceeds mean background levels by 10 to 100-fold (10 - 100) and 5) exceeds mean background levels by more than 100-fold (>100). Only metals with at least five reported samples for a given were included in the analysis.

Environmental hazard assessment

The hazard assessment indicated high variability for the mining areas of different geographic regions. We only report the measured concentrations that exceeded more than 10 (high hazard levels) or more 100 times (very high hazard levels) the standard thresholds, while the rest are shown in Figure 6A. For sediment samples, Hg showed very high hazard levels in at least one location in the geographic regions CA, NWA SA and SWA, varying from 1.5% of the samples in NWA to 8% of samples in SA. Exceedance of more than 100 times (very high hazard level) above TEL or PEL were also found for Cd in the NWA (50 % of the samples) and the NA (9 % of the samples) regions, and more than 5 % of the samples of Cu, Pb and Zn in the NWA region.

For water samples, the Hg, Fe, Cd, Cu, Pb, Ni and Zn were detected above the short term exposure and long-term exposure thresholds proposed by the Canadian Environmental Quality Guidelines (CCME, 2002), and/or the acute and chronic standards set by the United States Environmental Protection Agency (US EPA, 1994), except for Ni in the SA region, and Cd, Cu and Pb in the SWA region (Figure 6B). Hg samples exceeded more than 10 times the standards in at least one location in all regions, and more than 100 times the short term threshold in a significant number of samples of the NWA (83% of the samples), NA (47% of the samples), CA (16% of the samples) and SA (10% of the samples) regions, while the chronic standard was surpassed in the NWA (42% of the samples) region. In the NA region, the water concentrations of Fe exceeded more than 100 times the short-term (100% of the samples) and the chronic (50% of the samples) standards. In the NWA region, more than 10% of the samples of Cd, Cu, Pb, Ni and Zn exceeded such standards. Particularly, 41% of the Pb exceeded the chronic exposure threshold, 59% of the Cd samples exceeded long term exposure threshold, and 55% of the Cu samples exceeded the short-term exposure threshold.

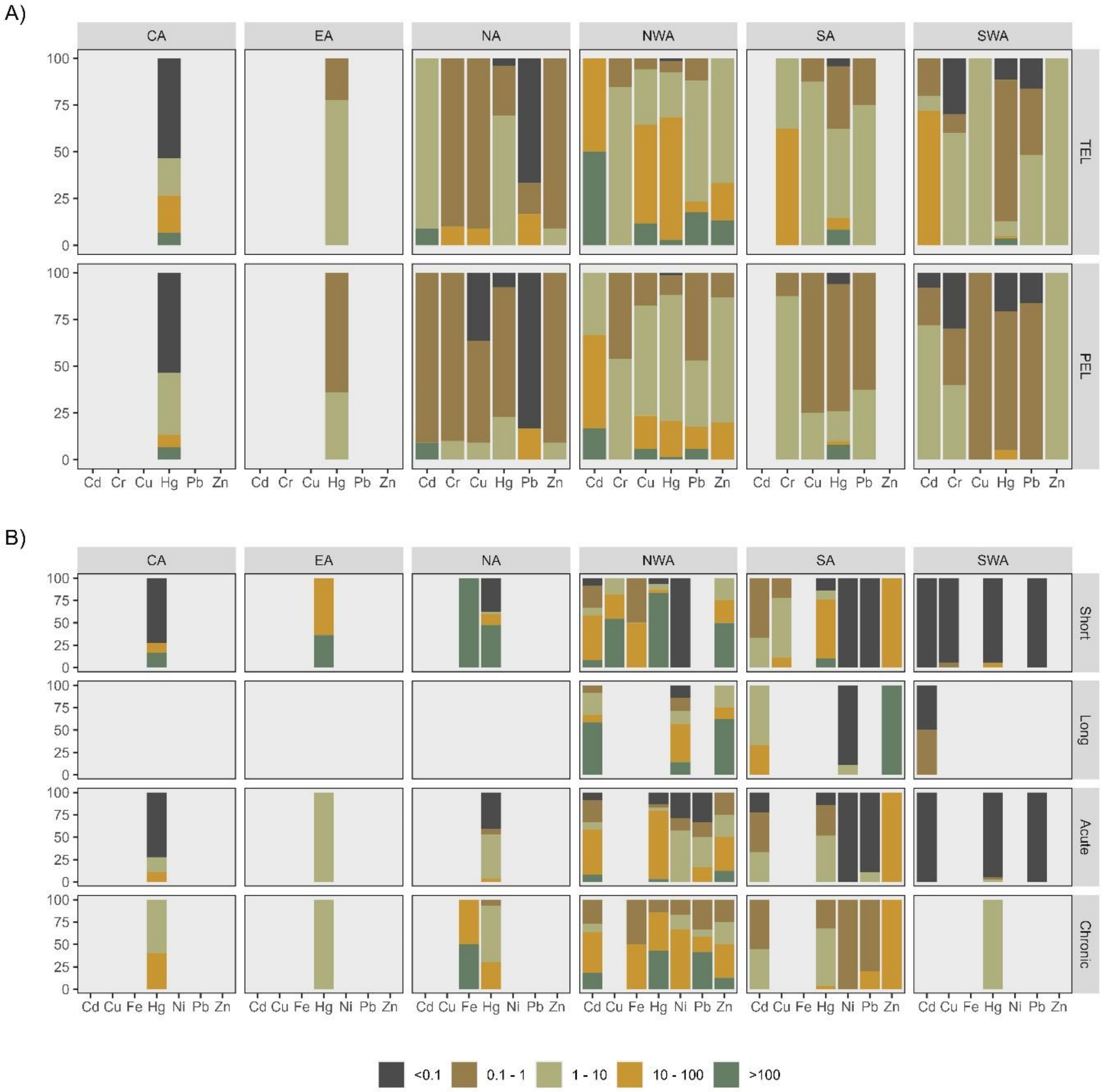

Figure 6. Hazard assessment for A) sediment and B) water samples in the different Amazon regions. The graphs display the percentage of samples that fall in each of the established hazard categories in relation to the toxicity thresholds determined for sediment (i.e., TEL and PEL values established by the Canadian Environmental Quality Guidelines; Long et al., (1995)), and water (i.e., short term and long-term exposure standards proposed by the Canadian Environmental Quality Guidelines; CCME (2002); and the acute and chronic standards set by the United States Environmental Protection Agency; US EPA, (1994)). Environmental hazards were classified as no hazard when the ratio between the measured concentration and the standard was < 0.1, potential hazard when the ratio was 0.1-1, moderate hazard when the ratio was 1-10, high hazard when the ratio was 10-100, and very high hazard when the ratio was >100. Empty bars indicate the absence of or less than five samples in the different regions. For

water samples, the absence of thresholds are also indicated by empty bars. The absences of thresholds correspond to short term exposure for Pb and Ni, long term exposure for Cu, Fe, Ni and Pb, acute exposure for Cu and Fe, and chronic exposure for Cu.

Discussion

Metal background levels

Based on our literature review we were able to determine metal background levels in all the Amazonian geographic regions for the metals As, Hg, Mn, Fe, Cd, Cu, Cr, Pb, Ni and Zn, for both water and sediment samples. NWA was the region where more sediment samples had been collected (57% of the total), followed by the CA region. NWA is formed by the dominant soil types Dystric Cambisols, Eutric Gleysols, and Haplic Acrisols, which contain clay-rich metals as compared to the other Amazon regions (Quesada et al., 2011). Indeed, fluvial sediments of many rivers flowing from NWA into the CA are metal-rich (Hoorn and Wesselingh, 2011; Quesada et al., 2011), as fluvial dynamics have intensively eroded local sediments, exposing metal-rich and high-clay geological formations (Rossetti et al., 2005; Ruokolainen et al., 2019). Intensive sampling in these regions could be related to accessibility (Carvalho et al 2023). For instance, in CA most of our data come from samples taken along the Negro and Solimões rivers, which are highly navigable. In NWA, most data come from Ecuadorian Amazonia and from the Acre state of Brazil, areas that are accessible by road. Therefore, knowledge gaps in less accessible areas still exist, and further sampling campaigns should prioritize those (Carvalho et al 2023).

Hg was the metal with the highest occurrence in sediment samples. About 41% of the total samples had been analyzed for Hg. Previous studies performed in the basins of the two largest Amazon tributaries, the Madeira and Negro rivers (both with river`s course mostly in CA), suggest that geochemical processes such as alluvial terrace deposit erosion and the accumulation of high Hg levels in superficial soil layers during the geological timescale may be responsible for naturally high Hg concentrations in soils and sediments (Lechler et al., 2000; Wasserman et al., 2007). In this regard, fluvial Amazon basin sediments have been found to contain considerable amounts of lithogenic Hg, ranging from 0.04 to 0.34 mg kg^{-1} (Lechler et al. 2000), which is in line with the values found in non-mining areas.

Regarding water samples, Mn was the metal with the highest occurrence. About 26% of the samples had determined Mn concentrations. This element is concentrated in lateral soils (ferricrete), which represent 80% of the Amazon basin. This element is abundant in floodplain areas (locally called *várzeas*) (Richey et al., 1989). A direct exchange of suspended sediments between floodplain areas and the main river takes place through entrainment and deposition processes, which control, at least partially, temporal Mn concentrations (Dunne et al., 1998).

Metal enrichment in mining areas

Mining activities are widespread through different regions of the Amazonian basin and range from small-scale artisanal gold mining along alluvial terraces to large industrial mining according to the mining possibilities of each region. By calculating background levels, we were able to provide information on metal enrichment in different geographic regions due to the presence of nearby mining activities. We acknowledge that the amount of data sources in each region may affect the calculation of background levels, as well as the metal enrichment assessment. For this reason, we applied a conservative approach and considered as clear metal enrichment only those samples that had concentrations above 100 times the calculated geomean for each region (i.e., the determined background level). Still, underestimations are possible concerning the number of samples presenting concentration values above such reference value, particularly since the distribution of monitoring campaigns in the Amazonian territory was not homogenous.

We found that metal concentrations in sediment and water collected next to mining areas exceeded background levels more than 100 times in all geographic regions. Amazonian sediments are characterized by having high concentrations of lithogenic metals (Lechler et al. 2000; de Oliveira et al. 2001). However, the sediment and water enrichment levels found here point at anthropogenic metal remobilization and river discharge from mining settings (Fadini and Jardim, 2001; Roulet et al., 1998).

Concerning sediment samples, about 5% of the samples presented Hg concentrations that denote clear enrichment, while clear metal enrichment in water samples was found in more than 50% of the samples taken in the NWA, CA and NA regions. Besides Hg, the NWA region showed enrichment by several metals in more than 85% of the samples. The western border of the Amazon basin has received eroded sediments from the Andes, which may also contain naturally high metal concentrations (Hoorn et al., 2010). However, significant metal enrichment has been found in this region for water and sediment, suggesting that it is one of the most impacted areas by mining activities. Concerning water samples, Hg concentrations at mining sites exceeded the mean background concentration in NWA, NA and CA. Mercury-dependent artisanal and small-scale mining is the most significant source of Hg pollution in the Amazon (Afrifa et al., 2019; Asner and Tupayachi, 2016; Esdaile and Chalker, 2018), and therefore the most likely cause of this contamination.

The high Hg enrichment in mining sites is explained by the indiscriminate use of Hg in the amalgamation process to concentrate and extract gold and silver from low-grade minerals (Lacerda et al., 1991; Veiga and Hinton, 2002), releasing this metal to the environment without any legal control whatsoever (Crespo-Lopez et al., 2021; Esdaile and Chalker, 2018; Maurice-Bourgoin et al., 2000). In efficient amalgamation processes, approximately 1 kg of Hg is used for every kg of gold. However, artisanal and small-scale mining 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, in fact, estimated to have released approximately 196,000 t of Hg into the environment between 1570 and 1900 (Strode et al., 2009). This type of mining may partly be responsible for the high fluxes of Hg in many parts of South America and the high background levels of this metal globally (Nriagu, 1994), as it can be transported hundreds of kilometers by rain or wind and can be easily concentrated and transformed to methylmercury by bacteria, increasing its toxicity, bioaccumulation capacity and food chain transfer (Crespo-Lopez et al., 2021). In Amazonia, artisanal and small-scale mining is responsible for emitting more than 200 metric tons of mercury annually, the equivalent to about 27% of global artisanal and small-scale mining emissions and 80% of total emissions in South America (Siqueira et al., 2018). However, mining and especially artisanal small-scale gold mining have increased significantly in recent decades in the entire Amazon basin (Teixeira et al., 2018).

Fe and Mn were present at the highest concentrations in both sediment and water from mining areas. These elements are abundant in Amazonian soils that correspond mainly to the family of red ferralitic soils (Bernoux et al., 2001; Quesada et al., 2011; Sombroek, 2000), whose mineralogy is dominated by quartz, Al and Fe oxides and kaolinite, interspersed with other minerals such as anatase and zircon (Seyler and Boaventura, 2003). However, especially in the NWA region, these metals exceeded the background values in mining areas by 100 times or more. Our results also indicate that the mean concentrations of Cd, Cu, Cr, Ni, Pb and Zn, in the sediment and in water from the mining sites exceed background mean values. Cd is mostly associated with the bioavailable fraction of the sediment of anthropic origin, and its presence in the environment is closely linked to mining activities (da Silva et al., 2002). The other metals could be enriched probably due to cassiterite extraction, which mobilizes metals from rocks and soils, with rain contributing to metal transport to rivers (Ribeiro et al., 2017), but also from gold mining (Capparelli et al. 2019). Therefore, just like Hg, the enrichment of Fe, Mn, Cd, Cu, Cr, Ni, Pb and Zn could be related to remobilization due to mining activities.

Although the number of samples with background information was small (less than five) to allow calculations of metal enrichment, the mean As concentration in sediment samples from the mining sites also exceeded the mean background value in the SWA region. The source material that most contributes to the occurrence of As in Amazon soils is arsenopyrite (FeAsS), present in metamorphic rocks and in different geological Amazon basin formations (Tallarico et al., 2000). Moreover, recent studies have argued that much of Hg is directly related to As concentrations (Barats et al., 2020), as high correlations between these metals suggest that they are derived from the same source. Mining companies do not use As in the Hg amalgamation process, but both As and Hg are commonly enriched in gold deposits. Therefore, further assessment of As concentrations could help to disentangle whether mining activities could be contributing to As enrichment in Amazonia (de Souza Neto et al. 2020).

Environmental hazard assessment

The results of this study show that mining areas constitute hot spots of metal contamination, with concentrations that exceed sediment and water standards set for the protection of aquatic life. All tested metals, regardless if they are considered essential or nonessential to biological systems, can cause damage to aquatic life by affecting the reproductive physiology of fish and invertebrates (Galarza et al., 2021), can cause adverse effects on the endocrine systems, such as liver necrosis (Viana et al., 2020), and can induce carcinogenicity and genotoxicity (Vasco-Viteri et al., 2023). In fact, several studies have denoted significant changes in the structure of aquatic invertebrate and fish communities in locations nearby mining areas in the Amazon (Caparelli et al. 2021; Azevedo-Santos et al. 2021). However, the individual toxicity of each of these metals to aquatic fauna and flora of the Amazonian basin has been seldom investigated. The most studied element has been Hg. Besides its potential direct toxicity, it has been investigated how the methylation process to form an organometallic complex (characteristic of stagnant waters) facilitates its biological uptake, contributing to its biomagnification in food chains of the Amazon region (Guimaraes et al. 2000; Achá et al. 2011). In fact, several studies have shown that methylmercury accumulates in detritivores and carnivorous fish of the Amazon (Rodríguez Martín-Doimeadios et al. 2014; Souza-Araujo et al. 2016), posing a potential hazard for large vertebrates and for the local population that consume them (Crespo-Lopez et al. 2021).

Our study shows that besides Hg, other metals that deserve immediate attention regarding their ecological hazards are Cu, Zn, Cd and Pb. It should be noted that such conclusions have been taken after the evaluation of measured environmental concentrations and environmental quality standards set for the protection of aquatic life in North America. The conditions of Amazonian freshwater ecosystems may be different to those representative of rivers of the North American region, with some rivers holding lower concentrations of free ions and extremely low pHs. Under such circumstances, metal complexation and speciation processes are expected to vary, thus potentially modifying their bioavailability and toxicity. For example, Duarte et al. (2009) found that the toxicity of Cu to fish species from the Amazon was two orders of magnitude lower under the ion-poor waters of the Negro River than under the standard medium recommended for toxicity tests. In a similar study, Holland et al. (2017) assessed the toxic effects of Ni in autochthonous fish species at concentrations characteristic of mining wastewaters and concluded that the differences in dissolved organic carbon (DOC) concentration among three of the most important Rivers of the Amazon (Negro, Solimoes, Tapajós) significantly affect its toxicity. The NWA region was the one showing the largest relative environmental threshold exceedances in our study. This region contains a varied range of water characteristics (including ion-poor waters with humic-like DOC); therefore, it is expected that the toxicity potential of such metals is somewhat underestimated in some of its areas when using the North American guidelines.

Metal contamination from mining activities is a widespread problem that affects ecosystems kilometers away from the emission source. Metal transport and accumulation in biota can affect human health and the food security of riverine populations (Da Silva et al. 2020; Galarza et al. 2023). The continued expansion of such (illegal) activities towards deeper areas of the Amazon is putting ecosystems as well as riverine and indigenous populations in peril (Crespo-Lopez et al. 2021). Therefore, continued monitoring of their activity as well as the metal concentrations in water, sediment, and biota of nearby locations is recommended. Moreover, trans-national research should focus on describing the actual establishment of mining locations in the Amazon basin, their impact zone, and the potential ecological and societal conflicts that may arise from them, particularly in protected areas.

Conclusions

The compiled evaluations of metal exposure in Amazonia are not uniformly distributed. The largest number of studies were carried out in the Brazilian Amazon, with evaluations focusing on Hg contamination in water and sediment samples. The number of studies was lower in the other countries that make up the Amazon basin, especially in the northern and southern peripheral areas. It is a matter of concern that information on metal contamination is still restricted to few areas, as several studies have revealed that artisanal and industrial mining activities are spreading towards less populated areas, with serious implications for the health of ecosystems and indigenous people. Our study shows that background metal concentrations differed among different regions depending on their geomorphological origin. It also suggests that mining activities are a major source of metal enrichment in water and sediment of the Amazon basin. Metal enrichment were particularly high in the NWA region. The NWA region was also the one showing the largest number of samples increasing the established environmental standards for water and sediment, with Cd, Pb, Zn, Cu and Hg posing the largest environmental hazards in sediment, and Hg, Fe, Cd, Cu, Pb, Ni and Zn in water. It should be noted, however, that the quality standards used in this study are based on North American rivers, which present significantly different physico-chemical characteristics as compared to the Amazonian rivers. Thus, the development of metal quality standards for the different regions of the Amazon basin, considering the background levels elucidated in this study and their bioavailability for aquatic life, is paramount for conducting refined risk assessment studies in the region.

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