Integrated Environmental Assessment and Management — Volume 19, Number 3—pp. 706–716

Received: 7 May 2022 | Revised: 30 August 2022 | Accepted: 10 October 2022

Special Series

Human health risk assessment of metals and metalloids in mining areas of the Northeast Andean foothills of the Ecuadorian Amazon

Emily Galarza,[1] *Gabriel M. Moulatlet,*[2] *Andreu Rico,*[3,4] *Marcela Cabrera,*[5] *Veronica Pinos-Velez,*[6,7] *Andrés Pérez-González,*[8] *and Mariana V. Capparelli*[9]

[1]*Facultad de Ciencias de La Tierra y Agua, Universidad Regional Amazónica Ikiam, Tena, Ecuador*
[2]*Red de Biología Evolutiva, Instituto de Ecología, A.C. INECOL, Xalapa, Veracruz, México*
[3]*IMDEA Water Institute, Science and Technology Campus of the University of Alcalá, Alcalá de Henares, Spain*
[4]*Cavanilles Institute of Biodiversity and Evolutionary Biology, University of Valencia, Paterna, Spain*
[5]*Laboratorio Nacional de Referencia Del Agua, Universidad Regional Amazónica Ikiam, Tena, Ecuador*
[6]*Departamento de Recursos Hídricos y Ciencias Ambientales, Facultad de Ciencias Químicas, Universidad de Cuenca, Cuenca, Ecuador*
[7]*Departamento de Biociencias, Facultad de Ciencias Químicas, Universidad de Cuenca, Cuenca, Ecuador*
[8]*Grupo de Investigación en Quimiometría y QSAR, Facultad de Ciencia y Tecnología, Universidad del Azuay, Cuenca, Ecuador*
[9]*Instituto de Ciencias del Mar y Limnología-Estación El Carmen, Universidad Nacional Autónoma de México, Ciudad del Carmen, México*

EDITOR'S NOTE:

This article is part of the special series "Diversity of Knowledge for a Sustainable Future in Latin America" and highlights timely research presented at the virtual SETAC Latin America 14th Biennial Meeting (2021). These articles reflect the urgent need to combine different knowledge sources and expertise to face current environmental challenges, decision-making, and problem solving. Risk, recovery, restoration, modeling, regulations, anthropic impact, and human health are some of the global environmental issues covered in this special series.

Abstract

Gold mining (GM) is a major source of metals and metalloids in rivers, causing severe environmental pollution and increasing the exposure risks to the residents of surrounding areas. Mining in Ecuadorian Amazonia has dramatically increased in recent years, but its impacts on Indigenous local populations that make use of rivers are still unknown. The aim of this study was to assess the risks to adults and children caused by the exposure to metals and metalloids in freshwater ecosystems contaminated with tailings released by GM activities in 11 sites of the upper Napo River basin, Ecuador. We selected a carcinogenic and a noncarcinogenic risk assessment method to estimate the hazard index (HI) and total cancer risk (TCR). The concentration of Ag, Al, As, Cd, Cu, Fe, Mn, Pb, Zn, B, and V in water and sediment samples was considered to assess the risks to human health. The calculated HI was 23–352 times greater than the acceptable limits in all sites for both children and adults. Mn and Fe were the main contributors (75% in water and 99% in sediment) to the total calculated risk based on the HI. The calculated TCR for children and adults exceeded approximately one to three times the permissible threshold in all sites. As and Pb contributed up to 93% of the total calculated risk based on TCR for both children and adults. This study demonstrates that the emission and mobilization of metals and metalloids caused by mining activities increase the risk to human health, to which we recommend further monitoring of freshwater contamination in the area and the implementation of preventive health management measures. *Integr Environ Assess Manag* 2023;19:706–716. © 2022 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Carcinogenic and noncarcinogenic; freshwater ecosystems; human health risk assessment; metals and metalloids; Napo province

This article contains online-only Supporting Information.
Address correspondence to marivcap@gmail.com
Published 14 October 2022 on wileyonlinelibrary.com/journal/ieam.

INTRODUCTION

Gold mining (GM) has historically affected riverine areas of the Amazon basin (Pan et al., 2018; Rehman et al., 2020; Saha et al., 2017). Intensive gold exploitation results in land-use modifications (Guzmán-Martínez et al., 2020), causes freshwater contamination (Capparelli et al., 2020, 2021), and endangers human health (Teixeira et al., 2021). In the eastern Andes of Ecuador, at the transitions with Amazonia lowland, concessioned and illegal GM have caused severe environmental pollution problems (Galarza et al., 2021) and negative social impacts (Guayasamin et al., 2021). New GM concessions were awarded in the Napo province during the previous decade (Roy et al., 2018). Although artisanal small-scale GM (mining without heavy machinery and granted to small companies or local communities) is the most common authorized concession, industrial GM accounts for 98% of the total territory for gold exploitation in the Napo province (33 718 ha). Nevertheless, illegal GM in Amazonia has increased sharply in recent years (Mestanza-Ramón et al., 2022a). Given the proliferation of mining concessions, and the substantial increase in illegal mining activities (Mestanza-Ramón et al., 2022b), gathering information on the risks to human health caused by this activity is crucial.

Metals and metalloids are commonly released as by-products of GM and are persistent compounds with a high bioaccumulative capacity (Saha et al., 2017). They can cause neurotoxic and carcinogenic effects in humans when inhaled, ingested, or through dermal contact (Guzmán-Martínez et al., 2020; Ogola et al., 2002; Wang et al., 2014; Zheng et al., 2020). The toxic effects of the exposure to metals and metalloids have been widely reported using human health risk assessment (HHRA) methods (Li et al., 2013, 2018; Sun et al., 2018). Human health risk assessments can be used to identify metals and metalloids that pose major human health hazards as well as to determine areas that require management and intervention (Castresana et al., 2019; Huang et al., 2018; Singh et al., 2019). In addition, HHRAs in mining areas may indicate whether residents are at risk caused by exposure to PTEs through multiple exposure routes and whether children have greater or less vulnerability than adults based on different exposure routes and their common behavior (Marrugo-Negrete et al., 2020; Rashid et al., 2019).

Artisanal and small-scale GM in the Ecuadorian Amazon is carried out on river margins and in small streams because gold deposits are often concentrated in the alluvial terraces. As a consequence of GM, concentrations of metals and metalloids greater than established environmental thresholds have been detected in rivers of the southern provinces of Sucumbios and Orellana (Carrillo et al., 2021; Escobar-Segovia et al., 2021; Rivera-Parra et al., 2021). In the Napo province, studies carried out in areas affected by GM have also detected metals and metalloids in environmental concentrations exceeding quality standards for both water and sediment (Capparelli et al., 2020, 2021; Galarza et al., 2021). Based on the dataset of Capparelli et al. (2020), the HHRA made by Jiménez-Oyola et al. (2021) suggests that local populations in the Napo province are at risk through contact with multiple exposure routes (i.e., mining, urban pollution, fish farming, and lixiviate from dumping areas). However, no study has been dedicated to applying HHRAs exclusively to mining activities in this area. Given that GM has intensified, an HHRA using solely data from mining areas would help to understand the risks caused by metals and metalloids to local Indigenous populations inhabiting areas near GM exploitation. Thus, our study aims to assess the carcinogenic and noncarcinogenic risks posed by the exposure to metals and metalloids through water and sediment in GM areas of the Napo province of Ecuador.

METHODOLOGY

Study area

This study was carried out in the tributaries of the Anzu, Jatunyacu, and Napo rivers in the Napo province in northern Ecuadorian Amazonia. This area is a geodiversity hot spot because of the diverse content of high-value minerals in alluvial deposits. Important local urban centers are Puerto Napo, Misahualli, Ahuano, and Carlos Julio Arosemena Tola (Figure 1). More than half of the 18 200 inhabitants are self-identified as Indigenous people, distributed in either urban or rural areas (INEC, 2010). The region is characterized by annual precipitation greater than 4000 mm and by the presence of an extensive hydrographic network.

Sampling collection and analyses

Data on metal and metalloids concentration in surface water and sediments were obtained from Capparelli et al. (2021). The water samples were collected at the center of the stream at mid-depth (according to the possibilities of each stream), and superficial sediment samples were collected at the riverbank at a depth of 15 cm. Samples were taken from 11 sites downstream from GM areas located within or right at the limits of the federal mining concessions. From the 44 compounds analyzed in Capparelli et al. (2021), we selected 12 (Ag, Al, As, B, Ba, Cd, Cu, Fe, Mn, Pb, V, and Zn) because of their potential toxicity to human health. Nine of these compounds (Ag, Al, As, Cd, Cu, Fe, Mn, Pb, and Zn) exceeded national or international regulatory standards for water and two (B and V) for sediments (Tables 1 and 2).

Human health risk assessment

The exposure pathways included in the HHRA were water ingestion, dermal contact via water, and dermal contact via sediment, based on the sum of the risk across all metals and metalloids in each site following the methodology described by Lee et al. (2005). For the HHRA calculations, we estimated the chronic daily intake (CDI) according to the proposed USEPA (2004) equations. The parameter values used in the exposure assessment are presented in Table 3.

Carcinogenic and noncarcinogenic risks

Clinical and epidemiological studies have related metals and metalloids with increased cancer risk and/or mortality caused by poisoning in human populations exposed to those substances (Cao et al., 2010; Dooyema et al., 2012). Noncarcinogenic risks were calculated using hazard quotients (HQs) measured for each metal and

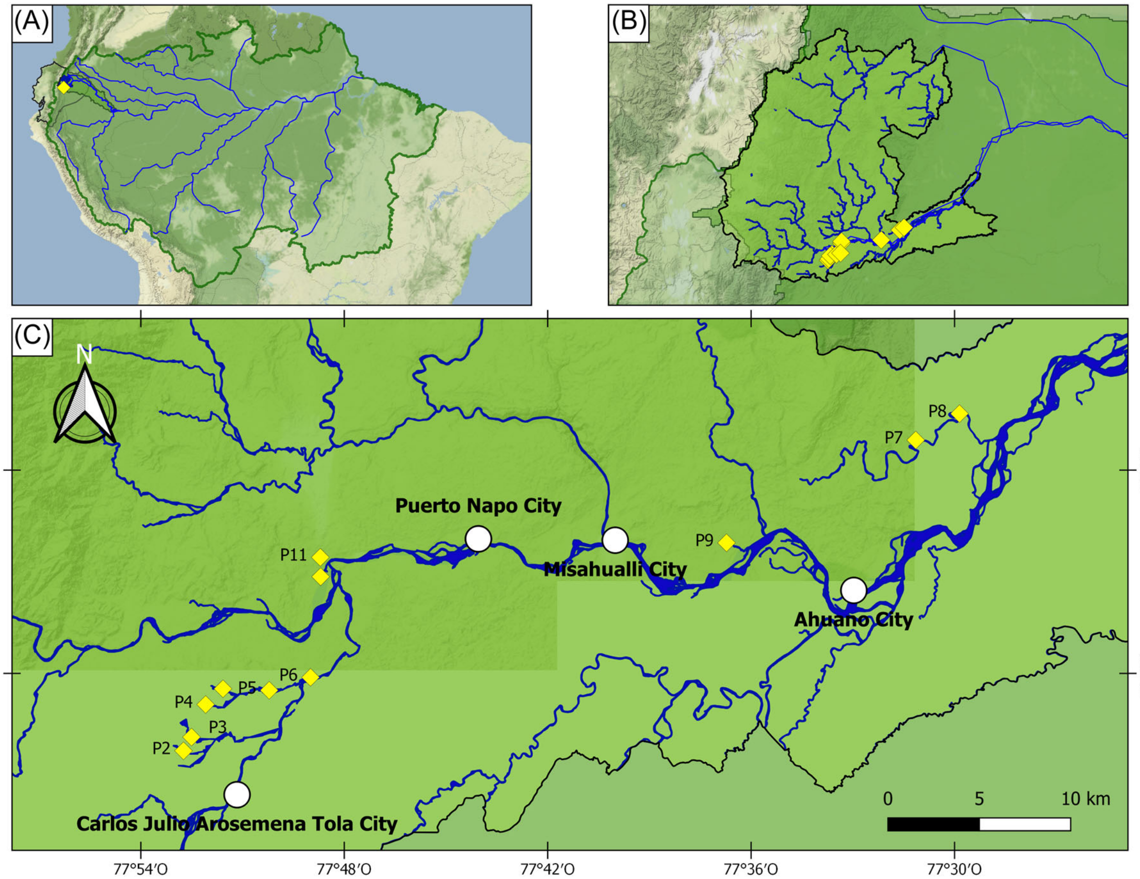

FIGURE 1 (A) Study area in the Amazon basin. (B) Napo province of Ecuador, and (C) location of the sampling sites along rivers (yellow diamonds). The 11 sites are located along rivers directly affected by medium- to industrial-scale gold mining

metalloid (Table 4, Equations 5 and 6). The human health HQs for noncarcinogenic risk were characterized by a threshold dose of toxicity, which is expressed by the reference dose (RfD). The RfD values are different for each metal and metalloid, and they were obtained from the Risk Assessment Information System (RAIS) website (https://rais.ornl.gov; Supporting Information: Table S1). Then, the cumulative hazard index (HI) was calculated by the sum of all calculated HQs (Table 4, Equation 7). Hazard index values lower than 1 indicated the absence of risk, and HI values greater than 1 indicated risk (USEPA, 2001).

As there is no toxicological threshold for carcinogenic substances, the total carcinogenic risk (TCR) for each site was calculated as the sum of the carcinogenic risk (CR) values for water ingestion multiplied by the cancer slope factor (CSF) of all metals and metalloids found in the same site (Table 4, Equations 7 and 8). CSF values were available only for the PTEs As, B, Cd, and Pb in the RAIS (Supporting Information: Table S1). Then, TRC values were compared with the permissible reference values (USEPA, 2001). We decided to use a single model for each element, avoiding the use of metal-specific models in order to obtain results comparable with previously published studies (Covre et al., 2021; E. S. de Souza et al., 2017). Calculated TCR values greater than 1×10^{-4} were considered to pose unacceptable risks (with high certainty), whereas values lower than 1×10^{-6} were considered to pose insignificant risks (with high certainty), and values ranging between 1×10^{-4} and 1×10^{-6} were considered to pose potential risks (Fryer et al., 2006; Hu et al., 2012).

RESULTS

Human health risk assessment

Overall, the HHRA indicated toxicological risks to human health in all sites. The HI exceeded the permissible thresholds for children and adults to be considered noncarcinogenic risk in all sites by at least one- to threefold. The HI values for children and adults were ranked as: P6 > P9 > P10 > P2 > P11 > P5 > P4 > P3 > P1 > P7 > P8. The P6 site had the highest value exceeding the permissible limit for both children and adults, 352 and 154, respectively (Supporting Information: Table S6), and they would experience the highest noncarcinogenic effects caused by exposure to metals and metalloids at this site. The P8 site had the lowest value for both children and adults, whereas the

TABLE 1 PTE concentrations in water and sediments used for the calculation of the HHRA

Source	Metals	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11
Water	Ag*	0.19	0.04	0.34	0.04	0.10	0.04	0.1	0.84	0.04	0.07	0.07
	Al*	158	133	288	93	231	378	147	253	249	350	406
	As*	2.2	1.7	6.7	1.4	2.3	1.8	3.4	2.8	2.7	5.7	3.7
	B	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	9.7	4.0
	Ba	345	32	113	60	154	817	46	61	223	938	339
	Cd*	0.49	0.73	0.18	0.19	0.17	0.43	0.18	0.78	0.35	0.46	0.27
	Cu*	24	6.0	12	6.4	8.0	11	5.6	11	11	9.4	8.4
	Fe*	373	229	558	227	326	237	513	548	536	371	309
	Mn*	456	14	153	105	275	486	49	74	513	598	259
	Pb*	6.1	10	5.7	0.7	2.4	14	1.7	1.7	2.4	4.4	5.5
	V	8.4	6.5	21	6.7	11	12	9.7	9.7	13	16	24
	Zn*	88	30	43	9.3	23	144	19	51	50	31	23
Sediment	Ag	0.01	0.03	0.03	0.02	0.02	1.2	0.02	0.01	0.03	0.02	0.03
	As	0.71	2.0	1.0	1.7	1.8	3.6	1.3	0.8	1.6	2.0	1.7
	B*	2.1	0.0	1.1	0.5	0.5	1.8	2.6	1.3	0.5	2.0	0.6
	Ba	33	37	56	76	74	137	66	18	135	113	90
	Cd	0.01	0.01	0.01	0.02	0.02	0.04	0.02	0.02	0.03	0.03	0.02
	Cu	3.4	4.4	4.1	7.1	6.9	10.6	3.7	1.3	5.4	5.2	4.0
	Fe	3447	11 155	5898	6071	7470	17 035	5654	2123	11 910	9956	7921
	Mn	126	368	140	225	318	632	179	68	459	438	370
	Pb	0.38	1.2	0.86	1.0	1.2	2.2	1.0	0.34	1.1	1.2	1.0
	V*	16	66	22	31	42	107	19	8.1	81	31	23
	Zn	6.1	11	6.8	11	12	21	9.5	3.5	15	10	8.2

Notes: Data were retrieved from Capparelli et al. (2021). Elements that exceed regulatory standards determined by the Ecuadorian (TULSMA) or the Canadian Environmental legislation (CCME) are indicated with an asterisk.
Abbreviation: HHRA, human health risk assessment.

risk to children was double that for adults (55 and 24, respectively). Higher HI values were obtained for children than for adults in all sites, meaning that children are more susceptible to toxicological risks due to water ingestion and water and sediment dermal contact (Figure 2A).

The TCR values for children and adults were ranked as: P3 > P10 > P11 > P6 > P2 > P7 > P1 > P8 > P9 > P5 > P4. Sites P3, P10, and P11 had the highest values for both children and adults, exceeding by almost three times the limit to be considered a risk, 1×10^{-6}, whereas P4 had the lowest risk value (Supporting Information: Table S6). However, none of the TCR values exceeded the threshold value of 1×10^{-4}, above which unacceptable risks are expected with high certainty. According to our calculations, children were more susceptible to cancer risks than adults at all sites (Figure 2B). The spatial distribution of HI and TCR across the study area is shown in Figure 3. Overall, the sites located in the western part of the study area had higher HI and TCR values than the eastern parts.

The presence of Mn and Fe in water and sediments contributed more than 75% and 99%, respectively, to the HI (Figure 4A,B). In almost all sites, the contribution of Mn to the HI in water was greater than 60% for children and adults; whereas in sites P7 and P8 the contributions of Mn and Fe were very similar, approximately 40% each. As for sediments, Fe contributed up to 71% to the HI for children and adults. The HI results suggested that, for both adults and children, the HI risk for Mn and Fe from sediment dermal contact was the primary exposure pathway (Figure 4A,B; Supporting Information: Tables S2, S3, S7). Regarding the TCR, in both adults and children, the exposure to As and Pb contributed up to 93%. Total cancer risk indicated that the primary pathway of exposure was derived from water ingestion (Figure 4C,D; Supporting Information: Tables S4).

 DOI: 10.1002/ieam.4698

TABLE 2 Exposure assessment equations by exposure pathways

Exposure pathways	Equations	
Water ingestion	$CDI_{Ing\ w} = \frac{C_W \times EF \times ET \times IR_W \times ED}{AT \times BW} \times CF$	(1)
Dermal contact water	$CDI_{derm\ w} = \frac{C_W \times EF \times ET \times ED \times SA \times K_p}{AT \times BW} \times CF$	(2)
Dermal contact sediment	$CDI_{derm\ s} = \frac{C_S \times EF \times ET \times SA \times AF \times ABS}{AT \times BW} \times CF$	(3)

Note: The exposure factors considered in the CDI are described in Table 3 (USEPA, 2011).
Abbreviations: ABS, dermal absorption factor; AF, adherence factor; AT, averaging time; BW, body weight; CDI, chronic daily intake; CF, conversion factor; ED, exposure duration; EF, exposure frequency; ET, exposure time; K_p, permeability constant; SA, skin surface area.

DISCUSSION

Potential impacts of PTEs on human health

This study was motivated by the high levels of metals and metalloids reported in the Napo province by Capparelli et al. (2021) and the concern these authors raised for the health of local freshwater ecosystems and Indigenous populations. The study suggests chronic toxicological risks in all sites evaluated and potential carcinogenic risks in most of the sites. Similar findings were reported by Castilhos et al. (2015) and E. S. de Souza et al. (2017) in GM areas of the Brazilian Amazonia. In our study, the maximum HI was up to 352 times greater than the established threshold for children and 153 times greater for adults. The TCR for adults and children was approximately three times greater than the established threshold for risk. The calculated TCR's highest values were for water ingestion for daily activities such as drinking, cooking, and human hygiene, corroborating the results of Jiménez-Oyola et al. (2021).

The elevated TRC was caused by the high concentration of As and Pb in the water. Our results are in line with those of Carvalho l Ferreira et al. (2016), who also reported elevated HI and TCR values in areas that had been affected by mining tailings in Portugal. In both cases, As exposure was related to incidental ingestion of water. Chronic and acute As toxicities have been associated with negative health effects (Chen et al., 2019), and high concentrations of As in areas close to mining sites may expose human populations to an endemic contamination risk (Souza Neto et al., 2020). Exposure to Pb is of great concern because between 8% and 57% of total Pb exposure is associated with drinking water. The risk of the exposure to Pb has been reported before (Jennings & Duncan, 2017). Regarding Cd, the high concentration of this metal has been linked to diarrhea, dermatitis, allergy, asthma, cancers, and other dysfunctions (Fallahzadeh et al., 2018; Satarug & Moore, 2004).

Human populations that are in constant contact with the above-mentioned metals are at elevated risk of developing acute and chronic diseases caused by long-term exposure. Additionally, given the high contribution of As, Cd, Pb, and Cr to the HI and TCR, local people should be informed and protected from exposure to contaminated water and sediments. Therefore, we advocate the provision of alternative water sources, the incentivizing of information campaigns, the facilitation of medical care, and the monitoring of the food chain supply, because metals can be easily transferred to edible plant parts (Gerson et al., 2021; Romero-Estévez et al., 2019), to invertebrates (Capparelli et al., 2021), and to

TABLE 3 Parameters used for the health risk estimations via consumption of water and dermal contact of water and sediments for children and adults, given by the USEPA (2011)

Parameters	Units	Children (C)	Adults (A)
PTE concentration in water (w) or sediment (s), C	µg/L	Table 1	Table 1
Permeability constant, K_p	cm/h	Supporting Information: Table S1	Supporting Information: Table S1
Exposure frequency, EF	Day/year	350	350
Exposure duration, ED	Year	6	24
Exposure time, ET	h/event	0.58	0.58
Skin surface area (swimming), SA	cm²	2800	5700
Body weight, BW	kg	15	70
Ingestion rate of water, IR w	L/event	2	2
Averaging time noncarcinogen, AT nc	Day	2190	8760
Averaging time carcinogen, AT c	Day	25 550	25 550
Adherence factor, AF	mg/cm²	0.2	0.07
Dermal absorption factor, ABS	Unit-less	0.03	0.03
Conversion factor, CF	Dimensionless	1×10^{-6}	1×10^{-6}

TABLE 4 Equations to determine the HQ for each metal and metalloid, the cumulative HI, and the potential CR

	Equations	
HQ for ingestion	$HQ_{ing} = \frac{CDI_{ing\,w}}{RfD_{oral}}$	(4)
HQ for dermal contact	$HQ_{derm} = \frac{CDI_{derm}}{RfD_{derm}}$	(5)
HI	$HI = \sum HQ = HQ_{ing} + HQ_{derm}$	(6)
CR	$CR_{ing} = CDI_{ing} \times CSF_{oral}$	(7)
TCR	$TCR = \sum CR_{ing}$	(8)

Abbreviations: CDI, chronic daily intake; CR, carcinogenic risk; HI, hazard index; HQ, hazard quotient; RfD, reference of dose; TCR, total cancer risk.

fish (Benefice et al., 2010; Lima et al., 2022) along the food chain.

Sampling sites located at the outlets of the downstream basin (sites P6, P9, P10, and P11; Figure 3) had HIs and TCRs limits greater than the threshold for both adults and children. Human settlements are frequently located a short distance from river meanders, floodplains, and basin outlets, where washed mining sediments and mining tailings are immediately transported and deposited. For instance, sites P6 and P11 are located less than 1 km away from approximately 50 Indigenous communities that depend on rivers to obtain water for daily use. Moreover, the intensive flood regimes in the upper Napo basin rivers can lead to the storage of contaminated sediments along riverbanks near human settlements (Appleton et al., 2001; Lucas-Solis et al., 2021). The

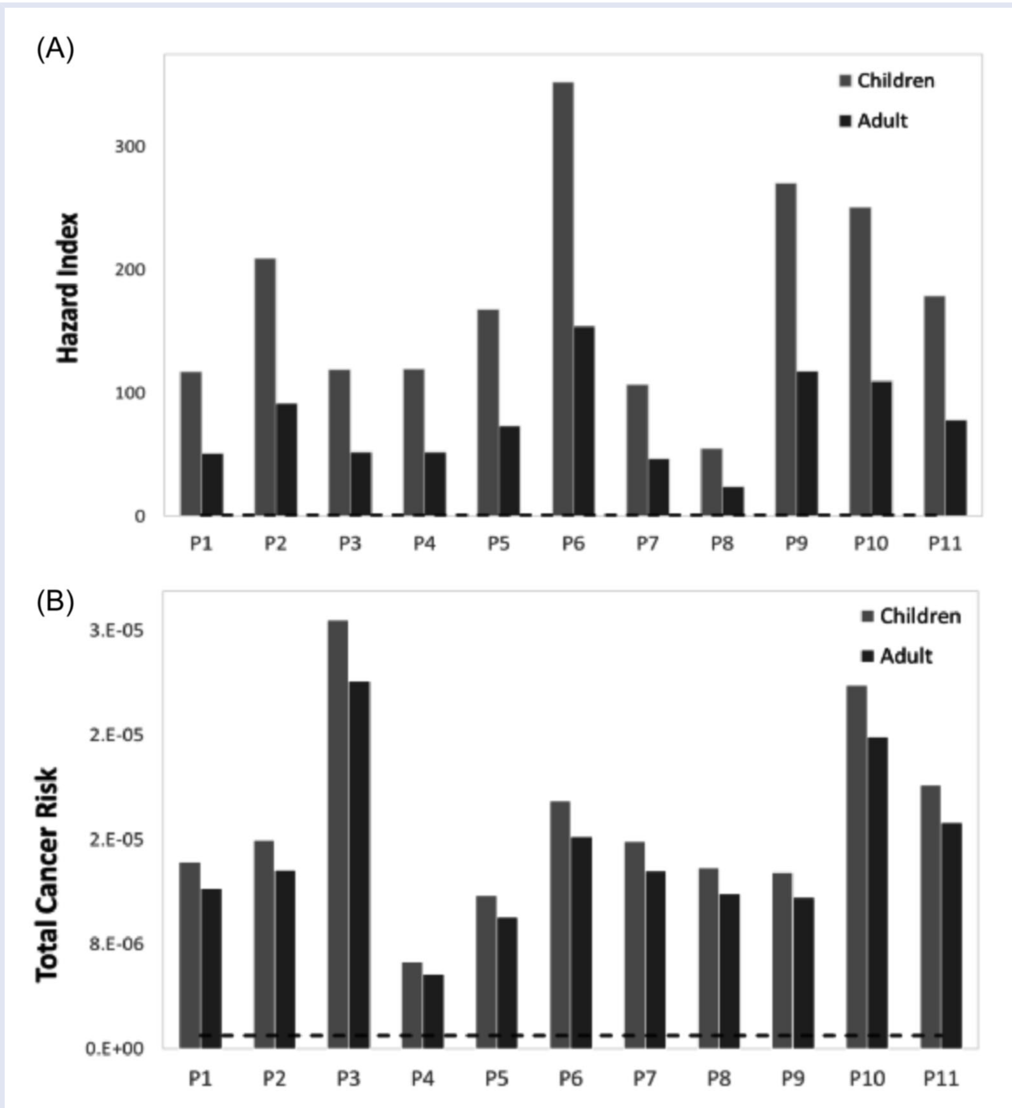

FIGURE 2 Results of the human health risk assessment (HHRA) for children and adults in each site. (A) Cumulative hazard index (HI); the horizontal line indicates the threshold value of 1, above which risks are expected. (B) Total cancer risk (TCR); the horizontal line indicates the limit established of 1×10^{-6}, above which carcinogenic risks may be expected (USEPA, 2001)

 DOI: 10.1002/ieam.4698

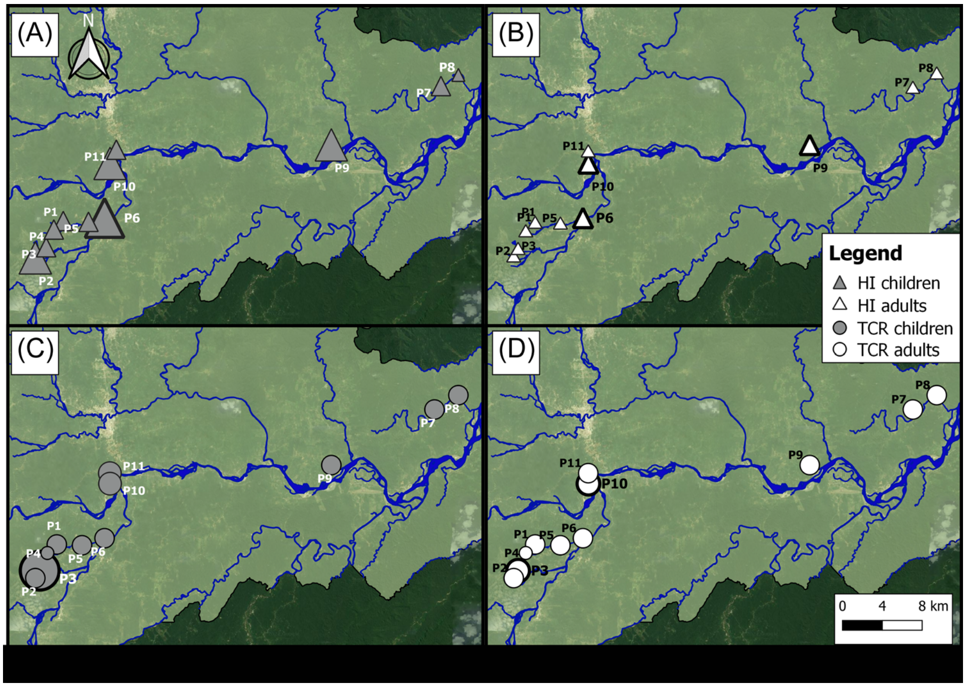

FIGURE 3 Spatial distribution of the hazard index (HI) values for (A) children and (B) adults and of the total carcinogenic risk (TCR) for (C) children and (D) adults. Symbol size represents the relative magnitude of either HI or TCR in sites where these indexes exceed permissible limits

degree of contamination of both water and sediments (Capparelli et al. 2021) and the HI and TCR calculated for these sites suggest that it might be possible that local communities have been consuming water with metal and metalloid levels greater than the recommended for a relatively long time. Thus, further examination of the temporal and spatial extensions of contamination and their impacts on the health of local Indigenous communities is recommended.

Perspectives on an Ecuadorian Amazonian scenario

Human health risk assessments are crucial to the design of further monitoring campaigns and to the establishment of corrective actions to areas affected by mining (De Miguel et al., 2014). Here, we based our HHRA estimates on the framework established by the USEPA, which includes a set of predefined exposure equations and parameter values. The calculation of risks to children and adults via water and sediment exposure was based on an exposure frequency of 350 (a value often used in other studies for Amazonian regions; Covre et al., 2021; J. J. de Souza et al., 2018) days per year, older than 6 years (for children) or 24 years (for adults; Table 3). However, contact with the aquatic ecosystem of Indigenous communities is expected to be greater than this, which could increase the risk of developing diseases related to metal and metalloid skin contact. Further research should be dedicated to refining the risk calculations by collecting a larger number of environmental samples for the critical elements defined in this study, adjusting water and sediment exposure calculations based on data that represent the habits of the Indigenous population of the Ecuadorian Amazonia.

The interaction of Amazonian communities with the rivers is the basis of their livelihood and cultural activities. If unable to use the river, these communities are forced to rely solely on accumulated rainwater for their daily needs. However, this is not enough for all the necessities, so the communities will still have to use river water for crop irrigation and watering cattle.

Because of the risk of cancer caused by the exposure to metals and metalloids, long-term strategic policies for reducing the exposure of local inhabitants are needed, as metal contamination can persist for decades in the ecosystem. The current policies of the Ecuadorian government aim to facilitate the legal mechanisms that allow mining concessions and other economic activities near or inside protected areas and Indigenous lands (Guayasamin et al., 2021). These policies are responsible for the highest rate of deforestation in the past 10 years, weakening the environmental protection legislation and human rights of traditional and Indigenous populations (Roy et al., 2018). With proper regulation, GM might represent economic gains to the country. However, it may harm the health of the communities and generate environmental problems (Mainville et al., 2006). In the past two years and during the COVID-19 pandemic, both legal and illegal mining activity has increased in Ecuador after the rise in the international price of gold (Mestanza-Ramón et al., 2022b). The data presented here were obtained in 2021, before the last expansion phase of GM activities in the upper Napo River basin. This study suggests that the human health risks were unacceptable before the mining increase in the

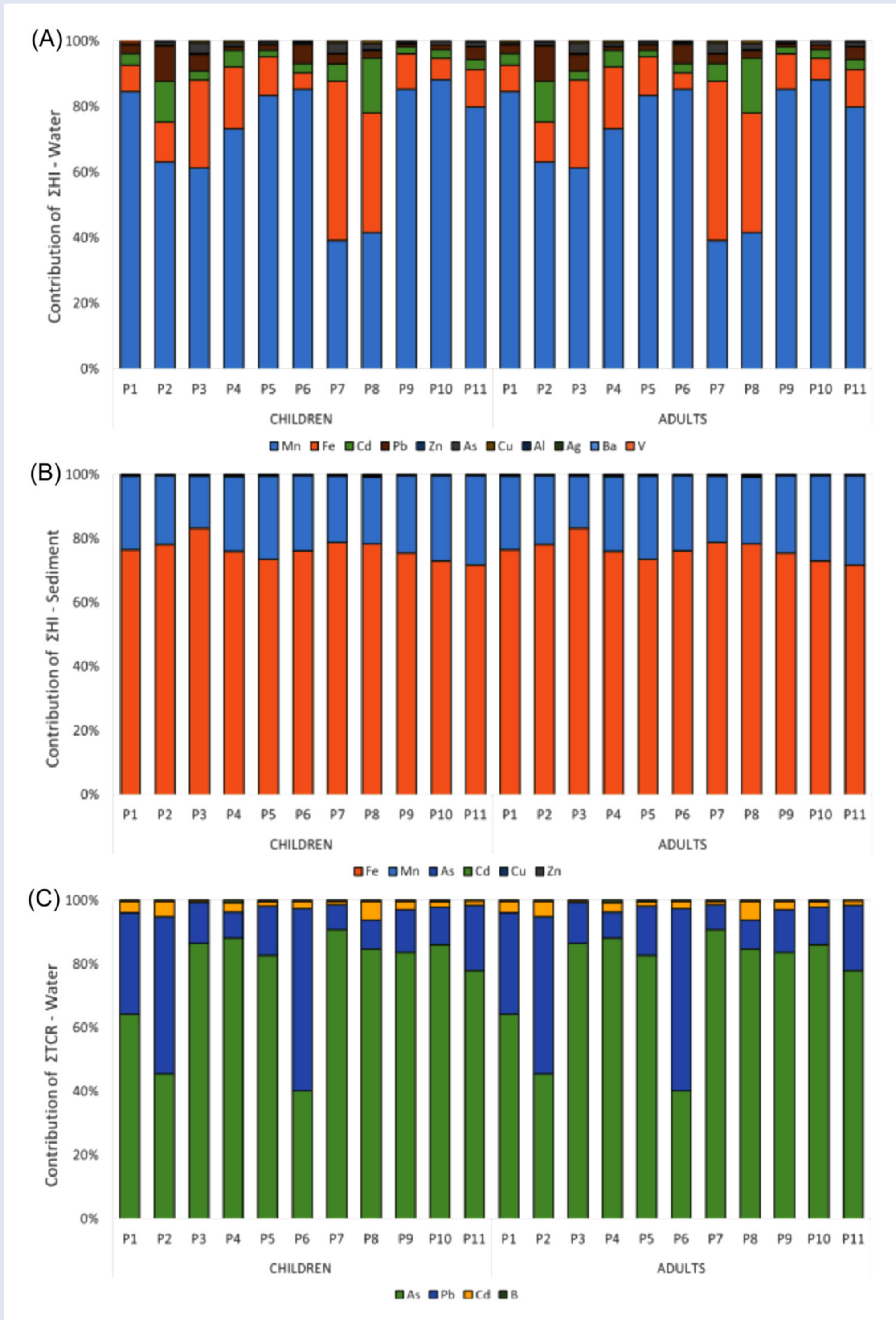

FIGURE 4 Contribution of each metal to the calculated hazard index (HI) in (A) water and (B) sediment. (C) Contribution of each metal to the total cancer risk (TCR) in water

region and calls for continued monitoring of metal and metalloid exposure and risk in the study region.

CONCLUSIONS

This study demonstrates that water and sediment exposure to metals and metalloids in the northeast Andean foothills of the Ecuadorian Amazon is greater than the established thresholds for producing carcinogenic and noncarcinogenic risks to the local population despite using exposure parameters that may slightly underestimate risk. Spatial analysis reveals that the rivers located at the end of the river basins (P2, P3, P6, P9, P10) are the most contaminated and, therefore, pose the greatest risk to the health of local communities. Although total concentrations of metals and metalloids can be used to quantify health risks, it is also advisable to assess bioavailable concentrations to obtain more reliable results. Policies to reduce exposure are necessary to avoid harmful effects on the health of local populations and should be accompanied by epidemiological studies to identify the occurrence of diseases associated with heavy metals(loids) through different exposure routes, that is, the consumption of contaminated water and food.

ACKNOWLEDGMENTS

This investigation received financial support from the European Union in coordination with the Spanish Cooperation International Agency for Development (AECID), granted to M. V. C., and A. R. A. R. acknowledges the Ramon y Cajal grant provided by the Spanish Ministry of Science and Innovation (RYC2019-028132-I). G. M. M. acknowledges the postdoctoral grant from the Project SEP-CONACYT CB-2017-2018 (#A1-S-34563).

AUTHOR CONTRIBUTIONS

Emily Galarza: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Resources; Software; Validation; Visualization; Writing—original draft; Writing—review and editing. **Gabriel M. Moulatlet**: Investigation; Validation; Visualization; Writing—original draft; Writing—review and editing. **Andreu Rico**: Conceptualization; Funding acquisition; Investigation; Validation; Writing—original draft; Writing—review and editing. **Marcela Cabrera**: Methodology; Validation; Visualization; Writing—original draft; Writing—review and editing. **Veronica Pinos-Velez**: Investigation; Validation; Visualization; Writing—original draft; Writing—review and editing. **Andrés Pérez-González**: Methodology; Validation. **Mariana V. Capparelli**: Conceptualization; Funding acquisition; Investigation; Methodology; Project administration; Supervision; Validation; Visualization; Writing—original draft; Writing—review and editing.

DATA AVAILABILITY STATEMENT

Data, associated metadata, and calculation tools are available from corresponding author Mariana V. Capparelli (marivcap@gmail.com).

SUPPORTING INFORMATION

Table S1. Reference doses (oral and dermal), cancer slope factor and permeability constant for some metals. NA, not available at the time of the study.

Table S2. Total hazard quotient (HQ) and hazard index (HI) in water for children and adults.

Table S3. Total hazard quotient (HQ) and hazard index (HI) in sediment for children and adults.

Table S4. Carcinogenic risk (CR) in water for children and adults.

Table S5. Cumulative hazard index (HI) and total cancer risk (TCR) to children and adults from all metals in each site classification by children and adults.

Table S6. Contribution of exposure pathways for children and adults by each site to each exposure assessment.

ORCID

Mariana V. Capparelli http://orcid.org/0000-0002-7517-7623

REFERENCES

Appleton, J., Williams, T., Orbea, H., & Carrasco, M. (2001). Fluvial contamination associated with Artisanal Gold Mining in the Ponce Enríquez, Portovelo-Zaruma and Nambija Areas, Ecuador. *Water, Air, and Soil Pollution*, *131*(1/4), 19–39. https://doi.org/10.1023/a:1011965430757

Benefice, E., Luna-Monrroy, S., & Lopez-Rodriguez, R. (2010). Fishing activity, health characteristics and mercury exposure of Amerindian women living alongside the Beni River (Amazonian Bolivia). *International Journal of Hygiene and Environmental Health*, *213*(6), 458–464.

Cao, H., Chen, J., Zhang, J., Zhang, H., Qiao, L., & Men, Y. (2010). Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. *Journal of Environmental Sciences*, *22*(11), 1792–1799. https://doi.org/10.1016/S1001-0742(09)60321-1

Capparelli, M. V., Cabrera, M., Rico, A., Lucas-Solis, O., Alvear-S, D., Vasco, S., Galarza, E., Shiguango, L., Pinos-Velez, V., Pérez-González, A., Espinosa, R., & M. Moulatlet, G. (2021). An integrative approach to assess the environmental impacts of gold mining contamination in the Amazon. *Toxics*, *9*(7), 149.

Capparelli, M. V., Moulatlet, G. M., Abessa, D., Lucas-Solis, O., Rosero, B., Galarza, E., Tuba, D., Carpintero, N., Ochoa-Herrera, V., & Cipriani-Avila, I. (2020). An integrative approach to identify the impacts of multiple metal contamination sources on the Eastern Andean foothills of the Ecuadorian Amazonia. *Science of the Total Environment*, *709*, 136088. https://doi.org/10.1016/j.scitotenv.2019.136088

Carrillo, K., Drouet, J., Rodríguez-Romero, A., Tovar-Sánchez, A., Ruiz-Gutiérrez, G., & Viguri Fuente, J. (2021). Spatial distribution and level of contamination of potentially toxic elements in sediments and soils of a biological reserve wetland, northern Amazon region of Ecuador. *Journal of Environmental Management*, *289*, 112495. https://doi.org/10.1016/j.jenvman.2021.112495

Carvalho I Ferreira, J., Diamantino, C., Rosa, C., & Carvalho, E. (2016). *Potential recovery of mineral resources from mining tailings of abandoned mines in Portugal*. https://www.researchgate.net/publication/308657907

Castilhos, Z., Rodrigues-Filho, S., Cesar, R., Rodrigues, A. P., Villas-Bôas, R., de Jesus, I., Lima, M., Faial, K., Miranda, A., Brabo, E., Beinhoff, C., & Santos, E. (2015). Human exposure and risk assessment associated with mercury contamination in artisanal gold mining areas in the Brazilian Amazon. *Environmental Science and Pollution Research*, *22*(15), 11255–11264. https://doi.org/10.1007/s11356-015-4340-y

Castresana, G. P., Roldán, E. C., Suastegui, W. A. G., Perales, J. L. M., Montalvo, A. C., & Silva, A. H. (2019). Evaluation of health risks due to heavy metals in a rural population exposed to Atoyac River pollution in Puebla, Mexico. *Water (Switzerland)*, *11*(2), 1–14. https://doi.org/10.3390/w11020277

Chen, Y., Yu, X., & Belzile, N. (2019). Arsenic speciation in surface waters and lake sediments in an abandoned mine site and field observations of arsenic eco-toxicity. *Journal of Geochemical Exploration*, *205*, 106349. https://doi.org/10.1016/j.gexplo.2019.106349

Covre, W. P., Ramos, S. J., Pereira, W. V., da, S., Souza, E. S., de, Martins, G. C., Teixeira, O. M. M., do Amarante, C. B., Dias, Y. N., & Fernandes, A. R. (2021). Impact of copper mining wastes in the Amazon: Properties and risks to environment and human health. *Journal of Hazardous Materials*, *421*, 126688. https://doi.org/10.1016/j.jhazmat.2021.126688

De Miguel, E., Clavijo, D., Ortega, M. F., & Gómez, A. (2014). Probabilistic meta-analysis of risk from the exposure to Hg in artisanal gold mining communities in Colombia. *Chemosphere*, *108*, 183–189. https://doi.org/10.1016/j.chemosphere.2014.01.035

de Souza, E. S., Texeira, R. A., da Costa, H. S. C., Oliveira, F. J., Melo, L. C. A., do Carmo Freitas Faial, K., & Fernandes, A. R. (2017). Assessment of risk to human health from simultaneous exposure to multiple contaminants in an artisanal gold mine in Serra Pelada, Pará, Brazil. *Science of the Total Environment*, *576*, 683–695. https://doi.org/10.1016/j.scitotenv.2016.10.133

de Souza, J. J., Ferreira, M. P., Gilkes, R., da Costa, L. M., & de Oliveira, T. S. (2018). Geochemical signature of Amazon Tropical Rainforest soils. *Revista Brasileira de Ciência do Solo*, *42*. https://doi.org/10.1590/18069657rbcs20170192

Dooyema, C. A., Neri, A., Lo, Y., Durant, J., Dargan, P. I., & Swarthout, T. (2012). Children's health outbreak of fatal childhood lead poisoning related to artisanal gold mining in northwestern Nigeria, 2010. *Environmental Health Perspectives*, *120*(4), 601–607.

Escobar-Segovia, K., Jiménez-Oyola, S., Garcés-León, D., Paz-Barzola, D., Navarrete, E., Romero-Crespo, P., & Salgado, B. (2021). Heavy metals in rivers affected by mining activities in Ecuador: Pollution and human health implications. *WIT Transactions on Ecology and the Environment*, *250*, 61–72. https://doi.org/10.2495/wrm210061

Fallahzadeh, R. A., Khosravi, R., Dehdashti, B., Ghahramani, E., Omidi, F., Adli, A., & Miri, M. (2018). Spatial distribution variation and probabilistic risk assessment of exposure to chromium in groundwater supplies; A case study in the east of Iran. *Food and Chemical Toxicology*, *115*, 260–266. https://doi.org/10.1016/j.fct.2018.03.019

Fryer, M., Collins, C. D., Ferrier, H., Colvile, R. N., & Nieuwenhuijsen, M. J. (2006). Human exposure modelling for chemical risk assessment: A review of current approaches and research and policy implications. *Environmental Science and Policy*, *9*(3), 261–274. https://doi.org/10.1016/j.envsci.2005.11.011

Galarza, E., Cabrera, M., Espinosa, R., Espitia, E., Moulatlet, G. M., & Capparelli, M. V. (2021). Assessing the quality of amazon aquatic ecosystems with multiple lines of evidence: The case of the Northeast Andean Foothills of Ecuador. *Bulletin of Environmental Contamination and Toxicology*, *107*(1), 52–61.

Gerson, J., Dorman, R., Eagles-Smith, C., Bernhardt, E., & Walters, D. (2021). Lethal impacts of selenium counterbalance the potential reduction in mercury bioaccumulation for freshwater organisms. *Environmental Pollution*, *287*, 117293. https://doi.org/10.1016/j.envpol.2021.117293

Guayasamin, J. M., Vandegrift, R., Policha, T., Encalada, A. C., Greene, N., Ríos-Touma, B., Endara, L., Cárdenas, R. E., Larreátegui, F., Baquero, L., Arcos, I., Cueva, J., Peck, M., Alfonso Cotes, F., Thomas, D., DeCoux, J., Levy, E., & Roy, B. A. (2021). Tipping point towards biodiversity conservation? Local and global consequences of the application of 'Rights of Nature' by Ecuador. https://doi.org/10.20944/preprints202108.0428.v1

Guzmán-Martínez, F., Arranz-González, J. C., Ortega, M. F., García-Martínez, M. J., & Rodríguez-Gómez, V. (2020). A new ranking scale for assessing leaching potential pollution from abandoned mining wastes based on the Mexican official leaching test. *Journal of Environmental Management*, *273*, 111139. https://doi.org/10.1016/j.jenvman.2020.111139

Hu, X., Zhang, Y., Ding, Z., Wang, T., Lian, H., Sun, Y., & Wu, J. (2012). Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China. *Atmospheric Environment*, *57*, 146–152. https://doi.org/10.1016/j.atmosenv.2012.04.056

Huang, Y., Zuo, R., Li, J., Wu, J., Zhai, Y., & Teng, Y. (2018). The spatial and temporal variability of groundwater vulnerability and human health risk in the Limin District, Harbin, China. *Water (Switzerland)*, *10*(6), 686. https://doi.org/10.3390/w10060686

INEC. (2010). *Fasiculo provincial Napo* (pp. 1–7).

Jennings, B., & Duncan, L. L. (2017). Water safety and lead regulation: Physicians' community health responsibilities. *AMA Journal of Ethics*, *19*(10), 1027–1035. https://doi.org/10.1001/journalofethics.2017.19.10.pfor1-1710

Jiménez-Oyola, S., Escobar Segovia, K., García-Martínez, M. J., Ortega, M., Bolonio, D., García-Garizabal, I., & Salgado, B. (2021). Human health risk assessment for exposure to potentially toxic elements in polluted rivers in the Ecuadorian Amazon. *Water (Switzerland)*, *13*(5), 613. https://doi.org/10.3390/w13050613

Lee, J. S., Chon, H. T., & Kim, K. W. (2005). Human risk assessment of As, Cd, Cu and Zn in the abandoned metal mine site. *Environmental Geochemistry and Health*, *27*(2), 185–191. https://doi.org/10.1007/s10653-005-0131-6

Li, F., Zhang, J., Cao, T., Li, S., Chen, Y., Liang, X., Zhao, X., & Chen, J. (2018). Human health risk assessment of toxic elements in farmland topsoil with source identification in Jilin Province, China. *International Journal of Environmental Research and Public Health*, *15*(5), 1040. https://doi.org/10.3390/ijerph15051040

Li, X., Chen, Z., Chen, Z., & Zhang, Y. (2013). A human health risk assessment of rare earth elements in soil and vegetables from a mining area in Fujian Province, Southeast China. *Chemosphere*, *93*(6), 1240–1246. https://doi.org/10.1016/j.chemosphere.2013.06.085

Lima, M. W., Pereira, W., Souza, E. S., Teixeira, R. A., Palheta, D., Faial, K., Costa, H. F., & Fernandes, A. R. (2022). Bioaccumulation and human health risks of potentially toxic elements in fish species from the southeastern Carajás Mineral Province, Brazil. *Environmental Research*, *204*, 112024. https://doi.org/10.1016/j.envres.2021.112024

Lucas-Solis, O., Moulatlet, G. M., Guamangallo, J., Yacelga, N., Villegas, L., Galarza, E., Rosero, B., Zurita, B., Sabando, L., Cabrera, M., Gimiliani, G. T., & Capparelli, M. V. (2021). Preliminary assessment of plastic litter and microplastic contamination in freshwater depositional areas: The case study of Puerto Misahualli, Ecuadorian Amazonia. *Bulletin of Environmental Contamination and Toxicology*, *107*(1), 45–51. https://doi.org/10.1007/s00128-021-03138-2

Mainville, N., Webb, J., Lucotte, M., Davidson, R., Betancourt, O., Cueva, E., & Mergler, D. (2006). Decrease of soil fertility and release of mercury following deforestation in the Andean Amazon, Napo River Valley, Ecuador. *Science of the Total Environment*, *368*(1), 88–98. https://doi.org/10.1016/j.scitotenv.2005.09.064

Marrugo-Negrete, J., Durango-Hernández, J., Díaz-Fernández, L., Urango-Cárdenas, I., Araméndiz-Tatis, H., Vergara-Flórez, V., Bravo, A. G., & Díez, S. (2020). Transfer and bioaccumulation of mercury from soil in cowpea in gold mining sites. *Chemosphere*, *250*, 126142. https://doi.org/10.1016/j.chemosphere.2020.126142

Mestanza-Ramón, C., Cuenca-Cumbicus, J., D'Orio, G., Flores-Toala, J., Segovia-Cáceres, S., Bonilla-Bonilla, A., & Straface, S. (2022a). Gold mining in the Amazon Region of Ecuador: History and a review of its socio-environmental impacts. *Land*, *11*(2), 221.

Mestanza-Ramón, C., Ordoñez-Alcivar, R., Arguello-Guadalupe, C., Carrera-Silva, K., D'Orio, G., & Straface, S. (2022b). History, socioeconomic problems and environmental impacts of gold mining in the Andean Region of Ecuador. *International Journal of Environmental Research and Public Health*, *19*(3), 1190.

Ogola, J., Mitullah, W., & Omulo, M. (2002). Impact of gold mining on the environment and human health: A case study in the Migori Gold Belt, Kenya. *Environmental Geochemistry and Health*, *24*(2), 141–157. https://doi.org/10.1023/a:1014207832471

Pan, L., Fang, G., Wang, Y., Wang, L., Su, B., Li, D., & Xiang, B. (2018). Potentially toxic element pollution levels and risk assessment of soils and sediments in the upstream river, Miyun Reservoir, China. *International Journal of Environmental Research and Public Health*, *15*(11), 2364. https://doi.org/10.3390/ijerph15112364

Rashid, A., Khan, S., Ayub, M., Sardar, T., Jehan, S., Zahir, S., Khan, M. S., Muhammad, J., Khan, R., Ali, A., & Ullah, H. (2019). Mapping human health risk from exposure to potential toxic metal contamination in groundwater of Lower Dir, Pakistan: Application of multivariate and geographical information system. *Chemosphere*, *225*, 785–795. https://doi.org/10.1016/j.chemosphere.2019.03.066

Rivera-Parra, J. L., Beate, B., Diaz, X., & Ochoa, M. B. (2021). Artisanal and small gold mining and petroleum production as potential sources of heavy metal contamination in Ecuador: A call to action. *International Journal of Environmental Research and Public Health*, *18*, 2794. https://doi.org/10.3390/ijerph18062794

Romero-Estévez, D., Yánez-Jácome, G. S., Simbaña-Farinango, K., & Navarrete, H. (2019). Distribution, contents, and health risk assessment of cadmium, lead, and nickel in bananas produced in Ecuador. *Foods*, *8*(8), 330.

Roy, B. A., Zorrilla, M., Endara, L., Thomas, D. C., Vandegrift, R., Rubenstein, J. M., Policha, T., Ríos-Touma, B., & Read, M. (2018). New mining concessions could severely decrease biodiversity and ecosystem services in Ecuador. *Tropical Conservation Science*, *11*, 194008291878042. https://doi.org/10.1177/1940082918780427

Saha, N., Rahman, M. S., Ahmed, M. B., Zhou, J. L., Ngo, H. H., & Guo, W. (2017). Industrial metal pollution in water and probabilistic assessment of human health risk. *Journal of Environmental Management*, *185*, 70–78. https://doi.org/10.1016/j.jenvman.2016.10.023

Satarug, S., & Moore, M. R. (2004). Adverse health effects of chronic exposure to low-level cadmium in foodstuffs and cigarette smoke. *Environmental Health Perspectives*, *112*(10), 1099–1103. https://doi.org/10.1289/ehp.6751

Singh, D. D., Thind, P. S., Sharma, M., Sahoo, S., & John, S. (2019). Environmentally sensitive elements in groundwater of an industrial town in India: Spatial distribution and human health risk. *Water (Switzerland)*, *11*(11), 1–19. https://doi.org/10.3390/w11112350

Souza Neto, H. F., Pereira, W., Dias, Y. N., Souza, E. S., Teixeira, R. A., Lima, M. W., Ramos, S. J., Amarante, C., & Fernandes, A. R. (2020). Environmental and human health risks of arsenic in gold mining areas in the eastern Amazon. *Environmental Pollution*, *265*, 114969. https://doi.org/10.1016/j.envpol.2020.114969

Sun, H., Cheng, H., Lin, L., Deng, K., & Cui, X. (2018). Bioaccumulation and sources of metal(loid)s in lilies and their potential health risks. *Ecotoxicology and Environmental Safety*, *151*, 228–235. https://doi.org/10.1016/j.ecoenv.2017.12.063

Teixeira, P. J., Johnson, M. W., Timmermann, C., Watts, R., Erritzoe, D., Douglass, H., Kettner, H., & Carhart-Harris, R. L. (2021). Psychedelics and health behaviour change. *Journal of Psychopharmacology*, *36*(1), 12–19. https://doi.org/10.1177/02698811211008554

ur Rehman, I., Ishaq, M., Ali, L., Muhammad, S., Din, I. U., Yaseen, M., & Ullah, H. (2020). Potentially toxic elements' occurrence and risk assessment through water and soil of Chitral urban environment, Pakistan: A case study. *Environmental Geochemistry and Health*, *42*(12), 4355–4368. https://doi.org/10.1007/s10653-020-00531-4

USEPA. (2001). Risk Assessment Guidance for Superfund (RAGS) Volume III–Part A: Process for Conducting Probabilistic Risk Assessment, Appendix B. *Office of Emergency and Remedial Response US Environmental Protection Agency*, *III*, 1–385. http://www.epa.gov/sites/production/files/2015-09/documents/rags3adt_complete.pdf

USEPA. (2004). *Risk assessment guidance for superfund (RAGS). Volume I. Human health evaluation manual (HHEM). Part E. Supplemental guidance for dermal risk assessment* (USEPA, 1(540/R/99/005)). https://www.epa.gov/sites/default/files/2015-09/documents/rags_a.pdf

USEPA. (2011). *Exposure factors handbook: 2011 Edition*. Environmental Protection Agency.

Wang, M., Beelen, R., Stafoggia, M., Raaschou-Nielsen, O., Andersen, Z. J., Hoffmann, B., Fischer, P., Houthuijs, D., Nieuwenhuijsen, M., Weinmayr, G., Vineis, P., Xun, W. W., Dimakopoulou, K., Samoli, E., Laatikainen, T., Lanki, T., Turunen, A. W., Oftedal, B., Schwarze, P., & Hoek, G. (2014). Long-term exposure to elemental constituents of particulate matter and cardiovascular mortality in 19 European cohorts: Results from the ESCAPE and TRANSPHORM projects. *Environment International*, *66*, 97–106. https://doi.org/10.1016/j.envint.2014.0

Zheng, S., Wang, Q., Yuan, Y., & Sun, W. (2020). Human health risk assessment of heavy metals in soil and food crops in the Pearl River Delta urban agglomeration of China. *Food Chemistry*, *316*, 126213. https://doi.org/10.1016/j.foodchem.2020.126213

