Human health risk assessment of potentially toxic elements 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 150150, 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, 28805 Alcalá de Henares, Spain

4. Cavanilles Institute of Biodiversity and Evolutionary Biology, University of Valencia, 46980 Paterna, Spain

5. Laboratorio Nacional de Referencia Del Agua, Universidad Regional Amazónica Ikiam, Tena 150150, Ecuador

6. Departamento de Recursos Hídricos y Ciencias Ambientales, Facultad de Ciencias Químicas, Universidad de Cuenca, Cuenca 010202, Ecuador;

7. Departamento de Biociencias, Facultad de Ciencias Químicas, Universidad de Cuenca, Cuenca 010202, Ecuador

8. Grupo de Investigación en Quimiometría y QSAR, Facultad de Ciencia y Tecnología, Universidad del Azuay, Cuenca 010204, Ecuador

9. Instituto de Ciencias del Mar y Limnología-Estación El Carmen, Universidad Nacional Autónoma de México, Ciudad del Carmen 24157, México

*correspondence author

Abstract

Mining activities are a major source of potentially toxic elements (PTEs) into rivers, causing severe environmental pollution and increasing the risk of exposure to the residents of surrounding areas. Mining in the Ecuadorian Amazonia has dramatically increased in the past years, but its effects on local indigenous populations that make use of local rivers are still unknown. The aim of this study was to assess the risks for adults and children caused by the exposure to potentially toxic elements (PTEs) in freshwater ecosystems contaminated with tailings released by gold mining activities in eleven rivers of the upper Napo River basin, Ecuador. We selected a carcinogenic and non-carcinogenic 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, Z, B, V, and Cr in water and sediment samples were considered to assess the potential adverse human health risks. For children, the calculated HI was almost 2 times above the acceptable limit in three sites; while for adults, the HI was above the established limit in one site. Mn and Fe were the major PTEs in HI method contributing 86% to the total risk. For children, TRC was above the limit acceptable in all sites and for adults this just happened in five sites. The two PTEs that contributed 95% were As and Pb. This study shows that PTES due to mining activities causes potential human health risk, to what we recommend that support health measures are taken and further monitoring of freshwater contamination in the area.

Keywords: Potentially toxic elements (PTEs), Napo Province, carcinogenic and non-carcinogenic risk assessment

INTRODUCTION

Gold mining (GM) has historically impacted 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), freshwater contamination (Capparelli et al., 2021, 2020) and puts human health at risk (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 (Capparelli et al. 2021) and negative social impacts (Guayasamin et al., 2021). In the last decade, new GM concessions have been approved in the Napo province (Roy et al. 2018), being about 60% of the concessions authorized for artisanal mining, leaving the remaining areas for industrial or medium-scale GM. The mining scale is defined by its extension, the processed volume of material, and the degree of financial investments. Even though artisanal small-scale GM (i.e. mining without heavy machinery and granted to small companies or local communities) is the most common authorized concession, industrial GM represents 98% of the total territory for the exploitation of gold in the Napo province (33,718 ha). Nevertheless, recent studies indicate that illegal GM has had a sharp increase in the past years in Amazonia (Mestanza-Ramón et al., 2022a). Given the proliferation of mining concessions, and the substantial increase of illegal mining activities (Mestanza-Ramón et al., 2022), information on the human health risks caused by this activity is crucial.

Potentially toxic elements (PTEs), such as metals and metal(loid)s, are commonly released as by-products of GM activities. These compounds are persistent, have a high bioaccumulative capacity (Saha et al., 2017), and can cause neurotoxic and carcinogenic effects to humans when inhaled, ingested, or via dermal contact. (Wang et al., 2014, Guzman-Martinez et al., 2020; Ogola et al., 2002; Zheng et al., 2020). The toxic effects of exposure to PTEs have been widely reported using Human Health Risk Assessment (HHRAs) methods (Kolawole et al., 2018; Li et al., 2014; Wang et al., 2017; Sun et al., 2018). HHRAs are useful to quantify the risk of exposure to chemical contamination (Huang et al., 2018, Singh et al., 2019), to determine the potential hazards caused by the PTE release into the environment, and to identify areas that require management and intervention (Castresana et al., 2019; Huang et al., 2018; Singh et al., 2019). HHRAs in mining areas indicate that residents, mainly children, are of great concern because they are often exposed to PTEs through multiple exposure routes and have a higher vulnerability (Hadzi et al., 2019; Marrugo-Negrete et al., 2020; Rashid et al., 2019).

Artisanal and small-scale GM in the Ecuadorian Amazon are carried out on river margins and streams because gold deposits are often concentrated in alluvial terraces (i.e. placer and paleoplacer deposits). As a consequence of mining, high concentrations of PTEs have been detected in rivers of the southern provinces of Sucumbios and Orellana due to GM contamination (Mora et al., 2018; Pérez et al., 2015; Moreno, 2017). In the Napo province, studies carried out in areas impacted by GM detected PTEs in environmental concentrations exceeding quality standards for both water and sediments (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 of the Napo Province of Ecuador are at high risk due to the contact with multiple environmental sources of freshwater contamination (i.e., mining, urban pollution, fish farming and lixiviate from dumping areas). However, no study has been dedicated to apply HHRAs related exclusively to mining activities in this area. Given that GM has intensified and that it is known as a pollutant activity, an HHRA using solely data from mining areas would help to understand the effects of the PTEs on local indigenous populations particularly affected by the mining impact. Thus, our study aims to assess the potential carcinogenic and non-carcinogenic risks posed by exposure to PTEs from GM areas of the Napo province of Ecuador based on water and sediment exposure concentrations, and provides recommendations for further research and monitoring.

METHODOLOGY

Study area

This study was carried out in the tributaries of the Anzu, Jatunyacu and Napo River, in the Napo province, in Northern Ecuadorian Amazonia. This area is known to be a geodiversity hotspot due to the diverse content of high-value minerals in alluvial deposits. Important local urban centers are: Puerto Napo, Misahualli, Ahuano and Carlos Julio Arosemena Tola (Fig. 1). The study area hosts about 18,200 inhabitants, distributed in both rural and urban areas (INEC, 2010). More than half of the population are self-identified like indigenous people, distributed in either urban or rural areas. The site is characterized by annual precipitation above 4000 mm/yr, and by the presence of an extensive hydrographic network. In addition to the great biodiversity of flora and fauna, the study area is known to be a geodiversity hotspot, given the content of high-value minerals, such as gold.

Sampling collection and analyses

Data on metal and metal(loid)s concentration (hereafter called as PTEs) in surface water and sediments were obtained from Capparelli et al. (2021). Samples were taken from eleven sites downstream from gold mining sites located within or right at the limits of federal concessions. From the forty-three PTEs species analyzed in Capparelli et al. (2021), we selected 13 metals or metal(loid)s due to their potential toxicity to human health (Ag, Al, As, B, Ba, Cd, Cr, Cu, Fe, Mn, Pb, V, and Zn), which include those in concentrations that exceed national or international regulatory standards for water or sediments (Table 1).

Human Health Risk Assessment

The HHRA was performed including different exposure pathways (i.e., water ingestion, sediment ingestion, dermal contact via water, dermal contact via sediment) and following previously described methods (Lee et al., 2005). For each possible exposure pathway (Table 2) we first estimated the chronic daily intake (CDI), according to the equations proposed by the USEPA (2004). The parameter values used in the exposure assessment are presented in Table 3. Moreover, we calculated the CDI for each PTE in each

Carcinogenic and Non-carcinogenic risks.

Carcinogenic and non-carcinogenic risk assessments were conducted to estimate potential health risks due to exposure to PTEs, as clinical and epidemiological studies have related PTEs with increasing cancer risk and/or mortality due to poisoning in human populations exposed to those substances (Cao et al., 2010; Dooyema et al., 2012).

The cumulative non-carcinogenic risk was quantified in terms of hazard quotients (HQs) for all the elements and exposure routes, according to equations (5) and (6) from Table 4. The human health hazard assessment for non-carcinogenic effects was characterized by the existence of a threshold dose of toxicity, which is expressed by the reference of dose (RfD). The values of RfD are different for each PTE, and they were obtained from the Risk Assessment Information System (RAIS) website (Table S1). Only for As, B, Cd Cr and Pb the RAIS defined cancer slope factor (SF) values of 0.002, 0.5, 0.006, 0.5 and 0.009 (mg/kg/day), respectively (USEPA, 2012). The sum of all HQs was expressed as the hazard index (HI), according to equation (7). HI values lower than 1 indicate that risks are not likely to occur, while HI values higher than 1 indicate non-carcinogenic risks (USEPA 2001).

For carcinogenic contaminants, there is no threshold dose of toxicity. Potential carcinogenic risk through ingestion of water and incidental ingestion of sediments was calculated according to Equation (8). The potential carcinogenic risk values for each PTE were then summed for each exposure route and expressed as a total cancer risk (TCR) before being compared to the acceptable reference values (USEPA 2001). Calculated TCR values greater than $1x10^{-4}$ were considered to pose unacceptable risks (with high certainty), whereas values lower than $1x10^{-6}$ were considered to pose insignificant risks (with high certainty) Values ranging between $1x10^{-4}$ and $1x10^{-6}$ were considered to pose potential risks (Hu et al., 2012, Fryer et al., 2006).

RESULTS

Human Health Risk Assessment

The risk assessment performed with the measured concentrations of the PTEs in the 11 areas evaluated, indicated potential toxicological risks for human health. P6 had the highest HI values for both children and adults, exceeding the established limits, while P8 had the lowest values (Fig. 2A). TCR in P2, P3, P6, P10, and P11 exceeded the permissible thresholds for children and adults (Fig. 2B). Higher HI and TCR values were obtained for children than for adults, meaning that children are more susceptible to cancer risks by metals due to water ingestion and water skin contact (Fig 2A-B). Children also showed a higher TCR than adults. The spatial distribution of HI and TCR indexes can be found in Fig 3.

For water and sediments, the presence of Mn, Fe, and Cr contributed to 86% to 99% of the HI (Fig. 4A). For children and adults, the highest contribution to the calculated risk was due to Mn (73% and 83%), and in sediment by Fe (63% and 64%). In sediments, the contribution of PTEs in all sites was similar for children and adults (Fig. 4A-B). The TCR results suggested that for both adults and children, the carcinogenic risk for Mn and Fe from accidental sediment ingestion was the primary exposure pathway (Figure 4A and Table 5). For sediment, Fe contributed over 64% to the index. For water, the highest PTE in all sites was Mn, except for the P8, where Ca had the largest contribution. For water and sediments, the presence of As and Pb contributed up to 95% to the TCR (Fig. 4C-D). In adults and children, TCR for As, derived from accidental water ingestion, was the primary pathway of exposure. It is noteworthy that the TCR (children and adults) for As is much higher than for other PTEs (up to 64%).

For water, out of the PTEs that exceed permissible limits (Fe, Mn, Al, Zn, Cu, Pb, As, Cr, Cd, Ag), none had an important contribution for HI; Fe, Mn, Cr, Cd contributed more than 3%, the others metals contribute down to 1% each. For TCR, As and Pb were the metals that had the highest contribution (above 21%). Cd and Cr contributed only 2% to the HI. For sediments, Ba, Cr, and V were metals that exceed permissible limits of concentration. Cr had a contribution above 11 % and the other metals contributed less than 1% for the HI. For TCR, Cr contributed to the index less than 2%

The HI mean values for children and adults were ranked respectively, as follows: P6>P9>P10>P2>P11>P5>P7>P4>P3>P1>P8 and P6>P9>P10>P2>P11>P5>P3 >P4>P7>P1>P8. Both have a very similar tendency, where the only difference relies on between the position of P7, P4, and P3. P6 site was the only site that exceeded the permissible limit for both children and adults (for children = 1.65, for adults = 1.09, Table 5), suggesting that they would experience non-carcinogenic effects due to the PTE exposure at this site.

The TCR values for different PTEs in the eleven sites decreased as follows: P3>P10>P6>P11>P2>P7>P9>P5>P1>P8>P4. The maximum value for children was 2.61 x10^{-6} and for adults was 1.65 x10^{-6} (Table 5). P4 site was the only site that did not exceed reference limits, suggesting no significant health effects for either children or adults. P2, P3, P6, P10 and P11 sites exceeded reference limits and are considered as having tolerable cancer risk for children and adults.

DISCUSSION

Potential Impacts of PTEs on Human Health

This study was motivated by the high levels of PTEs reported in our study area by Capparelli et al., (2021) and the concern these authors raised for the health of local indigenous populations. Our study showed that the probability of an individual developing cancer over a lifetime as a result of exposure to PTEs was higher than the acceptable levels. The presence of PTEs in surface waters and sediment samples might cause serious human health implications for both children and adults. Similar findings were reported by Castilhos et al. (2015) and de Souza et al. (2017) in gold mining areas of the Brazilian Amazon, who identified mining pollution as a potential hazard for residents nearby the mining areas. In our study, for children, the maximum calculated HI was 4 times above the established threshold. For adults, the maximum HI was 2 times above the threshold. The TCR for adults and children showed a potential tolerable carcinogenic risk, however, children could be more susceptible to TCR than adults, as they are generally more exposed to PTEs than adults, possibly due to the recreational contact with water. The calculated TCR's highest values were related to dermal contact and accidental ingestion of water and sediments, corroborating the results of Jiménez-Oyola et al., (2021) which shows a substantial contribution of TCR through accidental ingestion of sediments. Indeed, because water from the river is used daily for drinking, cooking, and human hygiene, water and accidental sediment ingestion is part of local people's routine.

The elevated TRC was due to the high concentration of As in water and sediment. Arsenic chronic and acute toxicity are associated with negative health effects (Chen, Yu & Belzile, 2019). High concentrations of As, including from mining waste or from mineral source material may expose human populations to an endemic contamination risk (Souza Neto et al., 2020). Similar results were found in gold mining polluted areas of Ghana

(Bempah and Ewusi, 2016) and Slovakia (Rapant et al., 2006, Shakoor et al., 2017), where the ingestion of contaminated drinking water was the main exposure pathway for As. Our results corroborate the findings of Carvalho et al. (2017), who reported HI values lower than 1 and TCR values higher than the safe limit due to As exposure in rivers during recreation activities in an old gold mining area in Portugal. The accidental ingestion of As through sediments was the most significant contributor to non-carcinogenic and carcinogenic risk outcomes in gold mining areas in the Bolivian Andes (Pavilonis et al., 2017), Mexico (Fernandez-Macías et al., 2020), and South Africa (Ngole-Jeme and Fantke, 2018). Overall, for both water and sediment, the As concentration was the crucial element for the risk evaluation in the study area.

In addition to As, the high Cd and Pb concentrations in water contribute to TCR. Pb's exposure has been a concern since 1991 when the USEPA estimated that between 14 and 20% of total Pb exposure was from drinking water (Jennings & Duncan, 2017). Regarding Cd, the high concentration of this PTE is of high concern since overexposure to Cd has been linked to diarrhea, dermatitis, allergy, asthma, lung cancers, high blood pressure, renal dysfunction, and negative effects on reproduction (Satarug & Moore, 2004, Fallahzadeh et al., 2018). For the sediments, Cr was the metal that had the highest contribution compared with V and Ba, with an 11% to the calculated HI. Cr has long been recognized as a toxic, mutagenic and carcinogenic metal. It is toxic to microorganisms, plants, animals and humans (Coetzeel et al., 2020).

The probability of an individual developing cancer over a lifetime caused by As, Cd, and Pb exposure through ingestion of water and the incidental ingestion of sediment was higher than acceptable levels, mainly for children. Therefore, due to those results, the population should be monitored for early signs of metal poisoning, and the protection of vulnerable people living in the study area should be prioritized. Exposure to sediment was below the safety limit and did not represent a risk to human health. Nevertheless, the food chain supply in the studied area should be monitored since these PTEs can be transferred to edible plant parts (Romero-Estévez et al. 2019, Gerson et al., 2021) and to benthic fish (de Lima et al., 2022, Benefice et al., 2010) and invertebrates (Capparelli et al., 2021).

Sampling sites located at the outlets of the downstream basin (Sites 6, 9, 10, and 11. Fig. 3) had HIs and TCRs limits above the allowed threshold for both adults and children. Human settlements are frequently a short distance from river meanders, floodplains and basin outlets, where washed mining sediments and mining tailings are immediately transported and deposited to. Moreover, the flood regimes in the upper Napo basin rivers can also lead to the storage of contaminated sediments along river banks, near human settlements (Lucas-Solis, et al., 2021; Miller et al., 1997). Sites P6 and P11, for example, are located less than 1 km away from around 50 indigenous Kichwa communities, with dret dependence of river to obtain drinking water. The degree of contamination of both water and sediments and the HI and TCR of these sites suggest that water and food sources might not be recommended for human consumption at those localities already. Therefore, it could be that local communities have been consuming water and fish with PTEs levels above the recommended for a relatively long period already. Thus, further examination of the temporal and spatial extension of contamination and their impacts on the health status of local indigenous communities is recommended.

Perspective on an Ecuadorian Amazonian scenario

HHRAs are crucial in the design of further monitoring campaigns and to establish corrective actions to areas affected by mining (De Miguel, E et a., 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. Further research should be dedicated to refining the risk calculations done in this study by collecting a larger number of environmental samples (for the critical elements defined in this study) and by adjusting water and sediment uptake rates to those that effectively represent the habits of indigenous population of the Ecuadorian Amazon. Considering the parameters used for health risk estimates via water and sediment consumption for children and adults provided by USEPA (2011), the calculated risks consider an exposure frequency of 120 days, over 6 years (for children) or 30 years (for adults) (Table 3). However, contact with the aquatic ecosystem of indigenous communities is much greater than this, which could considerably increase the risk of developing diseases related to PTEs exposure. Some studies in Amazonian countries outlined the complexity of the situation due to the multiplicity of factors which may increase exposure (Benefice et al., 2010), as these factors, may even be affected by individual, genetic, cultural and public health issues (Passos and Mergler, 2008, Barbieri et al., 2009).

The interaction of Amazonian communities with the rivers is the basis of their livelihood and cultural activities. In the study area, the probability of an individual developing cancer over a lifetime as a result of exposure to PTEs was higher than acceptable levels. Thus, strategic policies for reducing exposure are needed to avoid the detrimental health effects of the residents. In addition, future studies to assess the risk of the vulnerable populations, including children and pregnant women, should be carried out to identify the occurrence of PTE-associated diseases through different exposure routes. The risk related to the ingestion of edible plants and fish must also be monitored, which would raise the aggregate risk figures, since some PTEs can enter the human body through the food chain.

The current policies of the Ecuadorian government aim to promote mining and other economic activities, sometimes near or inside protected areas (Guayasamin et al., 2021) and indigenous lands. These policies are responsible for the highest rate of deforestation in the past 10 years (Roy et al., 2018), weakening the environmental protection legislation and human rights of traditional and indigenous populations. Due to incentives from the federal government, small-scale gold mining represents a great economic contribution to the country; however, it harms the health of the communities and generates environmental problems (Mainville et a., 2006). In the last two years and during the COVID-19 pandemic, both legal and illegal mining activity have increased in Ecuador following the rise in the price of gold (Mestanza-Ramón et al., 2022). 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 region, and calls for a continued monitoring of PTE exposure and risks in the study region.

CONCLUSIONS

This study reveals the high content of PTEs concentration in water and sediments and the corresponding danger to the health of the inhabitants of the Northeast Andean Foothills of the Ecuadorian Amazon. Spatial analysis shows that the rivers located at the end of the river basins (P6, P9, P10) are the most contaminated and, therefore, pose the greatest risk to the health of local communities. Although total concentrations of PTEs can be used to quantify health risk, it is advisable to assess bioavailable concentrations to obtain more reliable results. Policies to reduce exposure are necessary to avoid harmful effects on the health of residents, as well as epidemiological studies to identify the occurrence of diseases associated with heavy metals (loids) through different exposure routes, that is, the consumption of contaminated food.

Our results suggest that mining activities in the area represent a health hazard for the local human populations. For the indigenous populations of our study area, water consumption depends exclusively on the rivers, as no provision of drinking water and wastewater treatment is provided by local governments. If unable to use the river, these communities are forced to rely solely on the accumulated rainwater for their daily needs. Therefore, this study sheds light on the need for continuous environmental monitoring to identify the origin of PTEs in Amazon rivers and their effect on the health of the inhabitants. This information can support public strategies to control the quality and use of local rivers. Environmental and public health supervisory institutions should monitor the impact of anthropogenic activities in the area and adopt effective measures to decrease the risk to human health from exposure to pollutants.

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). GMM acknowledges the postdoctoral grant from the Project SEP-CONACYT CB-2017-2018 (#A1-S-34563).

REFERENCES

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., Cabrera, M., Rico, A., Lucas-Solis, O., Alvear-S, D., Vasco, S., ... & M Moulatlet, G. (2021). An Integrative Approach to Assess the Environmental Impacts of Gold Mining Contamination in the Amazon. Toxics, 9(7), 149.

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. doi: 10.1016/j.gexplo.2019.106349

Coetzee, J. J., Bansal, N., & Chirwa, E. (2020). Chromium in environment, its toxic effect from chromite-mining and ferrochrome industries, and its possible bioremediation. Exposure and health, 12(1), 51-62.

de Lima, M. W., da Silveira Pereira, W. V., de Souza, E. S., Teixeira, R. A., da Conceição Palheta, D., Faial, K. D. C. 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.

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

Dooyema, C. A., Neri, A., Lo, Y., Durant, J., Dargan, P. I., & Swarthout, T. (2012). *Research | Children ' s Health Outbreak of Fatal Childhood Lead Poisoning Related to Artisanal Gold*. *120*(4), 601–607.

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*(December 2017), 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

Galárraga, R., & Torres, M. C. (2001). Water Quality in the Napo River Basin (Ecuadorian Andean Amazonia): The Andean Amazon Rivers Analysis and Management project (AARAM). Mountain Research and Development, 21(3), 295-296.

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*(July). 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). https://doi.org/10.3390/w10060686

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). 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

Luo, X. S., Ding, J., Xu, B., Wang, Y. J., Li, H. B., & Yu, S. (2012). Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. *Science of the Total Environment*, *424*, 88–96. https://doi.org/10.1016/j.scitotenv.2012.02.053

Mari, M., Nadal, M., Schuhmacher, M., & Domingo, J. L. (2009). Exposure to heavy metals and PCDD/Fs by the population living in the vicinity of a hazardous waste landfill in Catalonia, Spain: Health risk assessment. *Environment International*, *35*(7), 1034–1039. https://doi.org/10.1016/j.envint.2009.05.004

Mestanza-Ramón, C., Cuenca-Cumbicus, J., D'Orio, G., Flores-Toala, J., Segovia-Cáceres, S., Bonilla-Bonilla, A., & Straface, S. (2022). 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. (2022). 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.

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). https://doi.org/10.3390/ijerph15112364

Raju, N. (2022). Arsenic in the geo-environment: A review of sources, geochemical processes, toxicity and removal technologies. Environmental Research, 203, 111782. doi: 10.1016/j.envres.2021.111782

Rehman, I. ur, 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

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.

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., Pereira, W., Dias, Y., Souza, E., Teixeira, R., & Lima, M. et al. (2020). Environmental and human health risks of arsenic in gold mining areas in the eastern Amazon. Environmental Pollution, 265, 114969. doi: 10.1016/j.envpol.2020.114969

U.S. EPA. (2011). *EPA-600-R-090-052F, Exposure Factors Handbook, 2011 Edition. September*, xv. www.epa.gov

US EPA. (2002). Supplemental Guidance for developing soil screening levels for Superfund sites. *United States Environmental Protection Agency*, *December*, 1–187. https://nepis.epa.gov/Exe/ZyPDF.cgi/91003IJK.PDF?Dockey=91003IJK.PDF

US EPA. (2012). United States Environmental Protection Agency. *Proceedings of the Water Environment Federation*, *2005*(16), 726–737. https://doi.org/https://rais.ornl.gov/cgi-bin/tools/TOX_search?select=chemtox

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 U.S. Environmental Protection Agency*, *III*(December), 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. *Us Epa*, *1*(540/R/99/005). https://doi.org/EPA/540/1-89/002

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

Table 1. PTEs concentration in water and sediments used for the calculation of the HHRA. 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.

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	0.07	0.84	0.04	0.07	0.07
	Al*	158.13	132.55	287.65	93.05	231.21	377.61	146.94	253.14	249.06	350.29	405.58
	As*	2.17	1.71	6.69	1.38	2.29	1.79	3.40	2.76	2.67	5.66	3.72
	B	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	9.75	4.01
	Ba	345.39	32.23	113.05	60.49	153.78	817.19	46.11	61.06	222.67	938.86	339.13
	Cd*	0.49	0.73	0.18	0.19	0.17	0.43	0.18	0.78	0.35	0.46	0.27
	Cr*	2.25	2.25	2.59	2.25	2.25	2.25	2.25	2.78	2.25	2.25	2.31
	Cu*	24.24	6.03	11.96	6.36	7.97	11.95	5.64	11.30	10.75	9.43	8.44
	Fe*	372.93	228.93	558.52	227.50	326.05	237.00	512.77	547.61	536.26	370.97	308.66
	Mn*	456.29	140.50	153.17	105.45	274.70	485.63	49.35	74.43	513.16	597.91	258.67
	Pb*	6.11	10.54	5.69	0.72	2.42	14.50	1.65	1.67	2.42	4.36	5.49
	V	8.36	6.52	20.62	6.69	11.04	12.42	9.67	9.72	13.16	15.58	23.95
	Zn*	88.40	30.05	43.41	9.26	23.34	144.19	18.94	50.85	50.64	30.82	23.30
Sediment	Ag	0.01	0.03	0.03	0.02	0.02	1.20	0.02	0.01	0.03	0.02	0.03
	As	0.71	2.00	0.96	1.66	1.83	3.63	1.31	0.83	1.58	2.03	1.67
	B*	2.10	0.00	1.12	0.54	0.47	1.81	2.60	1.31	0.54	1.98	0.56
	Ba	32.64	37.07	55.84	75.82	73.87	136.60	65.70	17.75	134.79	113.43	89.69
	Cd	0.01	0.01	0.01	0.02	0.02	0.04	0.02	0.02	0.03	0.03	0.02
	Cr*	4.76	19.09	11.36	10.12	12.90	36.73	9.95	4.32	11.90	11.49	7.10
	Cu	3.43	4.36	4.14	7.13	6.86	10.55	3.66	1.30	5.40	5.19	3.97
	Fe	3447.44	11154.96	5898.51	6070.85	7470.38	17035.00	5654.41	2123.42	11910.12	9956.71	7921.13
	Mn	125.59	368.47	139.56	224.78	318.22	632.34	178.77	67.82	459.05	438.03	370.43
	Pb	0.39	1.20	0.86	1.01	1.20	2.17	0.97	0.34	1.14	1.24	1.05
	V*	16.26	66.23	21.83	30.93	41.94	107.40	18.60	8.14	81.20	30.93	23.55
	Zn	6.09	11.34	6.84	10.57	11.65	20.82	9.49	3.52	14.59	10.19	8.21

Table 2. Exposure assessment equations by exposure pathways. The exposure factors considered in the calculation of CDI are described in Table 3 (USEPA, 2011).

Exposure Pathways	**Equations**	
Water ingestion	$CDI_{Ing\ w} = \frac{C_W\ x\ EF\ x\ ET\ x\ IR_W\ x\ ED}{AT\ x\ BW}\ x\ CF$	**(1)**
Sediment ingestion	$CDI_{Ing\ s} = \frac{C_S\ x\ EF\ x\ ET\ x\ IR_S\ x\ ED}{AT\ x\ BW}\ x\ CF$	**(2)**
Dermal contact water	$CDI_{derm\ w} = \frac{C_W\ x\ EF\ x\ ET\ x\ ED\ x\ SA\ x\ kp}{AT\ x\ BW}\ x\ CF$	**(3)**
Dermal contact sediment	$CDI_{derm\ s} = \frac{C_S\ x\ EF\ x\ ET\ x\ SA\ x\ AF\ x\ ABS}{AT\ x\ BW}\ x\ CF$	**(4)**

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

Parameters		**Unities**	**Children (C)**	**Adults (A)**
PTE concentration in water (w) or sediment (s)	C	ug/L		
Permeability constant	Kp	cm/hour		
Exposure frequency	EF	day/year	120	120
Exposure duration	ED	year	6	30
Exposure time	ET	hour/event	2.6	2.6
Skin surface area (swimming)	SA	cm^2	7280	23000
Body weight	BW	kg	15	70
Ingestion rate of water	IRw	L/event	0.09	0.053
Ingestion rate of sediments	IRs	mg/event	50	12.5
Averaging time non-carcinogen	AT nc	day	2190	10950
Averaging time carcinogen	AT c	day	25550	25550
Adherence factor-adults	AF	mg/cm^2	0.2	0.07
Dermal absorption factor	ABS	unit-less	0.001	0.001
Conversion factor	CF	dimensionless	1×10^{-6}	1×10^{-6}

Table 4. Equations to determine Hazard Quotients (HQ), Cumulative Hazard Index (HI) and Potential Carcinogenic Risk (CR). CDI = Chronic daily intake; RfD = reference of dose.

	Equations	
Hazard Quotients for Ingestion	$HQ_{ing} = \frac{CDI_{ing\,w}}{RfD_{oral}}$	**(5)**
Hazard Quotients for Dermal Contact	$HQ_{derm} = \frac{CDI_{derm}}{RfD_{derm}}$	**(6)**
Hazard Index	$HI = \sum HQ = HQ_{ing} + HQ_{derm}$	**(7)**
Potential Carcinogenic Risk	$CR_{ing} = CDI_{ing}\ x\ CSF_{oral}$	**(8)**

Table 5. Cumulative Hazard Index (HI) and Total Cancer Risk (TCR) to children and adults from all metals by each site classification by children and adults.

	Sites	**Hazard Index (HI)**	**Total Cancer Risk (TCR)**
Children	P1	0.50	**1.23×10^{-6}**
	P2	0.96	**1.77×10^{-6}**
	P3	0.56	**2.61×10^{-6}**
	P4	0.57	**1.01×10^{-6}**
	P5	0.78	**1.42×10^{-6}**
	P6	**1.65**	**2.53×10^{-6}**
	P7	0.63	**1.54×10^{-6}**
	P8	0.38	**1.23×10^{-6}**
	P9	**1.22**	**1.47×10^{-6}**
	P10	**1.19**	**2.60×10^{-6}**
	P11	0.85	**1.95×10^{-6}**
Adults	P1	0.34	7.75×10^{-7}
	P2	0.64	**1.12×10^{-6}**
	P3	0.37	**1.65×10^{-6}**
	P4	0.37	6.37×10^{-7}
	P5	0.51	8.99×10^{-7}
	P6	**1.09**	**1.59×10^{-6}**
	P7	0.33	9.75×10^{-7}
	P8	0.17	7.73×10^{-7}
	P9	0.78	9.30×10^{-7}
	P10	0.73	**1.64×10^{-6}**
	P11	0.51	**1.23×10^{-6}**

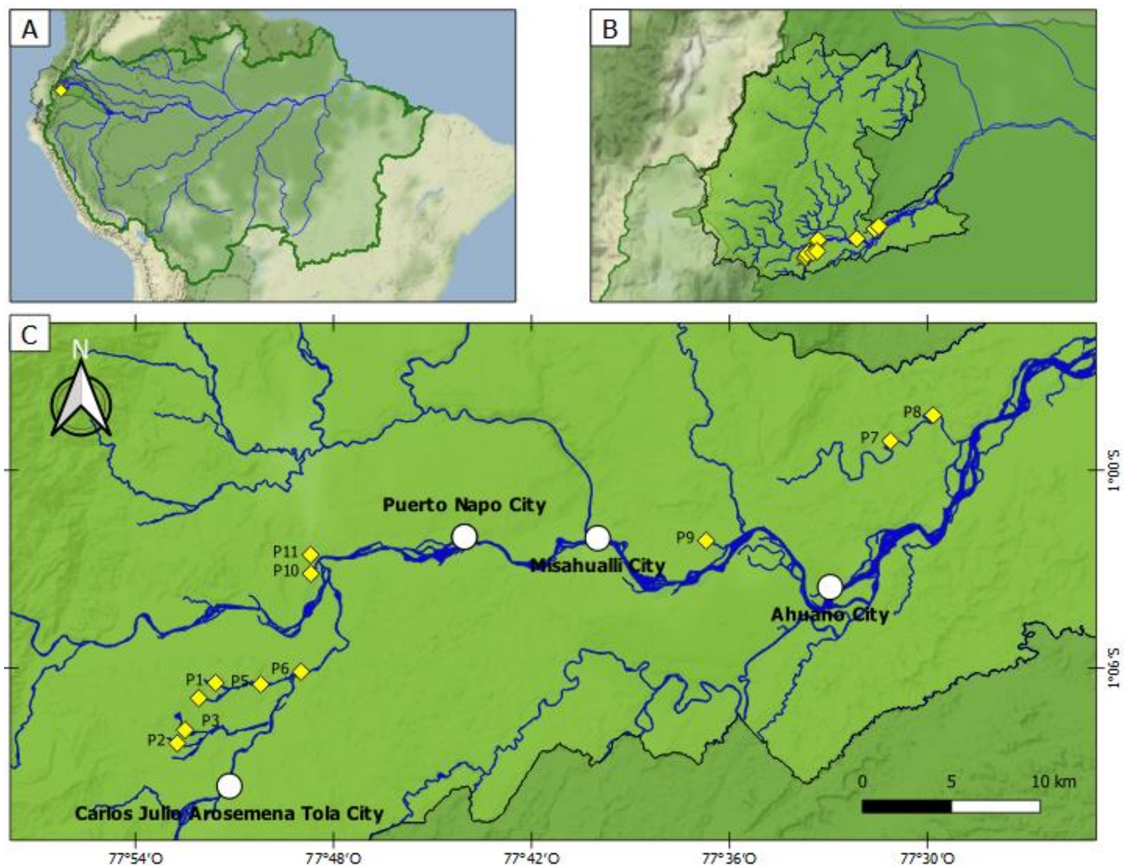


Fig 1. A) Location of the study area in the Amazon basin. (B) Napo province of Ecuador and location of the sampling sites along rivers (yellow diamonds). The eleven sites are located along rivers directly affected by medium-scale to industrial-scale gold mining.

by

the

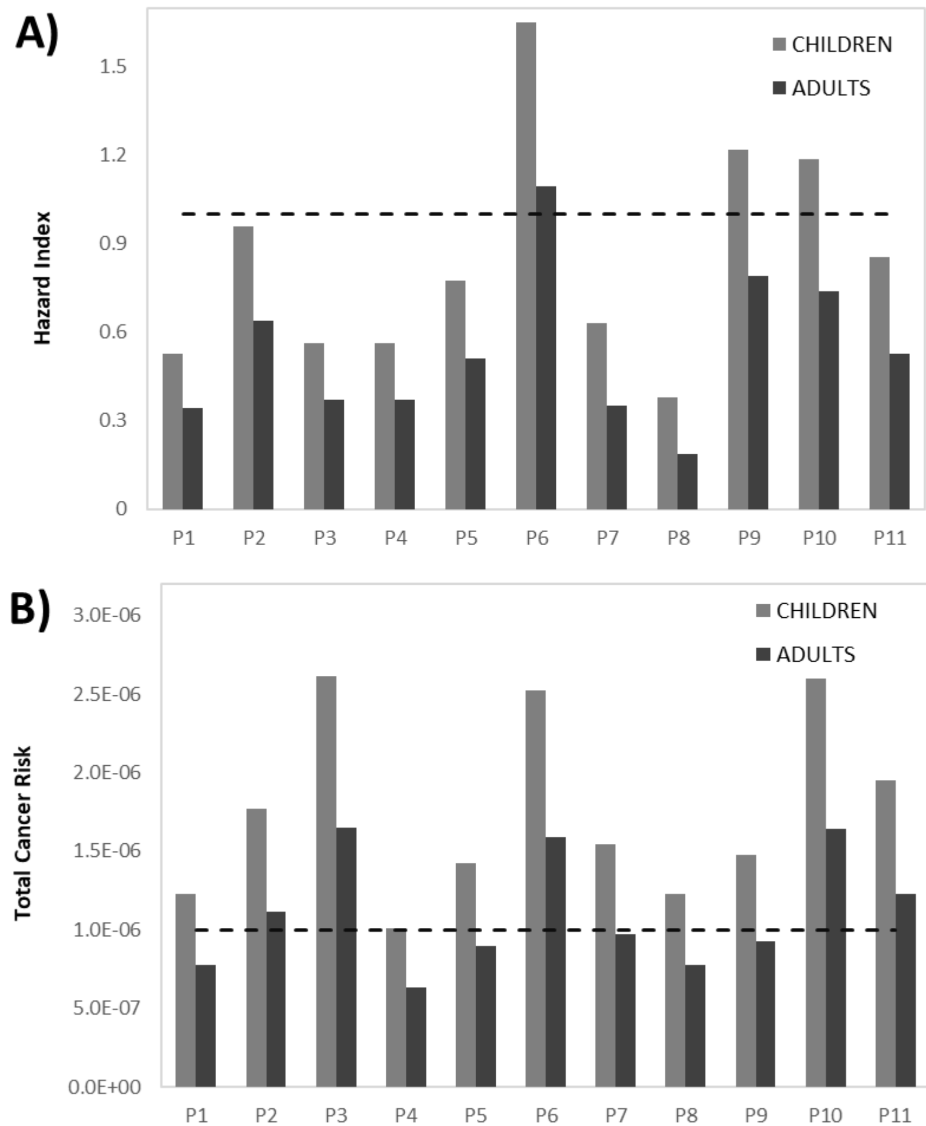


Fig 2. Results of children and adults of HRA each site. A) Cumulative hazard index (HI), horizontal lines, indicate the limit established where values upper to $1x10^{-6}$ are set as tolerable. B) Total Cancer risk (TCR), horizontal lines indicate limit established (USEPA 2001).

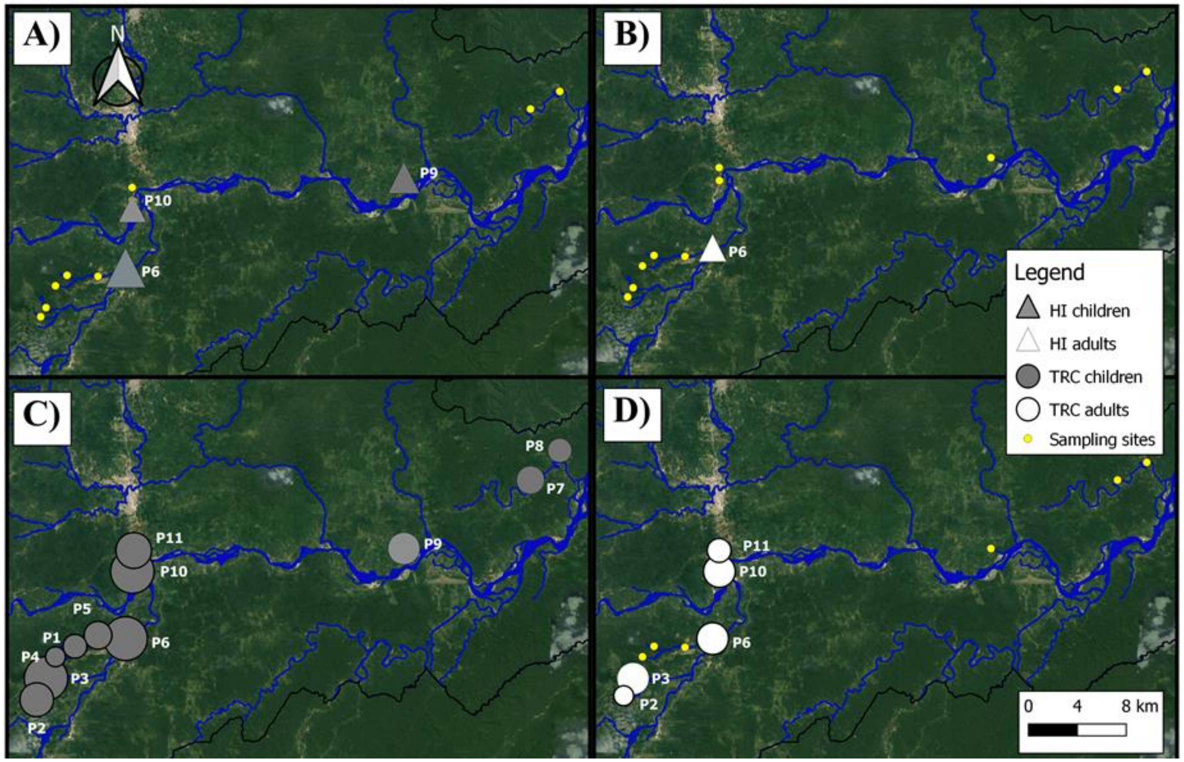
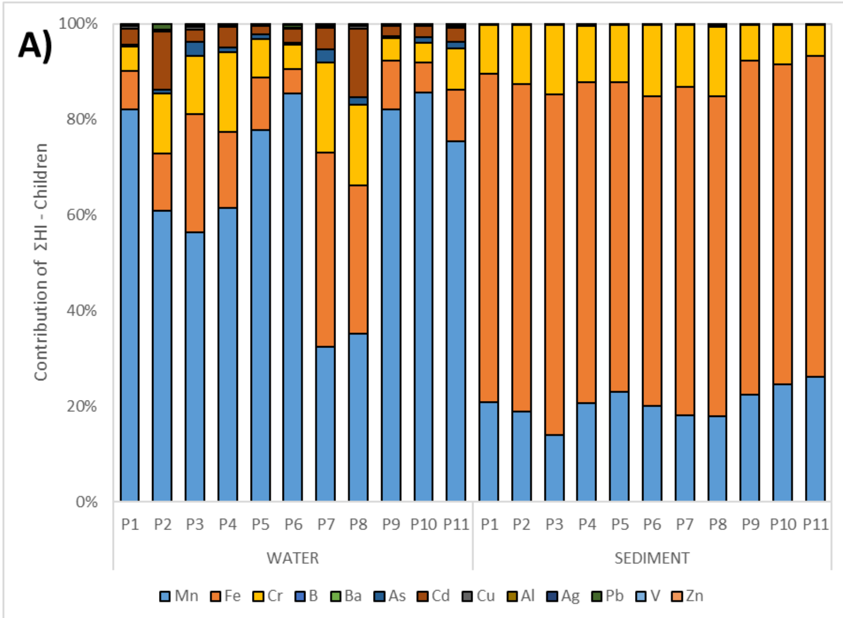
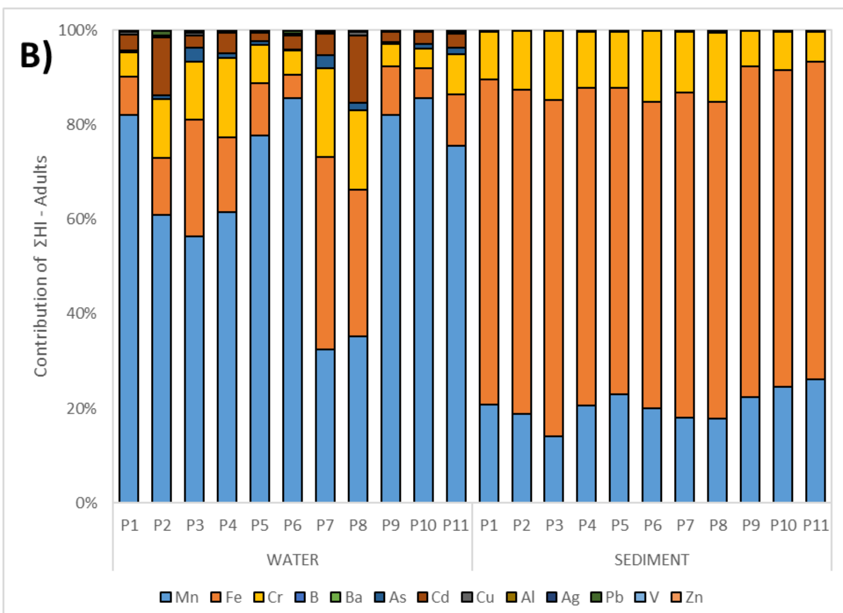
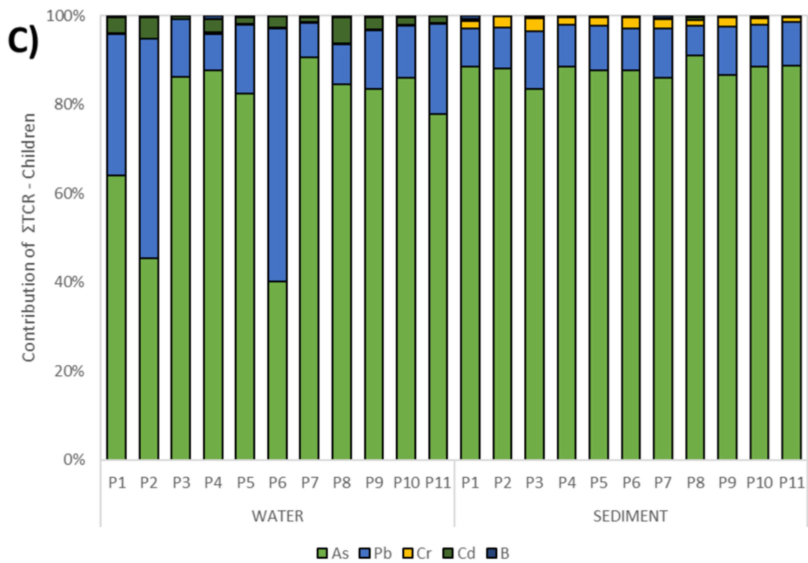


Fig 3. Spatial distribution of the Hazard index (HI) values for (A) children and (B) adults and of the Total Carcinogenic Risk (TCR) for (C children and (D) adults. Symbol size represents the relative magnitude of either HI or TCR in sites where these indexes exceed permissible limits. Otherwise sites are just represented by yellow dots.


A)
100%
80%
60%
40%
20%
0%
Contribution of ΣHI - Children
P1 P2 P3 P4 P5 P6 P7 P8 P9 P10 P11 P1 P2 P3 P4 P5 P6 P7 P8 P9 P10 P11
WATER
SEDIMENT
Mn Fe Cr B Ba As Cd Cu Al Ag Pb V Zn

42


B)
100%
80%
60%
40%
20%
0%
Contribution of ΣHI - Adults
P1 P2 P3 P4 P5 P6 P7 P8 P9 P10 P11 P1 P2 P3 P4 P5 P6 P7 P8 P9 P10 P11
WATER
SEDIMENT
Mn Fe Cr B Ba As Cd Cu Al Ag Pb V Zn



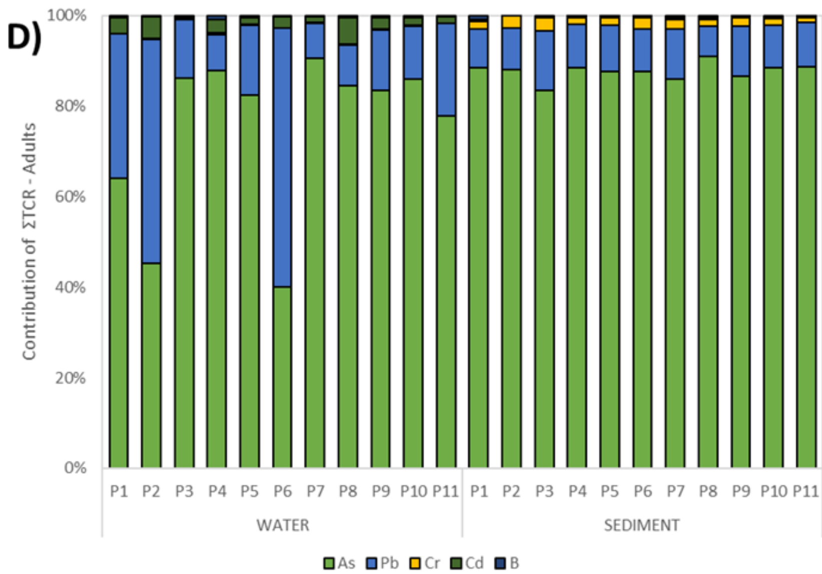


Figure 4. Contribution of each metal according to each site for water and sediment analyzed. Summary of the hazard index (ΣHI) A) Children and B) Adults. Summary of the total cancer risk (ΣCR) C) Children and D) Adults.