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Trace Metal Concentrations (Hg, Pb, As, Cd, Fe) in Fish Muscles from the Cavally River Impacted by Gold Panning in the Zouan-Hounien Department (Western Côte D'Ivoire)

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Abstract

Gold panning is a growing activity in the Zouan-Hounien department, and it has a significant impact on surface water resources. This study aims to determine the concentration of certain trace elements in *Clarias nigrodigitatus* muscles and assess the associated health risks to local populations. Mercury, lead, arsenic, cadmium, and iron concentrations in fish muscles complied with the FAO/WHO guide values recommended for consumption. The bioconcentration factors calculated for mercury, lead, cadmium, arsenic, and iron relative to sediments are less than one (BCF/sediments < 1) and greater than one relative to water (FBC/water > 1), indicating that fish concentrate trace elements in their muscles from the water. Additionally, the health risk assessment conducted on children and adults revealed hazard quotient (HQ) values below one (HQ < 1). This indicates that the population is not likely to develop non-carcinogenic diseases. Therefore, the estimated cancer risk values for adults and children are within the acceptable range for arsenic and cadmium ($10^{-6} \leq CR < 10^{-4}$) and not significant for lead ($CR < 10^{-6}$).

Keywords

Gold Panning, *Clarias nigrodigitatus*, Trace Metal Elements (TME), Health Risk, Cavally River

1. Introduction

The problems posed by the dispersion of pollutants in the environment, particularly in watercourses, have been of interest to the scientific community for many years now [1] [2]. Indeed, talking about environmental protection leads not only to a better understanding of the fate of these pollutants in the environment, but also of their effects on aquatic ecosystems. They are naturally present in the earth's crust. However, their high concentrations in the environment are the consequence of several anthropogenic activities such as industrial production, mining, agriculture, and transportation [3] [4]. Trace Metals (TME) are counted among the most persistent pollutants in aquatic ecosystems due to their resistance to decomposition under natural conditions and their capacity to bioaccumulate, making them a real threat to living organisms [5] [6].

In Côte d'Ivoire, fish is the main source of animal protein for consumers, accounting for a per capita consumption of 24 kg/year according to the Ministry of Animal and Fisheries Resources. In the department of Zouan-Hounien, the Cavally River is the main watercourse used by the local population for various purposes, such as fishing, supplying drinking water to the population, irrigation, etc. Unfortunately, this river is subject to the activities of illegal fishing boats. Unfortunately, the river is also subject to gold-panning activities that jeopardize its quality. Work carried out by [7] has revealed significant concentrations of mercury (Hg), lead (Pb), arsenic (As), and cadmium (Cd) in the river's surface waters and sediments. Once released into the aquatic environment, these trace metals can accumulate in the edible tissues of fish, representing a health risk for consumers [8]-[10]. This potential risk to human health from trace metal migration is assessed as a function of the quantity of fish consumed and the duration of exposure [11].

The fish species selected for this study is the catfish (*Clarias nigrodigitatus*). It is a commonly caught and widely consumed species in the area. Catfish are also demersal species. They feed on river sediments and are among the bioaccumulation fish [12]. According to [10], demersal fish can accumulate higher concentrations of trace metals than pelagic fish. [13] states that monitoring trace metal contamination in river systems using fish tissue enables the quality of aquatic ecosystems to be assessed. Building on previous research on water quality in the Cavally River, this study aims to determine the concentration of certain trace elements in the muscles of *Clarias nigrodigitatus* and assess the health risks to riverside populations.

2. Material and Methods

2.1. Presentation of the Study Area

The Cavally River is the primary waterway that drains the Zouan-Hounien department (**Figure 1**). Rising in Guinea north of Mount Nimba at an altitude of 600 metres, it is 700 km long. The 700 km-long Cavally River serves as a natural border between Côte d'Ivoire and Liberia in its middle and lower reaches [14]. The Zouan-Hounien department has a mountain climate, characterized by two seasons: a rainy season from March to October, and a dry season from November to February. The average annual rainfall is 1.87 mm (1970-2015). January is the least rainy month, with an average rainfall of less than 15 mm. Conversely, September is the wettest month, with an average rainfall of 236 mm and a maximum discharge of 196.01 $m^3 \cdot s^{-1}$. The fish species selected for this study was the catfish, scientific name *Clarias nigrodigitatus* (**Figure 2**), caught in the Cavally River during the low-water period.

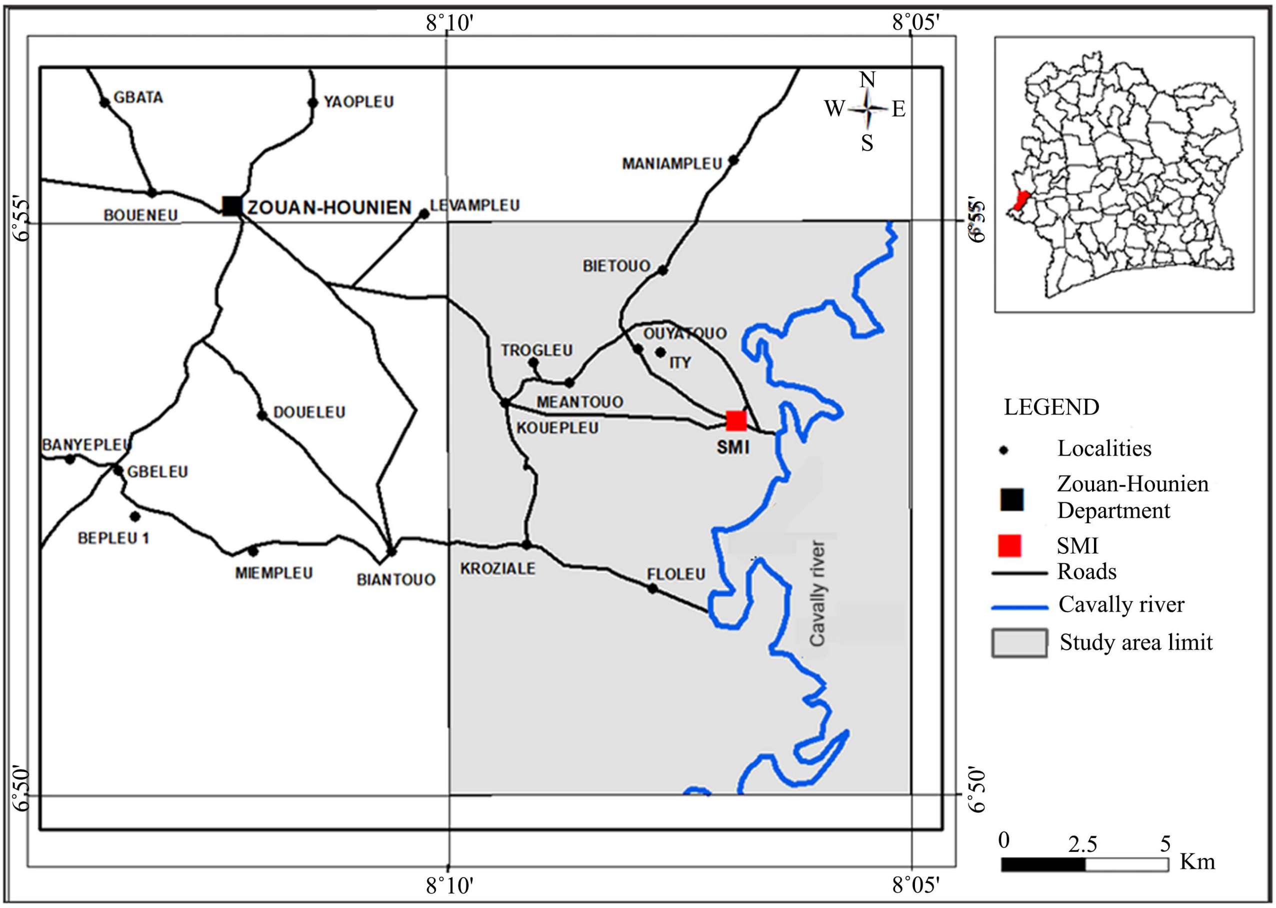

Figure 1. Presentation of the study area and the Cavally River.

Figure 2. A few samples of catfish (*Clarias nigrodigitatus*) were taken for laboratory analysis.

2.2. Fish Sampling

Fish samples were obtained during a single sampling campaign from local fishermen. Muscles were utilized as the fish components employed for TME determination, as they represent the edible portions of the fish and function as a circumstantial biological indicator, given their relative mass in comparison to other organs [15]. A total of 27 fish samples were collected, stored in a cooler containing ice cubes, and sent to the Central Laboratory for Food Hygiene and Agro-industry (LCHAI) of the National Laboratory for Support to Agricultural Development (LANADA) for chemical analysis in Abidjan. Upon arrival at the designated laboratory, the fish samples were stored in the freezer until the specific parts required for the TME assay were extracted.

2.3. Analysis of Mercury and Other TMEs

In the laboratory, the fish were measured from mouth to caudal fin tip (total length) and to the fork (standard length) using an ichthyometer, and then weighed on a 0.001 g precision electronic balance (total weight). For samples whose mass exceeded 5 kg, a pesola or load cell was employed for mass measurements. Subsequent to the collection of the aforementioned measurements, a 5 g sample of skinless dorsal muscle was obtained from each specimen. The fresh part was ground in an agate mortar and then placed in Teflon tubes, to which 6 ml of nitric acid (HNO3 68%) was added and closed with watch glasses. Subsequent to solubilisation, the tubes were placed in a sand bath at a gradual rate of heating to 130˚C, until the complete evaporation of the acid. The resulting pellets were then dissolved in hot distilled water. Following the cooling process, each acid-etch solution was transferred volumetrically to a 25 ml flask. Following homogenisation, the solution was filtered through filter paper. Concurrently, a 6 ml solution of 68% HNO_3 was prepared under identical conditions. With the exception of mercury, the presence of TME was detected by graphite furnace atomic absorption spectrometry (Perkin-Elmer spectrophotometer, model 3030).

2.4. Statistics

The intensity of contamination in fish is estimated by comparing the mean value of TME concentrations in each muscle sample with the guide values for the maximum limit concentrations of trace elements in fish [16] (**Table 1**).

Table 1. Limit values ($mg \cdot kg^{-1}$) for TME in fish [16].

Parameters / Reference	Hg	As	Cd	Pb	Fe
[16]	0.50	2.00	0.025	0.30	43.00

The assessment of metal contamination in fish was carried out by calculating the bioconcentration factor (BCF), a parameter linking the concentration of the contaminant in the organism of the species to that of the environment (water, sediment, soil, and air). It is used to describe the transfer of a contaminant from the biotope to the organism. It is expressed as the ratio of the concentration of the contaminant (inorganic parameter) in the organism (fish) to that of the contaminant in the biotope (water and sediment) [17]. The higher the ratio, the more intense the bioconcentration of TMEs in the organism [18]. Its formula is given by Equation (1).

Both concentrations are expressed in $mg \cdot kg^{-1}$. When BCF > 1, there is bioconcentration of the TME in the fish and therefore its transfer from the biotope to the fish.

$$\text{FBC} = \frac{\text{TME concentration in organism}}{\text{TME concentration in water or sediment}} \quad (1)$$

2.5. Health Risk Assessment Method

The health risk assessment method was developed by the U.S. National Research Council [19]. Adverse effects on human health resulting from environmental pollution are defined as the probability of such effects arising [20] [21]. It is a method for calculating the health risks to which a population exposed to a particular pollution of anthropogenic or natural origin is subject [22]. In the present study, the research question was posed and subsequently resolved in two distinct age demographics: namely, children (under 15 years of age) and adults (over 15 years of age). The application process is comprised of four distinct stages:

- Identification of chemical substance hazards is imperative in this context. The hazards in question refer to the concentrations of various trace elements that have been measured in fish muscles, including mercury (Hg), arsenic (As), lead (Pb), cadmium (Cd), and iron (Fe).
- Assessment of the dose-response relationship, resulting in Reference Doses which for Hg, Pb, Cd, As, and Fe are 0.3, 4, 0.3, 1, and 800 $\mu g \cdot kg^{-1} \cdot d^{-1}$, respectively.
- Exposure estimates are used to calculate the estimated daily intake according to Equation (2), obtained from the formula of [23] and **Table 2**;

$$\text{EDI} = \frac{C \times IR \times ED \times EF}{BW \times AT} \times 10^{-3} \quad (2)$$

where EDI = Estimated Daily Intake ($mg \cdot kg^{-1} \cdot day^{-1}$).

Table 2. Parameters for the health risk estimations of heavy metals.

Parameters	Unit	Children	Adults
Body weight (BW)	kg	15	70
Exposure frequency (EF)	$Days \cdot year^{-1}$	365	365
Exposure duration (ED)	Years	6	30
Average time (IR)	$mg \cdot day^{-1}$	200	100
Average time (AT)	$Days \cdot year^{-1}$	365 × ED	365 × ED

- **Risk characterization (Non-carcinogenic risk)**

This involves calculating the hazard quotient (HQ) for threshold effects. It is obtained from Equation (3) according to [23].

$$HQ = \frac{EDI}{RfD} \quad (3)$$

When HQ < 1, the probability of a toxic effect occurring is negligible. Conversely, when HQ > 1, the possibility of a toxic effect cannot be discounted.

In the context of this study, a hypothetical scenario has been postulated in which an individual (child or adult) is assumed to consume fish on a daily basis for a period of seven days. It is further postulated that the average annual quantity of fish ingested by a child will be equivalent to that of an adult [24]. Furthermore, no amount of the metal measured in the muscle will be considered lost or amplified during the cooking process, and therefore the ingestion dose will be equal to the contaminant dose absorbed [12].

- **Carcinogenic risk**

The carcinogenic risk is defined as the probability that a person will develop cancer due to exposure to a particular contaminant or a set of contaminants in the environment [25]. It is given by the ratio of the daily exposure dose to the carcinogenic slope factor (CSF) according to Equation (4) [25] [26].

$$\text{Carcinogenic risk} = EDI \times CSF \quad (4)$$

The cancer slope factors for Pb, Cd, and As are 0.0085, 0.63, and 1.5 mg/kg/day, respectively [25] [27].

Risks were categorized as negligible ($CR < 10^{-6}$), an acceptable range ($10^{-6} \leq RI < 10^{-4}$) and unacceptable ($RI > 10^{-4}$) based on the calculated values [25] [27] [28].

3. Results

3.1. TME Concentration in Fish Muscle

The mean concentrations of TME in fish muscle are presented in **Table 3**. The mercury concentrations ranged from 0 to 0.06 mg·kg^{-1}, with an average of 0.023 ± 0.01 mg·kg^{-1}. It is evident that all 27 fish samples have concentrations below the limit value of 0.5 mg·kg^{-1} set by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) [16]. This limit value is considered permissible for fish. Lead concentrations ranged from 0 to 0.46 mg·kg^{-1}, with a mean value of 0.25 ± 0.12 mg·kg^{-1}. In 29.62% of samples (8/27), lead concentrations exceeded the permissible limit of 0.3 mg·kg^{-1}. Cadmium concentrations ranged from 0 to 0.29 mg·kg^{-1}, with an average of 0.011 ± 0.004 mg·kg^{-1}. A total of 6 fish out of 27 (22.22%) had concentrations above the permissible limit of 0.025 mg·kg^{-1} for fish according to [16]. For arsenic, concentrations ranged from 0 to 0.40 mg·kg^{-1}, with an average of 0.09 ± 0.01 mg·kg^{-1}. All fish sampled had arsenic concentrations in line with recommended standards. Iron concentrations were highest, ranging from 5.56 to 41.36 mg·kg^{-1}, with an average of 17.07 ± 5.36 mg·kg^{-1}. However, all the fish analyzed (27/27), *i.e.* 100%, had Fe concentrations below the required standard of 43 mg·kg^{-1} for fish. These fish are therefore fit for human consumption. TME are abundant in fish sampled in Cavally River waters in the following order: Fe ≻ Pb ≻ As ≻ Hg ≻ Cd.

Table 3. Trace metal concentrations in fish muscles (*Clarias nigrodigitatus*).

TME	River	Min (mg·kg^{-1})	Max (mg·kg^{-1})	Average ± Standard deviation	[16] (mg·kg^{-1})
Hg	Cavally river	0.00	0.06	0.023 ± 0.01	0.5
Pb		0.00	0.46	0.25 ± 0.12	0.3
Cd		0.00	0.29	0.011 ± 0. 004	0.025
As		0.00	0.40	0.09 ± 0.01	2
Fe		5.56	41.36	17.07 ± 5.36	43

3.2. Bioconcentration Factors (BCF)

The results of the calculated bioconcentration factors for TMEs in water and sediments are reported in Table 4. This table shows that the bioconcentration factors relative to water for mercury, lead, cadmium, arsenic, and iron are greater than one (BCF > 1). These values reflect an accumulation of trace metal elements in fish muscles from water. Conversely, the BCF relative to sediment for all trace metal elements is less than one (BCF < 1), showing that fish do not concentrate TMEs in their muscles from sediments.

Table 4. Summary of trace metals bioconcentration factors in *Clarias nigrodigitatus* muscles in the Cavally river water.

Trace metal concentrations (μg·kg^{-1})	Hg	Pb	Cd	As	Fe
Fish	23	250	11	90	17,007
Water	0.87	1.6	0.04	0.66	2337.09
Sediments	97	610	20	510	15,512,220
BCF/Water	26.44	156.25	275	136.36	7.28
BCF/Sediments	0.24	0.41	0.55	0.18	0.001

3.3. Assessment of Human Health Risks in Fish (Catfish)

The results of the estimated daily intake (EDI), hazard quotient (HQ), and carcinogenic risk (CR) calculated for children and adults are shown in Table 5. EDI values for elements in children are lower than those in adults. Iron is the main element contributing to the risk of fish ingestion, with mean values well above those of the other elements. The estimated hazard quotient for all TME is less than 1 for both children and adults (HQ < 1). This indicates that there is likely no risk from eating catfish caught in the area. However, four out of eleven fish (4/11) recorded an HQ (As) greater than unity in children when considered individually.

Arsenic is the element with the highest non-carcinogenic risk value in both children and adults. All cancer risk values obtained for these three metals are within the acceptable limit for cadmium and arsenic ($10^{-6} \leq CR < 10^{-4}$) and not significant for lead ($CR < 10^{-6}$) in children and adults. These values show that long-term consumption of fish does not pose a cancer risk to the population.

Table 5. Results for exposure estimates (EDI), hazard quotients (HQ), and cancer risk (CR) of different trace elements in fish muscles from the waters of the Cavally River.

TME	EDI		HQ		CR	
	Children	Adults	Children	Adults	Children	Adults
Hg	9.20E−06	9.86E−06	0.03	0.03		
Pb	1.00E−04	1.07E−04	0.02	0.03	8.50E−07	9.11E−07
Cd	4.40E−06	4.71E−06	0.01	0.02	2.77E−05	2.97E−05
As	3.60E−05	3.86E−05	0.36	0.39	5.40E−05	5.79E−05
Fe	6.83E−03	7.32E−03	0.01	0.01		
			∑HQ = 0.44	**∑HQ = 0.47**		

4. Discussion

Sediments are important habitats and food sources for benthic organisms [29]. When TMEs enter the food chain directly or indirectly, their contamination is likely to endanger human health and the ecological environment. Catfish are demersal species that feed in river sediments, which makes them bioaccumulative fish [12] [30]. The obtained concentrations show that the average concentrations of all elements are in line with the standards set [16]. However, 25.92% (7/27) of fish in the Cavally River had lead concentrations above the standard. The high iron concentrations in *Clarias nigrodigitatus* muscle tissue compared to other elements are due to the fact that iron is naturally abundant in the soils of the study area. These soils are the main source of trace metals in the waters from which these fish originate. Similar observations were made by [30] in *Clarias gariepinus* muscles from the Eko-Ende dam in Nigeria. These authors also found high concentrations of Fe relative to Pb, As, Cd, Cu, and Mn. They attributed these high concentrations to the geological nature of the area. Nevertheless, the concentrations obtained in the present study (11.76 - 25.68 $mg \cdot kg^{-1}$) remain within the same range as those reported by [31] (20.25 $mg \cdot kg^{-1}$).

The bioconcentration factors calculated for mercury, lead, cadmium, arsenic, and iron relative to sediments are less than one (BCF/sediments < 1) and greater than one relative to water (FBC/water > 1), indicating that fish concentrate trace elements in their muscles from the water column and not from sediments. Typically, the uptake of TME occurs primarily through water, sediment, and food [31]. However, the efficiency with which they are concentrated may differ depending on factors such as the ecological requirements and metabolism of the fish, and contamination gradients in water, feed, and sediment [32]. The same applies to salinity, temperature, and interacting agents. In the present study, TME were not concentrated in sediments or water. This suggests that they originate from the fish's feeding habits. Catfish are omnivorous, demersal species that feed in river sediments and are among the bioaccumulating fish [12] [30]. According to [33], demersal, or bottom-dwelling, fish can accumulate higher concentrations of trace elements than pelagic fish. Sediments are indeed recognized as real contaminant accumulators [34] [35]. This characteristic makes sediments a potential source of contamination for benthic organisms [29]. However, bioconcentration factors show that fish do not accumulate heavy metals from sediments. These results could be explained by the release of heavy metals into the water column from sediments as a result of gold panning activities. Some gold miners are located in the bed of the Cavally River, using dredges to suck up bottom sediments, wash them on the surface, and then dump them back into the watercourse. This practice therefore leads to a change in the morphology of the riverbed [14] and high turbidity in the Cavally River.

[36] highlighted the negative effects of dredging on the aquatic biodiversity of the Baoulé River in the rural commune of Kémékafo, Dioila region, Mali. These impacts are manifested by high turbidity in the Baoulé River and the disappearance of several aquatic species. No significant correlation was found between the physical parameters of the fish (weight, standard length and total length) and the various TMEs. This suggests that accumulation is not necessarily age-related [37]. Several studies have demonstrated a positive correlation between the size of fish and high mercury concentrations in gold mining areas of the Amazon [38]-[40]. According to [10], mercury concentrations in exposed fish tissues may increase as the fish grow, since mercury is excreted slowly. For these authors, therefore, fish age is linked to length. Consequently, older (larger) fish have been exposed to environmental contaminants for longer and must therefore bioaccumulate more contaminants. The concentrations of lead (Pb) (0.25 mg/kg), cadmium (Cd) (0.011 $mg\cdot kg^{-1}$) and iron (Fe) (17.07 $mg\cdot kg^{-1}$) obtained in fish from the Cavally River are well below the values reported by [30] in the muscles of the same species of fish from the Yakoyo River in Nigeria: 3.41 $mg\cdot kg^{-1}$ for Pb and 253.24 $mg\cdot kg^{-1}$ for Fe. The low TME concentrations obtained in muscle tissue are due to the fact that this organ is not active in the accumulation of TMEs [41] [42].

A health risk assessment was conducted by calculating non-carcinogenic risk (HQ) and carcinogenic risk (CR) values, which revealed HQ values all below one. This indicates that there is no risk of non-carcinogenic toxicity for the population consuming these fish in general. Similar HQ results were reported by [27] for other fish species in the Buriganga River in Bangladesh.

Conversely, four out of eleven samples (36.36%) collected from the Cavally River exhibited an As HQ greater than one. Consequently, the habitual ingestion of fish poses a potential hazard to the general population. Notwithstanding the fact that the hazard quotient ascertained in fish is less than 1, the trace metal concentrations obtained in fish muscles should serve as a clarion call regarding the repercussions of artisanal mining activities in the area.

The cancer risk has been determined for arsenic and cadmium, which are classified by [43] as carcinogens, and for lead, which is classified as a potential carcinogen. Thus, all CR values obtained for these three metals are within the acceptable limit by [29], for cadmium and arsenic ($10^{-6} \leq CR < 10^{-4}$) and not significant for lead ($CR < 10^{-6}$) in children and adults, suggesting that there is no potential risk of carcinogenesis from consumption of fish from the waters of the Cavally River. The present study is in the same range as that of [44] on tilapia muscles in the waters of the Cauvery River in India.

5. Conclusions

Analysis of the level of contamination of catfish in the waters of the Cavally River in the Ity mining area in the Zouan-Hounien department revealed average concentrations of mercury, lead, cadmium, arsenic, and iron, all in line with the guideline values recommended by the FAO/WHO for fish intended for human consumption. The health risk assessment also highlighted the potential impact of fish consumption on human health. The calculation of non-carcinogenic risk indices (HQ) and carcinogenic risk (CR) showed that the occurrence of non-carcinogenic and carcinogenic risk effects linked to fish consumption is excluded.

However, the presence of TME in fish flesh in the waters of the Cavally River is attributable to the intense gold-panning activities that take place in and around the riverbed.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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