Health risk assessment and levels of toxic metals in fishes (*Oreochromis noliticus* and *Clarias anguillaris*) from Ankobrah and Pra basins: Impact of illegal mining activities on food safety

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ABSTRACT

Arsenic (As), mercury (Hg), Cadmium (Cd) and lead (Pb) are toxic heavy metals that naturally occur in the ecosystem. Their levels are on the rise due to anthropogenic activities posing threat to aquatic wildlife and humans. In Ghana, pollution of some water bodies has led to unsafe consumption of riverine fishes as well as a shortage of treated potable water principally because the cost of treating polluted water has become expensive across the country. This study aimed to assess the As, Hg, Pb and Cd concentrations in water and fishes from rivers Pra and Ankobrah where activities of artisanal gold mining were carried out resulting in gross pollution of the water bodies.

An experimental study was performed to ascertain the levels of As, Hg, Pb and Cd in fish species of Nile tilapia (*Oreochromis noliticus*) and mudfish (*Clarias anguillaris*) and aquatic media (water) from the Pra and River Ankobrah basins using the Atomic Absorption Spectrophotometer (AAS) (Varian AA240FS).

Both river water samples recorded ranges of 0- 0.0040, 0.0060- 0.0387, 0 - 0.0020, 0.006-0.0093 mg/l for Cadmium, Lead, Arsenic and Mercury respectively. For Cadmium and Arsenic, their levels were comparable (p > 0.05). However, detected values for Lead and Mercury were no comparable (p < 0.05). Toxic metals concentrations in the rivers decreased in the order of Hg > Pb > Cd > As. For the fish samples, values ranged 0-0.08, 0.04-0.42, 0-0.04, and 0.40- 0.60 mg/kg for Cadmium, Lead, Arsenic and Mercury respectively. Generally, appreciably high values were obtained for Mercury. Toxic metals concentrations in the rivers decreased in the order of Hg > Pb > Cd > As.

Human health risk assessment from heavy metal exposure through fish consumption from the Rivers for both children and adults showed no significant non-carcinogenic adverse health risk to humans since all calculated values for Hazard Quotient (HQ) were < 1. Nonetheless, Target Hazard Quotient (THQ) values calculated for children and adult exposure to Cadmium and Mercury were > 1 which implied a likely cause of adverse effects during a person's lifetime.

1. Introduction

Water is one of the most vital elements of the ecosystem. The water resources promote development in socio-economic issues crucial to society in general and more specifically for industries, agricultural activities, and domestic use. In this 21 st century, the provision of clean drinking (potable) water for the growing population of the world is one of the most challenging issues humans have had to encounter [1].
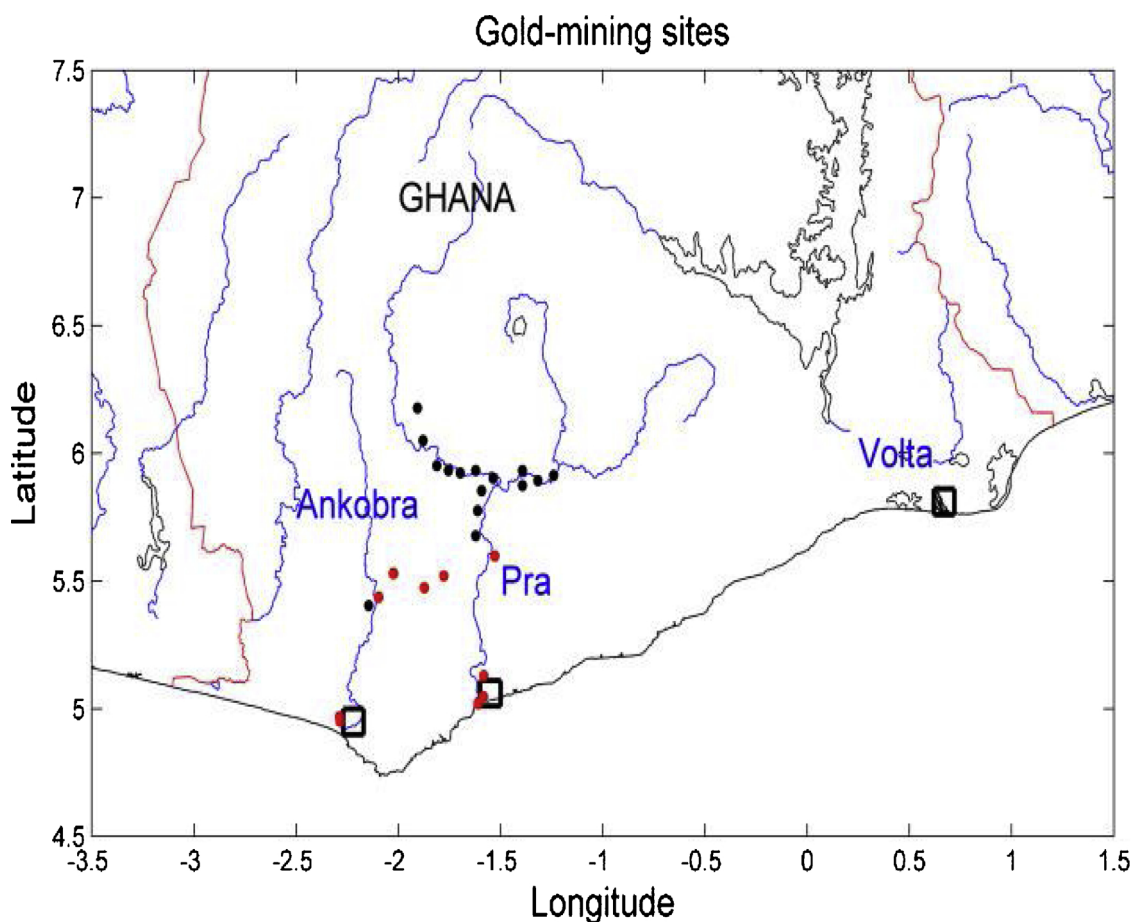

Fig. 1. Showing Rivers Ankobrah and Pra and its path of travel as it joins the Gulf of Guinea Note: Three sampling points along each river were taken and used. Colored dots represent sites of illegal mining activities. Scale: 1 cm to 15km.

Quality of water is predisposed by both biotic and abiotic factors. Except for the metals, man has created through nuclear reactions and other chemical processes, the others have existed on Earth since the formation of the planet [2]. Although there have some occurrences of local metal pollutions through natural weathering, in most cases, anthropogenic activities have caused metals to become an environmental health issue [3]. suggested activities of mining and smelting plants mainly, released metals from the bedrock to cause pollution. It is well acknowledged that natural processes likewise discharge or leachates from several anthropogenic activities are known causes of the incidence of heavy metals (HM) in aquatic environments [4].

Pollution due to heavy metals in the environment has universally become a challenge in this 21 st century because these metals are virtually indestructible while most of them are hazardous in aquatic systems [1]. Monitoring and evaluation programs as well as intensive research on heavy metals in the aquatic environment have become important due to concerns of over accumulation and toxic effects on aquatic organisms and eventually to humans through the food chain [4].

High levels of metals affect living organisms and pose considerable environmental risks [5,6,1]. Heavy metals can exist in sediments and freshwater systems for several years and this can affect human health and the environment [1,7]. In the evaluation of heavy metal (toxic) pollution, fish species are used as one of the indicators in freshwater systems [8]. Some metals such as Copper (Cu), Zinc (Zn), amongst others are essential because they play some roles in biological systems, conversely, others such as Cadmium (Cd) and Lead (Pb) are also non-essential metals which are needed by the human body in trace quantities but become toxic in unregulated quantities [9].

The increasing usage of Heavy Metals (HM) such as Arsenic and Mercury in the mining industry over the years has brought in its wake environmental pollution through effluents and emanation of grievous concern [11]. The main activities of the mining industries in Ghana are matters of concern as they negatively impact the environment. Their processing ore and methods of disposing of waste products are the main sources of HM pollution. Aquatic fauna and flora are easily destroyed by mine tailings which are left-behind in sedimentation ponds and accumulate for treatment. Unfortunately, these activities normally lead to the siltation of nearby water bodies usually by run-off. Eventual leach of elements like Lead, Cadmium, Iron, Mercury, Arsenic, Copper, Chromium, and Zinc from effluents, which then ends up polluting mainly underground water systems and occasionally rivers and streams [12]. Ingestion of HM such as mercury through food (fish and water) may expose one to respiratory, neurologic and psychological diseases [13].

According to FAO [10], illegal mining activities have adversely affected inland fishing activities due to pollution from these chemicals used in their mining activities. People living in the northern part of Ghana depend on these small streams and water bodies for fish supply because fisheries exploitation directly affects their employment, income, and also enhance the nutritional status of the local people living around these rivers and its catchment areas. Nonetheless, they no longer have sufficient fishes, so they have to rely on imported fishes because their water bodies have been messed up by illegal mining activities. Fish production from our "brackish" waters is eluding Ghana simply because they have become industrial waste reservoirs especially in Accra and other major cities.

Tilapia which is a species of fish is highly patronized in Ghana

owing to its delectable dishes they are used for. One such dish is "Banku" (a local dish prepared from gelatinized corn dough) and grilled tilapia served with chili pepper sauce is en vogue. Nonetheless, it is now unsafe to consume riverine tilapia due to heavy metal contamination arising from pollution by these mining activities.

The present study investigated the levels of toxic metals in water and fish samples obtained from the Pra and Ankobrah river basins. The human risk exposure to these toxic metals was also assessed.

2. Materials and methods

2.1. Study area and study design

An experimental study was undertaken to determine the concentration of heavy metals in fishes and aquatic media(water) from the Pra and Ankobrah river basins. This study was done in Southern Ghana (Ankobrah township) and River Pra in the Central Region in Ghana (Fig. 1).

The toxic metal analysis was of this work was carried out at the Chemistry Department of National Nuclear Research Institute, Ghana Atomic Energy Commission from January 2019 to May 2019.

Pra river is located in the easternmost of Ghana and is one of the most important. It is the largest of the three principal rivers that drain the area south of the Volta divide. The main tributaries are Offin, Anum and Birim rivers. The northern part was used for artisanal gold mining with metallic mercury, which is suspected to be contaminated. The geographical coordinates used in this study were Latitude 5° 01′8.87″ N and Longitude 1°37′33.53 W.

River Ankobrah is in southern Ghana. Rising Northeast of Sefwi-Wiawso and flows about 120 miles (190 km) south to the Gulf of Guinea west of Axim, the commercial center of the river basin.

The chief tributaries are the Mansi and the Bonsa rivers and much of its basin is shared with the Tano river to the west. Beposo was part of the study site because of artisanal gold and metallic mercury mining activities which cause some contamination. The geographical co-ordinates that were used for this study were 4°53′55″N 2°16′17W.

2.2. Sample collection

In total, 16 fish samples (2 different species) were collected from the local fishermen and used for the analysis of As, Hg, Pb, Cd. Water samples were collected from 3 locations along each river basin for analysis.

2.3. Sampling method

A simple random sampling technique was employed to collect fresh fish directly from the rivers by fishermen at the various landing sites of the study areas. The fishermen were contracted to catch fishes from the lower, middle and upper sections of the rivers of Pra and Ankobrah respectively. Water samples were also collected from sub surfaces of the same rivers.

2.4. Data collection, techniques, and tools

Fresh fish were obtained from the fishermen and were washed several times with distilled water and sorted into similar kinds/species. The sorted specimens were then packaged into plastic zip lock bags, labeled, transferred into a cooler with ice packs and finally transported to the laboratory for further treatment and analysis.

2.5. Digestion of samples

Fish samples were thawed at room temperature and cleaned with distilled water. One gram (1 g) of the skeletal muscle beneath the dorsal fin (epaxial muscle) of each individual weighed into an acid cleaned

vial and frozen at −20 °C. Dilute nitric acid was used to wash the materials used in cutting the muscles including the forceps and scalpel. The muscle tissues (1 g) were digested in concentrated nitric acid and hydrogen peroxide (BDH Laboratory Supplies, Poole England), homogenized and topped to 100 ml.

The calibration standards for Cd, Pb, As, and Hg were prepared, and together with the reagent blanks, subjected to same digestion procedure as the samples. Subsequently, the digested standards, reagent blanks, and samples were read at the wavelengths of 228.8 nm, 217 nm, and 193.7 nm using Varian Fast Sequential Atomic Absorption Spectrometer, model AA240FS for the determination of Cd, Pb, and As respectively in the samples. Acetylene gas was used as the carrier gas, for Cd, Pb, and As while inert argon was pass through the system to remove interfering gases between each reaction time. Cold vapor was used for Hg determination using 3% HCl in 1.1 % $SnCl_2$ and 3% HCl as the reductant at a wavelength of 253.7 nm

Ten milliliters (10 ml) portion of the water sample was transferred into a Teflon beaker. Solutions of HNO_3 (6 ml), concentrated HCl (3 ml) and H_2O_2 (1 ml) were added to the sample. The mixture was then digested for 40 min using the industrial microwave and complete digestion was indicated by a light-yellow color. Contents were washed down with distilled water. The filtrate was transferred into a 20 ml measuring cylinder and topped up to the 20 ml mark with distilled water before transfer into a test tube and allowed to cool down at room temperature for AAS analysis as described for the fish samples.

2.6. Human health risk assessment of heavy metals in fish

Different health risk estimation methods have been developed and used by some researchers [14–16] for the evaluation of the risk that the consumption of contaminated fish present to humans. The Estimated Daily Intake (EDI) is one method commonly used which helps to identify the number of pollutants consumed daily [17]. The EDI of potentially toxic elements (PTE) is directly proportional to the concentrations of PTE in the food and daily food consumption. Furthermore, human body weight has an important effect on the tolerance to contaminants [17]. Table 1 shows the tolerable limit of the heavy metals as prescribed by some international regulatory bodies.

2.7. Tolerable daily intake and estimated daily intake

The estimated daily intake (EDI) directly linked to the metal concentration, food consumption, and body weight. The following assumptions were made in this research to estimate the risk of heavy metals from fish consumption at the extreme; the ingested dose was equal to the absorbed pollutant dose [25]; cooking had no effect on the pollutants [26]; the average Ghanaians' adult body weight was 75 kg [27]; According to [27], the average daily consumption of fish in Ghana

Table 1
The tolerable values of some heavy metals in fish (mg/kg).
Source: [24]

Organization	Cd	AS	Hg (μg/kg)	Pb	References
UNEP	0.3			0.3	[18]
IAEA-407	0.18			0.12	[19]
TFC	0.05			0.2	[20]
Directive 2005/78/EC	0.05			0.2	[21]
FAO/WHO	0.5		0.5	0.5	[22]
JECFA		0.002	1.6		[23]

UNEP- United Nations Environmental Programme.
IAEA- International Atomic Energy Agency.
TFC- Turkish Food Codes.
EC- European Commission.
FAO/WHO- Food and Agriculture Organization/World Health Organization.
JECFA- Joint FAO/WHO Expert Committee on Food Additives.

Table 2

International guidelines of the toxic metal concentrations in water samples (mg/L).

Guidelines	Cd	AS	Hg	Pb	References
TSE- 266	0.005			0.01	[28]
WPCL	0.003			0.01	[29]
CIW	0.01			5	[30]
WHO	0.01		0.002	0.05	[31,22]
EPA	0.01			0.05	[32]
EC	5			10	[33]
OFJ –EC /GSA		0.025	0.05	0.0012	[34,35]

TSE- Turkish Standard Enstituso.

WPCL- Water Pollution Control Legislation.

CIW- Cevre II Wurdurlugu.

WHO- World Health Organization.

EPA- Environmental Protection Agency.

EC- European Commission.

OFJ-EC- European Commission (Regulation) Official Journal of the European Union.

GSA-Ghana Standards Authority.

is 74 g per day, and people living in the Ankobrah river basin would consume the same as Pra river basin. Therefore, the EDI of heavy metals for adults was calculated as follows:

$$EDI = \frac{CxCcons}{Bw} \qquad (1)$$

where C is the concentration of heavy metals in fish (mg/kg wet weight), C cons is the average daily consumption of fish in the local area (74 g/day Bw), and Bw represents the body weight (75 kg). Table 2 shows the international guidelines for each heavy metal.

2.8. Determination of target hazard quotient (THQ)

The THQ which is the ratio of the exposure dose to the reference dose (RfD), represents the risk of non-carcinogenic effects. If it is less than 1, the exposure level is less than the RfD. This points out the daily exposure at this level is not likely to cause conflicting effects during a person's lifetime, and vice versa. US EPA risk analysis [36] procedures were following in the dose calculations which were performed using standard assumptions from the combined. The model described by [26] was used for estimating THQ by the following equation:

$$THQ = \frac{EFrxEDtotxFIRxC}{RfDoxBwxATn}x10^{-3} \qquad (2)$$

Where; EFr is the exposure frequency (350 days/year); EDtot is the exposure duration (30 years); FIR is the food ingestion rate (g/day), while 10^{-3} is the unit conversion factor; C is the heavy metal concentration in fish (mg/kg wet weight); RfDo is the oral RfD (mg/kg day^{-1}); Bw is the average adult body weight (75 kg); and ATn is the average exposure time for non-carcinogens (365 days/year × number of exposure years, assuming 30 years).

2.9. Determination of hazard quotient (HQ)

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

where HQ is the hazard quotient and RfD is the reference dose (mg kg^{-1} day^{-1}). HQ values of < 1 signify unlikely adverse health effects, while HQ values > 1 indicate a likely adverse health effect.

2.10. Carcinogenic risk assessment

According to [37], carcinogenic risk assessment evaluates the

Table 3

Exposure parameters used for the health risk estimations via consumption of fish (US EPA, [37]).

Parameter	Unit	Child	Adult
Body Weight (BW)	Kg	15	75
Exposure Frequency (EF)	Days/ years	365	365
Exposure Duration	Years	6	30
Ingestion Rate (IR$_{fish}$)	mg/day	200	100
Average Time (AT)	Days/years		
For carcinogenic		365 × 70	366 × 70
For non-carcinogenic		365x ED	365x ED

likelihood of an individual developing cancer due to exposure to the potential carcinogen over a lifetime (Table 3).

In our estimations, a cancer slope factor was used to convert the EDI of the heavy metals over a lifetime exposure to the risk of an individual developing cancer [37].

Risk = Σ n, I = 1 EDI x CSF

CSF = Cancer Slope Factor

2.11. Determination of total target hazard quotient (TTHQ)

In this study, the total THQ was expressed as the arithmetic sum of the individual metal THQ values according to the method of [26]:

Total THQ (TTHQ) = THQ (toxicant 1) + THQ (toxicant 2) + THQ (toxicant n) (4)

2.12. Statistical analysis

Data of the elemental minerals are expressed as mean ± standard deviation (S.D.). Figures were plotted from data of mean ± standard deviation (S.D.) using Microsoft Excel for Windows 10. *P* values of less than α = 0.05 were considered significant.

3. Results

3.1. Heavy metals in water

The range of values recorded for the concentrations of toxic elements was generally low. Both river water samples recorded ranges of 0- 0.0040, 0.0060- 0.0387, 0 - 0.0020 and 0.006-0.0093 mg/l for Cadmium, Lead, Arsenic and Mercury respectively. For Cadmium and Arsenic, there was no significant difference (p > 0.05) observed in their concentrations. However, there were statistical differences (p < 0.05) observed for Lead and Mercury concentrations. Toxic metals concentrations in the rivers decreased in the order of Hg > Pb > Cd > As. Fig. 2 shows the concentrations of the heavy metals in each water sample

3.2. Heavy metals in fish samples from both rivers

For the mudfish samples, values ranged 0-0.08, 0.04-0.42, 0-0.04, and 0.40- 0.60 mg/kg for Cadmium, Lead, Arsenic and Mercury respectively (Fig. 3). Generally, appreciably high values were obtained for Mercury. There was no statistical difference (p > 0.05) observed between concentrations of Cadmium and Arsenic among all fish samples investigated. Furthermore, values (0.4 and 0.48 mg/kg) recorded for Mercury in mudfishes from both rivers, were comparable (p > 0.05). Lead concentrations in the fish samples from the Pra River were significantly (p < 0.05) higher than mudfish from the Ankobrah river. Toxic metals concentrations in the mudfish samples decreased in
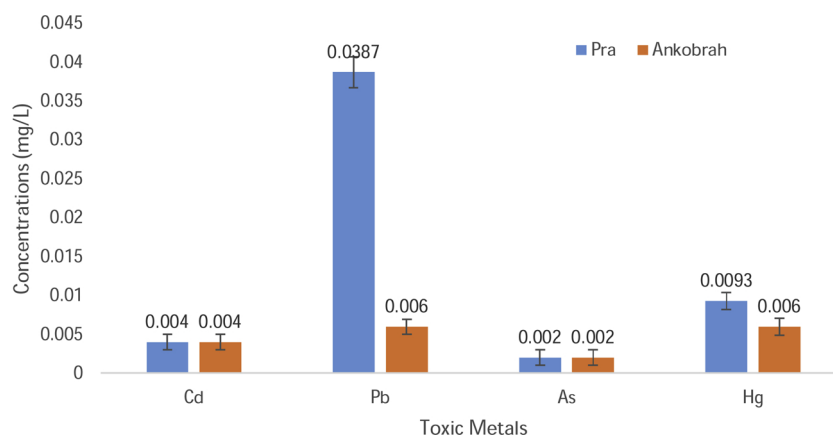
Fig. 2. Concentrations of toxic metals in rivers Ankobrah and Pra water samples. Mean ± standard deviation (n = 3).

the order of Hg > Pb > Cd > As. (Fig. 3)

A similar trend was observed in tilapia from the two rivers where there were no statistical differences (p > 0.05) observed in concentrations of Cd and As. Nonetheless, there were statistical differences (p < 0.05) recorded in Pb and Hg concentrations in tilapia from the two rivers (Fig. 4).

3.3. Risk assessment

Consumption of fish has many health benefits on humans such as protein-energy supplementation, a supply of some essential fatty acids as well as vitamins and minerals. Contrarily, if toxic substances are present in the fish, then their consumption can have detrimental consequences. The concentrations of Cd, Pb, and Hg determined in fish muscle tissue were compared to the maximum levels of these elements set by [38,39]. According to this research, the maximum concentrations of Cd, Pb, As and Hg in fish muscle tissues are 0.42 mg Pb/kgww, 0.08 mg Cd/kgww, 0.04 mg As/kgww and 0.5 mg Hg/kgww, respectively For Cd and Pb, these limit values were not reached in any sample.

The reference doses of the investigated metals were of range 1.0×10^{-3} - 3×10^{-4} and their corresponding cancer slopes are found in Table 4.

Table 5. shows the results obtained for the calculated EDI, HQ, THQ (both child and adult) for the two different fish species (*Oreochromis noliticus* and *Clarias anguillaris*) from the two river bodies (Ankobrah and Pra) ranged between 0.039- 0.5 mg/kg Bw/day. The Hazard Quotient values also ranged between 1.58×10^{-6} - 1.3×10^{-4}. Furthermore, Target Hazard Quotient values for children were of range 0.0340–5.114 while ranging 0.017–2.557 for adults.

Calculated values for the Total Target Hazard Quotient (TTHQ) for

adults who consume these fish species were greater than one (> 1) (Table 6). Values recorded for the tilapia fish species (*Oreochromis noliticus*) were 3.954 and 4.279 for the rivers Ankobra and Pra respectively. While for Mudfish species (*Clarias anguillaris*) recorded 4.79 and 4.279 for Ankobra and Pra respectively.

Cancer Risk assessment values calculated were not significant since it was below 1 (< 1) and ranged from 3.3×10^{-3}-0.0585.

4. Discussion

The obtained results of Cd, As, Hg and Pb concentrations in the water samples showed that they did not exceed limits set by WHO [31], EC [33], EPA [32], WPCL [29], CIW [30] and TSE-266 [28] guidelines (Table 2).

Cadmium concentrations for both river water samples were below the limits prescribed by CIW, WHO, TSE-266, EPA, and EC. Nonetheless, it was found to be slightly above limits set by WPCL. These concentrations were less than the 0.01 mg/l recommended by the WHO for drinking water [2].

Lead concentrations were found to be higher than limits set by WPCL, WHO, TSE-266 and EPA. Concentrations were however within limits of CIW and EC.

For Arsenic concentration levels in both rivers, they were found to be below-set limits (0.025 mg/L) [34,35]. Mercury concentration levels were also found to be below-set limits (0.05 mg/L) [34,35] but exceeding set limits for WHO [22].

In the criterions of the irrigation water report (CIW) given as a result of the Pra and Ankobrah River Basins study, maximum heavy metal concentrations allowed in irrigation waters have been aptly outlined by [30]. These values were compared with our results and it was found to
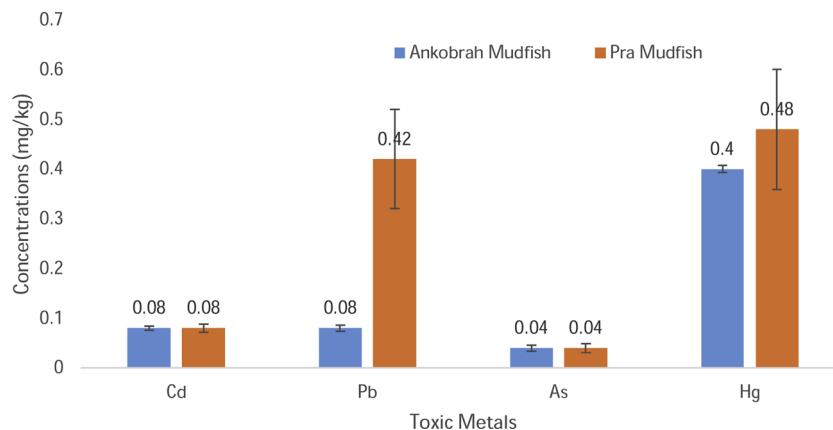

Fig. 3. Concentrations of toxic metals in mudfish from rivers Ankobrah and Pra (n = 3).
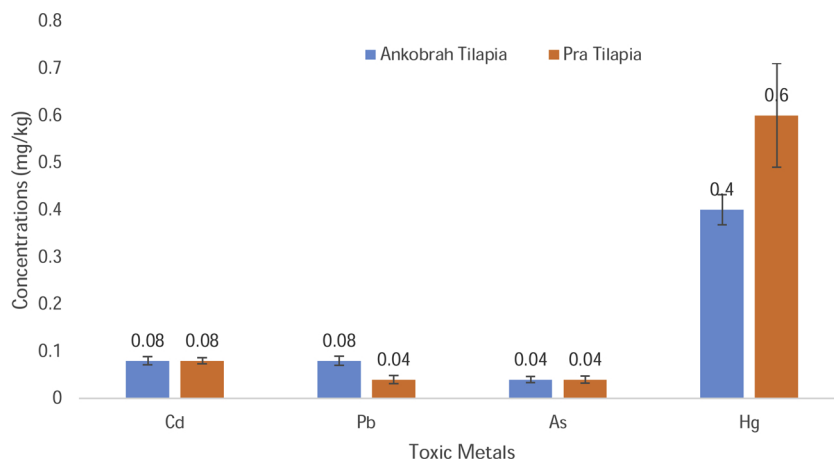
Fig. 4. Concentrations of toxic metals in Nile tilapia from rivers Ankobrah and Pra. Mean $\pm$ standard deviation (n = 3).

Table 4
Reference doses and cancer slope factors of some heavy metals.

Heavy metals	Reference Doses	Cancer slope factor	References
Arsenic	3.0×10^{-4}	1.50	[37,40]
Cadmium	1.0×10^{-3}	N/A	[40]
Lead	3.5×10^{-3}	8.5×10^{-3}	[37]
Mercury	3.0×10^{-4}	N/A	[41]

*NA- Not Available at the time of study.

Table 6
Estimated Total Target Hazard Quotient (TTHQ) of the two fish species from the rivers.

Fish specie	River	TTHQ
Tilapia	Ankobra	3.954
	Pra	4.279
Mudfish	Ankobra	4.79
	Pra	4.279

Table 5
The EDI and Hazard Analysis for carcinogenic risk evaluation expressed in mg/kg body weight/day for Tilapia and Mudfish from the two (2) rivers (Ankobrah and Pra).

Toxic Metal	Fish Type	River	EDI (mg/kg Bw/day)	HQ	THQ (child)	THQ (adult)	Cancer Risk
Cadmium	Mudfish (*Clarias anguillaris*)	Ankobrah	0.079	1.580×10^{-6}	4.091	2.046	N/A
	Nile Tilapia (*Oreochromis niloticus*)	Ankobrah	0.079	1.580×10^{-6}	4.091	2.046	N/A
	Mudfish (*Clarias anguillaris*)	Pra	0.079	1.580×10^{-6}	4.091	2.046	N/A
	Tilapia (*Oreochromis niloticus*)	Pra	0.079	1.580×10^{-6}	4.091	2.046	N/A
Arsenic	Mudfish (*Clarias anguillaris*)	Ankobrah	0.039	1.3×10^{-5}	0.340	0.170	0.0585
	Tilapia (*Oreochromis niloticus*)	Ankobrah	0.039	1.3×10^{-5}	0.340	0.170	0.0585
	Mudfish (*Claries anguillaris*)	Pra	0.039	1.3×10^{-5}	0.340	0.170	0.0585
	Tilapia	Pra	0.039	1.3×10^{-5}	0.340	0.170	0.0585
Lead	Mudfish (*Clarias anguillaris*)	Ankobrah	0.42	1.4×10^{-3}	0.358	0.179	0.0357
	Tilapia (*Oreochromis niloticus*)	Ankobrah	0.079	2.63×10^{-4}	0.068	0.034	6.7×10^{-3}
	Mudfish (*Clarias anguillaris*)	Pra	0.039	1.3×10^{-4}	0.034	0.017	3.3×10^{-3}
	Tilapia (*Oreochromis niloticus*)	Pra	0.039	1.3×10^{-4}	0.034	0.017	3.3×10^{-3}
Mercury	Mudfish (*Clarias anguillaris*)	Ankobrah	0.592	1.97×10^{-4}	5.114	2.557	N/A
	Tilapia (*Oreochromis niloticus*)	Ankobrah	0.394	1.31×10^{-4}	3.409	1.704	N/A
	Mudfish (*Clarias anguillaris*)	Pra	0.474	1.58×10^{-4}	4.091	2.046	N/A
	Tilapia (*Oreochromis niloticus*)	Pra	0.592	1.97×10^{-4}	5.114	2.557	N/A

TTHQ Ankobra Tilapia $= (2.046)Cd + (0.170)As + (0.034)Pb + (1.704)Hg$
$= 3.954$
TTHQ Ankobra Mudfish $= (2.046)Cd + (0.170)As + (0.017)Pb + (2.557)Hg$
$= 4.79$
TTHQ Pra Tilapia $= (2.046)Cd + (0.170)As + (0.017)Pb + (2.557)Hg$
$= 4.279$
TTHQ Pra Mudfish $= (2.046)Cd + (0.170)As + (0.017)Pb + (2.046)Hg$
$= 4.27$

contain slightly high concentrations. In this case, the water taken from Pra and Ankobrah is not proper for irrigation due to the tendency of bioaccumulation of these toxic elements by plants which will eventually end up in the food chain.

Arsenic (As) is a potentially toxic element that is present in the fish mostly as a consequence of its presence in the aquatic environment; As enters aquatic environments via the weathering of bedrock, but more often through anthropogenic origins [42]. Several health problems caused by chronic exposure to inorganic arsenic include; the gastro-intestinal and respiratory tracts, skin, liver, the nervous, cardiovascular and hematopoietic systems have been reported by [43]. Abiotic factors such as nature and intensity of pollution, alkalinity, water pH, temperature, as well as biotic factors such as size, age, feeding habits, and reproductive cycle all contribute to the degree of element accumulation in these fishes. Universally, arsenic leachate from geological sources is one of the most significant causes of As contamination of drinking water.

Suhendrayatna and Maeda, [44] reported that water living organisms can accrue the element As. Conversely, some researchers [45,46] found no bioaccumulation of As in some fish species (sterlet, northern pike, silver bream, and common carp). According to [46], concentrations of As in fish muscle tissue to a large extent reflects the water-soluble As concentrations.

Trace Arsenic residues were detected in muscle tissues of *Oreochromis niloticus* and *Clarias anguillaris* in this study. The concentration of As recorded in the muscles of examined fish species in this study were relatively lower than that reported by [1] (0.6 mg/Kg) and [47] (0.009 mg/Kg) wet weight in muscle tissues of *Oreochromis niloticus* from the Volta Lake, Ghana but contradicts findings of [48] who recorded values of 0.00 (nil) as mean As concentrations in muscle tissues of tilapia and mudfish species in Ala-river, Akure, Nigeria.

Variations in intensities of biotic as well abiotic factors could account for the differences observed. Furthermore, there is a likelihood of dissolved arsenic levels decreasing marginally from the upstream to the downstream. Also, studies conducted on some selected fish species recorded higher As levels from the "brackish" water environment towards the freshwater environment than in the marine environment. In line with this observation, [49] found low levels of HM in the marine environment along the coast of Ghana. Higher concentrations of As by [50] ranged from 0.80 to as high as 2.01 mg/kg in fishes including *Oreochromis niloticus* from the Tano river was linked to the assertion that fishes are better accumulators of As than Hg from both water and sediment. Arsenic has been classified by the International Agency for Research into Cancer (IARC) as a human carcinogen based on an increased incidence of cancers at sites where people are exposed to arsenic at work; in the environment or through their diet. Nonetheless, arsenic is also more acutely toxic than other metallic compounds. In both children and adults, recurrent low-level exposure to arsenic is linked with skin, vascular and nervous system disorders. Most of the arsenic in the diet is from fish and most of the arsenic in fish is in the less toxic organic forms.

For *Clarias anguillaris*, a range of 0.05 ± 0.01 – 0.15 ± 0.04 μg/g was reported by [51] from river Okpokwu, Apa in Nigeria. Skin lesions, malfunctioning of renal and reproductive systems have been linked to excessive intake of As [52]. Also [53], reported values of range 0.001–0.0469 mg/kg in mudfish from Laguna lakes in the Philippines.

Cadmium is among the toxic metals that have no known biochemical importance to humans [54]. The chief toxic effect of cadmium is its toxicity to the kidneys, although it has also been associated with lung damage (which includes induction of lung tumors) as well as skeletal changes in occupationally exposed populations. Cadmium is relatively poorly absorbed into the body, but once absorbed is slowly excreted, like other metals, and accumulates in the kidney causing renal damage.

In a related study, [22] recorded a range of 6.02 ± 1.03–11.05 ± 7.85 mg/kg wet weight for *Oreochromis niloticus* and *Heterotis niloticos* species from Ghana which were exceedingly higher than the stipulated limit (0.05 mg/kg) set by the European Union [55]. While [56] reported values of range 0.71–1.77 mg/Kg from Athi-Galana- Sabaki tributaries in Kenya. For mudfish [53], reported values of range 0.00241-0.30122 mg/Kg from Laguna lakes in the Philippines. Attributions to the high use of Phosphorus fertilizers as they contain several contaminants of which Cd is considered to be one of them has been made by [57]. Some fish species are also known to have bioaccumulative potentials for this toxic metal [58]. Diseases such as renal failure, osteoporosis, lung cancer and increased blood pressure [59] could arise from the consumption of fish with high concentration (> 0.05 mg/kg) of Cd and these will pose hazardous to humans… The concentrations for the examined fishes from the two rivers were also high in this study with concentrations as high as 0.08 mg/kg exceeding the guidelines set by [20] and that of Directive [21]. In a study by [60], they recorded a mean concentration of 0.02 μg/g of cadmium in the fish samples which was lower than the findings of this study. Variations in Cadmium levels could be attributed to the natural levels of its occurrence in the environment, the accumulation of Cadmium as a result of run-off water from events of agriculture involving some cultural practices such as land preparation, spraying crops with agrochemicals for the purposes of controlling weeds as well as pests and some other activities that wash off and empty into the river bodies. According to [60], fertilizers of phosphate base as well as other types contain averagely 13.4 μg/g of Cadmium which occurs as accumulation as fertilizers applied annually on farmlands. The concentration of Cadmium recorded for this study was lower than that reported by [61] of 0.24 mg/kg in *Hepsetus odoe* and *Tilapia zilli* along River Densu, Ghana. Ref. [2] highlighted that the estimated amount of Cadmium released into the environment naturally per year is about 25,000 tons while manufacturing and mining constitute human activities through which the rest are released [62]. Approximately half of this Cadmium is then released into rivers through weathering of rocks according to [2]. Disease conditions such as lung cancer, osteoporosis, and increased blood pressure may occur as a result of pollution of this kind [63]. The result of the present study could be an underlying factor for forecasting severe chronic Cd poisoning via the consumption of *Oreochromis niloticus* and *Clarias anguillaris* from the Ankobra and Pra river basins.

If proper measures are not taken and adhered to, to minimize the processing of gold ore into metallic gold as well as other activities such as illegal mining with the use of hazardous chemicals.

Mercury (Hg) is a globally known pollutant. However, of particular concern is MeHg, which can be converted from inorganic forms of Hg in aquatic ecosystems. Hg can enter freshwater ecosystems through atmospheric deposition or industrial wastewaters. Authman et al., [65] emphasized that the principal source of mercury and mercurial organic compounds in the environment are fungicides and organic fungicides respectively. It is noteworthy that mercury is associated with a wide spectrum of adverse health effects including damage to the central nervous system (neurotoxicity) and the kidney [27]. The main concern about the toxicity of mercury in the general population exposed to low levels of mercury in their diet relates to the potential neurotoxicity of organic forms of mercury in both children and adults.

Some degree of biological concentration likewise magnification of Hg has been reported in omnivorous and predator species. This is expected because it is well known that Hg concentration increases with fish age (size) and through the food web [66]. Lethal hepatotoxic, genotoxic as well as neurotoxic effects are some of the likely outcomes of the ingestion of elevated levels of Hg in fish [50]. During the development of the infants' brain, scaled-up intake of mercury is likely to disrupt its development, cause chest pains, shortness of breath, coughing up blood, paresthesia, and numbness in the hands and feet as symptoms mercury toxicity reported by [50]. Additionally, elevated levels of Hg result in irreversible damages, neurological impairment, lesions, behavioral and cognitive changes [27]. The concentration of mercury in this study exceeded the permissible limit of 0.5 mg/kg [67]. Results reported in this study agreed with findings of [27] who

recorded 0.56 $\pm$ 0.03 - 0.91 $\pm$ 0.91 mg/kg in as they studied the risk assessment of heavy metals in edible fish species(Tilapia) in the Barekese reservoir in Ghana. Their study attributed upsurge levels observed to artisanal Gold mining on River Offin and the use of Mercurial compounds in agricultural activities within the catchments of the reservoir. Abboah- Offei [68], reported Hg values of 0.341 and 0.388 mg/Kg for *Oreochromis niloticus* and *Clarias anguillaris* respectively in Ghana. Studies by [69] and [70] also showed low THg levels in muscle tissue of farmed tilapia in Sao Paulo (10–20 and 0.3–217 mg kg^{-1}, respectively). Botaro et al. [71] also reported values of 13.5–30.5 µg/kg of Hg in tilapia from Brazil. From the Philippines [53], reported Hg values of 0.00314-0.177 mg/kg for mudfish from Laguna lake. According to some previous researchers [72,71], total mercury (THg) concentrations may also be influenced by fish size likewise age and an overall increase with time.

Again, the presence of Pb in fish samples could be a consequence of anthropogenic activities, such as mining, chemical, and metal processing industries, refineries and urban runoff [73]. A relatively high concentration of 0.18 mg kg^{-1} of Pb was determined in the Danube roach, by [73]. The legislated regulations on permissible limits of Pb in fish according to the EU is 0.2 mg/kg wet weight. Concentrations of Pb were in a range of 0.04-0.4 mg/kg which exceeds the guidelines of [18,20] and [21] detected in the muscle tissues of *Oreochromis noliticus* and *Claries anguillaris* in this study. However, mean Pb concentration 0.8 $\pm$ 0.25 mg/kg wet weight recorded in *Oreochromis niloticus* exceeded the EU permissible limit. *Oreochromis noliticus* is aptly classified as benthopelagic species which feeds mainly on phytoplankton or benthic algae [74] hence its potential to biologically accumulate. The concentration of Pb recorded in this study was lower than the findings of [54] where a high Pb concentration of 6.82 $\pm$ 2.28 mg/kg was recorded in a study on concentrations of heavy metals in fish from the Fosu Lagoon in Ghana.

Van Aardt and Erdmann [75] reported Pb values of range 3.4-7.9 µg g^{-1} in mudfish from hard water dams in the Mooi River catchment in South Africa. From Nigeria, Abah et al. [51] also reported values of range 0.08 $\pm$ 0.03 µg/g - 0.34 $\pm$ 0.05 µg/g for *Clarias anguillaris* from river Okpokwu, Apa, Benue State. From the Philippines, [53] reported values that ranged from 0.007 to 4.41776 mg /kg in mudfish from Laguna lakes. Furthermore, Nzeve et al. [64] reported Pb concentration ranges of 0.643–1.078 mg/kg and 0.55-0.765 mg/kg for *Clarias gariepinus* and *Oreochromis spirulus niger* respectively from Masinga reservoir in Kenya.

Like mercury, Lead can accumulate in fish and shellfish and besides, can be found at higher levels in the offal (liver and kidney) of food animals. Children and adults eating diets rich in these foods may, therefore, be exposed to an unacceptable level of lead [76].

Increased reactive oxygen species (ROS) production leads to countless dysfunctions in the DNA, lipids, as well as proteins as emphasized by [65], are as a result of Lead depletion of sulfhydryl containing antioxidants and enzymes in the cell.

Consumption of *Oreochromis niloticus* from the Pra and Ankobra rivers could cause these dysfunctions.

4.1. Risk assessment

The results of human health risk assessment from Rivers Ankobrah and Pra are presented in Tables 1 and 2. Human health risk assessment of heavy metals in water showed that the estimated daily intake (EDI) for heavy metals in water from dermal and oral exposure was below the reference doses except for Pb which was greater than the reference dose for oral exposure. The THQ showed that for health risk through ingestion, Pb had the lowest THQ value while Cadmium and Mercury had the highest potential for risk with a value > 1 for both children and adults. Individual metals like Lead and Arsenic posed no health risk from their THQ values. Total Target Hazard Quotient (TTHQ) values were high (> 1) which suggested that Cancer risk was not high among all the metals investigated.

Recently, Ezemonye et al., [77] reported a summation of the individual THQs (TTHQ) values as above one (> 1) indicating possible health risk from the drinking of water from the Benin River in Nigeria. Calculated health risk through dermal exposure showed that Zn had the minimum THQ while Ni had the highest THQ. Individual THQs presented no possible health risk as they all had values < 1.

The results obtained in this study, disagreed with the published findings of Ezemonye et al., [77] as they recorded EDI values and THQ less than 1 (< 1) which suggested that no potential risks occurred from dermal exposure to water from Benin River. From their study, results of health risk assessments from consumption of shrimps and fish showed that the EDI values estimated for heavy metals in shrimps were below the reference doses which implied no potential risk while in fish only Pb recorded values above the reference dose. THQs of Pb were high in fish with a value of 1.93 which implied some likely health risks due to the presence of Pb. Amirah et al., [78] also reported values < 1 from their study of exposure through fish consumption from selected rivers in Kuatan. Compared to the present study, Krishna et al., [79] from their study of exposure through fish consumption in Andhra Pradesh India reported THQ values > 1 except for Cd which was < 1.

Yi et al., [80] also reported HQ values < 1 which suggested no injurious health effects of heavy metals on humans were discovered by consuming fish every day from the Yangtze River in China. Again, the total target hazard quotient (TTHQ) of 1.659 reported by them, exceeded 1 which implied the exposed population may encounter noncarcinogenic health risks from the aggregate effect of heavy metals they investigated.

Findings reported by Zhong et al. [81] demonstrated that the concentrations of heavy metals in the freshwater fish harvested from both central and eastern North China were relatively low, and did not cause significant human health risks.

From the results of our study, TTHQ values were > 1 (3.954–4.79) for both *Oreochromis niloticus* and *Clarias anguilaris* fish indicating potential risk from consuming fish and from Ankobrah and Pra Rivers. These current findings are a source of distress because of the potential health risk consequences from the intake of heavy metals through the consumption of water, fish and other similar aquatic organisms from the Ankobrah and Pra Rivers.

5. Conclusion

Toxic metals analysis showed that there were appreciable concentrations of Cadmium, Arsenic, Lead and Mercury in the two river water samples (Ankobra and Pra) as well as in the two fish species (*Oreochromis niloticus* and *Clarias anguillaris*) muscle tissues. All the examined fish species used in the study were within EU set limits, however, Hg exceeded the set limits of the WHO. Human health risk assessment from heavy metal exposure through fish consumption from the rivers for both children and adults showed no significant non-carcinogenic adverse health risk to humans since all calculated values for Hazard Quotient (HQ) were < 1. Nonetheless, Target Hazard Quotient (THQ) values calculated for both children and adult exposure to Cadmium and Mercury were > 1 which implied a likely cause of adverse effects during such a person's lifetime. Fishes (Nile tilapia) from Pra were above-set limits for human consumption hence is not safe for consumption. There was no cancer risk involved.

Education and awareness on the optimal levels of heavy metal in fish are crucial and such information must be made known to the public, to ensure that both nature and human health are in good harmony.

5.1. Limitations of this study

Although edible parts of the fish include the muscles, intestines, gills, and bones, data provided in this research article is on the muscles

of the fishes investigated which is the part principally consumed by Ghanaians. Also, lack of control river data as well as internal exposure data of children and adults were some of the limitations of this study.

Author statement

Authors declare that this research was carried out by all of us and we all agreed to its publication.

Authors' contributions

MEH, NKK and EKE performed the experiments and wrote the manuscript. NKK, MEH, NOB and FK were responsible for Toxic metal analysis. EKE, NKK, MA-A, NOB, PTA, SL, CT, and FK helped conceive the experiments and prepare the manuscript. NKK and MEH conceived the original study and NKK, MEH, SL and CT led the sampling and study in Ghana. All authors read and approved the final manuscript.

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