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Concentration of heavy metal in sediment, water, and fish from Ankobra and Tano River Estuaries, Ghana

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Abstract. *Awuah GK, Mensah JA, Fobil JN. 2020. Concentration of heavy metal in sediment, water, and fish from Ankobra and Tano River Estuaries, Ghana. Ocean Life 3: 94-101.* The heavy metals arsenic (As), mercury (Hg), and lead (Pb) are all poisonous and found in nature. The increase in their concentrations, however, is a result of human activities that pose a danger to both aquatic life and humans. The researchers set out to measure the levels of arsenic (As), hexavalent chromium (Hg), and lead (Pb) in sediment, water, and fish from the Ankobra and Tano Rivers in Ghana's Western Region. That was thought to be heavily polluted due to human activity, particularly artisanal gold mining. To assess the prevalence of As, Hg, and Pb in fish and the aquatic media (water and sediment) in the Tano of Jaway Wharf - Ellenda and Ankobra River of Sanwoma basins, an analytical cross-sectional study was carried out. The Atomic Absorption Spectrophotometer (AAS) Pinnacle 900T was used to determine the levels of As, Hg, and Pb in the tissues (muscles) of "Ekpoke" *Ctenopoma kingsleyae,* "Adwene" *Clarias gariepinus,* "Nzerma" *Pomadasys jubelini,* "Bile" *Parachanna obscura,* "Ekpoke" *Sarotherodon galilaues,* "Ekpoke" *Sarotherodon melanotheron,* and "Senzeke" *Parapenaeus longirostris* (n=53), water samples (n=30), and sediment samples (n=25) (Perkin Elmer, USA). STATA version 13 and the Excel spreadsheet from Microsoft version 10 were used for the statistical Analysis (StataCorps LP, Chicago, USA). Hg, As, and Pb levels were the highest in all the analyzed locations. In general, Hg (2.09 ± 1.29 mg/kg) and As (2.80 ± 1.52 mg/kg) were found in the highest amounts in fish, next by sediment (1.40 ± 1.78 mg/kg) and (0.61 ± 0.40 mg/kg), and water (0.09 ± 0.36 mg/L) and (0.06 ± 0.05 mg/L), respectively. Sediment (1.46 ± 4.26 mg/kg), water (0.14 ± 0.10 mg/L), and fish (0.11 ± 0.11 mg/kg) all had higher Pb concentrations than the other two. The total heavy metal variability in soil, water, and fish was not different (p=0.828, 0.570, and 0.978, respectively). Concentrations of As, Hg, and Pb in river water, sediment, and fish did not differ significantly between the Ankobra and Tano Rivers. Tano and Ankobra have As and Hg concentrations higher than those considered safe by the World Health Organization (WHO) for use in freshwater habitats.

Keywords: Arsenic, fish, lead, mercury, water

INTRODUCTION

There is widespread awareness about Heavy Metal (HM) exposure. It is the most pervasive environmental threat the mining industry poses worldwide. Water pollution endangers aquatic ecosystems, threatens food supplies, and harms human health (Akan et al. 2012; Ida 2012; Taylor 2012; Abualtayef et al. 2014; Retnaningdyah et al. 2014; Vikas and Dwarakish 2015; Krupnova et al. 2018; Laibu et al. 2018; Primadiani et al. 2018). Weathering of rocks and the subsequent conveyance of surface runoff and wind could naturally release heavy metals into aquatic systems. However, contamination of the environment, notably the aquatic environment, has grown due to human activities. The chemical composition of bedrock has been unlocked into water habitats due to the excavation of soil and minerals and the removal of enormous swaths of land for mining operations (Wuana and Okieimen 2011). Mining operations, such as rock crushing, may discharge heavy metals inside rocks into the surrounding environment. For instance, mining for gold (Au) often necessitates using poisonous chemicals like cyanide and mercury, which may wreak havoc on the ecosystem. In addition, the mining industry faces a significant environmental concern in the form of the waste produced after extraction (often referred to as tailing damp), which contains these harmful compounds and affects most countries and all mining sectors globally (Cobbina et al. 2015). Heavy metals from tailing damps are sometimes released into aquatic systems due to dike failure or the release of excess water from the tailing damp, both of which can happen accidentally or on purpose (Cobbina et al. 2015).

For people living in rural poverty, especially in Africa, Asia, and South America, rivers and streams are sometimes the only reliable supplies of drinkable water and household needs (Rijsberman 2006). However, introducing extra dissolved anions and cations causes water chemistry shifts, negatively impacting aquatic ecosystems. If aquatic organisms cannot endure the conditions or adapt physiologically, they will either be relocated or exterminated. Disruption of trophic levels and the consequent failure of aquatic ecosystems are the results. Because of this, communities dependent on the aquatic ecology within mining areas face food insecurity and health issues that can lead to malnutrition and extreme poverty (Falkenmark and Lundqvist 1998).

Mining is a major contributor to the seven-fold rise in heavy metal concentrations in the environment that has resulted from a confluence of human activity and climatic shifts. For example, researchers in Ghana have linked the continuous release of mercury (Hg), lead (Pb), arsenic (As), and cadmium (Cd), among other harmful and toxic metals, into aquatic habitats with gold mining activities (mineral exploitation, disposal of tailings and waste waters, ore transportation, smelting, refining) (Cobbina et al. 2015).

Increases in urbanization, agricultural runoff carrying fertilizers and pesticides, leaching from landfills, industrial and sewage effluents, and other human activities are all potential sources of heavy metal pollution of water and sediments (Akan et al. 2012; Sulardiono et al. 2018; Mwatsahu et al. 2020). Due to their inert nature, heavy metals remain in the aquatic environment indefinitely. They build up to toxic levels in the tissues of sedentary creatures like clams and are primarily found in sediments or are digested by microbes (Length 2011). Heavy metal accumulations in aquatic creatures often rise from lower to higher trophic levels. Proteins, minerals, vitamins, and omega-3 fatty oils can all be found in fish, making it an important part of a healthy diet for illness prevention and general well-being (Basim and Khoshnood 2013). Yet, fish may contribute to heavy metal pollution because of their natural bioaccumulation potential. Fish can accumulate heavy metals in their liver, gills, and bones, where they can remain for extended periods before being passed up the food chain to other animals, including humans (Asante et al. 2014).

Fish heavy metal contamination is related to pollution, diet, and sediments in the water. Because of their dual nature as pollutant "carriers" and "sinks," sediments help shape heavy metal contamination patterns in aquatic systems (Li 2014). However, the accumulation in fish varies on the mode of uptake, the kind of heavy metal, and the fish species. Therefore, due to these factors, fish is sometimes employed as a biomonitor to evaluate the environment's bioaccumulation and biomagnification of heavy metals (Begum et al. 2009).

Heavy metal pollution in fish increases the risk for various acute and chronic health problems (Anim-Gyampo et al. 2013). For example, evidence is mounting that toxicants including mercury (Hg), lead (Pb), arsenic (As), and cadmium (Cd) cause cognitive impairments, especially in children, as well as various cancers (with a disproportionately high rate of incidence in the upper gastrointestinal tract). In addition, toxicants could also weaken immune systems, malnutrition-related disabilities, fetal development retardation, kidney issues, reproductive disorders, skin lesions, vascular diseases, impaired psychological faculties, and endocrinological abnormalities (Cobbina et al. 2015).

While items like paints and agrochemicals are widely used and are known to contain heavy metals, regulations and control on the use of heavy metals are not adequately implemented in most developing nations. Despite being a member of the "International Convention on the Control of Trans border Movements of Hazardous Waste and their Disposal," or the "Basic Convention," Ghana has not yet enacted strict legislation governing the usage and disposal of hazardous waste (Dogbevi 2009). There are rules in place to restrict the use of trace metals, such as the Food and Drug Law (PNDC Law 305 B). However, they have not been properly applied. The Environmental Protection Agency (EPA) of Ghana established maximum contaminant levels (MCLs) for water sources as follows: 0.1 mg/mL for lead, ten micrograms per milliliter (mg/L) for zinc, ten micrograms per milliliter (mg/L) for iron, and 0.1 mg/mL for cadmium (Bannerman et al. 2003). Consequently, the purpose of this study was to evaluate the levels of arsenic, mercury, and lead in sediment, water, and fish from the Ankobra and Tano Rivers in the Western Region of Ghana. Those study locations where human activities, particularly artisanal gold mining, are thought to have significantly polluted the drainage systems.

MATERIALS AND METHODS

Study area

The research used two locations in the Ellembelle and Jomoro Districts of Western Ghana (Sanwoma and Jaway Wharf-Ellenda) (Figure 1).

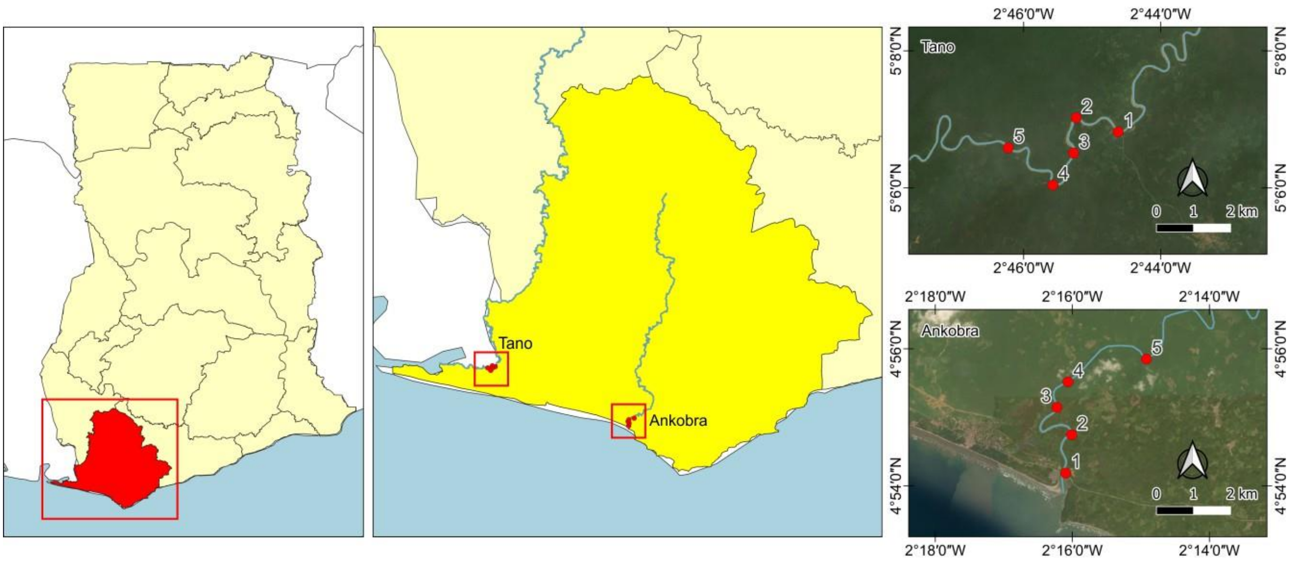

Figure 1. A map showing Tano and Ankobra Rivers Basins, Ghana

Figure 2. Ankobra River at Sanwoma (*left*) and Tano River at Ellenda Jaway (*right*), Ghana

Table 1. GPS coordinates

Point	GPS Coordinates			
	Ankobra		Tano	
	Latitude	Longitude	Latitude	Longitude
1	4° 54' 11.14" N	2° 16' 5.91" W	5° 6' 49.08" N	2° 44' 37.24" W
2	4° 54' 44.71" N	2° 16' 0.58" W	5° 7' 01.41" N	2° 45' 14.02" W
3	4° 55' 8.72" N	2° 16' 13.58" W	5° 6' 30.43" N	2° 45' 16.30" W
4	4° 55' 31.00" N	2° 16' 3.83" W	5° 6' 2.56" N	2° 45' 34.40" W
5	4° 55' 51.00" N	2° 14' 55.19" W	5° 6' 35.01" N	2° 46' 13.55" W

Sanwoma

The Ankobra River drains and forms the eastern border of Sanwoma. The Gulf of Guinea forms its southern border, while Asanta and Nkroful form its western and northern ones. As an estuary of the River Ankobra, fishing has long been the main source of income for the region. Additionally, there is some farming, albeit on a much lesser scale. The study region along the Ankobra River ran from 4° 54' 11.14" N, 2° 16' 5.91" W, to 4° 55' 51.00" N, 2° 14' 55.19" W in geographical coordinates.

Jaway Wharf-Ellenda

Jaway Wharf - Ellenda is a border town in the Tano River basin in the Jomoro District. People from around Ghana and Ivory Coast come here to trade items in the bustling markets. The Nzema communities of the Western area and other regions of the country rely heavily on tilapia caught in the Tano River, a key source of income for many locals. Tano River region coordinates ranged from 5°6'49.08" N, 2°44'37.24"W to 5°6'35.01"N, 2°46'13.55" W.

Variables of interest

Concentrations of heavy metals in fish, water, and sediments were the independent variables of interest.

Fish sample collection

Both freshwater and dark-water fish species were represented in the collection. Fifty-three (53) fish samples were gathered overnight in a trap set by local fishermen and analyzed for arsenic (As), mercury (Hg), and lead (Pb).

In the Ankobra and Tano Rivers, sediments were taken from five different spots (Figure 2). Fifteen sediment samples were taken from various points along the Ankobra River, with three replicates taken from each location (Figure 2). Additionally, for ten samples from the Tano River, two replicate sediment samples were obtained from each of the five sites or points across the river (Figure 2). Totally twenty-five (25) sediment samples were taken from the two rivers.

There were five sites on the Ankobra River at Sanwoma and on the Tano River at Jaway Wharf - Ellenda, where water samples were taken. There were a total of 15 water samples taken from each river, with three replicates taken at each of five locations throughout the river's length. Fifty-three (53) fish, thirty (30) water, and twenty-five (25) sediment samples were taken from the two rivers and studied.

Sampling method

A simple random sampling technique was employed to collect fresh fish directly from fishermen at the various landing sites of the study areas. Six fishermen were contracted to set up fish traps randomly overnight within the lower, middle, and upper sections of Rivers Ankrobra and Tano, respectively. Sediments were collected from each location using Ekman grab onboard a local canoe. Water samples were also collected from the sub-surface of the same area in the two rivers.

Data collection techniques and tools

As soon as the fishermen brought in their catches, they were cleaned and divided into species. The sorted samples were placed in plastic ziplock bags, labeled, and transported to the lab in a refrigerator with ice packs for further treatment and Analysis. The substrate was collected in labeled plastic bags and stored in a fridge with ice packs. A pre-cleaned acid-washed 250 mL sampling vial was used to collect the water samples. In addition, 1.5 mL of concentrated analytical-grade nitric acid was added to the water samples to acidify them (Apha 2008). Gamine eTrex GPS units were used to geo-reference the sample sites (Garmin Ltd, Schaffhausen, Switzerland). Table 1 shows the recorded GPS coordinates of the numerous sampling stations along the Ankobra and Tano Rivers.

Laboratory procedures

Thawed and identified using the FAO fish identification guide, the fish specimens were studied in the Department of Marine and Fisheries Sciences lab. Six fish families (Clariidae, Anabantidae, Cichlidae, Channidae, Haemulidae, Paenaediae) were represented in the Tano River, with a total of six fish species, including 'Ekpoke' *Ctenopoma kingsleyae* (Gunther, 1896); 'Ekpoke' *Sarotherodon galilaues (*Linnaeus, 1758*)*, 'Ekpoke' *Sarotherodon melanotheron* (Ruppel, *1852)*; 'Adwene' *Clarias gariepinus* (Burchell, 1822) and 'Bile' *Parachanna obscura* (Gunther, 1861).

Four distinct species were discovered in the Ankobra River. Because it is an estuary, the Ankobra was home to both freshwater and marine species. Among the freshwater animals were the "Adwene" *C. gariepinus (*Burchell, 1822) and "Bile" *P. obscura (*Gunther, 1861). However, 'Senzeke' *Parapenaeus longirostris* (Lucas, 1846) *and* 'Nzerma' *Pomadasys jubelini* (Cuvier, 1830) were the saltwater fish of choice. Analyses of mercury (Hg), arsenic (As), and lead (Pb) concentrations in fish (muscle), water, and soil sediments were performed at the Ecological Laboratory, Institute of Environment and Sanitation (ISA), the University of Ghana using an Atomic Absorption Spectrophotometer Pinnacle 900T (Perkin Elmer, USA).

Fish sample preparation

Fish samples were cleaned with de-ionized water to remove any remaining contaminants before having their muscles extracted and prepared for heavy metal analysis (Anim et al. 2011). (i) A macro-Kjeldahl digestion flask containing 5 g of fish was weighed, and then 20 mL of strong nitric acid and 20 mL of distilled water were added. By boiling the mixture, the volume was decreased to 20 mL; (ii) after the mixture had cooled, 10 mL of concentrated sulphuric acid was added and heated; and (iii) the mixture was again boiled after the addition of the concentrated acid. Next, nitric acid was added until the fish tissues were digested; (iv) after cooling, 10 mL of saturated ammonium oxalate solution was added and heated until abundant white fumes were created; the oxalate treatment helped remove the yellow coloration caused by nitro compounds such as lipids; (v) the solution was corrected to the 100 mL mark by adding distilled water; (vi) the solution was aspirated for heavy metals analysis using an Atomic Absorption Spectrophotometer Pinnacle 900T.

Nitric acid was added to distilled water and ammonium oxalate to make a blank solution for quality control. In addition to hydrogen peroxide, common oxidants include nitric acid, sulfuric acid, perchloric acid, and hydrochloric acid. As mentioned earlier, mixtures of two or more of the chemicals were suggested because of their combined benefits. Using a combination of oxidizing agents can potentially speed up the process greatly. Since less than 350°C is needed for oxidation, nitric acid can be utilized inexpensively. Moreover, there is less risk of element loss due to volatilization, and the process does not need constant monitoring.

Sediment sample preparation

Sediment samples were wet digested with a solution of nitric and perchloric acid, and then mercury, lead, and arsenic were aspirated using an atomic absorption spectrophotometer (Perkin Elmer Pinnacle 900T). (i) Sediment samples weighing between 0.2 and 1.0 g were weighed into a 125 mL Erlenmeyer flask after being oven-dried at 60°C to a constant; (ii) Under a fume hood, 10 mL of a ternary mixture was added (20 mL $HClO_4$; 500 mL HNO_3; 50 mL H_2SO_4); (iii) The materials were combined, then heated slowly on a hot plate at low to medium heat, all while being monitored by a perchloric acid fume hood; (iv) The sediment samples were digested until thick white fumes (sulfuric acid fumes) were produced; (v) After vigorously heating the mixture (between medium and high heat for half a minute), the liquid was cooled; (vi) 40 to 50 mL of distilled water were added, heated for thirty seconds, and then cooled; (vii) After filtering the resultant mixture into a 100 mL Pyrex volumetric flask, distilled water was added to get the volume up to the desired mark. Mercury, lead, and arsenic concentrations were measured in the stored solution.

Water sample preparation

Atomic absorption spectrometer Pinnacle 900T (Perkin Elmer, USA) was used to aspirate and analyze the acidified water samples for Hg directly, As, and Pb concentrations after they were mixed and agitated.

Quality control

Stringent quality control procedures were used to guarantee the reliability of the findings. After every ten samples were evaluated, a blank or duplicate was reanalyzed to verify precision and accuracy. All reagents and standard stock solutions were of analytical-reagent grade, and the instruments were calibrated using standard solutions of the various metals (Bortey-Sam et al. 2015).

Data processing and Analysis

The collected information was organized and analyzed using Microsoft Excel version 13 (Microsoft Corporation, Redmond, Washington, USA). The data in an Excel file was then transferred to STATA version 13 (StataCorp LP, Chicago, USA) for further statistical Analysis.

The data were summarized using means, standard deviations, ranges, p-values, and percentages. The data was tabulated and shown in bar charts and tables when necessary. The Kruskal-Wallis test was used to compare the concentrations of the samples. Parametric tests like the T-test and the Analysis of Variance (ANOVA) could not be utilized due to the nonparametric character or distribution of the data. Hence this test was employed instead. However, it resulted in highly skewed statistics. An in-text summary of the qualitative information was created. For a fair comparison with WHO-recommended values of heavy metals in fish, water, and sediments, mg/L concentrations were converted to mg/kg and mg/L.

Ethical considerations/issues

Before beginning the study, the researchers presented their plan to the Ghana Health Service's Ethics and Research Committee for approval. In addition, chiefs, fishermen, and assemblypersons from Sanwoma and Jaway Wharf-Ellenda were consulted for approval.

RESULTS AND DISCUSSION

The concentration of heavy metals in sediment

Sediment from the Tano and Ankobra Rivers was analyzed for the average quantities of arsenic, mercury, and lead, and the results are shown in Table 2. Tano had heavy metal concentrations of Pb (2.75 ± 6.68 mg/kg) > Hg (1.09 ± 0.73 mg/kg) > As (0.47 ± 0.29 mg/kg), while Ankobra had heavy metal concentrations of Hg (1.59 ± 2.21 mg/kg) > As (0.71 ± 0.46 mg/kg) >Pb (0.59 ± 0.30 mg/kg). Ankobra sediments had greater mercury concentrations (1.59 ± 2.21 mg/kg) than Tano sediments (1.09 ± 0.73 mg/kg). However, the difference was not statistically significant (p=0.828). Ankobra samples contained 0.71 0.46 mg/kg of arsenic, while Tano samples contained 0.47 ± 0.29 mg/kg. Again, no appreciable variations in water level were observed between the two rivers.

The concentration of heavy metals in water

The mean concentration of As, Hg, and Pb in water samples from the Tano and Ankobra Rivers are shown in Table 2. The mean concentration of heavy metal in water from Tano was in the order; Pb (0.11 ± 0.07 mg/L) > As (0.07 mg/L) > Hg (0.01 ± 0.01 mg/L), and Hg (0.15 ± 0.47 mg/L) > Pb (0.15 ± 0.11 mg/L) > As (0.06 ± 0.06 mg/L) in the Ankobra River. Higher levels of Hg were measured in water from the Ankobra (0.15 ± 0.47 mg/L) than in Tano River (0.01 ± 0.01 mg/L), although the difference was not statistically significant (p=0.680). Low but detectable levels of As were measured in water samples from Tano (0.07 mg/L) and Ankobra (0.06 ± 0.06 mg/L), respectively. The mean concentration of Pb in water samples from Ankobra (0.15 ± 0.11 mg/L) was slightly higher than that of Tano River (0.11 ± 0.07 mg/L), suggesting that Pb pollution in Ankobra water could be of much more concern than the levels determined in the Tano River. However, the two rivers had no significant difference (p=0.680).

The average levels of arsenic, mercury, and lead found in river water samples from the Tano and Ankobra are listed in Table 2. Tano's water had a mean heavy metal value of 0.11 0.07 mg/L for lead, 0.07 0.01 mg/L for arsenic, and 0.01 0.01 mg/L for mercury, whereas the Ankobra River's heavy metal concentrations were 0.15 0.47 0.11 0.06 mg/L for mercury, arsenic, and lead, respectively. Despite the lack of statistical significance (p=0.680), Hg concentrations in Ankobra water were higher (0.15 0.47 mg/L) than those in Tano River water (0.01 0.01 mg/L). Tano and Ankobra water samples contained measurable quantities of As (0.07 mg/L and 0.06 0.06 mg/L, respectively). Because the mean concentration of Pb in Ankobra water samples was 0.15 0.11 mg/L, and the mean concentration of Pb in Tano River water samples was 0.11 0.07 mg/L, the contamination of Pb in Ankobra water may be more of a problem than the levels determined in the Tano River. Still, comparing the two rivers, there was no discernible change (p=0.680).

The concentration of heavy metals in fish

Overall, the mean concentration of Hg, As, and Pb in the Tano and Ankobra Rivers were; (2.72 ± 1.36 mg/kg), (3.36 ± 1.52 mg/kg) and (0.12 ± 0.10 mg/kg) and (1.45 ± 1.21 mg/kg), (2.15 ± 1.54 mg/kg), and (0.10 mg/kg) respectively as shown in Table 2. Although fish from Tano had relatively higher heavy metal levels, there was no statistical difference in heavy metal levels between the two rivers.

The concentration of heavy metals in different fish species

The concentration of Hg in the different fish species from the Tano was; "Ekpoke" *S. melanotheron* (3.71 ± 2.01 mg/kg) > "Bile" *P. obscura* (2.96 ± 0.80 mg/kg) > "Adwene" C. *gariepinus* (2.66 ± 1.02 mg/kg) > "Ekpoke" *C. kingsleyae* (2.51 ± 1.28 mg/kg) > "Ekpoke" *S. galilaues* (1.73 ± 1.14 mg/kg) whereas As was in the order; "Ekpoke" *S. galilaues* (3.86 ± 1.29 mg/kg) > *"Bile "P. obscura* (3.54 ± 1.68 mg/kg)> *"Adwene" C. gariepinus* (3.48 ± 1.78 mg/kg) > "Ekpoke" *S. melanotheron* (2.86 ± 1.97 mg/kg) > "Ekpoke" *C. kingsleyae* (2.72 ± 1.33 mg/kg) as shown in Table 2.

There was no statistically significant difference between the variability of mercury and arsenic levels across fish species (p=0.524 and 0.8250, respectively). Hg levels in Ankobra River fish varied as follows: "Senzeke" *P. longirostris* (2.32 ± 1.95 mg/kg) > "Nzerma" *P. jubelini* (1.24 ± 0.48 mg/kg) > "Adwene" *C. gariepinus* (1.08 ± 0.69 mg/kg)> "Bile" *P. obscura* (0.98 ± 0.86 mg/kg) and that of As was in the order of "Adwene" *C. gariepinus* (2.22 ± 2.22 mg/kg) > "Senzeke" *P. longirostris* (2.07 ± 1.04 mg/kg) > "Bile" *P. obscura* (2.71 ± 1.38 mg/kg) > "Nzerma" *P. jubelini* (1.73 ± 1.70 mg/kg). There was no statistically significant variation in Hg levels between fish species in the Ankobra River (p=0.7200). As demonstrated in Table 2, As levels were higher than Hg levels for three of the four fish species sampled from the Ankobra, except for the "Senzeke," *P. longirostris*.

Comparative analysis of fish heavy metal concentration from fresh and brackish water in the Ankobra Estuary

Table 3 shows the concentrations of Hg (1.78. ± 1.21 mg/kg) and (1.03 ± 0.77 mg/kg), and As (1.90 ± 1.36 mg/kg) and (2.47 ± 1.81 mg/kg) in brackish and freshwater fishes from the Ankobra Estuary. The levels of Hg in brackish water were higher than those in freshwater, but the levels of As in freshwater were higher. On the other hand, neither estuary water type showed significantly different heavy metal concentrations (p= 0.338 and 0.621, respectively).

Comparative Analysis of heavy metal concentration in sediment, water, and fish from the Tano and Ankobra Rivers

Table 4 compares the heavy metal concentrations in the sediment, water, and fish of the Tano and Ankobra Rivers.

Table 2. Mean concentration, standard deviation, and p-values of mercury, arsenic, and lead in sediment, water, and fish from the Tano and Ankobra Rivers, Ghana

Source	Mercury concentration			Arsenic concentration			Lead concentration		
	Mean	SD	p-value	Mean	SD	p-value	Mean	SD	p-value
Sediment (mg/kg)									
Tano	1.09	0.73	0.828	0.47	0.29	0.570	2.75	6.68	0.978
Ankobra	1.59	2.21		0.71	0.46		0.59	0.30	
Water (mg/L)									
Tano	0.01	0.01	0.680	0.07	*	0.527	0.11	0.07	0.610
Ankobra	0.15	0.47		0.06	0.06		0.15	0.11	
Fish (mg/kg)									
Tano									
Ctenopoma kingsleyae	2.51	1.28		2.72	1.33	0.825	0.1194	0.1014	
Sarotherodon galilaeus	1.73	1.14		3.86	1.29		ND	ND	
Clarias gariepinus	2.66	1.02	0.524	3.48	1.78		ND	ND	NA
Parachanna obscura	2.96	0.80		3.54	1.68		ND	ND	
Sarotherodon melanotheron	3.71	2.01		2.86	1.97		ND	ND	
All species	2.72	1.36		3.36	1.52		0.1196	0.1014	
Ankobra									
Pomadasys jubelini	1.24	0.48		1.73	1.70	0.749	ND	ND	
Parapenaeus longirostris	2.32	1.95		2.07	1.04		ND	ND	
Clarias gariepinus	1.08	0.69	0.720	2.22	2.22		ND	ND	NA
Parachanna obscura	0.98	0.86		2.71	1.38		0.1024	*	
All species	1.45	1.21		2.15	1.54		0.1024	*	

Note: * Only one value recorded

Table 3. Shows the average levels of mercury and arsenic found in brackish and freshwater fish caught in the Ankobra River Estuary (Ghana), together with their standard deviations and p-values

Source	Mercury concentration (mg/kg)			Arsenic concentration (mg/kg)		
	Mean	SD	p-value	Mean	SD	p-value
Ankobra						
Blackish	1.78	1.21	0.338	1.90	1.36	0.621
Freshwater	1.03	0.77		2.47	1.81	

Table 4. Shows the average concentrations, standard deviations, and p-values of mercury, arsenic, and lead in sediment, water, and fish from the Tano and Ankobra Rivers, Ghana

Source	Mercury concentration			Arsenic concentration			Lead concentration		
	Mean	SD	p-value	Mean	SD	p-value	Mean	SD	p-value
Tano and Ankobra			0.828			0.570			0.978
Soil (mg/kg)	1.40	1.78		0.61	0.40		1.46	4.26	
Water (mg/L)	0.09	0.36		0.06	0.05		0.14	0.10	
Fish (mg/kg)	2.09	1.29		2.80	1.52		0.11	0.11	

The mean concentrations of Hg and As, overall, were highest in fish (2.09 ± 1.29 mg/kg) and (2.80 ± 1.52 mg/kg), next by sediment (1.40 ± 1.78 mg/kg) and (0.61 ± 0.40 mg/kg), and water (0.09 ± 0.36 mg/L) and (0.06 ± 0.05mg/L) respectively. On the other hand, the highest lead levels were in sediment (1.46 ± 4.26 mg/kg), next by water (0.14 ± 0.10 mg/L) and then fish (0.11 ± 0.11 mg/kg), respectively. However, the variability of overall heavy metal levels in sediment, water, and fish was not significantly different (p=0.828, 0.570, and 0.978, respectively).

In terms of mean concentrations, Hg and As were found to be most abundant in fish (2.09 ± 1.29 mg/kg) and (2.80 ± 1.52 mg/kg), then in sediment (1.40 ± 1.78 mg/kg) and (0.61 ± 0.40 mg/kg), and finally in water (0.09 ± 0.36 mg/L) and (0.06 ± 0.05mg/L). The sediment (1.46 ± 4.26 mg/kg) had the highest lead content, followed by the water (0.14 ± 0.10 mg/L) and the fish (0.11 ± 0.11 mg/kg). There was no statistically significant difference, however, between the sediment, water, and fish in terms of overall heavy metal variability (p=0.828, 0.570, and 0.978, respectively).

Discussion

This research aimed to quantify arsenic, mercury, and lead concentrations in sediment, fish, and water samples collected from the Ankobra and Tano River basins in Ghana's Western Region. Mining has occurred in the region between the Tano and Ankobra basins at least as far back as the 15th century, as reported by Akabzaa and Darimani (2001); as a result, industrial effluent, including heavy metal, is likely to flow into the streams that feed the Tano and Ankobra River. Comparisons were made between the heavy metal concentrations in aquatic medium and fish and previous findings, as well as the USA EPA, WHO, and US FDA standards and recommendations.

Generally speaking, the mean levels of mercury and arsenic were found to be at their highest in fish; (2.09 ± 1.29 mg/kg), (and 2.80 ± 1.52 mg/kg), respectively. It was followed by sediment; (1.40 ± 1.78 mg/kg), (0.61 ± 0.40 mg/kg), respectively, with water recording the lowest concentrations of mercury and arsenic; 0.09 ± 0.36 mg/L), (0.06 ± 0.05 mg/L), respectively. On the other hand, the lead concentration was highest in the sediments (1.46 ± 4.26 mg/kg), while it was about the same in the water (0.14 ± 0.10 mg/L) and the fish (0.11 ± 0.11 mg/kg) (Table 4).

Consistent with the notion that living things (biota) are exceptional at storing trace elements (Anim-Gyampo et al. 2013). Since fishes are known to bioaccumulate harmful metals, the higher levels of As and Hg detected in fish tissues, compared to sediment and water, are not surprising (Voegborlo and Adimado 2010). The fact that Pb has a higher affinity for sediment may explain why it is found in higher concentrations in sediment than in fish and water (Abouelnasr 2009). Tano appears to be more polluted than the Ankobra River, as evidenced by the greater levels of As and Hg in Tano fish than in Ankobra fish (Table 2). These results are in line with those found by Adjei-Kyereme et al. (2015), who discovered increased heavy metal concentrations in the Tano River and concluded that the presence of so many tributaries to the Ankobra River could be to blame for the apparent lack of a heavy metal concentration gradient between the two rivers. Both the As and Hg concentrations were higher than what is considered safe by the Australian and British governments (recommended level: 1 mg/kg; Neff, 1997; Edmonds and Francesconi, 1993) and the United States Food and Drug Administration (1.0 mg/kg mercury for fish and shellfish).

As levels in fish tissues were found to be highest in the "Bile" *P. obscura*, followed by the "Adwene" *C. gariepinus*, the "Senzeke" *P. longirostris*, and finally the "Nzerma" *P. jubelini*, among the various fish species found in Ankobra. *P. longirostris* and *P. jubelini* are diadromous species and thus do migrate between estuarine and marine environments. That is also reflected in increased As levels from the "brackish" water environment towards the freshwater environment. Voegborlo and Adimado (2010) also observed low concentrations of heavy metal in the marine environment off the coast of Ghana. Therefore, these findings are consistent with theirs. On the other hand, *P. obscura* and *C. gariepinus* are strictly freshwater species. Accordingly, it indicates that As contamination is higher in the Ankobra's freshwater section than in its brackish water section. The Hg concentrations in fish tissues, on the other hand, are highly variable and without any discernible trends. Being a demersal fish species (feeding on detritus), *P. longirostris* may have a high Hg concentration because of its relationship with sediment, which may contain high amounts of mercury (Johnston and Battram 1993).

As before, the arsenic (As) levels in fish tissues were frequently higher than the Hg values observed in Table 2 from the Tano River. A possible explanation is that fish absorb As from water and sediment more efficiently than Hg (Wayah and Gadima 2015). As a result, the As and Hg concentrations in the Tano River were significantly higher than the federal guidelines for safe exposure.

Table 2 shows that the levels of As (0.06 ± 0.06 µg/L), Hg (0.15 ± 0.47 µg/L), and Pb (0.15 ± 0.11 µg/L) in Ankobra's water were greater than those found in Tano with As (0.07 µg/L), Hg (0.01 ± 0.01 µg/L) and Pb (0.11 ± 0.07 µg/L). One possible cause is the influx of highly contaminated effluent from gold mining activities, especially artisanal (Galamsey) gold mining, into the Ankobra River basin via its many tributaries. In addition, the contaminated Hg levels were significantly higher than the acceptable threshold for both drinking water (2 µg/L) (WHO 2004) and pristine freshwater ecosystem (0.005 µg/L) (ATSDR, 1997). meanwhile, As (arsenic) concentrations were far higher than the safe limit of 50 g/L set by the World Health Organization (IPCS/WHO 1992).

Pb concentrations in sediments were found to be greater in Tano (2.75 ± 6.68 mg/kg) than in Ankobra 0.59 ± 0.30 mg/kg), although Hg and As concentrations were just slightly higher in Ankobra (Table 2). But the average levels of Hg, As, and Pb in the sediments of the two rivers were not significantly different from one another (p=0.828, 0.570, and 0.978, respectively). Adjei-Kyereme et al. (2015) found the same for Hg in the Tano and the Ankobra.

Since many of the fish used for human consumption in Ghana are taken in the Ankobra and Tano Rivers, the results of this study showing Hg, As, and Pb levels beyond the acceptable threshold from both study locations are somewhat worrying. Extreme neurotoxic and genotoxic consequences have been linked to the high amounts of Hg in fish (Hibbeln et al. 2007). In addition to causing symptoms like chest pain, shortness of breath, coughing up blood, paresthesias, and numbness in the hands and feet, a high mercury intake can slow down a baby's brain development. In addition, eating mercury-tainted foods can negatively affect the digestive system and lead to renal damage (Järup 2003). Increased toxicity from Hg has been linked to various negative outcomes for fish, including stunted growth and development, aberrant behavior, blood chemistry changes, decreased oxygen exchange, and even mortality (Folmar 1993).

A higher risk of skin cancer and other skin diseases, including hyperkeratosis and pigmentation alterations, has also been related to As contamination in food consumed at more than acceptable levels. A recent review by the World Health Organization (2004) found that exposure to arsenic in drinking water is causally linked to lung, kidney, bladder, and skin cancers, the latter of which is preceded by easily detectable precancerous lesions. These findings raise the possibility that exposure to environmental arsenic contributes to the development of Buruli ulcers (Gyasi et al. 2012). In addition, cancers of organs other than the lungs, bladder, kidneys, and skin are supported by data, as are hypertension and cardiovascular disease (Järup 2003).

Acute lead poisoning symptoms include headache, irritability, abdominal discomfort, and other symptoms connected to the nervous system, and they have been linked to exposure to greater Pb levels. Lead encephalopathy can cause severe symptoms such as acute psychosis, confusion, lowered consciousness, insomnia, and irritability. In addition, affected children may have trouble paying attention in class and displaying appropriate behavior. In mild cases, anemia due to disruption in hemoglobin production is the most noticeable symptom of lead poisoning.

Overall, the study found that the Ankobra and Tano Rivers, known to flow through several industrial and artisanal mining regions, contain heavy metal loads above the World Health Organization's (WHO) recommenced values for sediment, water, and fish. The mean levels of As, Hg, and Pb in the Tano River were higher than those in the Ankobra River. Because of this, Tano River sediment contains more metals than Ankobra River sediment. Since these heavy metals are regarded as toxic and can cause poor health of fish and other aquatic species, the health of aquatic life in these rivers is at risk. Communities' health that relies on these water sources for drinking, bathing, and other purposes are similarly threatened.

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