

Original Research Paper

Heavy Metals Pollution of Owerri and Asuokofi Rivers in Konongo, Ghana

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Article history

Received: 16-04-2021

Revised: 22-05-2021

Accepted: 03-06-2021

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Abstract: The effects of polluted water and soil resulting from anthropogenic activities have impacted negatively on the livelihood of both human and animal existence. A thorough study was therefore required to ascertain the extent of pollution caused by the undertakings of these anthropogenic activities particularly within the Asante Akim Central Municipality of Ghana. This study assesses the dispersions and the extent of heavy metal pollution within the Owerri and Asuokofi Rivers in the study area. Fourteen water and sediments samples were collected in fourteen locations from the upstream of two Rivers; Owerri and Asuokofi. The samples were collected and poured in clean (sterilised) plastic bottles. A Geographical Positioning System (GPS) “Garmin 62SC” was used to take coordinates for each of the sampled points using WGS 84 as the baseline. Collected samples were digested and analysed for Hg, Pb, As and Cd levels using Inductively Coupled Plasma Mass Spectrometry. The levels of Pb, Hg, As and Cd in the water samples were in the ranges of 0.8-9.5, 0.6-3.5, 0.02-51 and 0.2-5.2 µg/L respectively and that of sediments ranged between 7-89, 0.06-9.2, 10-998 and 0.1 -42 mg/kg respectively. The results showed that the levels of all the metals in water and sediment samples exceeded the World Health Organization (WHO) recommended levels in water and sediment.

Keywords: Heavy Metals, Illegal Mining, Contaminants and Water Quality

Introduction

Pollution of the environment, particularly water bodies has become a growing concern to governments all over the world (Inyinbor Adejumo *et al.*, 2018). Various anthropogenic activities such as illegal mining, deforestation, land-use and land cover changes among others are some of the key contributing factors of pollution of water bodies (Khatri and Tyagi, 2015). According to World Health Organisation (WHO) and the United Nation Children’s Fund (UNICEF) report (2013), access to improved drinking water sources Haiti has declined in the last 25 year; and the access on-premises to improved water has also decreased from 15 to 7%. About 24% of the rural populace drinks contaminated water in Ecuador; 21% of children are stunted and 18% are underweight (Andres *et al.*, 2018). Bangladesh has E-coli present in about 80% of water taps sampled and a similar rate collected from rivers and ponds (Hasan *et al.*, 2019). In Indonesia, only 5% of urban water is safe to be treated and supplied to consumers (kooy *et al.*, 2018). In

Nigeria, over 60% of the rural populace live more than 30 min away from a good water source. In Ghana, about 60% of water bodies are polluted with most of them in critical conditions (Ampomah, 2017).

The pollution of water bodies has caused a devastating impact on the livelihood of various countries and communities around the world. Biodiversity and aquatic ecosystems are affected as a result of the pollution of water. Sometimes the colour of the water is changed with an increase in the mineral content of the water (eutrophication), which adversely impact on the life of the water. The drinking or being in contact with polluted water may result in the contraction of certain diseases such as diarrhea, cholera, typhoid and dysentery or skin infection. According to Fiedler *et al.*, (2019), to attain the Sustainable Development Goals (SDG) on access to safely managed water by the year 2030, countries must spend \$150 million a year. This is due to the excessive pollution of freshwater bodies.

Mining which is the extraction of minerals from the earth’s crust makes a great impact on the landscape,

environment and the surrounding communities of the earth especially surface mining (Atayi *et al.*, 2016). This involves the clearing of a large area of the forest and agricultural land and these results in serious deforestation and land degradation.

Rapid growth in the mining sector has also attributed to the decrease and degradation of the land, forest cover and the biodiversity, though it serves as a great economic gain for a country economy (Kumar and Pandey, 2013). The mining industry is the second largest industry after agriculture at all scale and regions and it has played a vital role in the development of civilization from ancient times (Lodha *et al.*, 2009). As an example, according to (Seccatore *et al.*, 2014), Ghana's mining sector contributes about 40% of gross foreign exchange earnings, generates some 5.7% of GDP. During mining activities, large vegetation is cleared; huge pits dug to obtain the rocks rich in granite and limestone. The continuous extraction of the natural resources leads to the direct loss of the forest due to the frequent damage of the forest land, removal of the fertile topsoil layers (Berihu *et al.*, 2017), thereby resulting in the shortage of fuel woods, grazing area, increase in soil erosion and air pollution. This situation negatively affects people living within the mining areas (Nzunda, 2013).

Surface mining operations in Ghana have become a topical issue due to the devastating effects they are having on the environment. The extent of the devastation is assuming alarming proportions by the day and has destroyed both the environment and natural habitats (Emmanuel *et al.*, 2018). Some of the destructive occurrences instigated by this menace are the destruction of both vegetative and forest covers. Approximately 38% of the forest reserves in Ghana are depleted by mining activities (Levin, 2004). Excavated pits are left uncovered which results in some of them being stagnated with wastewater thereby breeding both reptiles and insects and serving as a death trap to the populace within these catchments (George, 2013). These defects on the environments give rise to the incidence of the outbreak of epidemic and people being drowned in water stagnated in trenches which are left uncovered. One of the most devious effects this menace has caused the environment is the pollution of water bodies with heavy metals and other contaminants (Bansah *et al.*, 2016). Heavy metal pollution in both water/sediments of rivers as well as soil within the affected catchments poses lots of health threats to both human and animal existence (Lu, 2012; Persaud *et al.*, 2017). In most of these affected catchments, farming is one of their primary source of employment. During the dry season, the farmers usually resort to streams and rivers as their source water for irrigating their farmlands. However, due to the over-exploitation of

these water bodies, the farmers are left with no option than to irrigate their farmlands with these polluted water. Consequently, both the soil and farmlands get contaminated by these pollutants and subsequently get ingested by both man and animals, thereby endangering lives (García *et al.*, 2015).

Metallic pollutants generally do not remain at the place of discharge but travel along the flow lines of the receiving rivers (Amankwah, 2013). The general question raising a concern with regards to today's mining activities includes the following: What are the use land-use changes in the atypical mining area, to what extent are these metallic pollutants dispersed in water, what are the levels of pollution these activities are generating, what is the impact on the water quality generally on the receiving rivers. To address these issues, this study was anchored on the following objectives: To ascertain the land cover changes as a result of the activities of small scale mining, to determine the effect of the mining activities on the water quality of the affected water bodies and to ascertain the level of contamination of the river sediments.

Materials and Methods

Study Area

The study area forms part of the districts under the jurisdiction of the Asante Region of Ghana (Fig. 1). The area lies within latitude 60 30' North and 70 30' North and longitude 00 15' West and 10 20' West. It spans over an area of 1,160 Km² with a population of 71,238 (Ghana Statistical Service, 2012). The study commenced from River Agogowa, a river that serves as a distributary to both the Owerri and Asuokofi Rivers. Mining activities are virtually non-existent within the enclave of River Agogowa which also serves as a control, but rather predominant within the catchment of the Owerri and Asuokofi. The area lies in the semi-tropical belt described by two precipitation maxima. The initial rainy season is from May to July and the subsequent from September to November. Mean yearly precipitation runs in the range of 855 and 1,500 mm. The normal stormy days for the year is in the range of 110 and 120 days. The dry harmattan season occurs between December and April and is related to dry conditions, high temperatures and early morning damp/mist and chilly climate conditions. Streams evaporate during this period. Temperature is observed to be consistently high throughout the entire year with a mean yearly temperature of 26°C. Humidity is high during the stormy season. Their area records extremely lower moisture conditions between December and February, (Boadi *et al.*, 2013).

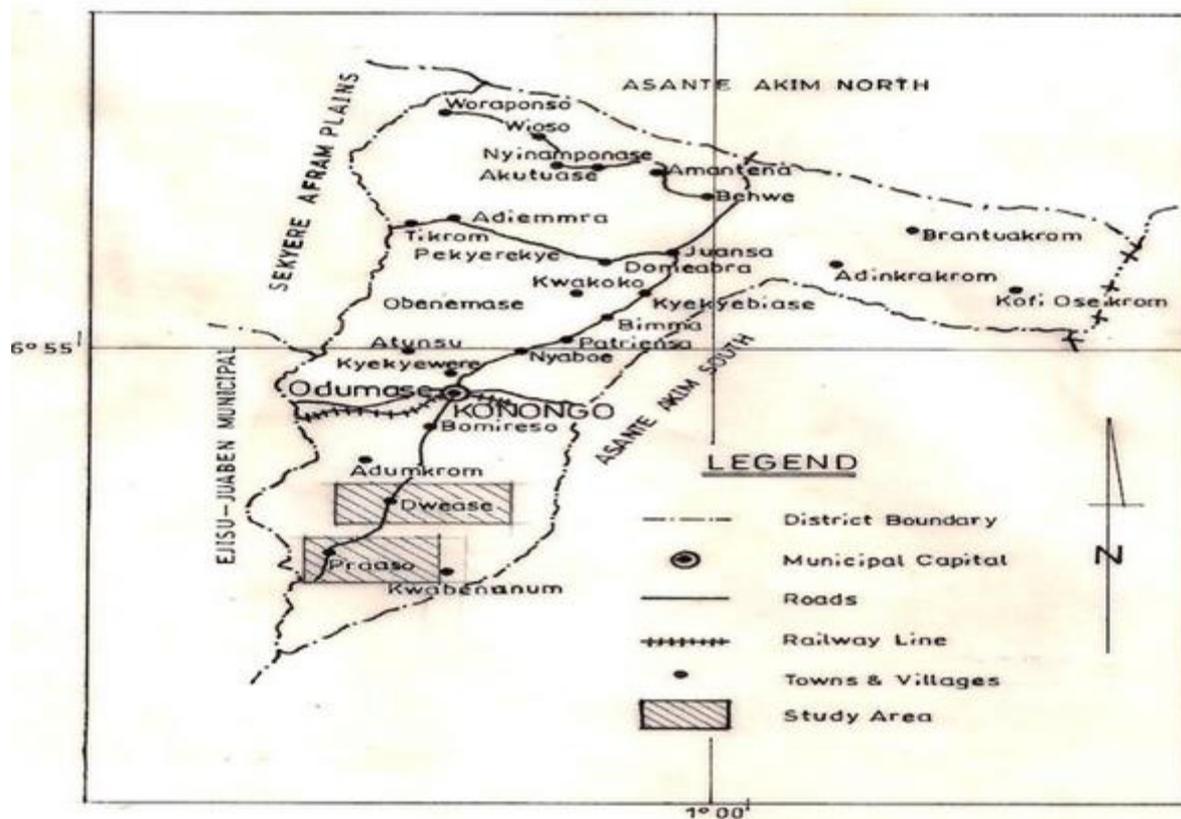


Fig. 1: Map of Asante Akim Central Municipality taken during the 2012 population and housing census in Ghana

Sampling Sites

The sampling sites were selected based on their strategic locations affected by the activities of small scale mining and its associated impact on water bodies in the area. The fourteen water and sediment samples (7 from each River) were identified and collected at locations affected mostly by the mining activities. Water and sediment samples were taken upstream from River Agogowa (Agogo), approximately 35 km from the study area, which has no record of small scale mining activity were taken and analysed to serve as a control. The sampled sites were given different designations. The aim was to ascertain the causes of the pollutants within the water and sediments of the two Rivers.

Sampling Methodology and Sample Treatment

The sampling was designed to cover eight months, spanning between March 2017 and November 2017. Fourteen water and sediments samples in fourteen locations from the Two Rivers/streams; Owerri and Asuokofi were collected into clean (sterilised) tetrafluoroethylene (Teflon) containers. The containers

were rinsed twice with water from the rivers. At each river/stream sampling points, about 0.25 L of water were collected from the centre of the river at a depth of 20 cm below the water surface (Shanbehzadeh *et al.* 2014). The containers were filled with the samples, leaving approximately 1% of the volume empty to allow for possible thermal expansion. Sediment samples weighing 250 g were also scooped using the sediment scoop sampler below the water surface from the centre of the river. The water samples were kept in pre-labelled Tetrafluoroethylene (Teflon) containers which had been rinsed with 10% HNO₃. About 4 cm³ of HNO₃ was added to the water samples before capping of the containers that contained the water samples to stabilize the heavy metals. The sediment samples were also collected into pre-labelled, polypropylene transparent bags. The bags were securely tied and placed in another bag, which was then sealed with duct tape. All the samples were stored in an ice chest with ice to maintain a low temperature of 4°C and then sent to the Ecological laboratory of the University of Ghana for analysis. A Geographical Positioning System (GPS) "Garmin 62SC" was used to take coordinates for each of the sampled points using WGS 84 as the baseline. Both

sediment and water samples for each of the sampled locations were taken with all the coordinated points converted into shape files using the geographic coordinate system. Geographic bound was considered to limit on the extent of the geographic area mapped but not the entire Municipality. For the digestion of the water samples, 20 mL of water samples were mixed with 5 mL of nitric acid and 2 mL hydrogen peroxide. The sediment samples were dried in an oven at 105°C for 24 h. The dried samples were powdered using an agate mortar and pestle to achieve a homogeneous mixture and then were passed through a 63-micron sieve. Thereafter, 1 g of the sediments was digested by adding a mixture of nitric acid and concentrated perchloric acid with a ratio of 4:1 through exposure to 40°C for 1 h and 140°C for 4 h. The total metal content of water and sediment samples was performed by Inductively Coupled Plasma Mass Spectrometry. Changes in Land Use Land Cover (LULC) maps of 1999, 2009 and 2017 were obtained by extracting shape files from Asante Akim Municipality.

Quality Control

Duplicate samples were taken, digested and analysed the same way as the samples. All the instruments used in the measurement were well-calibrated to minimise any measurement uncertainty by ensuring the accuracy of test equipment. Digestion Blank approach was employed to assess for possible contamination introduced during sample preparation activities.

Results

The land use classification in the Asante Akim Central is based on the forest/open forest, settlement/bare land and grass/farmland. Figure 2 shows the land cover classification of the study area in the year 1999 when the menace of illegal mining was virtually non-existent. The area was practically covered by forest/open forest as well as grass/farmland with fewer settlements clustered around the Owerri River ostensibly serving as their major source of water. After ten years (2009), the dynamics of the land use classification changed significantly. The forest/open forest cover and grass/farmlands started depleting with increase in settlement (Fig. 3). This is the period that license were given to small scale miners to mine at the enclave. Due to unemployment in the area, majority of the youth were engaged by the operators of these small scale mining. In 2017, a lot of illegal mining (galamsay) activities had literally engulfed the entire municipality and practically depleting the forest and grass/farmland cover with corresponding increase in the settlement (Fig. 4). Majority of the illegal mining activities were the alluvial method. This method of mining has the propensity of heavily polluting the soil and water bodies with harmful metals like Hg, As, Pb and Cd.

The forest, grassland/farmland and settlements had an estimated land cover of 59.9, 36.9 and 3.2% respectively (Table 1). These statistics give credence to the fact that the land use of the area has not been static but rather drifted from being a forest belt to grassland/farmland and settlements. These changes in land use might be necessitated by the community's over-reliance on farming as their essential source of income.

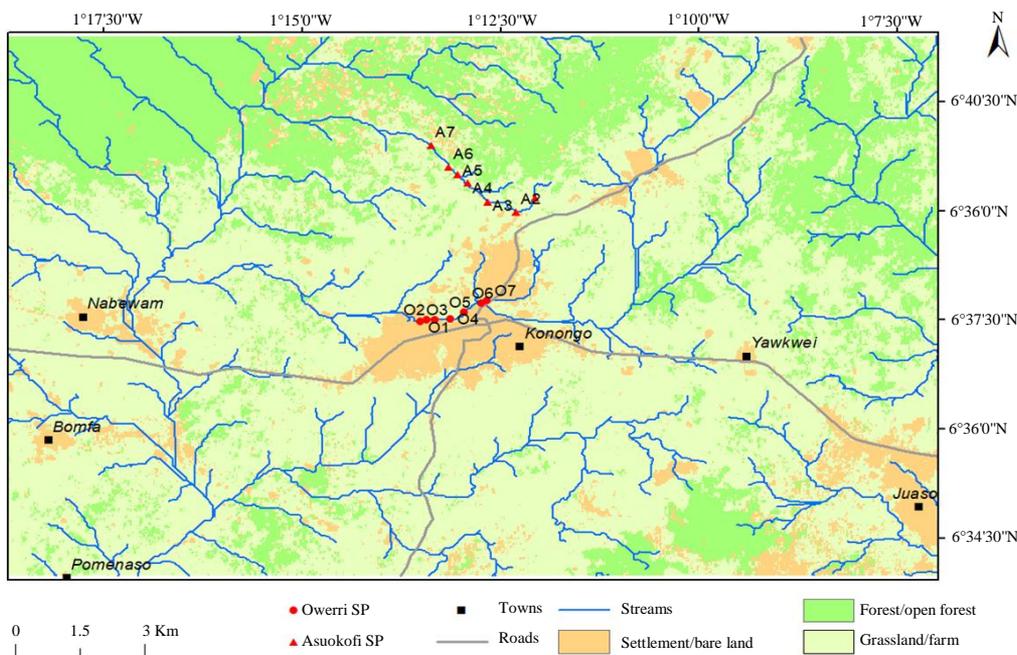


Fig. 2: Land use land cover classification for 1999 in Asante Akim central

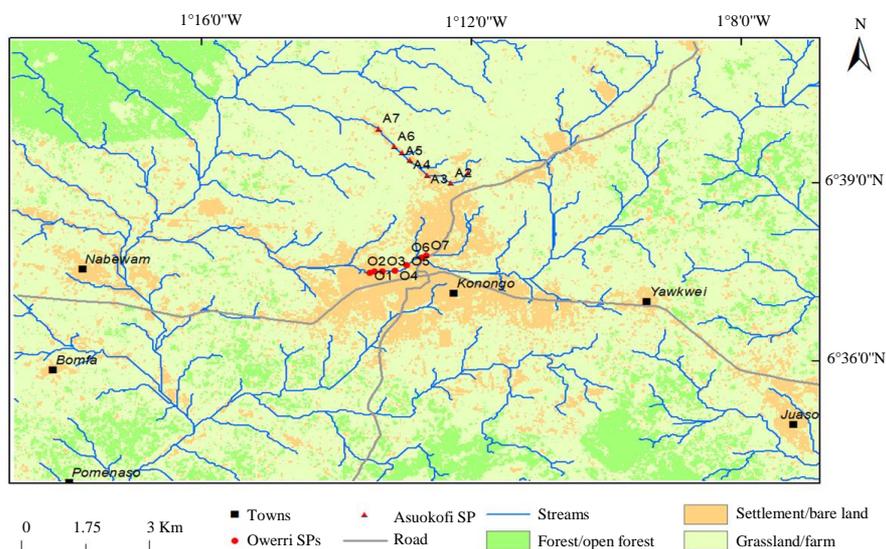


Fig. 3: Land use land cover classification for 2009 in Asante Akim central

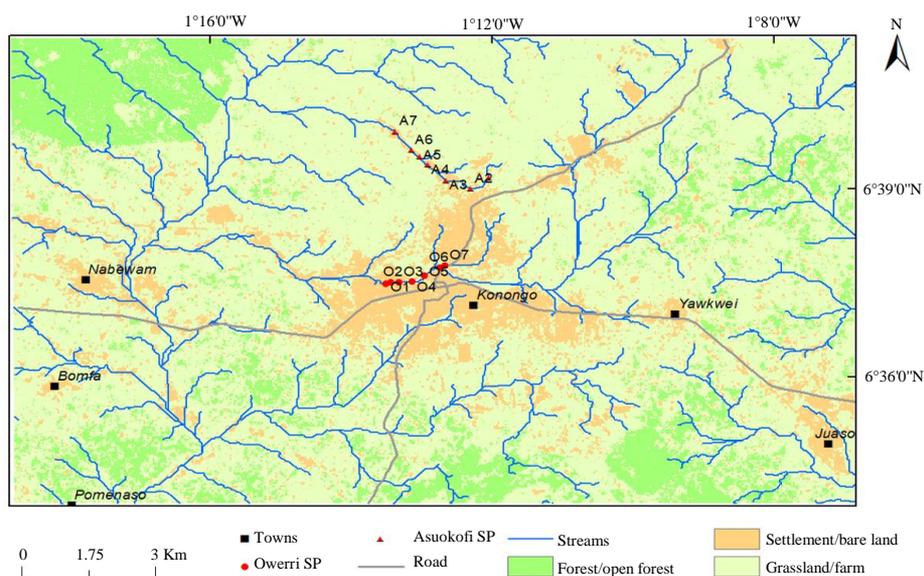


Fig. 4: Land use land cover classification for 2017 in Asante Akim central

Table 1: Land use/land cover changes in the Asante Akim central

Classification	Years of coverage with percentages					
	1999 (Km ²)	%	2009 (Km ²)	%	2017 (Km ²)	%
Forest	180.1	59.9	81.2	26.9	45.4	15.1
Grass/Farmland	110.8	36.9	189.4	63.0	180.9	60.2
Settlement	9.7	3.2	30.1	10.0	74.4	24.7
Total	300.6	100.0	300.6	100.0	300.6	100.0

According to Ghana's 2010 Population and Housing Census for the Asante Akim Central Municipality, the Agriculture, forestry and fishing industries employed the most significant number of the populace above the age of 15

years (33.6%). This was followed by wholesale and retail; repair of motor vehicles and motorcycles (20.8%). These two industries accounted for a little over half (54.4%) of the persons employed. This was expected as workers in the

informal sector dominate the municipality. Other significant industries include manufacturing (10.1%), accommodation and food services (6.1%), education (5.6%) and mining and quarrying (4.7%).

The forest cover within the area depleted from 59.9 in 1999 to 26.9% in 2009 and then finally to 15.09% in 2017 (Table 1). Concurrently, the settlement cover increased from 3.2% in 1999, 30.06% in 2009 then finally to 24.7% in 2017. The total number of households in the Asante Akim Central Municipality according to the 2010 Population and Housing Census is 16,920. Out of this number, 8,467 (about 50%) of these households are engaged in agriculture. The farmland cover kept increasing over the period. The dominant agricultural activity is crop farming, which has a proportion of almost ninety-six per cent (95.7%). This is followed by livestock rearing (20.8%) with tree planting and fish farming constituting less than one per cent (0.6%). This trend is just the same for rural households in both urban and rural localities. These statistics give ample attestation of the community's reliance on the available water resources for their livelihood. The two significant sources of water in the community are the Owerri and Asuokofi Rivers from which the citizenry depends largely on for drinking, irrigation of farmlands and other purposes. Unfortunately, the activities of Small-scale mining in the Asante Akim Municipality became prevalent between the years 2008-2016 (George, 2013) and it was largely dominated within the enclave of the Owerri and Asuokofi Rivers. The activities of the illegal miners in no doubt polluted these Rivers and consequently became a threat to both humans and livestock.

Apart from the activities of illegal mining, there are other activities such as an auto mechanic workshop, farming and market along the banks of the Two Rivers.

Levels of Heavy Metals in Owerri and Asuokofi Rivers

Figure 5-8 shows the levels of the heavy metals in the water samples of the Owerri and Asuokofi Rivers. The illegal mining activities were sited along both Rivers at locations (Points) 1, 2 and 3 within the study area (Ashante Akim Central).

Levels of Lead and Mercury in the Owerri and Asuokofi Rivers

The levels of Pb at each of the sampled points in the Asuokofi River were all above the levels at the control location (Fig. 5). The levels of Pb was high at sampled locations 1 and 2 and declined afterwards along the flow lines all through to sampled location 7. Except for

sampled locations 6 and 7 in the Owerri River, all the other points sampled had the Pb levels above that at the control location. Location 1 of Owerri recorded the highest levels of Pb and consequently declined drastically to location 2. There was a marginal increase in the levels of Pb from location 2 to 3 in the Owerri River but subsequently declined after location 3 through to location 7. The occurrence of Pb prevalently at tested areas 1, 2 and 3 might be ascribed to the draining of leaded gas from a portion of the hardware excavators, mechanized plants or tromeles utilized by the diggers just as the exercises of the automobile shop situated at the mining locales apparently to fix the gear of the excavators. When the Pb was leached into the Rivers at these points, they were expected to flow along the flow lines downstream, however, there were decreasing levels of Pb downstream and this could be as a result of the possible settling of Pb at the sediments of the River.

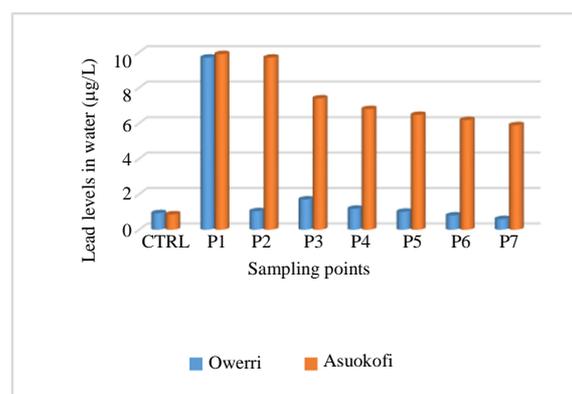


Fig. 5: Dispersion of Pb within Owerri and Asuokofi streams

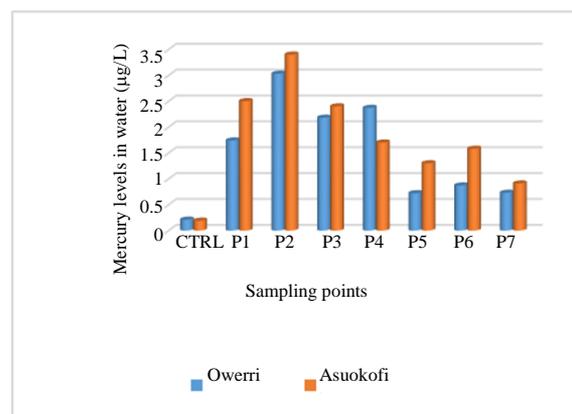


Fig. 6: Dispersion of Hg within Owerri and Asuokofi streams

The levels of Hg in both Owerri and Asuokofi Rivers were all above the levels recorded in the controlled sample. There was a gradual increase in the levels of Hg from location 1 to location 2 within the two Rivers, consequently, the levels of Hg declined steadily from location 2 through to location 7. Before long, Hg is used to removing gold from mineral as an amalgam. The amalgamation is usually separated by hand and thereafter warmed to refine the Hg and segregate the gold. The technique of amalgamation is reiterated three times to enhance the removal of the gold. This may account for the high levels of Hg at sampled points 1, 2 and 3 which incidentally happens to be where the activity of illegal gold mining was prevalent. Mercury is stable and does not easily dissolve in water but will float on the surface or form alloys in most metals and they can only dissolve in fats and oils. The Hg was likely collected together with the River water by the inhabitants to either irrigate their farmlands or used for other domestics purposes at some points along with the flow of the River. The levels of Hg at other locations where the activity of illegal mining was not prevalent (4, 5 6 and 7) along the flow lines were not considerably lower than the locations where the activities were prevalent. This may be attributed to the inability of Hg to easily dissolve in water at normal temperatures.

The mean and standard deviation of the physicochemical parameters of the two rivers are indicated in Table 2. The mean levels of Pb and Cd in the rivers are 5.33 ± 0.4 and 1.78 ± 0.1 respectively which are lower than the WHO standards of 10 and $5.0 \mu\text{g/L}$ respectively. The mean levels of Hg and As are respectively 1.27 ± 0.2 and 12.83 ± 0.7 , higher than the WHO standard values of 1.0 and $10 \mu\text{g/L}$ respectively. The level of pH in the rivers (6.30 ± 0.1) was within the WHO standard of 6.5-8.5. Conductivity, TDS and Turbidity values were 159.60 ± 1.7 , 107.23 ± 1.0 and 4128 ± 3.1 respectively. With the exception of TDS, levels of Conductivity and Turbidity are above the WHO standards of 5NTU and $500 \mu\text{S/cm}$.

Levels of Arsenic and Cadmium in the Owerri and Asuokofi Rivers

The dispersion of As within the Owerri River was virtually non-existent, on the other hand, As recorded the highest levels at location 1 and further declined along the flow lines to location 7 in the Asuokofi River. The levels of As within the Asuokofi River were high at locations 3-5, indicating high pollution within those catchments (Fig. 7). Arsenic occurs normally in rocks and soil, water, air, plants. Volcanic movement, the disintegration of rocks and minerals and backwoods flames are common sources that can discharge As into the environment. Adsorption of As to fine particles in water and precipitation with aluminium or iron hydroxides makes As enter develop. After some time arsenic may isolate a little while later significant to decrease responses. Arsenic blends may expeditiously separate in the water and in this way their dynamic lessens in their levels along the streamlines of the Asuokofi River.

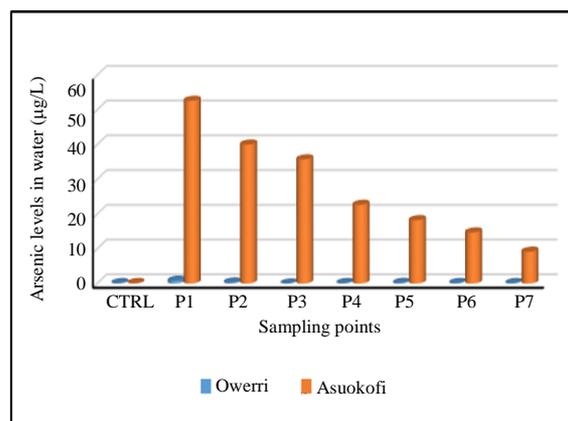


Fig. 7: Dispersion of As within Owerri and Asuokofi streams

Table 2: Levels of contaminants in the two rivers

Dependent variables	Sample type	N	Mean±SD	WHO Standard
Lead(Pb)	Sediments (mg/kg)	30	32.14 ± 28.26	35.8mg/kg
	Water ($\mu\text{g/L}$)	30	5.33 ± 4.01	$10 \mu\text{g/L}$
Mercury(Hg)	Sediments (mg/kg)	30	1.57 ± 1.34	0.18mg/kg
	Water ($\mu\text{g/L}$)	30	1.27 ± 1.72	$1.0 \mu\text{g/L}$
Arsenic(As)	Sediments (mg/kg)	30	256.88 ± 49.45	9.79mg/kg
	Water ($\mu\text{g/L}$)	30	12.83 ± 20.07	$10 \mu\text{g/L}$
Cadmium(Cd)	Sediments (mg/kg)	30	1.70 ± 1.49	0.99mg/kg
	Water ($\mu\text{g/L}$)	30	1.78 ± 1.96	$5.0 \mu\text{g/L}$
pH	Sediments (mg/kg)	-	-	-
	Water ($\mu\text{g/L}$)	30	6.30 ± 1.15	6.5-8.5
Conductivity($\mu\text{S/cm}$)	Sediments (mg/kg)	-	-	-
	Water ($\mu\text{g/L}$)	30	159.60 ± 14.77	5NTU
TDS(mg/l)	Sediments (mg/kg)	-	-	-
	Water ($\mu\text{g/L}$)	30	107.23 ± 30.05	259-500mg/L
Turbidity(NTU)	Sediments (mg/kg)	-	-	-
	Water ($\mu\text{g/L}$)	30	4128 ± 843	$500 \mu\text{S/cm}$

The levels of Cd within Owerri River were well dispersed along the flow lines at locations 2 and 3 with the highest levels of Cd (Fig. 8). However, the levels within the Asuokofi were minimal and were dispersed along the flow lines (Fig. 8). Cadmium, an uncommon yet broadly scattered component, is found normally in nature. It is discharged into nature through mining and purifying. The presence of Cd particularly in the Owerri River could be as a result of the activities of intense mining within the affected catchment (Fig. 8).

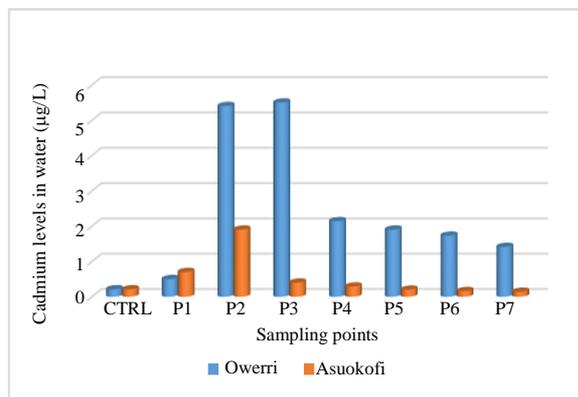


Fig. 8: Dispersion of Cd within Owerri and Asuokofi streams

Levels of Heavy Metals in the Sediments of Owerri and Asuokofi Rivers

Figure 9-12 shows the levels of Pb, Hg, As and Cd in the sediments of both the Owerri and Asuokofi Rivers.

Levels of Lead and Mercury in the Sediments of Owerri and Asuokofi Rivers

The levels of Pb in the sediments of Owerri River were well dispersed and much higher than those within the Asuokofi River. The levels of Pb at the sampled points 1-7 in the Owerri River were all higher than that at the source (control), indicating the influence of the illicit mining undertakings within the affected catchments (Fig. 9). Except for sampled points 6 and 7, the levels of Pb in the sediments of Asuokofi were all above that at the control. Conversely, the levels of Pb in the stream (water) of Asuokofi and Owerri were all below that of the sediments. The average depth of flow in both Rivers was about 0.8 m so there is the likelihood of Pb easily settling and dissolving in the sediments of the Rivers (Duncan *et al.*, 2018). The remediation of Pb by macrophytes will be much easier with higher levels in the sediments than the water. Therefore the remediation of Pb in the two Rivers will not take much time.

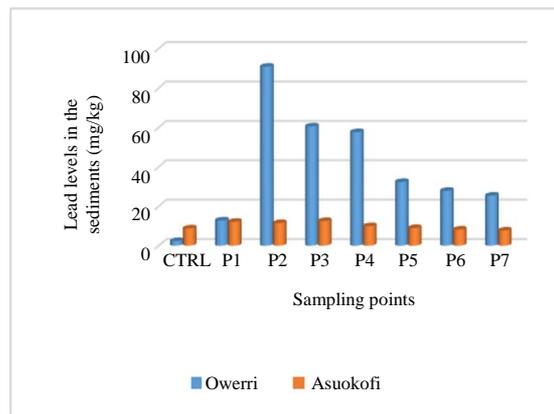


Fig. 9: Dispersion of Pb within sediments

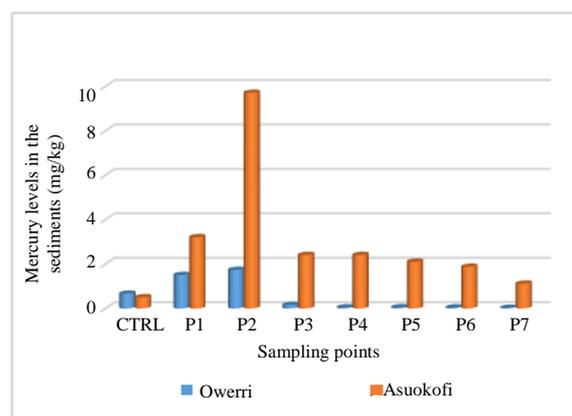


Fig. 10: Dispersion of Hg within sediments

The levels of Hg in the sediments of Asuokofi were well dispersed and much higher than those within the Owerri River. The levels of Hg in the sediments of Asuokofi were above the levels in the water samples of the same River (Fig. 10). This could be the high deposition rate of Hg at the sediments resulting from the inability of the Hg to dissolve in the water. However, this argument cannot be held for Owerri as the levels in the water samples were above that of the sediments. Mercury may have formed alloys with other metals in the Owerri River that could have led to the lower levels of Hg in the sediments of Owerri than the water samples.

Levels of Arsenic and Cadmium in the Sediments of Owerri and Asuokofi Rivers

The levels of As in the sediments of Asuokofi were very minimal and almost at the same levels with the source location. On the contrary, the levels of As in the sediments of Owerri were high at sampled locations. In other words, the

levels of As in the sediments of Owerri were higher than that of the Asuokofi River. The levels of As in the water samples of Owerri were much lower than that within the sediments of the same River. This is an indication of the fact that almost all the As metal settled at the sediments of the Owerri River, there is the tendency of the As metal to easily dissolve into the stream (water) at the slightest of subsidence of movement of the ground within that enclave. Particular attention must be given to the remediation of As in the Owerri River in all sampled locations.

The levels of Cd in the sediments of Asuokofi were well dispersed along the flow lines (Fig. 12). Except sampled point 2 which recorded the highest levels of Cd, the levels of Cd in the sediment of the rest of the sampled points were low.

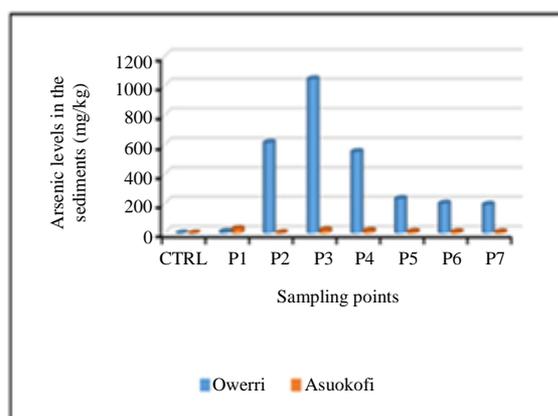


Fig. 11: Dispersion of Arsenic within sediments

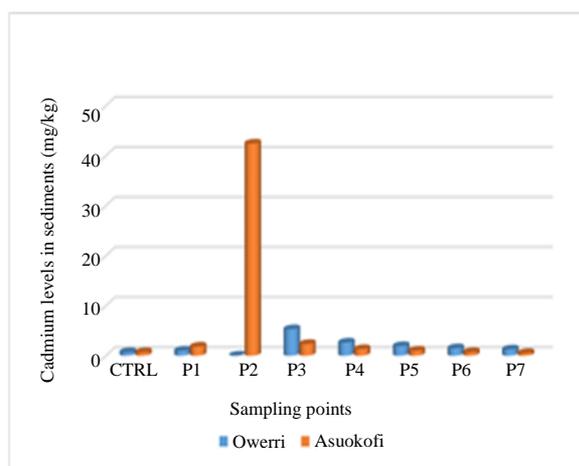


Fig 12: Dispersion of Cadmium within sediments

There is a positive correlation between Pb and As (0.88) (Table 3). The higher the levels of Pb in the stream, the

higher the corresponding levels of As. The level of correlation between Pb and As is statistically significant (t value = 0.00). This is an indication that there would be more than 95% chance to see both pollutants moving in the same direction. The correlation between Pb and Cd is negative (-0.04). The increase in the levels of Pb in the river would be associated with the decrease in the levels of Cd and vice versa. However, the negative correlation between Pb and Cd is not statistically significant (T-value = 0.77). The correlation between Pb and pH is positive (0.465). The rise in the level of Pb might see a corresponding rise in the pH level of the water. The correlation between Pb and pH is statistically significant (T-value = 0.01). The rise in the level of Pb in water would cause the pH level to also rise. There is a negative correlation between Pb and conductivity as well as TDS (-0.89 and -0.33 respectively). The rise in levels of Conductivity, TDS and Turbidity might cause a decrease in the levels of Pb in water. However, the negative correlation between Pb and conductivity, TDS as well as turbidity is not statistically significant (0.64, 0.08 and 0.49 respectively). This means that there wouldn't be any basis to predict an increase in Conductivity, TDS and Turbidity with a decrease in Pb.

The correlation between Hg and Cd as well as As are negatively correlated (Hg r Cd = -0.33 and Hg r As = -0.36). Statistically, the correlation between Hg and Cd as well as between Hg and As are significant. An increase of Hg in water may cause a corresponding decrease of Cd and As. There is a 95% chance of lower levels of Cd with the increase in Hg levels in the water. There stand a 99% chance seeing higher levels of Hg with corresponding decrease levels of As in water. Hg has a positive correlation with pH (0.42) and the level of correlation between Hg and pH is not statistically significant. Conductivity and turbidity have a positive correlation with Hg (Hg r conductivity = 0.002, Hg r turbidity = 0.31), however, the correlation between Hg and Conductivity as well as turbidity are not statistically significant. Hg has a negative correlation with TDS (-0.48) and the levels of correlation between them are statistically significant (t = 0.007). This means an increase in the levels of Hg might see a decrease in the levels of TDS.

There is a positive correlation between As and Cd (0.26) and the level of correlation is statistically significant (Table 3). The levels of As and Cd moves in the same direction in the water. The correlation between As and pH together with turbidity are positively correlated and the levels of correlation between them are statistically significant. Thus, the higher the levels of As in the water, the higher the pH and turbidity levels respectively. The correlation between As and TDS is negatively correlated (-0.05) and the level of correlation is not statistically significant (t = 0.79).

Table 3: Correlation analysis between measured samples

Variables	Statistics	Lead (Pb)	Mercury (Hg)	Arsenic (As)	Cadmium (Cd)	pH	Conductivity ($\mu\text{S/cm}$)	TDS (mg/l)	Turbidity (NTU)	Colour (Pt/Co)
Lead (Pb)	Correlation	1	-0.30*	0.88**	-0.04	0.46*	-0.09	-0.32	0.13	0.29
	Sig. (2-tailed)		0.02	0.00	0.77	0.01	0.64	0.08	0.49	0.19
Mercury(Hg)	Correlation	-0.30*	1	-0.36**	-0.33*	0.42*	0.00	-0.48**	.31	0.59**
	Sig. (2-tailed)	0.02		0.01	0.01	0.02	0.99	0.01	0.09	0.00
Arsenic (As)	Correlation	0.88**	-0.36**	1	0.26*	0.47**	0.30	-0.05	0.65**	0.79**
	Sig. (2-tailed)	0.00	0.01		0.04	0.01	0.10	0.79	0.00	0.00
Cadmium (Cd)	Correlation	-0.04	-0.33*	0.26*	1	-0.54**	0.09	-0.05	-0.17	-0.33
	Sig. (2-tailed)	0.77	0.01	0.04		0.00	0.63	0.81	0.36	.075
pH	Correlation	0.46*	0.42*	0.47**	-0.54**	1	0.53**	-0.20	0.09	0.19
	Sig. (2-tailed)	0.01	0.02	0.01	0.00		0.00	0.278	0.64	0.32
Conductivity ($\mu\text{S/cm}$)	Correlation	-0.09	0.00	0.30	0.09	0.53**	1	0.29	0.45*	0.22
	Sig. (2-tailed)	0.64	0.99	0.10	0.63	0.00		0.12	0.01	0.24
TDS(mg/l)	Correlation	-0.32	-0.48**	-0.05	-0.05	-0.20	0.29	1	0.40*	0.06
	Sig. (2-tailed)	0.08	0.01	0.79	0.81	0.28	0.12		0.03	0.77
Turbidity (NTU)	Correlation	0.13	0.31	0.65**	-0.17	0.09	0.45*	0.40*	1	0.84**
	Sig. (2-tailed)	0.49	0.09	0.00	0.36	0.64	0.01	0.03		0.00
Colour (Pt/Co)	Correlation	0.29	0.59**	0.79**	-0.33	0.19	0.22	0.06	0.84**	1
	Sig. (2-tailed)	0.13	0.00	0.00	0.08	0.32	0.24	0.77	0.00	

*. Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

The correlation between Cd and pH is negatively correlated (-0.54) and the level of correlation is significant ($T = 0.00$). Conductivity has a positive correlation with Cd (0.09), however, the level of correlation between conductivity and Cd is not statistically significant. There is a negative correlation between Cd and TDS as well as turbidity ($Cd \text{ } r \text{ } TDS = -0.049$, $Cd \text{ } r \text{ } turbidity = 0.17$). However, the level of correlation between Cd and TDS as well as turbidity is not statistically significant. This is to say, the levels of TDS has no bearing on the levels of Cd.

Discussion

The results obtained indicated the contamination of the Two Rivers; Asuokofi and Owerri in the study area as a result of the activities of illegal mining. All the four heavy metals identified; Hg, As, Pb and Cd were all found to be in elevated levels within the two Rivers (Table 2). The levels of the heavy metals at the source (control) of both Rivers were lower than that at locations 1-5. There was no activity of illegal mining at the source of the streams and hence this observation validates the assertion that the activity of illegal mining could be part of the main causes of heavy metal pollution in both Rivers. The presence and dispersion of the heavy metals along the flow lines were higher in the water samples for the Asuokofi than the Owerri River but the reverse was for the sediments (Table 2). It was observed that the higher the levels of the heavy metals in the water samples, the lower it is in the sediments and vice versa. However, the levels of some of the heavy metals (Lead) in the sediments were higher than those in the water column, this may be due to the ability of the metals to dissolve in the sediments and flow along the flow lines downstream. The Mercury levels in Asuokofi were higher than those of the Owerri River both in the water column and sediments. The levels in the sediment and water were higher; this may be due to the incessant usage of the Hg in amalgamating the gold ore in the Asuokofi River more than those in the Owerri River. The

levels of the As were higher in Asuokofi water sample than that of the Owerri River but the levels were extremely higher in the sediments of the Owerri River than the Asuokofi River. This may be attributed to the higher occurrence of arsenopyrite in the Owerri river course than Asuokofi leading to higher arsenic in the Owerri River. The levels of cadmium metal in the Owerri River were higher than that of the Asuofi for both the water column and sediments.

Generally, the levels of metals in the sediments were above that of the water column (Table 2). This is because; most metals are insoluble in water but are easily bound to the sediments. Furthermore, the metals in the aquatic ecosystems are mainly deposited in sediment and sediment acts as a source and as a sink. As a consequence, benthic biota living in a metal-polluted environment can have a very high level of metals (note: Benthos organisms such as mussels are used in biomonitoring of heavy metal pollution in the marine environment). The presence of these contaminants in sediments may influence a high peril of human infection due to resuspension by natural turbulence or human activities. The levels of almost all the heavy metal pollutants under consideration in both River especially Asuokofi were well dispersed and well above the WHO guidelines (Table 2) and the control point levels along the flow lines. There was a gradual decrease in the levels of pollutants from the upstream to the downstream. There is the tendency of the levels of pollutants in the sediments to further dissolve in the water whenever there is a disturbance at the bed of the streams which may further increase the levels of the metal way above the World Health Organisation (WHO) standards thereby endangering the lives of the communities. Comparing this results with other similar studies conducted in Dunkwah-on-offin (Kpan *et al.*, 2014) and Tarkwah (Boamponsem *et al.*, 2010) in the Central and Western Regions respectively of Ghana, confirm that the activities of illegal mining contribute to heavy metal pollution in water

and sediments. Their findings also confirm the decline of the heavy metal concentrations along the flow lines downstream.

From the maps shown in Fig. 2-4, most of the vegetation/farmlands and settlements are very close (about 20 m) to these streams where the illegal mining is being carried out of which the communities rely heavily on irrigation and domestic uses. The high levels of the heavy metals in the sediments give rise for concern on the impact of food security in the area. There is the tendency for the crops grown within the mining enclave to bio accumulate some of the heavy metals and subsequently to be consumed by both man and animals. The Physicochemical parameters analysed for the two streams were; pH, conductivity, TDS and Turbidity. The average Hvalue obtained was 6.3. Except for Turbidity, all the samples fell within the WHO range for potable water. The average turbidity was 4128 NTU which is far above, the limit 5NTU. The Electrical Conductivity (EC) for all samples fell within the permissible limit of 500 μ S/cm set by WHO. TDS value was generally 107.23 mg/L which was within the WHO permissible limit. This showed that the two-stream water in the area was quite fresh in most locations.

Conclusion

The pollution of the Owerri and Asuokofi can be attributed to the activities of illegal mining within their enclave. The activities of illegal mining within the catchment could also be as a result of land use and land cover changes. The predominant pollutant within these rivers is mostly Hg, As, Cd and Pb. The levels of these pollutants within the water substrate and sediments are above the WHO standards. Unfortunately, these pollutants are not localized but can disperse along the flow lines of the River. This further endangers the lives of the inhabitants both at the upstream and downstream. There is both a positive and negative correlation between the pollutants, indicating the predictability of one pollutant with levels of the other pollutant.

Acknowledgment

We acknowledge the immense contribution by the Water Resources Commission of Ghana and Ghana Environmental Protection Agency for making available to us all the necessary resources and permit rendered to us to carry out this very important research.

Author's Contributions

Samuel Wiafe: Conceptualized the research topic, formulated the objectives and methodology of the research and participated the data collection and analysis.

Richard Buamah: He carried out both the Laboratory and Field Investigation as well as the Data Curation of the research work.

Helen Essandoh: He carried out Laboratory work and also assisted in the writing of the manuscript.

Ethics

This manuscript has never been published in any journal or sent to any journal for consideration and publication. Strict scientific ethical standard were adhered to.

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