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Determination of the Physico-Chemical Properties and Heavy Metal Status of the Tano River along the Catchment of the Ahafo Mine in the Brong-Ahafo Region of Ghana

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Abstract

The study was conducted to determine the physico-chemical properties and heavy metal status of the Tano River along the catchment of the Ahafo Mine in the Brong-Ahafo Region of Ghana. To achieve this, water samples were taken at access points of the Tano River at Ntotroso (upstream) and Kenyase (downstream) and analyzed at the KNUST Central Laboratory to determine pH, Conductivity, Total Dissolved Solids, Turbidity and Dissolved Oxygen and the concentrations of Arsenic, Lead, Copper, Cadmium and Mercury. Data collected were analysed using the Statistical Product and Service Solution (Version 20). The results from the analysis showed that the physicochemical properties of the river investigated were all within the recommended range of acceptable water quality except for DO which was slightly lower than recommended threshold. The concentrations of heavy metals were also relatively low and all fall within tolerable threshold of the EPA and WHO except for the concentrations of lead which were slightly higher than the recommended threshold at both the upstream and downstream. The study recommends that frequent monitoring of all surface water bodies should be done to ensure the quality of the water is not compromised.

Keywords: Heavy metal; Conductivity; Agricultural activities

Introduction

Minerals exploration is an ancient economic activity that takes place in most countries of the World. As an economic activity, mineral exploration has significantly turned around the economic fortunes of many countries. Whether on small scale or large scale, mining operations have reportedly contributed significantly to the Gross Domestic Product (GDP), employment and revenue of many nations across the world [1]. In Ghana, the mining industry accounts for 5% of the country's GDP and contributes to 37% of total export. According to Akabzaa et al. [2], the mining sector is one of the highest contributors to government revenue through the payment of mineral royalties, employee income tax and corporate tax.

Mineral mining in Ghana, especially gold started a very long time ago. It has been reported that as early as the tenth century, Ghana, Mali and Senegal started gold trade with Europe [3]. During this period, it is believed that more than a quarter of a million ounces of gold were exported to Europe from African sources. Most of the gold came from natives working on the numerous gold deposits in both bedrock and placer throughout Senegal, Guinea, Sierra Leone, Ghana, Nigeria and other African nations using limited technology [4]. Since the beginning of the nineteen century when colonialism started, there has been a proliferation in mineral mining by European companies with the advent of modern scientific mining techniques. Since 1983 when Ghana's Economic policy changed, there has been an increase in the production and investment in the gold sector, resulting from considerable growth in the number of new mines and exploration companies [4]. According to Hilson et al. [3], the number of mining companies in Ghana reached 60 by 1990, with 3 engaged in mineral exploration and 20 of them being foreign companies. To dates, there are over 100 mineral exploration companies of both foreign and local descent.

While the developments and expansion of the mining sector may signify possibilities for the generations of mineral wealth and economic development, the concomitant impacts of the exploration on finite natural resources has become apparent. Damage to the Ajenua Bepo Forest Reserve and pollution of water bodies around the Akyim Mines area as well as increasing cyanide concentration in surface water bodies in the Ahafo mines area have all been strongly linked with the activities of mining operators [5]. As noted by Sangodoyin and Ogedengbe et al. [6], effluents from mineral exploration have almost always resulted significant negative effect on the quality of nearby water bodies. Mining activities, wheher done by large scale mining companies or small scale artisanal miners, require use of large quantities of water for cooling and other operational purposes. The result from the mining activities especially waste generated also mostly end up in nearby water bodies to an extent that has impeded their usability for consumptive and recreational purposes [2].

In Ghana, pollution of soil, water, air and destruction of vegetation has all been strongly linked with mineral exploration [7]. Water bodies in mining communities in Ghana are notable and reportedly affected by mines operation through acid rock drainage, heavy metals pollution and leaching [8]. Incidence of cyanide spillage into River Yaakyei, which flows into River Asunua at Kantinka before joining River Subri and finally flowing into River Tano at Achirensua, has caused tension between local communities and mining companies such as the Newmont Gold Ghana Limited 2009. Most of the rivers that are feared been polluted continue to serve as important source of water for consumptive and other domestic purposes. The Tano river in particular is the main

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source of water for domestic use and agricultural activities and use by the Ghana Water Company Limited (GWCL) at Akyerensua to services communities such as the Hwidiem, Kenyase No.1, Kenyase No.2, New Dormaa and a host of other communities within the Ahafo mining area. Against the backdrop of the acrimony between mines operators and local communities over pollution of water bodies in the Asutifi North District, it is important to establish empirically, the current status of water quality of the Tano river in terms of physico-chemical parameters and exntent of heavy metals concentration. This information will be important for inform actions and also extent the frontier of knowledge regarding the influence of mining activities on water resources quality in Ghana.

Objectives of the study

The main objective of the study was to determine the physico-chemical properties and heavy metal status of the Tano River along the catchment of the Ahafo Mine in the Brong-Ahafo Region of Ghana. The specific objective of the study were to:

- Determine the effects of the mining activities on the physicochemical properties (*pH*, conductivity, TDS, turbidity and DO) of the Tano River.
- Examine the variations in heavy metals (As, Cd, Cu, Pb and Hg) concentrations in the Tano River attributable to mining activities.
- Make comparison of water quality in the upstream and downstreams of the Tano River.

Literature Review

The evolution of gold mining activities in Ghana: The history of gold mining not only in Ghana but Africa at large is a very rich story. Ghana and most other countries in Africa have been the major areas of gold mining for a very long time. Historical records show that gold mining in West Africa dated as far back as the fifth century [4]. In Ghana, although it is uncertain exactly when gold mining started, it has been widely accepted that gold mining in the country pre-dated the arrival of the first European in 1471 [9,10]. The earliest available records indicate that gold has been mined in the modern day Ghana for several centuries before the arrival of the first Europeans. Ghana is acknowledged as a country with a rich depot of gold and has been a major player in the gold mining industry globally and in Africa in particular for centuries [11]. From the early days of gold mining when very limited technology was used to the present day, gold mining has increased in Ghana. Ofosu-Mensah et al. [3] evaluated the evolution of gold mining in Ghana in three main categories viz. panning, shallow-pit surface mining and deep-shaft mining. Ofosu-Mensah et al. [3] noted that in the early days of gold mining, the common method used involved "panning" that is washing for alluvial gold along the banks of streams and rivers and along ocean shores, particularly those near river estuaries.

The second method, Ofosu-Mensah et al. [3] referred to as shallow-pit mining involved digging of shallow holes and trenches in areas supposed to have sufficient deposit of gold. This method he noted involved a large number of workers and resulted in a large quantity of gold mined relative to the panning method. The third type is the deep-shaft mining used in mining for reef gold. Until recent times when gold mining became a full-time livelihood strategy, Gold mining was largely a seasonal activity. Evidence of panning for gold in Ghana in the pre-colonial period was reported in the findings of Peters et al. [12].

In the course of time when not much quantity of gold could be obtained at the river banks and streams, miners began to fabricate tools and implements that could enable them to dig deep into the soil for gold. Gold mining methods in Ghana, despite the fact, was fairly different across the regions; the trend had been moved from rudimentary hands-on tools and implements to some sophisticated methods using locally fabricated iron tools and implements. Historical records show that in the early years of gold mining in Ghana especially between the fifteenth and nineteenth centuries, mining activities were wholly an African business that relied on simple but effective technologies [4]. However, by the second half of the nineteenth century, there was an extensive European take-over of the mining industry in Ghana causing a decline in native gold mining efforts [12]. Since the European entered into the gold mining industry, there has been revolution in the gold mining industry in terms of technology and intensity of mining activities. The use of European technology in the mining industry of Gold Coast stalled the growth of the indigenous technology that was used in mining. Many of the Africans (Ghanaians) also joined the European mining companies as hired labours.

However, few years down the line, many of the formerly employed Africa nationals who worked for the European companies deserted them to embark on the extraction of gold by themselves using a combination of traditional mining methods and some scientific mining practices including the use of mercury and cyanide to recover gold [4]. The mining industry of today still have people using a combination of these methods, that is the traditional mining techniques and modern scientific methods especially for those in small-scale artisanal mining (galamsey) business [4].

Radical reforms and liberalisation in Ghana's mining sector as a result of the Ghana Structural Adjustment Programme (SAP) in 1983 stimulated increased investment with new multi-national mining companies coming on board as well as the rehabilitation of old mines [13]. Currently, gold mining in Ghana is dominated by mineral exploration firms with origin in Canada, Australia, and South Africa at zenith and companies from United States, United Kingdom, Norway and China also joining the industry recently. Following the merger of the Ashanti Goldfields and Anglo Gold, and the emergence of the USA based mining company Newmont (Newmont Gold Ghana Limited), the country has suddenly become the preferred destination for most mining investors of the world. The major gold mining companies in Ghana today are about eleven companies operating eight gold mines in Ghana. Those currently in operation in the country include; Goldfields Ghana Ltd (Tarkwa and Abosso mines); Anglo Gold Ashanti (Obuasi and Iduapriem mines); Central Africa Gold (formerly, AngloGold Ashanti Bibiani Mines) Golden Star Resources (Bogosu/Prestea and Akyempim mines); and recently Redback Mining Ltd (Chirano mine) and Newmont Ghana Gold Ltd (Ahafo and Akyem mines). With the exception of Anglo Gold Ashanti, which still operates an underground mine at Obuasi, all the other mines are surface mine operations [1].

Effect of gold mining on the physical environment: Despite the economic and social benefits that mining operation brings about, it appears in almost all cases that explorations of mineral resources often come at the expense of the physical environment as well. There is a profusion of evidence that suggest that mining or mineral exploration is inherently destructive to the environment and have caused a significant negative impact on several environment components [14,15] noted that inappropriate and wasteful working practices that are common among mining activities practised in developing countries have resulted in most of the environmental deterioration caused by mining. Preparation of access routes to mining sites, topographic and geological mapping, geophysical work, hydro-geological research and establishment of new settlements are common activities done at the beginning of mines operations. These activities undoubtedly often lead to severe land degradation, erosion and silting of the land, reduction of the water table, contamination of the air, water and the land, destruction of natural habitats of endemic fauna and flora species among others [16]. The use of chemical substances in mines operations such as cyanides, concentrated acids and alkaline compounds, and the production of dust, gases and toxic vapour also affect many units of the environment [17,18] has pointed out that major environmental problems in most mining communities of Ghana are largely brought about by the mining boom which requires massive vegetation clearance and excavation, waste disposal, mineral processing and misuse of mining chemicals leading to decline in quality of surface water bodies, air pollution, loss of ecological biodiversity, decreasing forest cover, destruction of agrarian livelihood and obliteration of human settlements.

Effects of mines operations on water resources: In addition to the damages that are caused to vegetation, lands and the lithosphere in general, mineral explorations have also been noted through research to have affected the compositions of the hydrosphere. Mining activities have caused serious pollution to rivers and streams and have also changed watercourses as a result of excessive siltation [16]. Most mining operations in Ghana have increased sedimentation in rivers, especially through the use of hydraulic pumps and suction dredges, which sometimes leave scars on the landscape and as well make the water resources of the country unsafe as a result of introduction of poisonous chemicals into the river [2,19].

Mines operations and changes in physicochemical properties of water: The earth's hydrological cycle driven by evaporation and gravity has been depended on by all life forms in the ecosystems and human societies. The growing populations and dependence of humans and other life forms put stress on natural waters by impairing both the quality of the water and the hydrological budget [20]. Stress, especially from anthropogenic activities that lead to the production of water pollutants, determines the fate of the hydrological cycle and Physicochemical processes. One of such anthropogenic activities that affect the Physicochemical properties of water resources is mining. Several studies have associated mining with changes in Physicochemical properties of water. Physicochemical properties especially the pH, Dissolved Oxygen, Total Dissolved Solids, Total Suspended Solids and True colour are the commonly affected.

pH: The term pH is used as a standard measure of the degree of acidity or alkalinity of any medium. The maintenance of a desired pH range has important implications for life processes, agriculture, industry and the environment. The pH of any particular medium provides important information about many chemical and biological processes and indirect correlations to a number of different impairments that are present in the medium. In unpolluted or pure waters, the pH is influenced by the exchange of carbon dioxide with the atmosphere. However, in the presence of alkaline earth metals such as sodium, carbonates and bicarbonate formed from the solubilisation of CO will interact with sodium to increase the alkalinity and hence shift the pH up over 7. Therefore changes in pH can be indicative of the presence of an industrial pollutant, photosynthesis or the respiration of algae that is feeding on a contaminant [21]. Rocks in open pit contain significant quantities of sulphide minerals predominantly pyrite (FeS). When the pyrite in these rock types is exposed to atmospheric oxygen, it can oxidise according to the following overall reaction:

$2FeS+7O+2HO \Rightarrow 2Fe^{+}+4\ SO^{2-}+4H^{+}$

Pyrite+Oxygen+Water=>Ferrous Iron+Sulfate+Hydrogen ion (acid)

If this reaction is allowed to continue in an uncontrolled manner, low pH conditions can develop. Also, during mines operation, large quantities of rock containing sulphide minerals are excavated from an open pit or opened up in an underground mine; these rocks when reacted with water and oxygen form sulphuric acid. Water passing through these rocks can then leach by way of run-off and carry the potential contaminants into water bodies increasing the acidity and adversely the quality of water resources [22]. Acid formation in rock is a natural process. However, excavation of rocks usually during gold mining accelerates the process of acid formation because it exposes rock to atmospheric oxygen [23]. The effect of this on the environment is felt through acid drainage and the associated increase in the solubility and leaching of metals into groundwater, rivers and streams. Examples around the world where this has happened include West Rand (Witwatersrand) in South Africa, Tinto river in Spain and Shamokin Creek stream in Pennsylvania. Local examples exist in around most mining areas in Ghana. Frimpong et al. [24,25] both reported incidences of acid mine drainage in the wetland areas where mining is done. Mensah et al. [26] also observed acid mine drainage in parts of the Sakumono and Kpeshie Lagoon.

Dissolved oxygen (DO): Dissolved Oxygen (DO) measures the amount of dissolved oxygen in a sample of water. Its unit of measurement is milligrammes per litre (mg/L) that is the number of milligrammes of oxygen dissolved in a litre of water. DO of water may vary depending on variables such as temperature, sunlight, atmospheric pressure, salinity, and plant life and water turbulence. The solubility of oxygen decreases as temperature and salinity increases. The DO of fresh water at sea level will range from 15 mg/l at 0°C to 8 mg/l at 25°C. Concentrations of unpolluted fresh water will be close to 10 mg/l [23]. However, in waters contaminated with fertilisers, suspended material, or petroleum waste or other industrial pollutants or waste the DO level is often low. Microorganisms that break down these contaminants require oxygen to break them down. And as more of the oxygen is consumed to break down contaminants, the water will become anaerobic to an extent where the DO level is too low to support the lives of other organisms such as fish.

Anthropogenic activities such as farming and mining are known to be the sources from which contaminant or waste enter most surface water bodies. And as the amount of contaminants increases, the Biological Oxygen Demand (BOD) of the water increases leading to low DO and death of aquatic species. The impact of mining on DO is compounded by the release of heavy metals that gets into the water and increase the BOD significantly. Evidence of mining activities resulting in low DO and death of aquatic animals in Ghana are presented in the study of Asamoah et al. [27] on impact of small-scale mining on quality of water in the Birim river; Dorleku et al. [21] on groundwater contamination with toxic metals through small-scale mining within the lower Pra basin; and Asamoah et al. [27] study on the effect of illegal small-scale gold mining operations (galamsey) on the water quality of the Birim River in the East Akim Municipality of the Eastern Region. Little evidence of the effects of mining activities in the Asutifi North District on the amount of DO in surface water has been documented. The present study seeks to bridge the gap in knowledge.

Electrical conductivity: Electrical conductivity (EC) of water refers to the normalised measure of the water's ability to conduct electric current. It is measured in Siemens per meter (S/m). All natural water contains dissolved minerals, and there is a relationship between the amount of dissolved minerals and the ability of the water to conduct electrical current; generally, the greater the concentration of dissolved minerals, the higher the conductivity. However specific minerals also influence the conductivity value differently. The presence of ions such as sodium, potassium and chloride in water significantly influence the level of conductivity Karato et al. [28]. The types of dissolved minerals present in a sample of water and their concentrations vary greatly from stream to stream and area to area, depending on the type of rock and soils in a given watershed, the land use activities, and the influences of other water bodies on a stream. Water from mines or mineral wastes usually has high electrical conductivity due to the presence of dissolved ions. As a result of this many scientists have regarded measurement of electrical conductivity of a water sample as a useful and quick estimate of total dissolved solids in the water and the extent of pollution. Water not polluted or high-quality drinking water usually have conductivity value of from 10 to about 200 micro Siemens/centimetre (μS/cm) whereas mine waters usually have conductivity level ranging from 100 to 38,000 micro Siemens/centimetre.

Turbidity and total suspended solid: The turbidity which is also a measure of the Total Suspended Solids (TSS) measured in Nephelometric Turbidity Unit (NTU) is the amount of the material in water that affects the transparency or light scattering of the water. The turbidity of natural water usually ranges from 1 NTU to about 2000 NTU. High values of turbidity usually come as a result of the presence of fine clay or silt particles, plankton, organic compounds, inorganic compounds or other microorganisms [27]. And although these materials can be released into water bodies through natural and other anthropogenic activities, mining remains one of the most pervasive causes of increasing concentration of these materials in water. Turbidity is closely related to total suspended solids (TSS), but also includes plankton and other organisms. The turbidity of natural waters tends to increase during runoff events as a result of increased overland flow, stream flow, and erosion [29]. Turbidity itself is not a major health concern. However, high turbidity results in eutrophication of the water and this may interfere with disinfection and provide a medium for microbial growth. Many fish species are also sensitive to prolonged exposure to TSS, making TSS monitoring an important indicator of water quality [27].

Mining activties and heavy metals concentration in surface water bodies: Mining activities expose metals that have been relatively immobile in a tightly bound subsurface causing them to leach into surface and ground waters in large quantities when the mined rocks are exposed to air and water. Metals at very low dissolved levels and the presence of such heavy metals above a certain threshold can be injurious to human health and the environment, particularly aquatic life. Since waste rock dumps are not lined, containment of contaminants from waste rock is often a challenge [30].

The impact of mining on the concentration of heavy metals in surface water bodies depends on the mineralogy of the rock materials, the availability of water and oxygen generated at both abandoned and active mine sites. These same factors also influence acid mines drainage. Acid mines drainage occurs at mine sites when metal sulphide minerals which are common constituents in the host rock associated with metal mining activity are oxidised. The activities of mining and other operations at mines sites often increase the rate of these same chemical reactions by removing sulphide rock material and exposing the material to air and water. Mined materials (waste rock or tailings) used for construction or other purposes (e.g., roadbeds, rock drains, fill material) or off a mine site can also develop acid drainage. The potential of mines operations in contamination of water bodies surrounding mines increases with increasing usage of various chemicals in the mining process as well as the extent to which metals are removed from the ground with the ore. Therefore large amounts of water produced from mine drainage, mine cooling, aqueous extraction and other mining processes increases the potential for heavy metal contamination of ground and surface water. A number of studies conducted in the Ahafo mines and other areas of significant mines operation have shown that surface water bodies in these areas are highly polluted with groundwater iron, arsenic and other heavy metals with values exceeding the maximum permissible World Health Organization (WHO) guide values as a result of uncontrolled run-off and acid drainage from mining sites [7,16]. The heavy metals commonly found associated with mines operation in Ghana include Mercury (Hg), Arsenic (As), Cadmium (Cd), Copper (Cu), Lead (Pb) Nickel (Ni) and Iron (Fe) [16,22]. In the Ahafo mines area Mercury, Arsenic, Cadmium, Copper and Lead are known to be prevalent. This is due to the fact that the mineralogy and rock types at the Ahafo mines are significant lithogenic sources of these metals. The rock types at the Ahafo area are mainly organic-rich fine-grained sedimentary rock with bituminous sands that are enriched with large quantities of heavy metals and other trace elements [31].

Research Methods

Study area

The study was conducted in the Asutifi North District of the Brong-Ahafo Region of Ghana specifically in the Tano river that passes through mining communities in the District. The geology of the study area is made up of predominantly of the Birimain and Dahomeyan formations. The soil and rocks types of the Birimian and Dahomeyan formation are known to be natural sources of granites, clay, sand, gold, diamond and other minerals. The Birimian formations, for instance, are known to be the gold-bearing rocks and a high potential source of Manganese and Bauxite. Currently, gold is being mined by Newmont Ghana Gold Limited (NGGL) in certain areas of the District especially Kenyase No. 1 and 2, Ntotroso, Gyedu-Wamahinso and other smaller communities. There is also a widespread deposit of sand and clay in the District and rounded out-crops of granite also found over the Birimian rocks at Kwadwo Addaekrom, Goa Asutifi, and other smaller communities [32].

The Tano River

The Tano River is a river in Ghana that passes through Ivory Coast into the ocean. It rises near Techiman and flows for 400 kilometres into Ehy Lagoon, Tendo Lagoon and finally Aby Lagoon in the Ivory Coast where it enters the Atlantic Ocean. It is navigable from its mouth for about 60 miles (95 km) to Tanoso, where further travel is blocked by the Sutre Falls. The Tano and the parallel Ankobra drain the western portion of a shallow basin lying south-west of the Kwahu Plateau, the main watershed of Ghana. The Ankobra-Tano Basin is important for mining (gold, bauxite), timber, copra, palm oil, and rubber. The lower course of the Tano River forms the Ghana-Ivory Coast boundary [33].

As the principal river in the Asutifi North District, the Tano River receives inflows from a number of streams that drain the Ahafo Mines project area. Seasonal streams and rivers have divided the Ahafo mines area into different basins some of which include the subika basin, Amoma basin and the Awonsu basins. All these basins and their tributaries dry up usually from November to end of April. The Tano River remains the most significant surface water resource in the project area. It serves as the main source of water for domestic use and agricultural activities. Water from the Tano River is pumped and treated by the Ghana Water Company Limited (GWCL) at Akyerensua and used to services communities such as the Hwidiem, Kenyase No.1, Kenyase No.2, New Dormaa and a host of other communities within the project area (Figures 1 and 2).

Water sampling and treatment

Water samples for the study were taken from the Tano River. In all twenty-four (24) samples were taken in duplicates from access point to the Tano River at Ntotroso (upstream) and at Kenyase (downstream). The samples were taken 100 metres apart at access points to the river. The samples were taken into clean bottles of volume 1.5 litres in two weeks interval between 9 am to 12 pm on each sampling day. At the sampling points, 5 ml of HNO_3 were added to each sample for preservation. The samples were placed in ice chest with ice and then transported to the Laboratory to the Central Laboratory at the Kwame Nkrumah University of Science and Technology for analysis.

Determination of parameters

Physicochemical properties: The Physicochemical properties that were measured included pH, Conductivity, Total Dissolved Solids (TDS) Turbidity and Dissolved Oxygen (DO) levels. The pH of each sample was determined using the pH meter (PHYME cobros 3 basic unit USB, Germany). The turbidity for the samples was determined using a turbidity meter (Hanna instrument LP 2000, Italy) with the turbidity measured in Formazin Turbidity Unit (FTU). The electrical conductivities of the samples and total dissolved solids of the samples were determined with Jennway Conductivity meter (Jenway model 4010, UK). The Amount of dissolved oxygen in the samples were also determined using the Winkler's Method.

Heavy metals concentration: The heavy metals that were analysed for in the samples include Arsenic, Lead, Copper, Cadmium and Mercury. The amount of mercury in the samples was determined using Automatic Mercury Analyzer (Model HG 5000, USA). For the concentration of arsenic, lead, copper and cadmium in the samples, the Atomic Absorption Spectrophotometer (AAS) (Unicam 929, USA) were used. The samples for AAS were digested with concentrated nitric acid before analysis. The filtered samples and the unfiltered samples were stored in the refrigerator at 4 °C for further analysis. In the first part of the analysis, a blank solution prepared from distilled water as well as the standard reference solution for the individual parameters were used to calibrate the instrument after the required lamp has been fixed into the instrument. The instrument was then adjusted until the acceptable calibration was achieved and the samples run to determine the concentration of each of the metals under investigation (Table 1).

Data analysis techniques: The data collected were analysed using the *International Business Machines* Corporation's Statistical Package and Service Solution (IBM SPSS version 20). The analysis involved both descriptive and inferential statistics. Descriptive statistics used involved frequencies, percentages, measures of central tendencies and dispersion. Inferential statistics used included independent sample t-test comparison of mean performed to find if there is a statistical difference in the values of the physicochemical properties and the concentration of heavy metals in the upstream and downstream of the Tano River.

Results and Discussion

The results from analysis of data collected for the study are presented as follows:

Descriptive analysis of physicochemical paramters levels/ Concentration in the Tano River

The study examined the concentration and levels of five physicochemical properties of water in the Tano River namely pH, Conductivity, Total Dissolved Solids, Turbidity and Dissolved oxygen (DO). In all these paramaters were analysed from 24 samples collected at both the upstream and downstream of the Tano River within the catchment of the Ahafo mining. The results from the analysis of the data collected are presented in Table 2. The results and discussion in relation to each of the physicochemical parameters are as follows.

pH: The pH of the water measures the amount of hydrogens ions in the water. From the results in Table 2, it noted that the upstream pH of the Tano river ranges from 6 to 7.86 whereas the downstream ranges from 5.95 to 7.81. The recommended acceptable threshold for pH is 6 to 9 and 6.5 to 8.5 respectively for the Environmental Protection Agency of Ghana (EPA) and the World Health Organisation (WHO). The results therefore means that upstream pH was generally within the EPA threshold, the downstream were lower than both the EPA and WHO thresholds. According to Dorleku et al. [21] rivers or water bodies polluted by mining activities tend to have low pH as a result of reactions between rock minerals and water and atmospheric oxygen. A low pH value in water bodies have often been used as proxy measure of the extent of pollution by mining activities. Essumang et al. [34] have observed that acidity of water in mining areas is often influenced by drainage from metal-rich rocks in the soil that are displaced by the mining operation. In this study, the down stream samples recorded a minimum pH that is lower than that of the upstream. Since the downstream area was characterised by mining activities, the slight acidity of the water could be as a result of the mining operations. It is however important to note that the difference between the uopstream

Parameters	Instrument/Method/Technique	Unit
Physicochemical Parameters		
pH	PHYME cobros 3 basic unit USB pH meter	
Turbidity	Hanna instrument LP 2000 turbidity meter	FTU
Conductivity	Jenwey 4010 conductivity meter	µS/cm
Total Dissolved Solid	Jenwey 4010 conductivity meter	mg/L
Dissolved Oxygen	Modified Winkler Method	mg/L
Heavy Metals		
Arsenic	Atomic Absorption Spectrophotometer (AAS) (Unicam 929, USA)	mg/L
Lead	Atomic Absorption Spectrophotometer (AAS) (Unicam 929, USA)	mg/L
Copper	Atomic Absorption Spectrophotometer (AAS) (Unicam 929, USA)	mg/L
Cadmium	Atomic Absorption Spectrophotometer (AAS) (Unicam 929, USA)	mg/L
Mercury	Automatic Mercury Analyzer (Model HG 5000, USA)	mg/L

Table 1: Water Quality Parameters and Measuring Instruments.

		Ntotroso (Upstream)		Kenyase No. 2 (Downstream)		Standards	
Parameters	N	Mean	Std. dev.	Mean	Std. dev	EPA	WHO
Conductivity (μS/cm)	12	203.33	35.50	224.25	44.70	1500	1400
Total Dissolved Solid (mg/L)	12	103.67	18.41	114.5	23.20	500	1000
Turbidity (FTU)	12	30.67	12.87	55.17	28.65	75	75
Dissolved Oxygen (mg/L)	12	4.43	0.64	3.95	0.71	-	6.1
pH	N	Min	Max	Min	Max	6-9	6.5-8.5
	12	6	7.86	5.95	7.81		

Table 2: Physicochemical properties of samples from the Tano River.

pH and that of the downstream was relatively small. This implies that impact of the mining activities on the river with regards to pH is very low.

Conductivity: Conductivitiy of water measures the amount of dissolve ions in the water. From the results in Table 2, it is noted that the conductivity of the downstream samples from the Tano river was higher than that of the upstream. The average conductivity at the upstream was 203.33 ± 35.50 μS/cm while that of the downstream sample was 224.25 ± 44.70 μS/cm. The EPA and WHO threshold limits for conductivity is 1500 μS/cm and 1400 μS/cm respectively. The results therefore means that while the conductitivty at both the downstream and upstream were within tolerable of the EPA and WHO thresholds, the downstream nevertheless have high conductivity than the upstream. The conductivity of water is influenced by several factors. The common condition that influences conductivity of water is the presence of dissolved minerals. Karato et al. [28] have postulated that the presence of ions such as sodium, potassium and chloride in water significantly influence the level of conductivity. Diffusion of Manganese (Mg^{2+}), iron (Fe^{2+}) and hydrogen have also been noted to play a significant role in the electrical conductivity of water largely because of the high mobility and potentially large concentration of hydrogen in minerals [28]. Activities that lead to the release of rock minerals into water have been noted to influence conductivity of water [27].

The results of this study showing low conductivity in both the Tano at both the downstream and upostream can be explained by several principles. According to American Public Health Association (APHA) [35], water that runs through areas with granitic bedrock tends to have a reduced conductivity due to the fact that granite is made up of inert materials that do not ionised. The low conductivity could, therefore, be possible due to the presence of inert materials in the water. Karato et al. [28] have also indicated that the presence of ions such as sodium, potassium and chloride whose presence is often related to mining pollution or other anthropogenic disturbances determines the conductivity of water. In this vain, it can be said that the low conductivity of the river means that there is no or limited anthropogenic disturbance of the water. Previous study by Asamoah et al. [27] also recorded no or minimal impact of mining on the conductivity of water in Ghana.

Total Dissolved Solids (TDS): Total Dissolved Solid measure the amount of materials in the water that affect the transparency and light scattering of the water. The study determines the concentration TDS in the Tano river at both the upstream and downstream as shown in the results in Table 2. Clearly as the results have shown, TDS at the upstream (103.67 ± 18.41 mg/L) were lower than that of the downstream (114.5 ± 23.20 mg/L) but both were also lower (within acceptable threshold) of the EPA threshold of 500 mg/L and WHO threshold of 1000 mg/L. High values of (TDS) are indications for high amount of inorganic salts, organic matter, and other dissolved materials [36]. While natural activities can result in the presence of TDS in water, its association with human activities such as mining or agricultural activities has been reported [37].

Although both the downstream and upstream TDS were within acceptable threshold, it is nevertheless important to examine factors that mya account for variation between the two points. The downstream is characterised by mining and related activities which potentially influenced the TDS values. Lottermoser et al. [38] reported that mining disturbances increase the concentrations of suspended particles and metals, and hence result in increased values of TDS in surface water bodies in mining area. The activities of mining at the downstream are quite intensive with large-scale operations and small-scale artisanal mining all on-going. These activities result in the weathering of rocks, displacement of particles which are drained into the Tano River and thereby may have accounted for the slight difference in the TDS values of the water (Table 3).

Turbdidity: The turbidity of the samples taken from the Tano river at both Ntotroso and Kenyasi are presented in Table 4. All turbidity measures were recorded in Formazin Turbidity Unit (FTU). From the results it is that clear that the mean turbidity values of the Tano river at both locations (Ntotroso and Kenyasi) were below the threshold value of GEPA for river. The mean turbidity values recorded for the samples taken at downstream 55.17 ± 32.05 FTU. was higher than that of the upstream samples of 30.17 ± 14.95. The EPA recommended threshold for turbidity is 75 FTU, meaning the mean values and minimum values obtained for samples from locations along the river fall below the recommended threshold.

Dissolved Oxygen (DO): Dissolved Oxygen (DO) of a sample of water measure the quantity of oxygen dissolved in the water. DO of water vary depending on factors such as temperature, sunlight, atmospheric pressure, salinity and water turbulence. From the results of the study presented in Table 2, the average DO recorded at the upstream was 4.43 ± 0.64 mg/L while that of the downstream was 3.95 ± 0.71 mg/L. Quite clearly as the resuls have shown, the DO level at the downstream was also higher than that of the upstream. In comparison with the WHO standard, it is noted that the DO level at both the upstream and downstream were lower than the acceptable threshold of 6.1 mg/L. Lower solubility of oxygen in water is associated with an increase in temperature and salinity. Simpson et al. [39] noted that warmer temperatures decrease the solubility of oxygen in water but also increases metabolic rates that affect sediment oxygen demand. Importantly, Barnes et al. [40] reported that pollutants such as acid rock drainage which result from mining activities produce direct chemical demand on oxygen in the water for certain oxidation-reduction reactions and thereby influence the amount of DO.

The amount of DO in water is very critical for the survival of aquatic organisms. Asamoah et al. [27] reported incidence of massive death of aquatic organism in the Birim river in Ghana as a result of lower DO caused by mining operations. The impact of mining on the DO of water is related to the fact that mining activities often result in introduction of heavy metals and other pollutants into the water. And as the amount of contaminants increases, the Biological Oxygen Demand (BOD) of the water increases leading to low DO and death of aquatic species. The findings of this study with DO lower than recommended standards is an indication of increasing BOD in the river. With the upstream having also a lower DO may be due to other anthropogenic activities in addition to mining are also responsible for the lower DO level.

Comparison of physicochemical properties of upstream and downstream samples: In order to established whether the difference in the physicochemical parameters of the samples from the upstream and that of the downstream were significantly different, an indepenedent sample t-test was performed. The t-test was performed to compare the mean difference between the upstream samples and the downstream samples. The results from the t-test are presented in Table 3. From the results, it is shown that no significant difference between the mean conductivity value of the water samples taken from upstream (203.33 ± 35.50 μS/cm) and that of samples taken from downstream (224.25 ± 44.70 μS/cm), t(22)=-0.197 p=0.218, two-tailed. The results also show no significant difference in the TDS of the samples taken from upstream (103.67 ± 18.41 mg/L) and that of those from downstream (114.5 ± 23.20 mg/L), t (22)=-0.194, p=0.218, two-tailed. The results, however, show that turbidity of samples taken from upstream (30.67 ± 12.87 FTU) and that of those taken from downstream (55.17 ± 28.65 FTU) were significantly different, t(22)=-2.703, p=0.013, two-tailed. The turbidity of the water at the downstream was significantly higher than that of samples taken from upstream.

The results in Table 3, imply that while there are difference in the mean conductivity, TDS and DO of the upstream and downstream samples, these differences were not 'big enough' statistically. The result implies that the activities mining at the downstream of the river did not exert a significant impact on the Tano River to have resulted in significantly different values from that of the upstream. With regards to the turbidity however, the difference were statistically significant. This means that the turbidity in the upstream were significantly different from that of the upstream samples. Many reasons may account for the significant difference in the turbidity. It is possible that the mining activities that takes place in the downstream result discharge wastewater from their gold processing activities as well as run-off of clay or silt particles, which could be responsible for the high turbidity values at the downstream [41]. Mining activities are also characterised by excavations and breakdown of rocks which increase the rate of weathering and susceptibility to erosion and run-off into surface water bodies, thereby increasing turbidity [27].

Heavy metal concentration in the Tano River

The study also examined the concentration of heavy metals specifically Arsenic (As), Lead (Pb), Copper (Cu), Cadmium (Cd) and Mercury (Hg) in the both the upstream and downstream of the Tano River. A descriptive analysis of the data collected are presented in Table 3.

Arsenic (As): From the results in Table 4, it is noted that the As concentration at the upstream of the Tano River was 0.003 ± 0.002 mg/L and that of the downstream was 0.004 ± 0.002 mg/L. The conscntration As at both the upstream and downstream are considered acceptable as the both the EPA and WHO threshold limit is 0.01 mg/L. Arsenic presence in the environment comes from both natural and anthropogenic activities. Naturally Arsenic occurs in rocks and gold ore such as arsenopyrite [27]. If undisturbed, the may remain in the rocks and beneath the earth surface for many years. Human activities however often result in the release of them into the environment. Mining of gold from arsenic-containing rocks, especially as it happen in the Ahafo mines often release the metal into the soil and into the water bodies. The lower concentration of Arsenic in the Tano River indicates that the mining operations do not result in a significant displacement of the metal into the water. This observation contradicts suggestions that Arsenic pollution is pronounced in water bodies near areas that mining operations are taking place. The results also contradict Opoku-Ware et al. [16] suggestions that there is a significant Arsenic concentration in surface water bodies at the Kenyase Ahafo mines areas and its environs.

Lead (Pb): The concentration of Lead in water in mining areas is often attributed to the mining activities. From the results of this study, lead concentration was slightly lower in the upstream (0.017 ± 0.004 mg/L), relative to the downstream of 0.018 ± 0.006 mg/L. In comparison with the EPA and WHO standard of 0.01 mg/L, it can be inferred that Lead concentration in both the upstream and downstream were higher than acceptable threshold. Many rocks contain significant quantities of Lead. Once these rocks are broken during mining operation, the Lead present gets release and get drained into surface water bodies. The high above standard concentration of Lead is attributable to the mining operations on-going at the Asutifi North District. The presence of lead in the study area may also be due to the excavations activities of miners resulting in weathering and leaching metal from waste rock dumps. The Birimian rock predominant in the study area contains high levels of lead [27]. The weathering of these rocks, therefore, becomes source of lead pollution.

Copper (Cu): Copper in optimum quantity in its natural sources may not cause any environmental problem, however, when

Parameters	N	Upstream (Mean ± SD)	Downstream (Mean ± SD)	p-Value
Conductivity (μS/cm)	12	203.33 ± 35.50	224.25 ± 44.70	0.218
TDS (mg/L)	12	103.67 ± 18.41	114.5 ± 23.20	0.218
Turbidity (FTU)	12	30.67 ± 12.87	55.17 ± 28.65	0.013
DO (mg/L)	12	4.43 ± 0.64	3.95 ± 0.71	0.086

Table 3: Independent t-test of upstream and downstream physicochemical properties.

Parameter	Ntotroso (Upstream)		Kenyase No. 2 (Downstream)		Standards	
Parameters	Mean	Std. dev.	Mean	Std. dev	EPA	WHO
Arsenic (mg/L)	0.003	0.002	0.004	0.002	0.01	0.01
Lead (mg/L)	0.017	0.004	0.018	0.006	0.01	0.01
Copper (mg/L)	0.308	0.024	0.326	0.009	5.00	2.00
Cadmium (mg/L)	0.006	0.002	0.004	0.002	0.01	0.03
Mercury (mg/L)	0.002	0.001	0.002	0.001	0.005	0.001

Table 4: Heavy metal concentration of samples from the Tano River.

overabundant quantities of copper are released into the environment, it becomes a problem. From the results of this study presented in Table 4, Copper concentration in the upstream of the Tano river is 0.308 ± 0.024 mg/L while that of the downstream was 0.326 ± 0.009. The EPA standard for Copper is 5 mg/L while that of the WHO is 2 mg/L. The results of this study therefore indicate that the concentration of Copper in both the upstream and downstream are within acceptable standard of both the EPA and the WHO. According to Rodricks et al. [42], anthropogenic activities such as copper smelting often lead to the release of overabundant quantities of copper. As a trace element Copper is essential to organisms, but when they are in excess quantity they tend to be toxic [43]. According to Asamoah et al. [27], copper is relatively prevalent and it is in high concentration in surface water bodies polluted by mining activities in Ghana. Common activities that lead to the release of copper include copper smelting and other anthropogenic activities. From the findings of this study, the concentration of copper in the Tano River is very low and hence it is conclusive that mining activities in the Ahafo Mines have had very little impact on copper concentration in the Tano River.

Cadmium (Cd): Cadmium (Cd) is one of the most toxic elements with reported carcinogenic effects in humans [44]. High concentrations of Cd have been found to lead to chronic kidney dysfunction. From the results of this study presented in Table 4, the average Cadmium concentration at the upstream of the Tano river was 0.006 ± 0.002 mg/L while that of the downstream was 0.004 ± 0.002 mg/L. The EPA and WHO standards are respectively 0.01 mg/L and 0.03 mg/L. The results implies that while the upstream recorded higher concentration of Cadmium than that of the downstream, point sides concentration of Cadmium were within acceptable threshold limits of both the EPA and the WHO statndards. High Cadmium concentration is of environmental and health concern. Rieuwerts et al. [45] noted that ingestion of high level of Cadmium can result in toxicity of the kidney and skeletal system and may result in cardiovascular diseases. But as the finding shows in the Tano River the Cadmium is relatively low and is unlikely to pose health threat. The results therefore suggest that the mining activities at the Ahafo mines have not resulted in a higher concentration of Cadmium in surface water bodies as found by Tay et al. [46] in the coastal regions of Ghana.

Mercury (Hg): As quicksilver, mercury is found in nature in various forms as released into the environment through natural processes such as volcanic eruptions, the weathering of rocks, and forest fires and a number of anthropogenic activities [47]. But as an element, mercury does not break down in the environment but instead is cycled between the atmosphere, land, and water, and can travel large distances from the original source [46]. Mercury can also build up in humans and animals and become highly concentrated in the food chain [48-53]. In this study, the concentration of Mercury was determined at both the upstream and downstream of the Tano River. From the results presented in Table 4, the average concentration of Mercury was the same for both the upstream and downstream. Both points recorded Mercury concentration of 0.002 ± 0.001 mg/L while the EPA and WHO standards are 0.005 mg/L and 0.001 mg/L respectively. Base on the results in Table 4, it can be inferred that there is low concentration of Mercury in Tano river The findings of this study, commensurate well with earlier studies on the concentration of Mercury in the Ahafo mines area. Yeboah et al. [22] found Mercury concentration of the upstream surface waters of the Ahafo mine were generally within the tolerable limit of 0.002 mg/L. The finding of this study also reflects Yeboah et al. [22] conclusion that Mercury concentration in surface water bodies within the Ahafo mines area is within tolerable limits.

Comparison of heavy metal concentration in upstream and downstream samples

To find out if the heavy metals concentration in the upstream were higher than those taken from downstream; an independent-samples t-test was performed. The results of the analysis as presented in Table 5 show that there was no significant difference between the mean concentration of Arsenic upstream (0.003 ± 0.002 mg/L), and downstream (0.004 ± 0.002 mg/L), $t(22)=-0.881$, $p>0.388$, two-tailed; concentration of Lead upstream (0.017 ± 0.004 mg/L) and downstream (0.018 ± 0.006), $t(22)=-0.233$, $P>0.818$, two-tailed; concentration of Cadmium upstream (0.006 ± 0.002 mg/L) and downstream (0.004 ± 0.002 mg/L), $t(22)=1.281$, $p=0.214$, two-tailed and the concentration of Mercury upstream (0.002 ± 0.001 mg/L) and downstream (0.002 ± 0.001 mg/L), $t(22)=0.235$, $p=816$, two-tailed.

The results, however, show the difference in the concentration of Copper in the upstream (0.308 ± 0.024 mg/L) and downstream (0.326 ± 0.009 mg/L) were statistically significant, $t(22)=-3.136$, $p=0.006$, two-tailed. The implication of the results is that, despite the fact that nominal difference exists in the mean concentration of these metal, the difference were not statistically significant since the P-values were greater than 0.05 at confidence interval of 95%. The result also implies apart from copper, the concentration of the heavy metals considered in the study were comparatively equal in the downstream and upstream. Overabundant concentration of copper in water poses environmental concern. Despite the fact that copper was highly concentrated in the downstream than the upstream, the mean concentration values at both the upstream and downstream were within the recommended threshold of the EPA and WHO. This implies that the concentration of copper was not too high to be of environmental health concern. As a trace element, copper is essential to organisms [43,54]. High uptakes of copper, however, may be harmful as it has been associated with metal fume fever, Wilson's disease among others [27].

Parameter	N	Upstream (Mean ± SD)	Downstream (Mean ± SD)	p-Value
Arsenic (mg/L)	12	0.003 ± 0.002	0.004 ± 0.002	0.388
Lead (mg/L)	12	0.017 ± 0.004	0.018 ± 0.006	0.818
Copper (mg/L)	12	0.308 ± 0.024	0.326 ± 0.009	0.006
Cadmium (mg/L)	12	0.006 ± 0.002	0.004 ± 0.002	0.214
Mercury (mg/L)	12	0.002 ± 0.001	0.002 ± 0.001	0.816

Table 5: Comparison of Heavy metals concentration between downstream and upstream.

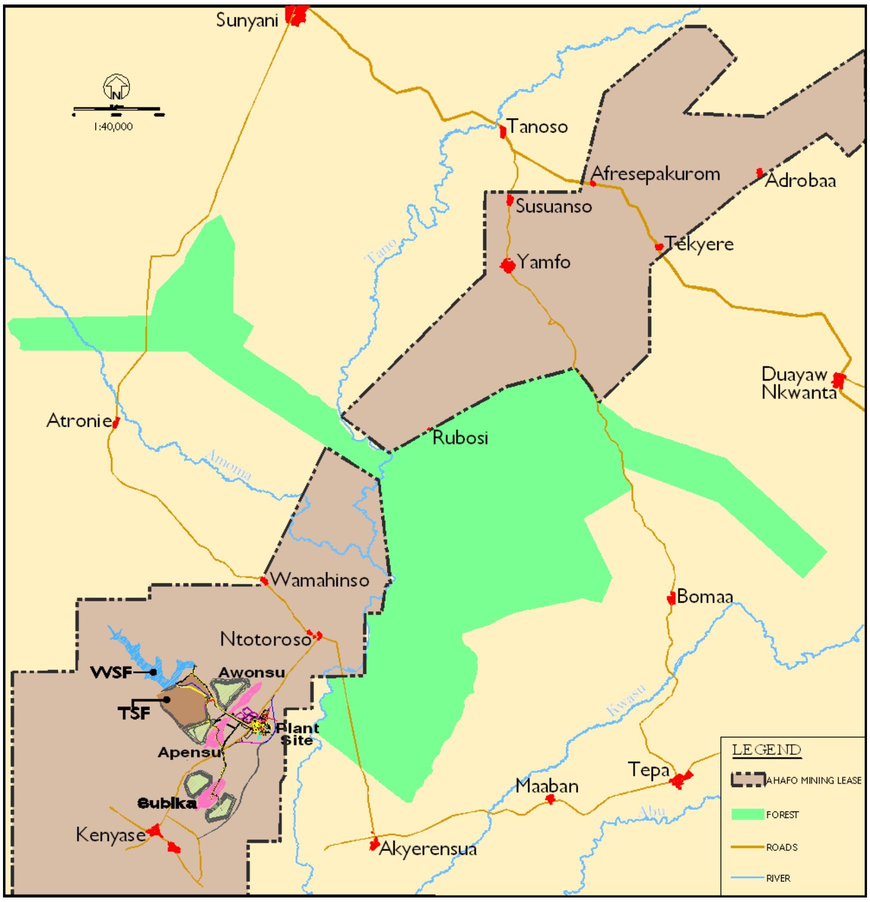

Figure 1: Map of Study Area (Ahafo Mine Catchment).

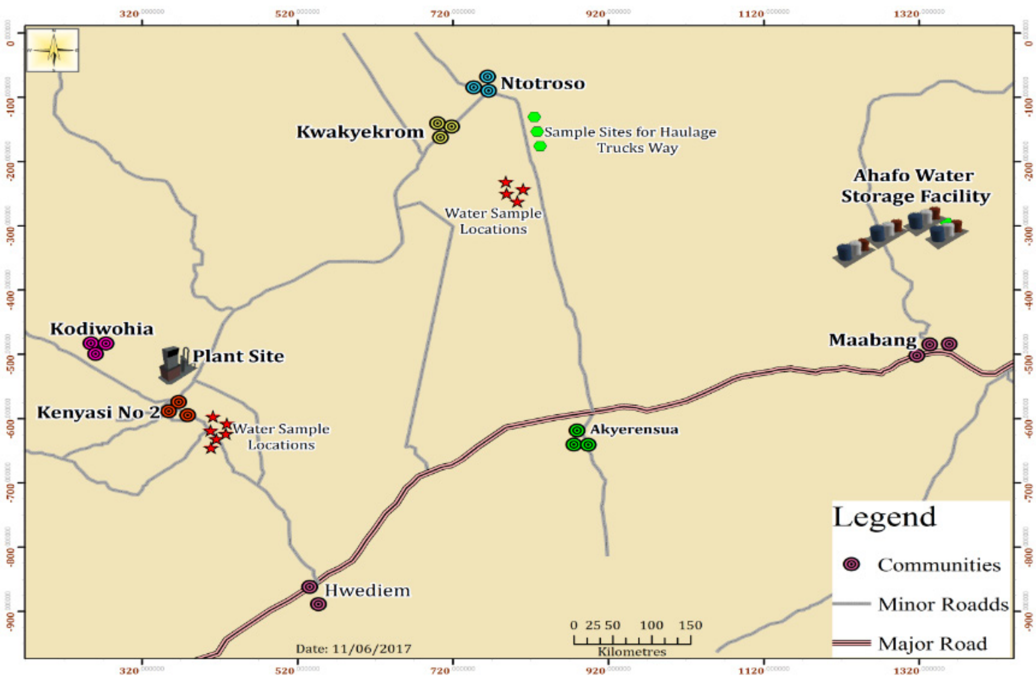

Figure 2: Map Showing sampling points.

Conclusion

Mines waste are undisputable sources of heavy metals. The activities of mining activities especially exploration and processing activities, therefore, pose a threat to nearby surface water bodies such as rivers. The results from analysis of the empirical data collected to determine the impact of mining activities on the Tano River show that the operations of the mines have very limited effect on the quality of the water in the Tano River. Apart from Dissolved Oxygen, all the other physicochemical properties of the river investigated had values within the recommended range of acceptable water quality by GEPA and WHO. The concentration of heavy metals such as Arsenic, Lead, Copper, Cadmium and Mercury were relatively low showing that little disturbance of the Tano River quality is attributable to the operations of the Mining activities. Additionally, apart from the turbidity of the water and the concentration of Copper, no significant difference was found between the physicochemical properties and heavy metal concentration of samples taken from the upstream and that of the downstream. Many of the differences in the quality of the Tano River based on the physicochemical properties and heavy metal concentration were not significant. The finding, therefore, leads to the conclusion that the mining activities in the Asutifi North District have had very minimal impact on the quality of the Tano River.

Recommendations and Implication for Future Research

Based on the findings of the study, the following recommendations have been suggested. Regular monitoring and enforcement of regulation on mining should be strengthened to ensure that mining operation in the Asutifi District do not adversely affect the quality of surface water bodies in the District. Aside from the Tano River, there are other surface water bodies such as wells, ponds, lakes among others that are potential sinks for waste generated from mining activities. Steps must be therefore be taken to ensure mining activities are regulated to prevent pollution of the water bodies. Further research should also consider the impact of mining on ground water in the Ahafo mines catchment.

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