

## Determination of the Concentrations of Physicochemical Parameters in Water and Soil from a Gold Mining Area In, Ghana

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**Abstract:** The study assessed the concentration of U, Th and K as well as other trace metals, anions and the physical parameters in water and soil samples in a goldmine and its surroundings using NAA, AAS, UV-VIS spectrophotometer and gross alpha/beta counter. The mean concentrations of the U, Th and K were 0.020, 0.029 and 1.19 mg/L. The concentration of U, Th and K were variable in soil and rock samples taken from different locations in the study area with mean values varying in arrange of 0.2 to 1.8  $\mu\text{g/g}$ , 0.9 to 2.6  $\mu\text{g/g}$  and 7037 to 71360  $\mu\text{g/g}$ , respectively. The concentrations of U, Th and K are comparable to world average values in similar studies. The calculated Th/U ratios show that there has not been significant fractionation during weathering or involvement in metasomatic activity of the radioelements with a mean value of 2.5. The concentrations of the other trace metals, anions and the physical parameters are within the WHO guideline levels in drinking water. The mean values of the gross- $\alpha$  and gross- $\beta$  activity concentrations were 0.012 and 0.137 Bq/L. These values are below the WHO recommended guideline values for drinking water. In general, the concentrations of U, Th and K in water and soil/rock samples were generally low even with the acidic conditions of the study area. The results obtained in this study also shows that the background radiation levels are within the natural limits and compared well with similar studies for other countries.

**Key words:** Gamma spectroscopy, goldmine, mineral processing, natural radioactivity, neutron activation

### INTRODUCTION

In Ghana there are over two hundred registered gold mining companies operating from small to large scale mining. Most of these mining companies are located in the Wassa West District in the Western Region of Ghana whose administrated capital is Tarkwa. All the mining companies are engaged in open pit (surface) mining. Even though mining contributes significantly to Ghana's Economic Recovery Program, it is at a great environmental cost as exploitation of the gold puts stress on water, soil, vegetation and poses human health hazards (Amonoo-Neizer and Amekor, 1993). Previous studies in the study area have shown that for gold mining, mercury, arsenic and cyanide are common pollutants at high concentrations in urine of the inhabitants of the mining communities (Asante *et al.*, 2007). Also many chemicals including those from less known e-wastes also enter the environment and remain environmental issues in Ghana (Asante and Ntow, 2009).

The source of the pollutants could be due to wastes arising from mining and mineral processing activities, manufacturing and use of synthetic products (e.g., pesticides, paints, batteries, industrial wastes, and land application of industrial or domestic sludge

(USDA, 2000). Most of these environmental pollutants also occur naturally through natural weathering processes. Published reports also indicate that, mainly mining and smelting plants release metals from the bed-rock (Walker and Sibly, 2001).

The study area is noted for its heavy mining activities from small scale to large scale mining. The concession of the mine is located at about 4 km from Tarkwa Township and also dotted around the concession are 8 small communities. The total population of the study area is about 94, 000 (GFGL, 2008). The main occupation of the inhabitants is farming. However, potentially contaminated soils may occur as a result of discharges of mines wastes that may contain environmental pollutant. For instance excess heavy metal accumulation in soils could be toxic to humans and other animals. The exposure to these pollutants is normally chronic through the food chain.

The source of water supply to inhabitants in the study area is ground water. The mining company in other to meet the demands for portable water has constructed boreholes and hand dug wells in the communities affected by their operations (Kortatsi, 2004). In addition, surface water from river Bonsa at Bonsaso is treated by the Municipal Water Supply Company for use by the inhabitants in the study area. Runoff of environmental

pollutants as a result of the mining and mineral processing of the Mining Company may also contaminate these water sources. A study on the multi-elemental contamination covering 22 trace elements in drinking water and urine from mining town of Tarkwa, in Ghana has been published (Asante *et al.*, 2007).

The current study focused on quantifying the metals concentration with special interest in uranium (U), thorium (Th) and potassium (K), anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ) as well as the physical parameters such as pH, temperature, conductivity and total dissolved solids (TDS). Uranium and thorium which are rare earth elements, beside their chemical toxicity also have associated with them radiological hazard. The U, Th and K are amongst the most incompatible elements and are normally concentrated in granitic rocks that are most abundant plutonic rocks in continental crust. They are generally similar in geochemical behavior with U and Th belonging to the actinides series and both exist in the tetravalent state under reducing conditions. Whilst K is found mainly in feldspar, mica, leucite, etc minerals, trace quantities of U and Th are found in major minerals such as quartz and feldspar (Galbraith and Saunders, 1983). However, the concentrations of U and Th could be higher in accessory minerals such as orthite or allanite, monazite, zircon, etc which are concentrated in granitic rocks (Valkovic, 2000). The content of U and Th generally increases with silicon dioxide ( $\text{SiO}_2$ ), during differentiation, fractional crystallization, partial melting, etc., in final stages of magmatic procedures (Rollinson, 1993).

Natural waters contain several alpha and beta emitting isotopes in widely varying concentrations mainly due to U, Th and K in groundwater. When the water is ingested by humans they contribute to internal dose to the body. Alpha ( $\alpha$ ) emitters are particularly of concern because of their high Linear Energy Transfer (LET). Some studies on radioactivity content of bottled drinking water in Australia and Spain have reported values exceeding the recommended limits (Cooper *et al.*, 1981; Martin Sanchez *et al.*, 1999). In Ghana, regulations on the levels of radioactivity in drinking water are based on the World Health Organisation (WHO) recommended values (WHO, 2004). The recommended levels in Ghana are set by the Ghana Standards Board (GSB, 2005). According to WHO guidelines, gross alpha radioactivity includes all the alpha emitters with the exception of radon; gross beta radioactivity includes all beta emitters, except  $^3\text{H}$ . These guidelines ensure an exposure lower than 0.1 mSv/yr assuming a water consumption rate of 2 L/day. In Ghana regulation for the quality of drinking water with regards to limits for radioactivity content are not carried out. For this reason, studies of the quality of the water used in the study area were performed in order to guarantee a low level of radioactivity. As a result the radiological quality

of the samples in the study area was analyzed to determine alpha and beta activities.

Physical parameters such as pH temperature and conductivity influence the concentration of many pollutants by altering their availability and toxicity. The temperatures at which environmental samples are collected and at which physicochemical measurements are made are important for data correlation and interpretation (Tay *et al.*, 2009). Also at high temperatures, the toxicity of many substances may be increased. Also in addition to microbial activities, within an aquatic medium, temperatures and pH are two important parameters that govern the methylation of elements such as Lead (Pb) and Mercury (Hg) (Von Loon, 1982). The Electrical Conductivity (EC) is also a useful indicator of mineralization in a water body which has a correlation with the Total Dissolved Solids (TDS) in the water body.

The aim of this study was to determine the concentration of physicochemical parameters in water and soil/rock in the study area as a means of assessing the quality of water use by the inhabitants and also determine if the farmlands have received heavy loading of pollutants such as U and Th and other metals that could have implications on farming in the area.

## METHODOLOGY

**Description of the study area:** The study area is Tarkwa Goldmine and its surrounding communities including Tarkwa Township within the mines area of concession. The study covered a period of two years from October 2008 to September 2010. The Tarkwa Goldmine is located in the Wassa West District in the Western Region of Ghana. The Tarkwa township is located at latitude  $5^{\circ}15' \text{ N}$  and longitude  $2^{\circ}00' \text{ W}$ . Figure 1 shows the concession of the mine and the surrounding communities where sampling was carried out. The concession of the mine covers an area of 294.606  $\text{km}^2$ .

Geologically, the gold ore are located within the Tarkwaian system, which forms a significant portion of the stratigraphy of the Ashanti Belt in south western Ghana. Intrusive igneous rocks contribute to about 20 % of the total thickness of the Tarkwaian system in the Tarkwa area (Karpeta, 2000). The ore body consist of a series of sedimentary banket quartz reef units similar to those mined in the Witwatersrand of South Africa where gold ore have associated with it uranium in commercial quantities. The existing surface operation currently exploits narrow auriferous conglomerates from six pits namely: Pepe, Atuabo, Mantraim, Akontansi, Terberebie and Kottraverchy. The geological formation of the mine is such that gold bearing ore is situated between waste belts with the major rock type being sedimentary. The local geology is dominated by sedimentary Banket series which consists of a well sorted conglomerates and pebbly

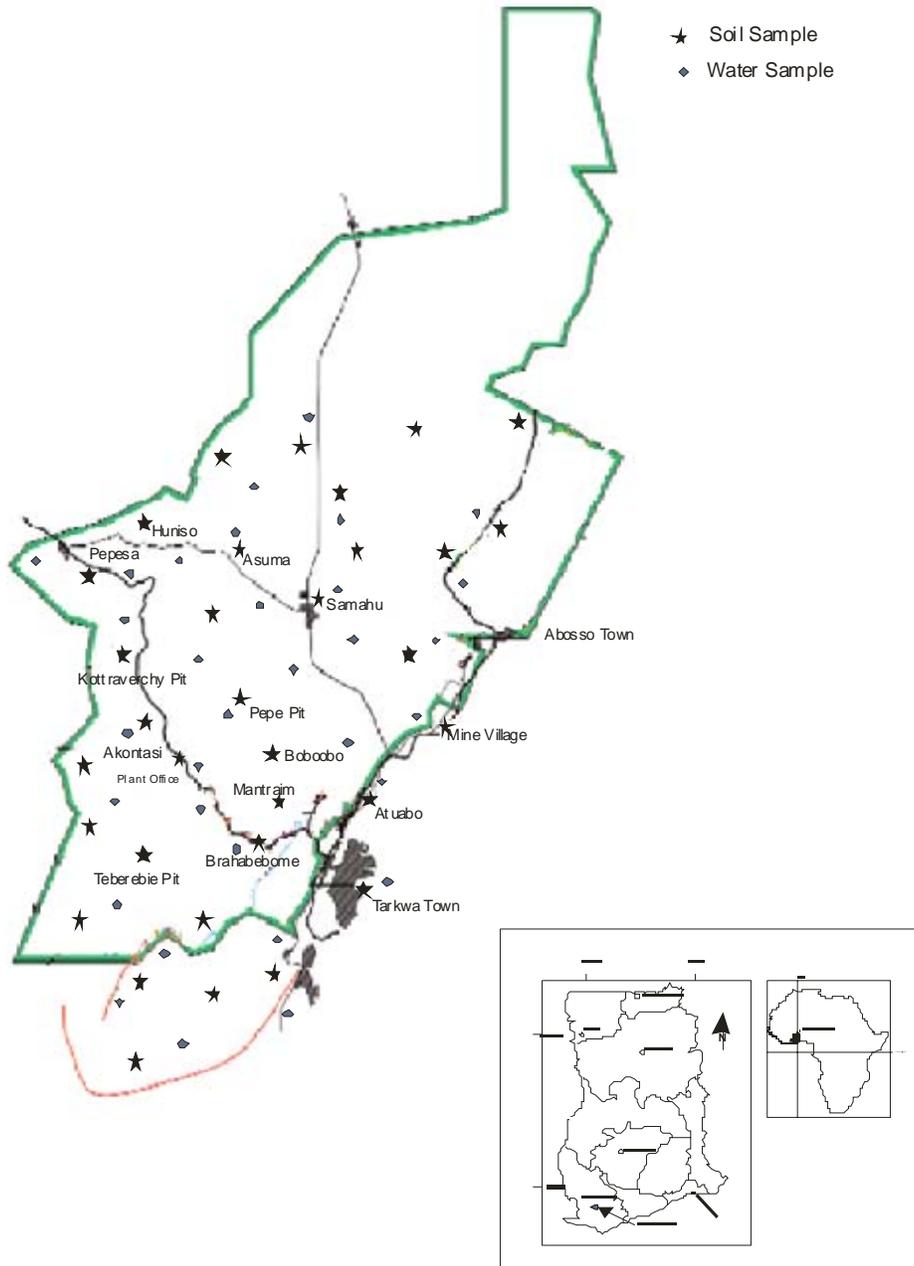


Fig. 1: Layout of the study area showing the water and soil/rock sampling points

quartzite with clasts generally considered to be Birimian in origin and containing significant gold mineralization, hosting the Tarkwa ore body. The rocks of the Tarkwaian system consist of the Kawere Group, the Banket series, the Tarkwa Phyllite and the Huni Sandstone. Most of the rocks that resemble sandstone at the surface are weathered equivalents of parent quartzite (Kuma and Younger, 2001). Gold ore is the alluvial type and non-sulphidic associated with the conglomerates of the

Tarkwaian formations. Two main methods are used by the Tarkwa Goldmine to recover gold from the ore, namely the Carbon in Leach (CIL) and the heap leach (HL) (GFGL, 2007).

Hydrogeologically, most of the major towns and villages except Tarkwa Township in the Wassai West District depend on groundwater as the main source of water supply through boreholes and hand dug wells (Kortatsi, 2004). Two types of soils exist in the Tarkwa-

Prestea area and these are forest oxysol in the south and forest ochrosol-oxysol integrates in the north (Kortatsi, 2004).

The climate of Tarkwa is the tropical type characterized by two wet seasons; March-July and September-November. Data obtained from the mines Environmental Department shows that the total annual rainfall figures measured for the year 2008 was 1744 mm with an average of 145 mm. The average rainfall figure from January to July 2009 was 256.6 mm in a range of 2.2 mm in January to 283 mm in June. The relative humidity for the area was in the range of 73-98% with an average of 86%. The average atmospheric pressure was 100.2 kPa in the range of 99.0-100.7 kPa and outdoor temperatures in the range of 28-39°C with an average value of 34°C.

**Sampling:** Soil and rock samples were collected from the following locations within the mines and the surrounding communities including Tarkwa Township, Abekoase, Brahabeom, Huniso, New Atuabo, Pepesa, Samahu and Bonsanso (control). The selection of the sampling locations was based on the accessibility to the public and proximity to the mine. Within the mines, soil samples were collected at satellite nursery, rehabilitation plantation, ore stockpiles, tailings dams, heap leach pads, wastes dumps, open pits and the plant site. In the communities samples were taken in areas (farms) where crops were grown. The sampling locations were marked using a Geographical Positioning System (GPS), Geo Explorer II. The soil samples were taken using a coring tool to a depth of 5-10 cm. One kilogram (1 kg) of each sample was collected for analysis. The samples were transported to the laboratory where they were spread on trays and allowed to air dry for seven days. Finally all the samples were oven dried for preparation and subsequent analysis.

The water samples were taken from water sources within the Goldmine, Tarkwa Township and in the communities. These include Tarkwa Municipal water treatment plants (raw and treated water), Tarkwa Goldmine water treatment plant, tap water in houses, open pits, tailings dams, rivers, streams, boreholes and underground water sources. The samples were collected into labeled 2.5 L plastic bottles. The bottles were acid washed with 1M HNO<sub>3</sub> before filling with the water to ensure radionuclides remain in solution rather than adhering to the walls of the container. The bottles were also filled to the brim without any head space to prevent CO<sub>2</sub> being trapped and dissolved in water that might affect the chemistry of the water (pH). The water samples were then transported to the Laboratory and stored in a refrigerator prior to preparation and analysis. The samples were analyzed for U, Th and K and other metals Fe, Mn, Cu, Zn, Cr, Pb, Cd, Hg and As, and anions SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and Cl<sup>-</sup>.

**Physicochemical analyses:** The pH of the water samples were measured in the field and in the laboratory using pH meter model HANNA pH 211. The pH meter was calibrated with standard buffer solutions with pH 4.01, 7.0 and 9.21. The Total Dissolved Solids (TDS), conductivity and salinity were also measured in the laboratory using HACH multi-meter, model SanSion 5. The equipment was calibrated with the following standard solutions, 0.01M KCl and 0.1M KCl.

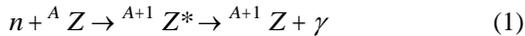
The following anions were determined in the water samples using a UV-VIS Spectrophotometer, model UV-1201, manufactured by HIMADZU of Japan; phosphate (PO<sub>4</sub><sup>3-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and chloride (Cl<sup>-</sup>). For quality control purposes the equipment was calibrated with a set of five (5) standard solutions of each analyte of interest.

The trace metals in the water samples were determined using Atomic Absorption Spectrophotometer (AAS). The water samples were first digested with a mixture of 3 mL concentrated HCl (35%), 6 mL concentrated HNO<sub>3</sub> (65%) and 0.25 mL industrial grade H<sub>2</sub>O<sub>2</sub> (30%) using automatic microwave digestion system ETHOS D Labstation. Reference standards for each element of interest, blanks and repeat of some samples were digested in the same way as the actual samples. After digestion, the following metals were determined using AAS Model Varian AAS240FS in an acetylene-air flame; Hg, As, Cd, Pb, Zn, Cu, Fe, Mn and Cr.

The trace metals in soil and water samples were determined using Neutron Activation Analysis (NAA). For the trace metals analysis in the soil samples, IAEA-SOIL-7 reference materials were used. The soil samples were prepared by weighing 0.1 g of the finely ground powder into a polyethylene film and sealed using a soldering rod and labeled with the sample code. The sample was then placed in a rabbit capsule and sealed again before the samples were irradiated. For water samples, 0.5 g of the sample was prepared in polyethylene vials of 1.2 cm diameter and 2.3 cm height for irradiation. In order to ensure that the sample was intact during the irradiation, the sample was doubly encapsulated by placing the smaller polyethylene vial into a bigger capsule of diameter 1.6 cm and height of 5.5 cm. The prepared samples, standards and blank, were irradiated using Ghana Research Reactor-1 (GHARR-1) at the Ghana Atomic Energy Commission, operating at 15 KW with a thermal flux of 5x10<sup>11</sup> n/cm<sup>2</sup>s. The samples were transferred into the irradiation sites via pneumatic transfer system at a pressure of 0.6 Mpa. The samples were irradiated with a scheme for medium to long radionuclide for one hour (1 h) and allowed to decay for 48 h to two weeks until a suitable dead time was achieved. After irradiation, radioactivity measurement of the induced radionuclides was performed by a computer based gamma spectrometry set-up. The gamma spectrometry system

consists of an n-type HPGE detector coupled to a computer based Multi-Channel Analyzer (MCA). The relative efficiency of the detector is 20% with energy resolution of 1.8 keV at gamma ray energy of 1332 keV of <sup>60</sup>Co. Through appropriate choice of cooling-time, the detector's dead time was controlled to be less than 10%. The irradiated samples were each counted for two hours on the HPGE detector. The identification of individual radionuclides was performed using their gamma ray energies and the quantitative analysis of the radionuclides was performed using gamma ray spectrum analysis software, ORTEC MAESTRO-32.

During irradiation, thermal neutrons collide with the nucleus and a number of reactions may occur the most useful of them in NAA being radiative capture and the reaction is generally represented by Eq. (1) (Landsberger, 1994).

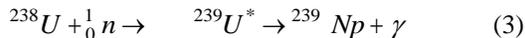


Where; <sup>A</sup>Z is the target nucleus, <sup>A+1</sup>Z\* is the compound nucleus in an excited state which de-excites with the emission of prompt gamma rays, <sup>A+1</sup>Z is the product after irradiating the target nucleus. The concentration of the metals in the samples was determined by comparator method represented by the Eq. (2).

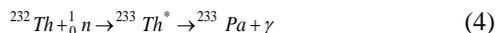
$$C_{sam} = C_{std} \left( \frac{A_{sam}}{A_{std}} \right) \quad (2)$$

Where; C<sub>sam</sub> is the unknown concentration of the element in the sample, C<sub>std</sub> is the known concentration of the element in the standard, A<sub>sam</sub> is the activity of the sample and A<sub>std</sub> is the activity of the standard.

The concentrations of uranium and thorium in µg/g (ppm) and other metals were determined from <sup>238</sup>U and <sup>232</sup>Th radionuclides using the following nuclear reactions and gamma energy lines of 277.7 and 311.9 keV, respectively (Landsberger, 1994).



The <sup>239</sup>U formed after the neutron capture has very weak gamma energy and undergoes a beta-decay to form <sup>239</sup>Np which emits gamma rays with energy of 277.60 keV and this was used to determine <sup>238</sup>U activity concentration. Similarly for <sup>232</sup>Th, the <sup>233</sup>Th formed after the neutron capture undergoes beta-decay to form <sup>233</sup>Pa with the emission of gamma rays with energy of 312.17 keV was used to determine <sup>232</sup>Th activity concentration.



**Natural radioactivity in water samples:** Twenty-nine (29) water samples taken from bore-holes, tap water, water treatment plants streams and waste water from the gold treatment plant were analyzed for gross alpha (α) and gross beta (β) radioactivity. Five hundred milliliters (500 mL) of each water sample was acidified with 1ml of concentrated HNO<sub>3</sub> and evaporated to near dryness in on a hot plate in a fume hood. The residue in the beaker was rinsed with 1M HNO<sub>3</sub> and evaporated again to near dryness. The residue was dissolved in minimum amount 1M HNO<sub>3</sub> and transferred into a weighed 25 mm stainless steel planchet. The planchet with its content was heated until all moisture has evaporated. It was then stored in a desiccator and allowed to cool and prevented from absorbing moisture.

The prepared samples were then counted to determine alpha and beta activity concentrations using the low background Gas-less Automatic Alpha/Beta counting system (Canberra iMatic™) calibrated with alpha (<sup>241</sup>Am) and beta (<sup>90</sup>Sr) standards. The system uses a solid state Passivated implanted Planar Silicon (PIPS) detector for alpha and beta detection. The alpha and beta efficiencies were determined to be 36.39±2.1 and 36.61±2.2%, respectively. The background readings of the detector for alpha and beta activity concentrations were 0.04±0.01 and 0.22±0.03 cpm.

## RESULTS AND DISCUSSION

The results of the physical parameters' pH, conductivity, temperature and Total Dissolved Solids (TDS) as well as the chemical parameters such as metals and anions in water sources in the study area are presented in Table 1.

The pH of the water sources studied varied in the range of 3.55 to 8.95 with an average value of 5.94. As can be observed in Table 1, almost all the water sources were acidic with pH less than 7.0. The WHO recommended pH range for drinking water is 6.50-8.50 (WHO, 2004). Out of the 29 water samples studied, only 42% of the water samples had pH in the WHO recommended pH range. This implies that, majority of the water sources had pH values below the pH of 6.50. The pH of water generally influences the concentration of many metals by altering their availability and toxicity. The most acidic of the water samples had a pH of 3.55 which was taken from Pepe pond within the mines which is not used for drinking or domestic purposes. The mean concentrations of U, Th and K in the Pepe water samples were low with values 0.02, 0.03 and 1.2 mg/L, respectively. The provisional guideline value of U based only on chemical toxicity in drinking water recommended by the WHO is 0.015 mg/L (WHO, 2004). The mean values of U, Th and K as shown in Table 1 were generally

Table 1: Comparison of the physic-chemical parameters of the water samples studied

Community	pH	T/°C	Cond. /µScm	TDS	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Fe	Cu	Zn	Pb	As	U	Th	K
				mg/L												
Abekoase	6.12	26.6	539.0	238.2	31.0	2.30	0.060	51.9	0.09	0.010	0.008	<0.001	0.004	0.015	0.030	1.47
Brahabebome	5.18	25.6	277.0	130.1	62.0	1.30	0.010	35.1	0.16	0.005	0.012	<0.001	0.003	0.040	0.040	1.01
Huniso	5.49	27.1	289.2	152.3	5.0	2.40	0.025	34.0	0.42	<0.001	0.068	0.04	0.007	0.015	0.025	1.21
New Atuabo	5.45	26.2	385.5	181.9	83.0	0.75	0.020	6.50	<0.001	<0.001	0.080	<0.001	0.004	0.025	0.030	0.81
Pepesa	5.55	26.6	519.5	229.5	6.0	2.35	0.010	88.8	0.22	0.086	0.147	0.07	0.005	0.015	0.025	2.43
Samahu	6.17	26.3	162.8	71.4	18.2	1.75	0.025	15.6	0.21	<0.001	0.030	0.04	0.004	0.020	0.035	1.94
Tarkwa	6.08	26.7	562.0	245.2	59.2	1.46	0.014	32.0	0.03	<0.001	0.013	0.08	0.004	0.014	0.030	0.99
Mine Site	6.67	26.4	332.8	235.5	26.3	3.20	0.073	85.9	0.12	0.007	0.009	0.17	0.005	0.023	0.032	0.85
Control	6.82	26.5	57.2	24.4	2.0	1.90	<0.514	10.1	0.41	<0.003	0.009	0.02	0.003	0.010	0.010	0.04
Min	3.55	25.5	2.4	17.3	0.2	0.2	<0.514	4.30	<0.001	<0.001	<0.001	<0.001	0.002	0.010	0.010	0.02
Max	8.95	27.3	1208.0	893.0	150.0	9.9	0.28	285.9	0.43	0.086	0.283	0.168	0.008	0.040	0.060	3.84
Mean	5.94	26.4	347.2	167.6	32.5	1.93	0.030	40.0	0.21	0.027	0.042	0.07	0.004	0.020	0.029	1.19
Stdev	0.57	0.41	173.5	79.9	29.1	0.72	0.024	30.3	0.14	0.048	0.048	0.05	0.001	0.009	0.008	0.69

low. In general, the concentrations of Th were higher than those of U which is unusual due to the relatively low solubility of Th as compared to U, and this could be attributed to the fact that, the water samples were not filtered prior to analysis. Thorium is generally transported with particulate matter and become deposited in water bodies. The concentrations of U and Th in water depend on the location of the water. In mineralized aquifers, values in a range of 0.10-0.46 ppm have been reported by various researchers (Fix, 1956; Denson *et al.*, 1956). Values in a range of 0.001-0.013 ppm have also been reported in sedimentary rock drainage (Adams *et al.*, 1958). The results in this study on underground water samples are typical of similar studies that have been reported in mineralized aquifers.

The concentration of other metals in the water samples such as Fe, Cu, Zn, Pb, As, Hg, Cd and Cr were variable from one location to another. The concentrations of Cr, Hg and Cd in all the water samples studied were below their detection limits. For Fe mean concentrations of all the water samples were below WHO guideline level of 0.3 mg/L (WHO, 2004) except the water sample from Huniso and river Bonsa at Bonsaso about 30 km from the mine site which was taken as a control. For Cu, Zn and As, the mean concentrations were all below the WHO guideline values of 2.0, 3.0 and 0.01 mg/L, respectively (WHO, 2004). The mean concentrations of Pb were variable with some water samples having values below the detection limit (Abekoase, Brahabebome) whilst the rest had values exceeding the WHO guideline levels of 0.01 mg/L (WHO, 2004).

For the anions Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> studied in the water samples, the mean concentrations were all below the WHO guideline levels in drinking water of 250, 50, 0.3 and 250 mg/L, respectively. The concentrations of the metals and anions, and the physical parameters were generally low and as a result not expected to cause any health hazards or caused water quality problems. In general, chemical and biogeochemical processes could result in lowering of pH and as a result, dissolution of trace metals as well as radionuclides into the ground water systems resulting in high concentrations. This could lead

to the water becoming hazardous for human consumption. For instance trace metals such as Cd, Hg, Cr, Pb and U are known to be powerful nephrotoxins (Doul *et al.*, 1980). Exposure to metals such as Fe, Pt, Sb, As, Au and Tl are known to cause renal damage (Maher, 1976). Based on the concentration of the metals in this study, the mine operations do not lead to any human risk.

The results of the mean concentrations of metals of interests U, Th and K measured in soil and rock samples as well as other metals such Mn, Si, V, Al, La, As, Cr, Sr, Sc, Fe, Co, Ti, Mg, Ca, Na are shown in Table 2. The mean elemental concentrations of U and Th varied in a range of 0.2-1.8 and 0.9-2.6 µg/g. All the mean concentration values were below the world average values of 2.8 and 7.4 µg/g reported by UNSCEAR (2000). This result indicates that the mean concentrations of the radioactive elements U and Th obtained from the formations studied are by a factor of two to fourteen times lower than the worldwide reported values. In general, the original uranium, thorium and potassium concentrations in rocks may vary due to alteration or metamorphic processes (Verdoya *et al.*, 2001). The most abundant of the three radioelements K is of less concern because K is an essential element for growth. The mean concentration of K varied in a range of 7037 to 71360 µg/g in soil. The means concentrations of the other metals in various materials studied were variable. The mean concentrations of Si were in a range of 1345 µg/g in soil to 5329 µg/g in rock which is an indication of silica (SiO<sub>2</sub>) saturated rock type of the area. Studies have shown that, the content of U and Th generally increases with silicon dioxide (SiO<sub>2</sub>), during differentiation, fractional crystallization, partial melting, etc in final stages of magmatic procedures (Rollinson, 1993). The results in this study did not reflect this trend where the concentrations of U and Th tend to be high with SiO<sub>2</sub>.

The results of the major metals such as Fe, Mg, Ca, Na and k were quite high in the soil and rock samples indicating that these essential metals are not highly leached even though the study area is known to have very high rainfall patterns. This also means that agricultural

Table 2: Summary of metals concentration and analytical uncertainties ( $\mu\text{g/g}$ ) of soil, tailings and rock samples of the mine by NAA

Element/ $\mu\text{g/g}$	Type of sample with number of samples (N) in parentheses						
	Rock (ore) (N = 6)	Soil (pit) (N = 6)	Rock (pit) (N = 9)	Rock (CIL plant) (N = 9)	Rock (HL plant)	Soil (communities) (N = 24)	Soil (Tarkwa) (N = 18)
Mn	176±29	426±28	1309±21	3400±111	193±28	285±22	56±15
Si	5086±322	1347±425	2640±239	5329±143	4198±209	3335±399	2077±341
V	12±0.4	32±6	459±19	241±17	1.8±0.6	8.4±0.4	115±7
Al	1911±111	1843±299	2169±423	9532±370	7722±310	3.5±0.03	5179±260
La	57±9	21.3±3.6	113.5±13	35±4	17.6±2.2	5.4±0.7	23±3
As	3.5±0.3	<0.00001	<0.00001	<0.00001	3.9±0.04	9.0±0.8	14±0.6
Cr	150±55	124±39	<0.01	170±34	<0.01	<0.01	360±48
Sr	<0.10	2.4±0.3	116±36	<0.10	<0.10	<0.10	194±56
Sc	2.5±0.4	1.7±0.02	4.6±0.4	4.5±0.15	4.5±0.35	<0.001	9±0.44
Fe	2316±773	4692±886	7307±105	2330±863	2920±813	<0.10	2143±393
Co	5.8±1.0	<0.001	<0.001	<0.001	6.5±1.0	<0.001	2±0.1
Ti	<0.10	2159±135	3579±160	4274±140	370±31	828±535	3200±383
Mg	8300±600	<0.10	2354±565	5820±375	2272±158	2809±173	<0.10
Ca	<1.00	<1.00	7143±142	1429±571	<1.00	754±452	<1.00
Na	11900±74	2446±18	19904±74	5171±30	11560±52	3505±100	2465±21
K	52648±216	7037±363	71360±3256	14190±616	36904±2064	7051±368	7643±566
U	1.8±0.9	0.2±0.1	0.4±0.1	0.52±0.17	1.80±0.60	1.3±0.69	1.4±0.55
Th	2.6±0.4	0.9±0.3	2.1±1.1	1.28±0.43	2.60±0.70	1.5±0.74	1.6±0.67
Th/U	1.4	4.5	5.3	2.5	1.4	1.2	1.1

CIL: carbon-in-leach; HL: heap leach; N: number of samples

Table 3: Gross- $\alpha$  and gross- $\beta$  activity concentrations (Bq/l) in water samples from the surrounding communities

Community	Activity concentration, Bq/l	
	Gross $\alpha$	Gross $\beta$
Abekoase	0.013	0.246
Brahabebome	0.011	0.096
Huniso	0.012	0.084
New Atuabo	0.013	0.063
Pepesa	0.012	0.374
Samahu	0.010	0.080
Tarkwa Township	0.008	0.071
Mine Site	0.017	0.101
Control	0.016	0.116
Mean	0.012	0.137

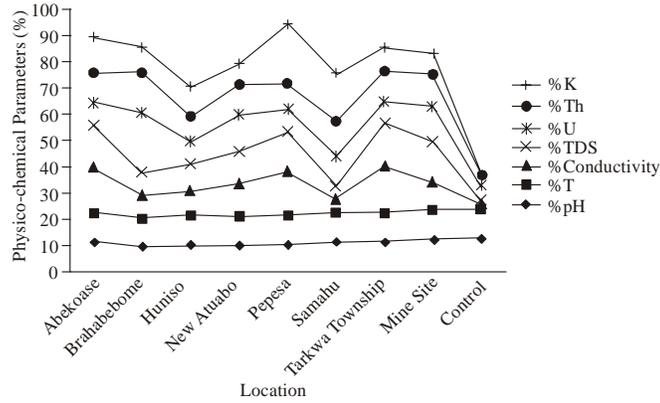
activities could still flourish in the study area. The concentrations of the rest of the trace metals As, Sr, Cr, Co, etc., were very low and in some cases below detection limit. This could be as a result of leaching of these metals due to the high rainfall of the area and the acidic conditions of the area as result of the high sulphides and pyrites.

By comparison, the concentrations of the trace metals were far lower than the major metals measured in the soil/rock samples. The reasons for the low levels of trace metals as compared to the major metals could be due to the clayed nature of the soil in the study area as well as heavy rains and low pH values of the area, which could facilitate the leaching of the trace metals. Soils with large surface areas such as clay minerals have large adsorption of major cations such as  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  etc and on the other hand low adsorption for trace metals such as arsenic. This is because ions have different tendencies to form complexes with different substances. For instance, many cations can form complexes with hydroxyl ( $\text{OH}^-$ ) or carboxyl group ( $\text{COOH}$ ) and as a result many metals become easily adsorbed to surfaces of these groups (Asklund and Eldvall, 2005). The concentrations of the

nutrient metals are very high which means that the soil type is an intermediate between the forest oxisols and the forest ochrosol which are normally less leached and contained all of their nutrients suitable for plant growth.

The activity concentrations of gross- $\alpha$  and gross- $\beta$  in water samples used in the various communities of the study area are shown in Table 3. The dominant oxide minerals in the study area include sandstone (quartz), pyrites, silica, hematite, specularite, magnetite and leucoxene with sandstone. Radionuclide concentrations in groundwater depend on the dissolution of minerals from rock aquifers. It has also been established that the water samples studied are acidic and this could facilitate the dissolution of radionuclides and other metals. The activity concentrations of gross- $\alpha$  in the water samples varied in a range of 0.008 Bq/L in Tarkwa Township to 0.017 Bq/L from the mine site (not intended for drinking or domestic purposes) with an average value of 0.012 Bq/L. For the gross- $\beta$ , the activity concentrations varied in a range of 0.063 Bq/L at New Atuabo to 0.374 Bq/L at Pepesa with an average value of 0.137 Bq/L. The WHO screening levels for drinking water below which, no further action is required are 0.5 Bq/L for gross- $\alpha$  and 1.0 Bq/L for gross- $\beta$  (WHO, 2004). The guideline values ensure an exposure lower than 0.1 mSv/year assuming a water consumption rate of 2 L/day. Comparing these results with the WHO guideline values, it can be observed that all the values of the gross- $\alpha$  and gross- $\beta$  are lower than the guideline values. This indicates that all the water sources in the study area which are designated for drinking and domestic purposes do not have significant natural radioactivity.

Figure 1 shows the concession of the mine and the surrounding communities where sampling of water and soil/rock were carried out. The soil/rock samples were collected from ore stockpiles, waste dumps, tailings dam, farmlands and other undisturbed areas within the mines.



Legend: K: potassium; Th: thorium, U: uranium, TDS: total dissolved solids; T: temperature

Fig. 2: A comparison of percentage weighted values of pH, temperature, conductivity, TDS, U, Th and K in soil and rock samples in the study area.

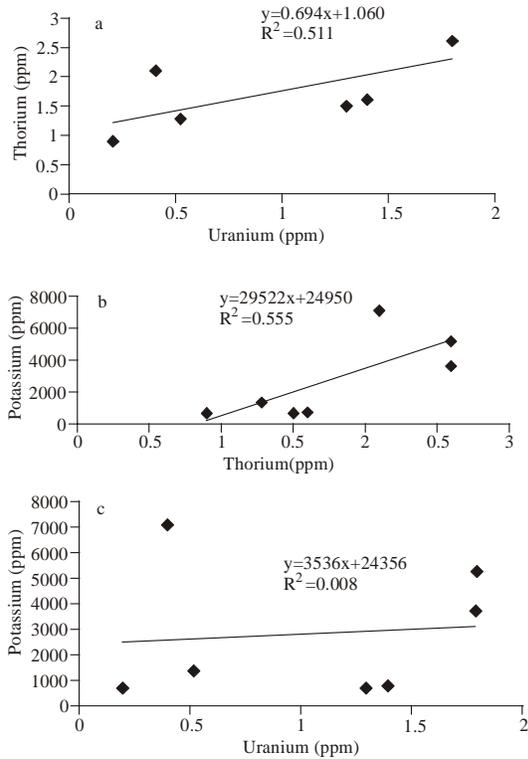


Fig. 3: Mean concentrations of U, Th and K in soil and rock samples in the study area. (a) U versus Th, (b) K versus Th and (c) K versus U. The solid straight lines represent the best fitting lines and their corresponding correlation coefficients.

Figure 2 is a comparison of the percentage weighted values of pH, temperature, conductivity, total dissolved solids, and concentrations of uranium, thorium and potassium in soil and rock samples. Studies have shown that, U, Th and K are generally similar in geochemical

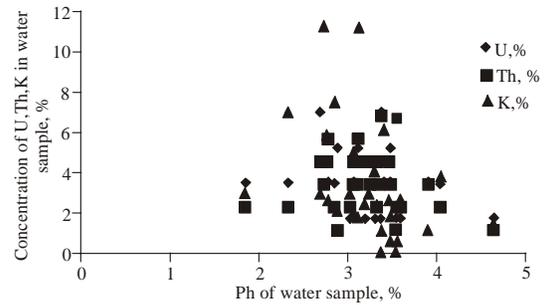


Fig. 4: Correlation between U, Th, K in the water samples and the pH of the samples.

behavior with U and Th belonging to the actinides series and both exist in the tetravalent state under reducing conditions (Adams *et al.*, 1958). As can be observed in Fig. 2, the results show that the three elements behave in the same manner under same environmental conditions of temperature, pH, conductivity and total dissolved solids.

The Th/U ratio which gives an indication of the relative depletion or enrichment of radioelements was also calculated for the different types of soil and rock samples. The Th/U ratio for normal continental crust varies from 3.8- 4.2 (Plant and Saunders, 1996) with a typical value of 3.0. The results of the ratios, Th/U, K/Th and K/U are shown in Fig. 3a, b and c, respectively. The calculated Th/U ratios are also shown in Table 2 with values varying in a range of 1.1 in soil in Tarkwa to 5.3 rock sample in a mine pit with a mean value of 2.5. The best fitting relations between Th/U, K/Th and K/U are linear with correlation coefficients of 0.511, 0.555 and 0.008 respectively. The value obtained for this study is closed to the theoretical value. This means that, there seems to be no significant fractionation during weathering or involvement in metasomatic activity of the radioelements. Figure 4 to 7 show comparison of the normalized values

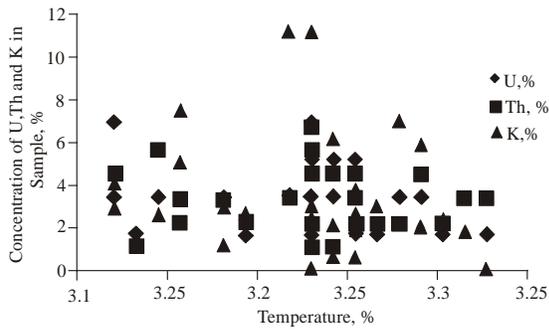


Fig. 5: Correlation between the concentrations of U, Th, and K and the temperature conditions of the study area

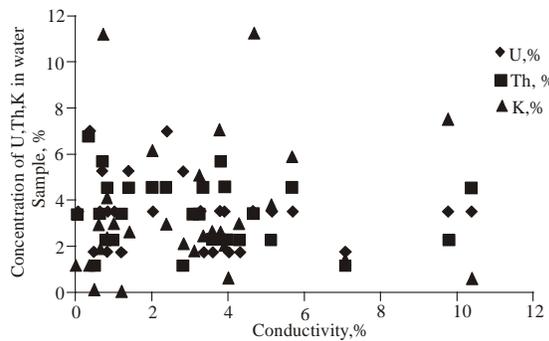


Fig. 6: Correlation between the concentrations of U, Th, and K and the conductivity of the water samples

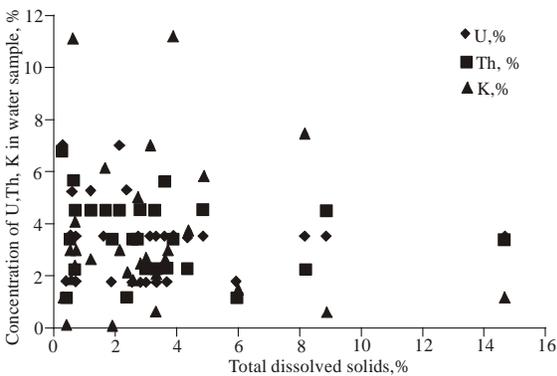


Fig. 7: Correlation between the concentrations of U, Th and K and the total dissolved solids of the water samples.

of the physical parameters pH, temperature, conductivity and total dissolved solid each with U, Th and K. As in the case of Figure 2, U, Th and K showed the same behavior with each of the physical parameters. This shows that U, Th and K behave in the same manner under the same conditions of pH, temperature, conductivity and total dissolved solids in water samples in the environment. Since U and Th behave similarly under reducing

conditions (+4 oxidation state), it implies the U and Th exist in the reduced state in the water samples studied.

### CONCLUSION

Various analytical methods have been used to determine the concentrations of trace elements, anions and physical parameters in water and soil/rock samples from Tarkwa Goldmine and its surroundings. The mean concentration of uranium in the water samples was 0.020 mg/L in a range of 0.010-0.040 mg/L. The mean concentration of thorium was 0.029 mg/L in a range of 0.010-0.060 mg/L. For K, the concentrations varied in a range of 0.02 to 3.84 mg/L with a mean value of 1.19 mg/L. The pH of majority of the water sources is acidic with values below the minimum recommended guideline value of 6.50. The results in study are typical of similar studies that have been carried in mineralized aquifer waters. In the case of the other metals, the concentrations were variable with some of the metals having concentrations below detections limits of the equipment used and others with concentrations below the WHO guideline values. For the anions, the concentrations of the samples were below the guideline values. A comparison of the behavior of U, Th and K with physical parameters such as pH, temperature, conductivity, total dissolved solids also showed that all the three radioelements showed the same trend and showed the same behavior under the same environmental physical conditions.

In soil and rock samples, the concentrations of U, Th and K were in a range of 0.2-1.8  $\mu\text{g/g}$ , 0.52-2.6 and 7037-71360  $\mu\text{g/g}$ , respectively. These results also compare well with results of normal continental crust rocks. The mean Th/U ratio of all the samples was 2.5 and this also compared well with normal continental crust rock value of 3. This means that the radioelements have not undergone any enrichment or depletion during weathering of the rocks of the study area.

The activity concentrations of gross- $\alpha$  and gross- $\beta$  in the water samples were all below the WHO recommended guideline values. However, it was observed that where the concentration of K is high in the water samples the gross- $\beta$  activity concentration tends to be higher due to contribution of beta radiation from  $^{40}\text{K}$ . The results obtained in this study show that the levels are within the natural background radiation limits and compared well with similar studies other countries. The data from this study can be used as baseline for future investigations

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