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Comparative studies of cyanide, cadmium, arsenic and mercury in cassava (*Manihot esculanta*) and water cocoyam (*Colocasia esculenta*) on mined and reclaimed mined lands in a mining community in Ghana

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ABSTRACT

Cassava (manihot esculanta) and water cocoyam (colocasia esculenta) have gained increased importance in the diets of majority of people in developing countries such as Ghana and for that matter the inhabitants of some mining communities. These root tuber crops absorb or uptake toxic chemicals from the soil thereby exposing the people who feed on them to the harmful effects of arsenic, cadmium, cyanide and mercury. The levels of arsenic, cadmium, cyanide and mercury in cassava and water cocoyam of a mined land and a reclaimed mine land were measured in this study. Cassava and water cocoyam samples were obtained from Tarkwa Goldmine areas, precisely from both mined land and demonstrations (reclaimed old mined land) farms and analysed for arsenic, cadmium, cyanide and mercury using various standard analytical methods. Most of the heavy metal and cyanide levels measured were slightly higher than the WHO acceptable limits. The result of the analysis showed that the reclaimed mine land had relatively lower levels of arsenic, cadmium, cyanide and mercury in the food crops analysed than the mined lands. As a result, though not equally safe, the inhabitants should be encouraged to use the reclaimed mined land for farming.

Key words: Cassava, water cocoyam, *Manihot esculanta, colocasia esculenta,* Galamsey

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INTRODUCTION

Gold, like no other metal has a fascinating history and a special place in the world. It has long been considered as one of the most precious metals and the most used in a range of everyday applications essential to modern life. Its main uses are jewellery, dentistry, adornments on buildings and in electronic gadget. The mining of gold in Ghana is considered one of the highest foreign exchange earners and contributes greatly to the socio-economic development of the country. Mining of gold is either by using mercury via amalgamation or by using the cyanide method to extract the gold [1]. Mining activities begins with the exploration of the deposit by geologists and drilling of holes filled with explosives which break up the ground to obtain the ore. The ore is crushed or placed directly on lined leach pads where a cyanide solution is applied to the surface of the heap. The solution percolates down through the ore and leaches the gold, which then flows to a central collection location [2].

$$4Au+8NaCN+O_2+2H_2O \rightarrow 4Na(Au(CN)_2)+4NaOH.$$

The gold bearing solution is pumped through electro-wining cells or through zinc precipitation circuit where the gold is then melted in a furnace. After, the gold is then refined into pure gold. The mined land is reclaimed for future use such as farming, fish farming and forest reserve. About 12% of the land space in Ghana is currently under some form of concession for mineral exploration [3], with more than 250 companies being engaged in surface mining [4]. Quite apart from the concessions, there are numbers of illegal mining (“galamsey”) activities which equally degrade vast acreage of land resulting in environmental contamination. Their activities take place right in the farming areas which makes the crops more susceptible to heavy metal contamination.

The geology of Wassa West District makes it highly attractive for mining and large areas have been granted to mining companies. It is reported that, gold deposits are usually found on various sites, particularly, in reef formations or alluvial deposited along riverbanks and in valleys [5]. The gold boom in a way triggered rapid surface mining development in the Wassa West District in the early 1980s [6] and today several large surface mining enterprises are extracting gold along the Ashanti belt (Fig. 1). Mining has indeed been an important industry in a resource-rich country like Ghana. Its contribution to the nation's overall GDP has tripled over the years from barely 2% of GDP in 1991 to 6.3% of GDP in 2009 [7]. With the rising tide of mining operations has come with it an increased risk to the environment. Chemical pollution in the mining environment is therefore on the rise.

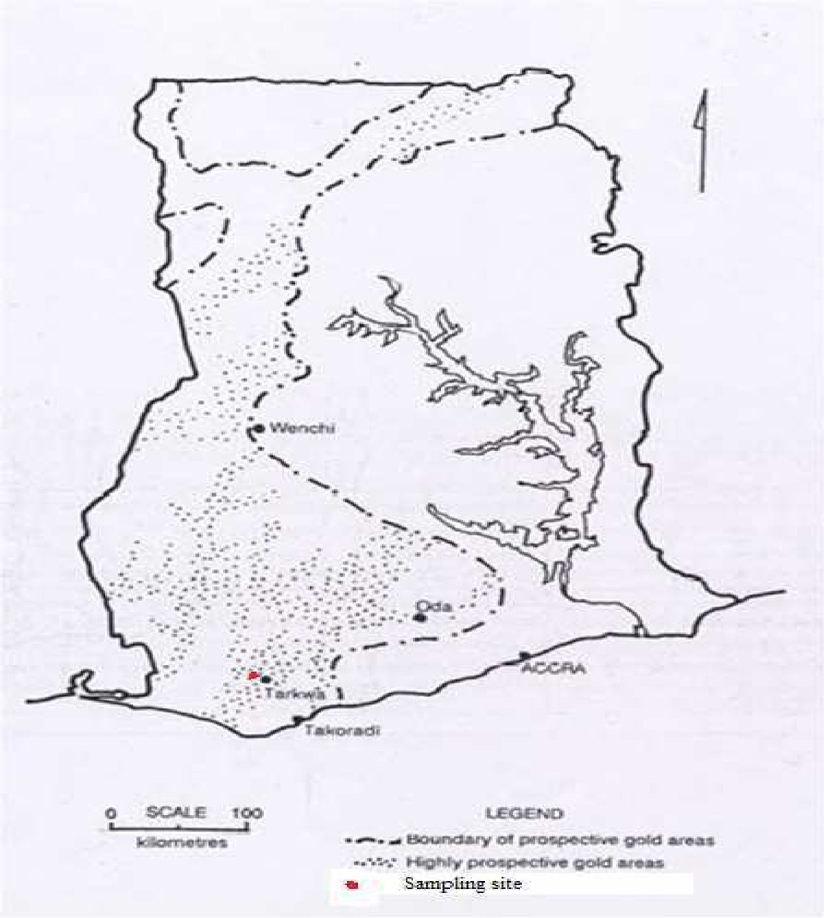


Figure 1: Map of prospective gold mining regions in Ghana

The mined lands are reclaimed to grow food crops such as cassava and water cocoyam which are staple food for a lot of Ghanaians and for that matter, the people of Tarkwa [8]. The reclamation which usually involves re-vegetation implementation may not completely remove all the toxic chemicals though; it is believe that, the reclaimed land may not contain some residues of toxic chemicals such as arsenic, cadmium and mercury. The mining process releases cyanide and mercury as well as other trace metals which comes out with the gold ore as impurities and contaminate the soil. Food crops are however, grown on these soils thereby contaminating them.

As defined by the web dictionary, trace metals are metals which are normally found in trace amounts due to their insolubility or to their relative lack of abundance in the earth crust. It also defines it as metallic elements that are essential for growth but only in very small quantities. These also include metals such as cadmium and mercury that normally occur in water and sediments at concentrations less than one part per million. Trace metals could be essential element or non-essential toxic trace elements. The essential trace elements are Zn, Cu, Fe, Mn, Se, Cr, Mo, Co, Vn and the non-essential, toxic trace elements are Pb, Cd, Ni, Be, As, Hg, Sb and Te [9]. The metals being dealt with in the scope of this study are therefore toxic elements such as: As, Cd and Hg including one other important toxic mining processing by-product CN^-. These metals could also be termed as heavy metal which refers to any metallic elements that has a relatively high density and is toxic or poisonous at very low concentration.

Heavy metals are natural components of earth crust and cannot be destroyed. They enter our bodies to a small extent through food, drinking water and air. Some trace elements are essential to maintain the metabolism of the human body; however, higher concentrations can lead to poisoning. In another development the inclusion of cyanide in this study is because of poisonous nature of the cyanide anion as an inhibitor of the enzyme cytochrome c oxidase (also known as aa_3) in the fourth complex of the electron transport chain (found in the membrane of the mitochondria of eukaryotic cells) [10].

According to Kurniawan, [11], a gold mining activity by Newmont, which uses either cyanide or mercury in gold extraction, released high levels of cyanide and other chemicals such as mercury, cadmium and arsenic in Buyat Bay which resulted in the reduction of the catch of local fishermen. Diseases such as brain damage and spasm affected the health of the local people [12]. The health effect of mining has been reported extensively in literature [13-17]. This means that, every effort should be made to ease the health burden of those living in and around mining communities.

Cassava and water cocoyam are staple foods for a lot of Ghanaians and in this case, the people of Tarkwa. Cassava is grown as a crop for starch, alcohol, cattle feed, liquid fuel, and it serves as food because the vast bulk of cassava production are for human consumption.

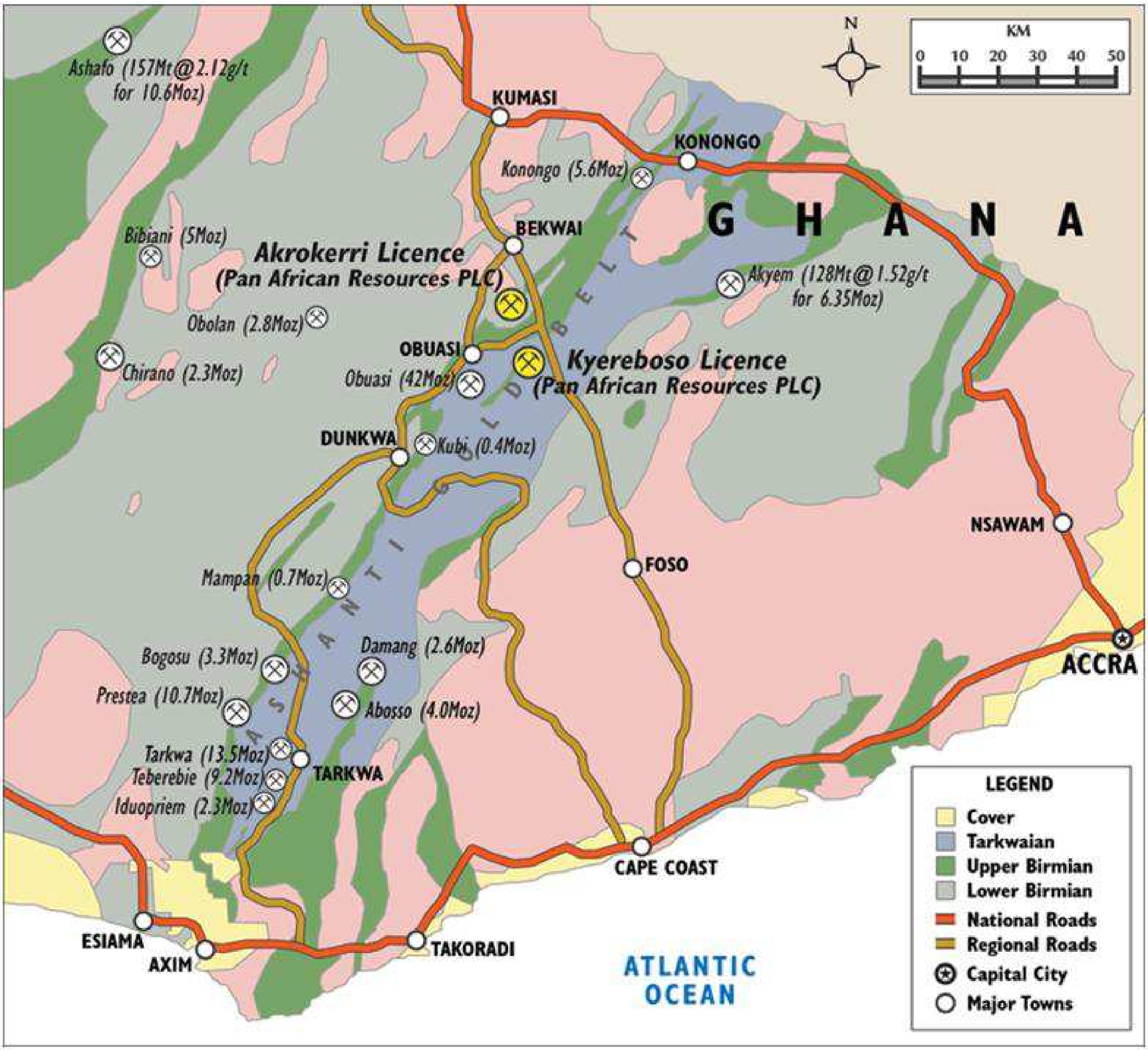
The possible uptake of toxic chemicals by cassava and water cocoyam endangers the lives of the people in the locality of Tarkwa and its environments. Essumang et al. [18] determined the levels of arsenic, cadmium, and mercury in Cocoyam (X. *sagititolium)* and Watercocoyam (C. *esculenta*) in Tarkwa and its surrounding villages and found the levels of arsenic, cadmium and mercury in X. *sagititolium* and C. *esculenta* were higher than the WHO recommended levels.

The Wassa West District, which includes three of the country's largest surface mine concessions: Bogoso-Prestea, Tarkwa, and Damang has most of the gold mining activities in Ghana. Tarkwa, covering an area of 11,400 ha is the oldest gold (surface) mine in Ghana, dating back to the early 1980s [6]. This concession has been mined by different enterprises, most recently AngloGold, Aboso gold field, Gold field Ghana, Ashanti Corp. and Goldfields Ghana Ltd. The mining activities both legal and illegal (galamsey) has left a vast land not properly reclaimed though the impact assessment procedure requires good mitigating practices. A number of them have made attempt in reclaiming some of the mined land. We decided to study the levels of some heavy metals and cyanide contamination in the tuber crops in the country's oldest surface mining area. The main thrust, was to determine mercury, cyanide, arsenic and cadmium levels in fresh and cooked cassava and water cocoyam from a mined land and a reclaimed mine land in Tarkwa, a mining community in Ghana and to compare the levels of contamination of the two sampling sites in order to make some recommendations.

EXPERIMENTAL SECTION

Study Region

Wassa West District in Ghana's southwest covers 2,354 km^2 and is the country's oldest and arguably most important gold mining region (Fig. 2). The hilly topography is characterized by gentle slopes and wide valleys. Elevation ranges from 30 to 200 m above sea level. The climate is tropical with an annual precipitation of 1,900 mm and year-round day temperatures between 26-29 ^oC. Ferralsols are the dominating soils in the region. Wassa West District belongs to the Eastern Guinean Forest ecoregion. Natural vegetation is wet evergreen rainforest with canopy heights of up to 60 m and dominating tree species of the genera Lophira, Heritiera, and Cynometra [19]. Land use has substantially altered the region's natural vegetation communities, and today rainforest covers less than 20% of the district, mostly within the Bonsa (210 km^2), Ekwumi (173 km^2), and Neung (158 km^2) forest reserves [6, 20]. About 46% of the district is used for agriculture, mostly oil palm and other cash crop plantations as well as some subsistence farming [20]. Wassa West District has a total population of about 254,100 (in 2002) and annual population growth is estimated at 2.9% [20]. Roughly 64% of the population lives in rural areas and the rest in the two large cities (Tarkwa and Prestea). Agriculture provides income for 48% of the total working force and the average farm size is about 1 ha [20].



Source: http://www.customdigitalmaps.com/portfolio/par/panafrican-portfolio.htm

Fig. 2: Map showing Tarkwa the sampling area

Sample Collection

Cassava and water cocoyam samples were obtained from Tarkwa Goldmine areas in the Western region of Ghana. The samples were taken from farms within the confines of the mining area, precisely from their demonstration farms (mined land). The samples were washed with distilled water in the laboratory and peeled with a stainless steel knife, chopped into small sizes. Each sample was divided into two and one part was boiled. Both the boiled and the fresh cassava and water cocoyam samples were air dried in the laboratory and then ground into fine powder and stored prior to chemical analysis.

Methodology

Digestion of Cassava Samples and Analysis of the Digested Samples

About 1.0 g of the cooked sample was weighed into a 100 mL beaker and 20 mL of Concentrated HNO_3 was added and set on a hot plate in a fume chamber for 20 minutes. It was removed from the plate and allowed to cool. This was filtered through a pre-washed filter paper into a 50 ml volumetric flask and the filtrate was topped up to the mark with double distilled water. The digest was then stored for the analysis of Arsenic and Cadmium.

In the case of mercury, to 1.0 g of the sample, 4 mL each of concentrated H_2SO_4 and HNO_3 was added, mixed thoroughly and heated over a water bath at 80 ^{0}C for 30 minutes and allowed to cool. After the cooling, 6 mL of hydroxylamine hydrogen chloride was added to remove the excess permanganate. It was filtered into 50 mL volumetric flask and topped to the mark with deionised water and stored for analysis. The same method was repeated for the fresh samples.

Arsenic and Cadmium concentrations in the samples were determined by direct analysis using Shimadzu AAS model No. 6401 (oxy-acetylene flame AAS) whilst mercury was determined by the cold vapour technique. All reagents used in the analysis of were of the analytical grade [21]. Quality control studies were also done alongside the analysis.

The Determination of Cyanide

About 10 g of the cooked sample was put in an 800 mL round bottom flask and 200 mL of water was added. This was allowed to stand for four hours and steam distilled.

One hundred millimetres of distillate was collected in sodium hydroxide solution. 100 mL of the distillate was diluted to 250 mL and 100 mL aliquot was taken. 8 mL of 6 M NH_4OH and 2mL 5% KI solution were added and titrated with 0.02 M $AgNO_3$ using a micro burette. The end point colour detected was a permanent turbidity which was easily recognized against a black background. This method was repeated for the fresh samples [22-23]. Quality control studies were also done alongside the analysis.

Preparation of Blank

About 8 mL of 6 M NH_4OH and 2 mL 5% KI solution were added to double distilled water. The blank was titrated against 0.02 M $AgNO_3$ solution.

RESULTS AND DISCUSSION

Quality Control

The quality control studies gave acceptable recoveries for the metals analyzed. From the results, the percentage of Arsenic, Cadmium and Mercury recovered in the reproducibility test is 89%, 88% and 92% respectively. The standard errors calculated were all less than 1; which indicates that the methods used to analyze the metals are reproducible. Also, the percentage of total cyanide recovered in the reproducibility test is 89% and a standard error of 0.002. The standard error is less than 1; this indicates that the method used to analyze total cyanide is also reproducible.

Results of the samples from the mined land

The concentrations obtained from the analysis for the fresh water cocoyam were little higher than the standard level by WHO. However, for the cooked water cocoyam, cadmium and mercury showed a slight decrease which was a little lower than the standard results (Table 2).

Table 1: Average levels of heavy metals and cyanide in Cassava (*manihot esculanta*) samples from both the mined land and the Demonstration farm

Analyte	*Permissible level by WHO mg/g*	*Average levels of analyte (mg/g)*			
		Cassava (*manihot esculanta*) Samples From mined land		Cassava (*manihot esculanta*) Samples From The Demonstration Farm	
		fresh	cooked	fresh	cooked
Arsenic	3.00 x 10^{-4}	1.73 x 10^{-2}	1.02 x 10^{-2}	1.40 x 10^{-2}	1.10 x 10^{-2}
Cadmium	5.04 x 10^{-4}	2.00 x 10^{-3}	4.00 x 10^{-3}	1.60 x 10^{-3}	1.25 x 10^{-3}
Mercury	3.00 x 10^{-4}	1.50 x 10^{-4}	1.30 x 10^{-4}	4.00 x 10^{-4}	3.50 x 10^{-4}
Cyanide	2.00 x 10^{-4}	3.42 x 10^{-4}	2.13 x 10^{-4}	2.10 x 10^{-4}	2.05 x 10^{-4}

Table 2: Results of water cocoyam (*Colocasia esculenta*) samples from both the mined land and the Demonstration Farms

Analyte	*Permissible level by WHO mg/g*	*Average levels of analyte(mg/g)*			
		Water Cocoyam (*Colocasia esculenta*) Samples From The mined land		Water Cocoyam (*Colocasia esculenta*) Samples From The Demonstration Farm	
		fresh	cooked	fresh	cooked
Arsenic	3.00 x 10^{-4}	4.32 x 10^{-2}	1.21 x 10^{-2}	3.21 x 10^{-2}	7.70 x 10^{-3}
Cadmium	5.04 x 10^{-4}	4.00 x 10^{-3}	9.00 x 10^{-4}	3.41 x 10^{-3}	1.00 x 10^{-3}
Mercury	3.00 x 10^{-4}	1.35 x 10^{-4}	1.80 x 10^{-4}	2.40 x 10^{-4}	1.70 x 10^{-4}
Cyanide	2.00 x 10^{-4}	3.25 x 10^{-4}	2.02 x 10^{-4}	2.15 x 10^{-4}	2.13 x 10^{-4}

The concentrations which were obtained for the fresh cassava were generally all higher than the standard values. The cooked cassava showed a decrease in the concentration, nevertheless, they were still higher than that of the WHO standards (Table 1& 2).

Levels of arsenic, cadmium, cyanide and mercury in food crops (cassava and water cocoyam)

The maximum permissible levels of daily oral intake of trace metals such as arsenic, cadmium and mercury in food crops (cassava and water cocoyam) and cyanide set by the World Health Organization (WHO), are used as baseline to determine the level of pollution or harm caused with regards to the uptake of arsenic, cadmium, cyanide and mercury by water cocoyam and cassava grown in the study area and the levels obtained in this study as shown in the Tables 1 and 2.

It was seen that the concentration of the Cd, As, CN- and Hg in the fresh samples obtained were higher than the cooked samples. It could be deduced that cooking the food samples reduces the levels of toxic chemicals in them. For example, cyanide is very volatile, so by boiling cassava and water cocoyam would cause some levels of cyanide to volatilize. Results obtained from the study (Table 1&2) shows that in all the samples, arsenic recorded the highest concentration (7.70×10^{-3} - 4.32×10^{-2} mg/g) compared to the others, which indicates that arsenic pollution in the study areas is very high. Cadmium (9.00×10^{-4} - 4.00×10^{-3} mg/g) was the next highest followed by mercury (1.30×10^{-4} - 4.00×10^{-4} mg/g) and cyanide (2.25×10^{-4} - 3.42×10^{-4} mg/g). This confirms our previous work and other studies conducted in 2007 and 2013 that the mining activities in the Tarkwa environment is introducing toxic heavy metals and cyanide into the food chain [18 & 24] and strict measures should be put in place to minimize the situation.

Results of samples from the demonstration farms

The levels of the metals and cyanide obtained for the fresh water cocoyam were all higher than the standard results as well as some of the cooked water cocoyam which were also high except for mercury which had levels a little lower than the standard values (Table 2).

The fresh cassava samples had Cd, and As levels exceeding the required levels by WHO but that of mercury was just below that of the standard and this was same for the cooked cassava (Table 1). This also shows that, the mercury concentration was within safe limits. The levels for mercury were however very low as compared to the rest, Arsenic, Cadmium and Cyanide. This may be attributed to the fact that, for some years now mercury has not been employed in large scale mining and it is only being used for small scale mining by the “Galamsey” operators. Comparing both the cooked and the fresh cassava and water cocoyam, it was realized that cassava contains the highest amount of cyanide. This is because cassava in its natural state contains some amount of cyanide.

Comparing both the results from the mined land and that from the demonstration farm, it was realized that there was relatively significant decrease As, Cd, CN^- and Hg levels from the demonstration farm since the results obtained from the demonstration farm were relatively lower. Similar report of food crops pollution by heavy metals due to mining activities has been reported in the vicinity of Dabaoshan mine, south China and Idrija Hg mine area [25-26]. Türkdoğan *et al.* [27] suggested that the high prevalence of upper gastrointestinal cancer rates in the Van region of Turkey was related to the high concentration of heavy metals in the soil, fruit and vegetables. It may be good for the farmers to cultivate their food crops on the demonstration farms. With the maximum permissible levels of daily oral intake of these toxic chemicals in food (Cassava and Water Cocoyam), set by the World Health Organization (WHO) as a baseline to determine the level of pollution, it was observed that the concentration obtained were all higher than the standard levels.

CONCLUSION

From the results of the study, the mean levels of Arsenic, Cadmium, Mercury and cyanide in cassava and water cocoyam from the mined land Tarkwa mining area are higher than the WHO recommended limit. However, those from the reclaimed mined land had comparatively lower levels of the studied toxic chemicals. Farmers may have to be encouraged to farm on the reclaimed mined lands. Also, mining companies should be encouraged to make every effort to do some form of mined land reclamations for the local farmers. Finally, it is worth noting that consumption of cassava and water cocoyam from the mining sites by human beings may pose some serious health risk to them. Mining activities undoubtedly increases the levels of arsenic, cadmium, cyanide and mercury in the soil and subsequently its uptake by crops such as coco yam and water cocoyam [28].

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