

## Studies of the Levels of Some Toxic Elements in Soil and Tailings from Bibiani Mining Area of Ghana

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**Abstract:** The concentrations of the toxic elements As, Cd, Cr, Hg and V in soil and tailings samples from the Bibiani mining area in the Western Region of Ghana have been measured using Instrumental Neutron Activation Analysis (INAA) with the aim of assessing the impact of mining activity on the Bibiani mining environment. All samples and standards were irradiated with thermal neutrons in the Ghana Research Reactor-1 (GHARR-1) facility at the Ghana Atomic Energy Commission, Kwabenya-Ghana, followed by counting with a conventional counting system. The concentrations of the elements measured in the soil were in the ranges: As, 0.46-996 mg/kg; Cd, 0.69-4.15 mg/kg; Hg, 0.01-0.06 mg/kg and V, 60-204 mg/kg. In the tailings, the concentrations of the elements were in the following ranges: As,  $(2.70-3.50) \times 10^3$  mg/kg; Cd 1.35-3.36 mg/kg; Cr, 19-87 mg/kg; Hg, 0.01-0.02 mg/kg and V, 48-93 mg/kg. The soils were near neutral and reducing (except sample LS, taken from Lineso, a galamsey mining area which had a pH of 4.99) with pH ranging from 4.99 to 7.54 and an average Eh of -64 mV, as were the tailings with pH ranging from 6.63 to 7.62 with an average Eh of -53 mV. Very high levels of As were measured in the tailings and some soil samples very close to the tailings dams of the Central African Goldmine, as well as some areas that used to be galamsey mining areas. This gives the indication that the tailings dams and galamsey mining activities might be the source of As pollution in the area. It was also realized that high levels of the elements As, and V occurred generally in both the soil and tailings samples. The levels of As in the tailings were far higher than in the soil whilst the levels of V in the soil were higher than those in the tailings. The levels of Cr measured in the tailings were quite high but our inability to measure Cr in the soil makes it difficult for us to tell whether these levels have in anyway influenced the levels of Cr in the soil. On the contrary, the levels of Cd and Hg in both soil and tailings samples were relatively low and therefore, did not give any indication of contribution from mining activities, especially large scale mining which was the main focus of this study.

**Key words:** Dam, Eh, galamsay, NAA, pH, pollution

### INTRODUCTION

There have been several instances of pollution of food crops and water resources by anthropogenic activities notably mining, agricultural practices, industrial activities and vehicular emissions in Ghana and other parts of the world. For example, through mining activities toxic elements such as As, Hg and Cr are often released into the atmosphere, soil, water and onto vegetation (Serfor-Armah *et al.*, 2006). Even though wastes such as tailings produced by some mining companies are stored in special containment systems such as tailings dams,

spillage of wastes from such storage systems are not uncommon. There have been a number of instances where some of these dams gave way as a result of earth quake, faulty construction, erosion, flooding, etc. resulting in spillage of the waste stored in them. For example, on Tuesday 18th June, 1996, Teberbie Goldfields Ltd spilled cyanide into the Angonabeng stream, a main tributary of the Bonsa River. This affected nine villages along the river bank (Lassey, 1999).

Soils polluted through anthropogenic activities such as mining are a potential danger. Toxic substances in such soils can be released to the atmosphere through

dusts; can be leached or washed by rain water to contaminate water bodies (streams, rivers, lakes etc). According to Bohn *et al.* (1985), terrestrial water receives most of its solutes from soil where weathering is most active. By the same way, through soil-water and soil-atmosphere interactions, poisonous substances released into the atmosphere eventually return to the soil, (Bohn *et al.*, 1985). Some plants are able to absorb some of these toxic elements that settle on them through their leaves thereby entering the food chain. Also toxic elements present in contaminated soil can possibly find their way into plants by root up-take. For example, contamination of soil by Cd is of concern because Cd is taken up efficiently by plants and therefore enters the food chain (Elinder, 1992).

Toxic elements are associated with a number of different toxicological effects which begin to manifest when a particular toxic element is present in the human body above a certain threshold (e.g., WHO value). Arsenic for example is associated with a number of toxicological effects including abdominal pain, vomiting, diarrhea, muscular pain and weakness (with flushing of the skin). These symptoms are often followed by numbness and tingling of the extremities, muscular cramping and the appearance of a popular erythematous rash (Murphy *et al.*, 1981). The ingestion of Cd in food or in drink can cause symptoms such as nausea, vomiting, abdominal cramp and headache within minutes of ingestion. In severe cases, diarrhoea and shock can also develop (Reilly, 1980).

Ingestion of 1-5 g of "chromate" results in severe acute effects such as gastrointestinal disorders, haemorrhagic diathesis, and convulsions. Death may occur following cardiovascular shock (Janus and Krajnc, 1990). Respiratory carcinogenicity following occupational exposure to Cr(VI) has been reported (WHO, 2003a). The two main effects of mercury poisoning are neurological and renal disturbances. Neurological disorders are characteristic of poisoning by methyl and ethyl mercury (II) salts. Renal disorders on the other hand are associated with poisoning by inorganic mercury (WHO, 2003b).

There is the need, therefore, for investigations to be carried out to assess the impact of mining activity on the water, soil and food samples in the area. This is of utmost importance since there is limited data on the levels of toxic elements in foodstuffs, water, soil and tailings in the area due to the fact that not much research have been carried out in the study area in that respect. The objective of this research is to determine the levels of the toxic elements, As, Cd, Cr, Hg and V in soil and tailings from Bibiani mining area in fulfillment of a broader objective

of assessing the impact of mining activity on the Bibiani mining environment by way of the levels of toxic elements in water, soil, tailings and foodstuffs in the area.

## MATERIALS AND METHODS

**Study area:** Bibiani, the town in which this work was carried out, is the capital of the Bibiani-Anhwiaso-Bekwai District of the Western Region of Ghana, West-Africa, Fig. 1. It is about 86 km by road from Kumasi, the capital of the Ashanti Region (Kesse, 1985). It is one of the oldest mining towns in Ghana where "galamsey" (galamsey is a term used to refer to small-scale gold mining) as well as large scale mining takes place. Both activities have been going on as far back as the early ninety's (Kesse, 1985). The mining company operating in the town as at the time this work was being carried out was Central African Gold Ghana Ltd., (CAG, 2007).

The population of the entire Bibiani-Anhwiaso-Bekwai District stands at 120,869 whilst that of Bibiani town alone is 26,186, according to the district survey conducted in 2005 (BABDA, 2006). The Bibiani-Anhwiaso-Bekwai district is located between latitudes 6° and 3°N and longitudes, 2° and 3°W and covers a total land area of 873 Km<sup>2</sup>.

The annual rainfall of the district averages between 1200 and 1500 mm. The pattern of the rainfall is bimodal, falling from March - August and September - October. The dry season occurs between November and January. The average temperature throughout the year is about 26°C. There is a high relative humidity averaging between 75% in the afternoons and 95% at nights and early mornings (BABDA, 2006).

In Bibiani Township, only a few surface waters are available for use for drinking purposes and as a result, wells with average depth of about six metres deep have been constructed to tap water from underground for drinking and other uses. Farming is a major economic activity of the people in the area where food crops such as cassava, plantain, cocoyam, corn etc. are grown. Cocoa, a major cash crop in Ghana, is also grown in the area (BABDA, 2006).

**Geology of the Bibiani area:** The geology of the district is dominated by the Precambrian Metamorphic rocks of the Birimian and Tarkwaian formation (BABDA, 2006) (Fig. 2). The oxisols soils are rich in mineral deposits making mining a lucrative economic activity in the district (BABDA, 2006).

The Bibiani Gold deposit lies within Birimian metasediments and related rocks which occur within the

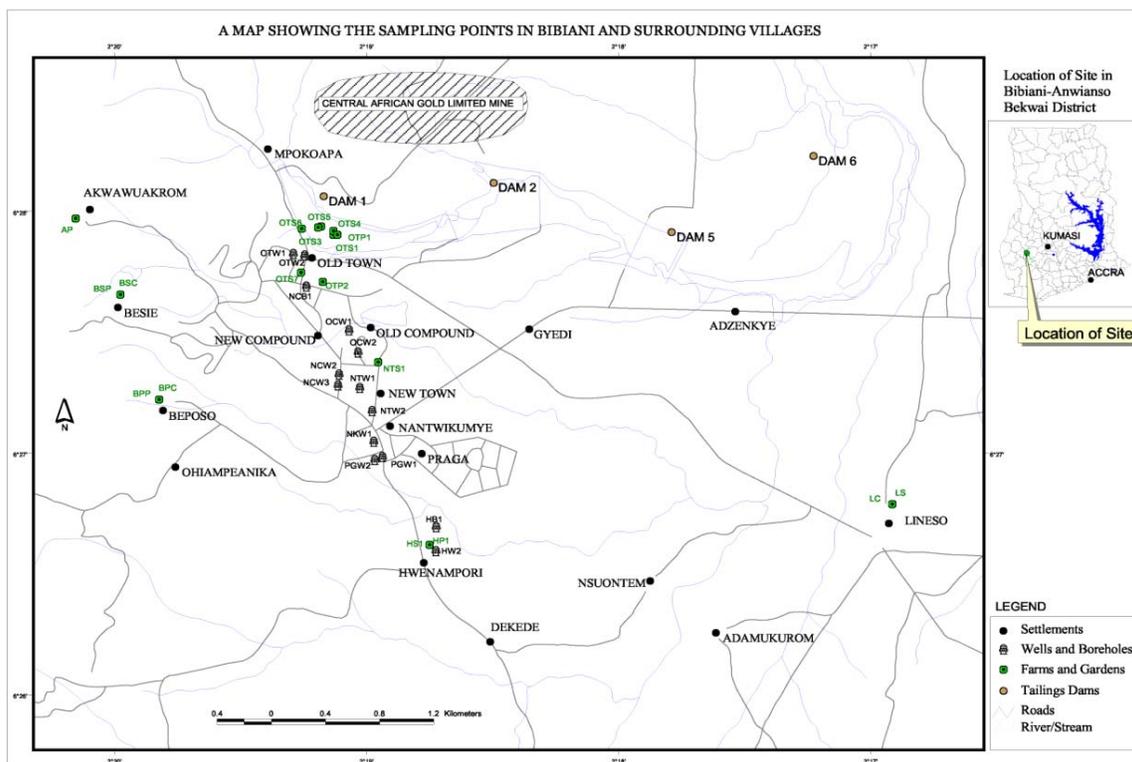


Fig. 1: Map of the study area showing sampling points

Proterozoic Sefwi Belt of southern Ghana (AA, 2006). Typical rock types include phyllites, schist, tuff and greywacke (CAG, 2007) (Fig. 2). This geological formation is intruded by rocks of the Eburnean Plutonic Suite namely micaceous granite, pegmatites, delorite dykes gabbros, Hornblende rich granites, granodiorites and monzonites, (Asiedu *et al.*, 2004) (Fig. 2).

The Bibiani ore body is a mesothermal lode type deposit hosted by a predominantly metasedimentary package of carbonaceous shales and lesser volcanoclastics with subordinate but important quartz porphyry intrusions. It is characterised by intense carbonate alteration, silicification and sulphidation (mostly pyrite and minor arsenopyrite) (CAG, 2007).

**Sampling and sample preparation:** Ten soil samples were collected and coded as; OTS1, OTS2, OTS3, OTS4, OTS5, OTS6, OTS7 (from Old Town), NTS1 (from New Town), HS1 (from Hwenampori) and LS (from Lineso), all in the Bibiani mining area as shown in Fig. 1, in September, 2007. All the soil samples were collected from different farms/gardens. Four tailings samples were

collected from four tailings dams (tailings dams 1, 2, 5 and 6) of the Central African Goldmine (CAGmine) as shown in Fig. 1, during the same period.

With a pair of gloves on, the soil samples were collected from the surface to about 15 or 20 cm depth with hand auger and plastic shovel (Davies, 1998) and transferred into pre-cleaned polyethylene bags (Adomako *et al.*, 2008). After taking each sample, the plastic shovel and the auger were washed with Deionized Distilled Water (DDW) and the hand gloves replaced to avoid contamination. The same procedure was repeated at all the sampling points. All the soil samples were doubly bagged and boxed for safe transport from the field to the laboratory (Adotey, 2003). The same procedure was followed when collecting the tailings samples.

At the laboratory, the soil and tailings samples brought from the field were spread on pre-cleaned polyethylene sheets for gloved-hand-picking of stones and plant materials. The samples were then dried in Memmert oven at a temperature of 40°C to a constant weight for 48 h (Boadu *et al.*, 2001).

The oven-dried soil and tailings samples were disaggregated with ceramic mortar and pestle and sieved

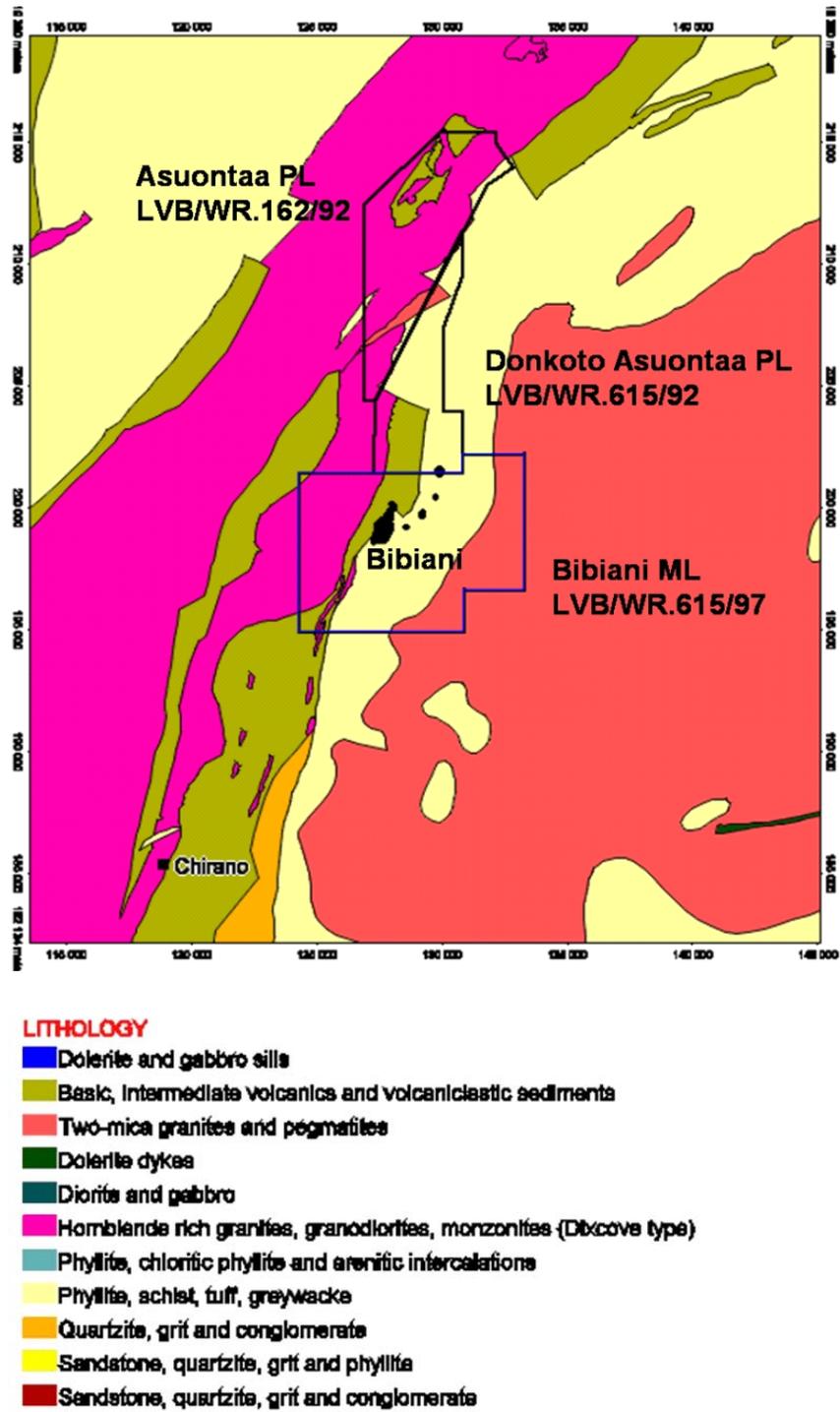


Fig. 2: Geological map of Bibiani (CAG, 2007)

through a British Standard Laboratory sieve N° 35 of 500 mm size (Endecotts Limited, London, England). The fine particles that passed through the mesh were collected into clean polyethylene sample packets and labeled. Portions of these samples were used for all NAA analyses.

One hundred milligrams (100 mg) of each sample were weighed onto pre-cleaned polyethylene sheets wrapped and heat-sealed. For each soil sample, eight (8) sub samples were weighed whilst twelve (12) sub samples were weighed for each tailings sample. Four (4) sub samples were irradiated for short lived nuclides and another four for medium lived nuclides as described earlier. The final set of four tailings sub samples was used for the determination of Cr through its long lived nuclide <sup>51</sup>Cr. For the determination of the short-lived nuclides, each parcel of 100 mg soil or tailings sample wrapped in polyethylene sheet and heat-sealed was placed in a 7.0 mL polyethylene vial. The space left in the vial was filled with cotton wool and the vial was heat-sealed. The samples to be used for the determination of the medium and long-lived nuclides were on the other hand separately packed into the 7.0 mL polyethylene vial as many as the vial could contain and heat-sealed.

**Irradiation, counting and analysis:** All the samples and the reference materials were irradiated with thermal neutrons in the Ghana Research Reactor-1 (GHARR-1) facility, which is a miniature neutron source reactor (MNSR), at Ghana Atomic Energy Commission, Kwabanya.

The samples were sent into the inner irradiation sites of the reactor by means of a pneumatic transfer system operating at 448 kpa. At the inner irradiation site the samples were irradiated with a thermal flux of  $5 \times 10^{11}$  n/cm<sup>2</sup>s while the reactor operated at 15 kW (Adotey, 2003; Serfor-Armah, 2006). Different timing schemes were used for the irradiation, decay and counting of the short, medium and long-lived radionuclides. The irradiation scheme ( $t_i$ :  $t_d$ :  $t_c = 0.5$ -2: 1: 10 min) was used for the short-lived, ( $t_i$ :  $t_d$ :  $t_c = 1$ : 24 - 48: 0.5 h), for the medium-lived and ( $t_i$ :  $t_d$ :  $t_c = 1$ : 14 - 21d: 5 h) for the long-lived radionuclides (Serfor-Armah, 2006).

The timing for the various irradiation schemes were chosen based on the matrix being dealt with (whether geological or biological matrix), the half-lives of the radionuclides to be determined, safety (to avoid exposure to high doses of radiation during handling) and optimization of counts and at the same time reducing pulse pile up (dead time). Also, the timing schemes were chosen with regard to the time available for analysis as well as to reduce interference from other radionuclides present in the sample.

The samples were counted on a computer-based gamma-ray spectroscopy system which consists of an N-type High Purity Germanium (HPGe) detector model GR 2518, a High Voltage Power Supply (model 13103), and a Spectroscopy Amplifier (model 2020, Canberra Industries Incorporated). ACCUSPEC Multi-Channel Analyzer (MCA) emulation software card and a microcomputer for data acquisition, evaluation and analysis were also used. Both quantitative and qualitative analyses were done using the Gamma Spectrum Analysis Software, MAESTRO 32 (Adotey, 2003).

## RESULTS AND DISCUSSION

The reference material IAEA SOIL - 7 was analysed for the elements As, Cd, Hg, and V using INAA. The results obtained from the analysis of the reference materials (Table 1) were comparable with the recommended/certified values. This shows that INAA analytical technique used for this work was reliable.

**Mineralogy of the Bibiani area:** The minerals that constitute the rocks of the Bibiani are: pegmatites, granites, plagioclase, Hornblende, muscovites, biotites, anorthite, albite, pyroxene, micas and arsenopyrites (Hirds *et al.*, 2009). These minerals are mainly made up of the elements, Al, As, Au, Ca, Fe, K, Mg, Na and Si (Alloway, 1995). Other elements that occur as trace elements together with the minerals are: Ba, Co, Cr, Ga, Mn, Ni, Rb, S, Sc, Se, Ti, V and Zn (Alloway, 1995).

**Physical parameters:** The physical parameters pH and Eh play important roles in determining the fate of elements in an environment such as soil. They also play crucial roles in determining bioavailability of both toxic and nutrient elements to plant. For example, Cr(III) has very low solubility and low reactivity resulting in low mobility in the environment and low toxicity to living organisms (Barnhart, 1997). Under oxidizing conditions in soils, Cr(III) is converted to Cr(VI) which may be present as  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$  (James *et al.*, 1997). In this form Cr(VI) is relatively soluble, mobile and toxic to

Table 1: Comparison of levels (mg/kg) of elements in reference materials measured by INAA with recommended/certified values

Elements	This work	Recommended value
As	14.2±0.7	13.4±0.9
Cd	1.41±0.6	1.3±0.8
Hg	0.05±0.02	0.04±0.03
Sb	1.8±0.2	1.7±0.3
V	68.0±5.0	66.0±7.0

Table 2a: The pH and Eh of soil samples

Sample I.D.	pH	Eh (mV)
BPS	7.03	- 59
HS1 (Control)	7.51	- 90
LS	4.99	55
NTS	16.66	- 39
OTS	16.43	- 20
OTS	27.01	- 59
OTS	37.06	- 57
OTS	47.35	- 79
OTS	57.28	- 67
OTS	67.34	- 76
OTS	77.54	- 86
Average	6.93	- 64

Table 2b: The pH and Eh of tailings samples

Sample I. D.	pH	Eh (mV)
Dam1	6.67	- 41
Dam 2	6.63	- 37
Dam 5	7.62	- 85
Dam 6	6.93	- 50
Average	6.96	- 53

Table 3a: Average concentrations of elements (mg/kg unless indicated otherwise) in soil samples with standard deviations

Elemental concentrations				
Sample	As	Cd	Hg	V
BPS	00.46±0.06	<0.07*	0.010±0.001	204±4.00
HS1	15.56±0.25	<0.07*	<0.010*	073±1.12
LS	20.70±0.32	<0.07*	0.063±0.003	130±2.00
NTS1	879±19	4.15±0.07	0.035±0.001	060±1.05
OTS1	474±10	<0.07*	0.024±0.001	150±1.20
OTS2	225±7	<0.07*	0.021±0.001	094±1.15
OTS3	105±1.35	<0.07*	0.026±0.004	075±1.02
OTS4	251±3.26	<0.07*	0.060±0.020	069±0.90
OTS5	069±1.04	<0.07*	<0.010*	109±1.50
OTS6	996±13	<0.07*	0.010±0.003	154±2.51
OTS7	200±3.01	0.69±0.03	0.056±0.020	077±1.30

\*: Detection limit

living organisms (ATSDR, 2000). In deeper soil where anaerobic conditions exist, Cr(VI) will be reduced to Cr(III) by  $S^{2-}$  and  $Fe^{2+}$  present. The reduction of Cr(VI) to Cr(III) is facilitated by low pH (Cary, 1982; EPA, 1990; Saleh *et al.*, 1989).

Lower pH may also facilitate leaching of acid soluble Cr(III) and Cr(VI) compounds in soil (ATSDR, 2000). Low soil pH increases the uptake of Cd by plants (Alloway *et al.*, 1990). The toxicities of the phytotoxic elements Al and Mn to plants are strongly pH dependent (Bohn *et al.*, 1985).

The ranges of pH values were 4.99-7.54 pH units for the soil samples (Table 2a) and 6.63-7.62 pH units for the tailings samples (Table 2b). The average Eh values for the soil and tailings were -64 and -53 mV, respectively (Table 2a and b). The soil and tailings samples as indicated by their pH and Eh values are both near neutral

and reducing except the soil sample LS which is acidic (pH 4.99) and oxidizing (Eh 55 mV). The pH values of the soil and tailings samples do not pose any threat regarding leachability of toxic elements. However the acidic pH of the soil sample LS might be as a result of anthropogenic activity since it was from a galamsey area. Elemental concentrations:

**Elemental concentrations:** The major elements (i.e., elements whose concentrations averaged above 100 mg/kg) determined in the soil were As, and V. The concentrations of Cd measured (with an average of 2.42 mg/kg) were at minor levels (i.e., the concentrations ranged between 1 mg/kg and 100 mg/kg) whilst mercury (with average concentration, 0.034 mg/kg) was at trace level (i.e., the concentrations were less than 1 mg/kg) (Table 3a). In general, the concentrations of As were relatively higher in the soil samples collected from sampling points close to the CAG mine (like OTS6 at a distance of 230 m from the mine/tailings dam). The concentrations of As in the soil samples generally decreased with increasing distance of the sampling locations from the mine/tailings dam; suggesting that the tailings dams may probably be the source of As in the soil around the vicinity of the mine.

Anomalies were observed with soil samples OTS7 (680 m away from the mine/tailings dam) and NTS1 (1280 m away from the mine/tailings dam). The soil sample OTS7 was taken from a garden very close to a 'galamsey' area. The 'galamsey' activity might be responsible for the level of arsenic in OTS7. The area from which NTS1 was taken may probably have a history of 'galamsey' mining. The concentration of As in sample HS1 taken from a household garden, a distance of 2.8 km from the mine was 15.56 mg/kg. Sample BPS taken from a farmland over 5 km from the mine however, had the least concentration of As (0.46 mg/kg) (Table 3a).

Arsenic occurred in the tailings as a major element with an average concentration of  $(3.20±0.01)×10^3$  mg/kg (Table 3b). The elements determined at minor levels in the tailings were Cr (48 mg/kg), Cd (2.02 mg/kg) and V (70±5 mg/kg), with their average concentrations indicated in parenthesis. The only element that occurred at trace level in the tailings was Hg ( $1.5×10^{-2}$  mg/kg) (Table 3b).

The high levels of Arsenic in the tailings are not unexpected because according to Kesse (1985) and the geology of the area, arsenopyrite ( $FeAsS_2$ ), a compound that contains As, occur naturally in close association with gold in Bibiani north. However these high levels of arsenic in tailings coupled with the trend shown by the levels of arsenic in the soil - which is higher in soil closest

Table 3b: Average concentrations of elements (mg/kg unless indicated otherwise) in tailings samples with standard deviations

Elemental concentrations					
Sample	As ( $\times 10^3$ )	Cd	Cr	Hg	V
Dam 1	2.70 $\pm$ 0.01	1.36 $\pm$ 0.20	54 $\pm$ 0.16	0.010 $\pm$ 0.002	64 $\pm$ 0.23
Dam 2	3.50 $\pm$ 0.01	3.36 $\pm$ 0.50	87 $\pm$ 3.02	0.020 $\pm$ 0.005	48 $\pm$ 0.15
Dam 5	3.20 $\pm$ 0.02	<0.07*	33 $\pm$ 2.02	<0.010*	93 $\pm$ 0.45
Dam 6	3.50 $\pm$ 0.02	1.35 $\pm$ 0.21	19 $\pm$ 1.23	<0.010*	78 $\pm$ 0.55

\*: Detection limit

to the tailing dams and reduces as the soil gets father away from the tailings dam-gives the indication that mining activity greatly contributes to the levels of As in the soil, especially in areas close to the mines. When arsenopyrite ores are being processed by roasting, As is converted to As<sub>2</sub>O<sub>3</sub> which is released into the atmosphere in the form of dust. Sulphur is also converted to the SO<sub>2</sub> responsible for acid rain. The As<sub>2</sub>O<sub>3</sub> dust later settles on vegetation, soil, water and roofs of buildings in the environment accounting for the high levels of As in the vicinity of the mine.

The levels of Cr in the tailings were also quite high (average concentration 48 mg/kg, Table 3b) and that is not surprising since chromium is among the trace elements associated with the geology of the area. However, our inability to measure chromium in the soil makes it difficult for us to tell whether mining activity has had any impact on the levels of chromium in the soil. Cadmium and mercury are elements that occur naturally at low concentrations in the environment. The approximate concentration of Cd in the environment is 1 mg/kg and Hg in rocks is 0.5 mg/kg (MCPA, 1999). Comparing these concentrations with the average concentrations of cadmium, 2.42 mg/kg and mercury, 3.40 $\times 10^{-2}$  mg/kg measured in the soil and the concentrations, 2.02 mg/kg and 1.50 $\times 10^{-2}$  mg/kg of cadmium and mercury respectively measured in the tailings, there is no clear indication of anthropogenic inputs. However, the most likely anthropogenic source of Mercury in the area is galamsey activity which involves the use of mercury in gold extraction. Fossil fuel combustion, as a result of movement of heavy vehicles in and around the mining site could also constitute a possible anthropogenic source of both cadmium and mercury (MCPA, 1999).

The average concentrations of the elements Cd, Hg and V were higher in the soil than in the tailings. On the contrary, As showed a higher average concentration in the tailings than in the soil. The elements As and V showed the most significantly different average concentrations in the soil and tailings. The average concentration of As in the tailings was 3.50 $\times 10^3$  mg/kg compared to 300 mg/kg

measured in the soil, thus confirming that the tailings could be the source of As pollution in the area.

## CONCLUSION

Bibiani in general is a place that, by virtue of its geology, one would not be surprised to find As in its soil. However from the results of this study it could be said that activities of both galamsey and large scale mining somewhat contribute to the levels of As in the soils, especially soils in the vicinity of these mines. This is evidenced by the finding that the levels of As in the soil in the vicinity of the Central African Goldmine/tailings dam were higher than those of soil far from the mine. Also pockets of high level As occurrence were identified in “galamsey” mining areas or areas with history of galamsey mining. It was also realized that high levels of the elements As, and V occurred generally in both the soil and tailings samples. The levels of As in the tailings were far higher than in the soil whilst the levels of V in the soil were higher than those in the tailings. The levels of Cr measured in the tailings were quite high but our inability to measure Cr in the soil makes it difficult for us to tell whether these levels have in anyway influenced the levels of Cr in the soil. On the contrary, the levels of Cd and Hg in both soil and tailings samples were relatively low and therefore, did not give any indication of contribution from mining activities, especially large scale mining which was the main focus of this study.

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