



## Levels of As, Cd, Hg, Sb and V in well and borehole water (groundwater) samples from Bibiani mining area of Ghana

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### ABSTRACT

The concentrations of the toxic elements As, Cd, Hg, Sb and V in well and borehole water, samples from the Bibiani mining area in the Western Region of Ghana have been measured using instrumental neutron activation analysis (INAA) following irradiation with thermal neutrons and counting with a conventional counting system. This study was conducted to assess the impact of mining activities on the ground water resources of the Bibiani mining area. The concentrations of the elements measured in the rainy season water samples were in the ranges: As, 0.04 – 6.08 mg/L; Hg, 1.63 – 2.05 mg/L; Sb, 0.52 – 0.96 mg/L and V, 0.06 – 0.62 mg/L. The concentrations of Cd were below 0.01 mg/L (i.e. the detection limit) in all the rainy season samples. In the dry season samples, the concentration ranges of the various elements were: As, 0.67 – 4.71 mg/L; Cd, 0.35 – 2.80 mg/L; Hg, 0.30 – 4.93 mg/L; Sb, 0.08 – 0.70 mg/L and V, 0.07 – 0.52 mg/L. In the rainy season, the concentrations of As in 54% of the samples, Hg in 31% of the samples, and Sb in 23% of the samples were above their respective World Health Organization (WHO) limits whereas in the dry season water samples, the concentration of As in 31% of the samples, Cd in 62% of the samples, Hg in 23% of the samples and Sb in 15% of the samples were above their respective WHO limits. The pH values of all the water samples ranging from 3.90 to 5.93 pH units fell below the lower limit of the range 6.5 – 8.5, the WHO (1985) pH range for good quality drinking water. Therefore it could be concluded on this grounds that the wells and boreholes studied in Bibiani mining area were polluted hence not suitable for human consumption.

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### Introduction

The indispensability of water to the survival of plants and animals is never in doubt. For example, according to Ashton *et al* (2001), globally, water is considered the most fundamental and indispensable of all natural resources and without it social and economic development and environmental diversity cannot be sustained. However, meeting the demand for this precious commodity is a very challenging situation that virtually every country is faced with as a result of burgeoning population (Ashton *et al*, 2001). In the first place, out of 70% of water that the planet earth is made of, fresh water accessible to man for drinking and other domestic uses constitutes only 0.76% (the remaining 99.24% is made up of freshwater in the form of polar ice, snow and soil water (which together constitute 1.74%) and salt water (97.5%)). Out of this 0.76%, groundwater constitutes 98% whilst rivers, lakes and spring water (referred to as surface water) constitute the remaining 2% (IAEA WRP, unknown year).

Groundwater is an important water resource not only because it is the largest reservoir of freshwater, but also because it supplies water to more than 1.5 billion urban dwellers, (UNESCO 2002). In Bibiani district, groundwater serves as the major source of water, ranking first ahead of the other main sources of water in the district, namely streams, rivers, and pipe-borne water. Groundwater in the form of well/borehole water alone supplies more than 57.4% of the entire population of the district with water (BABDA, 2006). A lot more people depend

on ground water during the dry season where most streams and rivers dry out or become unusable and during periods that the taps are not running. Also, since Bibiani is a mining district, most of its inhabitants prefer groundwater to streams/rivers because ground water is relatively less vulnerable to pollution by mining activities; and also because they cannot afford to purchase or do not have access to pipe-borne water which is the best option.

It is rather sad to note that, increasingly, human activities such as mining, rapidly growing cities, burgeoning industries, and the continuous use of chemicals in agriculture have, and continue to, undermine the quality of many water resources including aquifers (groundwater) and surface water such as streams, rivers and lakes on which we all depend (UNESCO 2002, SDWF unknown year). Mining by its nature consumes, diverts and can seriously pollute water resources. Four main mining impacts on water namely: Acid Mine Drainage; Heavy Metal Contamination and Leaching; Processing Chemicals Pollution and Erosion and sedimentation, have been spelt out (SDWF, unknown year). Through these impacts, a wide range of elements, including essential, potentially toxic and toxic elements could be released by mining activities into water bodies.

The group of elements, As, Cd, Hg, Sb and V are being studied because they are elements that have the tendency to be deadly poisonous to man when taken into the body above a certain concentration threshold (WHO values), even though very

useful to mankind industrially, and for that matter economically. The infamous *itai tai* incident that occurred in Japan in the 1940s bears witness to the deadly nature of Cd. Vanadium salts for instance is reported to have caused mild gastrointestinal disturbances in the short term, and anorexia, weight loss, and abdominal pain in the long term when administered in patients suffering from either diabetes mellitus or coronary artery disease (Evangelou 2002). Acute exposure of Sb to humans by inhalation has been reported to have caused rashes consisting pustules around sweat and sebaceous glands, and ocular conjunctivitis. Chronic exposure to antimony in humans causes antimony pneumoconiosis, alterations in pulmonary function, chronic bronchitis, chronic emphysema, inactive tuberculosis, pleural adhesions and irritation (ATSDR, 1992; USDHHS, 1993). The toxicological effects of Cd and Hg have already been described (Quarshie *et al.*, 2011).

With the high dependency of the people of Bibiani district on groundwater, bearing in mind ground water is not completely immune to pollution by mining activities, it was very necessary that this study be carried out. The aim of this study was to assess the impact of mining activities on groundwater resources in the Bibiani area by indication of the levels of the elements As, Cd, Cr, Hg and V in the wells and boreholes in the area.

#### Materials and methods

**Study area:** A detailed description of Bibiani, the study area, as well as a description of the geology has already been done in an earlier publication by same authors (Quarshie *et al.*, 2011). A map showing the sampling areas as well as geological map of the study area could be found in the same publication.

**Sampling and Sample Preparation:** A total of 14 water samples were taken from dug-wells/boreholes in seven communities of Bibiani on bimonthly basis from September, 2007 to April, 2008. The water samples collected were coded as; OTW1, OTW2 (from Old Town), OCW1, OCW2 (from Old Compound), NCB1, NCW2, NCW3 (from New Compound), NTW1, NTW2 (New Town), NKW1 (from Nantwikumye), PGW1, PGW2 (from Praga) and HBI, HW2 (from Hwenampori). Apart from wells coded OTW2 and NCB1 all the wells were sampled twice, i.e. during the rainy season and the dry season. The well coded NCB1 was not sampled during the rainy season because it was not identified during the rainy season sampling trip. The well coded OTW2 on the other hand had dried-out during the dry season.

Pre-cleaned plastic bottles were used to collect the water samples whilst wearing rubber hand gloves. The wells and boreholes were sampled following standard methods (Harter, 2003). At each of the water sources sampled, the plastic bottles were each rinsed three times with the water to be sampled before filling to the brim. About 10 drops of Analar nitric acid was added to one of the duplicate water samples (the sample intended to be used for analysis of toxic elements) to bring its pH to <2. This was done to keep metal ions in a dissolved state and also to minimize microbial activities (Serfor-Armah *et al.*, 2006; Adomako *et al.*, 2008). The pH and Eh were measured in situ using Accumet PORTABLE AP6 pH and Eh meter.

The water samples were filtered through a 0.45 $\mu$ m cellulose acetate Whatmann membrane filter fitted in a filtration unit (SM 16 510, Sartorius D-3400 Göttingen, Fed. Rep. Germany) connected to a suction pump (Phillips suction pump type, PU 9003, NC 9423 390 03011, № 413636 made in England). A volume of 0.5 ml each of the filtered water samples was transferred with calibrated Eppendorf tip ejector pipette

(Brinkmann Instruments, Inc. Westbury New York) into pre-weighed 1.5 ml polyethylene vials to obtain a mass of 500 mg (Serfor-Armah *et al.*, 2006; Adomako *et al.*, 2008). A piece of clean cotton wool (pre-weighed) was put gently into the water sample in the vial, capped and heat sealed. The cotton wool was added as a safety measure to avoid the water spilling and spreading radiation in case the vial opens in the reactor or whilst coming out of the reactor.

Four replicates of each water sample were weighed. Two were used for the determination of vanadium through its short-lived nuclide  $^{52}\text{V}$ , and the other two for determining antimony, arsenic, cadmium, and mercury through their respective medium-lived nuclides Sb $^{122}$ ,  $^{76}\text{As}$ ,  $^{115}\text{Cd}$  (as  $^{115\text{m}}\text{In}$ ) and  $^{197}\text{Hg}$ . For the determination of the short lived nuclides a 1.5 ml vial was put into a 7.0 ml polyethylene vial and heat sealed for irradiation. The space left in the polyethylene vial was filled with cotton wool to make sure that the sample is maintained at the correct geometry and heat sealed. For the medium-lived nuclides, four (4) 1.5 ml vials, each containing a sample, were packed into a 7.0 ml polyethylene vial and heat sealed for irradiation (Serfor-Armah *et al.*, 2006).

Aliquots (5 ml) of 1000 mg/L standard stock solutions of each of the elements; As, Cd, Hg, Sb and V (Manufactured by Tecknolab AB, Sweden and distributed by Industrial Analytical (Pty) Ltd., South Africa) were fetched and mixed together in a 500 ml volumetric flask and topped up to obtain a solution (House Reference Material) containing 10 mg/L of the various elements. For Quality Control/ Quality Assurance purposes (QA/QC), six replicates of 500 mg of the standard were weighed and prepared for irradiation per the description above. Also, a standard each was irradiated alongside the samples for the determination of the short and medium lived nuclides to aid quantification of the various elements in the samples via the comparator method.

**Irradiation, counting and analysis:** Irradiations were performed using the Ghana Research Reactor-1 (GHARR-1) facility at Ghana Atomic Energy Commission, Kwabenya. GHARR-1 is a miniature neutron source reactor (MNSR). Thermal neutrons were used to irradiate all the samples and the reference materials.

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  $5 \times 10^{11} \text{ ncm}^{-2} \text{ s}^{-1}$  while the reactor operated at 15kW (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 ( $t_i$ :  $t_d$ :  $t_c = 0.5 - 2: 1: 10$  mins) was used for the short-lived, ( $t_i$ :  $t_d$ :  $t_c = 1: 24 - 48: 0.5$  hrs), for the medium-lived and ( $t_i$ :  $t_d$ :  $t_c = 1: 14 - 21\text{d}: 5$ hrs) for the long-lived radionuclides (Serfor-Armah, 2006).

The timing for the various irradiation schemes were chosen based on 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 discussions

Six replicates of the House Reference Material (HRM) were analysed using INAA and the results obtained i.e., the mean concentration, precision and accuracy, presented in Table 1 below. The mean concentrations were comparable with the actual concentrations of the HRM's. This shows that INAA analytical technique developed in this work was reliable.

**Mineralogy of the Bibiani area:** The rocks of the study area are composed of the minerals, pegmatites, granites, plagioclase, Hornblende, muscovites, biotites, anorthite, albite, pyroxene, micas and arsenopyrites (Asiedu et al, 2004). These minerals are composed of, Al, As, Au, Ca, Fe, K, Mg, Na and Si (Alloway, 1995), as the major elements whilst Ba, Co, Cr, Ga, Mn, Ni, Rb, S, Sc, Se, Ti, V and Zn (Alloway, 1995) are the associated trace elements.

Oxidation of sulphur, which is one of the elements associated with the mineralogy of the area, could be responsible for the low pH observed for the ground water. This is possible when minerals containing sulphur such as arsenopyrites are exposed to atmospheric oxygen as is the case in Bibiani mining area where the tailings are left uncovered (WRC, 2000). This oxidation reaction is likely to occur at a faster rate in tailings because tailings are made up of fine particles due to the crushing and milling that the rocks are subjected to. Also iron in the form of Fe<sup>3+</sup> is able to oxidize sulphur resulting in low pH (Kortatsi, 2006; Asklund et al, 2005).

**Physical parameters:** The pH and Eh of water are important parameters in that they determine the species, mobility, bioavailability and toxicity of elements present. For example, under reducing conditions, sulphate ions are reduced to sulphides which precipitate cations of chromium and cadmium reducing their solubility. Also, the concentration of Cd in water decreases with increasing pH because sorption of Cd increases with increasing pH (ATSDR, 1999).

The pH values of the water samples obtained in both rainy and dry seasons were all below 7 pH units (Table 2), suggesting acidic character. On the average, the dry season water samples were more acidic than the rainy season samples. Out of a total of fourteen (14) samples, nine (9) samples namely, NCW2, NCW3, NKW1, NTW1, NTW2, OCW1, OCW2, PGW1 and PGW2 recorded more acidic pH in the dry season than in the rainy season. This may be due to the fact that during the dry season there was less rainfall hence the rate of dilution of ground water by rainfall decreased. As a result the dry season water became more concentrated (in terms of hydrogen ions) than the rainy season water, therefore having a lower pH. The pH of the rainy season samples ranged between 4.42 and 5.88 pH units with an average of 5.09 pH units. The pH values for the dry season samples on the other hand ranged from 3.90 to 5.93 pH units with an average value of 4.70 pH units (Table 2). This pH values are of concern because they provide favourable conditions for most metals to remain dissolved in water hence becoming bioavailable and toxic.

The ranges of the Eh values of the water samples were 43 – 133 mV for the rainy season and 30.9 – 160 mV for the dry

season samples (Tables 2) indicating that the water samples were oxidizing. The pH values of all the waters samples fell below the range of 6.5 – 8.5 (WHO, 1985) suggesting that the water samples are not suitable for drinking. This acidity could be due to the mineralogy of the area or to the infiltration of acidic water from the mine into the ground water system in the area – acid mine drainage.

**Elemental concentrations:** Vanadium occurred at detectable levels in almost all the water samples (Tables 3a & 3b) except the sample PGW1 in which it was not detected. Contrary to this, As, Cd, Hg and Sb were not detected in most samples except a few samples in which they occurred at levels above their respective WHO values. It may be inferred from this observation that vanadium is widely distributed (MPCA, 1999) relative to the other elements which appear to be present only in certain areas.

The concentration ranges of the elements measured in the rainy season water samples were: As, 0.04 – 6.08 mg/L; Hg, 1.63 – 2.05 mg/L, Sb, 0.52 – 0.96 mg/L and V, 0.06 – 0.62 mg/L. The concentrations of cadmium in all the rainy season samples were below detection limit (Table 3b). In the dry season, the concentration ranges of the various elements were: As, 0.67 – 4.71 mg/L; Cd, 0.35 – 2.80 mg/L; Hg, 0.30 – 4.93 mg/L; Sb, 0.08 – 0.70 mg/L and V, 0.07 – 0.52 mg/L.

The WHO guideline values for the elements As, Cd, Hg and Sb in drinking water are: As (0.01 mg/L), Cd (0.003 mg/L), Hg (0.001 mg/L) and Sb (0.005 mg/L) (WHO, 2006). In the following rainy season samples (Table 3a) the concentration of the elements indicated in parenthesis were above their respective WHO values: HB1, HW2, OCW1 and OCW2 (As); NCW3 (As, Sb); OTW1 and PGW1 (As, Hg); OTW2 (Sb); NTW1 (Sb, Hg) and NCW2 (Hg). Also in the dry season the following samples were found to contain the elements indicated in parenthesis in concentrations above their WHO values: NCW3 and OCW2 (As); NKW1 (As, Hg, Cd); OTW1 (As, Hg, Sb, Cd); PGW2 (Hg, Cd); HW2 (Sb, Cd) and HB1, NCB1, NCW2 and PGW1 (Cd) (Table 3b). The sample NTW2 was the only sample in which during both rainy and dry seasons, none of the elements As, Hg, Sb and Cd was found above the WHO value. Vanadium was not mentioned because WHO has not set a guideline value for it (vanadium) in drinking water.

It could be seen from the above results that more of the sampled wells and boreholes contained elements whose concentrations were above the WHO values in the rainy season than in the dry season, contrary to what was expected. It was expected that due to loss of water through evaporation and decrease in dilution of well/borehole water with inflowing water from the recharge area, the dry season well/borehole water would be more concentrated hence more of the elements would have concentrations above the WHO value.

The departure of the observation made in this study from this expectation could be explained by these scenarios: Firstly, that the toxic elements are not resident hence rely on the water flowing into the well/boreholes as a means of transport. In that case, as the inflow of water decreases in the dry season so do the concentrations of the toxic elements that are transported by the inflowing water.

The other alternative is that the toxic elements are resident but rather some dissolved substances that are transported to the wells/boreholes by the inflowing water complex/adsorb the toxic elements causing them to precipitate hence removing them from solution. As the inflows increase during the rainy season, and as

the pH becomes more basic, as observed from the results in table 2, more of the toxic elements are immobilized hence their concentrations fall below the WHO value.

Other important factors that come to play in determining the outcome of the above processes are the rate of flow of the water into the wells/boreholes and the rate of abstraction (as applies to existing wells that are frequently being fetched like in our case) or the time elapsed between the rainy season sampling and the dry season sampling (in the case of monitoring wells).

#### Conclusion:

The measured concentrations of the elements As, Cd, Hg, and Sb in almost all the water samples were above their respective WHO limits except a few samples in which the concentrations were below the detection limit of INAA. In the rainy season water samples, the concentration of As in 54% of the samples, Hg in 31% of the samples, and Sb in 23% of the samples were above their respective WHO limits whereas in the dry season water samples, the concentration of As in 31% of the samples, Cd in 62% of the samples, Hg in 23% of the samples and Sb in 15% of the samples were above their respective WHO limits. Also, the pH values of all the water samples ranging from 3.90 to 5.93 pH units fell below the lower limit of the range 6.5 – 8.5, the WHO (1985) pH range for good quality drinking water. Based on the findings above, the conclusion could therefore be drawn that all the dug-well/boreholes were polluted and hence not good for human consumption. There were indications that mining activities might have had some impact on the groundwater resources in the area. However, due to some challenges encountered during sampling, no concrete evidence could be gathered to attribute the pollution to mining activities.

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**Table 1: Comparison of actual levels (mg/L) of elements in HRM with the levels measured by INAA in this work**

Elements	This work (avg conc.)	Precision (%)	Actual value	Accuracy (%)
As	9.94	1.00	10.00	0.60
Cd	9.86	1.43	10.00	1.40
Hg	9.76	1.47	10.00	2.40
Sb	9.89	1.38	10.00	1.10
V	9.98	0.99	10.00	0.20

**Table 2: The pH and Eh values of the rainy and dry season water samples**

Sample codes	pH		Eh (millivolt)	
	Rainy season	Dry season	Rainy season	Dry season
HB1	5.88	5.93	43	35
HW2	4.67	4.76	112	108
NCB1	#	5.81	#	42
NCW2	4.77	3.90	110	160
NCW3	4.86	4.19	105	142
NKW1	4.75	4.70	111	112
NTW1	4.62	4.02	115	30.9
NTW2	5.62	4.15	59	145
OCW1	4.42	3.96	133	156
OCW2	5.11	4.50	90	123
OTW1	5.80	5.81	51	42
OTW2	5.78	#	55	#
PGW1	5.08	4.92	92	98
PGW2	4.80	4.43	108	128

**Table 3a: Average concentrations of elements (mg/L) in water samples collected during the rainy season, with standard deviations**

Sample codes	Elemental concentrations				
	As	Cd	Hg	Sb	V
HB1	0.15±0.02	<0.01*	<0.01*	<0.001*	0.35±0.050
HW2	0.23±0.03	<0.01*	<0.01*	<0.001*	0.06±0.009
NCW2	<0.001*	<0.01*	2.05±0.31	0.52±0.08	0.41±0.060
NCW3	0.65±0.10	<0.01*	<0.01*	<0.001*	0.17±0.030
NKW1	<0.001*	<0.01*	<0.01*	<0.001*	0.23±0.030
NTW1	<0.001*	<0.01*	1.82±0.27	0.96±0.14	0.13±0.020
NTW2	<0.001*	<0.01*	<0.01*	<0.001*	0.20±0.030
OCW1	6.08±0.90	<0.01*	<0.01*	<0.001*	0.62±0.090
OCW2	0.55±0.08	<0.01*	<0.01*	<0.001*	0.32±0.020
OTW1	1.10±0.15	<0.01*	0.90±0.13	<0.001*	0.08±0.020
OTW2	<0.001*	<0.01*	<0.01*	0.54±0.05	0.29±0.030
PGW1	0.04±0.002	<0.01*	1.99±0.25	<0.001*	0.10±0.010
PGW2	<0.001*	<0.01*	<0.01*	<0.001*	0.22±0.020
WHO values	0.01 <sup>a</sup>	0.003 <sup>a</sup>	0.001 <sup>a</sup>	0.005 <sup>a</sup>	-

\*Detection limit

<sup>a</sup>WHO Guidelines for Drinking-water Quality, 2006**Table 3b: Average concentrations of elements (mg/L) in water samples collected in the dry season with standard deviations**

Sample codes	Elemental concentrations (Dry season)				
	As	Cd	Hg	Sb	V
HB1	<0.001*	1.46±0.28	<0.01*	<0.001*	0.27±0.05
HW2	<0.001*	2.65±0.41	<0.01*	0.70±0.08	0.19±0.02
NCB1	<0.001*	0.88±0.12	<0.01*	<0.001*	0.07±0.01
NCW2	<0.001*	1.78±0.25	<0.01*	<0.001*	0.52±0.06
NCW3	0.89±0.11	<0.01	<0.01*	<0.001*	0.14±0.02
NKW1	4.71±0.71	2.80±0.32	0.30±0.02	<0.001*	0.10±0.02
NTW1	<0.001*	<0.01*	<0.01*	<0.001*	0.11±0.01
NTW2	<0.001*	<0.01*	<0.01*	<0.001*	0.16±0.02
OCW1	<0.001*	<0.01*	<0.01*	<0.001*	0.15±0.01
OCW2	0.67±0.10	<0.01*	<0.01*	<0.001*	0.12±0.007
OTW1	2.22±0.25	0.35±0.04	0.90±0.13	0.08±0.01	0.24±0.03
PGW1	<0.001*	2.25±0.25	<0.01*	<0.001*	<0.001*
PGW2	<0.001*	0.60±0.007	4.93±0.69	<0.001*	0.24±0.02
WHO values	0.01 <sup>a</sup>	0.003 <sup>a</sup>	0.001 <sup>a</sup>	0.005 <sup>a</sup>	-

\*Detection limit

<sup>a</sup>WHO Guidelines for Drinking-water Quality, 2006