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*Full Length Research Paper*

# Urinary arsenic and mercury levels in artisanal miners in some communities in the Obuasi Municipality of Ghana

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**There are a large number of small-scale artisan gold miners who use mercury in the extraction of gold in Ghana. The extraction process releases arsenic and mercury into the environment with its associated risk to human health. Human exposure to arsenic and mercury was assessed in artisanal miners involved in illegal mining activities in five communities at Obuasi municipality, a historic mining area in Ghana. Subjects completed an exposure assessment questionnaire and also provided the first urine voided upon waking up in the morning. Total urine-As and urine-Hg were simultaneously determined using neutron activation analysis. The highest mean urine-As value recorded at the high risk level (> 35 µg/L) was 53.57 ± 5.58 µg/L. Seventeen percent of the miners recorded urinary-As levels above the biological exposure index of 35 µg/L; 38% were found in the moderate risk level (20-35 µg/L) while 45% were in the low risk bracket (< 20 µg/L). The highest mean urine-Hg concentration at the high risk level was 38.55 ± 3.83 µg/L, recorded by 2% of the miners. Five percent of the miners had urine-Hg concentrations in the moderate risk bracket while 93% were at the low risk level. Fifty five percent of the artisanal miners recorded values above the WHO recommended range of 5 to 20 µg/L for urine-As.**

**Key words:** Mercury, arsenic, urine, neutron activation analysis.

## INTRODUCTION

Toxic emissions from industry and mining are still major cause of diseases in developing countries. Illegal artisanal gold mining often result in the release of toxic materials into the environment posing health risks to the miners and surrounding communities (Blacksmith Institute, 2006). The miners work in difficult and often hazardous conditions and without any regulations or standards. Artisanal gold miners frequently use toxic chemicals such as mercury to extract the gem. Due to its high volatility, mercury can disperse to distant uncontaminated locations. This results in deterioration of air and water quality and subsequent deleterious effects on living organisms (Donkor et al., 2006).

Arsenic, in the form of arsenopyrite (FeAsS), occurs as an impurity in gold ore and in many other mineral deposits (Eisler, 2004). Arsenic and mercury are therefore two highly toxic elements that could be discharged into the environment through artisanal gold

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mining activities. Soluble inorganic arsenic is acutely toxic. Ingestion of sub-lethal doses of arsenic may result in bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy and encephalopathy in humans (IPCS, 1980). Mercury can affect nerve cells causing twitching eyelids, headaches, memory loss and other neurological problems. Inhaling mercury vapour damages lungs and cause coughing and lung scarring. Long term mercury exposure will damage the kidneys (IPCS, 1990). Mercury and arsenic contamination resulting from artisanal gold mining activities is of a great concern in Ghana because mercury is used to effectively extract gold in small-scale mining. Indeed, mercury pollution of river water, sediments, soil and mine workers in Ghana has already been reported (Abrefah et al., 2011; Ansong-Asante et al., 2007; Donkor et al., 2006).

Toxicological studies suggest that urinary arsenic could be considered as a biomarker of arsenic exposure (Bera et al., 2010; Caceres et al., 2005; Hughes, 2006). A part of ingested arsenic gets to the liver where it is metabolized through various biotransformational processes (Gregus et al., 2000; Thomas et al., 2001; Vahter, 2002) and excreted through urine (Aposhian et al., 2004). The urine, faeces and hairs samples of subjects exposed to arsenic will contain significant concentrations of arsenic. Hence, urine may be considered as potential biomarkers of exposure to arsenic (Bera et al., 2010; Datta et al., 2010). The present study determined the occupational exposure to arsenic and mercury in the urine of artisanal gold miners in five communities within the Obuasi municipality where artisanal mining activities, known locally as “galamsey”, take place briskly. We also attempted collating data on the ailments the artisanal mine workers most often complain of.

## MATERIALS AND METHODS

### Study area

Obuasi is located in the south-central part of Ghana and is about 300 km northwest of the capital, Accra. It is located between latitude 5.35 and 5.65 N and longitude 6.35 and 6.90 N. The Obuasi municipality covers a land area of 162.4 $km^2$ and has undulating topography. The climate is of the semi-equatorial type with a double rainfall regime. Mean annual rainfall ranges between 125 and 175 mm. Mean average annual temperature is 25.5°C and relative humidity is 75 to 80% in the wet season (Akoto et al., 2011). The population of the municipality is estimated at 205,000 using the 2000 Housing and Population Census (Ghana Statistical Services, 2000) as a base and applying 4% annual growth rate. As a historical mining town that has seen continuous mining operations since the 1890s, mining activity presents the predominant potential source of trace element contamination in the area (Antwi-Agyei et al., 2009). Figure 1 is the map of the study area showing the sampling spots.

### Study population

Twenty small-scale artisanal miners with an average age of 27.54 ± 8.38 years, and having an average of 6.02 ± 2.95 years of practice were randomly selected from each of the five communities; Sansu (Sa), Ahansonyewodea (Ah), Nyameso (Ny), Anwona (An) and Dokyiwaa (Do) in the Obuasi municipality. Control sample comprising 20 subjects (average age of 28.14 ± 9.73 years) living in communities far away from mining activities but located in the Obuasi municipality was also pooled. Sampling was repeated after 3 months. All the 120 subjects were males in order to avoid any bias that sex differences could introduce; artisanal gold mining is mostly carried out by males. After obtaining their consent, each of the subjects was helped to complete an exposure assessment questionnaire. Background variables and other information (e.g., work experience, education, health, smoking and alcohol habits) relevant for the interpretation of the results were recorded.

### Sample collection, processing and analyses

The total collection consisted of one hundred and twenty urine samples (obtained on voluntary basis). Subjects provided their first urine voided upon waking up in the morning (first morning void). Each subject was given a common specimen collection system and a resealable plastic bag to contain the sample during transport. Up to 50 ml urine sample was provided by each of the subjects. Each collection vessel was placed in a heavy duty plastic bag and the seal closed. Urine samples were stored in a cold chest with frozen refrigerant packs and transferred to a refrigerator at the Environmental Laboratory of AngloGold Ashanti, Obuasi where they were stored at -20°C prior to analysis. Concentrations of mercury and arsenic were determined using the neutron activation technique in a reactor situated at the Ghana Atomic Energy Commission, Accra, Ghana. Sample irradiation was carried out in the 30 kW miniature neutron source reactor at a neutron flux of $5 \times 10^{11}$ neutrons $cm^{-2}$ $s^{-1}$.

Prior to analyses, samples were thawed and mixed thoroughly. A representative 1.0 ml aliquot was transferred to a polyethylene vial and heat-sealed. Single-element standard solutions of arsenic and mercury were also prepared in the same manner as the urine samples. The irradiation vials containing the samples and standards were then placed into a bigger vial and heat-sealed (double encapsulation). Samples and standards were transferred into the reactor via a pneumatic transfer system operating at a pressure of 0.6 mPa and samples irradiated for 1 h. They were then removed from the reactor and allowed to decay for 24 to 36 h. The induced γ-activities of the radioisotopes; $^{76}As$ ($t_{1/2}$ = 26 h; $E_\gamma$ = 559.1 keV) and $^{196}Hg$ ($t_{1/2}$ = 64.1 h; $E_\gamma$ = 77.3 keV) were measured using a coaxial high purity germanium (HPGe) semi-conductor γ-ray detector. The ORTEC MAESTRO-32 γ-spectroscopy software was used to acquire the γ-spectrum of the radioisotopes (De Corte et al., 1987). Two certified reference materials (CRMs) for human urine were used to validate the analytical procedure; SRM 3133 for Hg and SRM 3103a for As were purchased from National Institute of Standards and Technology (Gaithersburg, USA). Analytical calibrations based on peak areas of appropriate concentration points were carried out. Reproducibility of the method was evaluated by comparing the signals obtained from five determinations of the CRMs. The limits of detection (LOD) and limits of quantification (LOQ) were evaluated as 3 and 10 times the estimated regression standard deviation, respectively, based on five replicate determinations.

## RESULTS AND DISCUSSION

### Method validation

Table 1 gives the quality control parameters of the

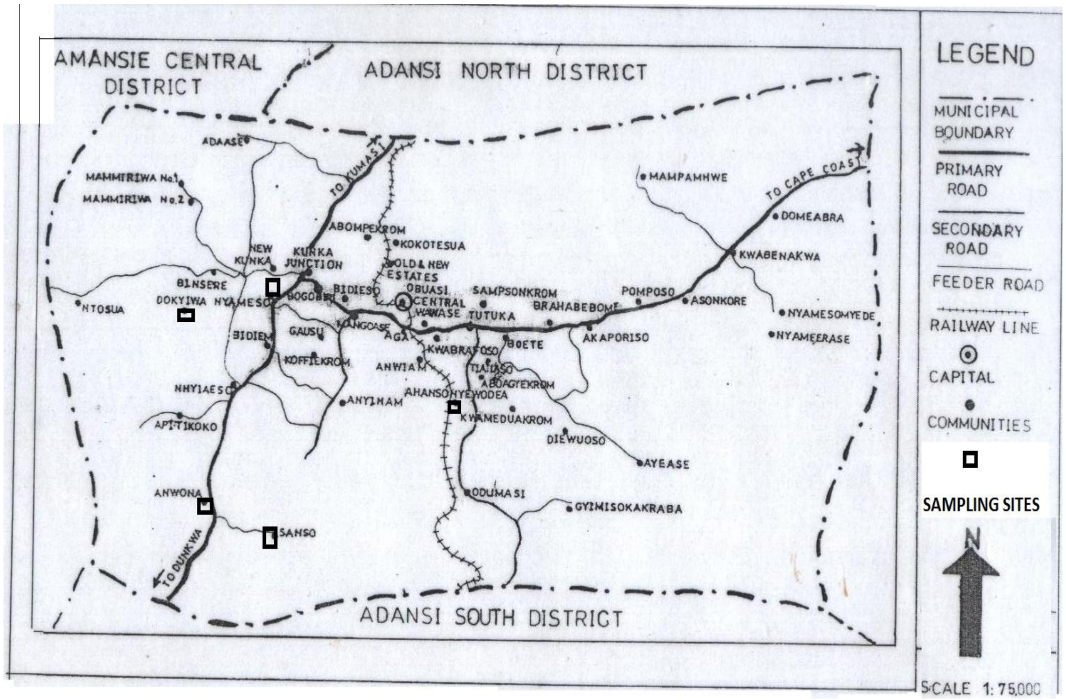


**Figure 1.** Map of study area showing sampling sites.

**Table 1.** Analytical quality control parameters determined using SRM 3133 for Hg SRM 3103a for As.

| Element | SRM 3133 | | | SRM 3103a | | | LOD ($\mu gL^{-1}$) | LOD ($\mu gL^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | Certified ($\mu gL^{-1}$) | Found ($\mu gL^{-1}$) | Rel. error (%) | Certified ($\mu gL^{-1}$) | Found ($\mu gL^{-1}$) | Rel. error (%) | | |
| Hg | 10.00 | 10.08 (0.65) | 0.8 | - | - | - | 0.04 | 0.12 |
| As | - | - | - | 8.00 | 8.05 (0.19) | 0.6 | 0.06 | 0.18 |

analyses. Accuracy of the determinations, expressed as relative error between the certified and the observed values of the CRMs were less than 1% for both mercury and arsenic. The precision of the measurements expressed as relative standard deviation on five independent determinations, was also satisfactory, being lower than 3% (Huber, 2003). The LOD was 0.04 ± 0.01 $\mu gL^{-1}$ for Hg and 0.06 ± 0.20 $\mu gL^{-1}$ for As. The LOQ was less than 0.2 $\mu gL^{-1}$ for the elements.

The mean levels of total urine arsenic and mercury measured in urine samples from artisanal gold miners in five communities in the Obuasi municipality is presented in Table 2. The highest urine-As concentration (>35 µg/L), designated as high risk level was recorded at Sa where 30% of the artisanal miners had mean urine-As levels of 53.57 ± 5.58 µg/L in a range of 38.26-76.63 µg/L (Table 2). This was followed by Do, where 20% of the artisans had a mean urine-As concentration of 40.33 ± 4.51 µg/L. Ah and An had 15% of the artisans having mean urine-As levels of 38.09 ± 2.72 and 38.88 ± 3.75 µg/L, respectively. None of the control nor subjects from Ny had urine-As in the high risk range. The values recorded at the high risk level were above the biological exposure index of 35 µg/L for urinary arsenic (ACGIH, 2001).

Subjects pooled from Sa and Do, again recorded the highest values of urine-As at the moderate risk level (20 to 35) µg/L; 40% recorded urine-As of 30.41 ± 2.91 µg/L and 27.52 ± 3.09 µg/L, respectively. At the moderate risk level (20 to 35 µg/L), Ah, Ny and An had 45, 30 and 35% of artisanal gold miners recording mean urine-As values of 24.57 ± 4.49, 24.35 ± 2.51 and 23.95 ± 2.81 µg/L, respectively.

Ah had 40% of the subjects recording the least mean urine-As value of 7.73 ± 4.57 µg/L in the low risk level (< 20 µg/L). Dokyiwa had 35% of the artisanal miners recording mean urine-As of 11.00 ± 5.71 µg/L. All the urine-As concentrations recorded in the control subjects were found in the low risk level. The control recorded mean concentration of 2.45 ± 1.17 µg/L. The mean of urine-As recorded in the present study at all the five communities were lower than those obtained by

**Table 2.** Mean urinary arsenic and mercury levels among small scale artisanal gold miners in five communities in the Obuasi Municipality.

| Community | Urinary concentration of As (µgL$^{-1}$) | | | Urinary concentration of Hg (µg L$^{-1}$) | | |
|---|---|---|---|---|---|---|
| Risk level | <20 Low | 20-35 Moderate | >35 High | <20 Low | 20-35 Moderate | >35 High |
| **Sansu** | N = 6 | N = 8 | N = 6 | N = 15 | N = 3 | N = 2 |
| Mean ± SD | 10.52 ± 6.69 | 30.41 ± 2.91 | 53.57 ± 5.58 | 7.41 ± 6.12 | 23.58 ± 3.92 | 38.55 ± 3.83 |
| Range | 2.21-18.26 | 22.74-34.93 | 38.26-76.63 | 1.28-16.30 | 20.82-26.34 | 35.83-41.26 |
| **Ahansonyewodea** | N = 8 | N = 9 | N = 3 | N = 20 | - | |
| Mean ± SD | 7.73±4.57 | 24.57±4.49 | 38.09±2.72 | 6.78±5.02 | | - |
| Range | 1.11-14.30 | 20.06-28.34 | 35.22-40.63 | 0.68-14.71 | | |
| **Nyameso** | N = 14 | N = 6 | N = 0 | N = 20 | | |
| Mean ± SD | 9.47 ± 5.28 | 24.35 ± 2.51 | - | 4.73 ± 3.40 | - | - |
| Range | 0.86-18.30 | 20.86-27.82 | - | 0.42-12.15 | | |
| **Anloga** | N = 10 | N = 7 | N = 3 | N = 20 | | |
| Mean ± SD | 8.48 ± 5.42 | 23.95 ± 2.81 | 38.88 ± 3.75 | 7.13 ± 4.14 | - | - |
| Range | 2.22-18.67 | 20.74-28.42 | 36.68-43.22 | 1.10-14.10 | | |
| **Dokyiwaa** | N = 7 | N = 8 | N = 5 | N = 18 | N = 2 | |
| Mean ± SD | 11.00 ± 5.71 | 27.52 ± 3.09 | 40.33 ± 4.51 | 9.43 ± 6.14 | 29.36 ± 3.98 | - |
| Range | 2.46-19.24 | 24.10-34.22 | 35.83-46.76 | 0.94-18.10 | 26.54-32.17 | |
| **Control** | N = 20 | N = 0 | N = 0 | N = 20 | | |
| Mean ± SD | 2.45 ± 1.17 | - | - | 1.14 ± 0.54 | - | - |
| Range | 0.40-4.51 | - | - | 0.24-2.11 | | |

Ansong-Asante et al. (2007) where urine-As concentrations varied between 34 and 700 µg/L with a mean value of 260 µg/L. The mean urine-As recorded in the current study at the low risk level (< 20 µg/L) were comparable to the mean urine-As values of 14.75 ± 1.62 µg/L recorded for gold processing workers at south western Ghana (Abrefah et al., 2011). However, the mean values recorded at moderate (20 to 35 µg/L) and high risk levels were higher than those recorded by Abrefah et al. (2011). Uchino et al. (2006) recorded urine-As concentration of 2.78 µg/L for mild, 30.7 µg/L for moderate and 118 µg/L for high arsenic affected families. Buchet et al. (1981) measured urinary excretion of arsenic in 10 workers ranging between 10 and 941 µg/L compared to a range of 7.6 to 59 µg/L in the control subjects. They concluded that the high urinary arsenic concentrations in the workers were more related to oral intake due to poor hygienic practices.

Fifty-five percent of the miners recorded values above the WHO recommended range of 5 to 20 µg/L for arsenic. Majority of the miners may be considered to be at risk of arsenic poisoning. Arsenic levels at Obuasi have been reported to be one of the highest in the world and have been linked to the principal gold bearing ore in the region which is rich in arsenopyrite (FeAsS) mineralization (Antwi-Agyei et al., 2009).

The concentrations of urine-Hg recorded in all the five communities were lower than the urine-As levels recorded. Mean urine-Hg concentrations for high risk levels were recorded only at Sa; 2 out of the 20 subjects had mean urine-Hg concentration of 38.55 ± 3.83 µg/L. The mean urine-Hg concentration of 38.55 ± 3.83 µg/L recorded for Sa at the high risk level is lower than the WHO recommended value of 50 µg/L for Hg in urine (Van-Straaten, 2000). Three of the subjects from Sa and 2 from Do recorded mean urine-Hg concentrations of 23.58 ± 3.92 and 29.36 ± 3.98, respectively (moderate risk level). Subjects from Ah, Ny, An and the control recorded values only in the low risk level with mean urine-Hg values of 6.78 ± 5.02, 4.73 ± 3.40, 7.13 ± 4.14 and 1.14 ± 0.54 µg/L, respectively.

The mean urine-Hg recorded at the low risk level in the five communities with the range (0.42-18.10 µg/L) were far higher than those recorded by Abrefah et al. (2011), which were in the range (0.40-0.74 µg/L) for casual mine workers and (0.38 to 0.76 µg/L) for permanent mine workers. Adimado and Baah (2002), recorded mean concentration of urine-Hg levels of 34.2, 2.6, 6.4 and 7.3 µg/L, respectively, in mine workers sampled from Anwiaso, Sahuma, Tanoso and Elubo in the Ankobra and Tano river basins. The concentration of urine-Hg recorded by Adimado and Baah (2002) were comparable to those obtained in the current study. The World Health Organization recommends the highest limit of urinary-Hg of 50 µg/L (IPCS, 1980). The mean urine-Hg concentration recorded at the low risk level in the five communities (93% artisanal miners) were comparable to the values obtained by Asante et al. (2007), where a maximum urine-Hg concentration of 12 µg/L was recorded. Sa community has a long history of artisanal mining which serves as economic activity for the youth. The high concentrations of urine-As and urine-Hg recorded for artisans at Sa could be attributed to the fact that the community is close to a mine shaft. Moreover, AngloGold Ashanti has an open pit located in the community. The area has also been used as a waste dump in surface mining operations. During heavy downpours, sediments from waste dumps wash directly into the Saa River which served as a source of drinking water for the community. AngloGold Ashanti (Obuasi) has a tailing dam at Dokyiwa where illegal mining activity is rampant. The indiscriminate illegal mining activities could have contributed to the moderately high levels of urine-As and urine-Hg at Do. Anloga is one of the communities where AngloGold Ashanti has one of its effluent discharges which have the potential of contaminating source of drinking water with arsenic. Ny community is not close to any of the surface mining consignment of AngloGold Ashanti. The artisanal gold miners in this area obtain their raw materials from other sites or go to these sites to work. The relatively low levels of arsenic and mercury in urine compared to the other communities studied may be attributed to the fact that the subjects stay far away from the mine site.

The data gathered using the questionnaire indicated that the use of personal protective equipment was non-existent among the artisans. The level of education helps people to better understand the risk associated with work they do and also take precautionary measure for their health and safety. Twenty one percent of the subject had no formal education, 74% have had only basic education and only 5% have attended ordinary level or senior high school education.

Reported illnesses that were compiled from the structured questionnaire administered to the miners included fatigue (88%), palpitations (32%), parasthesia (64%), headaches (72%) and gastrointestinal problems (56%). The effort to associate hygienic practices with arsenic and mercury exposure revealed that 84% of the miners wash their hands with only water (without soap) before eating while 42% do not wash their working clothes regularly. A significant proportion of miners (92%) indicated that they had meals at least once in a day at the workplace. These lifestyle factors could contribute to additional arsenic and mercury exposure in and outside the workplace.

## Conclusion

From the study conducted, it was observed that the levels of both arsenic and mercury were relatively high compared to other studies. This could be as a result of the fact that none of the artisanal gold miners used any personal protective equipment in the course of their work coupled with poor hygienic practices. Thus the moderately high urinary arsenic concentrations found inthe miners may be more related to oral intake due to poor hygienic practices.

The artisanal miners need to be educated on the dangers of eating and drinking at the workplace, that is, segregate work and eating areas; establish clothes changing facility in order to protect their health. They need to be encouraged to improve on their working methods and procedures and to use personal protective equipment in order to minimize exposure at the workplace. Furthermore, the miners need to be sensitized on the need to take regular medical examination to maintain their health.


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