

The impact of small-scale mining activities on the levels of mercury in the environment: The case of Prestea and its environs

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(Received May 27, 2004)

To obtain the baseline information of mercury pollution due to gold mining activities in Prestea and its environs total mercury (T-Hg) concentrations were measured in water and stream sediment. The samples were analyzed by instrumental neutron activation analysis (INAA). They were irradiated and counted without any preconcentration. Higher levels of T-Hg concentration were found in samples at the sites with extensive small-scale “galamsey” gold mining activities than at the sites with low small-scale “galamsey” activities. Concentrations varied between 6.80–19.82 mg/l for water and 28.90–84.30 mg/kg in sediment at sites with extensive small-scale mining activities. At low small-scale mining sites concentration levels for T-Hg varied between 0.50–9.10 mg/l and 1.20–22.75 mg/kg in water and sediment, respectively. The concentration levels of T-Hg in water from all the sampling sites are in excess of the WHO tolerable limit of 0.001 mg/l for drinking water.

Introduction

Ghana produces over 45 tons of gold per annum, which has now overtaken cocoa as the country's chief foreign exchange earner, bringing more than USD 600 million annually.¹ Over 90% of gold produced in Ghana is from large-scale underground or surface mining. A greater proportion of the remaining 10% is from small-scale mining locally referred to as “galamsey” (gather and sell), and this activity employs over 120,000 people. Rural employment and development are also some of the benefits of the mining industry in general. It is important to note, that, in some communities “galamsey” is the only viable economic activity since the land has been rendered infertile for farming by earlier mining activities. While economically significant, the processes involved are not carefully controlled and cause adverse effects to the environment including the diversion of water bodies and water pollution from the introduction of sediments and mine effluents. Mercury contamination associated with small-scale gold mining and processing represents a major environmental and human concern.^{2,3} Studies by gravimetric material flow analysis show that 70–80% of Hg is lost to the atmosphere during processing, 20–30% are lost to tailings, soils, stream sediments and water.³

Mercury is widely considered to be among the highest priority environmental pollutants.⁴ Amalgamation (Hg–Au amalgam) is the predominant gold extraction technique used by the “galamseys”. The miners make extensive use of mercury in the gold recovery process. All the mercury used is released into the environment, since there is no system in place to recover the used mercury. In the gold extraction process, the anthropogenically introduced mercury is lost to soils,

tailings, stream sediments and water close to the processing sites.¹ Inorganic mercury released into the aquatic environment undergoes biological methylation into methylmercury (Me–Hg), the most toxic form of mercury. The methyl–Hg ultimately bio-accumulates to significant levels in fish and may biomagnify through the food chain.^{4,5} Humans are exposed to mercury through the ingestion of contaminated water and food.⁵ The people living near gold mining areas may be contaminated with at least two forms of mercury. These are inorganic Hg and Me–Hg. Humans may be contaminated simultaneously from surrounding air, diets and water.⁴ Thus, people living along the river and depending on riverine products are easily exposed to Me–Hg and may develop toxic levels through repeated consumption of these contaminated fish. Therefore, there is the need to monitor both workers and inhabitants on regular basis to assess the effect of “galamsey” mining activities.

Studies of occupationally exposed humans to Hg vapor have shown slight adverse effects on the central nervous system and kidneys and probably on the thyroids.^{6,7} Mercury poisonings is manifested in various neuromuscular malfunctions ranging from numbing of the extremities to the loss of eye sight, paralysis and even death. When Me–Hg enters the human system, it readily crosses the walls of the gastrointestinal tract due to its fast transport through biological membranes, thus accumulating in the envelopes of the nerve cells causing neurological damage.^{8–10} The high toxicological profile of mercury, demands constant and extensive environmental monitoring of mercury levels, especially, in small-scale gold mining areas. However, not much work has been done on mercury pollution in Ghana.

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The present work was undertaken in order to: (1) determine the extent of Hg contamination in the aquatic environment, (2) gather data and use it as a scientific basis for further and future monitoring, and (3) to assess the Hg levels at greater distances from the point of discharge.

The study area was Prestea, a gold mining town and some of its surrounding villages in the Western region of Ghana. The area was chosen as a case study, owing to its well-known history of small-scale gold mining using amalgamation. In addition, the magnitude of present small-scale gold mining activities contributed to its selection.

Small-scale gold (galamsey) extraction process

The processing of gold by “galamsey” involves the crushing of gold-bearing rocks using mechanical crushers. A flow diagram of the essential processes involved is shown in Fig. 1. The crushed ore is milled mechanically. The fine gravel obtained is mixed thoroughly with water, and allowed to flow down an inclined “sluice board” covered with jute sack. Gold dust is trapped on the jute sack due to gravity concentration. The trapped gold dust is washed with water into a pan. Metallic mercury is added in excess to the gold dust and hand-mixed thoroughly to form a homogeneous Hg–Au amalgam. “Raw gold” is obtained by subjecting the amalgam to roasting in open charcoal fire contained in a coal pot. Air is blown periodically from the mouth to maintain the high temperatures so as to quicken the roasting process.

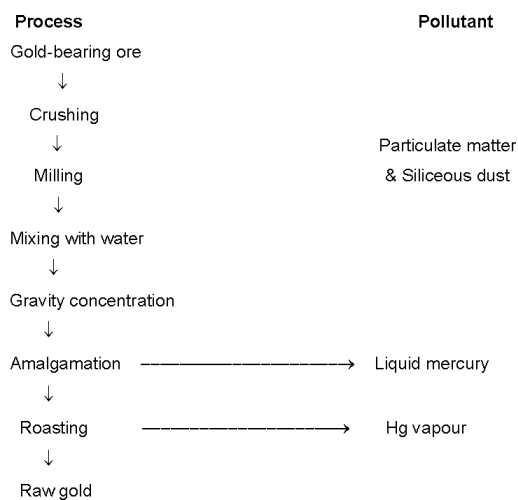


Fig. 1. Schematic flow diagram of the essential processes involved in gold extraction by “galamsey”

Experimental

Sampling

Samples of surface water and sediment were collected from the sampling points during January 2002–April 2003. Samples were collected on three-month basis from all the sampling points. The sampling location and sampling sites are presented in Fig. 2. At each sampling point, water and sediment were collected. Sampling points P1, P2, P3 and P4 are located at Dagarti compound, a suburb of Prestea, whilst B1 to B9 are located at Bondae, also in Prestea locality. There is an abandoned gold mine shaft at Bondae.

The collection of water samples from the streams was done with gloved hands. The direction of flow of water was faced and particles in the water stirred up by the feet allowed to settle down. Pre-cleaned capped polyethylene 1-liter sampling bottles were immersed about 10 cm below the water surface, uncapped and container filled with the water. At the sampling site, the bottles were rinsed at least three times with the water to be studied before taking the sample to be used for analysis. The water samples were filtered using a preconditioned plastic Millipore filter unit equipped with a 0.45 µm filter membrane (Gelman Instrument Co., London). Two sets of water samples were collected at each sampling site. One was used for the measurement of pH. The pH measurement was done on the field with a TOA pH-meter (TOA Electronics Ltd., Tokyo, Japan). The other was acidified with 1% nitric solution. This acidified sample was used for the INAA measurement. The addition of the acid is to keep the metal ions in the dissolved state. Samples were kept over ice in an ice chest and transported to the laboratory. The samples were stored in a refrigerator until analysis.

Collection of sediment was done with a pre-cleaned polyethylene shovel.^{11,12} The polyethylene shovel was used to scoop the top 10 to 15 cm of the sediment. With gloved hands, the sediment samples were transferred into pre-cleaned polyethylene bags and double bagged. No preservatives were added to the samples.³ The samples were immediately placed into an ice chest.

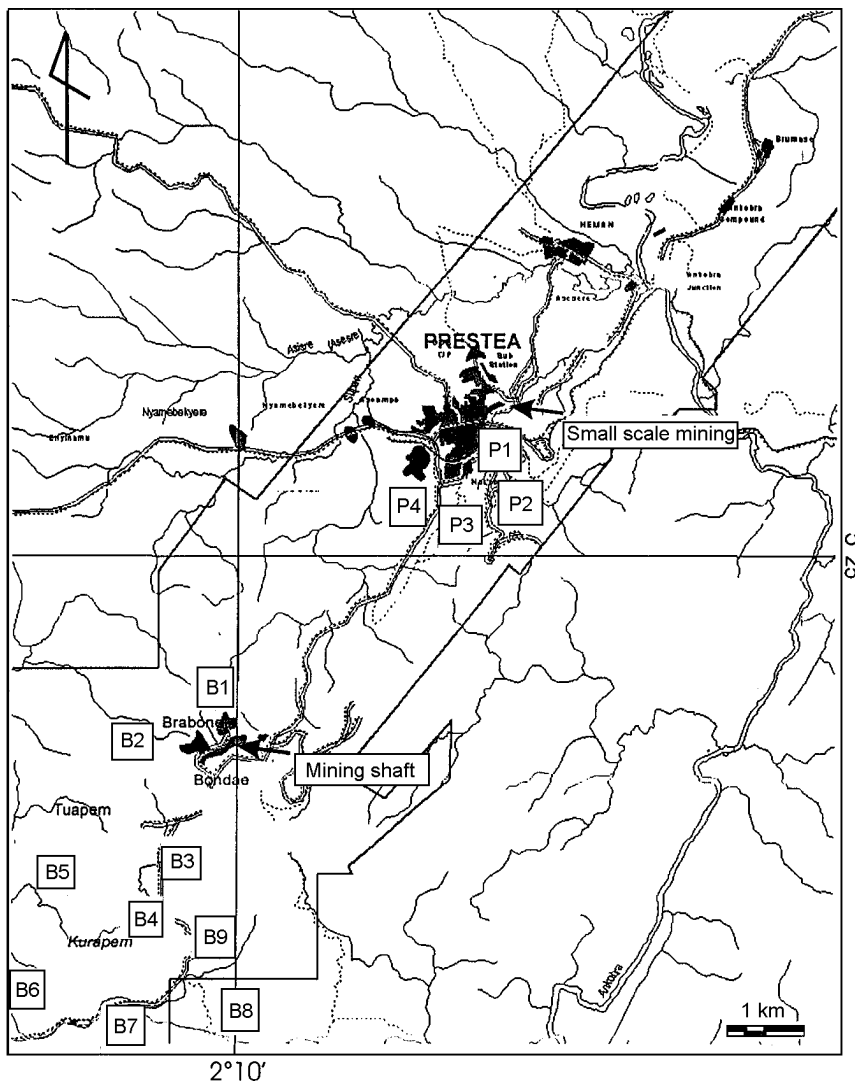


Fig. 2. Map of Prestea showing the sampling points

Sample preparation

0.5 ml of each water sample was pipetted using Eppendorf tip ejector pipette (Brinkmann instruments, Inc., Westbury, New York) into clean pre-weighed 1.0 ml polyethylene vials, weighed and heat-sealed. Two of these sample vials were placed into a 7.0 ml polyethylene vial and heat-sealed. Six replicates were prepared for each sample. 5 ppm and 10 ppm Hg standard (BDH, Spectrosol) solutions were prepared and used to spike the water samples. The spiking was done throughout the analysis.

Each sediment sample was homogenized using a polyethylene spatula and air dried at 18 °C for 72 hours in a clean environment. Organic debris, shelly fragments, stones and macro-organisms were glove-

hand picked from each sample. The dried samples were gently crushed using an agate mortar and pestle. Samples were sieved through an 85-mesh USA standard testing sieve (Fisher Scientific Co., USA). The samples were stored in air-tight polyethylene vials until analysis. 100.0 mg of each sediment sample were weighed onto polyethylene film. The films were wrapped and heat-sealed. Six replicate sub-samples were prepared for each sample, packed into polyethylene irradiation capsule and heat-sealed.

The accuracy of the analytical method was evaluated using reference material (RM) IAEA-405 (Trace Elements and Methylmercury in Estuarine Sediment) obtained from the International Atomic Energy Agency. Six replicates of the RM were prepared and packed in a similar manner as the samples.

Sample irradiation and counting

Irradiation and counting of samples have been described earlier.^{13,14} Samples and standards were irradiated using the Ghana Research Reactor-1 (GHARR-1) facility at the Ghana Atomic Energy Commission (GAEC). The miniature neutron source reactor (MNSR) operates at 15 kW with a neutron flux of $5.0 \cdot 10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Instrumental neutron activation analysis (INAA) was selected because of its relatively high selectivity, sensitivity and high precision. INAA is also very fast and multielemental in nature. Samples were transferred into the inner irradiation sites of the reactor by means of pneumatic transfer systems at a pressure of 65 psi and irradiated for one hour. At the end of irradiation, the capsules were returned and allowed to cool down for 24 hours until the activities reached acceptable handling levels. Samples and quality control standards were irradiated, decayed and counted under identical conditions and geometries. Blank polyethylene irradiation vials were also subjected to the same irradiation, decay and counting conditions.

Counting of samples was done on a PC-based gamma-ray spectroscopy system (Canberra Industries Inc.). Samples were placed on the detector and counted for 30 minutes. During the counting period, the intensities of the spectra accumulated on the computer

by means of a multi-channel analyzer (MCA). The accumulated spectra intensities were analyzed qualitatively and quantitatively. The qualitative analysis involved the identification of the photopeak of Hg using the 77.3 keV of ^{197}Hg . The quantitative analysis involved the conversion of the counts (area) under the photopeak of ^{197}Hg into concentration by comparator NAA¹⁵ method using a pure Hg standard solution.

Results and discussion

The results of the mean total mercury concentrations in water and sediment at the various sampling sites are presented in Table 1. The mean values are obtained from six replicate measurements with their precisions calculated as the percentage relative standard deviation (%RSD) of the six measurements. Table 2 shows the values of some elements of the reference material (RM) obtained in this work and those reported by the issuing agency (recommended values). As seen, the accuracy of the method can be inferred by the favorable comparison between our values and the recommended values. The spiking experiment indicated that there was no loss of Hg due to evaporation, volatilization, transpiration, etc. Analysis of the blank irradiated polyethylene vials showed no Hg contamination.

Table 1. Mean values of total Hg concentrations in water and sediment

| Sampling point | No. of measurements | Water, mg/l | Sediment, mg/kg dry weight |
|----------------|---------------------|------------------|----------------------------|
| P 1 | 6 | 6.80 ± 0.20 | 31.95 ± 0.90 |
| P 2 | 6 | 19.82 ± 0.50 | 62.60 ± 3.50 |
| P 3 | 6 | 12.70 ± 0.95 | 84.30 ± 4.95 |
| P 4 | 6 | 8.50 ± 0.02 | 28.90 ± 0.17 |
| B 1 | 6 | 4.10 ± 0.28 | 12.30 ± 1.30 |
| B 2 | 6 | 2.90 ± 0.35 | 14.75 ± 0.90 |
| B 3 | 6 | 0.50 ± 0.08 | 1.20 ± 0.20 |
| B 4 | 6 | 3.25 ± 0.70 | 6.85 ± 1.01 |
| B 5 | 6 | 6.20 ± 0.63 | 10.25 ± 1.20 |
| B 6 | 6 | 5.70 ± 0.80 | 20.20 ± 3.10 |
| B 7 | 6 | 6.20 ± 0.72 | 22.75 ± 3.30 |
| B 8 | 6 | 7.25 ± 0.95 | 17.54 ± 1.10 |
| B 9 | 6 | 9.10 ± 0.80 | 19.25 ± 1.95 |

Table 2. Results of reference material, IAEA-405 (Trace Elements and Methylmercury in Estuarine Sediment) showing our values and recommended values (in mg/kg)

| Analyte | No. of measurements | This work | Recommended value | 95% Confidence interval |
|---------|---------------------|-------------------|-------------------|-------------------------|
| As | 6 | 25.30 ± 2.02 | 23.6 | 22.9–24.3 |
| Co | 6 | 12.50 ± 2.90 | 13.7 | 13.0–14.4 |
| Cr | 6 | 83.15 ± 2.30 | 84 | 80–88 |
| Hg | 6 | 0.91 ± 0.01 | 0.81 | 0.77–0.85 |
| Mn | 6 | 489.03 ± 3.42 | 495 | 484–506 |
| Sb | 6 | 2.10 ± 0.10 | 1.81 | 1.62–2.00 |
| V | 6 | 90.00 ± 9.80 | 95 | 90–100 |

For water samples the range of total mercury concentration was between 0.50–19.82 mg/l (points B3 and P2). Also, the range of total mercury concentration for the sediments was between 1.20–84.30 mg/kg (points B3 and P3). Generally, the total mercury concentrations for both water and sediment samples at sites P1, P2, P3 and P4 were relatively higher than the values obtained at sites B1 to B9. This trend could be explained by the fact that there is a larger and more intensive “galamsey” mining activities around sites P1, P2, P3 and P4 than a sites B1 to B9. At sites P1, P2, P3 and P4 large amount of mercury is used, and, therefore, get released into tailings, which eventually ends up in water bodies through rain-washing. Occasionally, there are accidental spillage of mercury into the environment due to careless handling. Through rain-washing the spilled mercury also get into streams and sediment. Dumping of mercury-containing ashes from coal-pots used for the roasting the amalgam also accounts for the presence of mercury in the water bodies and sediment.

The highest total mercury concentration levels in water samples were recorded at sites P2 and P3. It was realized that apart from the activities of the permanent “galamsey” workers, these sites also serve as “treatment sites” for other “galamsey” workers who do not have treatment sites of their own. They bring their gold-bearing rocks and sediment from other places to sites P2 and P3 for treatment to obtain raw gold. This contributes to the mercury load in the aquatic environment. This important factor, among others, could be used to explain the highest values of mercury in the sediment samples at P2 and P3. The values were 62.60 and 84.30 mg/kg, respectively. It was generally observed that the mercury concentrations in the sediment samples were far higher than in the water samples. This is expected because of the self-cleansing mechanism of water for a number of heavy metals. These form insoluble precipitates with cations that are dissolved or suspended in natural waters. They may also get adsorbed or co-precipitated onto clay particles.¹⁶ Thus, these particles settle gradually onto the sediment thus increasing the mercury content of the sediments. Another factor which may increase the mercury content of the sediment, is the tendency of heavy metals to form hydro-oxo compounds or complexes (in aqueous medium) which precipitate out of solution, hence, increasing the concentration in the sediment. The relatively low total mercury concentration at site B3 for the water and sediment may be due to the almost non-existence of “galamsey” mining activities in the catchment area of B3.

The detection of mercury in water and sediments from sites with intensive and extensive small-scale mining activities, as well as sites with little or no

“galamsey” mining may be attributed primarily to rain-washing of top-soils containing mercury that was accidentally spilled unto the soil due to careless handling,² to direct discharge and transport into waterways or indirectly through wet and dry deposition from air or through rain.¹⁷ This is because elemental mercury vapour released from amalgam processing is converted to soluble forms and deposited by rain into soil and water.¹⁸

Conclusions

The assessment of total mercury concentration levels due to small scale gold mining at Prestea and its environs has indicated the serious status of Hg pollution in Ghana. Total mercury levels in water were high compared to the WHO limit. The concentration levels of total mercury in water from all the sampling sites were in excess of WHO tolerable limit of 0.001 mg/l. Total mercury concentration levels in the sediments were also high. Workers and inhabitants should be monitored to assess the impact of “galamsey” mining activities.

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Some financial support for the work from the National Nuclear Research Institute is highly appreciated. The authors thank Messers Nick OPATA and Ekow QUAGRAINE, the technicians at the NAA laboratory for their contribution during preparation, irradiation and counting of samples. We also thank the team of reactor operators.

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