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Mercury hotspots in tailings from artisanal gold mining areas of the Asutifi district, Ghana

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ABSTRACT
As mercury (Hg) amalgamation is an inexpensive, quick and simple way to extract gold, it is currently the method most commonly used in Artisanal gold mining in Ghana and most developing countries. However, the activities of these Artisanal miners result in the release of Hg into the environment by amalgamation tailings and amalgam burning. These amalgamation tailings often left behind forms Hg "hotspots" in both terrestrial and aquatic ecosystem, forming the main source of Hg dispersion. An investigation was conducted in the Asutifi district, hosts for several artisanal gold mining centres to ascertain the levels and the degree of mercury contamination in amalgamation tailings. The degree of contamination were assessed using mathematical model index approach, geoaccumulation index (I_{geo}) and enrichment factors (EF). The average I_{geo} for Hg in tailings (0.5) denoted uncontaminated to moderately contaminated, whilst the EF indicated very high to extremely high enrichment.

Introduction

Artisanal gold mining (AGM) also referred to as 'galamsay' (meaning gather and sell) is an important activity in Ghana as it provides a source of income particularly in rural communities where economic alternatives to agriculture are limited. Artisanal or small-scale gold mining in Ghana just like in most developing countries is a low technology, mainly labour-intensive and peasantry which was regularized by mining laws and policies passed in 1989 (PNDC law 217, 218, 219). The artisanal gold miners apply rudimentary methods mainly traditional in manual winning of gold, featuring simple tools like shovels, pick-axe, pans, chisels and hammers. The AGM operations still use the secular mercury (Hg) amalgamation technique to extract gold from the "gold ore". Despite the promulgation of mercury law in 1933 banning Ghanaian gold miners from using Hg in their operations, the practice continued (Akabzaa and Dramani, 2001; Hilson, 2001) till the legalisation of small-scale gold mining in 1989 by Provisional National Defence Council Law 218 (PNDC law 218). The legalisation of small-scale gold mining has escalated the activities of artisanal gold mining with Hg, thus providing employment to over a million people and playing a significant role in the economy of Ghana (Donkor et al, 2006). While economically significant to the miners, artisanal gold mining has been the target of strong opposition in recent years mainly because of its adverse environmental and social side effects. Foremost of this is mercury pollution.

The method of processing used by the artisanal gold miners involves mining of gold ore via underground to a maximum depth of 12 m (Aryee et al., 2003), or surface soils or river bed sediments. The ore pulled out is transported to processing sites to be crushed and milled. The resulting fine gravel is mixed with water, and then gently washed in 'sluice box' where gravity concentration occurs on hemp tissues (or towel). The obtained gravity concentrate is refined by washing it in a pan and then amalgamated with Hg. The Hg is added progressively, until the amalgam appears homogenous. The amalgam is then placed in a piece of fabric and squeezed to eliminate residual water and excess mercury. Gold is then recovered by burning the amalgam in open pans without any retorting facility.

Mercury from AGM activities is released into the environments by the amalgamation tailings and by amalgam burning. The majority of Hg emitted by the burning process is deposited near the emission source, contaminating the local areas (Gunson, 2004; Viega, 1997). While, amalgamation tailings often left behind forms Hg "hotspots" in both terrestrial and aquatic ecosystems. These hotspots can have dimensions of a few square meters to hundreds of square meters and are the main source of Hg dispersion. Thus, the Hg rich tailings remaining in most mining sites subsequently become susceptible to leaching, erosion and volatilisation. The high organic matter content in tropical aquatic and terrestrial environments also favours metallic Hg transformation by biotic or abiotic pathways into methylmercury (Larcerda and Solomons, 1998). Hence, Hg-loaded tailings from artisanal mining have been linked with higher levels of methylmercury (Baker, 2002). Fishing communities near artisanal gold mining operations have been found to exhibit symptoms of methylmercury poisoning, especially along the Tapajos River in Brazil (Gunson, 2004; Harada et al., 2001). This study therefore seeks to identify some Hg hotspots from artisanal gold mining sites from the Asutifi district in Ghana and assess the level of Hg contamination.

Study Area

The study was conducted in three artisanal gold mining (AGM) communities in the Asutifi District, one of the twenty-two districts in Brong Ahafo Region of Ghana. It lies between latitudes 6°40′ and 7°15′ North and Longitudes 2°15′ and 2°45′ West. The district lies within the Wet semi-equatorial zone in Ghana. It is marked by an annual double rainfall maxima

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pattern; June and October with a mean annual rainfall between 125 cm to 200 cm (Owusu et al., 2006; Smith, 2005).

A variety of crops ranging from cash to food crops grow well in the district. Also, with limited economic alternatives to agriculture, the indigenes depend on artisanal gold mining (AGM) activities in some streams and rivers in the area for their livelihoods.

The district is drained by Tano River and its many tributaries which include Nsubin, Goa, Ntotro, Aboabo, Subin, Suntim and other rivers exhibiting a dendentric pattern. These youthful fast flowing rivers have cut up the plateau surface giving rise to the dissected nature of the plateau. About 15 percent of the inhabitants have no access to potable water and rely on rivers and streams (Owusu et al., 2006) which are located close to AGM sites. The study was conducted in AGM sites located in three communities; Kenyasi, Wuramumuso and Nkaseim. These sites are also located along three rivers; River Suntim, Wuramumu and Aboabo stream before joining the Tano River to enter the Gulf of Guinea. Inevitably, Hg from processed waste ore is released to rivers and mine tailings.

Methodology

Sampling collection

The tailings hotspots were identified from AGM sites from three communities in the Asutifi district of Ghana. Tailings were collected from AGM sites at Kenyasi (TK1 –TK5), Nkaseim (TN1-TN3), and Wuramumuso (TW1-TW2). Tailings samples were taken from mining amalgamation sites and amalgam roasting points along the above rivers. At each sampling site, three tailings of about 1kg were collected from the average depth of 10 cm to 40 cm with a polypropylene scoop into acid pre-cleaned polyethylene containers. The samples in the polyethylene bags were placed in zip locks and sealed. All collected samples were then stored under ice and transported to Ghana Atomic Energy Commission (GAEC) laboratory for total Hg analysis.

Sample analysis

The tailings samples were air-dried and sieved and the < 0.2 mm fraction (about 1.50 g) was used for digestion with $HCl/HNO_3/H_2O_2$ acid mixtures (Report code 308 of the Milestone Acid digestion cookbook, 1996) in sealed teflon pressure vessels by microwave heating (ETHOS 900 Microwave digester). The mixture on cooling was diluted to 20 ml with deionised water into a test tube. Aliquots (10 ml) of the digestate were analysed for total Hg by CV-AAS after $NaBH_4$ reduction and detection by AAS.

For quality assurance (QA)/quality control (QC) purposes, reagent blanks and certified reference material (CRM), IAEA-Soil-7 obtained from the International Atomic Energy Agency (IAEA), was run with all T-Hg digestions and analyses. Recoveries on IAEA- Soil-7 averaged 95 ± 8 % for total- Hg (n=6). Recovery test also performed using AAS mercury standard solutions prepared from 1000 ppm Spectrascan (ISO 9001) Standard solution (Industrial Analytical Ltd, Technolab AD, Sweden) ranged from 94 – 97 %.

Other metals; Arsenic (As), Cadmium (Cd), Manganese (Mn), Copper (Cu) and Aluminium (Al) were analysed from the tailings samples using instrument neutron activation analysis. The process of sample preparation, irradiation, counting and analysis are described in Adomako et al., 2007. The results for the T-Hg and the other metals are presented in Table 1 and Table 2.

Results and discussion

Total mercury concentrations in Tailings

The total-Hg concentrations vary widely among piles of tailing samples collected from Kenyasi, Wuramumuso and Nkaseim artisanal mining sites. On the average, the total-Hg levels observed in tailings from the Kenyasi artisanal mining site was 0.8 and 0.7 orders of magnitude greater than those observed in Wuramumuso (0.340 ± 0.002 mg/kg) and Nkaseim (0.390 ± 0.027 mg/kg) sites respectively. The peak levels of T-Hg observed in TK2, TK3 and TK4 from Kenyasi could be attributed to high level of artisanal mining activity and probably the technique for processing. Also, recovery of gold (Au) from gold tailings from previous extraction processes due to comparatively long years of operation in Kenyasi than Wuramumuso and Nkaseim may be responsible for the high levels of T-Hg in Kenyasi. The mean T-Hg values from the three artisanal mining sites are higher than those tailings and soil samples reported in the Pra River system (Donkor et al., 2006). The elevated T-Hg concentrations in the gold tailings are as a result of Hg physically lost by the artisanal or small-scale miners during amalgamation process.

The extent of contamination of these tailing samples were evaluated using geoaccumulation index (I_{geo}) and enrichment factors (EF). The geoaccumulation index (I_{geo}) introduced by Muller (1969) is expressed as:

$$I_{geo} = \log_2 \frac{C_{Hg}}{1.5B_{Hg}}$$

Where, C_{Hg} is the measured total concentration of Hg in the fine-grained tailing fraction (mg/kg). B_{Hg} represents the geochemical background value of mercury (mg/kg). Average shale value as well as regional background has been frequently used to estimate I_{geo}. The factor 1.5 is the background matrix correction factor due to lithogenic effect. The index of geoaccumulation includes seven grades (0-6) ranging from unpolluted to very highly polluted. The I_{geo} calculated ranged from -0.8 to 3.8. The average I_{geo} (0.5) denoted uncontaminated to moderately contaminated tailings sample, the maximum value at TK2 (3.8) classified the tailings as heavily contaminated and the minimum value (-0.8) classified the tailings sample as considerably uncontaminated. From the three sampling sites (Kenyasi, Wuramumuso and Nkasiem), it was realised that tailings from Kenyasi were highly contaminated than that in Wuramumuso and Nkaseim from the calculated I_{geo} values (Table 1).

Also, Enrichment factor (EF) was used to identify anomalous concentration of Hg by normalisation of the Hg data to a conservative element, such as Aluminium (Al), Iron (Fe), Scandium (Sc), Rubidium (Rb), and Lithium (Li) (Ram et al., 2009) was employed. In this study, Al was used to normalize the Hg because it has been used successfully by several authors (Donkor et al., 2006; Rubio et al., 2000; Balls et al., 1997). The enrichment factor (EF) is calculated using the equation (Ram et al., 2009; Donkor et al., 2006):

$$EF = \left(\left[\frac{Me}{Al} \right)_{sample} \Big/ \left(\frac{Me}{Al} \right] \right]_{background}$$

Where $(Me/Al)_{sample}$ is the ratio of metal to aluminium concentration determined in the tailing and $(Me/Al)_{background}$ is similar to ratio based on background values or shale reference data. Shale reference data was taken from Turekian and Wedepohl (1961). The interpretation of results is as follows: EF-values lower than and around 1.0 indicate that the element in the

sediment originates predominantly from the crustal material and / or weathering processes (Zhang & Lui, 2002), EF < 2 deficient to minimal enrichment; EF = 2 - 5 moderate enrichment; EF= 5 - 20 significant enrichment; EF = 20 - 40 very high enrichment; and EF > 40 extremely high enrichment (Donkor et al., 2006; Loska et al., 2004).

Similarly to the I_{geo} values, the EF calculated revealed low EF values in Wuramumuso and Nkaseim and high values in Kenyasi.

The tailings collected from Wuramumuso and Nkaseim were mostly very highly enriched while the EF values recorded at Kenyasi had extremely high enrichment (Table 1). The Hg rich tailings remaining in these mining sites may subsequently become susceptible to leaching, erosion and volatilisation which contaminate the groundwater, surface water and the atmosphere.

Levels of other metals beside Hg

Mine tailings are usually hotspots for heavy metal contamination. The results of the mine tailings analysed showed comparatively low levels of Arsenic (As), Cadmium (Cd) and Copper (Cu) and very higher levels of Manganese (Mn) and Aluminium (Al) (Table 2).

The means in mg/kg (range in bracket) are: Cd, < 0.01; As, 24.13 (< 0.01 – 99.66); Mn, 425.26 (131.51 – 662.51); Cu, 11.92 (<0.01 – 32.52); Al, 2489.77 (1340.22 – 3895.32). The concentrations of heavy metals were of the following order Al > Mn > As > Cu > Cd. Cadmium concentrations in the mine tailings were all below detection limit (less than 0.01 mg/kg) in all sample sites and this confirms the low levels of Cd ores/minerals in the tailings samples. Considering the arsenic (As) concentrations from the three locations (Kenyasi, Wuramumuso and Nkaseim), high levels of As were recorded in tailings from Nkaseim which are most probably related to As content of the inherent mineralogy of the ores which may contain the mineral arsenopyrite ($FeAsS_2$) or other arsenic ores.

The highest As concentration recorded was 99.66 mg/kg which is quite significant. Naturally occurring As in surface soil typically range from 1-50 mg/kg and concentrations above 10 mg/kg are considered as potentially phytotoxic (Bowen, 1979). In addition concentrations of As greater than 0.39 mg/kg may cause carcinongenic effects in humans and concentrations above 22 mg/kg may result in adverse non-carcinogenic effects. Copper concentrations on the other hand were high in tailings collected from Kenyasi which may also be due to high Copper ores (e.g chalcopyrite) in the area. The remaining elements however, did not show much difference in their concentrations among the three locations.

Conclusion

High total-mercury levels in tailings were observed at the Kenyasi artisanal mining site due to high mining activities. The distribution pattern of T-Hg in the tailings sample according to I_{geo} index and EF, the tailings were highly polluted and enriched.

With respect to the other metals, there were elevated levels of Al, Mn, Cu and As in tailings from the study area. The elevated levels is due to the release of heavy metals from waste rocks or tailings as a result of weathering and the leaching effect of the water draining the waste dumps in the gold mines. The release of the heavy metals from their hosts' rocks and ore minerals in the study area is accelerated by mining activities like excavation, crushing and gravity concentration.

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Table 1 Concentration of T-Hg, EF, and Igeo of Tailings collected from the artisanal gold mining sites at Kenyasi, Wuramumuso and Nkaseim

Communities	Sample sites	Hg Mean ± SD (mg/kg)	I_{geo}	EF
Kenyasi	TK1	0.504 ± 0.100	-0.3	71
	TK2	8.466 ± 1.732	3.8	1263
	TK3	3.535 ± 0.001	2.6	197
	TK4	1.406 ± 0.056	1.2	88
	TK5	0.788 ± 0.088	0.4	40
Wuramumuso	TW1	0.341 ± 0.042	-0.8	31
	TW2	0.339 ± 0.011	-0.8	40
Nkaseim	TN1	0.419 ± 0.573	-0.5	43
	TN2	0.386 ± 0.034	-0.6	21
	TN3	0.365 ± 0.221	-0.7	37

Shale reference data (Turekian and Wedepohl, 1961); Hg (0.4), Al (80000)

Table 2 Total metal concentrations in mg/kg dry weight in tailings samples collected from the study area.

Communities	Sample sites	As (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Al(mg/kg)
Kenyasi	TK1	< 0.001	< 0.01	131.51	23.18	1411.44
	TK2	< 0.001	< 0.01	160.42	32.52	1340.22
	TK3	< 0.001	< 0.01	662.51	6.58	3587.94
	TK4	1.70	< 0.01	474.51	7.00	3188.27
	TK5	0.35	< 0.01	389.02	< 0.01	3895.32
Wuramumuso	TW1	16.13	< 0.01	599.76	< 0.01	2208.65
	TW2	1.73	< 0.01	248.36	4.02	1677.39
Nkaseim	TN1	12.97	< 0.01	453.42	4.46	1954.38
	TN2	36.39	< 0.01	630.21	< 0.01	3637.23
	TN3	99.66	< 0.01	502.84	5.67	1996.87
	Mean	24.13		425.26	11.92	2489.77
	STD	35.62		190.63	11.26	985.39
	Minimum	< 0.001		131.51	< 0.01	1340.22
	Maximum	99.66		662.51	32.52	3895.32

STD, Standard deviation; Detection limit of Cd (0.01 mg/kg), As (0.001 mg/kg), Cu (0.01 mg/kg)