



Comparative study of mercury (HG) in surface soil in gold and non-gold mining towns in Ghana

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ABSTRACT

Comparative study of levels of mercury in surface soil samples in gold and non-gold mining towns were conducted from Sikakrom of Kenyasi No. 1 and Dadiesoba of Asutsifi District in the Brong-Ahafo Region of Ghana. The mercury concentrations of acid digested dried samples were measured by Cold Vapour Atomic Absorption Spectrometry. Higher levels of T-Hg concentrations were found in surface soil samples at the sites with extensive small-scale “galamsey” mining activities than at the non small-scale “galamsey” mining sites. Levels of Hg in surface soil samples were in the range of 38.56 $\mu\text{g kg}^{-1}$ to 93.34 $\mu\text{g kg}^{-1}$ for the extensive small-scale “galamsey” mining sites at Sikakrom of Kenyasi No.1. The concentration levels of T-Hg in surface soil from all the sampling sites are in excess of the WHO tolerable limit of 0.001 $\mu\text{g/kg}$ for soil. The concentration levels of total mercury at Dadiesoba were lower than the WHO tolerable limit of 0.001 $\mu\text{g/kg}$. The influence of the off-shore sea breeze might have affected this observation. Hg levels obtained in this research were higher than the natural background levels of Hg. Obviously; Hg is a major metal pollutant at Sikakrom of Kenyasi No.1. Recovery and Repeatability test were done to check for the accuracy and reproducibility of the analytical method. Regression analysis on surface soil mercury concentrations showed proportionately less deposits at higher distances in 10 cm soil zone. In general, these findings suggest evidence of severe mercury pollution in Sikakrom of Kenyasi No. 1 in the Asutsifi District of the Brong Ahafo Region of Ghana.

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Introduction

The increase in public awareness and concern about the state of the earth and our local environments in recent years have been accompanied by evidence on the extent to which pollution has caused severe environmental degradation.

Harmful substances in the environment have been shown to have many effects on human health, agriculture productivity and natural ecosystem (Alloway and Ayres, 1993). It has been known that several metals are toxic to man, animals and plants; however some biochemical reactions within living organisms such as enzyme activities and components of controlled mechanisms (in muscle) have been found to involve several metallic elements. Some are referred to as essential trace elements and thus essential to life, but others are non-essential, detrimental or toxic to life.

Non-essential trace metals or heavy metals for example Hg, Cd, Pb and As present detrimental and toxic effect to life under normal background concentration. The detrimental effects of these metals include competition for sites with essential metabolites and the replacements of ion reactions on –SH groups and the damage to cell membranes.

Mercury used by some small-scale gold miners (Galamses in Ghana) is widely considered to be among the highest priority environmental pollutants. Amalgamation is the predominant gold extraction technique used by the ‘galamses’ and other miners. The miners make extensive use of mercury in gold extraction 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 the soils, tailings, stream, sediments, water and air close to the processing sites.

Inorganic mercury released into the aquatic environment undergoes biological methylation into methylmercury (Me-Hg), the most toxic form of mercury. The methylmercury ultimately bio-accumulates to significant levels in fish and may biomagnify through the food chain. Humans are exposed to mercury through the ingestion of contaminated water, food and air. The community around the mining area may be affected with at least three forms of mercury. These are Me-Hg, phenyl mercury and inorganic Hg. Humans may be contaminated simultaneously from surrounding air, diets and water. Thus communities along the rivers and depending on riverine products are easily exposed to Me-Hg and may acquire toxic levels through consumption of these contaminated fish and drinking water. Therefore, there is the need to monitor both workers and inhabitants on regular basis to assess the effect of mercury from ‘galamsey’ (extraction of gold with mercury).

Materials and Methods

Descriptions and Location of Sampling Sites

The study was done in a small-scale gold mining community. The samples investigated were surface soils. Sites (1, 2 and 3) were located within the vicinity of Sikakrom (small-

scale mining area) of Kenyasi No.1 and Dadiesoaba (control site) of Asutifi District (Brong-Ahafo Region).

Y. Serfor- Armah, B. J. B. Nyarko, D. K. Adotey, D. Adomako, E. H. Akaho.(2004) The impact of small-scale mining activities on the levels of mercury in the environment: the case of Prestea and its environs.

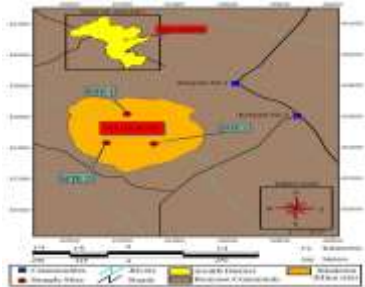


Figure 1: A Map of Kenyasi Community Showing the Sampling Sites

Sample Collection

Surface soil samples were collected from the three sampling sites 1, 2 and 3 (as shown in Figure 1) from the study area, during October 2009 and March 2010. These surface soil samples, were collected once every three months from all the three sampling site (close to the mining site and some kilometres away from the mining site). At each sampling point, five replicate samples were collected. The sampling town, Kenyasi No 1, is also presented in Figure 1. The same sampling procedure was used at the control site (Dadiesoaba) which has no history of mining activities.

The collection of the surface soil samples was done with a Teflon-coated soil auger while wearing polyethylene gloves. Samples were collected from the top 5cm and 10 cm at a distance of 5 km apart using the Teflon-coated soil auger. The soil samples were transferred into pre - cleaned polyethylene containers and sealed. During sampling, the Teflon-coated soil auger was washed with distilled water after sampling at each sampling point to avoid cross contamination. Each container was labelled and conveyed to the laboratory.

Sample Treatment and Storage

At the laboratory, soil samples were spread out on polyethylene sheets and freed off pieces of roots, other foreign objects and air-dried. The soil samples were dried at room temperature for three days. The dried samples were ground and homogenized in a porcelain mortar, sieved with a 500 μm size mesh and made into composite sample. They were finally transferred into polyethylene containers, sealed, labelled and stored for Hg levels analysis in the laboratory.

Digestion of Soil Samples for Mercury Determination

1.5 g of soil samples were weighed into 100 ml Teflon tube, 3 ml of 36% Conc. HCl, 6 ml of 67% HNO₃ and 0.25 ml of 30% H₂O₂ were added to the sample in the Teflon tube.

Each of them were mixed and placed in a microwave oven and digested for 45 minutes. At the end of the digestion, the Teflon tubes were removed and cooled in a water bath, transferred into a 5 ml test tube and diluted to 20 ml with double distilled water. 0.01 g of 99% solid Potassium Dichromate (K₂Cr₂O₇) was added to each sample for stabilization of the mercury present.

Mercury Analysis

The Cold Vapour Technique coupled with AAS was employed to determine the concentration of Hg in the sample. The blank solution was used to zero the instrument, before analysing the digest.

The sample blank and digest were mixed with a carrier solution of 5 ml HCl and reducing agent 0.3% (v/v) NaBH₄ prepared in 0.5% NaOH in a mixing chamber. Generated argon (Ar) gas was bubbled through the resulting solution, which vaporized the free Hg in the aqueous solution in the presence of reducing agent in the Hg vapour generator. The Hg vapour generated was swept into the absorption cell mounted on the AAS and measurement made automatically.

The cell was aligned in the path of Hg hollow cathode lamp operating at 4 mA and monitored at the 253.7 nm resonance lines. Analysis was done by sucking 7 ml volume of the blank, sample digest containing unknown amounts of Hg. Elemental Hg was aerated into the path of the Hg lamp, in which Hg atoms absorb radiations from the Hg cathode at 253.7 nm.

The absorption measured by the instrument is proportional to the concentration of the Hg atoms in the flame, hence the Hg concentrations in the digested samples.

The concentration of Hg was calculated using the equation: (USEPA, 1992)

$$C_{\text{Hg}} = \frac{A \cdot B \cdot 100}{M}$$

where C_{Hg} is mercury concentration, $\mu\text{g kg}^{-1}$.

A is concentration of mercury in digested solution, $\mu\text{g L}^{-1}$.

B is final volume of digested solution, mL

M is sample weight, g.

Results and Discussion

Levels of Hg were determined for a period of eight months and a summary of the results shows mean values of the Hg and their standard errors at each site in Tables. Figures illustrating variation of metal ions concentration with distance of the soil in vicinity of gold mine understudy are shown. The calculated equations and graphs of the line of regression and correlation coefficients of metal mean concentrations to the distances are also presented in tables. From the results, 99.2% and 99.5% of the mercury was recovered and the coefficient of variation was 5.263%. This showed that the results were consistent.

Mean Concentrations of Hg in Surface Soil Samples Sikakrom (Site 1)

At Site1 (Sikakrom), Hg concentration on samples were relatively higher than Site 2 and Site 3. The mean Hg concentration in the surface soil samples varied from 41.64 $\mu\text{g kg}^{-1}$ to 93.34 $\mu\text{g kg}^{-1}$ for 5cm soil zone with their standard errors ranging from 0.04 to 0.12 (Table 1). The 10 cm soil zone had mean concentration from 38.55 $\mu\text{g kg}^{-1}$ to 91.67 $\mu\text{g kg}^{-1}$ with their standard errors ranging from 0.02 to 0.05. This sampling site showed a decreasing trend of soil Hg concentration from the surface topsoil to the subsurface layer. This trend suggests that the source of Hg in the soil is aerial or air bone. The concentration levels of total mercury at Site 1 were in excess of WHO tolerable limit of 0.001 $\mu\text{g/kg}$. These high mercury concentration levels might be due to the other small-scale mining site scattered within the area of study. Also, the wind might have brought Hg dust from other gold mines such as Newmont Goldmines. The soil Hg levels obtained at Sikakrom (Site 1) are higher than the natural background soil Hg levels of 0.001-0.50 ppb. This is therefore an indication of Hg pollution at Site 1. The small standard errors obtained might be due to the soil being homogenous. The surface soil Hg levels obtained were lower than those obtained by Golow et al. (2002 a.). Golow et al (2002 a) centred their research around Continental Goldfield and its environs at Dunkwa-On-Offin. Golow et al (2002a) reported that the mean soil Hg levels were between 100 $\mu\text{g kg}^{-1}$ and 274 $\mu\text{g kg}^{-1}$. The surface soil Hg levels obtained

were higher than those obtained by Nartey V.K. et al. (2006). They centred their research along the Pra river basin in the southern Ghana.

Table 1: Result showing mercury concentration in surface soil samples in Sikakrom (site 1)

Sikakrom (Site 2).

At Sikakrom (Site 2), the soil mean mercury concentrations in the 5 cm soli zone ranged from $68.44 \mu\text{g kg}^{-1}$ to $78.47 \mu\text{g kg}^{-1}$ with the standard errors between 0.13 and 0.15 being lowest among the high levels registered by other soil zones. The 10 cm soil zone mean concentrations ranged from $65.55 \mu\text{g kg}^{-1}$ to $75.51 \mu\text{g kg}^{-1}$ with standard errors between 0.05 to 0.06. The result obtained were significantly higher than the natural background occurrence of 0.5 ppb and also beyond contaminated level of 50 ppb. The lowest levels of Hg concentrations might be due to the geochemistry of the soil, topography of the land (weathering and erosion) and anthropogenic sources among others could count for the above observation. The concentration levels of total mercury at Site 2 were in excess of WHO tolerable limit of $0.001 \mu\text{g/kg}$. The surface soil Hg levels obtained were higher than those obtained by Siekpe (1997). Siekpe (1997) centred his work on Obenemase Goldfield at Konongo. The mean Hg levels were lower than those obtained by Y.Serfor-Armah et al (2004). They also centred their work in Prestea and its environs. The standard errors observed also showed that the soil was homogenous. The surface soil Hg levels obtained were higher than those obtained by Doamekpor L. K. et al. (2006). They centred their research along the Pra river basin in the southern Ghana.

Table 2: Result showing mercury concentration in surface soil samples in Sikakrom (site 2)

Sikakrom (Site 3)

At Site 3, the soils mean Hg concentrations in the 5 cm soil zone registered values between $57.72 \mu\text{g kg}^{-1}$ and $83.95 \mu\text{g kg}^{-1}$ with standard errors ranging between 0.22 and 1.22 (Table 3). These levels are higher than the normal background level of 0.5 ppb. Therefore there is an indication of Hg pollution. The 10 cm soil zone also registered values between $58.47 \mu\text{g kg}^{-1}$ and $74.32 \mu\text{g kg}^{-1}$ with their standard errors 0.13 and 0.70. At 15 km the mean Hg concentration increased with depth and there was irregular trend of levels with distance. The concentration levels of total mercury at Site 3 were in excess of WHO tolerable limit of $0.001 \mu\text{g/kg}$. Anthropogenic sources among other sources might be responsible for the high levels obtained. Geochemistry of the soil might also be the cause. This observation is in agreement with a similar observation made by Peter van Straaten, (2000) and A.K. Donkor et al (2006). The surface soil Hg levels obtained were lower than those obtained by V.K. Nartey et al (2004). V.K. Nartey et al (2004) centred their research selected small-scale gold mining communities in South Western Ghana. The low standard errors obtained evidenced homogeneity of Hg in the soil.

Table 3: Result showing mercury concentration in surface soil samples in Sikakrom (site 3)

Dadiesoaba (control sites)

The Hg levels obtained at the control sites indicated that the spread of Hg by air could not get as far as Dadiesoaba, perhaps the direction of the wind towards a different area or town. The concentration levels of total mercury at Dadiesoaba were lower than the WHO tolerable limit of $0.001 \mu\text{g/kg}$. The influence of the off-shore sea breeze might have affected this observation. Hg levels obtained in this research were higher than the normal background. Obviously, Hg might be major metal pollutant at

Sikakrom. Anthropogenic sources among others might be responsible for the high levels obtained.

Table 4: Results of control sample of mercury concentrations in surface soil samples in Dadiesoaba

Other possible reasons for the relatively high Hg levels at these sites (Site 1, Site 2 & Site 3), which are higher than the normal background level of 0.5 ppb might probably be due to:

- Deposition of the vapourized Hg to soil by rain. Jenne (1970) confirmed that elemental Hg emitted to the atmosphere returns to the soil environment when it rains.
- Unintentional spilling of Hg unto the ground due to careless handling.
- Dumping of Hg-containing ash in coal-pots used for amalgam roasting by some miners unto the ground.
- High organic matter levels in the soils. Organic matter level is an indicator of the role played by the organic fraction of soils in the transport, deposition and retention of trace metals. Generally, high organic matter levels in soils results in high trace metal concentration.

Statistical Analysis

Correlation and Regression analysis were employed upon the raw data to prove their linearity statistically. Correlation analysis measures the strength of the linear relation between a pair of variables. The variables in this case are; concentrations of Hg of different surface soils samples, and distances of the sampling sites from the mines. Regression analysis is used to quantify the relation between two or more variables so that you can predict the value of one variable based on the values of another. Regression also develops an equation to predict the value of a dependent variable base on the values of one variable (Sommers et al., 1987; Christian et al., 1982; Miller et al., 1994; Bauer, 1971).

Mercury Level Analysis for Site 1

The Hg levels from Sikakrom (Site 1) recorded relatively high values in the soil samples. The correlation coefficient, r for 5 cm, and 10 cm soil zones were 0.99 and 0.99 respectively. The 5 cm and 10 cm soil zones showed strong positive linear correlation between Hg levels in soil zones and the distance. These suggest that as the distance from the mine increased, the Hg concentrations in the soil zones decreased. This trend might be due to the fact that Hg vaporizes easily, escape into the atmosphere and is carried along at distances away and changes its direction to where its activities might be paramount.

The equations of linear regression of the Hg levels in the surface soil upon distances from Site 1 were obtained as $y = -17.077x + 109.66$ for 5 cm soil zone and $y = -17.497x + 108.6$ for 10 cm soil zone; with y and x variables represent the metal concentration in the sample and the distance of the sampling sites from the centre of the mine. The graphs of the above equations are linear with slopes: $-17.077 \mu\text{g/kg/km}$ for 5 cm soil zone and $-17.497 \mu\text{gkg}^{-1}\text{km}^{-1}$ for 10 cm soil zone. The slopes suggest that the Hg levels in 5 cm and 10cm soil zones decreased with $-17.077 \mu\text{gkg}^{-1}$ and $-17.497 \mu\text{gkg}^{-1}$ in the surface soil upon every kilometer distance from the mine respectively (Table 5). The above findings suggested that the metal source might be aerial. This observation is in agreement with a similar observation made by Gasokpoh-Adjorlolo (2008). However, other sources might also be contributing factors such as geochemistry of the area and climatic conditions such as temperature, pressure and speed of wind and detection.

The graphical representation showing the strong positive linear correlation between Hg levels in soil zone and the distances at Sikakrom (Site 1) is shown below.

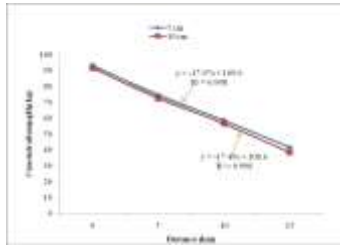


Figure 2: Graph showing Hg levels in surface soil sample from Sikakrom (Site 1)

Table 5: Equation of Linear Regression of mercury levels in surface soil upon distance from Sikakrom (Site 1) and their Correlation Coefficient, r

Mercury Level Analysis for Sikakrom (Site 2)

Levels of Hg in surface soil from Sikakrom (Site 2) were strongly, positively, linearly correlated with distance from the mine for the 5 cm and 10 cm soil zones. The correlated coefficients obtained were 0.98 and 0.96 respectively. The findings declared the presence of activities that release Hg into the environment prominent in the area with distance. This suggests that Hg source in the surface soil might be aerial. However, the soil nature does not enhance effective leaching since linearity decreases with depth. Perhaps, the soil properties including its pH and soil adsorption capacity might be contributing factors.

The equations of the lines of regression of Hg levels in surface soil upon distance from Sikakrom (Site 2) were $y = -3.392x + 82.54$ for 5 cm soil zone and $y = -3.386x + 79.96$ for 10 cm soil zone. The slopes were $-3.392 \mu\text{g kg}^{-1} \text{km}^{-1}$ and $-3.386 \mu\text{g kg}^{-1} \text{km}^{-1}$ respectively (Table 6). From the slopes obtained, it is evidence that Hg levels decreased from initial mine Hg soil levels of $82.54 \mu\text{g kg}^{-1}$, $79.96 \mu\text{g kg}^{-1}$ by $-3.392 \mu\text{g kg}^{-1}$ and $-3.386 \mu\text{g kg}^{-1}$ in every unit kilometer away from the mine for 5 cm and 10 cm respectively.

The graphical representation showing the strong positive linear correlation between Hg levels in soil zone and the distances at Sikakrom (Site 2) is shown below.

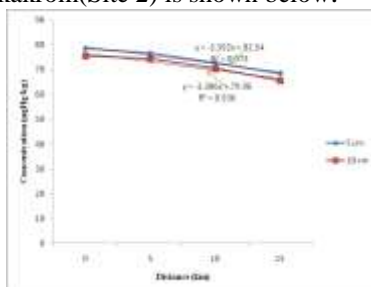


Figure 3: Graph showing Hg levels in surface soil sample from Sikakrom (Site 2)

Table 6: Equation of Linear Regression of mercury levels in surface soil upon distance from Sikakrom (Site 2) and their Correlation Coefficient, r

Mercury Level Analysis for Sikakrom (Site 3)

Levels of Hg in surface soil from Sikakrom (Site 3) were strongly, positively, linearly correlated with distance from the mine for the 5 cm and 10 cm soil zones. The correlated coefficients obtained were 0.96 and 0.93 respectively. The findings declared the presence of activities that release Hg into the environment prominent in the area with distance. This suggests that Hg source in the surface soil might be aerial. However, the soil nature does not enhance effective leaching since linearity decreases with depth. Perhaps, the soil properties including its pH and soil adsorption capacity might be contributing factor.

The equations of the lines of regression of Hg levels in surface soil upon distance from Sikakrom (Site 3) were $y = -9.607x + 95.61$ for 5 cm soil zone and $y = -6.037x + 81.255$ for 10 cm soil zone. The slopes were $-9.607 \mu\text{g kg}^{-1} \text{km}^{-1}$ and $-6.037 \mu\text{g kg}^{-1} \text{km}^{-1}$ respectively (Table 7). From the slopes obtained, it is evidence that Hg levels decreased from initial mine Hg soil levels of $95.61 \mu\text{g kg}^{-1}$, $81.255 \mu\text{g kg}^{-1}$ by $-9.607 \mu\text{g kg}^{-1}$ and $-6.037 \mu\text{g kg}^{-1}$ in every unit kilometer away from the mine for 5 cm and 10 cm soil zones respectively.

The graphical representation showing the strong positive linear correlation between Hg levels in soil zone and the distances at Sikakrom (Site 3) is shown below

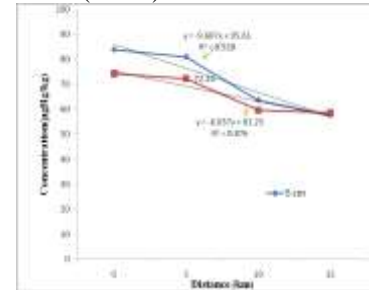


Figure 4: Graph showing Hg levels in surface soil sample from Sikakrom (Site 3)

Table 7: Equation of Linear Regression of mercury levels in surface soil upon distance from Sikakrom (Site 3) and their Correlation Coefficient, r

Conclusion

The results from the study showed that mining activities introduced Hg into the environment of the mine. Surface soil Hg levels revealed values from $38.56 \mu\text{g kg}^{-1}$ to $93.34 \mu\text{g kg}^{-1}$ for soil samples from Sikakrom (Site 1). $65.55 \mu\text{g kg}^{-1}$ to $78.47 \mu\text{g kg}^{-1}$ being Hg levels obtained in surface soil from Sikakrom (Site 2), and those from Sikakrom (Site 3) were between $58.47 \mu\text{g kg}^{-1}$ to $83.95 \mu\text{g kg}^{-1}$. These Hg levels were higher than the contamination limit of $50 \mu\text{g kg}^{-1}$; hence the surface soil of the study area is contaminated with Hg.

Generally Hg levels of surface soil at the study areas recorded a regular trend with distance; however there was an increase in Hg level at a depth between 5 cm and 10 cm soil zones (15 km from the source) in Sikakrom (Site 3) with distance than Sites 1 and Sites 2. The correlation analysis on the Hg levels at the study area gave linearity in all cases with distance. Regression analysis on the surface soil Hg levels showed proportionately less Hg deposits on the topsoil at higher distances from the mine while the Hg accumulated proportionately less at higher distances from the mine in the 10 cm soil zone. These suggested that the source of the Hg were aerial. This observation is in agreement with a similar observation made by Gasokpoh-Adjorlolo (2008). The geochemistry of the soil, topography of the land (weathering and erosion) and anthropogenic sources among others and change in the direction of the wind could account for the above trends. The geochemistry of the soil, topography of the land (weathering and erosion) and so on will have to be studied for more definitive conclusions to be drawn.

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Table 1: Results showing mercury concentrations in surface soil samples from Sikakrom (Site 1)

Distance (km)	Depth (cm)	Concentration (μgkg^{-1})	
		Mean	Standard Error
Point source	5	93.34	0.12
	10	91.67	0.05
5	5	74.28	0.22
	10	72.41	0.02
10	5	58.61	0.03
	10	56.77	0.03
15	5	41.64	0.03
	10	38.56	0.02

Table 2: Results showing mercury concentrations in surface soil samples from Sikakrom (Site 2)

Distance (km)	Depth (cm)	Concentration (μgkg^{-1})	
		Mean	Standard Error
Point source	5	78.46	0.15
	10	75.51	0.05
5	5	76.58	0.10
	10	74.45	0.04
10	5	72.75	0.14
	10	70.47	0.05
15	5	68.44	0.13
	10	65.55	0.06

Table 3: Results showing mercury concentrations in surface soil samples from Sikakrom (Site 3)

Distance (km)	Depth (cm)	Concentration (μgkg^{-1})	
		Mean	Standard.
Error	5	83.95	1.22
	10	74.32	0.70
Point source	5	81.04	0.39
	10	72.34	0.45
5	5	63.69	0.32
	10	59.52	0.15
10	5	57.71	0.22
	10	58.47	0.13

Table 4. Results of control sample of mercury concentrations in surface soil samples (Dadiesoaba)

Distance (km)	Depth (cm)	Concentration (μgkg^{-1})
Point source	5	< 0.001
	10	< 0.001
5	5	< 0.001
	10	< 0.001
10	5	< 0.001
	10	< 0.001
15	5	< 0.001
	10	< 0.001

0.001 is the detection limits.

Table 5: Equation of Linear Regression of mercury levels in surface soil upon distance from Sikakrom (Site 1), and their Correlation Coefficients, r.

Sample type	Equation Linear Regression	Correlation Coefficient
Soil zone		
5 cm	$y = -17.077 x + 109.6$	0.99
10 cm	$y = -17.497 x + 108.6$	0.99

y is concentration of mercury x is distance from the mine

Table 6: Equation of Linear Regression of mercury levels in surface soil upon distance from Sikakrom (Site 2), and their Correlation Coefficients, r.

Sample type	Equation Linear Regression	Correlation Coefficient
Soil zone		
5 cm	$y = -3.392 x + 82.54$	0.98
10 cm	$y = -3.386 x + 79.96$	0.96

y is concentration of mercury x is distance from the mine

Table 7: Equation of Linear Regression of mercury levels in surface soil upon distance from Sikakrom (Site 3), and their Correlation Coefficients, r.

Sample type	Equation Linear Regression	Correlation Coefficient
Soil zone		
5 cm	$y = -9.607 x + 95.61$	0.96
10 cm	$y = -6.037 x + 81.26$	0.93

y is concentration of mercury x is distance from the mine