ORIGINAL ARTICLE



Geospatial Distribution of Mercury in Surface Soils Across Ghana

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Abstract

The presence of mercury in soils has become a concern as artisanal gold mining activities in Ghana have increased significantly. This study assessed mercury concentration, spatial distribution, and potential ecological effects in surface soils throughout Ghana. Mercury concentrations were analyzed in 327 soil samples collected at 25 km by 25 km grid intersections using a Lumex Zeeman RA 915M mercury analyzer equipped with the Pyro-915 + attachment. The arithmetic mean and median values for mercury in the current study, 0.024 mg/kg and 0.011 mg/kg, respectively, are low when compared to the global average for permissible levels of 0.07 mg/kg. The pH of the soil ranged from 5.20 to 8.38, with mean and median concentrations of 5.81 ± 0.84 and 5.81, respectively, indicating that it was acidic. The root mean square error of the spatial distribution of mercury in the soil was 0.004, indicating an accurate result, and the map accurately predicted a concentrations in the Ashanti, Eastern, Western, and Western North regions, exceeding the global standard average. The southwestern region of Ghana exhibited relatively higher mercury pollution levels than other regions. Geo-accumulation and potential ecological risk indices demonstrated that the soil was uncontaminated, and the potential ecological risk was low. These findings provide baseline information on mercury concentrations in surface soils in Ghana that can inform policymaking for sustainable resource management and environmentally friendly solutions for agricultural production, industrialization, and mining activities.

Keywords Artisanal small-scale gold mining · Environmental pollution · Empirical Bayesian kriging · Semi-variogram

1 Introduction

The release of mercury into the environment is a global concern due to its high volatility [1], persistence [2], and toxicity [3]. The mercury discharge in the environment is either from natural causes (volcanic eruptions and emissions from the ocean) or anthropogenic sources (mining, burning, industrial water discharge, melting). Globally, an estimated 19.6 million metric tons of mercury were released into the

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atmosphere in 2010 [4]. In Ghana, the release of mercury into the environment is a major concern due to rapid urban growth and the huge explosion in artisanal small-scale mining activities. Globally, artisanal and small-scale gold mining (ASGM) is the leading source of anthropogenic mercury emission [5]. The small-scale miners in Ghana use mercury to process the gold ore [6–9]. Ghana is estimated to have released 57,488 kg of mercury in 2010 [4]. Of this, 91.32% is due to ASGM activities, 8.23% to non-ferrous metals, 0.27% to cement production, 0.16% to waste products, and 0.02% to oil and gas burning. The Ghana Government reports that the country inputs an estimated 81,060 kg of mercury per year into the environment [10]. The anthropogenic emissions continue to add significantly to the global pool of mercury.

Artisanal small-scale gold mining (ASGM) is mainly conducted along river banks rich in alluvial gold [7]. Mercury from ASGM activities enters rivers and is deposited into sediments [8, 9]. This is the primary source of mercury in water bodies and fish. Methylmercury, which is highly toxic, can be transported to pristine areas by rainwater, water currents, and volatilization [11], and is responsible for mercury poisoning. Mercury remains elevated in soil long after anthropogenic emissions are reduced [12, 13]. ASGM miners extensively use mercury, and emissions into the atmosphere and soil pose significant risks [5, 14]. Soil and atmospheric contamination are particularly significant near gold extraction and refining activities [15]. The main ways in which humans are exposed to mercury are through dust inhalation, consumption of contaminated fish, and occupational exposure, particularly for those involved in amalgamation or burning of mercury without protective gear [16]. Infants exposed to mercury through breastmilk can experience life-long cognitive defects [17]. A study conducted in Obuasi and Tarkwa municipalities in Ghana showed that more than 33.3% of babies living in mining towns were exposed to mercury [18]. Exposure to mercury can cause memory loss, miscarriages, psychotic reactions, kidney problems, respiratory failure, and neurological damage in humans [19].

Soil mapping is crucial for comprehending soil properties, adopting sustainable practices, and preventing soil degradation [20]. Direct observation of soil has limitations [21], necessitating predictions for inaccessible areas to facilitate risk management and awareness. Spatial prediction is essential for high-quality mapping, which can be achieved through interpolation [22–24]. Interpolation methods like inverse distance weight and ordinary kriging [25, 26] are commonly used for mapping pollutants such as heavy metals in soil. The study employed empirical Bayesian kriging, which improves interpolation results based on numerous simulations considering distance and nearby values, unlike classical ordinary kriging.

Soils are important players in the global mercury cycle, serving as both a sink and a source of contaminants. The accumulation of pollutants in soil degrades its quality, affecting plant growth, and high concentrations of mercury in soil can have toxic effects on plant growth and development. Mercury stress disrupts plant cellular structure, leading to stunted seedling growth, root development, and reduced yield [26]. With 69% of Ghana's land devoted to agriculture [27], the presence of high concentrations of mercury in agricultural soils will ultimately affect crop yield and pose health risks to consumers as it bioaccumulates in the body. While many studies [28-36] have been conducted on mercury concentrations in areas suspected to be contaminated with Hg due to mining and other industrial or urban activities, establishing contaminant levels typically present in soil to serve as a base map for pollution studies is crucial for pollution studies. This study aims to determine the mercury concentration in Ghana's surface soil, investigate Hg's spatial distribution, and assess the potential ecological risk to humans and surrounding ecological systems.

2 Materials and Methods

2.1 Study Area

The study covers the entire land surface area of Ghana (Fig. 1). The country, which is located in West Africa and is bordered by Cote d'Ivoire, Burkina Faso, Togo, and the Gulf of Guinea. The country covers an area of 232,139.40 km² and has a population of approximately 24,658,823 people. The majority of the labour force is engaged in agriculture, which contributes 54% of Ghana's GDP [38]. Gold mining is a major source of mineral revenue and has increased tenfold since 1989 [14], employing at least one million people directly and supporting four to five million others. ASGM activities are more prevalent in the southern section of the country.

2.2 Soil Sampling

A total of 327 surface soils were collected across the country from May 2018 to February 2019. random sampling technique (Fig. 1). The intersection of the gridded lines was used as sample points. The region was gridded at 25 km by 25 km from the first arbitrary point selected. These sample points were traced with a handheld global position system receiver. The land use information about the locations were documented. They included farmlands, forests, open vegetation, water banks, savanna, settlements, sand winning areas, cemetery, mountain, and roadside. The soil samples taken were at a depth of up to 10 cm using a stainless steel hand trowel since anthropogenic sources of pollutants contaminate the upper layers of soil [39]. At each sampling point, composite samples were taken (200 g) and homogenised to give a good representation of the sampled area. The samples collected were stored in labelled polyethene zip lock bags and sealed to avoid loss and external contamination of samples before transporting to the laboratory.

2.3 Analysis of Soil Samples

The collected samples were air-dried indoors to help prevent loss of Hg through vaporization. Close attention was given to each soil sample to avoid cross-contamination. The dried soil samples were sieved with 0.2 mm mesh nylon sieve to remove debris, stones, and pebbles. Total Hg contents in the soils were determined using the Lumex PYRO-915M Zeeman Mercury Analyser (Lumex, St. Petersburg, Russia). It was calibrated based on a pre-set calibration coefficient from the activated charcoal reference material (Cat: 500292 Lumex, Russia). In analyzing for the Hg contents, Soil sample of 0.3 g was weighed into the injection spoon of the



Fig. 1 Map Ghana showing the sampling points

PYRO-915 + attachment [40]. Samples were analyzed three times to check the consistency of the data. Mercury concentrations recorded were aggregated and averaged to represent the concentration of a particular sample site. A portable pH meter was used to determine pH.

2.4 Geo-Accumulation Index (I_{aeo})

The environmental impact of metals and the pollution level in the soil was assessed using geo-accumulation index (I_{geo}). Geo-accumulation index (I_{geo}) method is widely used for quantifying the enrichment or pollution degrees of heavy metals in soil by comparing the current background elements concentrations [38]. In this study, the quantity I_{geo} is calculated using the global average shale data [41]. The I_{geo} was calculated using Eq. 1.

$$Igeo = log_2 \frac{Cn}{1.5Bn} \tag{1}$$

where C_n is the measured concentration (mg kg⁻¹) of Hg at site n; and C_0 is the mean Hg background concentration in soil (mg kg⁻¹). Factor 1.5 is the background matrix correction factor due to the lithologic variation in the soils. The contaminated soils are categorized into seven classes as shown in Table 1.

2.5 Potential Ecological Risk Index

The Potential Ecological Risk Index (Er) was adopted to evaluate the potential ecological risks of mercury [41]. This method comprehensively considers the toxic level, concentration and environmental sensitivity of the contaminant. The potential ecological risk index (Er) of mercury is defined in Eq. 2:

$$EF = \frac{Cm}{Cb} / \frac{Cmref}{Cbref}$$
(2)

Class	Values	Interpretation
1	$I_{reo} < 0$	Uncontaminated
2	$0 < I_{geo} \le 1$	Uncontaminated to Moderately Contaminated
3	$1 < I_{geo} \le 2$	Moderately Contaminated
4	$2 \le I_{geo} < 3$	Moderately to Strongly Contaminated
5	$3 \le I_{geo} < 4$	Strongly Contaminated
6	$4 \le I_{geo} < 5$	Strongly to Extremely Strongly Contaminated
7	$I_{geo} \ge 5$	Extremely Contaminated

 Table 1 Geo-accumulation Index (Igeo)

Table 2 Potential Ecological Risk Index (PERI)

Values	Interpretation
Er < 40	Low potential ecological risk
$40 \le \text{Er} < 80$	Moderate potential ecological risk
$80 \le \text{Er} < 160$	Considerable potential ecological risk
$160 \le \text{Er} < 320$	High potential ecological risk
$Er \ge 320$	Significantly high potential ecological risk

where Tr = 40 is the toxic response factor for mercury [41, 42] C_i is the concentration of mercury in surface soil at site i (mg kg⁻¹), and C_0 is the regional background mercury values in the topsoil. The potential ecological risks of mercury in soils could be put into five classes based on the calculated values of PERI (Table 2).

2.6 Geostatistical Interpolation of Mercury

Kriging is an interpolation technique that models the variogram and fits it to an experimental model for subsequent analysis. It utilises a type of Bayesian inference that generates both a deterministic prediction and a standard error that can be used to quantify confidence intervals [21]. Kriging provides an unbiased linear estimation of a regionalised variable at unsampled locations. It works in a least-square sense where it aims to minimise the variance of estimation error. Kriging makes use of the basic tool known as the semi-variogram; which is half of the expectancy of deviation between values of samples separated by a distance h. In this case, it produces the spatial variability of the variable. Kriging makes use of a single semi-variogram which is a function of distance and direction separating two locations and then uses it to quantify the spatial dependence in the data. Every semi-variogram can be calculated using Eq. 3.

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left\{ z(x_1) - z(x_1 + h) \right\}^2$$
(3)

where $\gamma(h)$ = the experimental semi-variogram value at a distance h; N(h) = the number of sample value pairs within

distance h; and $z(x_1)$, $z(x_1 + h)$ = the sample value at two points separated by distance h. Empirical Bayesian Kriging (EBK) differs from the classical kriging as it accounts for error introduced by estimating the semi variogram model. A cross-validation method was adapted to validate the simulation and the model fitting effect. The level of accuracy was achieved by assessing the Root Mean Square Errors (RMSE). RMSE is used to evaluate the prediction accuracy and evaluate or validate the spatial prediction accuracy and the effect of the simulation model. The low RMSE indicates a good predicted results [43].

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left\{ (a(x_i) - b(x_i)) \right\}^2}$$
(4)

where *a* is the measured value; *b* is the predicted values.

2.7 Descriptive Statistical Analysis of Mercury

Descriptive statistical analysis was conducted using R statistical software to determine the arithmetic mean, standard deviations, sample variance, skewness and confidence interval at 95%.

3 Results and Discussions

3.1 Descriptive Statistics of Mercury Concentration in Soil

Figure 2 shows the descriptive statistics of the concentrations of mercury and pH of the samples analysed. The arithmetic mean and median values of mercury were found to be 0.024 ± 0.029 mg/kg and 0.011 mg/kg, respectively. These values were lower than the world average permissible levels of 0.07 mg/kg [44], indicating that the soil samples analyzed had a relatively low concentration of mercury. However, the coefficient of variation indicated a high dispersion of mercury in the surface soil, suggesting that the concentration of mercury was not uniformly distributed.

The pH levels of the soil samples ranged from 5.20 to 8.38, with a mean and median concentration of 5.81 ± 0.84 and 5.81, respectively. The mean and median values indicate that the soil was acidic. Soil pH is an essential factor in determining the availability of nutrients to plants and microorganisms. Generally, most plants grow well within a pH range of 6.0–7.5 [45]. Hence, soil with a pH value of 5.81 is relatively acidic and might require amendment to adjust the pH level for optimal plant growth.



Fig. 2 Boxplot showing the concentration of mercury in the soil and pH of soils across Ghana

3.2 Spatial Distribution Map of Mercury in Ghana

A Bayesian kriging was used for creating the prediction map of the spatial distribution of mercury in the surface soil (Fig. 3). The spatial distribution of mercury in the soil gave an RMSE of 0.004 (Fig. 4), indicating an accurate result [43]. The prediction map showed concentrations that ranged from 0 to 0.075 mg/kg.

Low levels of mercury were observed in the Upper West, North East, Northern and the Savannah Regions. The presence of mercury in low concentrations could be attributed to a natural constituent of mercury in soil. Concentrations ranging from 0.04 to 0.075 mg/kg were measured in seven regions; Ashanti, Eastern, Western, Western North, Central, Ahafo and Bono regions. Regional observation of the raw data reveals that Western North region have the highest mean concentration of mercury, 0.061 mg/kg, followed by Western and Ashanti regions with 0.54 mg/kg and 0.051 mg/ kg, respectively.

Generally, the northern part and the south eastern part of the country recorded low concentration as compared to the southwestern part of the country (Fig. 4). This could be attributed to the mining activities that are concentrated in the southwestern part of the country [33] other than the northern part of the country. When the data was assessed against the land use land cover information gathered from the field (Fig. 5), it confirmed that mining activities gave the highest mean concentration of 0.108 mg/kg. The mean concentration of mercury from mining areas was higher than the world average of 0.07 mg/kg [46]. Hence the need to monitor the soil, as further increase may be toxic to the ecosystem and may result in possible leaching of mercury into groundwater.

3.3 Relationship Between Mercury, pH, Population Density and Soil Type

Soil pH plays an important role in the mercury in the soil and as such influences its distribution in the soil. Soil pH ranged from 5.2 to 8.38. mercury concentration showed no strong correlation with pH (p > 0.05). Soil pH has a strong influence on metal solubility and retention in soil; higher soil pH results in greater retention and lower metal solubility [38]. The soil pH at most of the sampled points were in the pH range for natural soils which is usually 4.0–9.0. The lack of correlation in the soil properties could be attributed to the variation in the soil type with the study area [28, 47].

Soil type was found to be significantly associated with mercury (p < 0.01). The mean concentration of mercury concentration was higher in alisols, followed by acrisols and nitisols (Fig. 6). Alisols, acrisols and nitisols are dominated by significant accumulation of clay [48]. Soil clay content plays an important role in soil- mercury binding, which suggests that increased mercury sorption capacity in clayey soils may also relate to binding with organic matter [32]. It therefore reveals that elevated mercury levels are often associated with clayey soils. Rice paddy soil is susceptible to mercury due to the clay content in the soil [49]. Mercury presence in soil is however known to negatively affect seed germination and plant development [51].

Figure 7 is a map describing the population density of districts in Ghana was generated based on the 2010 population census [50]. It was to determine districts with high population density and its direct association with the mercury concentration observed in the district. An overlay of the population data and the mercury concentration showed that



Fig. 3 Spatial distribution of mercury concentration in soil



Regions in Ghana

Fig. 4 A histogram of mercury concentration in each region in Ghana

Fig. 5 A graph of land use land cover and mercury concentration in soils



Land Use Lnad Cover



Soil Type (Number of samples)

Fig. 6 A histogram of mercury concentration in soil against land use land cover

high population within a district did not directly reflect high concentration of mercury therefore suggesting negative correlation between high population density and the recorded concentrations.

3.4 Pollution Indices of Mercury in Soil and the Potential Ecological Risk Assessment

The Igeo results suggested that there is an absence of mercury pollution at these sampling sites. Ecological risk

assessment ranged from 0.464 to 10.526, it indicated that the ecological risk assessed was less than 40. The soil therefore posed a low potential ecological risk across the country. It is therefore suitable for agricultural activities.

Contrary to works done in mining areas in the Ashanti region such as Amansie [37, 51], studies showed high potential risk in mining sites and other landfill sites which could be injurious to plants, animals and human health. The distribution pattern of the ecological risk assessment map shows likely potential risk in the Ashanti, Western and Western



Fig. 7 Overlay of mercury concentrations on population density based on 2010 census

North regions. However, the concentrations reported from studies at the community and sub-national levels show high mercury concentration. In Bogoso, an artisanal mining community in Ghana reported mercury levels in soils ranging from 0.125 to 0.352 mg/kg [52]. In some non-mining communities in Ghana mercury concentration of ranging from 0.039 to 0.093 mg/kg were recorded in soil [53]. A review on soils in Ghana presented a range of 0.020-185.9 mg/kg of mercury in soil in an abandoned mine in Tarkwa and 0.297-330 mg/kg in a community in the Upper East region of Ghana [5]. An artisanal mining community in the Talensi district of Ghana measured mean mercury concentration from different groups of soil samples from Gbani; sites of active mining hotspots (7.1 mg/kg), line transects (2.7 mg/ kg), waste soil (1.5 mg/kg) and intersections of grid lines (0.5 mg/kg) [54]. All these values showed the effects of anthropogenic activity occurring at some parts of the country which can only be realized at the community levels.

4 Conclusions

The study investigated the nation-wide concentration and distribution trend of mercury. It further assessed the environmental risk of mercury in surface soil samples across Ghana and its impact on soil and living organism. The spatial distribution of mercury was closely correlated with ASGM activities as the major anthropogenic source. The hotspot areas are noted to be slightly above the world permissible limits of 0.07 mg/kg. The high concentrations observed in the Ashanti, Western and Western North regions were as a result ASGM activities. Generally, the mercury pollutions

in the southwestern part of Ghana (Ashanti, Western and Western North regions) are relatively higher than it is in the south eastern and the northern section of the country hence suitable for agriculture. The geo-accumulation Index across Ghana on the scale of 25 km \times 25 km showed that the soil is uncontaminated and has low potential ecological risk. On a country scale, the soils are not contaminated hence suitable for agriculture since it makes it a viable venture for farming activities in the northern section of the country to be intensified considering the very low concentration levels of mercury in the soils. There is, however, the potential risk of elevated concentration as a result of some ongoing ASGM activities in the soil. Mercury pollution could well be underestimated in areas of ASGM and other anthropogenic/ industrial activities mainly because few data were analysed from these sites based on the gridding system. Nonetheless, so long as ASGM activities persist with the use of mercury for amalgamation, there is the need to monitor the concentration of mercury in the soil to control the level of toxicity in the soil, especially in the southwestern part of the country, and ASGM areas as they are closer to human settlement and farmlands. Further studies should be carried out on other environmental media such as air and water to have a comprehensive analysis of the pathways of mercury in the Ghanaian environment. This study provides background information that will help effective formulation of pollution mitigation measure and policy-making on emission control, food safety, and public health protection in Ghana.

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest We declare that we have NO affiliations with or involvement in any organization or entity with any financial or non-financial interests in the subject matter or materials discussed in this manuscript.

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