Assessment of Bioaccessibility and Health Risk of Mercury within Soil of Artisanal Gold Mine sites, Niger, Northwestern part of Nigeria

Abiodun M. Odukoya[1], Bernard Uruowhe [1], Michael J. Watts[2], Elliott M. Hamilton[2], Andrew L. Marriott[2], Babajide Alo[3] and Nnamdi Anene [4]

[1]Department of Geology, University of Lagos, Akoka, Lagos, Nigeria, [2], Inorganic Geochemistry, Centre for Environmental Geochemistry, British Geological Survey, Nottingham, UK, [3]Department of Chemistry, University of Lagos, Akoka, Lagos and [4] Department of Artisanal and small- scale mining, Ministry of Mines and Steel Development, Nigeria.

Abstract

The occurrence of mercury (Hg) in the environment globally has been linked largely to its use for gold processing. In this research, ore samples, agricultural soil and mine wastes were taken within the vicinity of an artisanal gold mine and processing sites in Niger state, a northwestern part of Nigeria to determine Hg contamination in the environment and estimate the potential hazard to health. The values of Hg measured in ore, agricultural soil and mine wastes ranged between 0.03-5.9, 0.002-5.57 and 0.19-20.99 mg/kg, respectively, with the majority of samples observed above the crustal average values of 0.003 mg/kg. All of the samples were 100 times greater than the USEPA residential soil screening level (SSL) of 0.0023 mg/kg, but were lower than comparable mine sites within the same region. Contamination indices were used to demonstrate the potential exposure to Hg contamination in the study area which ranged from a medium to high level of contamination. Average Daily Dose (ADD) and Hazard Quotient (HQ) were calculated for adults and children in the study area and decreased in the following order: ADDvapour > ADDingestion >ADDdermal > ADDinhalation. The non-carcinogenic health risk index (HI) of Hg calculated for children and adults in the study area were children: 7.42, 2.19, 1.49 and adults: 4.45, 1.26, 1.19, for mine wastes, agricultural soil and ore respectively. All of these values were higher than a considered safe level (=1) and therefore showed that Hg posed a serious non-carcinogenic HI for both adults and children exposed to the soil in the study area. The bioaccessible fraction (BAF) as a measure of ingestion for Hg was generally <13% across all sample matrices, suggesting a low bio accessibility. An HQ incorporating bioaccessible data (BHQ) ranged between 0.000005 and 4.06 with a mean value of 0.62. Values for the BHQ were still >1, threshold limit in some samples and showed that Hg could present a risk to health via ingestion, although further research is required to assess dermal and inhalation bioaccessibility to

assess fully the risk to residents. However, the values were lower than the non-carcinogenic health risk index, which is assumed to be overestimated.

Keywords: Mercury; Gold; Mining; Processing; Health; Niger; exposure indices

Introduction

It is estimated that about 10 to 20 million persons are involved in artisanal small-scale gold mining (ASGM), responsible for approximately 12% of worldwide gold production (UNEP, 2008). Poor regulation and monitoring (especially in alleviating poverty) of the mining operations is responsible for the infiltration of artisanal small–scale mining (ASM) operators who are now responsible for over 95% mining activities in Nigeria (Ikenna *et al.,* 2015).

ASM operations have caused many environmental degradation issues due to poor monitoring and regulatory enforcement. Associated problems range from land degradation, soil and water contamination from toxic elements as well as occupational health and safety problems. One of the adverse effects linked with informal gold mining is the use of Hg for the processing of gold. Poor management of hazardous chemicals and waste like Hg can contribute to undermining health as highlighted in the SDG 3.9 which targets by 2030 a substantial reduction in the number of deaths and illnesses from hazardous chemicals via air, water and soil pollution (Esdaile and Chalker, 2018; Gibb, H and O'Leary K.G, 2014). For example, Hg can be released into the environment from the amalgamation of gold and tailings processing. Mercury is a highly toxic element and can affect human health via inhalation, ingestion or dermal absorption. The effect of Hg on people's health depends upon factors such as the level of exposure, the chemical form of Hg (e.g. organic, redox state), age of the exposed person, exposure pathway (e.g. inhalation, ingestion, dermal). The human health burden resulting from the release of Hg to the environment by miners as well as women and children who are typically processing the ore is considerable. Inhalation of Hg vapour by miners can result in impaired cognitive function, neurological damage, kidney damage, tremors, memory loss, respiratory distress and even death. Chronic exposure to Hg gas has also been linked to renal failure, tremors, movement disorders and memory impairment. Inorganic Hg can also cause kidney damage when consumed as well as soil and water contamination (Park and Zhang, 2012; Bose-O'Reilly *et al*., 2016). Mercury pollution from ASGM can also be converted into MeHg hence, poses a tremendous high risk that can be accumulated in food supplies such as rice

and fish (Reichelt-Brushett *et al.,* 2017). Rice reportedly accumulates MeHg, with up to 80% of MeHg in rice found in edible white rice (Meng *et al.,* 2013). In many studies, rice paddies were irrigated with Hg contaminated water and has led to Hg concentrations of up to 1.2 mg/kg in the edible grain, more than 10 times the threshold limit recommended by the World Health Organisation (Bose-O'Reilly, 2016). MeHg toxicity is particularly due to its ability to cross the blood brain barrier. The socio-economic consequences of Hg contamination have become a global concern during the last 2 decades (Kwokal *et al*., 2012; Taylor *et al.,* 2012; Driscoll *et al.*, 2013; Mondal *et al.,* 2015). Exposure to both Hg and its toxic organic form MeHg (CH_3Hg) effects neurological, cardiovascular and reproductive systems (US EPA, 1997; Wolfe *et al.,* 1998). Regulatory policies for Hg have been introduced (Driscoll *et al.*, 2013) to reduce its impacts from anthropogenic activities and govern transport mechanisms at local, regional and global scales. Health risks associated with MeHg include nerve and brain damage as well as kidney problems. There are also documented cases among miners that are suffering from frequent and severe headaches, dizziness, vision and motor disorders, among other health issues as a result of exposure to inorganic mercury (Gibb and O'Leary, 2014).

Hg and other toxic metals are known to bio accumulate from the abiotic environment through trophic transfer to living organisms (Ali and Khan, 2019). The implications for wildlife and human health consequences being contaminated through the food chain are a real concern in respect to populations who consume contaminated food e.g. fish, especially residents who live and work within ASGM sites (Fraser, 2016). Aside from obvious Hg-specific health problems, worth mentioning antagonistic effects for uptake of essential micronutrients (Selenium). It has been discovered that Se which is a micronutrient can inhibit the harmful effect of Hg exposure and this makes Se the most important micronutrient in rice as staple food (Khan and Wang, 2009; Zhang *et al.,* 2014). Supplementation of organic Se can prevent the oxidative damage from long-term Hg exposure in man (Li *et al.,* 2012; Zhang *et al*., 2014). The use of Hg in the processing of gold ore is undertaken in >65% of the ASGM locations in Niger state as observed during the fieldwork. The ore is treated with Hg after crushing, to form the Hg-gold amalgam, which is then subsequently heated with charcoal to remove the Hg (through evaporation). This process is often done by small children without any form of protection (Figures 1 and 2), with potential exposure via inhalation of Hg vapour, an observation in all the mine sites within the study area.

The Minamata Convention aimed to remove Hg for gold processing globally to protect human health and the environment from mercury related problems (Coulter, 2013). The contract for the execution of enabling activities for a National Action Plan (NAP) on Mercury in the Artisanal and Small-scale Gold Mining (ASGM) Sector in Nigeria was implemented in March 2017 according to the Federal Ministry of Environment in Nigeria through their bulletin. There are few coordinated environmental-human health studies with adequate data in Niger state, and across Nigeria for the estimation of exposure to mercury and potentially harmful metals. Therefore, the aim of this research was to provide a hazard exposure assessment for ASGM workers using contamination indices. This was achieved with the following objective:(1) Survey of ore, agricultural soil and mine wastes in proximity to artisanal gold mine and processing sites in Niger state in the northwestern part of Nigeria to determine mercury (Hg) contamination in the environment and (2) Estimate the potential hazard to health of both adults and children. Thus, this research will address the environmental and health impacts assessment of artisanal gold mining in Niger, northwestern part of Nigeria especially with regards to contamination of soil by mercury and the health implications on humans.

Material and Methods

The study area

The study area falls within Minna and its environs in Niger, northwest, Nigeria with latitude $3^{o}\,21^{'}$ East and longitude $11^{o}\,32^{'}$ North (Figure 3). The study area is rich in gold and mining activities carried out by artisanal miners within the country and those who migrated from neighboring countries. The mining of gold in the study area dates back to 1913 and was at the peak in 1930 mostly by artisanal miners (Olade, 2019). Gold mining activities are active in all the regions of the study area, including: Shakwata, ShidamTunganmaku, Anfani, Chanchaga, Gadoko, Kuchicko, SabonFegi, Koro, DabanWoko, NasarawaKainji, TakunPagi, DandankuChanchaga, Bukuchi, Daban Agua, UpChair/ TashalJatau, GonanZarumai, Kaniya, Kwakwakuta and Nasarawa.

The study area falls within Niger state which was created in 1976 with a total area of 76,363km^2 and population of 3,954,772 according to the 2006 Census. It is characterised by two climatic seasons from April to November for the wet season and December to March for the dry season with an average annual rainfall of 1230mm (Adefila, 2012). The vegetation can be classified as Savanna with lots of grass and few trees and shrubs species (Ayanwale *et al.*, 2013).

Gold Mining and Processing in the study Area

Most of the gold production in Nigeria is associated with alluvial deposits mainly from primary gold mineralisation in the western part of the country where schists are well developed (Obaje, 2009). The study area is within Maru schist belt and can be classified as the Minna-Birnin Gwari gold field (Woakes and Bafor, 1983). The two types of mining methods in this study area are open pit and Alluvial/Stream Bed Panning methods. The Schist Belt is made up of metasedimentary and metavolcanic rocks including low grade, metamorphic rocks. The belt trends from the northwest down to the south western part of Nigeria. Nigerian gold deposits occur in two different forms: as primary mineralization associated with veins bodies of quartz in the basement rocks(load) and alluvial deposits which are found in present river channels and in older buried placers. Primary gold deposits occur mostly within quartz veins in the host rock. Artisanal miners often target the veins by digging and chiseling out the gold ore. The pit is often demarcated into partitions with a given group of miners working on each of the partition. Others work in pits dug in the outcrop portion of the host rocks. Mercury (Hg) amalgamation is the preferred gold recovery method employed by artisanal gold miners for this deposit and its misuse can result in serious health hazards for miners involved in gold extraction as well as for surrounding community inhabitants, who may be exposed to mercury via the food chain (Hinton *et al.*, 2003). On the other hand, secondary gold deposits are mined by panning along riverbanks

including ancient river channels. In some of the sites, panning of stream bed sediments was done directly on the river channels or at the banks of the rivers. River sediments are usually shoveled into a head pan and panned directly inside the river. The rivers also serve as source of drinking water for the people (Figures 4 and 5). Because the river is seasonal, mining activities are predominant at the location during the dry season. This method does not need application of mercury most of the time.

The gold processing include ore crushing, sluicing, panning and amalgamation. Various activities including trading of gold, mercury and other chemical reagents also take place at the processing sites. The gold ore is usually bagged and brought from the mining sites to the processing sites. Mercury amalgamates with the gold (leaving behind the unwanted sediments) to form an amalgam of mercury and gold. In all the sites that use mercury, miners perform this process using bare hands. The tailings are normally thrown away together with the process water and some mercury retained in the sediments Mercury contaminated mine wastes are discarded onto tailings and the remaining water returned to the stream or surrounding land for irrigation, particularly for rice. Recycling of Hg which could reduce the amount of Hg released into the environment is not practiced in all the mine sites within the study area. Further refining is often undertaken by gold merchants at other locations including homes. Whole ore amalgamation was not the practice in any of the mines visited, instead concentrate amalgamation was the common practice.

Sampling and Sampling Preparation

Thirty-three samples, including thirteen gold ore samples, nine mine wastes and eleven agricultural soil from the adjacent farm land to the mine sites, were collected from different gold mining and processing sites within Minna and its environs, all in Niger, northwestern, Nigeria (Table 1 and Figure 3). The mining sites and processing sites are located in different areas while agricultural

soils were located very close and adjacent to the processing site. Top soil samples were taken at a depth of 0-10cm within the mining and processing sites, using a sterilised auger and then samples were securely stored in a polyethylene Ziplock bag and kept cool in the dark before transported to the laboratory as soon as possible. The samples were oven dried at 40°C and a porcelain mortar used for disaggregation. The samples were passed through a <2 mm sieve and the sieved samples were pulverized to <53 μm after proper homogenization in a pre-cleaned mechanical agate mill for geochemical analysis, with the exception of <250 μm for Hg analyses.

Sampling Analysis

Concentration of Mercury in soil

All of the samples were sent to the Inorganic Geochemistry Laboratories of the British Geological Survey for sample preparation and Hg analysis using a DMA 80 mercury analyzer as described by Chatterjee *et al.,* 2014 using 0.05g of <250 μm milled soil in a nickel boat placed into a quartz furnace where a four-stage thermal process of drying at 250 ºC for 60s. Sample decomposition and secondary decomposition in the catalyst at 650 °C for 720s for Hg reduction and volatilisation. Mercury vapours are trapped on a gold amalgamator while combustion gases are removed using an oxygen carrier gas from the detection cell. Mercury is then released from the gold amalgamator by heating at 850°C for 12s, carried to the detector where total Hg is determined using atomic absorption spectrometry at 254 nm. Certified reference materials TH-2 and PACS-2 were used to determine the accuracy and precision of the measurements and validate the applied methods. The average value for eight measurements were 0.69 ± 0.01 and 3.13 ± 0.03 mg/kg respectively. The percentage of recovery were 111 ± 4% and 103 ± 3% respectively and the precision (RSD) was lower than 5%.

Bioaccessibility of mercury in soil

Bioaccessible Hg extractions were undertaken according to Hamilton *et al.,* (2015). Analyses of these solutions followed the method described in Watts *et al.,* 2019 for trace and major element analyses using an Agilent 8900 series triple quadrupole inductively coupled plasma mass spectrometer (ICP-QQQ-MS) with an ISIS 3 sample introduction system. Helium gas (flow rate 5.1 ml min^{-1}) was introduced into the ORS to minimize the impact of polyatomic interferences (e.g. $^{186}W^{16}O^{+}$)

194 The instrument was calibrated at the beginning of every analytical run using at least three
195 standards and a blank. A mixed internal standard solution containing Sc, Ge, Rh, In, Te and Ir was
196 added to the samples at a fixed ratio of approximately 1:10 via a dedicated port in the sample
197 introduction valve. Quality control (QC) check standards were analysed at the start and end of
198 each run and after no more than every 20 samples. The quality assurance showed 95% confidence
199 limits of the recommended values given for the certified materials for precision and accuracy. The
200 Relative Standard Deviation (RSD) was between 5% and 10%. Duplicate samples, blanks, the
201 bioaccessibility guidance material BGS 102 and the standard reference material NIST 2711a were
202 extracted with every batch of UBM bioaccessibility extractions for quality control. The blanks
203 always returned results that were below the detection limit. The Hg recovery was 98% for BGS
204 102 and 101% for SRM NIST2711a. Mean repeatability (expressed as RSD%) was 5.6% for the
205 Gastric phase.

206 **Data Analysis**

207 Descriptive statistics (e.g. mean, standard deviation), as well as contamination indices including,
208 Enrichment Factor, Geo-accumulation index, Pollution index and health risk assessment of
209 mercury were determined and the formulas are as follows:

210 **Enrichment Factor (EF)**

211 Enrichment Factor was used to assess the degree of anthropogenic contamination of soil within
212 the mine sites (Simex and Helz 1981). EF can also be used to classify source of contamination as
213 geogenic or anthropogenic (Ghanavati *et al.,* 2019). EF can be calculated using the formula below;

214 $$\mathrm{EF} = \frac{(Ci/Cref)Sample}{(Ci/Cref)Background} \quad (1)$$

215 where $\frac{Ci}{Cref}$ = the ratio of toxic element in the sample collected to that of the background value of
216 the same element which is the Crustal Average Values (Taylor, 1964) in this case. Aluminum was
217 also used as the normaliser (Hsu *et al.,* 2016; Yongming *et al.,* 2006; Ghanavati *et al.,* 2019).
218 EF = 0.05≤EF≤1.5 represented contamination from geogenic origin while EF=>1.5 represented
219 anthropogenic origin. EF can further be categorized in agreement with Zhang and Liu, 2002 as
220 follows; EF<2 = deficiency to minimal enrichment; 2≤EF ≤5 = moderate enrichment; 5≤EF ≤20

=significant enrichment; 20≤EF ≤40 =very high enrichment and EF > 40 =extremely high enrichment (Namaghi *et al.,* 2011; Ghanavati *et al.,* 2019).

Geo-accumulation Index (Igeo)

Geo-accumulation Index is used widely for the evaluation of potentially harmful metal contamination (Mueller,1969) and the formula is expressed as:

$$Igeo = log2\frac{Cn}{1.5Bn} \quad (2)$$

Where Cn = Hg measured in the study area and Bn is the background value of the same element in average crustal values (Taylor, 1964), with 1.5 as a factor for possible variation adjustment in the background values as a result of lithologic differences.

The degree of contamination can be classified into seven categories based on the Igeo value for each trace elements; Igeo ≤0 (practically uncontaminated), 0 < Igeo ≤1 (uncontaminated to moderately contaminated), 1 < Igeo ≤ 2 (moderately contaminated), 2 < Igeo ≤ 3 (moderately to heavily contaminated), 3 < Igeo ≤ 4 (heavily contaminated), 4 < Igeo ≤ 5 (heavily to extremely contaminated), and Igeo > 5 (extremely contaminated) (Loska *et al.,* 2003; Fang et al., 2019).

Pollution Index (PI)

Pollution Index (PI) is the ratio of the concentration of element in the soil of the study area relative to the background crustal average values for Hg (Taylor, 1964). The three classes according to Wu *et al*., 2016 and reported in Odukoya *et al*., 2018 include PI ≤ 1 which indicated Low contamination, 1 < PI ≤ 3 indicated Middle contamination and PI > 3 that indicated High contamination.

$$\text{PI} = \frac{Cn}{Bn} \quad (3)$$

Health Risk Assessment of Toxic Elements

Human health risk assessment of toxic elements can be grouped as carcinogenic and non-carcinogenic risks. There are three exposure pathways of potentially harmful elements to humans, including oral ingestion, inhalation and dermal exposure according to USEPA, 1989, 2011. In addition, exposure of Hg via inhalation of vapor (D_{vapour}).

The different parameters used to calculate the health risk assessment are summarised in Table 2. In this study, the Average Daily Dose (ADD) based on the four exposure pathways of mercury to human body were determined using equations 4-7 (USEPA 2002; Zeng *et al*. 2010; Chen *et al*.,

2005 and Odukoya *et al*., 2018). The ratio of average daily dose (ADD) and reference values can be used in determining the health effect of toxic metals using equations 8 and 9. Reference Dose (RfD) is the threshold value used to determine harmful impacts of toxic elements in man and animal. The RfD for Hg used in this study was taken from the US Department of Energy's RAIS compilation (2004), summarised in Table 3.

Values lower than the reference dose indicate that there is no harmful health impact. On the other hand, the ADD value higher than the reference dose of Hg for different pathways (Table 3) indicates that the contact pathway will cause harmful human health effects (US EPA 1997).

$$ADDingnc = \frac{Csoil*IngR*CF*EF*ED*}{BW*AT} * 10^{6} \quad 4$$

$$ADDinhnc = \frac{Csoil*InhR*EF*ED*}{PEF*24*AT} \quad 5$$

$$ADDdermalnc = \frac{Csoil*SA*CF*AF*AABF*EF*ED*}{BW*AT} * 10^{6} \quad 6$$

$$ADDvapour = \frac{Csoil*InhR*EF*ED}{VF*BW*AT} \quad 7$$

Equations 8 and 9 were used to calculate Hazard Quotient (HQ) and Hazard Index (HI). Hazard Index represents the Total sum of Hazard Quotient (HQ) of several contaminants or exposure paths (US EPA, 1989). Therefore, a mixture of non-cancerous risk can be assessed by calculating the HI of every exposure pathway such as ingestion, dermal, inhalation and vapor (US EPA, 1989). The possible non-carcinogenic and carcinogenic risks were calculated by applying subsequent calculations (US EPA, 1989). Non-carcinogenic health risk is accepted when the HI value is below 1, and the degree of risk increases as HI increases (USEPA 2011).

$$HQ = \frac{ADDnc}{RfD} \quad 8$$

$$HI = \sum HQi \quad 9$$

Calculation of Bioaccessible fraction (BAF%)

The bioaccessible fraction (BAF%) of Hg in the ore, agricultural soil and mine wastes within the gold mining and processing sites in Niger, Central part of Nigeria was calculated as the ratio of the concentration of the Hg in stomach and intestinal phase to that in the total metal based on equation 10 based on Hamilton *et al*., 2015. The BAF is calculated from the highest concentration

of the two phases (stomach and stomach + intestine) to ensure the most conservative estimate of bio accessibility. The BHQ is the Bioaccessible Hazard Quotient calculated from the BAF and HQ as follows.

$$BAF\% = \frac{CBA\ Extracted\ Hg}{C\ Total\ Hg} * 100\% \quad (10)$$

$$BHQ = BAF * HQ \quad (11)$$

Results and Discussion

Concentration of Hg in the study area

Summary concentrations for Hg measured in 33 locations which included ore samples, mine wastes and agricultural soil from the adjacent farm land to the mine sites are shown in Table 4 while Figure 6 illustrates the descriptive statistics. The average crustal value of 0.08 mg/kg (Taylor, 1964) was used as the background value for Hg, whilst the concentration of Hg in the ore, agricultural soil and mine wastes ranged from 0.03-5.9, 0.002-5.57 and 0.19-20.99 mg/kg, respectively. Mean concentrations of Hg were 0.76, 1.23 and 5.58 for mine wastes, agricultural soil and ore respectively (Table 4 and Figure 6). Hg values in all the soil samples within the study area were above the USEPA residential soil screening level (SSL) (USEPA, 1996) and up to 100 times greater than the guidance value of 0.0023 mg/kg. All of the waste samples, five ore samples and one agricultural soil sample were above average crustal value of 0.008 mg/kg. The mean values for the three sample types were also above 0.056 mg/kg and 0.040 mg/kg which were cited as the guideline for maximum allowable limit of Hg in upper continental crust according to Wedepohl (1995) and Taylor and Mclema (1985), respectively (Table 5).

The concentrations of Hg observed in the study area can be classified as very high and a point of concern, and may be compounded by the use of Hg for gold processing which are common to the study area. Soil pH, grain size, organic matter, cation exchange capacity and electric conductivity have also been linked to the soil enrichment with Hg (Amadi, 2013). The pH of soils in the area ranged from 4.7 to 7.5 with a mean value of 6.5 indicating that the soils in the area were acidic. The low pH of soils in the area may increase the sorption rate of Hg to surrounding soils, with a long residual effect.

The mean concentrations of Hg in ore, agricultural soil and mine wastes for this study area were low in comparison with reported average Hg concentrations of 6.25 mg/kg in soil samples taken

from Anka, Zamfara, Northwest Nigeria (Lar Uriah *et al*., 2013). The mean value of Hg obtained in the study area was also lower than the mean value of Hg obtained in the soil within Madaka mining site in Rafi, also within Niger district (Amadi *et al*., 2017) (Table 5). The average value of Hg in the study area was however higher in comparison with the values reported in the soil within ASGM sites in Korea (0.204 mg/kg) (Han *et al*., 2012), Gilgit-Baltistan, Pakistan (0.27 mg/kg) (Arjumand, *et al*., 2018) and in Venezuela (0.049 mg/kg) (Garcıa-Sanchez *et al*., (2006). The elevated measured values demonstrate the potential impact of Hg used for gold processing in the study area and the need for further research on the ecological and human health exposure consequences, such as the use of contamination indices

Contamination Indices

In order to quantitatively estimate the level and extent of Hg contamination in the study area, environmental pollution indices were applied which include: geo-accumulation index, contamination factor and pollution index and the summary is presented in Table 6 and Figures 7-9.

Enrichment Factor (EF): EF of Hg in soil ranged between 0.004-13.02, 0.008-0.4 and 0.5-38.19 for agricultural soil, ore samples and mine wastes respectively (Table 6). The proportion of samples with a minimum enrichment, moderate enrichment, significant enrichment and very high enrichment were (60%, 100% and 20%), (20%, 0% and 20%), (20%, 0% and 30%) and (0%, 0% and 30%) for agricultural soil, ore samples and mine wastes respectively (Figure 7).

All of the ore samples were within minimal enrichment while 30% of the mine wastes fell within very high enrichment. The enrichment factor in the study area followed the order of mine wastes (10.36)> agricultural soil (6.57) > ore samples (1.09) (Table 6). The high enrichment of Hg indicates contamination in the study area.

Geo-accumulation Index (Igeo): The calculation of the geo-accumulation index ranged between -5.39-1.31, -5.69-5.54 and 0.63-7.54 for ore samples, agricultural soil and mine wastes respectively (Table 6). Igeo values calculated for Hg showed that 40%, 75% and 0% of agricultural soil, ore samples and mine wastes respectively fell below 1 which is the recommended value for uncontaminated soil. The percentages of soil that fell within low contaminated soil were 50%, 100% and 30% for agricultural soil, ore samples and mine wastes respectively. For agricultural

soil, only 20% can be classified as between moderately to heavily contaminated, 20% within heavily to extremely contaminated and 10% as extremely contaminated. Mine wastes showed that 10% can be classified as moderately contaminated, 30% within heavily to extremely contaminated and 30% within extremely contaminated (Figure 8). The IGeo in the study area also followed the order of mine wastes > agricultural soil > ore samples (Figure 8). All the wastes samples showed high Hg contamination while 25% of ore samples and 60% of agricultural soil showed different level of Hg contamination based on the geo-accumulation index.

Pollution Index: Assessment of different soil samples based on the calculation of a Pollution Index showed that the values for agricultural soil, ore samples and mine wastes showed the following ranges in mg/kg (0.03-69.63), (0.04-3.73) and 2.32-262.3), respectively (Table 6). The result showed that (20%, 62% and 0%), (20%, 0% and 0%), (20%, 38% and 20%) and (40%, 0% and 80%) of agricultural soil, ore samples and mine wastes can be classified as non-pollution, low pollution, medium pollution and high pollution respectively (Figure 9). The averaged pollution index in the study area followed the order of mine wastes (69.20) > agricultural soil (15.41) > ore samples (1.37) (Figure 9).

The result of different contamination indices generally showed that ore samples were minimally to moderately contaminated with Hg, agricultural soil samples can be classified as moderately contaminated while about 50% of the samples close to the processing sites were highly contaminated with Hg. Mine wastes taken from processing sites where Hg was used for processing of gold were within heavily contaminated to extremely contaminated. Only about 20% of mine wastes also fell within moderately contaminated especially those within mine sites. This also confirmed that the source of the Hg contamination in the study area is mainly from gold processing.

Health Risk Assessment of Hg in the study area

The results of non-carcinogenic risk for adults and children involved in ASGM and processing sites in Niger, Northwestern part of Nigeria are summarised in Appendix 1. They were calculated for different pathways, including ingestion, inhalation, dermal and vapourisation and based on the toxicity thresholds chronic reference dose (RfD) values and Average Daily Doses (ADD) values. The ADD values calculated for the four pathways were lower than the recommended RfDs except for ADDvapour. The average daily dose (ADD) and Hazard Quotient (HQ) values of Hg calculated for ore samples, agricultural soil and mine wastes for both adults and children were similar and decrease in the following order; ADDvapour > ADDing >ADDdermal > ADDinhalation. The

366 pathway from vapour showed that the highest ADD for adults and children compared to other
367 pathways (Appendix 1).
368 HQvapour and HQingestion contributed the most to the non-carcinogenic health risk index in all
369 of the soil samples taken in this study (Figures 10 and 11). HQvapour and HQingestion calculated
370 in samples taking from mine wastes, ore samples and agricultural soil contributed (52%, 52% and
371 91%) and (48%, 48% and 9%), respectively to the non-carcinogenic health risks in the study area.
372 The contribution of HQdermal and HQinhalation were very minimal in the study area (Figures 10
373 and 11). This shows that exposure to Hg in this setting through vapour and ingestion, especially in
374 children where most values were >1 can result in the non-carcinogenic harmful effects e.g. damage
375 to brain and tissues of children.
376 The non-carcinogenic health risk index (HI) for Hg in mine wastes, ore samples and agricultural
377 soil for children and adults in the study area were (7.42 and 4.45), (2.19 and 1.26) and (1.49 and
378 1.19) respectively (Appendix 1). All values were higher than the safe level (=1) and therefore,
379 showed that Hg posed a serious non-carcinogenic health risk index in the soil of the study area
380 (Appendix and Figures 10 and 11). The non-carcinogenic health risk index is higher for children
381 than adults due to their higher sensitivity to Hg exposure. The result also showed that mine wastes
382 samples constituted the highest risk, followed by agricultural soil and the least values were from
383 ore samples (Figures 10 and 11). Since most of the Hg used for gold processing end up in the mine
384 wastes, the results confirmed that the source of Hg in the study area is largely from gold processing,
385 with transfer to nearby agricultural soils within the adjacent farmlands in the study area.

Bioaccessible fraction of Hg in the soil of the study Area

Bioaccessible is the amount of a pollutant that can be dissolved in the gastrointestinal environment and show relative amount of the pollutant that can be absorbed by the body. The higher the bio accessibility, the greater the potential for absorbing pollutants (Zhou *et al.,* 2018). The risk assessment calculated using total content of heavy metal could be overestimated since it is not possible for body to absorb all the available Hg in the environment. The health risk of heavy metals is better assessed in soil using the value of bioaccessibility. The bioaccessible Hg in stomach and stomach + intestine in mg/kg range between (0.002-0.505) and (0.006- 0.061) with mean value of 0.063 and 0.017 respectively. 54% of the samples showed higher bioaccessible Hg in the stomach phase only compared to a combination of stomach+ intestine (Figure 12). The bioaccessible fraction (BAF), as the proportion of Hg which is bioaccessible from the sample matrix ranges from 0 to 13% with mean of 4%. Thus, large fractions of Hg in the soil samples are in forms that may not be available for absorption in the stomach or gastrointestinal tract following incidental ingestion. The BAF of Hg in the study area also fall within a low bio accessibility of less than 15% (Table 7, Figure 12)

The bioaccessible Hazard Quotient (BHQ) in the soil of the study area was determined using equation 11. The BHQ ranged between 0.000005 and 4.06 with a mean value of 0.62. BHQ values were >1 in some samples, especially agricultural soil and mine wastes hence it showed that Hg in the soil of the study area could cause damage to the health of the residents. However, the values were lower than the non-carcinogenic health risk index (Figure 13).

Conclusion

An environment that is free of toxic elements such as Hg is vital for human health and general well-being. Poor management of toxic elements in air, soil and water from mine wastes can jeopardises ecosystem and human health as addressed by the United Nations Sustainable Development Goals (SDG). For example, SDG 3.9 cites that "By 2030, substantially reduce the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination" (UNEP, 2018). Progress towards achieving the SDGs in the study area is at risk from illegal artisanal mining, use of Hg for gold processing, indiscriminate dumping of mine wastes, use of agro-chemicals as well as intense weathering in the study area have contributed to

the dispersion of Hg. The concentration of Hg for all of the samples were up to 100 times greater than the USEPA residential soil screening level (SSL). More than 70% of soil taken from the mine sites and farms in the vicinity of the mine sites, which included soils used for cultivation had a moderate to very high level of pollution based on contamination indices with the decreasing trend of Mine wastes > Agric > Ore samples. The health risk assessment calculated for Hg in the study area showed that Hg has potentially very high non-carcinogenic harmful impacts on children and adults. The HQ values for all the soil samples for the major pathways decrease as follows in children and adults: Vapor >Inhalation >Ingestion >Dermal. HI also showed the decreasing trend as follows: Mine Wates >Agric soil> Ore. The bioaccessible fraction of Hg in the samples was low and reduced the hazard assessment, BHQ compared to HI, which ranged between 0.000005 and 4.06 with a mean value of 0.62. BHQ values were >1, considered as the safe limit for agricultural soil and mine wastes, hence it showed that Hg in the soil of the study area could pose a hazard to the health of residents. However, the values were lower than the non-carcinogenic health risk index, which is assumed to be overestimated (Lu Ying et al., 2011). Therefore, there is a need for mitigation steps such as looking for alternatives to the use of Hg for gold processing. Closer monitoring and regulation to reduce the hazard to health in these communities is also very important to facilitate SDG 3.9.

Acknowledgements

The lead author will like to appreciate Dr Michael Watts, The head of inorganic geochemistry laboratory, British Geological Survey, Nottingham, UK and his team for the support with regards to the analysis of the soil samples. The authors will also like to appreciate Hajia Mohammed, the mine officer in charge of Niger state in Nigeria for her support during the field work activities.

Declaration

Conflict of interest

There is no conflict of interest.

Funding Information

No funding was received for conducting this study.

Data Availability

All data are readily available

Author Contribution

All the authors contributed to the design, fieldwork, analysis and writing of the manuscript

Animal Research

Not Applicable

consent to participate

Not Applicable

consent to publish before reference in the manuscript

Not Applicable

References

Adefila, (2012). Spatial assessment of farmers' cooperative organizations in agricultural development in Gurara area of Niger State, Nigeria. *Journal of Ecology and the Natural Environment*, 4. 112-124.

Ali, H and Khan, E (2019). Trophic transfer, bioaccumulation, and biomagnification of non-essential hazardous heavy metals and metalloids in food chains/webs—Concepts and implications for wildlife and human health. *Human and Ecological Risk Assessment*. 25 (6).

Amadi, A.N and Nwankwoala, H.O (2013). Evaluation of heavy metal in soils from Enyimba dumpsite in Aba, southwest Nigeria using contamination factor and geoaccumulation index. *Energy and Environment Research*. 3(1).

Amadi, A. N., Ebieme, E. E., Musa, A., Olashinde, P. I., Ameh, I. M. and Shuaibu, A. M (2017). Utility of Pollution indices in Assessment of soil Quality around Madaga Gold Mining site, Niger State, North-Central Nigeria. *Ife Journal of Science*. 19 (2).

Arjumand Riaz, Sardar Khan, Said Muhammad, Caihong Liu, Mohammad Tahir Shah and Mohsin Tariq (2018). Mercury contamination in selected foodstuffs and potential health risk

assessment along the artisanal gold mining, Gilgit-Baltistan, Pakistan. *Environ Geochem Health* 40:625–635.

Ayanwale, A.V., Shokunbi, M.T., Olayemi, J.K., Chukwuemeka, V.I., Falusi. F.M and Erhabor, O.F (2013). A study of the Fish Fauna of Tagwai Lake Minna, Nigeria in relation to gear selectivity. *Pakistan Journal of Biological Sciences*. 16. 731-734.

Bose-O'Reilly S., Schierl R., Nowak D., Siebert U., William J.F., Owi F.T., Ir Y.I (2016). A preliminary study on health effects in villagers exposed to mercury in a small-scale artisanal gold mining area in *Indonesia. Environ. Res.*149. 274–281.

Broadway, A, Cave, M.R, Wragg, J, Fordyce, F.M, Bewley, R.J, Graham, M.C, Ngwenya, B.T and Farmer, J.G (2010). Determination of the bio accessibility of chromium in Glasgow soil and the implications for human health risk assessment. *Science of the Total Environment* 409. 267–277.

Carla, C., Eduardo, F., Paula, F.Á and João, P.T. (2014) Identifying Sources and Assessing Potential Risk of Exposure to Heavy Metals and Hazardous Materials in Mining Areas. The Case Study of Panasqueira Mine (Central Portugal) as an Example. *Geosciences*.4. 240-268.

Chatterjee, M., Sklenars, L., Chenery, S. R., Watts, M. J., Marriott, A. L., Rakshit, D., Sarkar, S. K. (2014). Assessment of Total Mercury (Hg_T) in Sediments and Biota of Indian Sundarban Wetland and Adjacent Coastal Regions. *Environment and Natural Resources Research*. 4: 50-64.

Chen, J., Tan, M., Li, Y., Zhang, Y., Lu, W., Tong, Y., et al. (2005). A lead isotope record of Shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline. *Atmospheric Environment, 39*. 1245–1253.

China Ying Lu, Wei Yin, Longbin Huang, Ganlin Zhang and Yuguo Zhao (2011). Assessment of bioaccessibility and exposure risk of arsenic and lead in urban soils of Guangzhou City. *Environ Geochem Health*. 33:93–102.

Coulter, M.A (2016). "Minamata Convention on Mercury." *International Legal Materials* 55 (3). 582-616.

Driscoll, C. T., Mason, R. P., Chan, H. M., Jacob, D. J., & Pirrone, N. (2013). Mercury as a global pollutant: Sources, pathways, and effects. *Environmental and Science Technology*. 47. 4967–4983.

Esdaile, J and Chalker, J.M (2018). The Mercury Problem in Artisanal and Small-Scale Gold Mining. *Chem.Eur*. 24. 6905 –6916.

Fang X, Peng B, Wang X, Song Z, Zhou D, Wang Q, Qin Z, Tan C (2019). Distribution, contamination and source identification of heavy metals in bed sediments from the lower reaches of the Xiangjiang River in Hunan province, China. Sci Total Environ. 689. 557-570.

Fraser B (2016). Peru's gold rush prompts public-health emergency. *Nature*.534(7606):162.

Garcıa-Sanchez, A, Contreras, F, Adams M and Santos, F (2006). Atmospheric mercury emissions from polluted gold mining areas (Venezuela). *Environ Geochem Health* 28. 529–540.

Ghanavati, N, Nazarpour, A and Watts, M.J(2019). Status, source, ecological and health risk assessment of toxic metals and polycyclic aromatic hydrocarbons (PAHs) in street dust of Abadan, Iran. *Catena* .177.

Gibb, Herman and O'Leary, Keri. (2014). Mercury Exposure and Health Impacts among Individuals in the Artisanal and Small-Scale Gold Mining Community: A Comprehensive Review. *Environmental health perspectives*. 122.

Hamilton, E.M, Barlow, T.S, Charles J.B. Gowing and Watts, M.J (2015). Bioaccessibility performance data for fifty-seven elements in guidance material BGS 102. *Microchemical Journal*. 123. 131-138.

Han Sik Kim and Myung Chae Jung (2012). Mercury contamination in agricultural soils from abandoned metal mines classified by geology and mineralization. *Environ Geochem Health* 34:55–69.

Hinton, J.J, Veiga, M.M, Tadeu, A and Veiga, C (2003). Clean artisanal gold mining: a utopian approach? *Journal of Cleaner Production*. 11. 99–115.

Hsu, C.-Y., Chiang, H.-C., Lin, S.-L., Chen, M.-J., Lin, T.-Y., & Chen, Y.-C. (2016). Elemental characterization and source apportionment of PM10 and PM2.5 in the western coastal area of central Taiwan. *Science of the Total Environment, 541*, 1139–1150.

Hua Zhang, Xinbin Feng, Chengxin Jiang, Qiuhua Li, Yi Liu, Chunhao Gu, Lihai Shang, Ping Li, Yan Lin b, Thorjørn Larssen (2014). Understanding the paradox of selenium contamination in mercury mining areas: High soil content and low accumulation in rice. *Environmental Pollution* 188. 27-36.

Ikenna, T.O., Jeremy, P., Richards, R.S., Theresa, G and Tara, M. (2015) Artisanal and small-scale mining in Nigeria. Experiences from Niger, Nasarawa and Plateau states. *The Extractive Industries and Society*. 2.694-703.

Khan, M.A.K., Wang, F.Y (2009). Mercury-selenium compounds and their toxicological significance: toward a molecular understanding of the mercury selenium antagonism. *Environ. Toxicol. Chem.* 28, 1567-1577.

Kwokal, Z, Sarkar, S K, Franci, S and Bilinksi,F (2012). Mercury Concentration in Sediment Cores from Sundarban Mangrove Wetland, India. *Soil and Sediment Contamination*, 21:525–544

Lar Uriah, Tsuwang Kenneth, Gusikit Rhoda and Mangs Ayuba (2013). Lead and Mercury Contamination Associated with Artisanal Gold Mining in Anka, Zamfara State, North Western Nigeria: The Continued Unabated Zamfara Lead Poisoning. *Journal of Earth Science and Engineering. 12.* 764-775

Lee, W.R, Eom, Y, Lee, T.G (2017). Mercury recovery from mercury -containing wastes using a vacuum thermal desorption system. *Waste management*. 60. 546-551.

Li, Y.-F., Dong, Z., Chen, C., Li, B., Gao, Y., Qu, L., Wang, T., Fu, X., Zhao, Y., Chai, Z (2012). Organic selenium supplementation increases mercury excretion and decreases oxidative damage in long-term mercury-exposed residents from Wanshan, China. *Environ. Sci. Technol*. 46, 11313-11318.

Louisa J. E and Justin M. C. (2018). The Mercury Problem in Artisanal and Small-Scale Gold Mining. *Chem. Eur. J*. 24. 6905 – 6916.

Loska, K.; Wiechula, D.; Barska, B.; Cebula, E.; Chojnecka (2003). A. Assessment of arsenic enrichment of cultivated soils in Southern Poland. *Polish J. Environ. Stud*. 12, 187–192

Lu, X.W., Zhang, X.L., Li, L.Y., Chen, H., (2014) Assessment of metals pollution and health risk in dust from nursery schools in Xi'an, China. *Environ. Res*.128.27–34.

Lu, Ying, Yin, Wei, Huang, Longbin, Zhang, Ganlin and Zhao, Yuguo (2011). Assessment of bioaccessibility and exposure risk of arsenic and lead in urban soils of Guangzhou City, China. *Environmental geochemistry and health*. 33. 93-102.

Luo et al., Luo, X.S., Yu, S., Zhu, Y.G., Li, X.D., (2012). Trace metal contamination in urban soils of China. *Sci. Total Environ*.17.421–422.

Mondal, Naba, Das, Chittaranjan and Datta, Jayanta. (2015). Effect of mercury on seedling growth, nodulation and ultrastructural deformation of Vigna radiata (L) Wilczek. *Environmental monitoring and assessment.* 187. 4484.

Medecins Sans Frontieres (2012). Lead -poisoning-crises-in-Zamfara-Nigeria.pdf. *MSF Briefing Paper*. https://reliefweb.int/sites. Accessed on 16th of June 2019.

Meng, Mei, Li, Bing, Shao, Jun-Juan, Wang, Thanh, He, Bin, Shi, Jianbo, Ye, Zhi and Jiang, Guibin. (2013). Accumulation of total mercury and methylmercury in rice plants collected from different mining areas in China. *Environmental pollution*. 184C. 179-186.

Muller, G. (1969) Index of geoaccumulation in sediments of the Rhine River. *Geol. J*., 2, 108–118.

Namaghi, H.H., Karami, G.H. and Saadat, S. A. (2011). Study on chemical properties of groundwater and soil in ophiolitic rocks in Firuzabad, east of Shahrod, Iran: with emphasis to heavy metal contamination. *Environmental Monitoring Assessment*, 174. 573-83.

Obaje, N.G. (2009) Geology and Mineral Resources of Nigeria. *Springer,* Dordrecht Heidelberg London New York, 221.

Odukoya, A.M, Olobaniyi, S.B and Oluseyi , T.O (2018). Assessment of Potentially Elements pollution and human health risks in soil of Ilesha Gold mining site, southwest Nigeria. *J Geol Soc India*. 91: 743.

Olade, M.A (2019). Solid Mineral Deposits and Mining in Nigeria: - A Sector in Transitional Change. *Achievers journal of scientific research*. 2. 1-15.

Park, D and Zheng, W (2012). Human Exposure and Health Effects of Inorganic and Elemental Mercury. *J Prev Med Public Health*. 45. 344-352

Peng Xing, GuoLiang Shi, GuiRong Liu, Jiao Xu YingZe Tian YuFen Zhang YinChang Feng and Armistead G. Russell (2017). Source apportionment and heavy metal health risk (HMHR) quantification from sources in a southern city in China, using an ME2-HMHR model. *Environmental Pollution*. 221, 335-342

Reichelt-Brushett, A.J, J. Stone, P. Howe, B. Thomas, M. Clark, Y. Male, A. Nanlohy, P. Butcher (2017). Geochemistry and mercury contamination in receiving environments of artisanal mining wastes and identified concerns for food safety. *Environ. Res*. 152, 407–418.

Simex, S. A and Helz, G. R. (1981). Regional geochemistry of trace elements in Chesapeake Bay. Environ. Geo. 3. 315- 323,

Taylor, S.N (1964). The continental Crust: Its Composition and Evaluation. Blackwell Scientific Publications, Oxford. 312.

Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: its Composition and Evolution*. Blackwell Blackwell Scientific, Oxford, 311p.

Taylor, D.L, Linehan, J.C, Murray, D.W and Prell, W.L (2012). Indicators of sediment and biotic mercury contamination in a southern New England estuary. *Mar Pollut Bull*. 64(4): 807–819

Tomlinson, D.L., Wilson, J.G., Harris, C.R. Jeffery, D.W (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgolander Meeresunters.* 33: 566.

United Nations Environment Programme (2008). The UNEP 2008 Annual Report. www.unep. Accessed on 6th of March 2019.

United Nations Environment Programme (2018). https://web.unep.org/globalmercurypartnership/our-work/artisanal-and-small-scale-gold-mining-asgm. Accessed on 10th of June 2020.

U.S. Environmental Protection agency (1989). Risk Assessment Guidance for Superfund: Human Health Evaluation Manual [part A]: Interim Final. Washington, DC, USA.

USEPA (1996). Office of Solid Waste and Emergency Response Washington, DC 20460 Publication 9355.4-23 Superfund Soil Screening Guidance: User's Guide 2nd Edition

U.S. EPA (1997). Exposure Factors Handbook (1997) Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA/600/P-95/002F a-c.

U.S. EPA (United States Environmental Protection Agency) (1997). Fate and Transport of Mercury in the Environment, Vos I-VII, EPA-452/R-97-005. US Environmental Protection Agency; Washington, DC: 1997. Mercury study report to Congress.

USEPA. (2011). Supplemental guidance for developing soil screening levels for superfund sites. OSWER 9355.4-24. Washington DC: U.S. Environmental Protection Agency

USEPA IRIS (US Environmental Protection Agency), (2002). Integrated Risk Information System. Environmental Protection Agency Region I, Washington DC 20460. http:// www.epa.gov/iris.

USDE (Department of Energy). (2004). RAIS: Risk assessment information system. Washington DC: US Department of Energy.

USDE (Department of Energy). (2004). RAIS: Risk assessment information system. Washington DC: US Department of Energy.

Watts, M.J., Middleton, D.R.S., Marriott, A.L., Humphrey, O.S., Hamilton, E.M., Gardner, A.,

Smith, M., McCormack, V.A., Menya, D., Munishi, M.O., Mmbaga, B.T. and Osano, O. (2019b)

Source apportionment of micronutrients in the diets of Kilimanjaro-Tanzania and Counties of Western Kenya, Scientific Reports, 9, 14447.

Wedepphl, K.H (1995). The composition of the continental crust Geochem. *Cosmochin Acta*, 59, 1217-1232.

Woakes, M and Bafor, B.E (1983). Primary gold mineralization in Nigeria," in GOLD 1982: The Geology, Geochemistry and Genesis of Gold Deposits, R. P. Foster, Ed., Geological Society of Zimbabwe Special Publication no. 1, Balkema, Rotterdam, The Netherlands.

Wolfe MF, Schwarzbach S, Sulaiman RA (1998). Effects of mercury on wildlife: A comprehensive review. Environ Toxicol Chem. 17:146–160.

WHO (1996). Permissible limits of heavy metals in soil and plants (Geneva: World Health Organization), Switzerland.

Wu, B., Zhao, D.Y., Jia, H.Y., Zhang, Y., Zhang, X.X., Cheng, S.P (2009). Preliminary Risk Assessment of trace metal pollution in surface water from Yagtze River in Nanjing Section, China. B. Environ. *Contam. Toxicol*. 4, 405.

Xiao, Q., Zong, Y., & Lu, S. (2015). Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. *Ecotoxicology and Environmental Safety,* 120, 377–385

Yongming, H., Peixuan, D., Junji, C. and Posmentier, E. S (2006). Multivariate Analysis of Heavy Metals Contamination in urban dusts of Xi'an, Central China. *Sci. Total Environ*., 355, 176-186.

Zhang, H., Feng, X., Jiang, C., Li, Q., Liu, Y., Gu, C., Larssen, T. (2014). Understanding the paradox of selenium contamination in mercury mining areas: high soil content and low accumulation in rice. *Environmental Pollution*, *188*, 27 -36. https://doi.org/10.1016/j.envpol.2014.01.012.

Zheng, N, Liu, J, Wang, Q and Liang, Z (2010). Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China *Sci. Total Environ*. 726.408.

Figure 1. Mercury used for gold processing in Niger, Northwest, Nigeria.

Figure 2. Heating of amalgam in Niger, Northwest, Nigeria

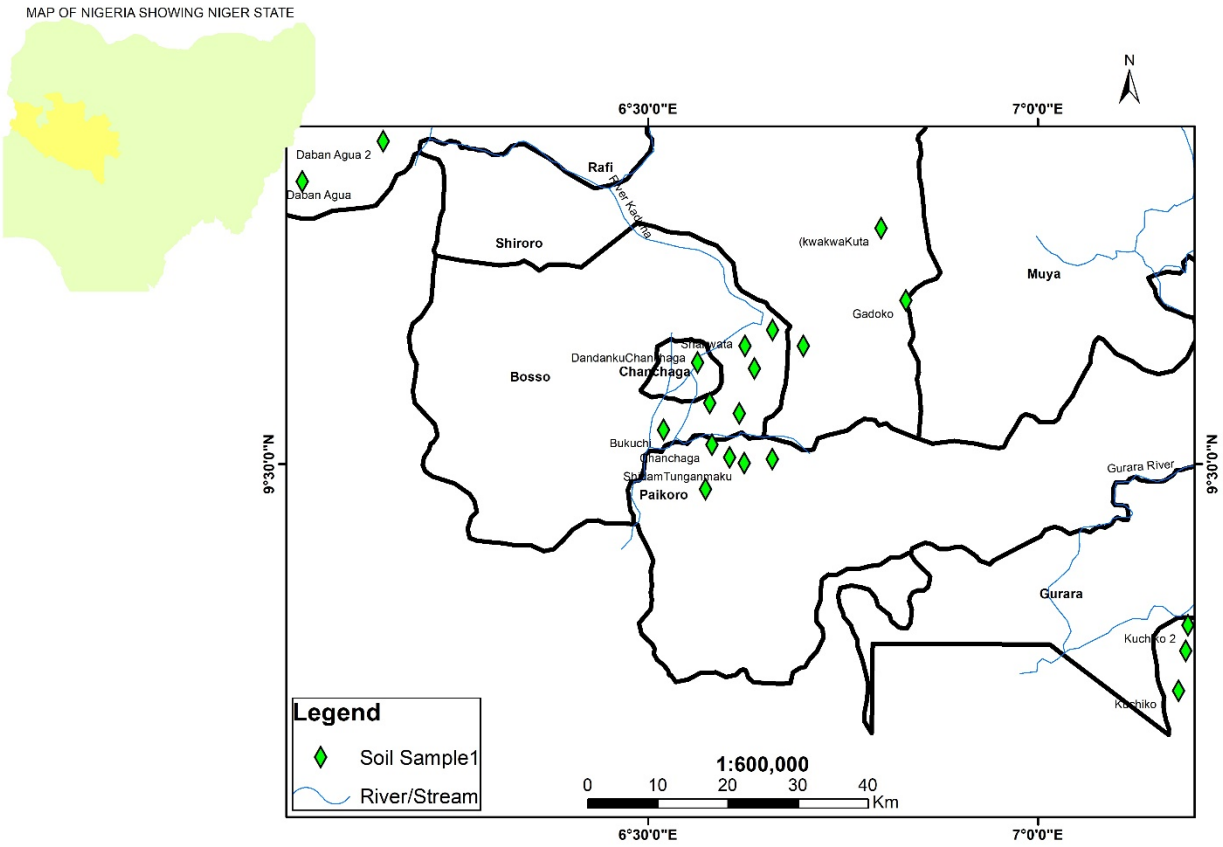

Figure 3. Map of the study Area and Sample Locations

Figure 4. Shakwata Open Pit Gold Mine in Niger, Northwest, Nigeria

Figure 5. Gold Panning of River Sediments in Niger, Northwest, Nigeria

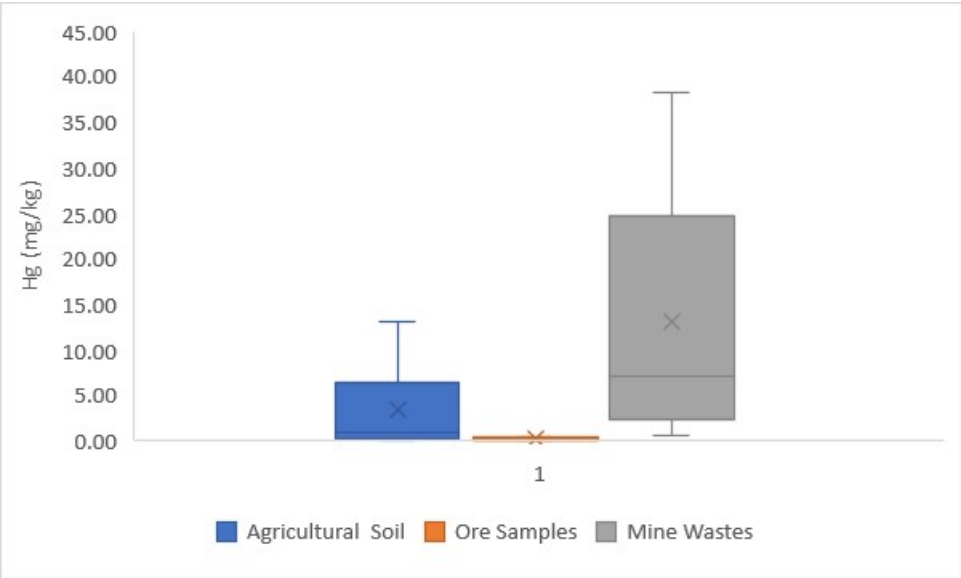

Fig 6. Concentration of Hg in different Soil Types

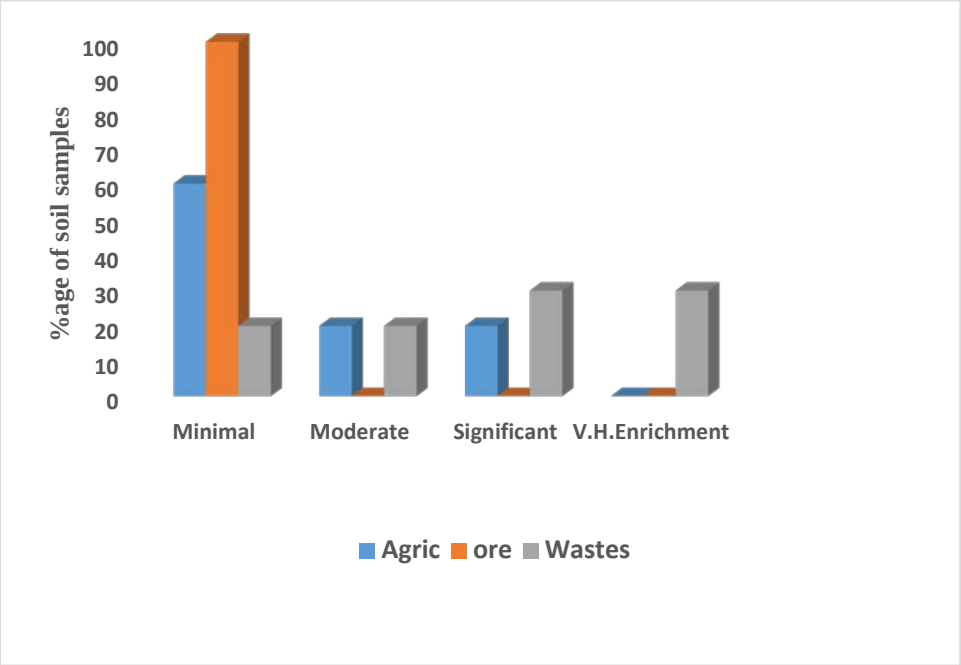

Figure 7. Classification of soil based on EF

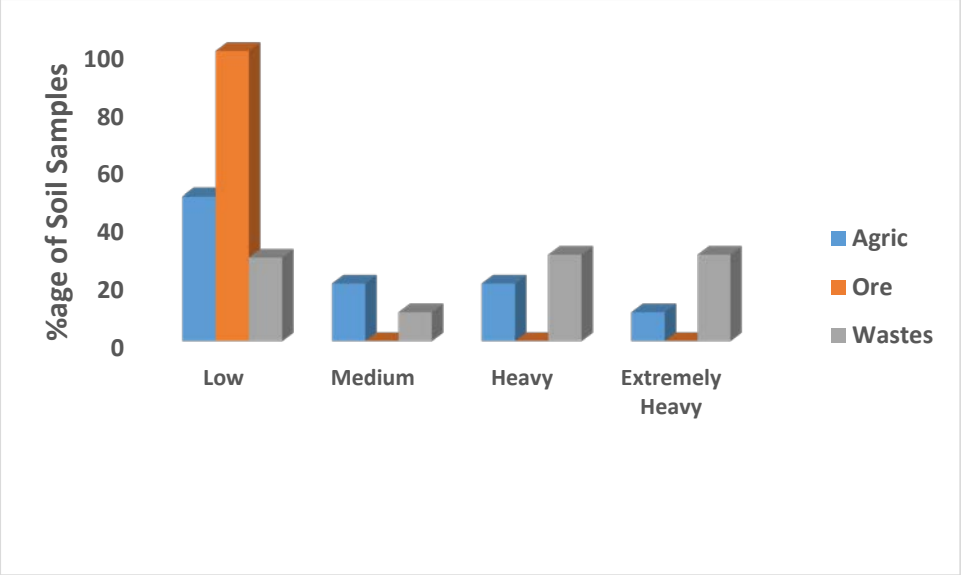

Figure 8. Classification of soil based on IGEO

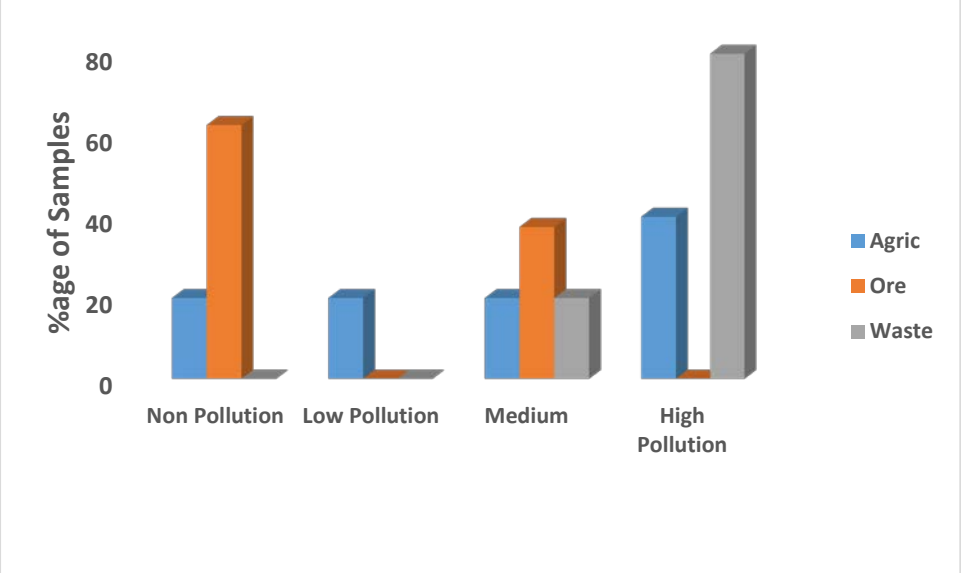

Figure 9. Classification of Soil based on PI

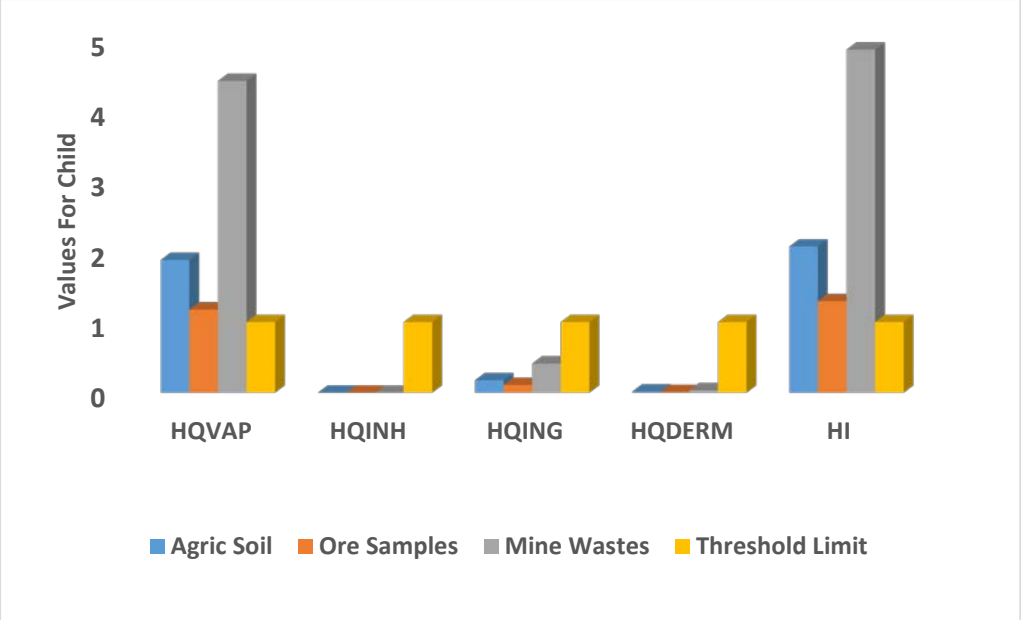

Figure 10. Hazard Quotient and Index Calculated for Child

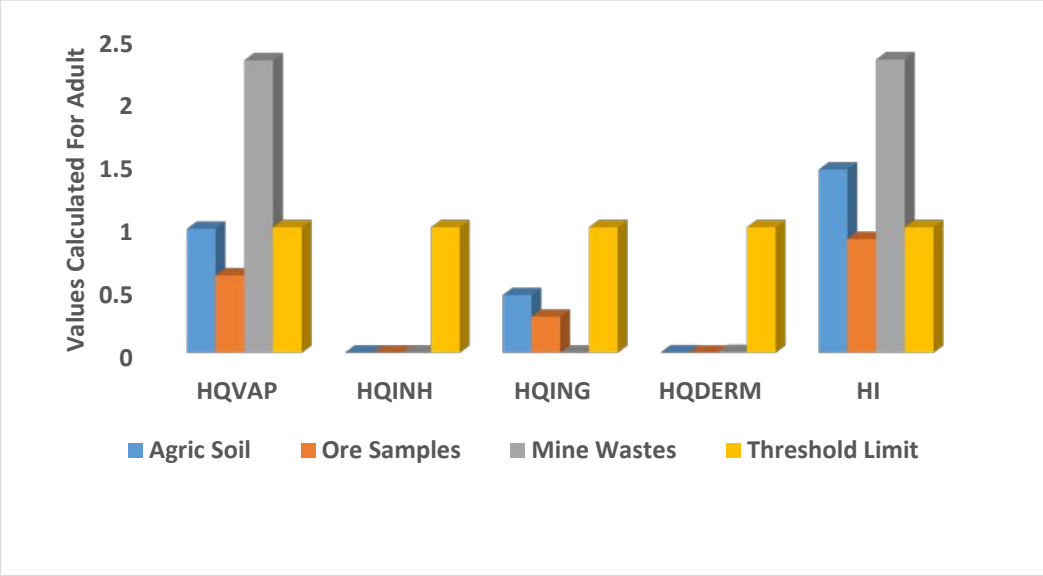

Figure 11. Hazard Quotient and Index Calculated for Adult

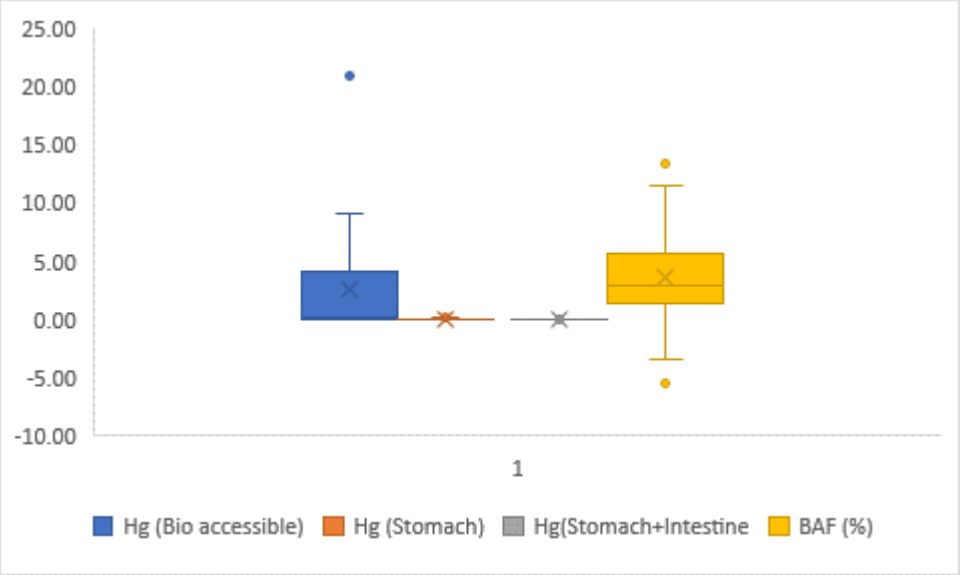

Figure 12. Summary of bioaccessible Hg in sample matrices.

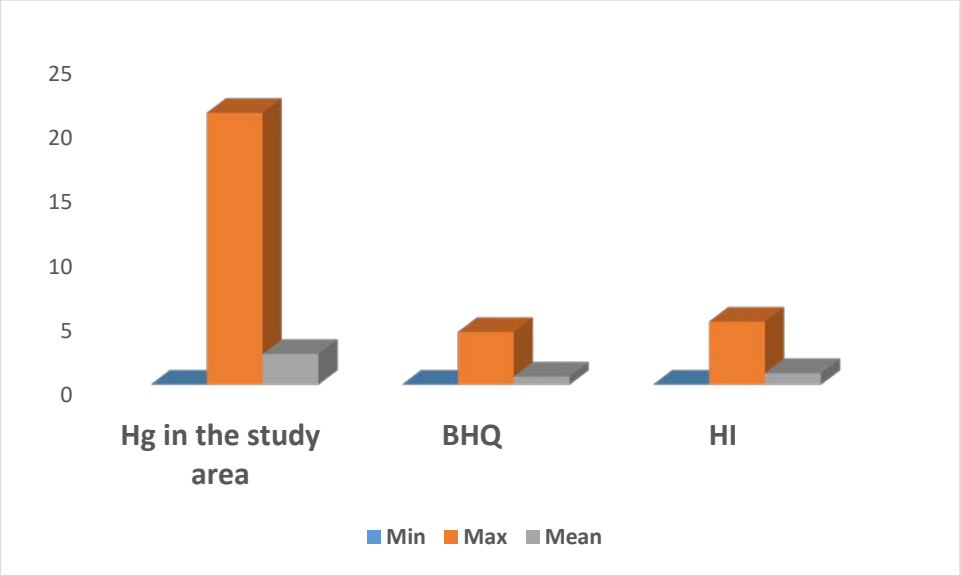

Figure 13. Comparison between Hg in the study area, BHQ and HI

Table 1. Sample Types and Locations in the Study Area

S/N	SAMPLE	CODE	LOCATION
1	Agricultural soil	S1	Gidanbire
2	Agricultural soil	S2	Metubi Crusher
3	Agricultural soil	S3	Mechanic Village
4	Agricultural soil)	S4	Shakwata
5	Agricultural soil	S5	Chanchaga
6	Agricultural soil	S6	Shidan Tungan Maku
7	Agricultural soil	S7	Shakwata
8	Agricultural soil	S8	Kuchiku
9	Agricultural soil	S9	Luku Chakwata
10	Agricultural soil	S10	Kuchiko
11	Agricultural soil	S11	Kuchiko Site II
12	Mine wastes	S12	Chanchaga
13	Mine wastes	S13	Shakwata
14	Mine wastes	S14	Gidanbiri Crusher
15	Mine wastes	S15	Chanchaga Crusher
16	Mine wastes	S16	Kuchiko Site II
17	Mine wastes	S17	Luku Chakwata
18	Mine wastes	S18	Kuchiko Site I
19	Mine wastes	S19	Old Gurusu
20	Mine wastes	S20	Metubi Crusher
21	Ore Sample	S21	Gidanbire
22	Ore Sample	S22	Metubi Crusher
23	Ore Sample	S23	Chanchaga Crusher
24	Ore Sample	S24	Old Gurusu
25	Ore Sample	S25	Luku Chakwata
26	Ore Sample	S26	Agua
27	Ore Sample	S27	Shakwata
28	Ore Sample	S28	Gandako
29	Ore Sample	S29	Borgu
30	Ore Sample	S30	Kuchiko Site II
31	Ore Sample	S31	Kuchiko Site I
32	Ore Sample	S32	Mechanic Village
33	Ore Sample	S33	Rafinzabo Sango

Table 2. Values of some parameters for the calculation of health risk assessment of Hg in mining soils as reported by Peng *et al.*, 2014

Factor	Definition	Units	Value		References
Csoil	Concentration of PTEs in soil	Mg/kg	Child	Adults	This Study
IngR	Ingestion Rate of soil	Mg/day	100	200	USEPA, 2001, Xiao, *et al.*, 2015
EF	Exposure Frequency	Day /year	350	350	Environmental site assessment guideline 2009, Xiao, et al., 2015
ED	Exposure Duration	Years	6	30	USEPA, 2001, Xiao, et al., 2015.
BW	Body weight of the exposed individual	Kg	16.2	61.8	Environmental site assessment guideline (2009), Xiao, *et al*., 2015.
AT_{nc}	Average Time	Day	365ED	365ED	USEPA, 1989, Xiao, *et al*., 2015.
AT_{ca}	averaging time for carcinogenic	Day	LT × 365	LT × 365	USDOE, 2011
LT	lifetime	Year	72	72	WHO,1996
AF	soil to skin adherence factor	Mg/cm^3	0.2	0.07	USDE, 2011
InhR	Inhalation rate of soil	m^3/day	10	20	Carla, *et a*l., 2010.
PEF	Particle emission factor	m^3/Kg	1.36 *10^9	1.36 *10^9	USEPA, 2001
SA	Skin surface area (SA)	cm^2	2800	5700	Carla, et al., 2010.
SAF	Soil adherence factor (AF)	mg/cm^2	0.07	0.2	Carla, et al., 2010.
IR	Soil ingestion rate-age adjusted	mg × year/kg/d	113	113	Luo, et al., 2012
DFS_{adj}	soil dermal contact factor-age-adjusted	mg × year/kg/d	362.4	362.4	Luo, *et a*l., 2012

Table 3. RfD values of Hg for different exposure pathways

RfD	Direct Ingestion	Dermal Absorption	Inhalation	Vapour
Hg	0.0003	0.00002	0.0000857	0.0000857

Table 4. Statistical values of Hg in the soil of the study area (mg/kg)

	Min	**Max**	**Mean**	**SD**	**Skew**	**CV**
Soil (Ore)	0.003	5.900	0.76	1.64	3.00	2.70
Soil (Agric)	0.002	5.570	1.23	1.88	1.76	3.20
Mine Wastes	0.190	20.99	5.58	3.38	1.91	11.43
Crustal Average (Taylor, 1964)	0.08					
USEPA Soil Screening Level (USEPA, 2013)	0.0023					

Table 5. Mean values of Hg in the Soil of the study area, other ASGM sites and different Guidelines

ASGM Locations and Guidelines of Hg	Mean Value of Mercury
Study Area Agric Soil Ore Sample Mine Wastes	 0.76 1.23 5.58
Crustal Average Value (Taylor 1964)	0.08
USEPA residential soil screening level (SSL) (USEPA, 1996)	0.0023
Upper crust Guideline (Wedepohl, 1995)	0.056
Upper Crust Guideline Taylor and Mclema, 1985	0.040
Anka, Zamfara, Nigeria (Lar Uriah, et al., 2013)	6.25
Rafi, Niger, Nigeria (Amadi et al., 2017)	50.17

Korea (Han et al., 2012),	0.204
Gilgit-Baltistan, Pakistan (Arjumand, et al., 2018	0.27
Venezuela (Garcıa-Sanchez et al., (2006)	0.049

Table 6. Summary of Contamination Indices of Hg in the study area

		EF	I-geo	PI
Agricultural soil	Min	0.004	-5.69	0.03
	Max	13.02	5.54	69.63
	Mean	6.57	1.15	15.41
Ore samples	Min	0.0008	-5.39	0.04
	Max	0.4	5.62	3.73
	Mean	1.09	0.47	1.37
Mine wastes	Min	0.5	0.63	2.32
	Max	38.19	7.45	262.33
	Mean	10.36	4.45	69.70

Table 7. Different Categories of BAF%

BAF	CATEGORY OF MOBILITY
Very High	>50
High	31-50%
Intermediate	16-30%
Low mobility	<15%

Appendix 1. Health Risk Assessment of Hg in the study Area Calculated for Child and Adult

		ADDVAP	ADDINH	ADDING	ADDDERM	HQVAP	HQINH	HQING	HQDERM	HI
Values Calculated for Child										
	Min	3.44E-06	8.27E-11	1.12E-06	6.3E-09	0.040161	9.65E-07	0.003749	0.0003	0.044211
Agric	Max	0.000161	3.88E-09	5.27E-05	2.95E-07	1.883361	4.52E-05	0.175799	0.014064	2.073269
	Mean	6.85E-05	1.65E-09	2.24E-05	1.25E-07	0.799001	1.92E-05	0.074581	0.005967	0.879569
	Min	4.17E-08	1E-12	1.36E-08	9.94E-11	0.000486	1.17E-08	4.54E-05	4.74E-06	0.000536
Ore	Max	0.000101	2.42E-09	3.3E-05	1.96E-07	1.177365	2.83E-05	0.109899	0.009313	1.296605
	Mean	2.23E-05	5.35E-10	7.28E-06	2.52E-08	0.259993	6.25E-06	0.024269	0.0012	0.285467
	Min	5.43E-08	1.31E-12	1.78E-08	1.33E-09	0.000634	1.52E-08	5.92E-05	6.31E-05	0.000756
Wastes	Max	0.000379	9.1E-09	0.000124	6.93E-07	4.417759	0.000106	0.412368	0.032989	4.863223
	Mean	4.78E-05	1.15E-09	1.56E-05	7.82E-08	0.558033	1.34E-05	0.052089	0.003725	0.61386
Values Calculated for Adults										
	Min	1.8E-06	4.34E-11	2.95E-06	1.18E-09	0.021056	5.06E-07	0.009827	5.6E-05	0.030939
Agric	Max	8.46E-05	2.03E-09	0.000138	5.52E-08	0.987393	2.37E-05	0.460833	0.002627	1.450876
	Mean	3.59E-05	8.63E-10	5.87E-05	2.34E-08	0.418894	1.01E-05	0.195505	0.001114	0.615523
Ore	Min	2.18E-08	5.25E-13	3.57E-08	1.42E-11	0.000255	6.12E-09	0.000119	6.78E-07	0.000375
	Max	5.29E-05	1.27E-09	8.64E-05	3.45E-08	0.617259	1.48E-05	0.288085	0.001642	0.907001
	Mean	1.17E-05	2.81E-10	1.91E-05	7.61E-09	0.136307	3.27E-06	0.063617	0.000363	0.200289
Waste	Min	2.85E-08	6.85E-13	4.65E-14	1.86E-11	0.000332	7.99E-09	1.55E-10	8.84E-07	0.000333
	Max	0.000198	4.77E-09	3.24E-10	1.29E-07	2.316107	5.56E-05	1.08E-06	0.006162	2.322325
	Mean	2.51E-05	6.02E-10	4.1E-11	1.63E-08	0.292561	7.03E-06	1.37E-07	0.000778	0.293346