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# Assessment of trace metal concentration and health risk of artisanal gold mining activities in Ijeshaland, Osun State Nigeria— Part 1

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ABSTRACT

This present study assessed the trace metal concentrations and human health risks associated with the activities of artisanal gold miners in Ijeshaland, Osun State, Southwestern Nigeria. Environmental samples, including surface water (rivers and streams), groundwater, bottom sediments, fish (Tilapia) and floating plants (ferns) were collected between 2011 and 2012 and analyzed for important parameters using standard procedures. Fifty four environmental samples were collected and analyzed for essential and nonessential trace metals. Data collected were subjected to simple descriptive and inferential statistics. Health risk indexes of noncarcinogenic and carcinogenic adverse effects of trace metals were determined in water and fish samples. Results of metal concentrations revealed Al ($305 \pm 950\ \mu g\ L^{-1}$) and Fe ($0.31 \pm 0.56\ mg\ L^{-1}$) in surface water higher than the World Health Organization (WHO) permissible limits in drinking water. The hazard quotient (HQ) values of Al and Fe (from surface and ground water), Mn (from groundwater) and Pb (from fish) were higher than 1.0 indicating noncarcinogenic adverse effects. The cancer risk (CR) values of Cd and Cr in groundwater, surface water and fish samples ranged between $7.9 \times 10^{-4}$ and $1.0 \times 10^{-2}$ thereby establishing their carcinogenic effects. The CR values of Ni and Pb in water consumed by infants and children were also higher than the acceptable limits of $1.0 \times 10^{-4}$. The results allow us to assert that the activities of the artisanal gold miners clearly affect human health.
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## 1. Introduction

The mining sector contributes to the economic development of any country through foreign exchange earnings, employment and improved standard of living. Gold mining in Nigeria could be dated back to 1913; but the production peak was experienced between 1933 and 1943 during which around 1.4 t of gold were produced (Australian Mine Limited, 2011; Gee, 2011). The gold production declined during the World War II period as mines were abandoned by the colonial companies. The Nigerian Mining Corporation, however, started exploring gold in the early 1980s but failed to be sustained due to lack of funds (MMSD, 2010). The discovery of petroleum as the mainstay of the country's economy also contributed to the lack of attention giving to gold mining despite its promising potentials (Paul, 2014). The Ijeshaland gold mining activities are mainly carried out by artisanal small-scale miners who worked with crude tools and equipment (Bradshaw, 1997; Gbadebo and Ekwue, 2014). Their activities include mining of gemstones (tourmaline, beryl, amethyst, aquamarine and garnet) and precious minerals (diamond and gold). These activities potentially result into environmental damages, social disruption and conflicts (Ako et al., 2014). Gold mining and processing operations (milling, grinding, concentrating ores) and disposal of tailings, along with mine/mill waste water are emission sources of environmental pollutants. Other environmental problems of gold mining include: land degradation, devegetation, loss of aquatic animals, soil pollution, water pollution and air pollution (Adriano, 1986). Apart from the environmental concerns of gold mining, the health problems of gold mining are numerous due to use of gravity concentration methods such as panning and sluicing during the processing operations (Adriano, 1986). Generally, metal contaminations may be linked directly to mineral exploitation, ore transportation, smelting and refining, disposal of the tailings and waste waters around the gold mines. Studies on health impacts of artisanal gold mining had been severally reported (Basu et al., 2015; Cobbina et al., 2015; Rajaee et al., 2015; Obiri et al., 2016). These studies revealed artisanal gold mining as the major exposure route to mercury. Artisanal mining releases 1000 t of mercury into the environment every year, which accounts for 30 to 40% of global mercury emissions (Basu et al., 2015). Mercury, cadmium, chromium and arsenic are metals of health concerns among the communities of gold miners (Obiri et al., 2016). Health problems associated with mercury include neurological disorder, cardiovascular diseases; increases in systolic blood pressure and diastolic blood pressure, and renal dysfunction (Rajaee et al., 2015, Choi et al., 2009; Goodrich et al., 2012). Cancer is the major health risk

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associated with exposure to cadmium, chromium and arsenic (Basu et al., 2015; IARC, International Agency for Research on Cancer, 2012). High levels of urinary aluminium, copper, manganese, lead, zinc, arsenic had been reported among the miners and community residents (Basu et al., 2015). The disposal of gold mine wastes often produces more environmental problems than the mining. The pollutants may be transported from the tailings and waste rock dumps to the nearby soils by acid mine drainage and/or atmospheric deposition of windblown dust. This depends on climatic and hydrologic conditions, which determines the locations of potentially contaminated areas (Aslibekian and Moles, 2003; Fernández-Caliani et al., 2009).

Recent studies had reported the negative impacts of gold mining activities of Ijeshaland gold city (Gbadebo and Ekwue, 2014; Ekwue et al., 2012; Ayantobo et al., 2014a; Olujimi et al., 2015). None of these studies had produced a detailed research on the multiple effects of the gold mining activities on surface water, groundwater, floating plants, bottom sediments and fish samples. The objective of this pilot study is to assess the trace metal concentrations and health risk associated with artisanal gold mining operations in the gold city of Ijeshaland, Osun State. The health assessment is very essential due to the fact that, groundwater, in form of hand-dug wells is mostly utilized for domestic and drinking purposes by the communities around the gold mines. Furthermore, during the dry season, people living around the area fetch water from the streams and rivers for domestic use.

## 2. Materials and method

### 2.1. The study area

The study areas are the gold mine sites in the gold city of Ijeshaland, Osun State. The sites are characterized by active artisanal and small scale gold mining activities. The main towns around the mining sites are Igun-Ijesha (24 carats alluvial gold), Iperindo (18 carats alluvial gold), Ijana Wasare (24 carats alluvial gold), Itagunmodi (18 carats alluvial gold), and Isanlu (18 carats alluvial gold). The mining sites are also characterized by varied vegetation, drainage pattern and geomorphic units. The sites are adequately accessible by a network of access roads and footpaths. The gold mine sites were within one of the six classes of the Basement Complex rock that is from slightly migmatised to nonmigmatised, metasedimentary, metasedimentary and metaigneous rock known as the Schist belt (Ayantobo et al., 2014a and b). This is a part of Ilesha-Ife Schist belt (Ademeso et al., 2013). The belt is one of the 11 Schist belts identified in Ademeso et al. (2013). The study area has two contrasting lithologies separated by NNE-SSW trending shear system- the Ifewara Fault Zone, which is occupied by the amphibole schist, amphibolites, talc-tremolite and pellitic rocks (TML, Tropical Mines Limited, 1996; Ayantobo et al., 2014 a, b). The eastern part has quartzite, quartz schist and amphibole schist. The gold deposit occurs in the eastern area that lies on the east of Ifewara fault zone. Gold occurs with ores such as: Pyrite, pyrrhotite and minor chalcopyrite, galena, sphalerite, magnetite and ilmenite. Adjacent to the gold bearing veins the host granite-gneiss has been hydrothermally altered to a sericitechlorite epidote assemblage (with also hematite and pyrite) (Ayantobo et al., 2014a and b). The geological setting of the study area is presented in Fig. 1 while Fig. 2 shows the map of sampling locations in the study area.

### 2.2. Sample collection and analysis

A total of fifty four environmental samples (surface water, groundwater; bottom sediment; floating plants and fish) were randomly collected within the vicinity of the gold mining sites between 2011 and 2012. Samples were analyzed for physical and chemical composition using standard procedures (APHA, American Public Health Association, 2005). Detailed analytical procedures would be discussed in the next section.

#### 2.2.1. Surface and groundwater samples

A total of 19 surface water (rivers and streams) and 9 groundwater samples were collected and analyzed for physical and chemical parameters. Water samples were collected with pre-washed white plastic bottles (2 L). Parameters analyzed were: pH, turbidity, fluoride, total cyanide (HCN), nitrate, bicarbonate and trace (essential and nonessential) metals. The essential trace metals were Co, Cr, Cu, Fe, Mn, Mo, Ni, Zn while the nonessential trace metals were Ag, Al, As, Au, Ba, Cd, Hg, Li, Pb, Sb, Ti, V). pH was determined using a pH meter (Combo Hi 98,130, Hanna USA) while turbidity, sulphate and nitrate were analyzed with UV–visible spectrophotometer (Hach DR/4000, UK) (EPA, 1980; APHA, American Public Health Association, 2005; EPA, 2009). Fluoride and total cyanide were also determined using the spectrophotometric method (Taiwo et al., 2012; EPA, 1980). Water samples for total HCN analysis were collected with separate bottles and preserved in-situ with 50% sodium hydroxide to pH of 12 (EPA, 1980). Bicarbonate, hardness, alkalinity was analyzed titrimetrically (Taiwo et al., 2012; Gbadebo et al., 2010). Samples for the measurement of metals were fixed in-situ with concentrated nitric acid (5 mL), before acid digestion (10 mL concentrated $HNO_3$). Details of acid digestion can be found elsewhere in Ayantobo et al. (2014a). All digested samples were sent to ACME Analytical Laboratory in Canada for metal analysis using the Inductively Coupled Plasma Mass Spectrophotometer (ICPMS) instrument. The procedures of ICPMS have been described in Taiwo et al. (2014).

#### 2.2.2. Bottom sediments

Ten bottom sediment samples were collected using a sediment sampler. The bottom sediments were air-dried, pulverized and allowed to pass through <0.5 mm sieve before an *aqua regia* (concentrated $HNO_3$ and HCl) acid digestion for analysis of metals as described in Taiwo et al. (2016). An Approximately 1.0 g (pulverized and sieved) bottom sediment sample was weighed into a 100 mL Erlenmeyer flask followed by introduction of 15 mL concentrated nitric acid and 5 mL concentrated hydrochloric acid. The mixture was heated at 95 ± 5 °C for 30–45 min inside a fume cupboard until a clear solution was obtained. The digested sample was allowed to cool and then filtered into a prewashed 100 mL

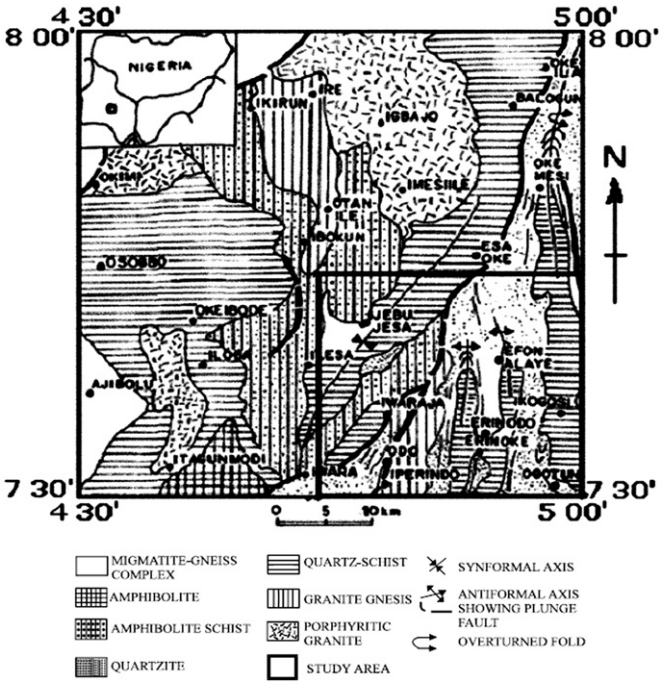


**Fig. 1.** showing the geological map of the study area (Source: Onyedim, 2007).

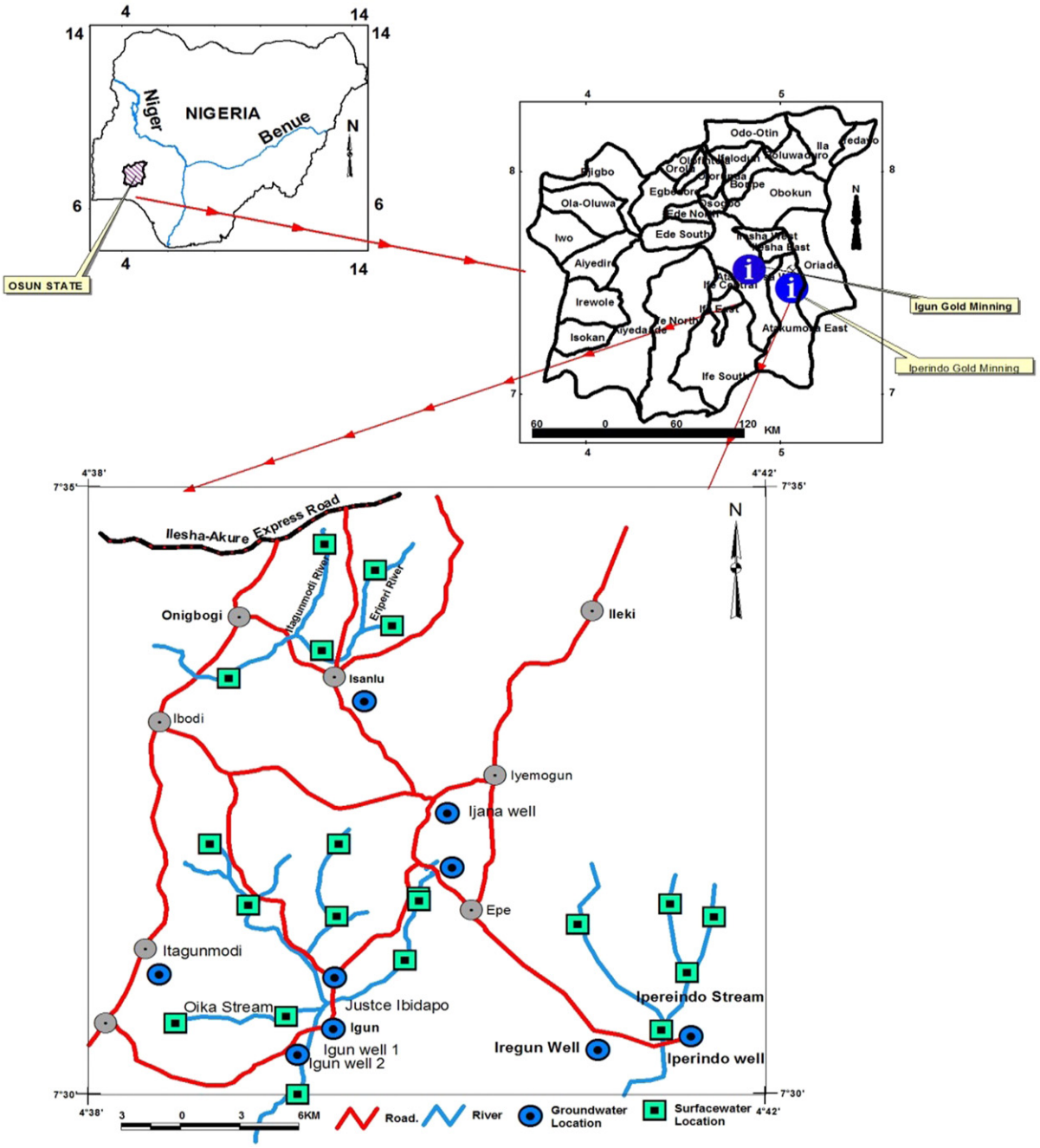


**Fig. 2.** Map showing the sampling sites in Ijeshaland, Osun State, Southwestern Nigeria.

plastic bottle which was made up to the mark with distilled water. The digested extract was analyzed for metals using the ICPMS instrument.

*2.2.3. Floating plant and fish*

Twelve floating plants (Ferns, *Salvinia natans*) and four fish (Tilapia) samples collected were oven-dried, ground and digested with mixed concentrated acids ($HNO_3$ and HCl) before analyzing for trace metals using the ICPMS instrument. The fish samples were collected from one of the rivers at the gold mining sites with the assistance of the local fishermen. The analyzed parts of fish samples were the gills, the guts and muscle. The digestion of plant and fish samples followed similar procedure as bottom sediments. This involves weighing 2.0 g of pulverized and sieved plant and fish samples into a conical flask. The mixture was then digested with mixed concentrated acids (15 mL $HNO_3$, 5 mL HCl) for 30–45 min under gentle heating at 95 ± 5 °C in a fume cupboard. The final extract was sent to ACME Laboratory in Canada for analysis of metals using the ICPMS instrument.

All chemicals used for analysis were of ultra-pure grade. Blank samples were also run to cancel the impurities introduced by analytical chemicals (Taiwo et al., 2014). Table 1 presents the detection limit of instrument, and accuracy error and precision of data. Detailed procedure for measurement of accuracy error and precision had been described in Cicchella et al. (2008). Detection limit was calculated using the six blank samples. Precision calculation was based on three in-house replicates and two blind duplicates. Accuracy was calculated on Acme's in-house reference material, TMDA-70. The laboratory accuracy error and

**Table 1**
Detection limit of instrument, accuracy error and precision of data.

| | Unit | Detection limit | Accuracy error (%) | Precision (%) |
|---|---|---|---|---|
| Nonessential metals | | | | |
| Ag | ppb | 0.01 | 7.3 | 67 |
| Al | ppb | 0.1 | 2.4 | 10.7 |
| As | ppb | 0.01 | 3.1 | 67 |
| Au | ppb | 0.01 | 0.0 | 57 |
| Ba | ppb | 0.01 | 6.2 | 30 |
| Cd | ppb | 0.01 | 3.1 | 44 |
| Hg | ppb | 0.01 | 0.0 | 156 |
| Li | ppb | 0.01 | 2.1 | 29 |
| Pb | ppb | 0.01 | 8.2 | 25 |
| Sb | ppb | 0.05 | 7.3 | 1.1 |
| Ti | ppb | 5 | 0.0 | 45 |
| **V** | ppb | 0.1 | 1.3 | 100 |
| Essential metals | | | | |
| Co | ppb | 0.1 | 2.4 | 29 |
| Cr | ppb | 0.1 | 2.2 | 45 |
| Cu | ppb | 0.1 | 4.7 | 9.1 |
| Fe | ppm | 0.001 | 1.2 | 32 |
| Mn | ppm | 0.001 | 3.3 | 52 |
| Mo | ppb | 0.1 | 1.3 | 89 |
| Ni | ppb | 0.1 | 1.9 | 29 |
| **Zn** | ppb | 0.5 | 1.9 | 19.5 |

precision were determined using formula presented in Eqs. 1 and 2 (Cicchella et al., 2008).

$$\text{Accuracy error} = [\text{abs}(X - TV)/TV] \times 100 \quad (1)$$

where,
X = laboratory's analysis result for the performance sample (standard sample)
TV = true value of the performance sample (standard sample).
The precision was calculated as Relative Percent Difference (%RPD) as:

$$\%RPD = [\text{abs}(SV - DV)/0.5 * (SV + DV)] \times 100 \quad (2)$$

where,
SV = the original sample value
DV = the duplicate sample value

### 2.3. Data analysis

Data collected were subjected to simple descriptive (mean and standard deviation) and inferential statistics (Analysis of Variance and Duncan Multiple Range Test, DMRT) using SPSS for Windows version 16.0.

### 2.4. Health risk assessment

The health risk assessments for trace metals were calculated for average daily dose (ADD), noncancer hazard index (HI) and cancer risk (CR) using the procedures described in USEPA (United States Environmental Protection Agency) (2002, 2007, 2012)), Batayneh (2010) and Ayedun et al. (2015).
Average Daily Dose (ADD) was calculated as:

$$ADD = \frac{C \times IR \times ED \times EF}{BW \times AT} \quad (3)$$

where,
ADD = Average Daily Dose in drinking water or fish ($\mu g\ kg^{-1}\ day^{-1}$).
IR = Ingestion rate of water or fish; water = 2 L $day^{-1}$ for an adult, 1 L $day^{-1}$ for a child, 0.75 L $day^{-1}$ for an infant (Ayedun et al., 2015); Fish = 24.7 g $day^{-1}$ for an adult based on the Food and Agriculture Organization (FAO) annual per capita fish consumption statistics for Nigeria given as 9.0 kg (FAO, 2008).
C = Concentration of trace metals in water ($\mu g\ L^{-1}$) or fish ($\mu g\ kg^{-1}$) samples.
BW = Body weight (kg); 60 kg for an adult, 10 kg for a child, 5 kg for an infant (Ayantobo et al., 2014a).
EF = Exposure frequency (day $year^{-1}$) = 350 days $year^{-1}$.
ED = Exposure duration (years) = 30 years for an adult, 6 years for a child and 1 year for an infant (USEPA, United States Environmental Protection Agency, 2001; enHealth, 2012).
AT = Averaging time = life expectancy (years).
AT = ED for noncarcinogenic effects while AT = 54.5 years (53 years for men and 56 years for women) for carcinogenic effects on adult (WHO, 2015a) (It should be noted that the averaging time for an infant and a child was based on their lifetime exposure where AT = ED).

$$\text{Provisional Tolerable Weekly Intake (PTWI)} = ADD * 7 \quad (4)$$

Noncancer hazard index (HI) was calculated as the sum of hazard quotients (HQ)

$$HI = \Sigma_{i=1}^{n} HQ \quad (5)$$

$i = 1 \ldots n$

$$\text{Hazard quotient (HQ)} = \frac{ADD}{RfD} \quad (6)$$

where,
ADD = Average Daily Dose in drinking water and fish ($\mu g\ kg^{-1}\ day^{-1}$),
RfD = Reference Dose ($\mu g\ kg^{-1}\ day^{-1}$) adapted from USEPA (United States Environmental Protection Agency) (2001)
N = numbers of elements observed.
HQ > 1 denotes noncarcinogenic adverse effects,
HQ < 1 denotes no adverse effects.
Cancer Risk was calculated as:

$$Risk = ADD \times SF \quad (7)$$

where,
ADD = Average Daily Dose in drinking water and fish ($\mu g\ kg^{-1}\ day^{-1}$),
SF = Slope Factor ($1/\mu g\ kg^{-1}\ day^{-1}$).

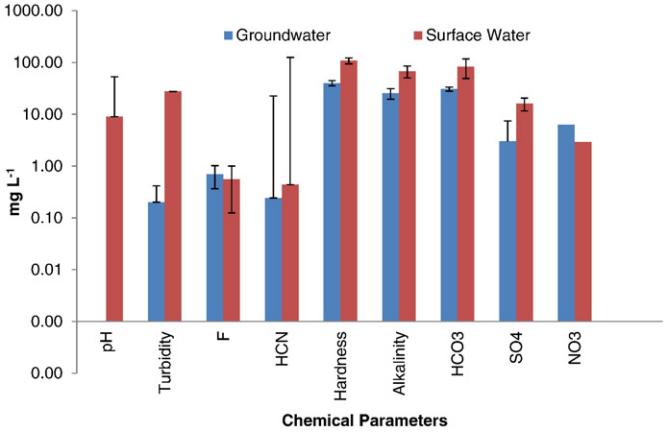


**Fig. 3.** Mean concentrations of important water quality parameters.

**Table 2**
Essential metal concentrations in environmental samples collected at the vicinity of the gold mines.

| | | Surface water (μg $L^{-1}$) | Groundwater (μg $L^{-1}$) | Sediment (μg $kg^{-1}$) | Fish muscle (μg $kg^{-1}$) | Fish gills (μg $kg^{-1}$) | Fish guts (μg $kg^{-1}$) | Plant (μg $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Metals | N | 19 | 9 | 10 | 4 | 4 | 4 | 12 |
| Co | Mean ± SD | 0.1 ± 0.1$^{a}$ | 2.8 ± 5.5$^{ab}$ | 7.7 ± 16.2$^{ab}$ | 4.9 ± 4.0$^{ab}$ | 14.9 ± 18.3$^{b}$ | 7.8 ± 8.5$^{ab}$ | 6.9 ± 13.2$^{ab}$ |
| | Range | <0.1–0.6 | <0.1–16.8 | <0.1–43.0 | 1.2–10.5 | 4.5–42.2 | 2.9–20.5 | 0.3–47.3 |
| Cr | Mean ± SD | 3.0 ± 1.8$^{a}$ | 8.3 ± 11.5$^{a}$ | 39.7 ± 96$^{ab}$ | 71.8 ± 69.6$^{b}$ | 70.2 ± 44.1$^{b}$ | 18.5 ± 22.1$^{ab}$ | 4.8 ± 4.7$^{a}$ |
| | Range | 1.5–9.8 | 0.8–34.4 | <0.1–299 | 2.9–156.6 | 15.6–121.4 | 2.9–49.8 | 1.4–18.2 |
| Cu | Mean ± SD | 2.0 ± 1.0$^{a}$ | 1.5 ± 0.7$^{a}$ | 8.5 ± 18.1$^{a}$ | 60.6 ± 18.7$^{b}$ | 319.8 ± 504$^{c}$ | 100.4 ± 40.3$^{b}$ | 5.1 ± 3.9$^{a}$ |
| | Range | 0.8–4.2 | 0.7–2.5 | <0.1–48.2 | 35.0–78.0 | 57.3–1076 | 78.0–160.6 | 0.7–14.5 |
| Fe* | Mean ± SD | 0.31 ± 0.6$^{a}$ | 0.01 ± 0.01$^{b}$ | 1.9 ± 3.6$^{b}$ | 7.4 ± 4.7$^{b}$ | 7.6 ± 9.2$^{a}$ | 7.7 ± 4.2$^{a}$ | 1.2 ± 2.1$^{a}$ |
| | Range | 5.0–2318 | 5.0–57.0 | BDL-9.1 | 1.9–12.5 | 1.5–21.2 | 1.8–11.4 | 0.0–7.2 |
| Mn* | Mean ± SD | 0.002 ± 0.002$^{a}$ | 0.1 ± 0.2$^{b}$ | 0.3 ± 0.1$^{a}$ | 0.7 ± 0.7$^{c}$ | 1.2 ± 1.9$^{d}$ | 1.0 ± 0.7$^{cd}$ | 1.2 ± 2.8$^{d}$ |
| | Range | BDL-0.01 | BDL-0.4 | BDL-0.5 | 0.6–1.6 | 0.1–4.1 | 0.2–1.8 | 0.04–10.0 |
| Mo | Mean ± SD | 0.6 ± 0.7 $^{a}$ | 0.6 ± 0.6$^{a}$ | 0.3 ± 0.4$^{a}$ | 7.6 ± 6.9$^{bc}$ | 8.6 ± 5.8$^{c}$ | 5.3 ± 6.2$^{b}$ | 0.9 ± 1.7$^{a}$ |
| | Range | <0.1–3.0 | <0.1–2.0 | <0.1–1.4 | 0.9–15.8 | 1.0–15.1 | 0.8–14.5 | <0.1–6.3 |
| Ni | Mean ± SD | 0.9 ± 0.7$^{a}$ | 6.1 ± 8.3$^{a}$ | 15.7 ± 18.1$^{b}$ | 28.0 ± 11.6$^{c}$ | 20.1 ± 4.4$^{bc}$ | 26.2 ± 5.3$^{c}$ | 2.3 ± 3.3$^{a}$ |
| | Range | 0.3–3.1 | <0.1–20.3 | <0.1–32.5 | 12.7–40.9 | 16.0–26.2 | 18.2–29.1 | <0.1–11.9 |
| Zn | Mean ± SD | 8.7 ± 7.7$^{a}$ | 15.4 ± 10.2$^{a}$ | 79.0 ± 22.6$^{b}$ | | | | 40.1 ± 22.3$^{c}$ |
| | Range | 1.8–27.9 | 5.1–29.8 | 63.0–95.0 | | | | 10.7–65.1 |

SD = Standard Deviation, Superscripts of similar letters are not significantly different at $p > 0.05$; * concentrations in ppm; BDL-Below detection limit (<0.001 ppm).

## 3. Results and discussion

### 3.1. Trace metal concentrations and other parameters measured in environmental samples

Fig. 3 shows the mean values of important water quality parameters measured in water samples. The pH of surface water (9.9 ± 0.1) was alkaline in nature and slightly higher than the World Health Organization (WHO) permissible range of 6.5–8.5 in drinking water (WHO, 2011). The average turbidity (27.6 ± 44 NTU) value in surface water was higher than the WHO limit of 5.0 NTU (WHO, 2011). The high turbidity value observed in surface water indicates water pollution probably from erosion of mining wastes into the rivers and streams. High turbidity in water body is usually associated with presence of microorganisms and clay particles (Taiwo et al., 2011; Taiwo et al., 2012). The mean total cyanide (HCN) concentration was significantly higher ($p < 0.05$) in surface water (0.4 ± 0.4 mg $L^{-1}$) than groundwater (0.2 ± 0.3 mg $L^{-1}$). The concentration of HCN obtained in this study was higher than the recommended safe limit of 5.2 μg $L^{-1}$ total cyanide (Tarras-Wahlberg et al., 2000) and 10 μg $L^{-1}$ free cyanide (Eisler, 2000; Eisler and Wiemeyer, 2004) that could be chronically exposed to in drinking water. The high concentration of HCN in water samples may be linked directly to the gold processing activities in the study area. The use of cyanide for gold extraction has been documented (Korte et al., 2000). HCN data depicting wide variations may be attributed to periodic pollution episode from gold mining activities.

The fluoride concentrations were generally <1.0 mg $L^{-1}$ in surface water and groundwater samples, but higher fluoride concentration was observed in groundwater samples. Exposure to high concentration of fluoride in drinking water may result into fluorosis; a condition characterized by staining and pitting of the teeth (WHO, 2015b). Other water parameters such as nitrate, sulphate alkalinity, and hardness measured in surface water and ground water were within the WHO permissible standards. Bicarbonate, HCN, hardness, alkalinity and

**Table 3**
Nonessential trace metal concentrations in environmental samples collected at the vicinity of the gold mines.

| | | Surface water (μg $L^{-1}$) | Groundwater (μg $L^{-1}$) | Sediment (μg $kg^{-1}$) | Fish muscle (μg $kg^{-1}$) | Fish gills (μg $kg^{-1}$) | Fish guts (μg $kg^{-1}$) | Plant (μg $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Metals | N | 19 | 9 | 10 | 4 | 4 | 4 | 12 |
| Ag | Mean ± SD | <0.01 | 0.1 ± 0.2$^{a}$ | 13.7 ± 9.5$^{a}$ | 100.8 ± 72.3$^{c}$ | 145.2 ± 69.4$^{d}$ | 82.7 ± 11.9$^{c}$ | 0.1 ± 0.2$^{b}$ |
| | Range | <0.01–0.1 | <0.01–0.6 | 0.1–30.6 | 11.1–175.2 | 51.3–214.7 | 76.1–100.6 | <0.01–0.6 |
| Al | Mean ± SD | 305 ± 950$^{a}$ | 21.8 ± 32.2$^{a}$ | 8.5 ± 6.2$^{a}$ | 2.3 ± 1.6$^{a}$ | 2.5 ± 2.6$^{a}$ | 1.6 ± 0.7$^{a}$ | 47.1 ± 47.8$^{a}$ |
| | Range | 0.5–4171 | 1.0–78 | 1.6–20.8 | 0.6–3.7 | 0.4–6.4 | 0.6–2.0 | 4.0–161 |
| As | Mean ± SD | 0.3 ± 0.1$^{a}$ | 0.4 ± 0.3$^{a}$ | 22.3 ± 15.7$^{b}$ | 2.1 ± 1.5$^{a}$ | 2.2 ± 2.4$^{a}$ | 2.2 ± 1.0$^{a}$ | 1.0 ± 1.5$^{a}$ |
| | Range | 0.3–0.8 | 0.3–1.1 | <0.01–52 | 0.7–3.8 | 0.7–5.7 | 0.7–2.9 | <0.01–5.1 |
| Au | Mean ± SD | <0.01 | 0.02 ± 0.03 | 0.1 ± 0.1$^{a}$ | <0.01 | <0.01 | <0.01 | 1.7 ± 3.6$^{a}$ |
| | Range | <0.01–0.1 | <0.01–0.1 | <0.01–0.1 | <0.01–0.1 | <0.01–0.1 | <0.01–0.1 | 0.1–12.5 |
| Ba | Mean ± SD | 52.1 ± 18.9$^{a}$ | 140.8 ± 91.7$^{b}$ | 56.3 ± 116$^{a}$ | 324.9 ± 167$^{c}$ | 209.2 ± 130$^{c}$ | 567.5 ± 547$^{d}$ | 160.1 ± 218$^{ab}$ |
| | Range | 20.4–92.4 | 54.7–337.8 | 2.5–355 | 117.2–525 | 68.9–382.6 | 134.5–1300 | 28.4–831.5 |
| Cd | Mean ± SD | <0.01 | 0.1 ± 0.1$^{a}$ | 2.7 ± 2.1$^{b}$ | 7.6 ± 1.4$^{c}$ | 6.5 ± 2.4$^{c}$ | 7.8 ± 2.5$^{c}$ | 0.5 ± 1.6 $^{a}$ |
| | Range | <0.01–0.2 | <0.01–0.2 | 0.1–6.8 | 6.7–9.6 | 4.5–9.8 | 6.1–11.6 | <0.01–5.5 |
| Hg | Mean ± SD | 0.1 ± 0.1$^{a}$ | 0.1 ± 0.1$^{a}$ | <0.01 | 1.5 ± 1.1$^{a}$ | 1.1 ± 0.6$^{a}$ | 0.8 ± 0.9$^{a}$ | 18.5 ± 14.9$^{b}$ |
| | Range | <0.01–0.4 | <0.01–0.3 | <0.01 | <0.01–2.6 | 0.4–1.9 | <0.01–1.9 | 4.0–45 |
| Li | Mean ± SD | 0.7 ± 0.6$^{a}$ | 3.1 ± 2.5$^{b}$ | 1.5 ± 2.8$^{a}$ | 1.2 ± 0.4$^{a}$ | 1.8 ± 1.9$^{a}$ | 1.0 ± 0.2$^{a}$ | |
| | Range | 0.2–2.4 | 0.3–7.9 | <0.01–7.4 | 0.9–1.7 | 0.8–4.7 | 0.9–1.3 | |
| Pb | Mean ± SD | 0.8 ± 0.8$^{a}$ | 0.6 ± 1.1$^{a}$ | 12.3 ± 2.9$^{a}$ | 78.5 ± 27.6$^{b}$ | 72.1 ± 10.2$^{c}$ | 57.0 ± 28.5$^{c}$ | 1.9 ± 1.7$^{a}$ |
| | Range | 0.1–2.7 | 0.1–3.3 | 10.2–14.3 | 39.0–98.1 | 60.2–85.2 | 39.0–98.9 | 0.3–5.9 |
| Sb | Mean ± SD | 0.6 ± 0.8$^{a}$ | 0.6 ± 0.5$^{a}$ | 0.3 ± 0.1$^{a}$ | 2.3 ± 0.5$^{b}$ | 4.8 ± 1.6$^{c}$ | 3.1 ± 2.4$^{b}$ | 0.1 ± 0.0$^{a}$ |
| | Range | <0.05–3.3 | <0.05–1.3 | 0.2–0.3 | 1.7–2.9 | 2.8–6.3 | 1.9–6.7 | <0.05–0.2 |
| Ti | Mean ± SD | 11.4 ± 22.9$^{a}$ | 5.0 ± 0.00$^{a}$ | 2.5 ± 1.4$^{a}$ | 297.8 ± 333$^{c}$ | 300.8 ± 230$^{c}$ | 161.3 ± 73.1$^{b}$ | 32.3 ± 30.0$^{ab}$ |
| | Range | 5.0–105 | 5.0–5.0 | 1.5–3.5 | 94.0–791 | 67.0–499 | 99.0–240 | 9.0–119 |
| V | Mean ± SD | 0.7 ± 1.4$^{a}$ | 1.2 ± 1.7$^{a}$ | 158.5 ± 55.9$^{c}$ | 1.8 ± 0.3 $^{a}$ | 2.8 ± 0.9$^{ab}$ | 4.8 ± 1.3$^{b}$ | 6.9 ± 9.2$^{b}$ |
| | Range | <0.1–4.7 | <0.1–4.0 | 119–198 | 1.0–1.8 | 1.8–2.8 | 3.2–4.8 | 1.0–33 |

SD = Standard deviation.

**Table 4**
Non-cancer Hazard Quotient (HQ) and Hazard Index (HI) values of elements in water and fish samples.

| Metal | RfD | Source of RfD | HQ surface water | | | HQ groundwater | | | HQ fish |
|---|---|---|---|---|---|---|---|---|---|
| | | | Adult | Child | Infant | Adult | Child | Infant | Adult |
| | $\mu g kg^{-1}$ $day^{-1}$ | | | | | | | | |
| Ag | 5* | | 0.05 | 0.001 | 0.001 | 0.001 | 0.002 | 0.003 | 0.08 |
| Al | 0.4 | IRIS | 9.2 | 25.7 | 38.6 | 1.7 | 5.2 | 7.8 | 22.7 |
| As | 0.3 | IRIS | 0.04 | 0.1 | 0.1 | 0.03 | 0.1 | 0.2 | 0.03 |
| Au | 5 | IRIS | 0.000 | 0.001 | 0.001 | 0.000 | 0.001 | 0.001 | 0.000 |
| Ba | 200 | IRIS | 0.01 | 0.02 | 0.04 | 0.02 | 0.07 | 0.10 | 0.01 |
| Cd | 0.5 | IRIS | 0.04 | 0.01 | 0.01 | 0.00 | 0.01 | 0.02 | 0.06 |
| Co | 30* | | 0.000 | 0.000 | 0.001 | 0.003 | 0.01 | 0.01 | 0.001 |
| Cr | 3 | IRIS | 0.03 | 0.1 | 0.1 | 0.1 | 0.3 | 0.4 | 0.1 |
| Cu | 1.1* | | 0.05 | 0.2 | 0.3 | 0.04 | 0.1 | 0.2 | 0.2 |
| Fe | 0.26* | | 37.9 | 113.9 | 170.9 | 1.3 | 4.0 | 6.0 | 113.4 |
| Hg | 0.3 | IRIS | 0.01 | 0.02 | 0.03 | 0.01 | 0.02 | 0.04 | 0.02 |
| Mn | 5(water)<br>140(food) | IRIS | 0.01 | 0.04 | 0.1 | 0.6 | 1.7 | 2.5 | 0.02 |
| Mo | 5 | IRIS | 0.00 | 0.01 | 0.02 | 0.00 | 0.01 | 0.02 | 0.01 |
| Ni | 20 | IRIS | 0.00 | 0.00 | 0.01 | 0.01 | 0.03 | 0.04 | 0.01 |
| Pb | 0.14* | | 0.2 | 0.6 | 0.8 | 0.1 | 0.4 | 0.6 | 2.2 |
| Sb | 0.4 | IRIS | 0.05 | 0.1 | 0.2 | 0.05 | 0.1 | 0.2 | 0.02 |
| V | 9* | | 0.001 | 0.004 | 0.01 | 0.002 | 0.01 | 0.01 | 0.000 |
| Zn | 300* | | 0.000 | 0.001 | 0.002 | 0.001 | 0.003 | 0.004 | 0.001 |
| **ΣHQ or HI** | | | 47.6 | 140.8 | 211.3 | 4.1 | 12.2 | 18.3 | 138.9 |

* RfD = http://web.ornl.gov/sci/env_rpt/aser95/tb-6-9.pdf. IRIS- Integrated risk information System, USEPA (United States Environmental Protection Agency) (2001, 2002).

sulphate were observed at higher concentrations ($p < 0.05$) in surface water than groundwater.

Table 2 presents the average concentration of essential trace metals observed in surface water, groundwater, bottom sediment, fish and the plant samples. Among the essential trace metals, Fe was measured at a significantly higher concentration ($p < 0.05$) in surface water than groundwater by 31 times, while Mn was observed 50 times greater in groundwater than surface water. Approximately 21% of the total sampled rivers and streams have the average values of Fe higher than the WHO permissible standard of 0.3 mg $L^{-1}$ in drinking water (WHO, 2011). Fe was also the most abundant essential trace metal in the bottom sediment, fish and plant samples. The WHO standard for Fe in sediments is 2% (20,000 mg $kg^{-1}$) (WHO, 2004), which was higher than the average Fe value obtained in this study. A study had shown Fe as the most abundant metal measured in Jimi River near the Obuasi gold mine in Ghana (Asare-Donkor et al., 2015). Other parameters measured in the bottom sediments were lower than the WHO (2004) permissible standard.

Cu and Mn were observed at significantly higher ($p < 0.05$) concentrations in fish gills than other parts of the fish samples. The copper concentrations observed in fish guts and gills were higher than the values reported in four fish species collected from Parangipettai Coast, South East Coast of India (Raja et al., 2009). Cu is an essential metal required for body metabolism, but can be toxic at higher concentration. Toxic effects of Cu include nausea, vomiting, stomach cramps or diarrhea (ATSDR, Agency for Toxic Substances and Disease Registry, 2015a). Animal studies had shown high ingestion of Cu to cause decreased fetal growth (ATSDR, Agency for Toxic Substances and Disease Registry, 2015a). Mn concentration was also observed higher in fish gills than the values reported in two fish species, *Aleper para and Atropus atropus* by Rajaee et al., 2015. Generally, most of the metals were concentrated in the gills as it serves as the respiratory and excretory organs for fish (Sharon et al., 2012). It is expected therefore, that the gills accumulate more pollutants from the aquatic environment than other parts of fish (Uzairu et al., 2009). In the plant samples, Fe and Mn were the most abundant essential metals. The order of abundance of metals in plants was Fe > Mn > Zn > Co > Cu. A similar study by Espinoza-Quinones et al. (2005) reported the order of abundance of metals in macrophytes sampled in a polluted river Brazil as Fe > Mn > Zn > Cu.

Table 3 represents the concentrations of nonessential metals measured in the environmental samples. Al was the highest measured nonessential metal in surface water while Ba was the highest measured nonessential metal in groundwater and plants. About 26% of the total sampled rivers and streams have the average values Al higher than the WHO standards of 0.20 mg $L^{-1}$ (WHO, 2011). Vanadium was the highest observed nonessential trace metal in the bottom sediment samples. In the fish samples, the most abundant nonessential metals were Ba, Ti, Ag and Pb. The occurrence of nonessential metals like Ag, Ba, Ti and Pb in fish muscle may be dangerous to human health when consumed. The mean value of Hg observed in the fish samples was lower than the value of 0.008 mg $kg^{-1}$ reported in fish samples collected from Manyera River near a gold mine site in Niger State (Idowu et al., 2013).

The most abundant trace elements measured in plant samples were Ba, Al and Cd. Nonessential metals such as Ag, Ba, Cd, Pb, Sb and Ti were observed at significant higher concentrations ($p < 0.05$) in fish than other environmental samples. This shows the evidence of bioaccumulation of trace metals in fish samples with consequent adverse effects on human health. According to Mansour and Sidky (2002), metal accumulation in fish tissues is an indication of water quality problem. The activities of the artisanal gold miners might be responsible for the high concentrations trace metals in fish samples. The presence of high value of Ba in plants may pose serious deleterious effects to aquatic organisms that consume the plants. Ba toxicity has been documented to include abdominal, cramp, diarrhea, muscle weakness, difficulty in breathing, vomiting, increased/decreased blood pressure, changes in hearth rythms and death (Mansour and Sidky, 2002). Au was observed at below detection limit (<0.01 μg $L^{-1}$) in surface water while low Au concentration of 0.03 ± 0.02 μg $L^{-1}$ was observed in groundwater samples. In one of the fish samples, Au concentration of 0.08 μg $kg^{-1}$ was observed in the muscle and 0.07 μg $kg^{-1}$ in the gills. Cd was also found at below detection limit (<0.01 μg $L^{-1}$) in surface water samples but occurred at a significant concentration ($p < 0.05$) in groundwater, bottom sediment, fish and plant samples.

Most of the metals measured at noticeable amounts in fish samples are toxic. For instance, Ni, Cr and Cd are human carcinogens while Pb affects the central and peripheral nervous system, damages kidney and causes death at high concentration (WHO, 2011). In 2010, >400 deaths (mainly children) were reported in Zamfara State, Nigeria due to lead poisoning (Galadima et al., 2011). Ag, Ba and Hg are also toxic metals with no physiological functions in human system (ATSDR, Agency for Toxic Substances and Disease Registry, 1990; Mansour and Sidky, 2002).

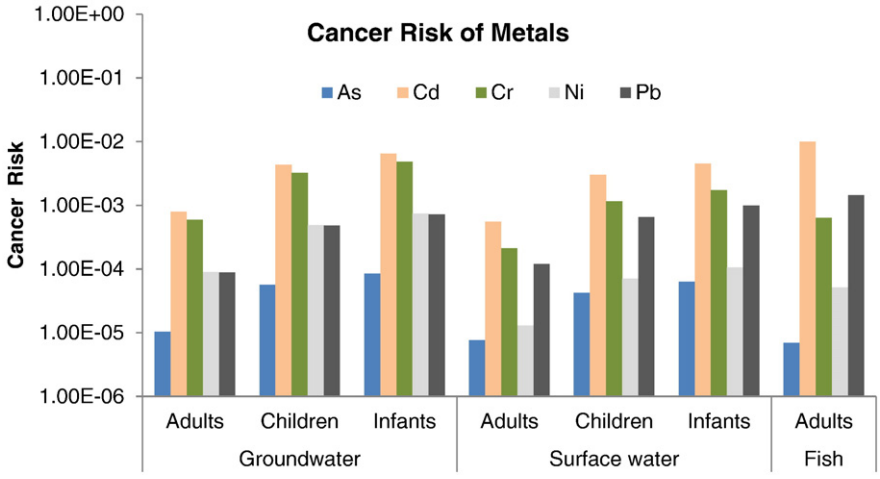


**Fig. 4.** Cancer risk of some toxic metals in water and fish samples.

Generally, wide data variations were observed in some environmental parameters due to factors like small data size and also an occurrence of outliers that might be traced to pollution peak episodes (Osborne and Overbay, 2004). Furthermore, some parameters showed higher values in groundwater than surface water similar to Ayantobo et al. (2014b) study in Igun-Ijesha where higher concentrations of As, Cd, Cr, Pb and Zn were measured in groundwater than surface water. Reasons might be linked to the gold mining types (e.g. underground pit or surface), tailing storage and disposal methods (Murray et al., 2003). Pit mining is widely practiced by the artisanal gold miners in the study area (Olujimi et al., 2015). The possibility of disposing mine wastes into abandoned mine pits may be eminent thus leading to groundwater contamination (Breitenbach, 2008). Similarly, a previous study had demonstrated higher values of Mn, Hg and Zn in groundwater than surface water at a gold mine site in Tarkwa, Ghana (Armah et al., 2010).

The study of Cobbina et al. (2015) at two gold mining sites in Northern Ghana demonstrated higher concentrations of Hg, As, Cd, Pb and Zn in surface water than the values measured in this study. However, the present study shows higher mean Pb concentration in surface water than the values reported from rivers around the gold mining areas of Prestea Huni Valley District of Ghana (Obiri et al., 2016).

### 3.2. Health risk assessment

Table S1 in the supplementary material shows the Average Daily Dose (ADD) values of the analyzed trace metals from water and fish samples. The ADD was calculated from the concentration of elements measured in water (groundwater and surface water) and fish (muscle) samples. The calculation was based on the assumption that a matured adult weighing 60 kg consumes 2 L of water per day while a child weighing 10 kg consumes 1 L of water per day and an infant weighing 5 kg consumes 0.75 L of water per day (USEPA, United States Environmental Protection Agency, 2002; 2007; Batayneh, 2010; USEPA, United States Environmental Protection Agency, 2012; Ayedun et al., 2015). The risk assessment results showed Ba ($4.5 \pm 2.9$ μg $kg^{-1}$ $day^{-1}$), Mn ($2.8 \pm 4.8$ μg $kg^{-1}$ $day^{-1}$) and Al ($0.7 \pm 1.0$ μg $kg^{-1}$ $day^{-1}$) as the most dosed toxic metals in groundwater by adults. In one week, the adult would have consumed $31.5 \pm 20.5$ μg $kg^{-1}$ $day^{-1}$ body weight $^{-1}$ of Ba, $19.8 \pm 33.5$ μg $kg^{-1}$ $day^{-1}$ body weight $^{-1}$ Mn and $4.9 \pm 7.2$ μg $kg^{-1}$ $day^{-1}$ body weight$^{-1}$ Al. In addition, the weekly dose values of the measured trace metals are presented in Table S2 in the supplementary material. A child that drinks 1 L of groundwater daily would take higher dose of trace metals 3 times than an adult. Despite the fact that an infant (of lower body weight) consumes less quantity of water compared to an adult (of higher body weight); an infant would take more of these toxic elements in water than an adult by five times. The order of ADD of trace elements from groundwater follows: Mn > Ba > Al > Cr > Fe > Cr > Zn > Ni > Ti > Li. The corresponding ADD and weekly intake values of metals from groundwater were similar to those of surface water for As, Au, Cd, Cu, Hg, Mo, Sb and Pb but higher for Ag, Ba, Co, Cr, Li, Mn, Ni, V and Zn. (Tables S1 and S2). Furthermore, a person would expose to higher dose of Ti (by 2 times), Al (5 times) and Fe (28 times) in surface water than in groundwater. The order of ADD for these metals from surface water follows: Fe > Al > Ba > Ti > Zn > Cr > Mn > Cu.

The weekly dose of Al in water samples (except for adults who consumed groundwater) was higher than the Joint Expert Committee on Food Additives (JECFA) Provisional Tolerable Weekly Intake (PTWI) value. The JECFA PTWI value for Al is 7.0 μg $kg^{-1}$ body weight$^{-1}$ (JECFA, J. F., 2008). The high PTWI value of Al observed for infants and children in this study indicates Al toxicity. The major health problem of Al toxicity in food or water is Alzheimer Disease (AD). A positive relationship has been established between aluminium and dementia/AD in drinking water (WHO, 1997). Even though there are no available PTWI data for Ba and Mn, the calculated PTWI values of these metals were high in groundwater consumed by infants (Table S2).

The average daily and weekly intake data of trace elements in fish samples were also presented in Tables S1 and S2. It was assumed that an adult weighing 60 kg consumes 24.7 g fish daily in Nigeria (FAO, 2008). The daily and weekly intake values for some of these toxic elements in fish were high for Fe, Al and Mn. Although, the weekly intake values of these metals were lower than the JECFA, J. F. (2008) PTWI values for As and Pb; but their long term impacts on humans' health may be severe (ATSDR, Agency for Toxic Substances and Disease Registry, 2007).

Table 4 shows the hazard quotient (HQ) and hazard index (HI = ΣHQ) values of metals calculated from surface water, groundwater and fish samples. This study revealed higher noncarcinogenic adverse effects of metals in surface water than groundwater despite measuring higher concentrations of some trace metals in groundwater. Among the observed metals, the HQ of Al and Fe were generally > 1.0 in water and fish samples consumed by infants, children and adults. The hazard quotient values of Mn from groundwater taken by children and infants were also > 1.0. The HQ value > 1.0 denotes noncarcinogenic adverse effects and a high level of health concern (Obiri et al., 2016).

The sum of HQ or HI value was also > 1.0 in water samples. The study of Obiri et al. (2016) had reported similar high HI value. The ΣHQ value for adult from groundwater was lower than the range value (26–886) reported by Ayantobo et al. (2014a) in groundwater samples collected from Iperindo gold mining site. However, the ΣHQ values for infants and children in surface water were higher than the range value (117–119) reported by Ayantobo et al. (2014a). Olujimi et al. (2015) also

reported the ΣHQ value of 3.97 in soil samples analyzed at the vicinity of Igun gold mine in Ilesha. The pattern of abundance of HQ for adults, children and infants in this study follows: Al > Fe > Mn > Pb > Cr > Co in groundwater and Fe > Al > Pb > Cu > Ag > Cd in surface water. The earlier work of Ayantobo et al. (2014a) had reported the HQ pattern as: Cr > Pb > Cd while Ayedun et al. (2015) reported the HQ orders of As > Cd > Cr. In the study conducted by Ayedun et al. (2015) on groundwater samples collected in Lagos State, the HQ value (0.59) reported was lower than the HI value obtained from groundwater in this study. This further confirms the negative impacts of the artisanal gold mining activities in the study area.

The major health concerns of consuming fish caught in the surface water samples from the study area were Fe, Al, and Pb showing HQs of 113.4, 22.7 and 2.2, respectively. The HI value from fish samples >1.0 is also an issue of health concern. This HI value was higher than the value previously reported by Onsanit et al. (2010) from two marine fish cultured in fish cages in Fujian province, China. The health problems associated with Al are dementia, damage to central nervous system, loss of memory, listlessness and severe trembling (http://www.lenntech.com/periodic/elements/al.htm). Fe is an essential element required for body metabolism; however, a large dose of Fe is associated with haemochromatosis (a disease characterized by liver cirrhosis), hepatocellular carcinoma and impaired pancreatic function (Beaton and Adams, 2007). Adverse effects including constipation, nausea, vomiting, heart disease, gastric upset, abdominal pain and faintness are also associated with excess dose of Fe (Whitlock et al., 2006; Aggett, 2012). The high HQ values of Mn from groundwater could pose deleterious health effects to water consumers in the study areas. Mn toxic effects include kidneys and urinary tract illness, disturbances of nervous system, effects on children's brain development, lung irritation, adverse changes in male reproductive performance and sperm damage (ATSDR, Agency for Toxic Substances and Disease Registry, 2015b). Also, the high HQ value of Pb from fish samples may result into numerous toxic effects including teratogenic, neurological disorder (central nervous system CNS and peripheral nervous system PNS), inhibition of haemoglobin, psychosis, damage to kidney and gastrointestinal tract (GIT), poor intelligence quotient (IQ) and poor development in children (Duruibe et al., 2007).

Fig. 4 presents the cancer risk (CR) values for As, Cr, Cd, Ni and Pb from groundwater, surface water and fish samples. In water samples, the CR calculated for As ranged from $7.7 \times 10^{-6}$ in surface water to $8.5 \times 10^{-5}$ in groundwater. The CR values of Chromium varied from $2.1 \times 10^{-4}$ in surface water to $4.8 \times 10^{-3}$ in groundwater while for Ni, the CR ranged from $1.3 \times 10^{-5}$ in surface water to $7.4 \times 10^{-4}$ in groundwater. The CR for Cd ranged from $5.6 \times 10^{-4}$ (surface water) to $6.5 \times 10^{-3}$ (groundwater) while the CR for Pb varied from $8.9 \times 10^{-5}$ (groundwater) to $9.9 \times 10^{-4}$ (surface water). The cancer risk values observed for Cd and Cr in surface water and groundwater were higher than the acceptable limit of $1.0 \times 10^{-4}$ indicating possible carcinogenic effects. Obiri et al. (2016) had shown higher cancer risk values for Cd ($1.2–9.8 \times 10^{-2}$) from surface water samples from the vicinity of gold mining sites in PresteaHuni Valley District, Ghana. The CR for Ni and Pb from groundwater exposed to by children and infants were higher than the permissible level. Pb cancer risk values were also high in surface water consumed by adults, children and infants. The CR value for Ni from surface water was higher than the acceptable limit of $1.0 \times 10^{-4}$.

In fish samples, the cancer risks were $6.9 \times 10^{-6}$ for As, $1.0 \times 10^{-2}$ for Cd, $6.4 \times 10^{-4}$ for Cr, $5.5 \times 10^{-5}$ for Ni and $1.5 \times 10^{-3}$ for Pb. The study therefore revealed the carcinogenic effects of Cd, Cr and Pb in fish samples as their CR values were higher than the acceptable limit of $1.0 \times 10^{-4}$. The sum of cancer risks was higher than the acceptable limit in groundwater, surface water and fish samples. Infants were at the greatest risk followed by children.

The sum of cancer risk in water and fish samples were 9–22 times higher than the acceptable limit of $1.0 \times 10^{-4}$; this therefore calls for public concerns and the need for cautions during the artisanal gold mining activities in Ijeshaland. The CR values of As, Cd, Cr and Pb obtained in this study were lower than the values reported by Ayedun et al. (2015) in groundwater samples collected in Lagos and Ogun States. In this present study, Cd formed the major contributor to the cancer risk constituting 50% and 81% of total cancer burden in groundwater and surface water, respectively. The order of risk of cancer in this study follows: Cd > Cr > Pb > Ni > As and deviated from the earlier observations of Ayedun et al. (2015) where Pb > Cr > As > Cd and Li and Tian (2008) where Cr > As > Cd. In fish sample, the pattern of CR was Cd > Pb > Cr > Ni > As. The previous study of Olujimi et al. (2015) had confirmed the carcinogenic impacts of Cr and Pb at the gold mining site of Igun-Ijesha, Oshun State. The high cancer risk values obtained for Cd and Pb in fish samples therefore calls for urgent attentions of the policymakers in the State to prevent high prevalence and incidence of cancer cases among the residents in the study area. A recent study had shown that >100, 000 annual cases of cancer are reported in Nigeria (Jedy-Agba et al., 2012). A cleanup exercise for these toxic metals in the gold city of Ijeshaland is therefore important to protect the public health.

## 4. Conclusion

This study has examined the metal composition and human health risks from environmental samples collected at the vicinity of the gold city of Ijeshaland, Osun State, Southwestern Nigeria. The mean values of Al and Fe in surface water were higher than the WHO standards in drinking water. Total cyanide was also measured at higher concentration in water samples than the permissible standard. Most of the measured water parameters were observed at higher concentrations in groundwater water than surface water. A high concentration of Ba was observed in fish and plants. Ti concentration was higher in fish than water, sediment and plant samples. The hazard quotient (HQ) risk assessment for individual element was generally <1.0 except for Al and Fe from all the environmental samples. Mn from water samples dosed by children and infants and Pb from fish showed HQ values >1.0. Hazard index (HI) value >1.0 indicated overall adverse noncarcinogenic effects, in which the infants were at the greatest risk. The pattern of HQ in this study was Al > Fe > Mn > Pb > Cr > Co in groundwater and Fe > Al > Pb > Cu > Ag > Cd in surface water. Exposure assessments and remediation measure for these toxic metals in the gold city of Ijeshaland are therefore important to protect the public health. This study had established the carcinogenic effects of Cd, Cr, Pb and Ni in the analyzed water and fish samples. The data obtained in this study showed that, the artisanal gold mining in the study area is hazardous to human health. Urgent action is therefore, required by the policymakers to combat the negative activities of the miners. More environmental, socio-economic and health researches should also be carried out on the activities of gold miners in the gold city of Ijeshaland. This study recommends further studies on environmental and health assessment of the artisanal gold miners in the study area. Environmental samples from locations outside the gold mining areas should be collected, analyzed and compared with data from the gold city.

## Conflict of interest

The authors has no actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

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## Appendix A. Supplementary data

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