

Health Risk Assessment of Heavy Metals in Soil from the Iron Mines of Itakpe and Agbaja, Kogi State, Nigeria

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ABSTRACT: The study evaluates associated health risks of heavy metals in the soil to inhabitants of two mining areas of Nigeria. For so doing, it collects and analyses nine homogenous soil samples for their lead, copper, cadmium, zinc, and chromium levels, using AAS. The samples are then used to calculate health risks to adults and children. For adult population in Agbaja community, the calculated hazard quotients fall below one in all considered pathways. Hazard index values for all the pathways are also less than one, taking the following order: Cu>Cr>Pb>Cd>Zn. It is shown that for all considered heavy metals, the adult population in Agbaja mining community was not at any risk of non-carcinogenic effects from these metals. As for the children in Agbaja, the calculated HQ values for Cd and Zn have been less than one in all the pathways, while the HQ values for Pb, Cr, and Cu have significantly surpassed 1, with the ingestion route being the main pathway. The HI values have been in the following order: Cu>Cr>Pb>Cd>Zn, which poses serious non-carcinogenic health risks to the children, living around this community. The carcinogenic risk has been calculated based on Pb, Cd, and Cr, with the former (Pb) proven to be the highest contributor to cancer risk. USEPA considers acceptable cancer risk within the range of 1×10^{-6} to 1×10^{-4} . Though insignificant in its values, carcinogenic risk for adults in Agbaja (2.95×10^{-4}) and Itakpe (4.71×10^{-4}) and for children in Itakpe (4.47×10^{-4}) have been higher than the acceptable values. Hence, the adults are more at risk, for whom ingestion is the main contributor to excess lifetime cancer risk, followed by dermal pathways. Considering the health hazards, entailed by the accumulation of these heavy metals, on human health, mining sites and areas require to get monitored properly.

Keywords: Iron ore mining, heavy metals, health risk, carcinogenic risk, hazard quotient

INTRODUCTION

Heavy metals in soils are of great concern to humans and the environment, due to their toxicity, bio-accumulative potentiality, biodegradability, and recalcitrant nature. Some metals are essential for life, playing an irreplaceable role as sources of vitamins and minerals for human organs to function. All living organisms require varying amounts of metals, but at higher concentrations they

become toxic (Adesuyi *et al.*, 2015). What is more, some metals do not play any useful role in human physiology and might be toxic even at low rates of exposure. They might continuously get accumulated in vital organs such as the brain, the liver, bones, and kidneys, for years or decades, in turn causing serious health problems (Kabata-Pendias, and Pendias, 2011).

Lead (Pb) is the second hazard in the priority list of heavy metal pollutants,

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designated by United States Agency for Toxic Substances and Disease Registry (2007). Regarded as a human mutagen and probable carcinogen (Podsiki, 2008), it is well-known to induce renal tumours, and disturb normal function of kidneys, joints, reproductive, and nervous systems (Kamunda *et al.*, 2016). Acute ingestion of Cd is also known to be toxic, even in low amounts, being regarded as a probable carcinogen as well. Severe exposure to Cd may result in pulmonary effects such as alveolitis, bronchiolitis, and emphysema (Adedokun *et al.*, 2016). It can also result in bone fracture, kidney dysfunction, hypertension, and even cancer (Kamunda *et al.*, 2016). What is more, some of its odd long-term effects include arthritis, diabetes, anaemia, cardiovascular disease, cirrhosis, reduced fertility, headaches, and strokes.

Zn and Cu are essential for human life, yet excessive intake of these metals may have non-carcinogenic impacts on human health. Higher concentrations of Zn have been associated with growth and reproduction impairment, whereas higher amounts of Cu are associated with liver damages (Adesuyi *et al.*, 2015; Kamunda *et al.*, 2016). While Chromium (III) is an essential element, chromium (VI) compounds are known to be mutagenic and carcinogenic. Inhaling high levels of chromium (VI) may cause asthma and shortness of breath. Also, long-term exposure to it might damage the liver and the kidneys (Podsiki, 2008). Ni, on the other hand, is known to cause cancer, both orally and intestinally. It is also responsible for health issues such as depression, heart attacks, haemorrhages, and kidney problems (NRC, 1999).

Both Itakpe Iron Mine (7.36 N, 6.61 E) and a prosperous mining site, Agbaja iron ore site, (7.982978 N, 6.649874 E) are located in Kogi State, Nigeia. The Itakpe Hills in and around the town of Itakpe contain very pure deposits of iron ore. Housing National Iron Ore Mining Company, it supplies the steel works of Ajaokuta and Aladja, not to

mention producing iron ore for export (Olatunji, 2008). Agbaja is also the site of a large iron ore deposit in Kogi State, believed to possess the biggest iron ore deposits in central Nigeria (Lar, 2012). Major mechanisms to transfer heavy metals from the mines take place in the air, ground water sources, and surface water body. Accumulation of these metals in soil, air, water, and edible parts of plants represents a direct pathway for their entry into human food chain. Although no health risk studies have ever been conducted in these mining areas, children and adults of mining communities have often reported incidents of chest pain, tuberculosis, diarrhoea, cough, and itchy skin (Kamunda *et al.*, 2016). Therefore, the current study intends to determine concentration levels of heavy metals in soils from the study areas, also estimating the health risks of exposure to heavy metals in the inhabitants of these areas.

MATERIALS AND METHODS

The study took place in Itakpe Iron Mine (7.36 N, 6.61 E) as well as a prosperous mining site Agbaja iron ore site (7.982978 N, 6.649874 E) both in Kogi state. The Itakpe Hills in and around the town of Itakpe contain very pure deposits of iron ore.

Sampling of soils was performed in August and September, 2016, in which a sum of eighteen soil samples (9 top and 9 subs) were obtained from the sites, using a calibrated steel soil auger. At each sampling location, five replicate samples were collected in a 2 m * 2 m grid. They were thoroughly mixed to give a homogenous sample, out of which 1 kg was packaged in a tagged polythene bags.

Control samples were obtained 2 km off the mining sites. All collected samples were properly tagged and identified by their sampling locations. Furthermore, the coordinates were obtained, using a Global Positioning System (GPS) receiver. The collected soil samples were taken to the

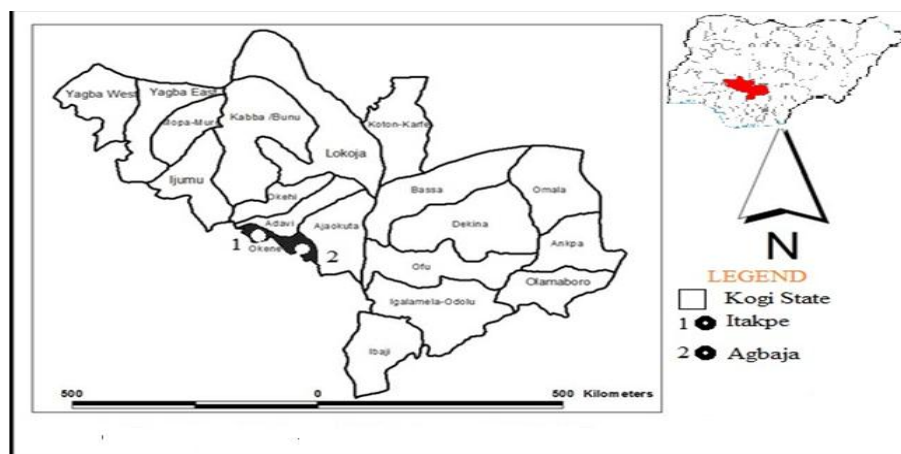


Fig. 1. Map of the study area, showing Itakpe (7.36 N, 6.61 E) and Agbaja (7.982978 N, 6.649874 E) iron ore mine

University of Lagos, Central Research Laboratory, for further processing.

The soil samples were air-dried and sieved to <0.25mm, then to get stored in desiccators prior to heavy-metal content analysis. To determine total heavy metal content, 0.25 g of the treated samples were weighed by an electronic analytical balance (Mettler Toledo-EL204). Afterwards the samples were put into digestion vessels and digested with HCl, HNO₃, HF, and HClO₄ by means of graphite furnace digestion instrument. Then the solutions were diluted into a final volume of 50 ml with 2% (v/v) HNO₃.

Zinc (Zn), lead (Pb), chromium (Cr), copper (Cu), and cadmium (Cd) levels were determined by Atomic absorption spectrometry (Hseu *et al.*, 2002). The readings were taken from the equipment and the results were converted to actual concentration of the metal in the sample, using this equation (Aderinola *et al.*, 2009):

$$\text{Concentration of metal} = \frac{\text{Calibration reading} \times \text{Volume of Digest}}{\text{Weight of Sample}}$$

where calibration reading was the reading from the instrument, volume of digest was 50 ml, and weight of sample, 2 g.

Human health risk assessment is a process to estimate the health effects that

might result from exposure to carcinogenic and non-carcinogenic chemicals (USEPA, 2001). The risk assessment process is made up of four basic steps: 1) hazard identification, 2) exposure assessment, 3) toxicity (dose-response) assessment, and 4) risk characterization (USEPA, 2001). The purpose of exposure assessment is to measure or estimate the intensity, frequency, and duration of human exposure to an environmental contaminant. In the current study, exposure assessment was carried out by measuring the average daily intake (ADI) of heavy metals, identified earlier through ingestion, inhalation, and dermal contact by adults and children from the study area. Adults and children were divided into separate groups, thanks to their behavioural and physiological differences (Wang *et al.*, 2005).

Dose-response assessment estimates the toxicity from exposure levels of the chemicals. The cancer slope factor (CSF, a carcinogen potency factor) and the reference dose (RfD, a non-carcinogenic threshold) are two important toxicity indices used. RfD values are derived from animal studies, which use the “No observable effect level” principle. For humans, RfD values are multiplied 10-fold to account for all uncertainties (USEPA, 1989; USEPA, 2010).

Risk characterization predicts potential cancerous and non-cancerous health risks for both children and adults in the study area by integrating all collected information to arrive at quantitative estimates of cancer risk and hazard indices (USEPA, 2004).

The potential exposure pathways for heavy metals in contaminated soils are calculated, based on the recommendations by several American publications. ADI (mg/kg-day) for different pathways were calculated, using the following exposure Equations (1)–(3) as prescribed by (USEPA, 1989).

Ingestion of Heavy Metals through Soil was calculated thus;

$$ADI_{ing} = \frac{C \times IR \times EF \times ED \times CF}{BW \times AT} \quad (1)$$

where ADI_{ing} is the average daily intake of heavy metals, ingested from the soil, in mg/kg-day, C indicates the concentration of heavy metal in mg/kg for soil. IR is the ingestion rate in mg/day; EF, the exposure frequency in days/year; ED, the exposure duration in years; BW, the body weight of the exposed individual in kg; and AT, the time period over which the dose is averaged in days. Also CF is the conversion factor in kg/mg.

Inhalation of Heavy Metals via Soil Particulates was calculated thus;

$$ADI_{inh} = \frac{Cs \times IR_{air} \times EF \times ED}{BW \times AT \times PEF} \quad (2)$$

where ADI_{inh} stands for the average daily intake of heavy metals, inhaled from the soil in mg/kg-day, CS indicates the concentration of heavy metal in soil in mg/kg, and IR_{air} and PEF are the inhalation rate in m^3/day and the particulate emission factor in m^3/kg , respectively. EF, ED, BW, and AT are as defined earlier in Equation (1) above.

Dermal Contact with Soil is calculated thus;

$$ADI_{dems} = \frac{C_s \times SA \times FE \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

where ADI_{dems} is the exposure dose via dermal contact in mg/kg/day. CS represents the concentration of heavy metal in soil in mg/kg, SA stands for exposed skin area in cm^2 . FE is the fraction of the dermal exposure ratio to soil; AF, the soil adherence factor in mg/cm^2 ; and ABS, the fraction of the applied dose absorbed across the skin. EF, ED, BW, CF, and AT are as defined earlier in Equation (1). Table 1 shows the exposure parameters, used for health risk assessment of standard residential exposure scenario through different exposure pathways.

Table 1. Exposure parameters, used for health risk assessment through different exposure pathways for soil (USEPA, 2004; DEA, 2010)

Parameter (Unit)	Child	Adult
Body weight (BW) kg	15 kg	70 kg
Exposure frequency (EF) (days/year)	350	350
Exposure duration (ED) (years)	6	30
Ingestion rate (IR) (mg/day)	200	100
Inhalation rate (IR_{air}) (m^3/day)	10	20
Skin surface area (SA) (cm^2)	2100 cm^2	5800 cm^2
Soil adherence factor (AF) (mg/cm^2)	0.2	0.07
Dermal Absorption factor (ABS)	0.1	0.1
Dermal exposure ratio (FE)	0.61	0.61
Particulate emission factor (PEF) (m^3/kg)	1.3×10^9	1.3×10^9
Conversion factor (CF) (kg/mg)	10^{-6}	10^{-6}
Average time (AT) (days) For carcinogens	365×70	365×70
For non-carcinogens	$365 \times ED$	$365 \times ED$

Non-carcinogenic hazards are characterized by a term, called Hazard Quotient (HQ), a unit-less number expressed as the probability of an individual suffering an adverse effect. It is defined as the quotient of ADI or dose, divided by the toxicity threshold value, which is referred to as the chronic reference dose (RfD) in mg/kg-day of a specific heavy metal, as shown in Equation (4) (USEPA, 1989):

$$HQ = \frac{ADI}{RfD} \quad (4)$$

For n number of heavy metals, the non-carcinogenic effect on population is as a result of the sum of all HQs due to individual heavy metals, which is referred to as another term called Hazard Index (HI), as described by USEPA (1989). Equation (5) shows the mathematical representation of this parameter:

$$HI = \sum_{k=1}^n HQ_k = \sum_{k=1}^n \frac{ADI_k}{RfD_k} \quad (5)$$

where HQ_k , ADI_k , and RfD_k are values of heavy metal k. If HI is less than one, the exposed population is unlikely to experience any adverse health effects, while if it exceeds this value, there could be some concern for potential non-carcinogenic effects (USEPA, 1989).

For carcinogens, the risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to potential

carcinogens. The equation to calculate excess lifetime cancer risk is:

$$Risk_{pathway} = \sum_{k=1}^n ADI_k CSF_k \quad (6)$$

where Risk is a unit-less probability of an individual developing cancer over a lifetime. ADI_k (mg/kg/day) and CSF_k (mg/kg/day) are average daily intake and cancer slope factor, respectively for the k^{th} heavy metal and for n heavy metals. The slope factor converts the estimated daily intake of the heavy metal averaged over a lifetime of exposure directly to incremental risk of an individual developing cancer (USEPA, 1989).

The total excess lifetime cancer risk for an individual can finally be calculated from the average contribution of the individual heavy metals for all pathways, using the following equation:

$$Risk_{total} = Risk_{(ing)} + Risk_{(inh)} + Risk_{(dermal)} \quad (7)$$

Both non-carcinogenic and carcinogenic risk assessment of heavy metals are calculated using RfD and CSF values, largely derived from the Department of Environmental Affairs (South Africa) and USEPA, as shown in Table 2.

The descriptive statistical parameters were calculated by means of GraphPad Prism software package (version 6.0), with Analysis of variance (ANOVA) being performed to test the significance of differences in total metal concentrations in plant and soil samples.

Table 2. Reference doses (RfD) (in mg/kg-day) and Cancer Slope Factors (CSF) for different heavy metals (USEPA, 1991; USEPA, 2007; USEPA, 2010; DEA, 2010; Luo *et al.*, 2012)

Heavy metal	Oral RfD	Dermal RfD	Inhalation RfD	Oral CSF	Dermal CSF	Inhalation CSF
Pb	3.60E-03	-	-	1.50E+00	1.50E+00	1.50E+01
Cd	5.00E-04	5.00E-04	5.70E-05	-	-	6.30E+0
Cr (VI)	3.00E-03	-	3.00E-05	5.00E-01	-	4.10E-01
Zn	3.00E-01	7.50E-02	-	-	-	-
Cu	3.7.00E-02	2.40E-02	-	-	-	-

RESULTS AND DISCUSSION

Table 3 shows metal levels in soil samples. The highest (48.16 ± 0.01 mg/kg) and lowest Pb (14.65 ± 0.05 mg/kg) levels were observed in the samples around Itakpe Iron ore mine. There were slight differences between the Pb levels in the mine area and control (10.35 ± 0.50 mg/kg), but there was no significant difference ($p > 0.05$) in all soil samples. Pb levels in all soil sampled around Itakpe and Agbaja did not exceed the international threshold values for Pb concentration in soils, set by EU (300 mg/kg), UK (70 mg/kg), and FAO/WHO (100 mg/kg). Cd levels ranged from 1.10 ± 0.05 mg/kg in Itakpe to 2.22 ± 0.005 mg/kg in Agbaja, showing a significant difference ($p < 0.05$). Cd concentrations in all soils, sampled around Itakpe and Agbaja, did not exceed the international threshold value of 3 mg/kg for the concentration of Cd in soil, set by EU, USA, and UK. Cr varied from 18.65 ± 0.01 mg/kg to 83.88 mg/kg, with the lowest amount, obtained from Itakpe, and the highest, from Agbaja.

There was no significant difference ($p > 0.05$) in Cr level in the soil samples. On the contrary, Zn level showed high variations (65.51% coefficient of variation) across all sampling areas, ranging from 2.02 ± 0.01 mg/kg to 14.79 ± 0.0 mg/kg. Zn levels in all soils, sampled around Itakpe and Agbaja, did not exceed the international threshold values for Zn concentration in the soil, set by EU (300 mg/kg), USA (200 – 300 mg/kg), and UK (100 – 200 mg/kg). Similarly, there were great variations in Cu at all sampling points (having a coefficient of variation equal to 100.84%). The levels of this metal ranged from 62.80 ± 0.05 mg/kg to 286.01 ± 0.01 mg/kg, and, around the sampling sites of Itakpe and Agbaja, they exceeded the international threshold values for Cu concentration in soils set by EU (130 – 140 mg/kg), USA (80 – 200 mg/kg), and UK (63 mg/kg). There were some variation among all heavy metals with significant difference for Pb and Cu, Cd and Cu, Cr and Cu, and Zn and Cu ($p < 0.05$).

Table 3. Heavy metal levels in the soil samples (mean \pm standard error) and International threshold values for heavy metal concentration in soils (mg/kg)

S/N	Site	Pb	Cd	Cr	Zn	Cu
1	Agbaja	47.04 ± 0.005	1.98 ± 0.01	58.32 ± 0.01	14.79 ± 0.0	277.7 ± 0.01
2	Agbaja	19.15 ± 0.00	2.22 ± 0.005	58.88 ± 0.005	5.02 ± 0.005	62.80 ± 0.005
3	Agbaja	29.44 ± 0.005	1.92 ± 0.01	68.34 ± 0.005	4.52 ± 0.005	182.02 ± 0.01
4	Agbaja	33.42 ± 0.02	1.74 ± 0.01	56.83 ± 0.005	3.94 ± 0.005	157.20 ± 0.01
5	Agbaja	20.07 ± 0.01	1.81 ± 0.01	45.29 ± 0.005	2.95 ± 0.000	254.51 ± 0.05
6	Agbaja	37.92 ± 0.005	2.15 ± 0.005	83.88 ± 0.000	4.47 ± 0.000	133.65 ± 0.01
7	Itakpe	17.21 ± 0.005	1.82 ± 0.01	22.95 ± 0.000	4.25 ± 0.005	272.51 ± 0.005
8	Itakpe	48.16 ± 0.01	1.67 ± 0.01	53.41 ± 0.005	10.65 ± 0.005	286.01 ± 0.01
9	Itakpe	14.65 ± 0.05	1.10 ± 0.05	18.65 ± 0.01	2.02 ± 0.01	210.0 ± 0.00
	Control	10.33 ± 0.50	0.56 ± 1.52	12.85 ± 4.55	2.00 ± 0.05	75.50 ± 1.56

The examined mining areas in this research were compared with studies from other countries, i.e., heavy metal concentrations in contaminated mining soils in Spain, South Africa, India, Iran, Vietnam, and China (Table 4). Numerous studies in these selected countries have shown that the surrounding environment of the mines is often polluted by heavy metals, dispersed from mining operations.

For example, mines in the southern and northern areas of Spain have operated for ages and have led to high metal concentrations in surrounding soils (Ordóñez *et al.*, 2011; Li *et al.*, 2014). In Vietnam, many metalliferous mines are located either in mountainous areas or in the upper reaches of lowland streams, where frequent flooding during the rainy season causes the dikes constructed around

the mines to collapse and not function properly, resulting in heavy metal pollution pouring into low streams and farmland areas (Kien *et al.*, 2010). Currently, there are about 72 mining areas in China with severely high levels of heavy-metal-contaminated soils (Li *et al.*, 2014). The mean concentrations of all listed heavy metals in the 3 mining area of Vietnam for Pb, Cd, Zn, and Cu are higher than the mean values in this study, as well as the ones carried out in South Africa, Spain,

and China, except for Cr level, which had its highest rate in India than all the rest. The mining areas in Vietnam have higher heavy metals than those in Nigeria, which is attributed to long-term mining operations in Vietnam, generating considerable amounts of heavy metal pollution (Ha *et al.*, 2011). Based on the above analyses, compared to the mining areas of other countries, the examined mining areas of Nigeria contained lower levels of heavy-metal-contaminated soils.

Table 4. Comparison of mean heavy metal concentrations, observed in this study with those found in other heavy-metal-soil studies (mg/kg)

Site	Pb	Cd	Cr	Zn	Cu	References
Nigeria (2 mine areas)	29.67	1.82	51.83	5.37	204.04	This study
South Africa (5 mines)	4.79	0.04	278.76	51.30	42.41	Kamunda <i>et al.</i> 2017
Spain (16 mines)	881.80	120.80	63.20	465.80	120.80	Ordóñez <i>et al.</i> , 2011
India (5 mines)	304.70	3.82	1509.00	338.80	63.49	Li <i>et al.</i> (2014)
Vietnam (3 mines)	30635.00	135.00	1501.00	41094.00	271.40	Kien <i>et al.</i> , 2010
China (72 mines)	641.30	11.00	84.28	1163.00	211.90	Li <i>et al.</i> (2014)

Non carcinogenic risk for adults and children were calculated based on RfD values, as presented in Table 1, and ADI values, in Table 5. The results for ingestion, inhalation, and dermal pathways were all presented in terms of HQs, as shown in Table 6. In risk assessment, when HQ and HI values are below 1, there is no obvious risk to the population, but if these values exceed 1, there may be some concern for potential non-carcinogenic effects (USEPA, 2004).

For the Adult population in Agbaja community, the calculated HQ values for Pb, Cd, Cr, Zn, and Cu were less than one in all considered pathways. HI values for all the pathways were also less than one, standing in the following order: Cu>Cr>Pb>Cd>Zn. For all the heavy metals considered, the adult population in Agbaja mining community were not at risk of any non-carcinogenic effects from these metals. As for the children, the calculated HQ values for Cd and Zn were less than one in all pathways, while for Pb, Cr, and Cu they were significantly greater than 1,

with ingestion being the main pathway. Pb has been shown to affect almost every organ and system in the human body. Researches have shown that Pb is a multi-target toxicant, affecting the gastrointestinal tract, cardiovascular system, central and peripheral nervous systems, kidneys, immune system, and reproductive system (RAIS, 2008). Irreversible brain damage has also been reported to occur when Pb level of blood exceeds 100 µg/dl in adults and 80-100 µg/dl in children (RAIS, 2008). Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to Pb dose above RfD (NSC, 2009), while the children are believed to be the most prone to toxic effects of Pb, suffering a breakdown of central nervous system (Ogunkunle *et al.*, 2013). The toxicological risk from oral exposure to Cr for children in the two mining communities was high, with daily oral intakes of the population being above RfD (0.003 mg/kg/day). This calls for greater attention because the predominant

Cr-containing substance in the soil could be the highly toxic hexavalent Cr [Cr(VI)], which when ingested has greater absorption rate (2-8%) than the trivalent species, though unstable in humans and may later be reduced to Cr(III) by ascorbate and glutathione in the body. Chromium is associated with allergic dermatitis in humans (Scragg, 2006, Adesuyi *et al.*, 2015). The Children and adults in both communities in this study were prone to health risk from Cu toxicity due to their daily oral ingestion estimate, which was greater than oral chronic RfD (0.04 mg/kg/day). This was translated into copper HQ above 1, posing much non-carcinogenic risk. Copper is indeed essential to humans but in high doses, especially above RfDs (reference doses), it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation (Wuana and Okieimei, 2011).

The HI values were in the order of Cu (4.63) > Cr (2.64) > Pb (1.11) > Cd (0.57) > Zn (3.82E-03), showing that children were at higher level of health risk with greater exposure to heavy metals. In a study on health risk assessment of heavy metals in soils from Witwatersrand gold mining basin, South Africa (Kamunda *et al.*, 2016), for the adult population, the Hazard Index value for all pathways turned out to be 2.13, making non-carcinogenic effects significant to the adult population. For children, the Hazard Index value was 43.80, a value greater than 1, which had serious non-carcinogenic effect on children, living in the gold mining area.

For the adult population in Itakpe mining community, the calculated HQ values for all metals and all the pathways did not exceed 1; similarly, HI values for all pathways were below one, meaning that the adult population of this community were not at risk of non-carcinogenic effects. For children populations, the HQ values for Cd, Zn, and Cu were lower than 1 for all pathways, while Pb and Cr hazard

quotient values were greater than one, mainly through the ingestion pathways. HI for Pb, Cr, and Cu were above one in the following order: Cr>Pb>Cu. This may pose a very high non cancer health risk to the children, living around the two mining communities. The results also indicates that for both children and adult populations of both communities, the ingestion pathway enjoyed the lion's share of non-carcinogenic risk, followed by the dermal pathway. The inhalation pathway was the least contributor to the risk. Similar observations have been previously reported by Xiao *et al.* (2017) in their investigation of health risk assessment of heavy metals in soils from partial areas of Daye City, China. Results from the current study were also consistent with the findings of Zhang *et al.* (2012), who reported that due to lead/zinc mining and smelting activities, environmental pollution and related health effects were concentrated in south-central and southwest China.

The degree of heavy metals' toxicity to human beings depends on their daily intake (FAO/WHO, 2004). The excess lifetime cancer risks for adults and children were calculated separately from the average contribution of individual heavy metals in soil for all pathways. Based on carcinogenic risk values of the calculated ADI (average daily intake) values, presented in Table 7, the results of the excess lifetime cancer risks are presented in Table 8. The values of ADI for adults and children for all pathways of heavy-metal exposure did not differ from one another, significantly, with the exposure routes for all metals being in the following order: Ingestion > dermal > inhalation for both adults and children in the mining communities. The average exposure dose of the three exposure pathways for adult population of Agbaja community was in order of Pb > Cu > Zn > Cr > Cd, while for the children in Agbaja as well as both adult and children populations in Itakpe, it was: Cu > Pb > Cr > Cd > Zn.

Table 5. Average Daily Intake (ADI) values in mg/kg/day for adults and children in the soil of mining areas for non-carcinogenic risk calculations

Receptor Pathways		Average Daily Intake (ADI) Values for Heavy Metals in mg/kg/day					Total
		Pb	Cd	Cr	Zn	Cu	
Agbaja – Adult	Ingestion	4.27E-04	2.69E-05	8.48E-04	8.15E-05	1.54E-02	1.68E-02
	Inhalation	4.61E-07	2.91E-08	9.15E-07	8.79E-08	1.66E-05	1.81E-05
	Dermal	1.06E-04	6.68E-06	2.10E-04	2.02E-05	3.81E-03	4.15E-03
	Total	5.33E-04	3.36E-05	1.06E-03	1.02E-04	1.92E-02	2.09E-02
Child	Ingestion	3.98E-03	2.51E-04	7.92E-03	7.60E-04	1.43E-01	1.56E-01
	Inhalation	1.53E-08	9.68E-10	3.05E-08	2.93E-09	5.53E-07	6.03E-07
	Dermal	5.10E-04	3.23E-05	1.01E-03	9.74E-05	1.84E-02	2.00E-02
Itakpe – Adult	Total	4.49E-03	2.83E-04	8.93E-03	8.57E-04	1.61E-01	1.76E-01
	Ingestion	4.47E-04	2.39E-05	5.23E-04	1.02E-04	3.83E-03	4.93E-03
	Inhalation	4.83E-07	2.58E-08	5.64E-07	1.10E-07	4.13E-06	5.31E-06
Child	Dermal	1.11E-04	5.92E-06	1.29E-04	2.53E-05	9.47E-04	1.22E-03
	Total	5.59E-04	2.99E-05	6.53E-04	1.27E-04	4.78E-03	6.16E-03
	Ingestion	4.18E-03	2.23E-04	4.88E-03	9.52E-04	3.57E-02	4.59E-02
Child	Inhalation	1.61E-08	8.58E-10	1.87E-08	3.66E-09	1.37E-07	1.76E-07
	Dermal	1.11E-04	2.85E-05	6.25E-04	1.22E-04	4.57E-03	5.46E-03
	Total	4.29E-03	2.52E-04	5.51E-03	1.07E-03	4.03E-02	5.14E-02

Table 6. Hazard Quotient (HQ) and Health Index (HI) values for heavy metals in adults and children for the soil of the mining areas

Receptor Pathways		Hazard Quotient (HQ)				
		Pb	Cd	Cr	Zn	Cu
Agbaja – Adult	Ingestion	1.2E-01	5.0E-02	2.82E-01	2.72E-04	4.16E-01
	Inhalation	-	5.11E-04	3.05E-02	-	-
	Dermal	-	1.34E-02	-	2.69E-04	1.58E-01
	Hazard Index (HI)	0.12	0.06	0.31	5.41E-04	0.57
Child	Ingestion	1.11	5.02E-01	2.64	2.53E-03	3.86
	Inhalation	-	1.69E-05	1.02E-03	-	-
	Dermal	-	6.46E-02	-	1.29E-03	7.66E-01
Itakpe – Adult	Hazard Index (HI)	1.11	0.57	2.64	3.82E-03	4.63
	Ingestion	1.24E-01	4.78E-02	1.74E-01	3.4E-04	1.04E-01
	Inhalation	-	4.53E-04	1.88E-02	-	-
Child	Dermal	-	5.05E-04	-	3.37E-04	1.26E-02
	Hazard Index (HI)	0.12	0.05	0.19	6.77E-04	0.12
	Ingestion	1.61	4.46E-01	1.62	3.17E-03	9.65E-01
Child	Inhalation	-	1.51E-05	6.23E-04	-	-
	Dermal	-	5.7E-02	-	5.08E-03	1.90E-01
	Hazard Index (HI)	1.61	0.50	1.62	8.25E-03	1.16

Cd, As, and Pb are classified by IARC as carcinogenic agents (Mahfuza *et al.*, 2017). The carcinogenic risk was calculated based on Pb, Cd, and Cr, with the former being discovered as the highest contributor to cancer risk. The US Environmental Protection Agency considers cancer risk in the range of 1×10^{-6} to 1×10^{-4} as acceptable for regulatory purposes (USEPA, 2004). The

cancer risk for adults in Agbaja (2.95×10^{-4}), adults in Itakpe (4.71×10^{-4}), and children also in Itakpe (4.47×10^{-4}) were found to be higher than acceptable values. Therefore in the current study, for Itakpe and Agbaja communities, adults were more at risk than children, and the ingestion route seemed to be the main contributor to excess lifetime cancer risk, followed by the dermal pathway.

Table 7. Average Daily Intake (ADI) values in mg/kg/day for adults and children in soil from the mining areas for carcinogenic risk calculations

Receptor Pathways		Average Daily Intake (ADI) Values for Heavy Metals in mg/kg/day					Total
		Pb	Cd	Cr	Zn	Cu	
Agbaja – Adult	Ingestion	1.83E-04	1.15E-06	3.63E-05	3.49E-06	6.60E-04	8.84E-04
	Inhalation	2.82E-09	1.77E-10	5.59E-09	5.37E-10	1.01E-07	1.10E-07
	Dermal	1.29E-08	2.86E-07	9.00E-06	1.23E-05	1.63E-04	1.85E-04
	Total	1.83E-04	1.43E-06	4.53E-05	1.58E-05	8.23E-04	1.07E-03
Child	Ingestion	3.41E-05	2.15E-06	6.78E-05	6.51E-06	1.23E-03	1.34E-03
	Inhalation	1.31E-09	8.30E-11	2.60E-09	2.51E-10	4.74E-08	5.16E-08
	Dermal	4.37E-06	2.88E-07	8.69E-06	8.35E-07	1.57E-04	1.71E-04
Itakpe – Adult	Total	3.85E-05	2.44E-06	7.65E-05	7.35E-06	1.39E-03	1.51E-03
	Ingestion	1.92E-04	1.02E-05	2.24E-04	4.37E-05	1.64E-03	2.11E-03
	Inhalation	2.95E-09	1.58E-10	3.45E-09	6.73E-10	2.52E-08	3.24E-08
Child	Dermal	4.75E-05	2.54E-06	5.55E-05	1.08E-05	4.06E-04	5.22E-04
	Total	2.40E-04	1.27E-05	2.80E-04	5.45E-05	2.05E-03	2.64E-03
	Ingestion	2.15E-02	1.15E-03	2.51E-02	4.90E-03	1.84E-01	2.36E-01
Child	Inhalation	2.96E-10	1.58E-11	3.46E-10	6.71E-11	2.52E-09	3.24E-09
	Dermal	9.83E-06	5.25E-07	1.15E-05	2.24E-06	8.40E-05	1.08E-04
	Total	2.15E-02	1.15E-03	2.51E-02	4.90E-03	1.84E-01	2.36E-01

Table 8. Cancer risk values of heavy metals for adults and children in soil from the mining areas

Receptor Pathways		Cancer Risk for all Pathways					Risk Total
		Pb	Cd	Cr	Zn	Cu	
Agbaja – Adult	Ingestion	2.75E-04	-	1.82E-05	-	-	
	Inhalation	4.23E-08	1.12E-09	2.29E-09	-	-	
	Dermal	1.94E-06	-	-	-	-	
	Total	2.77E-04	1.12E-09	1.82E-05	-	-	2.95E-04
Child	Ingestion	5.12E-05	-	3.39E-05	-	-	
	Inhalation	1.96E-08	5.23E-10	1.06E-09	-	-	
	Dermal	6.55E-06	-	-	-	-	
Itakpe – Adult	Total	5.78E-05	5.23E-09	3.39E-05	-	-	9.17E-05
	Ingestion	2.88E-04	-	1.12E-04	-	-	
	Inhalation	4.42E-08	9.95E-10	1.41E-09	-	-	
Child	Dermal	7.13E-05	-	-	-	-	
	Total	3.59E-04	9.95E-10	1.12E-04	-	-	4.71E-04
	Ingestion	3.22E-02	-	1.25E-02	-	-	
Child	Inhalation	4.44E-09	9.95E-11	1.42E-10	-	-	
	Dermal	1.47E-05	-	-	-	-	
	Total	3.22E-02	9.95E-11	1.25E-02	-	-	4.47E-04

Several studies have linked heavy metal accumulation to numerous several health diseases and abnormalities. They cause both short- and long-time safety along with environmental and health risk. If all other routes of heavy metal entry are considered, such as from food and water intake as well as air pollution (Adedokun *et al.*, 2016; Jolaoso *et al.*, 2016; Njoku *et al.*, 2016), the potential health risks for residents of these mining communities might actually be higher.

CONCLUSION

As shown in this study, for both adults and children, the ingestion pathway is the greatest contributor to non-carcinogenic risk, followed by the dermal pathway. The inhalation pathway is the least contributor to non-cancer risk. For carcinogenic effects, the ingestion pathway contributes the most to cancer risk, followed by the dermal pathway. Based on the results from the present study, it can be concluded that mining activities contribute to elevated

level of heavy metals in surrounding soils of the mining areas. Considering the health hazards from the accumulation of heavy metals, especially the high level of copper in this study, it is quite needed to properly monitor mining sites and areas. The present study provides a good basis for further research on the impact of mining and its various processes to the environment. There is a great need for educationist, environmentalist, and other interested stakeholders to have a keen interest in the operations of artisanal as well as small and large scale mining so as to address the problems, caused by their operations.

REFERENCES

- Adedokun, A.H., Njoku, K.L., Akinola, M.O., Adesuyi, A.A. and Jolaoso, A.O. (2016). Potential human health risk assessment of heavy metals intake via consumption of some leafy vegetables obtained from four markets in Lagos metropolis, Nigeria. *J Appl Sci Environ Manag.* 20(3): 530-539.
- Adekoya, J.A. (2003). Environmental effect of solid minerals mining. *Journal of Physical Science in Kenya*, 1: 625–640.
- Aderinola, O.J., Clarke, E.O., Olarinmoye, O.M., Kusemiju, V. and Anetekhai, M.A. (2009). Heavy metals in surface water, sediments, fish and periwinkles of Lagos Lagoon. *Amer-Eurasian J Agri & Environ Sciences.* 5(5): 609-617.
- Adesuyi, A.A., Njoku, K.L. and Akinola, M.O. (2015). Assessment of Heavy metals pollution in soils and vegetation around selected Industries in Lagos, South western Nigeria. *J GEP*, 3: 11-19.
- Department of Environmental Affairs (2010). *The Framework for the Management of Contaminated Land*, South Africa. 79pp.
- FAO/WHO (2004). *Fruit and vegetables for health: Report of joint FAO/WHO workshop*, 1–3 September 2004.
- Ha, N.T.H., Sakakibara, M., Sano, S. and Nhuan, M.T. (2011). Uptake of metals and metalloids by plants growing in a lead–zinc mine area, Northern Vietnam. *J Hazard Mater.* 186: 1384–1391.
- Hseu, Z.Y., Chen, Z.S., Tsai, C.C., Tsui, C.C., Cheng, S.F., Liu, C.L. and Lin, H.T. (2002). Digestion methods for total heavy metals in sediments and soils. *Water Air Soil Pollut.* 141: 189–205.
- Jolaoso, A.O., Njoku, K.L., Akinola, M.O., Adesuyi, A.A. and Adedokun, A.H. (2016). Heavy metal analyses and nutritional composition of raw and smoked fishes from Ologe and Lagos Lagoon, Lagos, Nigeria. *J Appl Sci Environ Manag.* 20(2): 277-285.
- Kabata-Pendias, A. and Pendias, H. (2011). *Trace Elements in Soils and Plants*. 4th Editions, CRC Press, Boca Raton. 520pp.
- Kamunda, C., Mathuthu, M. and Madhuku, M. (2016). Health Risk Assessment of Heavy Metals in Soils from Witwatersrand Gold Mining Basin, South Africa. *Int. J. Environ. Res. Publ. Health.* 13: 663 – 674.
- Kien, C.N., Noi, N.V., Son, L.T., Ngoc, H.M., Tanaka, S., Nishina, T. and Iwasaki, K. (2010). Heavy metal contamination of agricultural soils around a chromite mine in Vietnam. *Soil Sci. Plant Nutr.* 56(2): 344-365.
- Lar, U.A. (2012). *Solid Mineral sector and inclusive green growth strategy in Nigeria*. Commissioned by the African Centre for Shared Development Capacity Building, Ibadan, Nigeria, September 2012. 37pp.
- Li, Z., Ma, Z., van der Kuijp, T.J., Yuan, Z. and Huang, L. (2014). A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. *Sci. Total Environ.* 468–469: 843–853.
- Luo, X.S., Ding, J. and Xu, B. (2012). Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. *Sci. Total Environ.* 424: 88–96.
- Mahfuza, S.S, Rana, S., Yamazaki, S., Aono, T. and Yoshida, S. (2017). Health risk assessment for carcinogenic and non-carcinogenic heavy metal exposures from vegetables and fruits of Bangladesh. *Cogent Environmental Science*, 3: 1-17.
- Njoku, K.L., Rumide, T.J., Akinola, M.O., Adesuyi, A.A., and Jolaoso, A.O. (2016). Ambient Air Quality Monitoring in Metropolitan City of Lagos, Nigeria. *J Appl Sci Environ Manag.* 20(1): 178-185.
- NRC-National Research Council (1999). *Arsenic in Drinking Water*; National Research Council: Washington, DC, USA, 1999; pp. 251–257.
- NSC (2009). *Lead Poisoning*. National Safety Council. 6pp.
- Ogunkunle, C.O., Fatoba, P.O., Ogunkunle, M.O. and Oyedeji, A.A. (2013). Potential Health Risk Assessment for Soil Heavy Metal Contamination of Sagamu, South-west Nigeria due to Cement Production. *IJAST.* 3(2): 89-96.

- Olatunji, K.J. (2008). Heavy metal Contamination of Plants and Soil in Itakpe Iron Ore Deposit Area of Kogi State, Nigeria. *Environmental Research Journal*, 2(3): 122 – 124.
- Ordóñez, A., Álvarez, R., Charlesworth, S., De Miguel, E. and Loredó, J. (2011). Risk assessment of soils contaminated by mercury mining, Northern Spain. *J Environ Monit.*, 13:128–36.
- Podsiki, C. (2008). Chart of Heavy Metals, Their Salts and Other Compounds. 24pp.
- RAIS (2008). The Risk Assessment Information System, 2008.
- Scragg, A. (2006). Environmental biotechnology. Oxford, UK, Oxford University Press, 2nd edition. Pp. 1-67.
- U.S. Environmental Protection Agency. (2010). Recommended Use of BW3/4 as the Default Method in Derivation of the Oral Reference Dose.
- U.S. Environmental Protection Agency. (2007). Framework for Determining a Mutagenic Mode of Action for Carcinogenicity: Review Draft.
- U.S. Environmental Protection Agency. (1991). Human Health Evaluation Manual, Supplemental Guidance: Standard Default Exposure Factors; USEPA: Washington, DC, USA.
- U.S. Environmental Protection Agency. (1989). Risk Assessment Guidance for Superfund Volume 1: Human Health Evaluation Manual (Part A); Office of Emergency and Remedial Response: Washington, DC, USA, 1989.
- U.S. Environmental Protection Agency. (2004). Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment); USEPA: Washington, DC, USA.
- U.S. Environmental Protection Agency. (2001). Toxics Release Inventory: Public Data Release Report. USEPA: Washington, DC, USA.
- Wang, X., Sato, T. and Xing, B. (2005). Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *Sci. Total Environ.* 350, 28–37.
- Wuana, R.W. and Okieimen, F.E. (2011). Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecology*. doi:10.5402/2011/402647.
- Xiao, M.S., Li, F., Zhang, J.D., Lin, S.Y., Zhuang, Z.Y. and Wu, Z.X. (2017). Investigation and health risk assessment of heavy metals in soils from partial areas of Daye city, china. *IOP Conference Series: Earth and Environmental Science*, 64: 012066.
- Zhang, X.W., Yang, L.S., Li, Y.H., Li, H.R., Wang, W.Y. and Ye, B.X. (2012). Impacts of lead/zinc mining and smelting on the environment and human health in China. *Environ Monit Assess.* 184:2261–2273.

