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ENVIRONMENTAL TOXICANTS AND THEIR ECOLOGICAL AND HEALTH IMPLICATIONS: A STUDY OF FIVE LGAS IN KOGI STATE

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Abstract
Public health and environmental protection is increasingly becoming a serious concern for sustainable development and being disease free. Topography and slope aspects influence soil erosion and consequently have impact on the properties of soils. This study assessed the ecological and human health risk of environmental pollutants, their sources and water quality. Seventy-five (75) samples each of soil, plant and water samples were collected from five different local government areas of Kogi State, namely; Lokoja, Okehi, Ankpa, Yagba West, and Ajaokuta LGAs. The results showed that the mean concentration of heavy metals in the soils were in the order; Fe > Pb > Cr > Zn > Ni > Cu > Co > Sn > Sc > As > Cd. The heavy metals in the water was in the order; Fe > Zn ≥ Cr ≥ Pb ≥ Cu ≥ Ni ≥ Cd ≥ As ≥ Co. All the heavy metals in water were below their permissible levels for drinking water quality. The geo-accumulation index (Igeo), Contamination factor, Pollution load index (PLI) revealed that the overall pollution status of the soils ranged from no contamination to severe contamination while heavy metals posed low ecological and human health risk according to the ecological hazard factor and potential risk index. The human health risk assessment showed that children faced higher health risk than adults especially via the ingestion exposure pathway. The results of the physical, chemical and microbiological parameters of water quality revealed that most parameters measured were within and below the WHO/NSDWQ standard fr drinking water quality threshold except for the microbiological properties which were higher than the permissible limits for drinking water quality making the water not fit for drinking and other domestic uses. Regular soil and water testing and monitoring should be made mandatory for public health protection. Remediation of areas with heavy metals should be done to forestall further contamination and future hazards.

Keywords: *Ecological, Health Risk Assessment, Heavy metals, Pollution, Contamination, Remediation*

INTRODUCTION Background Information

In our world today, environmental pollution cum contamination is one of the leading cause of deadly diseases, immense morbidity, and high mortality rate. According to the World Health Organization (WHO) approximately seven (7) million deaths annually is associated with pollution, mostly due to environmental toxicants (Adewale et al. 2023; Yahaya et al. 2021; WHO, 2006). Incidence of heavy metals and pesticides contamination in some parts of Kogi State, Southern Guinea Savanna of Nigeria due to artisanal mining and use of chemicals (inorganic fertilizers, herbicides, pesticides for Agriculture have been reported to have resulted in the pollution of vast area of land and water.

Contamination of soil and water bodies by environmental toxicants from mining and intense use of chemicals for agriculture is an emerging concern in Kogi State and Nigeria at large (Majabi et al. 2023; Henry et al., 2021; Ekwule et al., 2021). Pollution of natural environment due to release of pesticides and heavy metals from various sources is a widespread problem throughout the world. Accumulation, toxicity and persistence of heavy metals, which are accumulated in our environment as a result of natural and anthropogenic activities, pose a serious environmental threat and problem in our world today. The illegal mining and intense mineral extraction in mining areas has produced a large amount of industrial waste material, leading to the release of toxic elements to the environment (Nuhu et al., 2014) particularly heavy metals (Abdu and Yusuf, 2013). Heavy metals and pesticides are common environmental pollutants and exposure to their significant levels can result in deleterious effects on humans, animals and plants. These illegal and intense mineral extraction produced a large amount of waste material accumulated on the heaps or tailings (Majabi et al., 2023) and without proper and precise managements, the minerals on the heaps and tailing serve as the source of heavy metals, which are washed out by precipitation and can pollute the environment (Li et al., 2015; Li et al., 2014).

Soils and water are rich ecosystems, composed of both living and non-living matter with a multitude of interaction between them. It is also a critical component because it can accumulate pollutants produced by natural and anthropogenic activities such as mining, industry, agriculture, vehicular movement etcetera. The interaction of the different processes of physical, chemical and biological means aid the transport of heavy metals and pesticides in soil (Shokunbi et al., 2020). However, these polluted soils usually become the source of contamination of the environment and consequently entering the food chain (Zhang et al., 2016; Yoon et al., 2006). The heavy metals and pesticides are known to be non-degradable and very persistent, their presence in soil is stable and long-term, and these pose risks to the environment and public health (Oteno et al., 2023). Environmental monitoring of soil and water sources is critical in understanding the impact of toxicants and soil/water interactions, as well as determining the potential accumulation in plants, resulting in food safety and security problems and potential human health risks (Majabi et al., 2023; Shokunbi et al., 2020).

Statement of Research Problem

There is a global concern for environmental pollution due to build-up of high levels of toxic substances especially heavy metals. Many diseases are a result of an interaction between our genetics (individual variabilities) and chemicals in our environment. Recent reports of high incidence of cancer and water related diseases is alarming. Reports of child mortality, morbidity and disorders in Kogi State and Nigeria is quite frightening (Adewale et al., 2023). This threat to human existence has called for this research, to provide adequate and accurate data for the public, farmers, drinking water producers and health institutions to help prevent risks of metal pollution and secure public health. The assessment of this pollutant load in selected LGAs is very necessary. Increased levels of heavy metal toxicity because of human or anthropogenic activities (Ying et al., 2016). This widespread effect of anthropogenic activities has become a threat to Agriculture, human health, and the environment at large.

As the human population continues to grow geometrically, great pressure is being placed on arable lands and water sources to provide adequate supply of food (crops and fish especially) which forces farmers to use chemicals indiscriminately in order to achieve market demand. The continuous application of these chemical may lead to the accumulation of heavy metals in the soil.

Furthermore, the population growth has led to substantial increase in the quantity and diversity of waste product more specifically or particularly the municipal solid wastes which one vital means or options for the disposal of this waste is through careful and safe dumping or application on the land as amendment which has raised concern over the concentration of heavy metals and pesticides such as cadmium, Copper, Lead and Zinc. Heavy metals are not degradable and can persist in the soil for decades and even centuries as they react with soil components through ion exchange, coprecipitation and complexation processes.

Justification of the Study

Incidence of heavy metals contamination in Kogi State Nigeria as a result of mining, waste dumping and chemical use in agriculture has captured a lot of attention, and many researches have been conducted to assess the levels of the heavy metals in the area (Peter et al., 2023; Majabi et al., 2023; Oteno et al., 2023; Sunday et al., 2022; Ekwule at al., 2021; Henry et al., 2021; Shokunbi et al., 2020; Adedeji et al., 2020; Salifu, 2017; Ocheje et al., 2018; Cooper, 2017; Oluokun et al., 2017; Michael et al., 2015; Musa et al., 2013; Matthews et al., 2012; Omanayi et al., 2011). However, to the best of my knowledge little or no study has been reported on the ecological and human health risk of these contaminated areas. Long-term, low-level exposure to common pollutants like heavy metals in our environment is detrimental to health (Yahaya et al., 2020), therefore there is need to assess the levels of this pollutant not only in contaminated soils but also to the soils and water sources of our environments, in order to provide information on the level of risks for proper managements.

Ecological and health risk assessment of environmental toxicants usually heavy metals and pesticides in polluted soil and water bodies has been receiving more attention in recent years (Yahaya et al., 2020; Ying et al., 2016; Wu et al., 2015). The ecological risk assessment will provide information on the possibility of soil or water being polluted and even for ecological function to be compromised/harmed by specific heavy metals and pesticides, while the human risk assessment can be used to provide information to public health workers, other stakeholders, government, and non-governmental organizations to make informed decisions (Yahaya et al., 2020). Furthermore, studying heavy metals concentration, its ecological and human health risk is of unique importance, as it can affect agricultural production due to adverse effects on food quality (Abdu et al., 2011a, 2011b, 2011c) reduces crop growth and yield (Abdu and Yusuf, 2013; Abdu, 2010), and as well causes health risk hazards either indirectly; by consuming contaminated products, or directly by inhaling contaminated dust or drinking contaminated water (Zhang et al., 2014).

In addition, Information of this study is necessary for developing strategies for soil/site remediation, water quality monitoring, mining restrictions and urban environmental quality management. Ecological cum Toxicological studies provides an interesting and exciting way to apply science to important problems of social, environmental, and public health significance (CLUI-IN, 2017; Wuana and Okieimen, 2011). These therefore necessitated this study with the aim to meet the under listed objectives.

Objective(s) of the Study:

Aims and Objectives

The main goal of this research is to assess the ecological and health risks associated with environmental toxicants in Kogi State, Nigeria. The study is designed with specific objectives to:

i. Assess the status of pesticides and heavy metal pollution in arable lands, mining sites waste dumpsites and water sources in the affected local government areas of Kogi State, Nigeria. ii. Assess the ecological risks of heavy metals contamination in the affected LGAs.

iii. Assess the human health risks and hazards because of pesticides and heavy metals contamination in the affected LGAs.

iv. Determine the water quality of surface and ground water sources in the affected LGAs for drinking and health implications.

REVIEW OF RELATED LITERATURE Environmental Toxicants

Synthetic or artificial products produced because of human activity such as liquid and solid waste products of the industry and mining are called toxicants. It could be put as a measure of the extent or degree to which a known substance can harm the body of an plant, animal and humans (organism) (Mbah and Anikwe, 2010). They can contaminate or pollute an environment and causes harm to its inhabitants (crops plants, animals, and human beings).

Sources of Water and Soil Pollutants

Surface water and soils can be contaminated by a point or nonpoint sources of environmental toxicants. Industrial wastes ideally constitute the highest pollution issues in soil and water. These contaminants include heavy metals (chromium, lead, zinc, cadmium, copper) organic wastes such as solvents, inorganic wastes. Contamination of soil and water results when by-product chemicals are not properly disposed of or conserved. In addition, industrial accidents may lead to severe local contamination. Domestic and municipal wastes, both from sewage and from disposal of chemicals, are another major source of chemical pollutants (Ihedioha et al., 2016). At the turn of the twentieth century, municipal wastes received no treatment and were discharged directly into rivers or oceans. Even today, many older treatment plants do not provide sufficient treatment, especially plants in which both storm water and sewage are combined.

Pesticides as environmental toxicants are ranked also as a major source of concern as water and soil pollutant due to their stability and persistence, the most hazardous pesticides are the organochlorine compounds such as DDT, aldrin, dieldrin, and chlordane. Persistent pesticides can accumulate in food chain. Herbicides also when used in large quantities can be viewed as a serious concern as potential toxic pollutants. However, mining is another source of environmental toxicants (Henry *et al.* 2021).

Water Quality and Pollution

Christopher and Olatunji (2018) carried out the assessment and classification of Ogbese River using quality index (QI) tool. The results obtained indicated that most of the parameter was within maximum permissible limit of World Health Organization, Food and Agriculture Organization (FAO) and Nigeria Standards for Drinking Water Quality (NSDWQ) with the exception of total dissolved solids, turbidity, electrical conductivity and total coliform in both seasons. Lead, Zinc and Iron were not detected in dry season, while their traces were recorded in wet season. The water quality indices indicated considerable degrees of pollution with classification numbers of 46.61 and 44.91 for dry and wet seasons respectively.

Adeaga et al. (2013) worked on the quality of surface water upstream of Niger Delta. The study focused on major ions and trace elements concentration and provides an update of trace metals and arsenic concentration in water of Niger Basin and of the region of Lagos, Nigeria for standardization and comparison with WHO maximum allowable concentrations in drinking water and mean annual European Quality Standards (EQS). The water quality assessment reflects the fact that the water resource from the Niger and Benue River Basins is moderately contaminated upstream of their confluence (Lokoja) except for Pb. Downstream of their confluence, particularly around the Lagos region, drinking water exceeds the WHO quality water for Mn, and to a lesser extent, Al. the arsenic concentrations are lower than the drinking water quality standards and are safe for consumption and irrigations upstream of the Niger Delta.

Akwanwa et al. (2011) worked on the ground water quality around open waste dump sites Ifejika and

Obosi in Anambra State Nigeria. The ground water quality was investigated using experimental method. Two dump sites were studied with a total of four Leachate samples collected from each dump site. Similarly, twelve ground water samples were collected from the vicinities of the dump sites during the rainy season. The physical, chemical and bacteriological parameters of the leachate of the ground water samples were analyzed using experimental method. The survey method was used to sample the opinions of people on the effect of the waste dumps on the ground water. The heavy metals were determined using AAS and the student t – test was used to analyze the data generated. The physical, chemical and bacteriological content of the leachates shows marked deviations from the acceptable standard in treated waste water discharge in Nigeria. The chloride, sulphate, Nitrite, Iron, total coliform and E-coli in both areas also shows deviations above the acceptable standard in drinking water quality in Nigeria. The high level of coliform and E-coli showed fecal contamination and human pathogenic bacteria in the ground water of the area. The heavy metals both in the leachate and the ground water samples were within the acceptable standard. The study recommends that ground water in the area be treated before use and the wastes dumped be closed or managed in an environmentally friendly way

Heavy Metals in our Environment

The presence of heavy metals in the soil is not an indication of contamination (McLean and Bledsoe, 1992) because of the geology of the parent material from which the soil is formed. Higher concentration of heavy metals in soils is closely associated with biological and geochemical cycles, and is influenced by anthropogenic activities (Abdu, 2010). Many industries such as textile industries, diaries, recycle facilities, fertilizer industries, tin and drug industries, are among primary causes of heavy metals pollution (Patil and Kaushik, 2016). Different chemical reactions occur between heavy metals and surfaces of clay minerals, metal oxides and oxyhydroxides, humic substances, plant roots, and microbes. These reactions control the toxicity, solubility, mobility, and bioavailability of metals in our environment. Heavy metals are non-degradable and toxic in soil and water bodies; hence it becomes a subject of several studies that draw global attention (Shafie et al., 2014) many physical and chemical properties of soil affect the concentration of heavy metals in soil of which organic matter and pH are the most important properties controlling the accumulation and availability of heavy metals in soil environment (Nyamanga and Mzezewa, 1999).

Heavy Metals Pollution Sources

Weathering of parent materials through pedogenesis released heavy metals into the soil environment at levels that are regarded as trace (<1000 mg/kg) and rarely toxic (Pierzynski et al., 2000; Kabata-Pendias and Pendias, 2001). While activities of man through various anthropogenic processes lead to the accumulation of one or more of the heavy metals above defined background values high enough to cause risks to human, plants, animals, or the entire ecosystems (D'Amore et al., 2005). Soils become more rapidly contaminated with heavy metals because; the rates of heavy metals generation through manmade activities are more rapid compare to the natural ones (Abdu, 2010), heavy metals are transferred from mines to random environmental locations where higher potentials of direct exposure occur, the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (D'Amore et al., 2005; Abdu and Mohammed, 2016).

A simple mass balance of the heavy metals in the soil can be expressed as follows (Alloway, 1995; Lombi and Gerzabek, 1998):

$$M_{total} = (M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip}) - (M_{cr} + M_l)$$

where "M" is the heavy metal, "p" is the parent material, "a" is the atmospheric deposition, "f" is the fertilizer sources, "ag" are the agrochemical sources, "ow" are the organic waste sources, "ip" are other inorganic pollutants, "cr" is crop removal, and "l" is the losses by leaching, volatilization, and so forth. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones (Kuo et al., 1983; Kaasalainen and Yli-Halla, 2003). Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources as discussed hereunder.

i. Application of fertilizers

Historically, the first major human influence on the soil was agriculture (Scragg, 2006). Plants require both macronutrients and micronutrients to grow and complete their lifecycle. Though the micronutrients are required in small amounts, some soils are deficient in the heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni and Zn) which are essential for healthy plant growth (Lasat, 2000). Hence crops may be supplied with these as an addition to the soil or as a foliar spray, and these may lead to their accumulation. In the intensive farming system, large quantities of fertilizers are regularly applied to the soils to provide adequate N, P, and K for crop growth. The compounds used to supply these elements contain trace amounts of heavy metals (e.g. Cd and Pb) as impurities. Therefore, continued application of fertilizers may significantly increase its content in soil (Jones and Jarvis, 1981). Also, application of certain phosphatic fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including F, Hg and Pb (Raven et al., 1998).

ii. Wastewaters disposal

Application of industrial and municipal wastewater to agricultural and non-agricultural lands is now a common practice in many parts of the world (Reed et al., 1995). Studies suggest that agriculture based on wastewater irrigation accounts for 50% of the vegetable supply to urban areas in several Asian and African cities (Bjuhr, 2007). The treatment of wastewater for irrigation in developing countries is limited, therefore raised a serious concern for the potential accumulation of heavy metals to these soils when irrigated with untreated wastewater. Abdu et al. (2011a) observed that the concentrations of Cd and Zn throughout the profiles understudy from five vegetable gardens under 30years of wastewater irrigation in Kano attained unsafe levels (Cd is 2.3 – 4.8 mg/kg and Zn is 13 – 285 mg/kg). This is attributed to the wastewater applied to the soil because natural soils of the Nigerian Savannah are characterized by low heavy metals concentrations due to their high weathering intensity and long period of pedogenesis (Agbenin and Latifatu, 2004). Although the wastewater effluents contain heavy metals at a relatively low concentration, long-term application of the wastewater to the soil can eventually result in heavy metals accumulation in the soils.

iii. Application of pesticides

To control pest and disease in agricultural and horticultural productions, pesticides are required. Several common pesticides that are used extensively contained substantial concentration of heavy metals. For instance, Bordeaux mixture (copper sulphate) and copper oxychloride are copper containing fungicidal sprays (Jones and Jarvis, 1981). For many years lead arsenate was used in fruits orchards to control some parasitic insects (Wuana and Okieimen, 2011). In New Zealand and Australia, arsenic containing compounds were also used extensively to control cattle ticks and to control pests in banana, timbers have been preserved with formulations of Cu, Cr, and As, and there are now many sites where soil concentration of these elements greatly exceed background concentrations (Wuana and Okieimen, 2011). The potentials of pesticides causing soil contamination is more compared with fertilizers, because the use of such materials has been restricted to particular sites or crops (McLaughlin et al., 2000).

iv. Air-borne sources

Generally heavy metals from airborne sources are released as particulates contained in the gas stream. Volatilization of some metals such as As, Cd, and Pb also occur during high temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained (Smith, 1995). Site-specific conditions play a vital role in determining the type and concentration of metals emitted from a source. The solid particles in smoke from fires and from industrial chimneys are eventually deposited on land or water bodies, and those deposited on water bodies may be taken to lands through irrigation. This raised the amounts of heavy metals in soils. For example, very high concentration of Cd, Pb, and Zn has been found in plants and soils adjacent to smelting works (Wuana and Okieimen, 2011). Another major source of soil contamination is the aerial emission of Pb from the combustion of petrol containing tetraethyl lead, this contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Zn and Cd may also be added to soils adjacent to roads, the sources being tyres, and lubricant oils (USEPA, 1996a).

v. Mining and processing of metal ores

Mining and milling of metals ores have resulted to the widespread distribution of heavy metals contaminants in soils. During processing of metals ores, larger and heavier particles are directly discharged into natural depressions, including onsite wetlands resulting in elevated concentrations of the metals (DeVolder et al., 2003). Abdu and Yusuf (2013) reported that gold ore contain Pb as impurity and hence Pb was developed in the soils during processing of the ore, and these resulted in a widespread Pb contamination in the villages and compounds where gold ore are processed. Extensive Pb and Zn ore mining and smelting have resulted in contamination of soils.

vi. Industrial discharges

Many industries such as tanning, petrochemicals, textile, pesticides, pharmaceuticals etc. disposed wastes which are highly variable in composition. Although some are disposed of on land, few have benefits to agriculture or forestry. In addition, many are potentially hazardous because of their contents of heavy metals (Cr, Pb, and Zn) or toxic organic compounds and are seldom, if ever, applied to land. Others are very low in plant nutrients or have no soil conditioning properties (Sumner, 2000).

vii. Application of manures and biosolids

Application of animal wastes especially from poultry, pigs, and cattle as manure to soil either as solids or slurries is now a common practice (Sumner, 2000). And these inadvertently lead to the accumulation of heavy metals such as Cd, Cr, Cu, Hg, etc. in the soil (Basta et al., 2005). This is as a result of metals been part of the additives to the feed and poultry health products. For example, Cu and Zn are added to diets of animals as growth promoters while As is contained in poultry health products (Chaney and Oliver, 1996; Sumner, 2000). The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn. Although most manures are valuable fertilizers, repeated application of thus in a restricted area of land can cause considerable buildup of these metals in the soil in the long run. Heavy metals where identified in biosolids (a primarily organic solid product, produced by wastewater treatment processes that can be beneficially recycled (USEPA 1994a)) of which the most commonly found are Pb, Ni, Cd, Zn, Cr, and Cu, and the metal concentrations are governed by the nature and intensity of the industrial activity, as well as the type of process employed during the biosolids treatments (Mattigod and Page, 1983). Therefore, there is high potential of soil contamination through biosolids application. An increase concentration of Cd, Ni, and Zn in drainage leachates was observed on some New Zealand soils treated with biosolids (Keller et al., 2002; McLaren et al., 2004).

Potential Health Risks and Soil Chemistry of Heavy Metals

Heavy metals have widespread environmental distribution. They are originated from natural and anthropogenic sources and constitute one of the common environmental pollutants that put human lives at risk (Bennett et al., 2003). The following metals are the most common heavy metals found at contaminated sites, these are; Pb, Cr, As, Zn, Cd, Cu, and Hg (USEPA, 1996b). These heavy metals contamination is being recognized to be dramatically increasing in large parts of the developing countries, especially in China and India (Cheng, 2003; Meharg, 2004). Those metals are important since they are capable of decreasing crop production and have the risk of bioaccumulation and biomagnification in the food chain. Therefore, the toxicity as a result of metal contamination arising from different sources is a great problem on ecological, evolutionary, nutritional, and environmental perspective (Nagajyoti et al., 2010; Jaishankar et al., 2014). Understanding the basic chemistry, environmental and associated health effects of these heavy metals is of important in knowing their speciation, bioavailability, and remedial options. The fate and transport of a heavy metals in soil depends significantly on the chemical form and speciation of the metal (Abdu and Mohammed, 2016). Heavy metals in soil are redistributed into different chemical forms with varying bioavailability, mobility and toxicity (Shiowatana et al., 2001; Buekers, 2007). This distribution is believed to be controlled by reactions of heavy metals in soils such as mineral precipitation and dissolution; ion exchange, adsorption, and desorption; aqueous complexation; biological immobilization and mobilization; and plant uptake (Levy et al., 1992).

Lead (Pb)

Lead is a metal with atomic number 82, atomic mass 207.2, density 11.4 g/cm3, melting point 327.40C, and boiling point 17250C. It belongs to group IV and period 6 of the periodic table. It occurs naturally with a bluish gray colour, and usually found as mineral combined with other elements like sulphur and oxygen. It ranges from 10 to 30 mg/kg in earth crust (USDHHS, 1999), and a typical mean concentration for the surface soils worldwide averages 32 mg/kg and ranges from 10 to 67 mg/kg (Kabata-Pendias and Pendias, 2001). The general forms of Pb that are released into surface waters, groundwater, and soil include ionic Pb, Pb (II), Pb oxides and hydroxides, and lead-metal oxyanion complexes (Wuana and Okieimen, 2011). The most common and reactive form among the Pb compounds is Pb (II), it has ability to form mononuclear and polynuclear oxides and hydroxides (GWRTAC, 1997). Above pH 6 insoluble Pb compounds such as Pb phosphate and Pb carbonate predominates the soil (Raskin and Ensley, 2000). Lead sulfide is the most stable solid form within the soil matrix (Wuana and Okieimen, 2011). Under anaerobic conditions a volatile organo-lead (tetra methyl lead) can be formed due to microbial alkylation (GWRTAC, 1997).

Humans can come into contact with Pb through inhalation and ingestion as the two major exposure routes, and the effects from both are the same (Wuana and Okieimen, 2011). Lead has the ability to accumulate in the body organs such as brain, kidney and central nervous system causing poisoning (plumbism) or even death. Children exposed to Pb are at risk for lower IQ, impaired development, shortened attention span, hyperactivity and mental deterioration, with children under the age of six being at a more substantial risk

(Wuana and Okieimen, 2011). For adults, it usually causes nausea, insomnia, anorexia, and weakness of the joints (NSC, 2009). Lead is not an essential element and plant do not absorb or accumulate Pb, but however, in soil testing high in Pb, it is possible for some Pb to be taken up (Wuana and Okieimen, 2011). Generally, it has been considered safe to grow crops in soil with total Pb levels less than 85mg/kg (DPR, 2002). But there is risk if the concentration rises above this level. And most of the risk is from Pb contaminated soil or dust deposits on the plants rather than from uptake of Pb by plant (Rosen, 2002).

Cadmium (Cd)

Cadmium is also a transition element with atomic number 48, atomic weight 112.4, density 8.65 g/cm3, melting point 320.90C, and boiling point 7650C. It belongs to d-block and period 5 of the periodic table. It occurs naturally as a soft, malleable and blue-white metal. Cadmium occurs as divalent Cd (II) ion. It is directly below zinc in the periodic table and has a chemical similarity to that of zinc, and hence substitutes zinc leading to malfunctioning of metabolic processes done by zinc (Campbell, 2006). Cadmium is present as impurities in several products, including phosphate fertilizers, detergents and refined petroleum products. Campbell (2006) reported that acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface-water concentration tends to increase as lake water pH decreases. The sources of Cd contamination to soil includes application of agricultural inputs such as fertilizers, pesticides, biosolids, disposal of industrial wastes, deposition of atmospheric contaminants, and from byproducts of zinc and occasionally Pb refining. Cadmium is being absorbed by plants, hence its bioavailability determines whether plant Cd uptake occurs to a significant degree (Weggler et al., 2004).

Many enzymatic functions are known to be affected by high Cd concentration in the body. It also reduces the activity of delta-aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase (Manahan, 2003). The itai-itai disease incidence experience by people of Jintsu River Valley, near Fuchu, Japan, makes Cd poisoning to be well known. It was attributed to consuming irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd (Wuana and Okieimen, 2011). The major threat of Cd poisoning to human health is it chronic accumulation in the kidneys leading to kidney dysfunction. The main route by which Cd enters the body is food intake and tobacco smoking (Manahan, 2003). Cadmium is not an essential element for metabolic activities.

Chromium (Cr)

Chromium is also a transition element with atomic number 24, atomic weight 52, density 7.19 g/cm3, melting point 18750C, and boiling point 26650C. It is a first-row d-block element belonging to group VIB and period 4 of the periodic table. It is one of the less common elements, found only in compounds with crystalline steel-gray appearance. Chromium is mostly obtained in mining as a primary ore product in form of the mineral chromite, FeCr2O4. Releases of Cr from electroplating processes and disposal of Cr containing wastes are the major sources of Cr contamination (Smith et al., 1995). The commonly found Cr at contaminated sites is Cr (VI), and it can also occur in +III oxidation state depending on pH and redox conditions. Wuana and Okieimen (2011) stated that Cr (VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. And it can be reduced to Cr (III) by soil organic matter, S2- and Fe3+ ion under anaerobic conditions in deeper groundwater. The most toxic among Cr ions is Cr (IV) and is also more mobile. While Cr (III) is less mobile as the mobility is decreased by adsorption to clays and oxide minerals below pH 5; and low solubility above pH 5 due to the formation of Cr (OH)3 (Chrostowski et al., 1991). The disease associated with Cr in humans is allergic dermatitis (Scragg, 2006)

Zinc (Zn)

Zinc is a transition element with atomic number 30, atomic mass 65.4, density 7.14 g/cm3, melting point 419.50C, and boiling point 9060C. It falls under group IIB and period 4 of the periodic table. It occurs naturally as a hexagonal crystal with bluish-white colouration (Shalini et al., 2017). It also occurs naturally in soil with a concentration of about 70 mg/kg in crustal rocks (Davies and Jones, 1988). It can be found freely or combine in air, soil, water and food materials. Drinking water also contains certain amounts of Zn, which may be higher when it is stored in metal tanks. Initially concentration of Zn in soil is low, but it is rising due to anthropogenic activities such as mining, coal, waste combustion, agricultural activities etc. (Bhagure and Mirgane, 2011). Zinc is a trace element that is essential for human and plant health, high concentration in drinking water and food chain can lead to health problems. Zinc shortages can cause birth defects (Wuana and Okieimen, 2011). It generally interrupts the activities in soils when it is high, as it negatively influences the activity of microorganisms and earth worms, thus retarding the breakdown of organic matter (Greany, 2005).

Nickel (Ni)

Nickel is also a transition metal with atomic number 28, atomic mass 58.69, density 8.902 g/cm3, melting point 14530C and boiling point 27320C. It falls under d-block and period 4 of the periodic table. It occurs naturally as a hard, malleable and silvery white metal. In acidic solution, it exists in the form of the nickelous ion (Ni (II)). While in neutral and slightly alkaline solutions, it precipitates as nickelous hydroxide (Ni (OH2)2), which is a stable compound. The nickelous hydroxide can be readily dissolves in acid solutions to form Ni (III) while in a very alkaline conditions it forms nickelite ion (HNiO2) that is soluble in water (Wuana and Okieimen, 2011). The major sources of nickel contamination to soil are combustion of fossil fuels, metal plating industries, and nickel mining and electroplating (Khodadoust et al., 2004). Nickel was first released into the air from the different sources and later settles into the grounds after undergoing precipitation reactions.

Even though it is required by both plant and animals for their metabolic activities, it can be dangerous when the maximum tolerable amounts are exceeded. These can cause various kinds of cancer on different sites within the bodies of animals, mainly those that leave near refineries. And also, microorganisms suffer from growth decline due to the presence of Ni, but they usually develop resistance to Ni after some time (Wuana and Okieimen, 2011). Nickel is not known to accumulate in plants or animals (Wuana and Okieimen, 2011) and as a result have no potential to biomagnified up the food chain.

Iron (Fe)

Iron is also a transition element with atomic number 26, atomic weight 55.85, density 7.874 g/cm3, melting point 15350C, and boiling point 27500C. It is malleable, ductile, silvery-white metal which when exposed to surfaces form red-brown oxides. It is relatively abundant in many cultivated soils with an average concentration of 20 to 40 g/kg (Cornell and Schwertmann, 2003; Raji et al., 2015) and it is also the most abundant trace mineral in the body and is an essential element in most biological systems (Goyer, 1996; Greentree and Hall, 1995). Iron in oxidation state of +II (ferrous state) is mainly present in primary minerals and some phyllosilicates. While its oxidation to iron (III) (ferric state) result in important pedogenetic changes (Stucki et al., 2002) resulting the formation of a series of 'conjugate base' where Fe is coordinated with water and hydroxyls (Sposito, 1989). Iron is an essential plant nutrient which is mainly involved in the process of plant photosynthesis, therefore the deficiency of Fe in soil can lead to chlorosis and stunted growth of plants.

Iron is also an essential element for developing aerobic life on Earth (Williams, 1990). But it is toxic to cells in excessive amounts. Acute iron poisoning is common and potentially lethal in dogs, cats, and many other animals. Iron is also a leading cause of unintentional poisoning deaths in children less than 6 years old (Albretsen, 2006).

Health Risk Assessment of Heavy Metals Contaminated Soils

Ecology as defined by Begon et al. (2006) is the scientific study of abundance, distribution, and relations of organisms and their interactions with the environment. Heavy metals are generally harmful and caused significant risk to both the ecosystem and human health, although some are essential for metabolic activities for both plants and animals, they can be toxic at higher concentration. Fan et al. (2017) observed in a near three mining areas in central China that a combined hazard index caused by five heavy metals was about 22.59 with total cancer risk of
0.1773, of which Cd contributed the most significant cancer risk, accounting for approximately
99.77% of the risk. They concluded that potential noncarcinogenic and carcinogenic health risk exist for local inhabitants. In the investigation of heavy metal toxicity by Li et al. (2015) in soils around a smelter in southern China, they found a significant pollution of local soils by Pb, Cd, As, Sb, and Hg, in which Pb has the highest concentration. Wu et al. (2015) reported that 74.6% of soil samples from Du'an county in China are contaminated with eight heavy metals understudy, with Cd having concentration to be 70.6% higher than the permitted standard. Investigation of some villages located in central Gansu Province, China, found that Pb concentrations for arid agricultural soils exceeded the threshold by about 72.46% (Li et al. 2008). Odat (2015) observed a behaviour of Cd along Irbid/Zarqa highway-Jordan to have an enrichment factor of 38.7 and geoaccumulation index of 1.41, suggesting that the higher concentration may be due to burning of fossil fuel and wear and tear of tyres. Okegye and Gajere (2015) observed that the concentration of Cr, Cu and Ni in surface and groundwater resources around Udege Mbeki mining district of north-central Nigeria, are generally within the permissible limit of the WHO (2006) guideline, whereas concentration of Fe, Co, Pd, and Cd exceeded the maximum permissible limit. They attributed the higher concentration to be caused by anthropogenic activities. Observation of former mining area before and after the end of mining activities by Demkova et al. (2017) revealed that the values for Hg, Zn, and Cd concentrations exceeded limit values at all sampling sites within both studied years. In a study by Ihedioha et al. (2016) on municipal solid waste dumpsite in Uyo, Nigeria, they found that Cd contributed 98 – 99% of the total potentially ecological risk, while no probable health risk was observed as the total hazard index of the metals was less than one. Different indices were used to access the degree of metal contamination, ecological risk, human health risk, sources of the metals contamination etc. they are discussed hereunder:

i. Enrichment factor, EF

Enrichment factor is an indication of the level of accumulation of the element of interest to the natural background level. Thus, it measures the geochemical trend and can be used in making comparisons between an area and overtime. The enrichment factor of the metals in soil are usually calculated based on equation proposed by Sutherland (2000). Mostly iron is used as a reference element since it is the most

naturally abundant element in soil (Okuo and Iyasele, 2007). Mostly iron is used as a reference element since it is the most naturally abundant element in soil (Okuo and Iyasele, 2007).
Thus, it is calculated using the equation below:

$$EF = \frac{\left(\frac{Msample}{Resample}\right)}{\left(\frac{Mref}{Reref}\right)}$$

Where EF is enrichment factor, Msample and Resample are the concentrations of the metal and the reference metal in the contaminated soil and Mref and Reref are concentrations of the metal and the reference metal in the reference soil (Abrahim and Parker, 2008; Abdu et al. 2011a).Sutherland (2000) categorize enrichment factor depending on the value of EF into five classes, these are: deficient to minimal enrichment, moderate enrichment, significant enrichment, very high enrichment and extremely high enrichment.

ii. Geo-accumulation Index, Igeo

Geo-accumulation index (Igeo) is used to determine and define metal contamination in the soils. It is done, by comparing current concentrations with pre-contamination levels. It was computed using an equation proposed by Ntekim et al. (1993). Hence;

$$Igeo = \log2 \left[\frac{Cn}{1.5\,Bn}\right]$$

Where Cn is the measured concentration of the examined metal n in the soil and Bn is the geochemical background concentration or reference value of the metal n. Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences (Abdu et al. 2011a; Ihedioha et al. 2016).
Seven classes of geoaccumulation index (Igeo) were distinguished by Muller as in Buccolieri et al. (2006), viz: Class 0 – unpolluted; Class 1 - unpolluted to moderately polluted; Class 2 - moderately polluted; Class 3 - moderately to strongly polluted; Class 4 - strongly polluted; Class 5 - strongly to extremely polluted; and Class 6 - extremely polluted.

iii. Contamination factor (CF)

Contamination factor is a measure used to identify the intensity of contamination of a given element in the soil sample. It was determined based on the equation proposed by Lacatusu (2000) as below;

$$CF = \frac{Concentration\ of\ the\ metal\ in\ the\ soil}{Target\ (Background) Value}$$

The target (background) value is a reference value of metals concentration (mg/kg) obtained from the standard table formulated by the Department of Petroleum Resources of Nigeria (DPR, 2002) for maximum allowable concentration of metals in the Nigerian soil in case of Nigeria, or the world crustal average contamination of the trace metals under consideration may be used as the target value (Abdu et al., 2011c). Contamination factor values greater than one defines the pollution range, while values lower than one defines the contamination ranges. The standard employed for interpreting soil heavy metals contamination/pollution index varies from country to country based on the chosen factors (Lacatusu 2000).

Ten contamination categories are recognized on the basis of contamination/pollution factor (CF) by Lacatusu (2000), these categories are: very slightly contamination, slight contamination, moderate contamination, severe contamination, very severe contamination, slight pollution, moderate pollution, severe pollution, very severe pollution and excessive pollution.

iv. Pollution load index (PLI)

The pollution load index as proposed by Tomlinson et al. (1980), is used to gives an estimate of the metals contamination status and the necessary action that should be taken. It is calculated using the equation below;

$$PLI = (CF1 \times CF2 \times CF3 \times CF4 \ldots \ldots \times CFn)^{1/n}$$

Where n is the number of metals studied and CF is the contamination factor calculated as described above. The value of PLI was classified into four groups by Wang et al. (2010), these are: no pollution, moderate pollution, heavy pollution and extreme pollution.

Ecological risk factor (ErF)

Ecological risk factor (ErF) quantitatively expresses the potential ecological risk of a given single contaminant. It is calculated based on equation proposed by Hakanson (1980) and is given as:

$$ErF = Tri \times CFi$$

Where Tri is toxic response factor of a given substance, CFi is the contamination factor. Five terminologies are used to describe ecological risks based on Hakanson (1980), these are: low potential ecological risk, moderate potential ecological risk, considerable potential ecological risk, high potential ecological risk and very high ecological risk Potential ecological risk index, RI.

The potential ecological risk index (RI) is in the same manner as degree of contamination/ pollution load index defined as the sum of the risk factors:

$$RI = (ErF1 + ErF2 + ErF3 \ldots\ldots + ErFn)$$

where ErF is the ecological risk factor, n is the number of element studied. The following terminologies have been used for the potential ecological risk index by Hakanson (1980), these are: low ecological risk, moderate ecological risk, considerable ecological risk and very high ecological risk.

Human health risk assessment

Human can come into contact with heavy metals directly through three exposure pathways: direct ingestion of particles containing heavy metals; dermal absorption of trace elements in particles adhered to exposed skin; and inhalation of the suspended particles through mouth and nose. The average daily dose or intake (ADD, mg/kg/day) for non-carcinogens through each of the three exposure pathways were normally used for the assessment and is calculated using the following equations as proposed by USEPA (1989, 1996a).

$$ADDinh = \frac{C \times Rinh \times EF \times ED}{PEF \times BW \times AT}$$

$$ADDing = \frac{C \times Ring \times EF \times ED \times 10\text{-}6}{BW \times AT}$$

$$ADDderm = \frac{C \times SL \times SA \times ABS \times EF \times ED \times 10\text{-}6}{BW \times AT}$$

Where:

ADDinh is average daily dose for inhalation, ADDing is average daily dose for ingestion, ADDderm is average daily dose for dermal contact, C is Concentration (mg/kg) of each metal in soil, Ring is ingestion rate, Rinh is inhalation rate, EF is exposure frequency, ED is exposure duration, SA is exposed skin area, SL is skin adherence factor, ABS is dermal absorption factor, PEF is particle emission factor, BW is average body weight and AT is averaging time for noncarcinogens.

The potential health risk of the soil heavy metal is estimated using a hazard quotient (HQ). The non-cancer hazard quotient (HQ) assumes that there is a level of exposure known as the reference dose (RfD), which is a daily intake rate that is estimated to pose no appreciable risk of adverse health effects, even to sensitive populations, over a 70-year lifetime (USEPA 2005a). The reference dose is an estimate of a daily exposure to the human population. Hazard quotient (HQ) is defined as the ratio of the average daily intake or dose (ADD) [mg/kg/day] to the reference dose (RfD), [mg/kg/day] (USEPA 2010).

$$HQ = \frac{ADD}{RfD}$$

ADD is average daily dose (mg/kg/day) for the different exposure routes and RfD is reference dose (mg/kg/day),

The overall potential risk posed by a mixture of heavy metals, expressed as a total hazard index (THI), is determined from the sum of the HQs for each heavy metal.

$$THI = HQ1 + HQ2 + \dots\dots\dots + HQn$$

If the THI is less than 1.0, it is highly unlikely that significant additive or toxic interactions would occur, so no further evaluation is necessary. When the THI exceeds 1.0, there may be concern for potential non-cancer health effect (Ihedioha et al. 2016).

Remediation Techniques for Heavy Metals Contaminated Soils

By way of definition, Soil remediation, from an environmental perspective, is the reduction of contaminant concentrations within soil. The fundamental objective of any heavy metal contamination remediation technique is to create a final solution that is friendly to human health and environment (Martin and Ruby, 2004). Each remediation is based on some certain regulatory requirements, and where such does not exist, is based on assessments of human health and ecological risks. The best remediation is the one that is centered on reducing bioavailability that is equated with reduced risk, or the one that the bioavailability reductions are demonstrated to be long term. Before embarking on any remediation technique, it is important to get information about the physical and chemical characteristics of the site and the type and level of contamination at the site, because physical and chemical form of heavy metal contaminant in soil strongly influences the selection of the appropriate remediation technique. Different goals exist in remediation of heavy metals; it includes total metal removal, removal of leachable metal in soil, or as some combination of both.

Different types of chemical, physical and biological techniques have been used for remediation of heavy metal contaminated soil. The approaches are generally classified as in-situ or ex-situ and some can be both. In-situ remediation involves treating the polluted material at the site while exsitu involves the removal of the polluted material to be treated elsewhere. Examples of both insitu and ex-situ includes; phytoremediation, bioremediation, soil vitrification, soil washing, solidification/stabilization, soil flushing, excavation and landfill etcetera. (Wuana and Okieimen, 2011; Sheoran et al., 2011; Liu et al., 2018).

MATERIALS AND METHODS Description of the Study Area

The study area comprised of five (5) local government areas of Kogi State, namely: Lokoja, Okehi, Ankpa, Yagba West and Ajaokuta. These experimental sites are chosen because of the history of pollution due to mining, waste dumping, intense cultivation, and use of chemicals for farming. Kogi State is within Southern Guinea Savanna of Nigeria. The coordinates and elevation of the study area was recorded using a global positioning system (GPS) during water, plant, and soil sampling as shown in table 1.

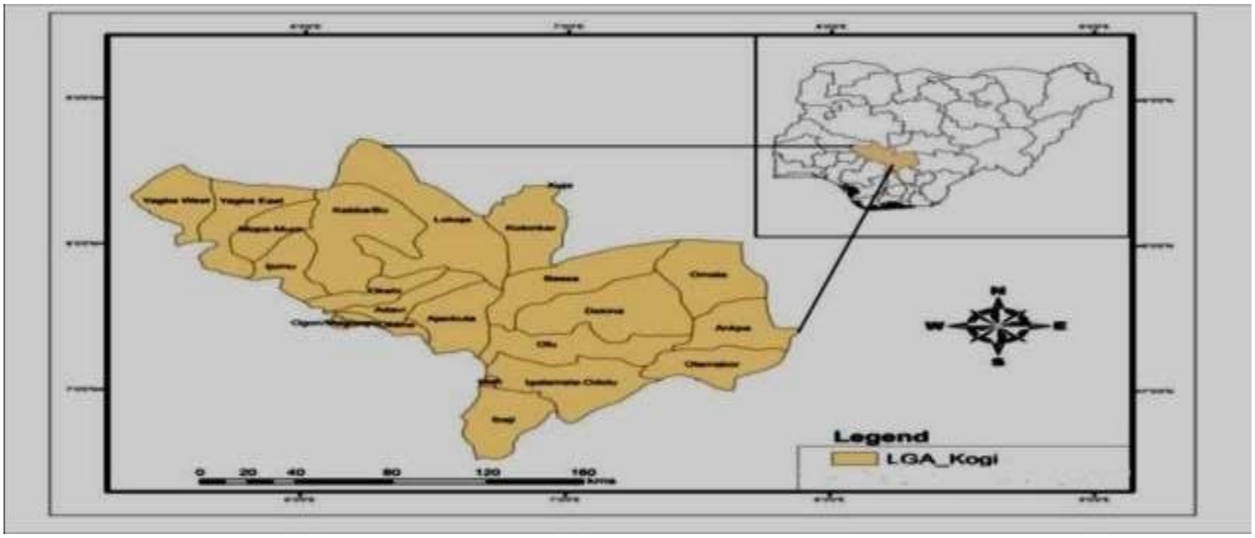

Figure 1: Map of Kogi State showing the study areas

Table 1: GPS and altitude information about sampling location

Locations	Sampling site	GPS Coordination/Coordinates		Altitude (m.a.s.l.)
		Latitude	Longitude	
Lokoja	1	7^0 29’ 24’’ N 8.2057^0 N	6 25’ 48’’ E 6.4451^0 E	137 86 m
Okehi	2	7^0 36’ - 7^0 39’ N 7^0 37’ 22.3’’ N	6^0 17’ E - 6^0 22’ E 6^0 12’ 6.8’’ E	235 m 217 m
Ankpa	3	7 25’ 21.6 ‘’N	7 38’ 55.1’’ E	390 m
Yagba West	4	8^0 15’ 0’’ N 8^0 11’ 18’’ N	5^0 33’ 0’’ E 5^0 36’ 22’’ E	306 m 297 m
Ajaokuta	5	7^0 44’ - 7^0 52’ N 7^0 33’ 44.2’’ N	6^0 40’ - 6 45’ E 6^0 39’17.9’’ E	186 m 187 m

m.a.s.l. – meter above sea level

Detailed Field Work Samples collection and preparation i. Soil sample collection and preparation

Soil samples was collected from the five (5) different locations. In each of the location, sampling was done from mining environment, roads, houses, dumpsites for waste, riverbank, and farms around the communities. At each sampling location, 15 samples were randomly collected at a depth of 0 – 30 cm. Each soil sample collected was placed inside polyethene bag. A total of 75 soil samples was collected. All the samples were taken to the laboratory and spread to air dry, some portion was used for the physical and chemical analyses, while the remaining was stored under room temperature and used for heavy metal analyses.

ii. Water sample collection and preparation

Water samples were collected from five (5) different locations. In each of the location, sampling was done from the domestic wells, boreholes, rivers, farm water sources, mining sites. At each sampling site, three subsamples was randomly collected. A total of 15 bottle samples was taken. Pre-cleaned sampling bottles was used for sampling. At each sampling point, the bottles were rinsed three (3) times with distilled water before collection of the sample. The samples were preserved by acidifying with $2cm^3$ of concentrated HNO3 to suppress microbial activities (Abdu and Yusuf, 2013) while other water samples were refrigerated at 4^0C till the studies were concluded.

iii. Plant sample collection and preparation

Plant samples were collected from all the five (5) locations. Samples were taken from the whole above ground portion of Vegetables and Gamba grass (*Andropogon gayanus*) (i.e. the most populous grass in all the study area). All the samples were collected in three replicates. A total of 15 plant samples were collected for each location. The plant samples were oven-dried at 65°C to constant weight, ground and sieved through 0.5 mm mesh and kept in a polythene bag before analyses.

Routine Soil Analysis of Experimental Soil

The routine analyses was carried out in the soil and water laboratory of the Kogi State Polytechnic, Itakpe Campus. The soil samples collected for routine analysis were spread out to dry and sieved through a 2.0 mm sieve. The analyses was carried out with the <2.0 mm soil sample and they include particle size analysis, organic carbon, total nitrogen, available phosphorus, exchangeable cations, exchangeable acidity, effective cation exchange capacity, soil pH, and electrical conductivity.

The pH and electrical conductivity was measured in a soil suspension (1:2.5 w/v dilutions) by digital pH meter and conductivity meter, Type M. C. S. Model EBB/10, respectively (IITA, 1982). Organic carbon was determined by potassium dichromate titration of Walkley and Black method (Nelson and Sommers, 1982). Particle size distribution was determined by the hydrometer method (Gee and Or, 2002). Total nitrogen was determined by the Kjeldahl method, Available phosphorus by Bray 1 extraction method (Bray and Kurtz, 1945), exchangeable cation by extraction with 1N NH4OAc solution as described by Rhodes (1982), exchangeable acidity by leaching the soil sample with 1N KCl solution as fully described by Agbenin (1995) and effective cation exchange capacity by the summation method.

Determination of heavy metals Determination of total heavy metals concentration

The soil samples were air dried and fine grind in a porcelain pestle and mortar. One gram of each sample was placed in a 250-mL conical flask, and a mixture of concentrated HNO3: HClO4: HF in the ratio 3:1:3 was added (Nwajei and Gagophien, 2000). The mixture was then be placed on a hot plate for 3 h at 800C. The digest was filtered into 100 mL standard flask and made to mark with deionized water. For the water samples, the samples were digested according to APHA procedure (APHA, 2005). Here, 1000 cm^3 of well mixed, acid preserved sample was transferred into a beaker. Exactly, 50 cm^3 of conc. HNO3 was added and heated to boiling. This was then evaporated on a hot plate to 20 cm^3. Heating and addition of concentrated HNO3 will continue until digestion was completed as indicated by a light colour, clear solution. The content was then transferred to 100 cm^3 plastic bottles, cooled and diluted to mark. Portions of this solution was used for heavy metals determination. For plant samples, the same procedure adopted for soil samples was used in the digestion.

The concentrations of metals in sample solutions were measured using flame atomic absorption spectrophotometry (Varian model-AA240FS). The blanks were prepared and analyzed in a similar manner but omitting the sample. This was done in order to remove occurrence of metal ions present in the reagent mixture. The metals determined includes; iron (Fe), lead (Pb), zinc (Zn), nickel (Ni), chromium (Cr), cadmium (Cd), and manganese (Mn).

Determination of extractable heavy metals

The labile concentrations of the heavy metals were extracted by saturating 10 g soil with 20 mL of 0.01M CaCl2, and shaking the mixture for 16hrs. The soil suspension was then filtered through Whatman No. 42 filter paper. The concentrations of the extractable heavy metals in the filtrate was then read with AAS (Varian model-AA240FS).

Determination of Pollution Indices

The use of pollution indices for processing, analyzing and conveying raw environmental information to decision makers, managers, technicians and the public is very useful (Caeiro et al. 2005). The following indices: contamination factor, pollution load index, geoaccumulation index and enrichment factor were used to measure the extent of pollution, while the ecological risk index was used to assess the ecological risk associated with heavy metal pollution in the study area. **i. Enrichment factor, EF**

Enrichment factor is an indication of the level of accumulation of the element of interest to the natural background level. Thus, it measures the geochemical trend and can be used in making comparisons between an area and overtime. The enrichment factor of the metals in soil was calculated based on Eq. (2) using iron as a reference element since it is the most naturally abundant element in soil (Okuo and Iyasele 2007)

$$EF = \frac{\left(\frac{Msample}{Resample}\right)}{\left(\frac{Mref}{Reref}\right)} \qquad \text{Eq. (2)}$$

Where EF is enrichment factor, Msample and Resample are the concentrations of the metal and the reference metal in the contaminated soil and Mref and Reref are concentrations of the metal and the reference metal in the reference soil (Abrahim and Parker, 2008; Abdu et al. 2011).

Five contamination categories are recognized on the basis of enrichment factor (Sutherland 2000). These categories are:

EF - < 2 - Deficient to minimal enrichment
EF - 2 – 4.99 - Moderate enrichment
EF - 5 – 19.99 - Significant enrichment

EF - 20- 39.99 - Very high enrichment
EF - ≥40 - Extremely high enrichment

ii. Geo-accumulation Index, Igeo

An index of geo-accumulation (Igeo) was used in order to determine and define metal contamination in the soils. This was done, by comparing current concentrations with precontamination levels. It was computed using Eq. (1). (Ntekim et al., 1993).

$$\text{Igeo} = \log 2 \left[\frac{C\,n}{1.5\,B\,n}\right] \qquad \text{Eq. (1)}$$

Where Cn is the measured concentration of the examined metal n in the soil and Bn is the geochemical background concentration or reference value of the metal n. The world average elemental concentrations in mg/kg (0.30 for Cd, 95 for Zn, 68 for Ni, 45 for Cu, 20 for Pb, 90 for Cr, 850 for Mn and 47,200 for Fe) reported by Turekian and Wedepohl (1961) in the earth's crust will be used as reference in the study. Factor 1.5 will be used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences (Abdu et al. 2011; Ihedioha et al. 2016).

Seven classes of geo-accumulation index (Igeo) was distinguished by Muller (Buccolieri et al. 2006), viz.

Igeo ≤ 0 - Class 0 - unpolluted
Igeo 0.1 – 1.0 - Class 1 - unpolluted to moderately polluted
Igeo 1.1 – 2.0 - Class 2 - moderately polluted
Igeo 2.1 – 3.0 - Class 3 - moderately to strongly polluted
Igeo 3.1 – 4.0 - Class 4 - strongly polluted
Igeo 4.1 – 5.0 - Class 5 - strongly to extremely polluted
Igeo > 5 - Class 6 - extremely polluted

iii. Contamination factor (CF)

The contamination factor will be derived by employing the model defined by Lacatusu (2000).

$$CF = \frac{\text{Concentration of the metal in the soil}}{\text{Target (Background)Value}} \qquad \text{Eq. (3)}$$

The target (background) value is a reference value of metals concentration (mg/kg) obtained from the standard table formulated by the Department of Petroleum Resources of Nigeria (DPR 2002) for maximum allowable concentration of metals in the Nigerian soil (Fe (5000), Mn (476), Pb (85), Cr (100), Cd (0.8), Zn (140), Ni (35)). Contamination factor values greater than one defines the pollution range, while values lower than one defines the contamination ranges. The standard employed for interpreting soil heavy metals contamination/pollution index varies from country to country based on the chosen factors (Lacatusu 2000).

Ten contamination categories are recognized on the basis of contamination/pollution factor (CF) (Lacatusu 2000). These categories are:

CF - < 0.1 - very slightly contamination
CF - 0.10 – 0.25 - slight contamination

CF - 0.26 – 0.5 - moderate contamination
CF - 0.51 – 0.75 - severe contamination
CF - 0.76 – 1.00 - very severe contamination
CF - 1.1 – 2.0 - slight pollution
CF - 2.1 – 4.0 - moderate pollution
CF - 4.1 – 8.0 - sever pollution
CF - 8.1 – 16.0 - very severe pollution
CF - > 16 - excessive pollution

iv. Pollution load index (PLI)

The pollution load index, proposed by Tomlinson et al. (1980), will be calculated using Eq. (4).

$PLI = (CF1\ x\ CF2\ x\ CF3\ x\ CF4 \ldots \ldots x\ CFn)1/n$ Eq. (4)

Where n is the number of metals studied and CF is the contamination factor calculated as described in Eq. (3). The PLI gives an estimate of the metal contamination status and the necessary action that should be taken.

The value of PLI was classified into four groups (Wang et al. 2010):

PLI - <1 - no pollution
PLI - 1.0 – 1.99 - moderate pollution
PLI - 2.0 – 2.99 - heavy pollution
PLI - ≥ - extreme pollution

v. Ecological risk factor (ErF)

Ecological risk factor (ErF) quantitatively expresses the potential ecological risk of a given single contaminant (Hakanson 1980) and is given as:

$ErF = Tri \times CFi$ Eq. (5)

Where Tri = toxic response factor of a given substance (lead = 5, zinc = 1, cadmium = 30, chromium = 2, nickel = 5); CFi is the contamination factor which has been evaluated from Eq. (3). Five terminologies are used to describe ecological risks based on Hakanson (1980).

These are

ErF - < 40 - low potential ecological risk
ErF - 40 – 79.9 - moderate potential ecological risk
ErF - 80 – 159.9 - considerable potential ecological risk
ErF - 160 – 319.9 - high potential ecological risk
ErF - ≥ 320 - very high ecological risk

vi. Potential ecological risk index, RI

The potential ecological risk index (RI) is in the same manner as degree of contamination defined as the sum of the risk factors:

$RI = (ErF1 + ErF2 + ErF3 \ldots\ldots + ErFn)$ Eq. (6)

where ErF is the ecological risk factor, n is the number of element studied. The following terminologies have been used for the potential ecological risk index (Hakanson 1980).

RI	-	< 150	-	low ecological risk
RI	-	150 – 299.9	-	moderate ecological risk
RI	-	300 – 599.9	-	considerable ecological risk
RI	-	≥ 600	-	very high ecological risk

vii. Human health risk assessment

Human can come into contact with heavy metals directly through three exposure pathways: direct ingestion of particles containing heavy metals; dermal absorption of trace elements in particles adhered to exposed skin; and inhalation of the suspended particles through mouth and nose. The average daily dose or intake (ADD, mg/kg/day) for non-carcinogens through each of the three exposure pathways will be used for the assessment and will be calculated using the following equations proposed by USEPA (1989, 1996).

$$ADDinh = \frac{C \times Rinh \times EF \times ED}{PEF \times BW \times AT} \qquad \text{Eq. (7)}$$

$$ADDing = \frac{C \times Ring \times EF \times ED \times 10\text{-}6}{BW \times AT} \qquad \text{Eq. (8)}$$

$$ADDderm = \frac{C \times SL \times SA \times ABS \times EF \times ED \times 10\text{-}6}{BW \times AT} \qquad \text{Eq. (9)}$$

Where:
ADDinh – average daily dose for inhalation
ADDing – average daily dose for ingestion
ADDderm – average daily dose for dermal contact
C – Concentration (mg/kg) of each metal in soil
Ring – ingestion rate (200 mg/day) for children and (100 mg/day) for adults (USEPA 2001)
Rinh – inhalation rate is 10m3/day for children and 20m3/day for adult (Van den Berg 1995)
EF – exposure frequency is 250 days/year (Ferreira-Baptista and De Miguel 2005)
ED – exposure duration is 6 years for children and 25 years for adult (USEPA 2001)
SA – exposed skin area is 2800 cm2 for children and 3300 cm2 for adult (USEPA 2001)
SL – skin adherence factor is 0.2mg/cm2/h for children and adult (USEPA 2001)
ABS – dermal absorption factor (unit less) is 0.001
PEF – particle emission factor is1.316 x 109 m3/kg (USEPA 2001)
BW – average body weight is 15 kg for children and 70 kg for adults (USEPA 1989)
AT – averaging time for non-carcinogens is ED x 365 days

The potential health risk of the soil heavy metal will be estimated using a hazard quotient (HQ). The non-cancer hazard quotient (HQ) assumes that there is a level of exposure known as the reference dose (RfD), which is a daily intake rate that is estimated to pose no appreciable risk of adverse health effects, even to sensitive populations, over a 70-year lifetime (USEPA 2005a). The reference dose is an estimate of a daily exposure to the human population. Hazard quotient (HQ) is defined as the ratio of the average daily intake or dose (ADD) [mg/kg/day] to the reference dose (RfD), [mg/kg/day] (USEPA 2010).

$$HQ = \frac{ADD}{RfD} \qquad \text{Eq. (10)}$$

ADD = average daily dose (mg/kg/day) for the different exposure routes

RfD = reference dose (mg/kg/day), RfDinh = RfC x 20 m3 per day/70 kg—for adult (USEPA 1994, 2005b), RfDinh = RfC x 10 m3 per day/15 kg—for children (USEPA 1994, 2005b) RfC = reference concentration, obtained from USDOE (2011).

The overall potential risk posed by a mixture of heavy metals, expressed as a total hazard index (THI), is determined from the sum of the HQs for each heavy metal.

$$THI = HQ1 + HQ2 + \ldots\ldots\ldots + HQn \qquad \text{Eq. (11)}$$

If the THI is less than 1.0, it is highly unlikely that significant additive or toxic interactions would occur, so no further evaluation is necessary. When the THI exceeds 1.0, there may be concern for potential non cancer health effect (Ihedioha et al. 2016).

Water Quality Analyses

Procedure for physicochemical and microbiolgical analysis of the water samples i. **pH of water** it is important to test for the pH level of surface water before consumption. The pH of the surface water sample will be measured by electromagnetic method using laboratory pH meter Hanna model H1991300 (APHA; 1998).

ii. Electricity conductivity determination

The conductivity of the water sample was determined decordy to APHA2010 guiding, mode/DDS-307 **iii. Turbidity determination**

The jar of the turbidity line was filled
2. The turbidity chart on the top edge of the jar was hold
3. The appearance of the secchi disk icon in jar to the chart was focused.
4. The result was recorded as the turbidity is in JTU.

iv. Total dissolves solid determination

The total dissolved solid was determined using APHA 2510A TDS tester (APHA 210).

Calculation:
$$TDS = \frac{(A - B)\,10^3}{\text{Sample volume in ml}}$$

Where: A= weight of dish solid (mg)
B= weight of dish before use (mg)

Summary of Water Quality Parameters for Analysis

v. Determination of Colour, Chemical Oxygen Demand, Turbidity and Fluoride by Colorimetric Method.

These parameters were determined using Hach Colorimeter model DR890, a semi automated colorimeter with 95 Hach programs permanently stored in memory.

vi. Determination of Conductivity, Total Dissolved Solids and Temperature by Conductivity/Total Dissolved Solids Meters

JENWAY Model 470 portable conductivity/total dissolved solids meter, a general purpose hand held meter offering direct calibration on standard solutions will be used for the determination of 49 conductivity, total dissolved solids and temperature in all the samples in-situ.

vii. Determination of Total Alkalinity by Potentiometric Titration

Two replicates of 10.0 mL of 0.05M Na2CO3 were pipetted into 100mL beakers. Each of the standards was titrated potentiometrically to pH 4.5 end-point using 0.02 M HCl,

viii. Determination of Ammonia, Nitrate, Nitrite, Sulphate, Phosphate, Hexavalent By UV/Visible Spectrophotometry
ix. Determination of Chloride by Argentometric Method as described by APHA, (1998) **x. Determination of the Heavy Metals** by Atomic Absorption Spectrophotometry.
xi. Determination of Sodium, Potassium and Calcium by Flame Emission Spectrophotometry **xii. Determination of Calcium Hardness** by Titrimetry

Statistical Analyses

Each sample collected was made into triplicate before analyses and the data collected was subjected to analysis using SAS 9.2 (SAS 2007) and Microsoft Excel (2010), where there were significant differences, Least Significant Difference (LSD 0.05) tests was used to separate the means. Correlation analyses was used to compare relationships between the variables. Principal component (PCA) analysis was performed to establish possible factors that contribute toward the metal concentrations and source apportionment. The number of significant principal components was selected based on varimax orthogonal rotation with Kaiser Normalization at eigenvalues greater than 1.

Quality Assurance and Control

Quality assurance and quality control is very important to ensure the reliability of measurements. In this study, all experimental reagents used were of analytical grade. Distilled water was used throughout the experimental procedure. Each soil and plant samples were analysed in triplicate, and one standard sample was analysed after every three experimental samples to ensure the accuracy of the results. Field blank and experimental blank samples were also analysed to ensure the accuracy of data obtained into 18 samples. Global Positioning System (GPS) was used to locate the points and recorded it. Soil morphological features/properties were identified for each sample at every sampling point (*in situ*). Each soil sample was bagged in individual, clean polyethene bags and labeled appropriately before they were transported to the laboratory for processing and analysis.

RESULTS AND DISCUSSION Soil Physio-chemical Properties of the study locations

The result of the physical and chemical properties of the soils assessed are shown in Table 2. The results obtained from the analysis of the experimental soils showed that the soil textural class was predominantly sandy clay loam and sandy loam in accordance to the USDA soil classification system (Arshad *et al.* 1996). The soil texture observed in this study is indicative of their suitability for agriculture as most crops do well in loam textured soils (Weil & Brady, 2017). The pH values ranged from 5.7 to 6.8 which are slightly acidic according to the United State Department of Agriculture, Natural Resources Conservation Services (SSDS, 1993), which is also in consonance with the classification of the Federal Ministry of Agriculture and Natural Resources of Nigeria (FMANR, 1990). The pH values recorded are characteristic of Nigeria guinea savanna soils (Raji *et al.* 2015). The cation exchange capacity ranged from 5.15 - 9.85 cmolkg^{-1} which rates low to moderate indicating that the soils have low to moderate nutrient retention capacity (Brady and Weil, 2002). Lokoja soils were found to have higher fertility/nutrient contents than other soils assessed. The low nutrient contents of the soil observed could be attributed to the lower organic matter status of the soil (Asmamaw *et al.* 2018) which betokened that nitrogen deficiency in the soils which is typical of Nigeria savanna soils (Salifu, 2022, Ogbe *et al.* 2020).

Heavy Metal Content of Soils

The results of the concentrations of the heavy metals in the experimental soils is presented in Table 3. Zinc (Zn) and Nickel (Ni) concentrations across all locations were less than the maximum permissible concentrations Zn (300 mg/kg) and Ni (50 mg/kg) respectively in the Nigerian soils guideline (FMEnv) and WHO/FAO according to UNEP reports (European Commission Standard). However, the levels accumulated already is tending towards significance which could pose a threat in the future which indicates that mining activities and waste dumping in Yagba West and Okehi LGAs have a great influence on these heavy metals accumulation.

Chromium (Cr) concentrations was observed to be less than the thresh-hold (limits 100 mg/kg) as set by the WHO/FAO and Nigerian Standard for heavy metals in soil and poses no health threat currently but potentially can increase in accumulation if mining and waste dumping activities are left unchecked especially in Yagba West LGA. Cr concentration is in the order Yagba West > Okehi > Lokoja > Ankpa >Ajaokuta LGAs. Chromium (Cr) concentrations in Yagba West LGA is above the permissible limits for Cr in the soil (100 mg/kg), hence, the pollution or contamination risk is very high if not remediated immediately and monitored for future occurrence.

Cadmium (Cd), Arsenic (As), Copper (Cu), and Lead (Pb) were observed to be below their permissible levels across the study locations except that lead concentration under Yagba West soils (325.1 mg/kg) exceeded the maximum allowable concentrations of Pb (100 mg/kg) by the FAO/WHO and Nigerian standard. Iron (Fe) have the highest concentration/accumulation than all other heavy metals determined which ranged from 10676.7 - 24501.8 mg/kg. This result aligns with those of Yahaya *et al.* (2021), Ademoroti (1996), Aluko and Oluwande (2003), Eddy *et al.* (2006) and Abdul *et al.* (2011) who reported significantly higher amounts/concentrations of Fe than other heavy metals suggesting that pollution of the environment cannot be exclusively linked to mining and waste dumping alone but other natural sources of iron (Fe) must be taken into account as Fe has been reported to be the most abundant element in Nigerian soils (Amusan *et al.* 2005). The concentration of the heavy metals in soils across all the study sites is in the following order: Fe > Pb > Cr > Zn > Ni > Cu > Co > Sn > Sc > As > Cd.

POLLUTION ASSESSMENT OF HEAVY METALS IN SOIL Enrichment of Heavy Metals in the Soil

Table 4 presents results of the accumulation of heavy metals in soils of the study area using enrichment factor (Ef). The results showed that Lead (Pb) enrichment evaluation showed that Yagba West LGA have an extremely high enrichment, while Okehi and Ankpa LGAs have moderate enrichment of Pb. Lokoja and Ajaokuta LGA soils have deficient to minimal Pb enrichment. The high Pb enrichmnent observed under Yagba west and other locations could be attributed to the intense mining and waste dumping activities going on in the LGAs. This is a clear indication that anthropogenic activities such as mining could lead to Lead (Pb) enrichment in the study areas. Table 4 results of heavy metals enrichment also revealed that Cadmium (Cd) have significant enrichment in Yagba west and Okehi LGAs while Ankpa has a moderate Cd enrichment. Lokoja and Ajaokuta LGAs have deficient to minimal enrichment of Cd. However, mining activities alone cannot be concluded to have caused the accumulation in these study locations but also account for other sources of Cadmium in the environment. This result is in line with those reported by Yahaya *et al.* (2021) and Mohammed (2014), who stated that human activities such as mining and waste dumping could increase cadmium (Cd) accumulation. The results also betokened that Zinc (Zn), Chromium

(Cr), and Nickel (Ni) in all the study areas have deficeint to minimal enrichment. This is indicative that mining and waste dumping actvities did not have significant impact on the accumulation levels.

Geo-accumulation of Heavy Metals in the Soil

Results of the geoaccumulation index (I-geo) of Lead (Pb), Cadmium (Cd), Chromium (Cr), Zinc (Zn), Nickel (Ni) and Iron (Fe) in soils from the five selected LGAs of Kogi State are presented in Table 5. The calculated I-geo for the soils of the study locations ranged from -18.57 to 3.42 for Lead (Pb), -11.42 to -1.62 for Cadmium (Cd), and -19.22 to -0.49 for Chromium (Cr). Nickel ranged from -18.40 to -4.50, Zn recorded a range of -3.14 to 1.23 and Fe ranged from -18.81 to 1.86. The results indicates that all the locations studied with respect to their Chromium (Cr), Zinc (Zn) and Nickel (Ni) accumulation is classified as class zero (0 = unplolluted), while Lokoja, Ankpa and Ajaokuta LGAs showed that the soils ar unpolluted (class 0) for Lead (Pb) accumulation. Okehi LGA have moderate pollution for Pb while Yagba West LGA showed that it was strongly polluted. Cadmium (Cd) showed moderate pollution under Okehi and Yagba West while Lokoja, Ankpa and Ajaokuta were rated unpolluted for Cd. Similar to the enrichment of these heavy meatls, Yagba West and Okehi have the trend of Lead (Pb) ad Cadmium (Cd) pollution to be moderate to significantly high pollution which confirms the impact of mining and dumping of waste as the major anthropogenic (human factors) activities leading to the pollution of these two (Yagba West and Okehi LGAs) study areas with Lead (Pb). This is inline with the reports of Mohammed (2014), Henry *et al.* (2020) and Yahaya *et al.* (2021) that study sites where mining activities takesplace were polluted with Lead 9Pb) andCadmium (Cd).

CONCLUSION

The overall ecological and human health risk of heavy metals assessed in this study showed that Yagba West and Okehi LGAs soil are polluted as a result of mining primarily and due to dumping of waste. The calculated enrichment factor, geo-accumulation index and contamination factor showed varied superficial enrichment for the metals, with Lead (Pb) and Cadmium (Cd) consistently having a higher score. The pollution load indexes and contamination assessment indicate that Yagba West has moderate pollution, while the remaining locations have no pollution load of the heavy metals. The result of human health risk assessment showed that only Yagba West LGA has a THI of >1.0 for child ingestion of heavy metals (i.e. non-cancer health risk for ingestion of heavy metals), while Okehi LGA have a THI ingestion of child approaching one (1). This indicates that most of the human health risk will be due to ingestion of soil particles rather than inhalation or dermal contact with the soil particles.

In conclusion, the findings of this study revealed that Lead (Pb) and Cadmium (Cd) exhibited the highest levels of enrichment, with most concentrations exceeding the maximum permissible limits set by WHO and FMEnv (Nigerian standard). These two heavy metals (Pb and Cd) were responsible for about 97.32% of the total potential ecological risk identified in the study area. Furthermore, the health risk assessment showed that, for both adults and children, ingestion was the primary exposure pathway for non-cancer risks, followed by dermal contact, while inhalation posed the least risk. This quantitative evidence underscores the urgent need for stringent mining regulations to safeguard both the environment and public health particularly that of children and highlights the importance of implementing remediation measures in contaminated areas. The results obtained from the physio-chemical and microbiological parameters of water quality indicates that pH, total hardness, alkalinity, conductivity, sulphate, heavy metals in water falls within and below the WHO/NSDWQ thresh-hold or permissible limits. The E. coli, total coliforms and microbial count were all higher than the permissible limits for drinking water quality (0 CFU/100 mL).

RECOMMENDATION

With respect to the associated danger in consuming water from such polluted source, it is recommended that the government create public awareness of the vulnerability of the people to the risks of using the water I the study area, mining activities and over use of fertilizers should be restricted. The practice of water treatment should be strengthened to help combat and protect the health of the water users as pollution can occur at any time from now. Waste dumping near the water sources should be out rightly discouraged and avoided.

Policies should be made to help in the assessment and remediation of heavy metals and water of ground and surface water sources within the study areas. Federal and State Government should empower agencies to always check the level of pollutants in soil and water around mining sites. Regular water testing and monitoring when made mandatory will help to protect the communities from public health associated hazards and risk.

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