ASSESSMENT OF HEAVY METAL CONCENTRATIONS OF SOIL AND WATER IN THE VICINITY OF GURMANA GOLD MINING SITE, NIGER STATE, NIGERIA

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ABSTRACT

The release of mining waste containing different toxic heavy metals have reached an alarming rate that deserves prompt attention. Hence, the purpose of this study was to determine extent of contamination of soil and water from Gurmana Gold Mining Site. A total of seventeen (17) samples comprising twelve (12) soil and five (5) water samples were collected. The samples were digested using nitric-perchloric acid mixture (3:1) and analysed for selected heavy metals (Cd, Cu, Cr, Pb, Mn, Ni and Zn) using an Atomic Absorption Spectrophotometer. The results revealed that the soil pH, organic matter and cation exchange capacity have values in the range of 6.37 – 6.80, 1.74 – 1.95% and 6.88 – 8.11 cmol/kg respectively. While pH of the water samples has a range 6.74 – 7.69 is lower than 6.5 – 8.5 (USEPA recommended standard). The heavy metal contents: Cu, Fe, Mn, Ni, Pb and Zn in soil samples had concentrations that ranged from 6.38±2.17 to 7.53 ± 1.25 mg/kg, 72.45±22.78 to 457.53±164.71 mg/kg, 11.05±4.95 to 27.93±20.39 mg/kg, 2.48 ±1.31 to 3.89±3.35 mg/kg, 1.38±1.38 to 3.34±3.34 mg/kg and 15.57±15.57 to 26.60± 26.60 mg/kg respectively. These concentrations were within the FAO/WHO maximum permissible limits of 100 mg/kg, 50,000 mg/kg, 2000 mg/kg, 50 mg/kg, 100 mg/kg and 200 mg/kg respectively except cadmium which was not detected all through the sampling sites. The water samples from well, spring, borehole and river from Gurmana revealed the presence of Cu, Fe, Mn, Ni and Zn in the range of 0.05 – 0.11 mg/dm^3, 1.93 – 48.78 mg/dm^3, 0.11 – 1.15 mg/dm^3, 0.02 – 0.07 mg/dm^3, and 0.02 – 0.07 mg/dm^3 respectively. Cd and Pb were below detection limit throughout in the water samples, while Fe was below detection limit in river and borehole samples and Zn was also below detection limit in the spring, borehole and river water samples. The contamination factor of soil samples ranged from very slightly contamination to slightly contamination, while that of water samples ranged from low contamination to a very high contamination level. The contamination of soil and water by these heavy metals could be attributed to mining activities in the area. The levels of potentially toxic heavy metals in soil and water should be assessed and monitored regularly in order to forestall the impending health risk associated with heavy metals arising from illegal mining activities.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Mining refers to the process of extraction of mineral from the surface of the earth or from beneath the surface and can only take place where minerals are present and are economically viable (Nnaji & Omotugba, 2016). Natural resources (metallic, non-metallic minerals and fossil fuels) are important in the development of any country; the general importance of the mining sector has been documented to include foreign exchange, employment and economic development (Fashola *et al*., 2016). However, lack of organized research techniques for gold, despite the great potential in the mines, coupled with high rate of unemployment and poverty, paved way for the invasion of the Nigerian gold fields by intense artisanal gold miners. Artisanal and small-scale mining is a means of livelihood adopted primarily in rural areas to complement traditional activities such as agriculture (Ngom *et al.,* 2020). When not formalized, organized, planed and controlled, artisanal and small scale mining can be viewed negatively by government and environmentalists, because of its potential for environmental damage, social disruption and conflicts (Emmanuel *et al.,* 2018).

Mining has been associated with the potential of impacting negatively on the quality of environment amongst the many anthropogenic activities by causing destruction of natural ecosystems (Abiya *et al*., 2019). Aside the physical habitat destruction, with accompanying loss of biodiversity resources, the accumulation of pollutants in different media has been reported around mining sites and therefore mining portend great toxicological challenges for the surrounding ecosystems and to human health (Okegye & Gajere, 2015). Processing of the ore bodies and disposal of mine tailings and wastewater rich in metals and metalloids are the main source of metal and metalloid release from gold mines (Ngole-jeme & Fantke, 2017) Heavy metals are one of the waste that have been implicated around mining sites which have received global attention by researchers, owing to their noxious effects on plants and animals (Abiya *et al.*, 2019). Due to variation in the physical and chemical properties of soil, heavy metals in tailings can translocate and accumulate in plants and animals (Uzoekwe & Richard, 2020). Even in small concentration, heavy metals can persist in soil and can enter into food chain through plant uptake (Ali *et al.*, 2019). Some heavy metals like lead (Pb), arsenic (As), mercury (Hg), and cadmium (Cd), are not essential for plants growth, since they are not known to perform any physiological function in plants (Okegye & Gajere, 2015). Other metals like iron (Fe), copper (Cu), nickel (Ni), manganese (Mn), cobalt (Co), molybdenum (Mo), and zinc (Zn) are essential elements required for normal plant growth and metabolism, but when they exceed the desired concentrations could portend danger to individual plants (Mofor *et al.*, 2017).

In order to evaluate the damage that gold mining activities exert on the environment, especially in areas in which crude methods are largely used, there is need to assess the extent of pollution through determination of heavy metal content and their relation to soil and plant (Abiya *et al.*, 2019).

Apart from environmental problems, health issues are not left out because of artisanal and small scale gold mining operations. The medium through which people are affected include drinking water, food, and inhalation of contaminated dust, oral ingestion of particles especially by children and through breast feeding (Ali *et al.,* 2019). Mining of gold has been left in the hands of artisanal miners who do not have enough resources and adequate equipment and technology required for the mining activities.

Niger State is endowed with an array of solid minerals scattered around the state and gold is one the most prominent solid minerals in the state which the government of the day have left unharnessed (Ako *et al.,* 2014). This has led to uncontrolled mining by the youth and adult alike in the areas where these minerals exist without due consideration to the effect of this activity on their health and the environment. Some of the areas where these minerals exist in the state and which illegal mining have been ongoing are Mokwa, Raffi, Jattau in Garingabas Nasarawa in Borgu, Maiwayo and Gada Eregi. Niger State has one of the major gold fields that suffer in the hands of artisanal miners particularly in Gurmana. This study assessed soil and water chemistry with special concern to heavy metal contaminations/pollutions in Gurmana mining site.

1.2 Statement of the Research Problem

Uncontrolled mining activities in Gurmana have increased and can cause the release of heavy metals into the immediate environment. The presence of these heavy metals can persist and accumulate in soil and water where they could translocate into the food chain with associated health risks (Zauro *et al.,* 2017). Also, there is inadequate information on the heavy metal contents of the soil and water around the Gurmana mining site.

1.3 Justification of the Study

It is important that research into sources and modes of heavy metal contamination of water and soils be undertaken so that toxic metals which threaten human health can be managed. The levels of selected heavy metals associated with mining activities and their consequent effects on the surrounding community of the study area will be established

1.4 Aim and Objectives of the Study

The aim of this research work was to determine the level of heavy metal concentrations in soil and water within Gurmana gold mining site in Shiroro Local Government area of Niger State, Nigeria.

The specific objectives set to achieve the aim are to:

i) Determine selected physicochemical properties such as organic matter (OM), electrical conductivity (EC), soil pH and cation exchange capacity (CEC) in the soil samples within the mining site;

ii) Determine selected physicochemical properties such as temperature, pH, electrical conductivity (EC), nitrate, phosphate, alkalinity, calcium, magnesium, total hardness, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) in the water samples from the mining site;

iii) Determine selected heavy metals (Cd, Cu, Fe, Ni, Pb, Mn, and Zn) in soil from the mining site using an Atomic Absorption Spectrophotometer (AAS).

iv) Determine selected heavy metals (Cd, Cu, Fe, Ni, Pb, Mn, and Zn) in water from the mining site using an Atomic Absorption Spectrophotometer (AAS) and

v) Evaluate the contamination factor and pollution load index of the metals in the soils and water.

1.5 Scope and Limitation of the Study

This research work will evaluate the levels of the selected heavy metal loads (Cd, Cu, Fe, Mn, Ni, Pb, and Zn) in soil and water collected from the mining area at Gurmana in Shiroro Local Government Area of Niger State

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Heavy Metals

Heavy metals are natural occurring metallic elements with atomic number greater than 20 and elemental density greater than 5 g/cm^3 (Ali & Khan, 2018). These include the transition metals some metalloids, lanthanides and actinides. Amounting to more than 20, metals generally exist in a positively charge forms and can bind onto negatively charge organic molecules. Being metals ions, heavy metal cannot be degraded or destroyed, their stability make them as the persistence toxic substances in environment (Ali *et al.,* 2019). Heavy metal as the environmental contaminants can be found in the air, soil and water which pose health hazard to the general public (Ali *et al,*. 2019).

Studies have shown that both long and short term contamination of soils have effects on microbial activities and energy activities in the soil (Fashola *et al.,* 2016). The toxicity and mobility of heavy metals in soil depend not only on the total concentration but also on their specific chemical form, bonding state, metal properties, environment factors, soil properties and organic matter content. Presence of heavy metal in water as contaminant is an indication of global industrialization, attributed to large scale inappropriate disposal and untreated waste water containing heavy metals from anthropogenic sources (Opaluwa *et al.,* 2020).

The concentration of heavy metals in soil, and their impact on ecosystem can be influenced by many factors such as the parent rock, climate and anthropogenic activities. Soil is often contaminated by human activities and this is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development (Odika *et al*., 2020). Materials that find their entry into the soil system persist and accumulate in toxic concentrations becoming sources of pollution in the soil

(Wang *et al.,* 2016). The main pathway through which these heavy metals contaminate the food chain is the soil, water, and other inorganic substances by the process of leaching and runoff, while human exposure is through ingestion, inhalation and dermal (Nkwunonwo *et al.,* 2020).

2.2 Gold Extraction and Processing

Gold mining can be open-pit or deep shaft mixed with other heavy metals (HM), such as mercury (Hg), copper (Cu), silver (Ag) and lead (Pb). Its location determines the type of mining process to be used in extraction and the amount of wastes that will be generated. In the past, small quantities of waste were generated by mining activities because higher grade ores were being exploited (Ngueyep *et al.,* 2021). There was also limited capacity to move large quantities of materials and so the waste generated was discarded within a few meters of the mine opening or pit. Open-pit mining produces eight to 10 times as much waste as underground mines because a greater amount of topsoil, overburden and barren or waste rock have to be removed. Gold mining in Nigeria over the centuries has resulted in the accumulation of thousands of voluminous tailings dumps which are scattered all over the country with lots of potentially negative impact on the environments (Nnaji & Omotugba, 2016).

To separate the gold (Au) from the mineral bearing rock, mercury is mixed with the ores dug from the ground or from stream beds to form an amalgam. The burning off; the amalgam leads to vaporization of the elemental mercury into a toxic plume leaving the gold behind. Mercury amalgamation was the initial method used for centuries to process gold and is still in use today by artisanal and small-scale gold mining (ASGM). Globally, ASGM is the second largest source of atmospheric mercury pollution after coal combustion. Another method of Au extraction uses cyanide in a two-stage process;

extraction and recovery. Gold is first dissolved using cyanide in the extraction stage and the dissolved gold is then recovered from the cyanide solution by cementing with zinc or adsorption onto activated carbon (Rasoul & Shipi, 2017). The cyanide extraction processes could be heap leach or vat/tank leach depending on the quality of the ores. In ores of higher gold content, the vat/tank leaching is employed, which involves leaching of the crushed and ground ore in large enclosed tanks equipped with agitators to dissolve the gold which then adheres to pieces of the activated carbon. The activated carbon and the gold are then stripped off the solution and the barren solutions together with the leached ore are discarded. The heap leach is used for low-grade ore and involves extraction of crushed oxide gold ore piled onto plastic-lined pads with leaching solvents such as acids or cyanide to dissolve the gold which is collected at the bottom of the pad (Nnaji & Omotugba, 2016).

2.3 Environmental Pollution from Gold Mine Tailings

Environmental pollution from gold mines is associated mainly with the release of harmful elements from the tailings and other mine wastes. The infiltration of water through sulphide- containing tailings piles and ponds, surface and underground workings, waste and development rock leads to leaching of large volumes of metals like Zn, Ni, Pb, As, Cu and sulphate ions into stream and river ecosystems (Slaveykova & Cheloni, 2018). This results in acid mine drainage (AMD) with severe detrimental effect on the receiving water bodies. Heavy metal pollution and acid mine drainage is a very important environmental concern where waste materials containing metal-rich sulphides from mining activity have been stored or abandoned (Concas *et al.,* 2005).

2.4 Heavy Metals Essentiality for Life

Heavy metals are classified as essential and nonessential (Ali & Khan, 2018). Essential heavy metals such as Mn, Fe, Cu, and Zn are important to living organisms and may be required in the body in quite low concentrations while, the nonessentials heavy metals such as Cd, Pb, and Hg are toxic and have no known biological role in living organisms (Rahim *et al.,* 2016). The heavy metals Cu, Co, Fe, Mn, Mo, Ni, and Zn are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nuclic acids, growth chemicals and secondary metabolites (Ali *et al.,* 2019). Either deficiency or excess of an essential heavy metal lead to diseases or abnormal conditions. However, the list of essential heavy metals may be different for different groups of organisms such as plants, animals, and microorganisms. It means a heavy metal may be essential for a given group of organisms but nonessential for another. The interactions of heavy metals with different organism groups are much complex (Ali *et al.,* 2019). Studies of the effect of heavy metals in soil, plants and water have been reported by Abiya *et al*. (2019), Okegye and Gajere, (2015), Mouhamed *et al.* (2020) and Dan-badjo *et al*. (2019).

2.5 Selected Heavy Metals

2.5.1 Cadmium (Cd)

Cadmium is a d-block white malleable metal with atomic number 48 which belongs to group 12 periods 5 in the periodic table. It has atomic mass of 112.2, density 8.65 g/cm^3, melting 321.07°c, boiling point 767°c.

Cadmium is one of the most toxic heavy metals to most organisms. Its concentration in unpolluted soil is usually 0.1 to 0.5 mg/kg (USEPA, 2018), but in gold mine tailings, concentrations up to 4.1 mg/kg have been reported in Ghana by Emmanuel *et al*. (2020). It occurs in gold bearing ore bodies as an isometric trace element in sphalerite and its concentration depends on the concentration of the sphalerite in the ore body. Cadmium is of serious concern as a result of its accumulation in the food chain, drinking water and soil. It has an exceptionally long biological half-life (>20 years), highly mobile in soil-plant systems and can also exert a great effect on the proper functioning of the ecosystems.

Chronic exposure to cadmium can lead to kidney disorder, anaemia, emphysema, cardiovascular diseases, renal problems and hypertension (Nkwunonwo *et al.,* 2020).

2.5.2 Zinc (Zn)

Zinc is a d-block bluish-white metal with atomic number of 30 located in group 12 period 4 in the periodic table. It has atomic number of 65.4, density 7.15 g/cm^3, melting point and boiling point of 419.53^{0}c and 907^{0}c respectively.

Zinc also occurs in gold ore bodies in the form of sphalerite (ZnS) which is often associated with galena. The average natural level of Zn in the Earth's crust is 50 mg/kg (dry weight), ranging between 10 and 300 mg/kg (Fashola *et al*., 2016). In gold mine tailings, concentrations ranging between 137.6 and 143.5 mg/kg have been reported by (Emmanuel *et al*., 2020). While a higher concentration of 1415 mg/kg was reported by (Atibu *et al*., 2016) in Congo. Though a micronutrient needed by plants, and human beings for vital cell functions, its presence beyond the normal physiological value can be toxic (Rahim *et al.,* 2016).

2.5.3 Lead (Pb)

Lead is a silver blue-white p-block metal. It is located in group 14 period 4 of the periodic table. Pb has atomic number 82, atomic mass 207.2, density 11.4 g/cm^3, melting and boiling point of 327.46°c and 1749°c respectively.

Lead is toxic at the lowest concentration and naturally non-degradable, unless it is removed from the medium where it is found. Standard mean concentration for Pb in surface soils worldwide averages 32 mg/kg with a range of 10–67 mg/kg but concentration range up to 2234.02 mg/kg have been reported in gold mine tailings by (Adewumi & Laniyan, 2020). It occurs in the form of galena (PbS) in gold ore and this form is found when sulphide concentration of the ore is high. Lead exists in various oxidation states (0, I, II, IV) and the most stable forms are Pb(II) and lead-hydroxy complexes. The ionic form, Pb(II) is the most reactive and most common form which forms mononuclear and polynuclear oxides and hydroxides. This ionic form together with lead oxides and hydroxides are the forms that are released into surface water, ground water and soil (Daichi *et al.,* 2020).

2.5.4 Copper (Cu)

Copper is a d-block red metal located in group 11 periods 4 of the periodic table. It has atomic number 29, atomic mass 63.5, density 8.96 g/cm^3, melting and boiling point of 1084.62°c and 2562°c respectively.

Copper is widely distributed in sulphides, arsenites, chlorides and carbonates in gold ores. The mean concentration of 5 to 70 mg/kg exists in unpolluted, soil while higher concentrations are found in contaminated environments like mining sites. Adewumi & Laniyan, (2020) found a concentration of 320.6 mg/kg in gold mine tailings of Anka Nigeria. Gold mining has greatly increased Cu concentration in the environment which upon release binds to particles of organic matter, clay minerals leading to great accumulation in the soil. Copper exists in two states, oxidized state Cu(II), and reduced state, Cu(I). The ability to exist in these two states makes this metal potentially toxic because the conversion between Cu(II) to Cu(I) could lead to a generation of superoxide and hydroxyl radicals. Copper toxicity can cause pink disease in infant and dermatitis (Nkwunonwo *et al.,* 2020).

2.5.5 Nickel (Ni)

Nickel is lustrous, metallic and silver, with a gold tinge in appearance. It belongs to group 10 periods 4 in the periodic table. It has atomic number 28, atomic mass 58.7, density 8.9 g/cm^3, melting and boiling point of 1455^{O}c and 2730^{O}c respectively.

It occurs in the environment at very low levels and is essential in small doses but can be dangerous when the maximum tolerable limit is exceeded. Some of its health risk include fibrosis, chronic bronchitis, impaired pulmonary function and emphysema (Nkwunonwo *et al.,* 2020). Nickel contaminations in the soil come from mining, electroplating, agricultural processes and combustion of fossil fuel (Bawuro *et al.,* 2018).

2.6 Physical Environmental Impact of Artisanal Miners

2.6.1 Land degradation:

This involves destruction of natural landscape of an area as a result of erosion. The heaps of rock wastes and tailings generated as a result of the mining activity are not easily disposed off and this also leads to the destruction of the natural landscape (Benjami *et al.,* 2018). Large pits are also created as a result of the mining activity; these pits can be dead traps to both man and animals. It could also become dangerous habitat for reptiles such as snakes which can cause harm to man (Ako *et al.*, 2014). Benjami *et al.* (2018) reported that the destruction of over 1000 hectares of arable farm lands and flooding of abandoned pits have become death traps due to artisanal mining of Azarabarytes deposition in Nasarawa State, Nigeria.

2.6.2 Loss of soil quality

The soil in the mined areas lost their quality due to the mining activities, erosion, sedimentation and contamination of the soil (Oramah *et al*., 2015). Similarly, Ezeaku (2012) reported that soils around the mine site in selected areas of Nasarawa State were coarse texture and acidic due to the influence of open cast mining of solid minerals. These have caused severe effect on the soil ecosystem, hence making the soil not to be suitable for plant life.

2.6.3 Soil erosion and sedimentation

The major effect of mining activity in an environment is soil erosion and sedimentation. Erosion and sedimentation are caused by land disturbances and removal of vegetation in the process of mining. Erosion from over burden and tailing piles often increases sediment loading in a nearby stream, thereby modifying the stream morphology by disrupting water channel, diverting stream flow and changing the slope or bank stability of the stream (Ako *et al*., 2014).

2.6.4 Destruction of vegetation

The clearing of the site for mining activities has resulted in deforestation. Large amount of vegetation has been destroyed and this exposes the soil to erosion and renders it unfit for crop production (Ako *et al*., 2014).

2.6.5 Deterioration of water quality

The act of getting gold out of the crushed rocks brings it into contact with people, ground and surface waters where heavy and dangerous metals contained in rocks and deposited (Ngueyep *et al.,* 2021). These activities are capable of polluting both surface and ground water system through the release of heavy metal contained in the host rocks, thereby posing a great health threat to humans, aquatic life stocks within the mine environment (Slaveykova & Cheloni, 2018).

2.7 Remediation of Heavy Metals

Soil and ground water contamination by heavy metals can be caused by silts or direct infiltration of sewage discharged from industrial activities, leachate from mine tailings or from industrial waste lagoons, air born emissions. Processed solid wastes/sluge sand purification of metals (Tyopine *et al.,* 2018). The unusual levels of heavy metals such Cu, Cd, Pb, Cr, As, Zn and Hg in soils represent a significant health and environmental hazard. Therefore, their remediation is paramount (Tyopine *et al.,* 2018).

Although all contaminated sites are unique and a site specific approach to remediation is often required, heavy metal contamination creates even more complex challenges. Depending on the site characteristics (geographical location, types of co-contaminants, climate, depth; soil type, pH level, water content, particle size, clay site specific alternatives must be evaluated carefully (Mallampati *et al.,* 2015). Remediation methods is divided into three broad categories; physical remediation which include: - Soil replacement, soil isolation, vitrification and electro-kinetic.

Biological method which generally includes: - Phytostabilization, phytoevaporation and phytoextraction

Chemical method which contains immobilization and soil washing. However biological and chemical methods can be applied jointly depending on the type of metal, soil, plant and chemical reagent (Khalid *et al*., 2016).

2.7.1 Physical remediation

2.7.2 Soil replacement

Soil replacement involves replacing the contaminated soil with non-contaminated one. Soil replacement method dilutes the concentrations of heavy metals in soil, thereby increasing soil functionality. The replaced soil is generally treated to remove heavy metals or dumped in other places. Soil replacement method can efficiently isolate the contaminated soil and ecosystem, thus reducing its effect in the environment. However this technique is costly due to high labour work (Khalid *et al*., 2017).

2.7.3 Soil isolation

Involves separation of heavy metal contaminated soil from the uncontaminated soil. Isolation techniques are generally designed to prevent off-site movement of heavy metal and other contaminants by restricting them within a specific area. Soil isolation technique is used to avoid further contamination of ground water by heavy metals when other remediation methods are not economically or physically feasible (Khalid *et al.,* 2016).

2.7.4 Vitrification

A high temperature treatment can be applied to the contaminated site to reduce the mobility of heavy metals (Mallampati *et al*., 2015), that can lead to the formation of vitreous materials. Vitrification can be applied majorly to the soils contaminated with inorganic (heavy metals) and organic contaminants. Vitrification can be done both *in situ* and *ex-situ,* although in situ method is preferred due to low energy requirement and cost. An *Ex-situ* vitrification process involves various stages such as excavation, mixing, pre-treatment, melting feeding, and casting of the melted product (Dellisanti, 2016). *Ex-situ* vitrification requires high energy for melting and is therefore costly.

2.7.5 Immobilization techniques

Immobilization involves decreasing of metal mobility, bioavailability and bioaccessibility in the soil by adding immobilizing agents to the contaminated soils. Heavy metals can be immobilized in soil by precipitation, complexation and adsorption reactions. These processes result in redistribution of heavy metals from soil solution to solid particles, thus limiting their transport and bioavailability in soil.

Immobilization is generally carried out using organic and inorganic amendment to soil (Hussein *et al*., 2017). The most commonly used amendments include clay, zeolites, cement, phosphates microbes, minerals and organic amendments (Sun *et al.,* 2016). It is understandable that organic amendments can immobilize heavy metals in soil through adsorption reactions or forming stable complexes (Salisu *et al*., 2016).

By –products of manure that contains low levels of metal are nowadays used as metal immobilization in soils (Venegas *et al*., 2015). Khan *et al.* (2015) reported that the use of farm yard manual (FYM) was highly effective in immobilizing Fe, Cr, Ni, Mn, and Pb, while di-ammonium phosphate (DAP) was more effective for stabilizing Cu, Cd, and Zn in soil.

2.7.6 Soil washing

Soil washing involves removal of heavy metals from soil using various reagents and extractants (Sun *et al.,* 2016) that can leach the heavy metals from the soil. During the soil washing, the contaminated soil is dug out and mixed with a suitable extractant solution depending on the type of metal and soil. The extractant solutions are mixed thoroughly for a specific time. Through the precipitation, ion exchange, chelation or adsorption. The heavy metals in soil are transferred from soil to liquid phase, and then separated from the leachate (Zhai *et al*., 2018).

Some of the reagents used in soil washing include synthetic chelating agents (EDTA, EDDS), organic acids, humic substances, surfactants and cyclodextins (Kulikowska *et al*., 2015).

2.7.7 Biological remediation

This is the one of the most effective options to detoxify and re-establish the natural condition of soil considered detrimental to environmental health. Bioremediation makes use of microoganisions/plants to detoxify or remove metals from the soil. Bioremediation is less cost, non-invasive and provides permanent solution (Khalid *et al.,* 2017).

2.7.8 Phytoremediation

Phytoremediation also known as vegetative remediation, botanoremediation, agroremediation, or green remediation comprises of techniques that make use of plants to remediate and revegetate contaminated sites. Phytoremediation is often seen environmental friendly, attractive, aesthetically pleasing, energy efficient, and cost effective techniques to clean up the site with low to moderate levels of heavy metals (Salisu *et al*., 2016).

2.8 Pollution Indices

Pollution indices are used to assess environmental potential risk that contaminants will pose on soil in an area. Some indices described below are used to evaluate environmental risk in which certain heavy metals will pose to the immediate environment.

2.8.1 Contamination/pollution index (C/P).

The contamination/pollution index (c/p) of metals in soils is calculated using the scheme formulated by Lacatusu (2000) and adopted by Olayinka *et al.* (2017).

C/P =concentration of metal in soil divided by target value from reference table (2.0).

The target value was obtained from the standard formulated by the Department of Petroleum Resources of Nigeria (DPR)/Cluster abundant values for maximum allowed concentration of heavy metals in soil in mg/kg (Cd: 0.8, Cu: 36, Fe: 50,000, Mn: 1000, Ni: 35, Pb: 85 and Zn: 140).

Contamination/pollution index value greater than one (>1), defines pollution range but when it is less than one (<1), it defines contamination range (Lacatusu, 2000).

Table 2.1 Interval of contamination/pollution index of heavy metals in soil and its significance

<0.1	very slight contamination
0.10-0.25	slight contamination
0.26-0.50	moderate contamination
0.51-0.75	severe contamination
0.76-1.00	very severe contamination
1.1-2.0	Slight pollution
2.1-4.0	moderately polluted
4.1-8.0	severe pollution
8.1-16.0	very severe pollution
>16.0	

Source: Lacatusu, (2000)

2.8.2 Contamination factor (CF) of water

The assessment of contamination of the water sources was also done using the calculation of contamination factors of the heavy metals in the water samples. This calculation was used to evaluate the potential risk of the heavy metals to the environment, using the formula below (Nnabo, 2015).

$$C_f = Ci/Cn \qquad (2.1)$$

Where Ci is the mean concentration of metal from the water sampling sites and Cn is taken as the USEPA maximum permissible limits of heavy metals in water as reference values.

Table 2.2 Maximum limits of metals permissible in water established by the united state environment protection agency (US EPA 2018)

Parameters	Limits (mg/dm^3)
Cu	2.0
Fe	0.3
Mn	0.02
Ni	0.01
Zn	5.0

Table 2.3 summaries the techniques used by various researchers for heavy metals analysis of soil water and plant samples, which shows that atomic absorption spectrophotometer (AAS) techniques was employed by 61.9%, followed by 23.8% of the researchers who used inductively couple plasma - mass spectrometry (ICP-MS), while inductively couple plasma - optical emission spectrometry (ICP-OES) and x-ray fluorescence (XRF) were used by 9.5% and 4.7% of the researchers respectively.

Table 2.3 Review of previous techniques and samples matrix used by different researchers in the analysis of heavy metals

Sample Matrix	Digestion Method	Analytical Technique	Analytes	Reference
Soil	HCl /NHO_3	AAS	As, Cd, Cu, Hg, Pb, Zn	Aung *et al.,* 2020
Soil and vegetable	HNO_3/$HClO_4$	ASS	Cd, Cu, Zn, Pb, Cr, Ni	Abdullahi & Mohammed, 2020
Soil, water and vegetable	$HClO_4$ / HCl H_2O_2	ICP – OES Varian Vista MPC, Varian palo Alto, California USA	Cd, Cu, Fe, Hg, Pb, Zn	Emmanuel *et al.,* 2020
Soil	HCl/HNO_3 /HF/ $HClO_4$	ICP – MS	As, Cd, Cu, Co, Ni, Pb	Zhiming *et al.,* 2020
Soil	HCl	AAS HPG_3	Cu, Fe, Mn, Zn	Ali & Vinod, 2020
Soil and Plant	HNO_3 /HCl	AAS	As, Cd, Cr, Cu, Pb, Ni, Zn	Abiya *et al.,* 2019
Soil	HNO_3 / H_2SO_4 / $HClO_4$	AAS shimadzu -700	Mn, Fe, Cu, Zn, Cl, Pb	Abu-Rayhan *et al.,* 2019
Soil and crops	HCl/ HNO_3	AAS contr AA300, Analytik Jena, Germany	Cd, Cu, Fe, Mn, Zn	Onyedikachi *et al.,* 2018
Soil		AAS	As, Hg, Cd, Cu, Cr, Ni, Pb, Zn	Gang *et al.,* 2018

Sample Matrix	Digestion Method	Analytical Technique	Analytes	Reference
Water		ICP- MS	As, Cd, Hg, Cu, Cr, Co, Al, Fe, Mn, Ni, Pb, V, Zn	George *et al.,* 2018
Water, kidney, liver and Blood	HNO_3	ICP – OES (perkin Elmer 8000 USA)	As, Pb, Ni, Cd, Se, V	Azubuike *et al.,* 2018
Soil		ICP-MS/AFS	Cd, Pb, Zn, Cu, Ni, As	Shunhung *et al.,* 2017
Soil	HCl/ HNO_3	AAS Contr AA300	As, Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn	Ngole-Jeme & Fankte, 2017
Soil		AAS	Hg, Cd, Cu, Fe, Mn, Pb, Zn	Eludoyin *et al.,* 2017
Soil		ICP – MS	As, Hg, Cd, Cu, Co, Cr, Ni, Pb, Zn	Caspah *et al.,* 2016
Soil		XRF	As Mn Pb	Solongo *et al.,* 2016
Water	HNO_3	AAS	Cd, As, Cd, Cu, Ni, Pb, Zn	Nnabo, 2015
Soil, water and crops	HNO_3 /$HClO_4$ /HF	AAS GBC 932AA (ICP- MS Agilent 7700×, USA)	Cd, Cu, Pb, Zn	Ping *et al.,* 2014
Soil	HCl	AAS (perkin elmer model 403)	Cu, Fe, Mn, Zn	Adewole & Adesina, 2011

CHAPTER THREE

3.0 MATERIALS AND METHODS

The equipment used in the research are listed in Table 3.1

Table 3.1 List of Equipment's

S/N	Name	Model	Manufacturer
1.	pH meter	EIL7045/46	Kent, England
2.	Weighing Balance	B300	OHAUS USA
3.	Orbital Shaker SSLI		United kingdom
4.	Conductivity meter	EIL5013	Kent, England meter
5.	Thermometer		
6.	AAS	HP-MY14470001Perkin Elmer,	UK

The chemicals and reagents used in the research are as listed below. All the chemicals and the reagents are of analytical grade.

The chemicals and reagents used in the research are provided in Table 3.2. All the chemicals were purchased and used without any further purification

Table 3.2 List of Reagents

S/N	Name	Formulae	%purity	Grade	Manufacturer
1	Trioxonitrate (V) acid	HNO_3	68	Analytical	KEM LIGHT India
2	Hydrochloric acid	HCl	36	Analytical	BDH, England
3	Tetraoxosulphate (VI) acid	H_2SO_4	98	Analytical	BDH, England
4	Sodium hydroxide	$NaOH$	99	Analytical	BDH, England
5	Silvertrinitrate (V) salt	$AgNO_3$		Analytical	BDH, England
6	Perchloric acid	$HClO_4$	72	Analytical	BDH, England
7	Potasiumheptaoxo dichromate(VI)	$K_2Cr_2O_7$		Analytical	BDH, England

3.1 The Study Area

Shiroro Local Government lies between latitudes $9^{O}57^{1}$ and 9^{O} 42^{11} N and longitudes 6^{O} 50^{1} and 6^{O} 13^{11} E in Niger State, Nigeria. The study area is a rural community of about 2000 people that engage predominantly in subsistence farming of rice, maize, millet and ground nut.

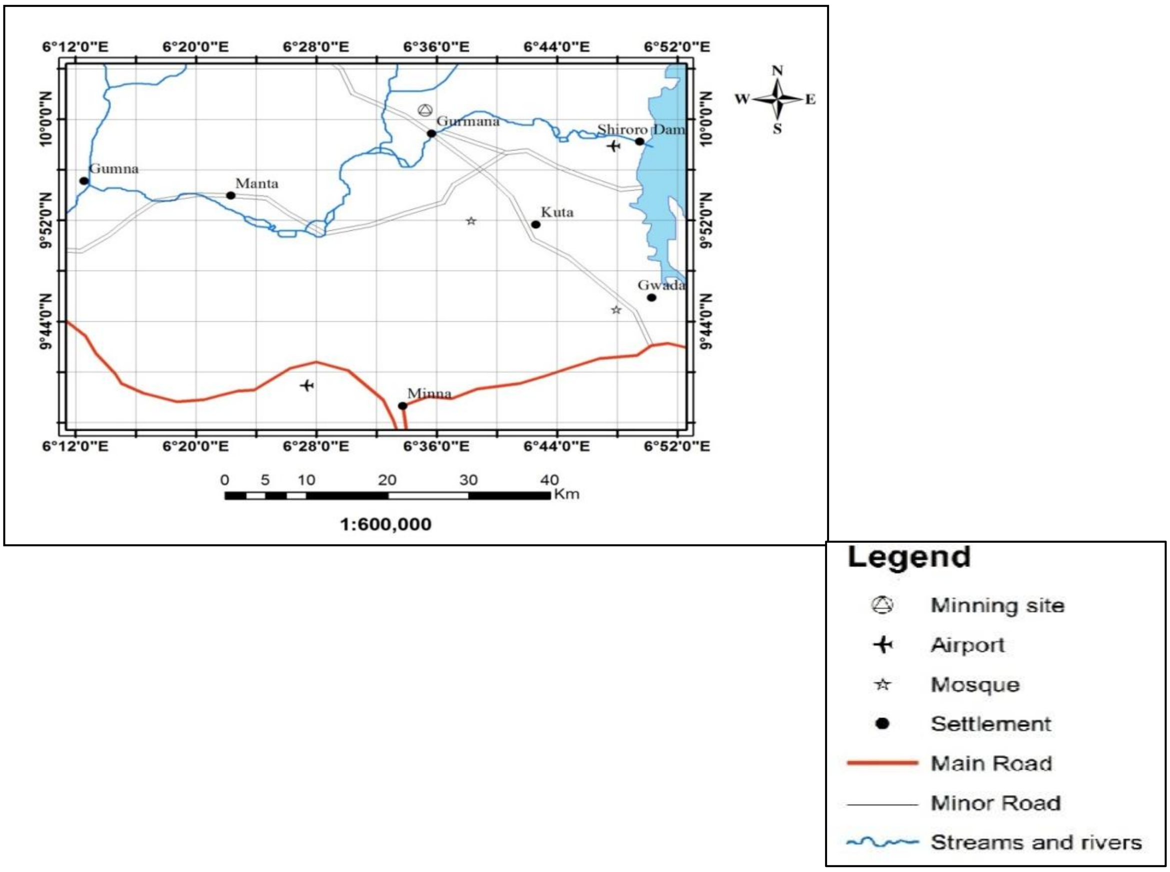

Fig 3.1: Map of the Study Area

Source: Open internet window

Plate I: Gold Mining Site in Gurmana

Plate II: Washing of Gold by Artisanal Gold Miners in Gurmana, Shiroro Local Government area, Niger State.

3.2 Preparation of Reagents

3.2.1 1.0M Potassium dichromate ($K_2Cr_2O_7$)

This was prepared by dissolving 49.04 g of $K_2Cr_2O_7$ in distilled water and diluted to 1 dm^3 in a volumetric flask.

3.2.2 0.5M Ferrous solution

To 100 cm^3 of distilled water was dissolved 196.1 g of ferrous ammonium sulphate $Fe((NH_4)_2SO_4)_2.6H_2O$ and 20.0 cm^3 of sulphuric acid and diluted to 1 dm^3 in a volumetric flask.

3.2.3 1.0M Sodium acetate solution

This was also prepared by weighing 136.0 g of sodium acetate trihydrate, dissolved in distilled water and diluted to 1 dm^3 in a volumetric flask.

3.2.4 1.0M Ammonium acetate solution

To 700 cm^3 of distilled water were added 57.0 cm^3 of concentrated acetic acid and 68.0 cm^3 of concentrated ammonium hydroxide, diluted to 1 dm^3 in a volumetric flask and adjusted to pH-7 by adding more of ammonium hydroxide.

3.2.5 0.05M Sodium carbonate

To a pyrex glass was weighed 5 g of Na_2CO_3 and dried at $250^{O}c$ in an ovun for 4 hrs, cooled in a desicator, and 2.50 g was weighed, dissolved in distilled water and made up to 1 dm^3 in a volumetric flask.

3.2.6 0.02M Sulphuric acid

This was prepared by transferring 1.96 g of H_2SO_4 stock into 1dm^3 volumetric flask containing some quantities of distilled water and made up to the mark with distilled water.

3.2.7 0.01M EDTA

For this solution, 3.723 g of di-sodium salt of ethylenediaminetetraacetic acid EDTA was weighed, dissolved in distilled water and diluted to 1 dm^3.in volumetric flask with distilled water.

3.2.8 Murexide reagent (ammonium purpurate) indicator

This was prepared by mixing 200 mg dye with 100 g solid NaCl ground to 40-50 mesh size.

3.2.9 12M Sodium hydroxide

For this solution, 3.50 g of NaOH was weighed into a 100 cm^3 beaker, and transferred into 1dm^3 volumetric and made up the mark with distilled water.

3.2.10 Buffer solution

To a 500 cm^3 beaker was weighed 16.9 g of NH_4Cl and dissolved in 143 cm^3 of concentrated NH_4OH. 1.25 g magnesium salt of ethylenediaminetetracetate (EDAT) was also added and diluted to 250 cm^3 with distilled water in a volumetric flask.

3.3 Sample Collection and Pre-treatment

3.3.1 Soil sample

Surface soil samples were collected using soil auger at a depth of 0-20 cm in the month of july, 2019. The mining site was divided into four according to cardinal points i.e

North, East, South and West. Three samples were collected from each direction at spacing of a 50 metre. The samples were placed in neat polythene bags. The soil auger was always cleaned after collecting sample from each point. Control sample was taken 5 kilometres away from the mining site. The collected soil samples were air dried for seven days, debris removed, ground into fine powder using pestle and mortar and screened through 2mm sieve to achieve uniform particle size.

3.3.2 Water sample

Water samples were collected from two hand dug well, spring, borehole and flowing River Shiroro in Gurmana. The water samples were collected during the day in plastic bottles which have been pre-cleaned with 1% nitric acid and rinsed with deionised water. The bottles were rinsed again severally at the point of sample collection. The sample containers were filled to the brim, tightly covered, stored in an ice chest and transported to the Water Resources, Aquaculture and Fisheries Technology Laboratory, Federal University of Technology Minna in the month of july, 2019.

3.4 Digestion of Soil Samples

To a 100 cm^3 beaker was weighed 1.0 g of the soil sample with 15.0 cm^3 of concentrated nitric-perchloric (3:1) acid mixture and allowed to stand overnight at room temperature. Each the sample was then heated in hot plate at constant temperature for about 45 min until the mixture release white fumes and become clear and semi dried. After cooling, 20.0 cm^3 of distilled water was added and then filtered through Whatman No. 42 filter paper into a 50 cm^3 volumetric flask and made up to the mark with distilled water (Mansour *et al.*, 2020).

3.5 Analysis of Soil Physicochemical Properties

All the physicochemical analyses were carried out according to the procedures outlined by Analysis of the Association of Analytical Chemical (AOAC, 2005).

3.5.1 Determination of soil pH

Into 100 cm^3 beakers was weighed 10.0 g of soil sample and 50.0 cm^3 of distilled water was added. The mixtures was shaken, stirred with a glass rod for about three hours and allowed to stand overnight. The mixture was then filtered into another clean beaker, the pH meter was then calibrated and the electrode immersed in the solution and the reading was recorded. The electrode was rinsed after each measurement with distilled water.

3.5.2 Measurement of electrical conductivity of soil

Into 100 cm^3 beaker was weighed 10.0 g of the soil sample and 50.0 cm^3 of distilled water was added. The mixture was then placed on mechanical shaker and shaken for about an hour. The mixture was allowed to settle and then decanted into a beaker. The conductivity meter was then calibrated using a standard solution of known conductivity. The probe was then submerged into the solution and reading was taken after the meter stabilizes.

3.5.3 Determination of organic carbon and organic matter

Into a 250 cm^3conical flask was weighed accurately 1.0 g soil sample. Then 10.0 $cm^3$of 1.0M $K_2Cr_2O_7$ and 20.0 cm^3 concentrated H_2SO_4 acid was added and placed on a fume cupboard. After 30 min, the mixture was removed and allowed to cool before quantitatively transferred into a titration vessel containing 100 cm^3 of distilled water. Four drops of o-phenanthroline indicator was added and titrated against 0.5M ferrous ammonium sulphate solution. Blank was also treated the same excluding the soil sample

Percentage organic carbon and organic matter were calculated using the following formulae:

$$\% \text{ (OC)} = \frac{(S-T) \times M \times 0.003 \times 1.33}{ADW} \times 100 \qquad (3.1)$$

Where

M = Molarity of dichromate solution

T = Volume of ferrous sulphate used in sample titration (cm^3)

S = Volume of ferrous sulphate used in blank titration (cm^3)

ADW = air dried sample weight (g)

% Organic matter = % Organic carbon x 2 (3.2)

Note, formerly a conversion factor of 1.72 was used, but there is evidence that unless specific information about the organic matter concerned is available a factor 2 is more appropriate (Nelson & Sommers, 1982).

3.5.4 Determination of cation exchange capacity (CEC)

Into 100 cm^3 beaker was weighed 1.0 g of air dried soil sample, 30 cm^3 of 1.0 M NH_4OAc was added, stired, covered and allowed to stand overnight. The solution was then filtered with suction through a Buchner funnel, the solution was leached with small portion of 1.0M NHO_4Ac until the total volume of the extract was 80.0 cm^3. The leachate was then transferred into a 100 cm^3 volumetric flask and made up to the mark with 1.0M NHO_4Ac and saved for analysis with a flame photometer.

3.6 Digestion of Water Samples

To 50.0 cm^3 water sample was added 10.0 cm^3 concentrated nitric acid. The solution was then heated in a hot plate for about 1 hr at a temperature of 80°c until the volume was reduced to one-third of its original volume. The solution was allowed to cool and filtered using Whatman No. 42 filter paper, into a 100 cm^3 volumetric flask, and made up to the mark with distilled deionised water (Kiros *et al.,* 2021).

3.7.1 Physicochemical properties of water

3.7.1 Determination of temperature and pH of the water sample

The temperatures of the water samples were determined with the aid of portable digital thermometer (Pen type model 8685) at the point of sample collection. The glass electrode was thoroughly rinsed with distilled water. The pH meter was calibrated with buffers 4 and 7. After which it was then inserted into a conical flask containing about 20 cm^3 of the raw water sample and allowed to stabilize and the readings were taken.

3.7.2 Determination of total alkalinity (TA)

To the water sample, 2 drops of methyl orange indicator was added and titrate against 0.02M sulphuric acid to an end point (Yellow – orange). Total alkalinity was calculated using the following equations

$$\mathrm{TA} = \frac{VA \times M \times 1000}{Vol\, Sample} \qquad (3.3)$$

Where m V_A = titre value

M = molarity of acid

3.7.3 Determination calcium

Into a flask containing 50.0 cm^3 of the water samples, 2.0 cm^3 of 12M NaOH and 0.2 g indicator mixtures were added and titrated against 0.01M EDTA to an end point (pink to purple). Calcium was calculated using the following equation below

$$\mathrm{Mg\ Ca/l} = \frac{A \times B\ 400.8}{Vol\, Sample} \qquad (3.4)$$

A= titrant vol.

$$B = \frac{Vol\ of\ standard\ Ca\ sol\ taken\ for\ titration}{Vol\ of\ EDTA\ titrant}$$

3.7.4 Determination of total hardness (TH)

Into a 100 cm^3 conical flask was measured 25.0 cm^3 of the water sample, diluted to 50.0 cm^3 with distilled water and then 2.0 cm^3 butter was added followed by 2 drops of indicator and titrated against EDTA titrant to an end point (red to blue). Total hardness was calculated using the following expression

$$TH = \frac{Tv \times 0.01 \times 100 \times 1000}{Vol\ Sample} \qquad (3.5)$$

3.7.5 Determination of magnesium

Calculation from total hardness and calcium

$$Mg\ Mg/l = TH\ as\ mg\ CaCO_3/l - Calcium\ hardness\ as\ mg\ CaCO_3/l\ X\ 0.243 \qquad (3.6)$$

3.7.6 Determination of phosphate

Into 250 cm^3 conical flask was measured 50.0 cm^3 of the water sample and then one drop of phenolphthalein indicator was added followed by 5.0 $cm^3$of 5.0M sulphuric acid and 8.0 cm^3 of combined reagents were added, mixed and allowed to stand for 30 minutes. The solution was then filtered and absorbance was read at 880 nm using UV spectrophotometer. Phosphate was calculated using the following equation

$$PO_4^{3-}\ mg/dm^3 = mg\ P\ from\ calibration\ curve\ x\ 1000 \qquad (3.7)$$

3.7.7 Determination of total dissolved solid

The water sample was filtered through a rinsed and dried glass fiber filter; the filtrate was collected into a pyrex glass container which was previously cleaned and weighed and placed in an oven and then heated at 180°c for about 8 hours in an ovun. After which it was removed and placed in a desicator to cool and then the differences in weight was taken.

Calculations

$$TDS\ mg/dm^3 = wt_{d+s} - wt_d/cm^3 sample \quad (3.8)$$

Where wt_{d+s} =weight of dish plus sample

W_{td} = weight of dish

3.7.8 Determination of biochemical oxygen demand (BOD)

Into 300 cm^3 BOD bottle was pipetted 20 cm^3 of the water sample, and then aerated. The dissolved oxygen (DO) content was determined and recorded and the bottle was incubated in the dark for five days at 20°C. At the end of five days, the final DO content was determined and the difference between the final DO reading and the initial DO reading was calculated. The decrease in DO was corrected for sample dilution, and represents the biochemical oxygen demand of the water sample (Sajad *et al.,* 2019).

$$[BOD]_5 = [DO]_{final} - [DO]_{initial} \quad (3.9)$$

3.7.9 Determination of chemical oxygen demand (COD)

Into a reflux flask was measured 50.0 cm^{3}of water sample and 10.0 cm^3 of potassium dichromate solution with 1.0 g mercuric sulphate was thoroughly mixed. Antibumping beads were added to control boiling of the solution. To this, 10.0 cm^3 of sulphuric acid reagent was added through the open end of the condenser and carefully mixed by swirling. The reflux apparatus was operated for about 1 hour and allowed to cool. The flask was removed, and its content was diluted to 150 cm^3 with distilled water. To the resulting solution, three drops of the ferroin indicator were added. This sample was titrated with standard ferrous ammonium sulphate to an end point where blue-green colour just changed to red-brown (Raji *et al.,* 2015). Blank sample was also treated the same excluding the water sample. The reactions taking place during the oxidation can be expressed by the following equations;

$Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 4H_2O + 3O$ (oxidation reaction)

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ (dichromate titration)

$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$ (chloride interference reaction)

$Hg^{2+} + 4Cl^- \rightarrow [HgCl_4]^{2-}$

$Cr^{3+} + 6Cl^- \rightarrow [CrCl_6]^{3-}$

$Ag^+ + Cl^- \rightarrow AgCl$

Chemical oxygen demand of the water sample was calculated using the following equation

$$COD = \frac{(a-b)\times C \times 8{,}000}{Vol\ of\ Sample} \qquad (3.10)$$

a = titrant used for sample
b =titrant used for blank
C = molarity of ferrous ammonium sulphate

3.8 Statistical Analysis

All the experiments were carried out in duplicates, statistical analysis of the data was performed using SPSS 16 software package. Pearson correlation significance was computed among various physicochemical parameters and concentrations of HMs in the soil and water at 0.95 and 0.01confidence levels. ($p<0.05$ and $p<0.01$) using 2-tailed test.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physicochemical Parameters and Heavy Metals in the Soil Samples

The results of the selected physicochemical parameters of soils from various sampling points are given in Table 4.1. From the results, it was observed that the concentrations of pH, electrical conductivity, organic matter and cation exchange capacity of the soils varied from one sampling point to another. The least pH value was observed in the North sited samples while the highest value was obtained in the East sited samples. South sited samples gave the highest electrical conductivity while lowest value was observed in North samples. The highest organic carbon and organic matter contents were observed in the South sited samples while lowest values were obtained in the North sited samples. As for the cation exchange capacity, highest value was obtained in the West sited samples while least value was obtained in the North sited samples.

Table 4.1 Physicochemical parameters of soil samples in gurmana gold mining site

Sample	pH	EC (µS/cm)	(%) OM	CEC (cmol/Kg)
NS	6.37±0.41^{a}	45.00±26.46^{a}	1.74±0.17^{a}	6.88±1.19^{a}
ES	6.82±0.04^{d}	96.33±75.16^{b}	1.800.30^{ab}	7.17±0.38^{b}
SS	6.60±0.27^{b}	200.33±148.30^{d}	1.95±0.04$_{b}$	8.11±0.64^{c}
WS	6.70±0.20^{c}	125.67±14.22^{c}	1.93±0.08^{b}	8.08±0.88^{c}
FAO/WHO 2014	6.90-8.00	16-175		-

Keys: EC: Electrical Conductivity, OM: Organic Matter and CEC: Cation Exchange Capacity, NS: North Cardinal Sample, ES: East Cardinal Sample, SS: South Cardinal Sample, WS: West Cardinal Sample*Means with different superscript along same column are significantly different from each other at ($p<0.05$). *Each value represents the mean of triplicate determination ± standard deviation

4.1.1 Soil pH

pH of soil plays an important role in regulating solubility and mobility of heavy metals. Most of the heavy metals are found to be available for plants in acidic pH (Wang *et al.,* 2018). The pH result from Table 4.1 indicates that the soil samples were slightly acidic compared to 6.90-8.00 as acceptable limits (USEPA, 2018).The range of the present study was 6.37-6.82. Such a decrease in soil pH could enhance the mobility of heavy metals in soil due formation of metal ions. (Mansour *et al.,* 2020). The result of the present finding is in agreement with pH range of 6.7-6.9 an earlier report by Emmanuel *et al.* (2020) on assessment of heavy metal pollution of soil-water-vegetative ecosystems associated with artisanal gold mining in Ghana.

4.1.2 Electrical conductivity (EC)

Electrical conductivity is used to estimate the concentrations of soluble salts in the soil. The electrical conductivity of soil samples in the present study was found to be in the range of 45.00-200.33 µS/cm, which is greater 16-175 µS/cm, USEPA (2018) permissible limit, which could be due to release of ions which ordinarily will be bound to rocks but are broken down and washed off during the gold mining and processing. This result is also greater than 1.73-11.52 µS/cm reported by Ngole-jeme & Fantke, (2017) on assessment of ecological and human health risks associated with abandoned gold mine tailings contaminated soil in Australia, and lower than 1180-574 µS/cm reported by Abiya *et al.* (2019) on assessment of heavy metal pollution in a gold mining site in southwestern Nigeria. The difference could be as a result of extent of anthropogenic activities carried out in the area.

4.1.3 Organic matter (OM)

Organic matter represents the organic constituents of the soil. Most of its are plants and animals residues. Which contribute positively to the soil structure, soil fertility and water holding capacity of soil. The organic matter of the soil samples in this study were in the range of 1.74-1.95% which is low. This could be due to the fact that the environment is devoid of plant nutrients, and slightly acid nature of the tailings would have hinder vegetation growth; limiting the amount of organic matter in soil thereby creating a conducive medium for heavy metal chelation formation (Olayinka *et al.,* 2017). The present finding corroborates with 2.73-4.17% previous reports by Bhatti *et al.,* (2016) in study of physicochemical properties and heavy metal contnts of soil and crops of Punjab India, and 0.20-0.85% by Mansour *et al.* (2020) in agricultural soil northern Nigeria.

4.1.4 Cation exchange capacity (CEC)

The cation exchange capacity (CEC) of a soil is a measure of the quantity of negatively charge sites on soil surface that can retain positively charged ions (cations) such as Calcium (Ca^{2+}), Magnesium (Mg^{2+}), and potassium (K^{+}), by electrostatic force (Ali and Vinod, 2020). The CEC result gave a ranged value of 6.88-8.11 cmol/kg. Low organic matter content of the soil would have contributed to the low CEC observed in the soil samples (Ngole-jeme & Fantke, 2017). This means the parameter has a strong relationship with organic matter. This result is greater than 3.12-3.26 cmol/kg reported by Abiya *et al.* (2019) on assessment of heavy metal pollution in a gold mining site in southwestern Nigeria.

4.2 Heavy Metals in Soil Samples

The results of the selected heavy metals of soil samples presented in Table 4.2 show that the concentrations of the selected heavy metals were higher than that of the control site while, Cd was not detected throughout the sampling points. Iron gave the highest mean concentrations among the heavy metals tested for.

Table 4.2 Heavy metal concentrations in soil samples around gurmana gold mining site (mg/kg)

Sample	Cd	Cu	Fe	Mn	Ni	Pb	Zn
NS	ND	6.78 ± 2.11^{ab}	72.45 ± 22.78^{a}	24.97 ± 35.71^{b}	2.48 ± 1.31^{a}	1.38 ± 1.38^{a}	15.65 ± 15.65^{a}
ES	ND	6.38 ± 2.17^{a}	157.27 ± 94.60^{b}	11.05 ± 4.95^{a}	3.20 ± 2.18^{b}	3.27 ± 3.27^{c}	26.60 ± 26.60^{c}
SS	ND	7.07 ± 3.13^{b}	378.47 ± 40.71^{c}	13.63 ± 4.42^{a}	3.84 ± 0.79^{c}	3.34 ± 3.34^{c}	15.57 ± 15.57^{a}
WS	ND	7.53 ± 1.25^{c}	457.53 ± 164.17^{d}	27.93 ± 20.39^{c}	3.89 ± 3.35^{c}	2.10 ± 2.10^{b}	19.08 ± 19.08^{b}
Control	ND	4.375	50.00	3.050	1.200	1.050	3.850
WHO/FAO (2014)	3.000	100.00	-	-	50.00	100.00	200.00

ND = Not Detected*Means with different superscript along same column are significantly ($p<0.05$) different from each other. *Each value represents the mean of triplicate determination ± standard deviation

4.2.1 Cadmium (Cd)

Cd is considered as one of the most ecotoxic heavy metals and have been reported to exhibit an adverse effect in soil health, plant metabolism, biological activities animals health and human beings (Sun *et al.,* 2016). The mean concentration of cadmium as presented in Table 4.2 was above the detection limit for all the soil samples and control. This result corroborated with the finding of Onyendikachi *et al.* (2018).

4.2.2 Copper (Cu)

Cu is an important essential element but when consumed in excess, can cause toxicity (Nkwunonwo *et al.,* 2020). The concentrations of copper in soil samples ranged from 6.38-7.53 mg/kg higher than that of control (4.37 mg/kg), but still within range of 100 mg/kg maximum permissible limit proposed by WHO/FAO (2014). This result is greater than 2.22-3.02 mg/kg reported by Eludoyin et *al.* (2017) which could be due extent of mining activities in the sampling stations of the study areas.

4.2.3 Iron (Fe)

Iron was found to be the most predominant metal ion among essential elements in soil. The range of Fe was 72.45-457.53 mg/kg, and was higher than the control value, which could be due to the fact that iron originates mainly from soil parent rock materials and pollute the soil through anthropogenic activities. A higher value of Fe (1496.40-2654.11 mg/kg) was reported by Onyedikachi *et al.* (2018) in quarry sites located in Abeokuta, Nigeria. While a lower value 9.67-24.32 mg/kg was reported by Mansour *et al.* (2020) for agricultural soil fertilized by fertilizer. The differences in results could be due to differences in the geological settings of the sampling sites and the extent of mining operation in the areas.

4.2.4 Manganese (Mn)

The mean concentration of Mn ranged from 11.05-27.93 mg/kg and is higher than that the of control site (3.05 mg/kg). The concentrations of manganese found in this site is similar to 6.92-18.52 mg/kg level of Mn in soil contaminated by applications of fertilizer as reported by Mansour *et al.* (2020). While a value of 219-780 mg/kg was reported by Fazeli *et al.* (2018) on anthropogenic share of metal contents in soils of urban areas of Iran.

4.2.5 Nickel (Ni)

The concentrations of Ni in the soil samples ranged from 2.48-3.89 mg/kg (Table 4.2). A higher concentration of Ni (17.4-105.3 mg/kg) was reported by Benjami *et al.* (2018) in artisanl gold-mining in a rural environment: land degradation in Kenya. While a lower concentration (0.08-0.081 mg/kg) was reported by Abiya *et al.* (2019) in mining site South Western Nigeria. The differences in concentrations could be attributed to extent of mining in the areas, method of mining and geological setting of the area (Emmanuel *et al.,* 2020).

4.2.6 Lead (Pb)

Low levels of lead (1.38-3.34 mg/kg) were generally observed in all the soil samples similar to low levels of Pb 0.216-0.278 mg/kg and 2.69-2.77 mg/kg earlier reported by Abiya *et al.* (2019) and Eludoyin *et al.* (2017) in mining sites in Nigeria. However, the levels of Pb reported here are also relatively low when compared to maximum values 131.73 and 1149 mg/kg levels reported from some contaminated sites by Adewumi & Laniyan, (2020) and Odumo *et al.* (2018).

4.2.7 Zinc (Zn)

The concentration range of zinc in the study area is 15.57-26.60 mg/kg lower concentration of 0.63-0.70 mg/kg reported by Abiya *et al.* (2019) and higher concentration of 47.14 mg/kg was reported by Adewumi & Laniyan, (2020) in Anka mining site Nigeria. The differences in concentrations could be due to the difference in geographical settings, methods and extent of mining in the sampling sites.

4.3 Physicochemical Parameters of the Water Samples.

The selected physicochemical parameters such as pH, electrical conductivity (EC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total hardness (TH), total alkalinity (TA), phosphate (PO_4), nitrate (NO_3), and total dissolved solid (TDS) was analysed for the water samples collected from two hand dug wells, spring, borehole, and flowing river Shiroro in Gurmana Shiroro Local Government Area of Niger State.

The data on water quality of the study area in different sampling sites is presented in Table 4.3, which shows the mean values of the various physicochemical parameters assessed from the different sampling locations for hand dug well water samples, spring water sample, borehole water sample and river water sample respectively

Table 4.3: Concentration of physicochemical parameters of water samples in the vicinity of gurmana gold mining site

Sample	pH	Temp. (°C)	Ec µs/cm	BOD mg/dm^3	COD mg/dm^3	TH mg/dm^3	Ca mg/dm^3	Mg mg/dm^3	TA mg/dm^3	PO$_4^{3-}$ mg/dm^3	NO$_3^-$ mg/dm^3	TDS mg/dm^3
WS1	6.74±0.05^{a}	28.50±0.05^{d}	188.00±2.12^{d}	7.65±0.21^{c}	12.79±0.33^{d}	95.00±1.41^{d}	8.52±0.14^{b}	42.08±0.71^{c}	56.00±0.07^{d}	0.76±0.05^{c}	1.88±0.07^{c}	60.18±0.71^{c}
WS2	7.08±0.21^{ab}	25.00±0.15^{b}	138.50±1.41^{c}	5.70±0.71^{c}	9.65±0.50^{c}	120.50±0.71^{e}	11.07±0.18^{b}	59.60±1.41^{d}	73.00±1.41^{e}	0.62±0.14^{c}	1.70±0.07^{c}	43.15±0.11^{b}
SPG	7.34±0.09^{ab}	27.50±0.12^{c}	43.25±1.06^{a}	4.00±0.13^{ab}	5.95±0.13^{a}	40.50±0.71^{a}	4.28±0.09^{a}	15.94±0.21^{a}	16.45±0.64^{a}	0.007±0.03^{a}	0.17±0.07^{a}	11.77±0.37^{a}
RS	7.69±0.16^{b}	24.50±0.03^{a}	65.85±1.20^{b}	5.40±0.42^{bc}	7.63±0.11^{b}	56.10±0.85^{b}	4.48±0.03^{a}	25.07±0.75^{b}	28.1±0.85^{b}	0.23±0.11^{ab}	3.28±0.18^{d}	40.32±0.71^{b}
BH	7.39±0.25^{ab}	30.50±0.02^{e}	389.50±8.49^{e}	3.75±1.06^{a}	5.28±0.25^{a}	77.50±0.71^{c}	85.74±2.21^{c}	227.90±2.97^{e}	45.50±0.71^{c}	0.34±0.09^{b}	1.33±0.99^{b}	122.19±2.56^{d}
U.S EPA (2018)	6.5.5-8.5	Ambient	1000	6.00	225	200	75	-	-	3.5	50	500.00

Keys: WS: Well water samples, SPG: Spring water sample, RS: River water sample, BH: Borehole water sample

EC: Electrical Conductivity, BOD: Biochemical Oxygen Demand, COD: Chemical Oxygen Demand, TH: Total Hardness, TA: Total Alkalinity, and TDS: Total Dissolved Solid. *Means with different superscript along same column are significantly different from each other at ($p<0.05$).

4.3.1 Temperature

Temperature plays an important role in the metabolic activities of organisms and is considered as a biologically significant factor, its variation depends on climatic condition and geographical area (Obaje *et al.,* 2020). Water temperatures during the study period range from 24.5°c – 30.5°c.

The result obtained in this study is agreement with that reported by Obaje et *al.* (2020) which ranged from 27.11°c - 27.41°c on water quality index of underground water sources in Doma, Nasarawa State.

4.3.2 pH

The pH of water is very vital as it measures the acidity or alkalinity of water and eventually its suitability for domestic or industrial uses (Obaje *et al.,* 2020). The pH of the water samples ranged from 6.74-7.69 as shown in Table 4.3, which is within 6.5-8.5 maximum permissible limit of USEPA but higher than 3.40-7.40 reported by Nnabo, (2015) on water samples in abandoned Pb-Zn mine site in Eyigba South Eastern, Nigeria.

4.3.3 Electrical conductivity (EC)

Electrical conductivity is the ability of water to transmit electric current and this depends on the presence of ions, their mobility, relative concentrations and temperature measurement (Yadav and Jamal, 2018). The mean range of EC in this study is 43.25-39.50 µS/cm. These values are higher than the mean range 7-23 µS/cm of EC for surface water from mining site in west Cameroon (Mouhamed *et al.,* 2020). The conductivity values for all the water samples in this study are within the recommended standard values (WHO/FAO, 2014).

4.3.4 Biochemical oxygen demand (BOD)

BOD is defined as the oxygen required by microorganisms for complete biological decomposition of organic matters in water under aerobic condition (Yadav & Jamal, 2018). The BOD reported for the water samples ranged from 3.75-7.65 mg/dm^3 and are higher than (2.13 mg/dm^3) reported by Raji *et al.* (2015) in the of physicochemical characteristics of river Sokoto, Northwest Nigeria. The slightly higher BOD observation in the water samples studied could be due to organic pollutant caused by poor treatment of wastewater.

4.3.5 Chemical oxygen demand (COD)

Chemical oxygen demand is the measurement of the oxygen required to oxidize soluble and particulate organic matter in water. The COD of the water samples studied range from 5.28-12.79 mg/dm^3 and is lower than 100.15-165.25 mg/dm^{3}earlier reported by Ma *et al.* (2020) in China on the levels of heavy metals in food waste water with environmental effects.

4.3.6 Total hardness (TH)

Calcium and magnesium are primarily responsible for the presence of hardness in water. Ground water may be categorized based on hardness values: < 75 mg/dm^3 (soft), 75-150 mg/dm^3 (moderately soft), 150-300 mg/dm^3 (hard) and > 300 mg/dm^3 (very hard), hard water do not form scum with soap and could also cause scale deposit in pipes (Obaje *et al.,* 2020). The range of hardness for water samples studied is 40.50-120.50 mg/dm^3, which fall within soft and moderately soft. These results corroborate with 90-125 mg/dm^3 reported by Obaje *et al.* (2020).

4.3.7 Total alkalinity (TA)

Alkalinity of water could be due to carbonate, bicarbonate and hydroxide contents of the water. The alkalinity of the water samples in this study ranged from 16.45-73.00 mg/dm^3, and is much higher than 8.87-9.24 mg/dm^3 as reported by Sajad *et al.* (2019) for water quality assessment of Al-sweib river, but lower than 150-250 mg/dm^3 reported by Ma *et al.* (2020) in the study of wastewater physicochemical properties.

4.3.8 Phosphate (PO_4^{3-})

PO_4^{3-} in the water samples ranged from 0.007-0.76 mg/dm^3, and is lower than 0.11-1.77 mg/dm^3 and 10.35-12.75 mg/dm^3 reported by Raji *et al.* (2015) and Ma *et al.* (2020) but similar to 0.018-0.073 mg/dm^3 reported by Kiros *et al.* (2021) for water samples from hand dug well.

4.3.9 Nitrate (NO_3^-)

Nitrates generally are contributed to water through discharge of sewage, industrial effluents and run off from agricultural fields (Qureshimatva *et al.,* 2015). The range of NO_3^- values in this work (0.17-3.28 mg/dm^3) is lower than 6.6-19.7 mg/dm^3 earlier reported by Raji *et al.* (2015) and 20.25-30.30 mg/L reported by Ma *et al.* (2020) but similar to 1.86-5.43 mg/dm^3 reported by Kiros *et al.* (2021).

4.3.10 Total dissolve solid (TDS)

Total Dissolved Solid depends on various factors such as geological character of watershed, rainfall and amount of surface runoffs and gives an indication of the degree of dissolved substances (Sajad *et al.,* 2019). The ranged values of the water samples were 11.77-122.19 mg/dm^3 lower than 1169.6-1665 mg/dm^3 reported by Sajad *et al.*

(2019). The differences in concentrations of physicochemical parameters of the water samples could be due to closeness of anthropogenic activities to the water sources.

4.4 Heavy Metals in Water Samples

The heavy metals concentrations in hand dug well water samples, spring water sample, borehole water sample and river water sample proximal to the artisanal gold mining area are presented in Table 4.4

Table 4.4 Heavy metal concentrations of water samples (mg/dm^3) in the vicinity of gurmana gold mining site

Sample	Cd	Cu	Fe	Mn	Ni	Pb	Zn
WS1	ND	0.09 ± 0.01^b	1.93 ± 0.07^b	0.56 ± 0.08^b	0.07 ± 0.01^b	ND	0.07 ± 0.03^b
WS2	ND	0.11 ± 0.02^b	11.42 ± 0.12^c	0.56 ± 0.09^b	0.02 ± 0.01^a	ND	0.02 ± 0.01^a
SPG	ND	0.05 ± 0.01^a	48.78 ± 0.64^d	1.15 ± 0.07^c	0.05 ± 0.02^b	ND	ND
RS	ND	0.06 ± 0.01^a	ND	0.11 ± 0.03^a	0.06±0.02b	ND	ND
BH	ND	0.06 ± 0.01^a	ND	1.05 ± 0.05^c	0.07 ± 0.01^b	ND	ND
U.S EPA (2018)	0.003	2.00	0.3	0.02	0.01	0.01	5.0

Keys: ND = Detected*Means with different superscript along same column are significantly different from each other at ($p<0.05$), WS: Well water samples, SPG: Spring water sample, RS: River water sample and BH: Borehole water sample.

The heavy metal concentrations in the two hand dug wells, spring, borehole and river water samples presented in Table 4.4 show that the concentrations of Fe in both the well and spring water sample are above USEPA maximum permissible limit for drinking water, of 0.3 mg/dm^3, Kiros *et al.* (2021) also reported a concentration range of 0.33-1.86 mg/dm^3 in hand dug well, while 0.80-1.78 mg/dm^3 was reported by Emmanuel *et al.* (2020) in well water within vicinity of artisanal gold mining site Ghana.

likewise, Mn and Ni concentrations in all the water samples studied are above USEPA maximum permissible limit of 0.02 and 0.01 mg/dm^3, this result agrees with the finding of Nnabo, (2015) who reported concentrations 0.01-3.46 and 0.08-3.63 mg/dm^3 for Mn and Ni from water sources in Eyingba Pb-Zn mining site South Eastern Nigeria. Also, Zn and Fe were not detected in spring, river and borehole water samples while Cd and Pb were not detected in any of the water samples studied. This corroborate with the finding of Ma *et al.* (2020) in the study of physicochemical properties of wastewater. This result indicated that Fe has contaminated the two well water and the spring water while Mn has contaminated all the water sources. Also, Ni did not contaminate in well two with others contaminated. The source of contamination could be through anthropogenic activities in the area. When pH of water decreases, most metal solubility increases making them to become available to aquatic organisms. The higher the acidity, the more soluble and mobile the metals, which makes the metal ions more likely to be taken up and accumulate in the ecosystem.

4.5 Correlations between various Physicochemical Parameters and Heavy Metals in Soil

The correlation between heavy metals and physicochemical parameters of soil are presented in Table 4.5 shows that there is correlation among various physicochemical parameters and concentrations of heavy metals in soil at 0.95 and 0.01confidence levels ($p<0.05$ and $p<0.01$) using 2 tailed test. Both positive and negative correlations were evident.

Table 4.5 Correlation coefficients between physicochemical parameters and heavy metals of soil in the vicinity of gurmana gold mining site

	pH	EC	OC	OM	CEC	Cu	Fe	Mn	Ni	Pb	Zn
pH	1										
EC	0.653	1									
OC	0.418	0.911 *	1								
OM	0.376	0.910 *	0.999**	1							
CEC	0.350	0.859*	0.991**	0.994**	1						
Cu	-0.099	0.414	0.697	0.717	0.786	1					
Fe	0.383	0.771	0.965**	0.965**	0.987**	0.833*	1				
Mn	-0.476	-0.393	-0.061	-0.035	0.072	0.669	0.180	1			
Ni	0.584	0.865*	0.980*	0.971**	0.964*	0.630	0.955*	-0.110	1		
Pb	0.707	0.709	0.498	0.471	0.380	-0.274	0.292	-0.884*	0.559	1	
Zn	0.819*	-0.199	-0.179	-0.223	-0.247	-0.547	-0.195	-0.478	0.013	0.451	1

** Correlation is significant at 0.01 level, * Correlation is significant at 0.05 level (2 tailed test) respectively.

EC: Electrical Conductivity, OM: Organic Matter and CEC: Cation Exchange Capacity, The correlation among various physicochemical parameters and concentrations of heavy metals in the soil at 0.95 and 0.01 confidence levels ($P<0.05\%$ $P<0.01$) using Pearson correlation with 2-tailed test as presented in Table 4.5, Pearson correlation with 2-tailed test showed that at 0.01 level ($P<0.01$), significant positive relationships exist between OM-CEC ($r=0.994$), OM-Fe($r=0.965$), OM-Ni($r=0.971$), CEC-Fe($r=0.987$), CEC-Ni($r=0.964$) and Fe-Ni($r=0.955$). The relationship between OM and CEC could be due to the fact that CEC sites are found primarily on clay minerals and organic matter surfaces, relationship between OM and metals could be due to the high affinity of metals to the soil organic matter. Similarly, significant positive correlation between CEC and metals could be due to the role CEC play in retention and mobility of the metals in soil. While positive correlation between heavy metals themselves suggest similar and identical origin of the metals. The present finding corroborates with the earlier results of Mansour *et al.* (2020).

At level 0.05 ($P<0.05$) there is also positive correlation between pH-Zn ($r=0.819$), EC-Ni ($r=0.865$), EC-CEC ($r=0.859$) and Cu-Fe ($r=0.833$) due to the fact that mobility of heavy metals also depends on pH. While there is adverse correlation between Mn-Pb ($r=-0.884$). Soil parameter has common sources or mutual dependence (Mansour *et al.,* 2020).

4.6 Correlation between Heavy Metals and Physicochemical Parameters of Water Samples in vicinity of Gurmana Gold Mining Site.

The correlation between heavy metals and physicochemical parameters of the water samples are presented in Table 4.6 the result which shows correlations among various physicochemical parameters and concentrations of heavy metals in water samples at 0.95 and 0.01 confidence levels ($p<0.05$ and $p<0.01$), using 2 tailed test. Both positive and negative correlations were evident from the result.

Table 4.6 Correlation between the heavy metals in water and the physicochemical parameters of water

	pH	**EC**	**BOD**	**COD**	**TH**	**Ca^{2+}**	**Mg^{2+}**	**TA**	**PO_4^{3-}**	**NO_3^-**	**TDS**	**Cu**	**Fe**	**Mn**	**Ni**
pH	1														
EC	-0.154	1													
BOD	-0.697	-0.181	1												
COD	-0.793	-0.153	0.985**	1											
TH	-0.643	0.338	0.528	0.620	1										
Ca^{2+}	0.166	0.933*	-0.514	-0.499	0.073	1									
Mg^{2+}	0.108	0.953*	-0.454	-0.430	0.183	0.994**	1								
TA	-0.636	0.387	0.513	0.602	0.999**	0.122	0.231	1							
PO_4^{3-}	-0.787	0.322	0.805	0.852*	0.891*	-0.026	0.069	0.894*	1						
NO_3^-	0.259	-0.080	0.449	0.327	0.184	-0.168	-0.131	0.186	0.310	1					
TDS	-0.027	0.979**	-0.163	-0.168	0.288	0.924*	0.942*	0.338	0.297	0.104	1				
Cu	-0.643	0.036	0.613	0.705	0.953*	-0.224	-0.114	0.935*	0.840	0.199	-0.015	1			
Fe	0.918*	-0.989*	-0.932*	-0.960*	-0.873*	-0.840	-0.824	-0.882*	-1.000*	-0.995*	-0.987*	-0.825	1		
Mn	-0.125	0.355	-0.596	-0.495	-0.234	0.473	0.427	-0.219	-0.352	-0.942*	0.197	-0.344	0.981*	1	
Ni	0.128	0.335	-0.012	-0.122	-0.540	0.339	0.266	-0.506	-0.183	0.095	0.401	-0.687	0.041	0.106	1

** Correlation is significant at 0.01 level, * Correlation is significant at 0.05 level (2 tailed test) respectively

EC: Electrical Conductivity, BOD: Biochemical Oxygen Demand, COD: Chemical Oxygen Demand, TH: Total Hardness, TA: Total Alkalinity, and TDS: Total Dissolved Solid.

pH shows a significant correlation with Fe (r=0.918), which means that the solubility and mobility of this metal depends on pH. Electrical conductivity (EC) shows significant correlation with TDS (r=0.979) and moderate correlation with Ca^{2+} (r=0.933) and Mg^{2+} (r=0.953) at $P<0.05$ and $P<0.01$. This shows that the presence of these ions in dissolved form in water can increase the conductivity of the water (Table 4.6).

BOD_5 shows a strong correlation with COD (r=0.985) since both determine the level of organic pollution in water. COD estimates biodegradable and non biodegradable contamination while BOD_5 defines the biodegradable fractions (MohdYawer *et al.,* 2020).

Total hardness (TH) also shows a perfect positive correlation with total alkalinity (TA) (r=0.999) at ($P<0.01$ and moderate correlation with PO_4^{3-} (r=0.891) and Cu^{2+} (r=0.953) and negative correlation with Fe (r=0.882) which shows that the presence of these ions in dissolved form can increase the total hardness of the water. Ca^{2+}shows strong correlation with Mg^{2+} (r=0.994) and moderate correlation with TDS (r=0.924).TA shows significant correlation with PO_4^{3-} (r=0.894) and Cu (r=0.935) which means presences of this ions in dissolved form could increase total alkalinity of the water. NO^{3-} and TDS show negative correlation with Fe while Fe shows significant correlation with Mn indicating identical source. This result corroborates with that reported by Kiros *et al.* (2021).

4.7 Contamination/Pollution Index (C/PI) of Soil

The results of the Contamination/Pollution index of soil samples from various sampling points are presented in Table 4.7, Contamination/Pollution index value greater than unity, signifies pollution range, while values less than unity, signifies contamination range

Table 4.7 Contamination/pollution index for heavy metals in soil samples of vicinity of gurmana gold mining site

Samples	Cu	Fe	Mn	Ni	Pb	Zn
NS	0.18	0.001	0.02	0.07	0.02	0.11
ES	0.17	0.003	0.01	0.09	0.04	0.19
SS	0.19	0.008	0.01	0.11	0.04	0.11
WS	0.21	0.009	0.03	0.11	0.02	0.14

Keys:NS: North Sample, ES: East Sample, SS: South Sample, WS: West Sample

Contamination and pollution index (Table 4.7), shows that the contamination factors are 0.17-0.21, 0.001-0.009, 0.01-0.03, 0.07-0.11, 0.02-0.04 and 0.11-0.19 for Cu, Fe, Mn, Ni and Zn respectively. This shows that the soil samples are very slightly contaminated with Cu, Fe, Mn, Ni, Pb and Zn, to slightly contamination. This result is lower than 1.86, 1.74, 0.64 and 1.41 for Pd, Zn, Mn and Cd respectively reported by Olayinka *et al.* (2017) in the study carried out levels of heavy metals in soil samples obtained from some selected anthropogenic sites in Abeokuta, Nigeria.

4.8 Contamination Factor (CF) of Water Samples

The results of contamination factors in heavy metals of the water samples from the various sampling points presented in Table 4.8, the values shows that the water samples are contaminated with heavy metals and ranged from low contamination levels to very high contamination levels.

Table 4.8 Contamination factors of heavy metals of the water samples in the vicinity of gurmana gold mining site

Sample	Cu	Fe	Mn	Ni	Zn
WS1	0.04	6.4	28	7.0	0.01
WS2	0.06	38	28	2.0	0.003
SPG	0.03	164	58	5.0	-
RS	0.03	-	5.5	6.0	-
BH	0.03	-	53	7.0	-

Keys: WS: Well water samples, SPG: Spring water sample, RS: River water sample and BH: Borehole water sample.

Fe shows very contamination factor in the two well and the spring water samples. Fe contributes to very high pollution of these water sources in Gurmana (Table 4.8).

Mn showed considerable contamination factor in the river water sample and very high contamination factor in the two well, spring and borehole water samples. While Ni shows moderate contamination factor in well two (WS2); considerable contamination factor in the spring and river water samples and very high contamination factor in well one (WS1) and borehole water samples. The high level of contamination expressed by the concentrations of Fe, Mn and Ni could be related to gold occurrence and mining in the study area.

This is also shown by the positive correlation that exists between Mn and Ni which indicates the effects of man's activities on the sources of the metals. This result corroborates with the finding of Nnabo, (2015), which revealed that both surface and ground water sources within the vicinity of Pb-Zn mining site in Eyingba Nigeria are contaminated with As, Cd, Co, Cu, Mn, Ni, Pb and Zn respectively.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The main goal of this research work was to assess the physicochemical and heavy metal concentrations of soil and water samples collected from a mining site, Gurmana Community of Shiroro Local Government Area, Niger State. A total of seventeen (17) samples were collected comprising of twelve (12) soil and five (5) water samples. The samples were analysed for physicochemical properties and heavy metals and the following conclusion were drawn;

i) The measured physicochemical parameters for soil samples were found to be below the normal standard which could be attributed to mining activities carried out in the area, while those of the water samples varied from one sampling point to another but still within the permissible limits set by standard organizations.

ii) The concentrations of the selected heavy metals in the soil studied were generally higher than the control site indicating some degrees of contamination. Mean concentrations of heavy metals in the soil were found to be in the increasing order of Pb (2.52 mg/kg) <Ni (3.40 mg/kg) <Cu (6.90 mg/kg) <Zn (19.23 mg/kg) <Mn (19.40 mg/kg) <Fe (226.43 mg/kg) respectively. While in the water samples, the concentrations Fe in the two wells and spring water samples were above the standard limit and that of Mn and Ni were also above the standard throughout the water samples.

iii) The contamination/pollution index (C/PI) showed that the soils were very slightly contaminated with Cu, Fe, Mn, Ni, Pb and Zn to slightly contamination. While the water samples were found to be slightly contaminated to a very high contamination level, which means the water samples are more contaminated.

Therefore, there is need for regular monitoring of the mining activities in order to forestall impending health risks that could arise from heavy metals concentrations in mining sites.

5.2 Recommendations

a) Further research work should be carried out on the effects of heavy metals using a more sophiscated techniques in Gurmana Community of Shiroro Local Government Area, Niger State.

b) The levels of other potentially toxic heavy metals in soil, water and plants should be assessed and monitored regularly in order to forestall the impending health risk associated with heavy metals

5.3 Contributions to knowledge

The findings from this study establishes that activities of artisanal gold mining in Gurmana impacted negatively on the heavy metal contents in water with Nickel concentrations of 0.02-0.07 mg/dm^3, while other metals were generally below USEPA recommended limit of 0.01 mg/dm^3. It also establishes that the contamination factor of soil samples ranged from very slightly to slightly contamination (0.001 to 0.21), while that of water samples ranged from low contamination to a very high contamination level (0.003 to 164) respectively.

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