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Determination of Some Heavy Metals in Wastewater and Sediment of Artisanal Gold Local Mining Site of Abare Area in Nigeria.

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Abstract

Wastewater and sediment samples from Abare artisanal gold mining and processing site Zamfara, Nigeria were analyzed for Lead (Pb), Mercury (Hg), Cadmium (Cd), Chromium (Cr), Copper (Cu), and Iron (Fe). The average values (ppm) of Pb, Hg, Cd, Cr, Cu, and Fe in the Wastewater and sediment samples are, 0.832, and 1733.031 for Pb, 7.278, and 2.540 for Hg, 0.004, and 0.005 for Cd, 0.0001, and 2.277 for Cr, 0.062, and 45.908 for Cu, 45.908, and 1024.459 for Fe respectively. Evidence of contamination of the study area by these elements was obvious when compared with World Health Organization (WHO) guidelines for portable water, as well as United State Environmental Protection Agency (USEPA) standard for heavy metals in soil. Given the reality of extreme poverty in Zamfara State, stopping mining operations without an alternative source of income is not realistic. It was recommended that, focus should instead be placed on informing about and implementing safer mining practices; enacting stronger regulation; and establishing areas outside of villages where ore could be securely stored and safely processed without posing significant threats to human health and the environment.

Key words: Gold mining, Environmental and negative effect of gold mining, Heavy metals, Lead poison in Zamfara state.

1 Introduction

Gold mining has been identified as one of the human activities which may impact negatively on the quality of the environment. As for many local communities around the world, many villages in Zamfara State, Nigeria have been associated with uncontrolled and illegal artisanal gold mining activities through which their socio- economic and basic life support systems have been sustained. The impact of these activities results in the destruction of natural ecosystems through removal of soil and vegetation and burial beneath the waste disposal sites. Generally, gold mining waste can be divided into two categories: (i) Mine tailings, generated when processing the ore. (ii) Waste rock produced during uncovering the ore body. The processing methods used involve grinding of rock and ores, recovery of the desired fraction and the disposal of the wastes, often as slurry, to a tailings or retention adits. More than 99% of the original material may finally become tailings when low quality ores are been utilized [1].

The environmental impacts of gold mining are particularly severe because of the chemical processes often used to extract gold. At the present time, most of local communities in Zamfara state used Mercury amalgamation method in extracting gold. This process is particularly damaging the environment, infringes the principle of sustainable development, consume large water and creates a morass of hazardous waste. Considering all of these consequences, the need to assess the quality of water bodies and their sediments in terms of their metallic load in all the gold mining areas of Zamfara state becomes imperative since water from these sources is being used for drinking, domestic irrigation and livestock activities by people living in the catchment areas. In view of the health implications that cut across the food strata. Several years of illegal and small scale gold mining activities in Zamfara state are a potential source of environmental pollution. However, knowledge of metals concentration in Wastewater s and sediments of these gold mining communities is not available or fairly limited.

The present study is planned to address these issues by taking into consideration, the assessment of concentration levels of Pb and other heavy metals known to be associated with gold ore through the following:

1. To quantify the contents of Pb and other heavy metals (Hg, Cr, Cu, Cd and Fe), in water and sediments from Abare artisanal gold mining and processing site using Atomic Absorption Spectroscopy (AAS).
2. To provide a comprehensive data on the concentration Pb and other heavy metals associated with the study area.

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3. To suggest remedial measures for various types of contaminations, if found in the study area.

This study will give a direction for rapid and coordinated intervention by State and Federal authorities, with the support of the international community, in making mining safer, cleaning up polluted villages, and treating those affected by lead poisoning, thereby, contributing to development of database of heavy metals in the geologic environment of Zamfara state, Nigeria.

1.1 Gold Minig Process

Gold as a precious metal found in small quantities, it's mining operations tend to cover wide areas, thus can inflict environmental damage over a geographically wide area. The mining process sometimes is complex and results in the release of highly toxic pollutants. Gold mining tends to have huge negative impacts on the environment from digging out a huge pit to disposing of the left over chemicals and tailings [1].

Heavy metals associated with gold mining are of particular interest for a number of reasons: (i) They show a tendency to accumulate in sediments and soils and have a long persistence time because they are not biodegradable. (ii) They are ubiquitous in sediments and soils arising from both natural and anthropogenic sources with pathways including inheritance from the parent rocks, application of water as well as local and long-range atmospheric and fluvial deposition of emissions from dust and mining. These metals can then enter the food chain via uptake by plants and animals including man. During the processing of the ores for the gold, poisonous substances such as oxides and sulphides of heavy metal pollutants are released into the environment. Other heavy metals associated with the gold, such as arsenic (As), cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) may be freed to enter streams. Mercury (Hg) may also enter streams if miners use it to recover fine particles of gold. The geochemical investigation of waters and sediments is of major importance in the study of aquatic systems, as they provide information about the heavy metals dissolved. The sediment of any water body contains a historical record of the natural and anthropogenic fluxes of heavy metals received into the water basin [2].

1.2 Use of Water in Gold Mining

Gold mining operations utilize large volumes of water, diverting local water resources away from other uses. Disposal methods for Wastewater are highly variable and depend to a large degree on local regulations. In many developing countries, Wastewater containing toxic chemicals can be discharged directly into the water supply. Because mining lobbies and environmental groups are constantly advocating on opposite sides of the issue, mining waste and water quality regulations also vary significantly over time. Even in areas with relatively strict waste-management standards, significant amounts of toxic chemicals and heavy metals contaminate nearby water sources. Strip mining and mountaintop removal can destroy entire watersheds and result in sedimentation of waterways. Many mining activities also use large volumes of water to process ore [3].

1.3 The Environmental Impacts on Water Sources Near Mine Dumps.

Mining processes result in large amounts of toxic waste, which need to be disposed of or stored. In developing counties, due to lax regulations, large amounts of mine tailings are simply sent into rivers, resulting in considerable ecological damage and contamination of human water supplies. Older abandoned mines often have exposed tailing piles that are poorly contained. Particulate mine tailings can be carried by wind to contaminate broad areas, including waterways. Modern mines utilize a variety of containment methods, including pond storage, which minimize but do not completely eliminate the spread of toxins into water sources. While mining regulations have become stricter, mining technologies result in higher productivity, leading to larger amounts of mining waste. Mines invariably contaminate surface and ground water, even when mines have containment systems in place. Chemicals such as sulfur, arsenic, mercury and cyanide seep into ground water during mining operations, or get washed away by rainwater, collecting in rivers, lakes and aquifers. Many abandoned mines leave toxic waste dumps that leach chemicals and heavy metals for decades, much of which ends up in water sources. Acid mine drainage frequently occurs with coal mines, polluting waterways and destroying terrestrial habitats in large areas surrounding the mines [3].

1.4 Types of Pollution Generated by Gold Mining.

Gold mining or prospecting has been performed in areas of the world for hundreds of years. While early excavation methods included the use of crude tools or picks and shovels, more productive techniques have evolved over the last one hundred years. Unfortunately, many modern gold mining practices have led to elevated air, soil and water pollution levels as a result. Mining gold from the earth can have grave environmental implications. Because mining is an inefficient process, large swaths of land must be used. Gold mining is a dangerous and environmentally dubious practice for several reasons. Mining is destructive to the natural environment around mines, creates waste rock disposal problems, and uses harsh chemicals which can be significant sources of waste and harm to workers and nature [3].

Gold mining can generate several types of pollution as follows:

1.4.1 Air Pollution

Air pollution is created from several processes associated with gold mining. Open air mining, sometimes called open pit mining, involves digging in vertical levels to prevent danger from falling rocks. Haul roads are placed near the mines to collect waste and ore. Mining close to the ground surface and driving to and from the mine site generates large amounts of dust, which pollutes the air. The process of refining the ore also causes pollution, particularly when the ore goes through a smelting process which heats the ore to melt the metal and release it from the surrounding material. The smelters release large amounts of lead as well as nitrogen and sulfur, which are returned to the earth in the form of acid rain [3].

1.4.2 Water Pollution

Once ore is gathered from mines, it can be extracted by using different methods. One such method, called leaching, is a low-cost method of removing ore from waste. During the process, workers pile low-grade gold ore into an outdoor heap and put a cyanide or mercury solution on it. The cyanide/mercury then dissolves the gold, which it runs down a slope into reservoirs before it is collected. In some countries, environmental laws require that the slopes and collection vats are impenetrable so that poisons cannot be released into the ground. However, lack of protections in other countries mean that the poisons are often leaked into the soil. These materials then make their way into local water supplies, lakes, rivers and streams. Drainage of this type raises acid levels in lakes which are harmful to both animals and people. Additionally, some mines intentionally dispose toxic wastes into oceans, lakes and rivers, while others place wastes or tailings in dammed reservoirs that can occasionally burst and flood areas, releasing mercury and other heavy metals into the water supply. Pollution from mines can cause drinking water contamination and high levels of mercury or heavy metals in fish [3].

1.4.3 Soil Pollution

Because a small amount of gold is extracted from large areas of land, large piles of toxic tailings and waste are the result of gold mines. These piles can cause heavy metals and other toxins to penetrate the soil, preventing plant life or creating high levels of toxins in plants. Animals that eat these plants can then be subject to disease or other health problems. Heavy metals and toxins can remain in soils for decades after mining, which leaves the areas unsuitable for use by humans and animals for some time [3].

1.5 Negative Effects of Gold Mining

Gold is a precious metal used around the world in jewelry, electronics and even dentistry. Extraction of gold requires mining for it beneath the Earth's surface. Mining for gold has some negative effects, including erosion, the use of mercury, loss of biodiversity, and disruption of indigenous communities [3].

1.5.1 Erosion

Erosion is when solid deposits are weathered over a period of time and moved from their natural spot to a new destination. Erosion occurs naturally in the wild, but can also occur as a negative effect of gold mining. Excessive amounts of gold mining can wash away soil into nearby rivers, as well as strip an area of soil altogether. Serious erosion can also strip an area of its ability to support agriculture [3].

1.5.2 Mercury

The chemical mercury is used in the extraction of gold from ore. It is very toxic to humans and animals. When the chemical enters the body, it suppresses the central nervous system causing respiratory failure and death. The mercury used in gold mining can get into the soil, and through the process of erosion can make its way into lakes and streams. This in turn can pollute local water supplies [3].

1.5.3 Loss of Biodiversity

In the gold mining process, land must be cleared for mining. Clear-cutting trees disrupts local ecosystems, causing animals to flee the area or perish. Also, when the chemicals used in gold mining make their way into the soil and the water, they disrupt the local wildlife by poisoning their sources of food and water. It is not unusual in gold mining for toxic chemicals to be simply dumped into local ponds [3].

1.5.4 Indigenous Communities

In many remote parts of the world, indigenous communities still exist and gold mining may disrupt their lives. Large gold mining companies will often secure land deals from the local governments, and in this process eject, often violently, the local indigenous population. Governments in these regions have been known to kill indigenous people for refusing to leave areas that have been sold to gold mining companies [3].

1.6 Heavy metals

Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. Although these elements are lacking in abundance they are not lacking in significance. Mercury and lead for example are widely used in technology but are so toxic that minute quantities can destroy life. In Nigeria today numerous studies indicated that industrial activities release heavy metals either as solid, gas and most especially liquids in the form of Wastewater or effluents allowed draining into water ways or bodies. Small scale road side activities are also significantly contributing to the transmission of these toxic species [4].

1.7 Macro-nutrients

These metals are required by body in good quantities for proper metabolism and functioning of body organs [5]. They are referred to as the trace elements. These include iron, zinc, calcium, magnesium, sodium, potassium, copper, and manganese. These elements, or their compounds, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products [4].

1.7.1 Iron (Fe)

The total amount of iron in the human body is approximately 4 g, of which 70% is present in red blood colouring agents. Iron is a dietary requirement for humans, just as it is for many other organisms. Men require approximately 7 mg iron on a daily basis, whereas women require 11 mg. The difference is determined by menstrual cycles. When people feed, normally these amounts can be obtained rapidly. The body absorbs approximately 25% of all iron present in food. When someone is iron deficit feed iron intake may be increased by means of vitamin C tablets, because this vitamin reduces tertiary iron to binary iron. Phosphates and phytates decrease the amount of binary iron. In food iron is present as binary iron bound to haemoglobin and myoglobin, or as tertiary iron. The body may particularly absorb the binary form of iron. When iron exceeds the required amount, it is stored in the liver. The bone marrow contains high amounts of iron, because it produces haemoglobin. Iron deficits lead to anaemia, causing tiredness, headaches and loss of concentration. The immune system is also affected. In young children this negatively affects mental development, leads to irritability, and causes concentration disorder. Young children, pregnant women and women in their period are often treated with iron (II) salts upon iron deficits. When high concentrations of iron are absorbed, for example by haemochromatose patients, iron is stored in the pancreas, the liver, the spleen and the heart. This may damage these vital organs. Healthy people are generally not affected by iron overdose, which is also generally rare. It may occur when one drinks water with iron concentrations over 200ppm. Iron compounds may have a more serious effect upon health than the relatively harmless element itself. Water soluble binary iron compounds such as $FeCl_2$ and $FeSO_4$ may cause toxic effects upon concentrations exceeding 200 mg, and are lethal for adults upon doses of 10-50 g. A number of iron chelates may be toxic, and the nerve toxin iron penta carbonyl is known for its strong toxic mechanism. Iron dust may cause lung disease. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens [6].

1.8 Micro-nutrients

These metals are required by the body in trace quantities and are essential for maintaining various body functions and metabolic activities. Metals such as silicon, nickel, boron, and vanadium are essential (but toxic at higher levels). These have biological functions in plants and some animals but essentiality for humans and their requirements are under research [5]. The toxicity details of some of the metal causing human disorders are described below:

1.8.1 Chromium (Cr)

Chromium does not occur freely in nature. The main chromium mineral is chromite. Chromium compounds can be found in waters only in trace amounts. The element and its compounds can be discharged in surface water through various industries. It is applied for example for metal surface refinery and in alloys. It may be polished and it does not oxidize when it comes in contact with air [6].

The human body contains approximately 0.03 ppm of chromium. Daily intake strongly depends upon feed levels, and is usually approximately 15-200 μg, but may be as high as 1 mg. Chromium uptake is 0.5-1%, in other words very small. The placenta is the organ with the highest chromium amounts. Trivalent chromium is an essential trace element for humans. Together with insulin it removes glucose from blood, and it also plays a vital role in fat metabolism. Chromium deficits may enhance diabetes symptoms, and are very rare. Chromium is a dietary requirement for a number of organisms. This however only applies to trivalent chromium [6].

Chromium water pollution is not regarded one of the main and most severe environmental problems, although discharging chromium polluted untreated Wastewater in rivers has caused environmental disasters in the past. Chromium (III) oxides are only slightly water soluble, therefore concentrations in natural waters are limited. Cr^{3+} ions are rarely present at pH values over 5, because hydrated chromium oxide ($Cr(OH)_3$) is hardly water soluble. Chromium (VI) compounds are stable under aerobic conditions, but are reduced to chromium (III) compounds under anaerobic conditions. The reverse process is another possibility in an oxidizing environment. Chromium is largely bound to floating particles in water. Lime or phosphate in soils may further decrease chromium susceptibility. Air-dried soil generally contains 2-100 ppm of chromium. Chromium solubility in soil water is lower than that of other potentially toxic metals. This explains the relatively low plant uptake. Under normal conditions plants contain approximately 0.02-1 ppm chromium (dry mass), although values may increase to 14 ppm. Chromium (VI) compounds are toxic at low concentrations for both plants and animals. The mechanism of toxicity is pH dependent. These compounds are more mobile in soils than chromium (III) compounds, but are usually reduced to chromium (III) compounds within a short period of time, reducing mobility. Soluble chromates are converted to insoluble chromium (III) salts and consequently, availability for plants decreases. This mechanism protects the food chain from high amounts of chromium. Chromate mobility in soils depends on both soil pH and soil sorption capacity, and on temperature. The guideline for chromium is agricultural soils is approximately 100 ppm. Chromium (III) toxicity is unlikely, at least when it is taken up through food and drinking water. It may even improve health, and cure neuropathy and encephalopathy [6].

Chromium (VI) compounds are toxics and known human carcinogens, breathing high levels can cause irritation to the lining of the nose; nose ulcers; running nose; and breathing problems, such as asthma, cough, shortness of breath, or wheezing. Long term exposure can cause damage to liver, kidney, circulatory and nerve disorders, as well as skin irritation [5].

1.8.2 Copper(Cu)

Copper is an essential substance to human life, but its critical doses can cause anemia, acne, adrenal hyperactivity and insufficiency, allergies, hair loss, arthritis, autism, cancer, depression, elevated cholesterol, depression, diabetes, dyslexia, failure to thrive, fatigue, fears, fractures of the bones, headaches, heart attacks, hyperactivity, hypertension, infections, inflammation, kidney and liver dysfunction, panic attacks, strokes, tooth decay and vitamin C and other vitamin deficiencies [5].

Copper enters the air, mainly through release during the combustion of fossil fuels. Copper in air will remain there for an eminent period of time, before it settles when it starts to rain. It will then end up mainly in soils. As a result soils may also contain large quantities of copper, after copper from the air has settled. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of copper each day by eating, drinking and breathing [6].

1.9 Toxic metals

Lead, cadmium, mercury, arsenic and their inorganic compounds, are toxic to human health as well as the environment. [5].The toxicity details of some of the metal caused human disorders are described below:

1.9.1 Lead (Pb)

Lead is a naturally occurring bluish-gray metal found in small amounts in the earth's crust. Lead can be found in all parts of our environment. Much of it comes from human activities including burning fossil fuels, mining, and manufacturing. Lead has many different uses. It is used in the production of batteries, ammunition, metal products (solder and pipes), and devices to shield X-rays [7].

The effects of lead are the same whether it enters the body through breathing or swallowing. Lead can affect almost every organ and system in your body. The main target for lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system. It may also cause weakness in fingers, wrists, or ankles. Lead exposure also causes small increases in blood pressure, particularly in middle-aged and older people and can cause anemia. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High level exposure in men can damage the organs responsible for sperm production [7].

Children are more vulnerable to lead poisoning than adults. A child who swallows large amounts of lead may develop blood anemia, severe stomachache, muscle weakness, and brain damage. If a child swallows smaller amounts of lead, much less severe effects on blood and brain function may occur. Even at much lower levels of exposure, lead can affect a child's mental and physical growth. Exposure to lead is more dangerous for young and unborn children. Unborn children can be exposed to lead through their mothers. Harmful effects include premature births, smaller babies, decreased mental ability in the infant, learning difficulties, and reduced growth in young children. These effects are more common if the mother or baby was exposed to high levels of lead. Some of these effects may persist beyond childhood. It is important to note that even children who seem healthy can have high levels of lead in their bodies [7].

Lead poisoning is most commonly caused by ingestion and inhalation of lead and lead compounds. Lead causes damage to multiple body systems, and the nervous system is particularly vulnerable, especially in young children. Chronic lead poisoning occurs when small amounts of lead are taken in over a longer period. The Centers for Disease Control and Prevention (CDC) defines childhood lead poisoning as a whole-blood lead concentration equal to or greater than 10 micrograms/dL. Acute lead poisoning, while less common, shows up more quickly and can be fatal, when a relatively large amount of lead is taken into the body over a short period of time. Children constitute the vast majority of such cases. Symptoms can include severe abdominal pain, diarrhea, nausea and vomiting, weakness of the limbs, seizures, and coma [7].

1.9.2 Mercury (Hg)

Mercury is a naturally occurring metal which has several forms. The most common one, methyl mercury, is produced mainly by microscopic organisms in the water and soil. More mercury in the environment can increase the amounts of methyl mercury that these small organisms make. Metallic mercury is used to produce chlorine gas and caustic soda, and is also used in thermometers, dental fillings, and batteries. Mercury salts are sometimes used in skin lightening creams and as antiseptic creams and ointments [7].

Exposure to mercury occurs from breathing contaminated air, ingesting contaminated water and food, and having dental and medical treatments. Mercury, at high levels, may damage the brain, kidneys, and developing fetus. Inorganic mercury (metallic mercury and inorganic mercury compounds) enters the air from mining ore deposits, burning coal and waste, and from manufacturing plants. It enters the water or soil from natural deposits, disposal of wastes, and volcanic activity. The nervous system is very sensitive to all forms of mercury. Methyl mercury and metallic mercury vapors are more harmful than other forms, because more mercury in these forms reaches the brain [7].

Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and developing fetus. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems. Short-term exposure to high levels of metallic mercury vapors may cause effects including lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes, and eye irritation. Very young children are more sensitive to mercury than adults [7].

1.9.3 Cadmium (Cd)

Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides. Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried sea weed. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by cadmium are: Diarrhoea, stomach pains and severe vomiting, Bone fracture, Reproductive failure and possibly even infertility, Damage to the central nervous system, Damage to the immune system, Psychological disorders, Possibly DNA damage or cancer development [6].

2 Materials and methods

2.1 Apparatus and Reagents

All the chemicals and reagents used in this study were of analytical grades, and the glass wares used were cleaned, rinsed with distilled water and air dried. They include: Weighting balance(Mettle P.M. 16k, Gallen Kamp UK), Filter Paper (What man (12cm), What Man LTD England), while oven, beaker, volumetric flask and digestion flask are pyran brand from Kort-Koll, Germany.

The analyses of the metals were carried out using Schimadzu AA 7000 atomic absorption spectrophotometer (model Schimadzu AA 7000. Spectrum, Philip) attached to graphite atomizer and a HP 960C Computer Printer.

2.2 Methods of Preparation of Reagents

The solvents used were prepared as described below:

(a) 5% Nitric acid (HNO_3): 5 mL concentrated HNO_3 was pipette into a 100 cm^3 volumetric flask and made up to mark with distilled water.

(b) 50% Nitric acid (HNO_3): 50 mL concentrated HNO_3 was pipette into a 100 cm^3 volumetric flask and made up to mark with distilled water.

(c) 1:1 (v/v) Nitric acid (HNO_3)/Distilled water: 125cm^3 of concentrated HNO_3 was measured into a 250 cm^3 volumetric flask and made up to mark with distilled water.

2.3 Sample Collection and Treatment

Sample containers were thoroughly washed with detergent, rinsed with water followed by distilled water before soaking in 5% HNO_3 for about 24 hours. Wastewater and sediment Samples were collected from gold processing site in Abare, Anka, Zamfara State.

2.4 Treatment of Samples for AAS Analysis

Wastewater Sample

The Wastewater samples (100cm^3) was filtered using cellulose nitrate filter papers (0.45µm pore size), acidified with 50% HNO_3 acid solution to achieve a pH of 2.0. The addition of acid to water sample is to keep the metal ions in the dissolved state, as well as to prevent microbial activities. The samples were then kept in a refrigerator until they were dispatched to the AAS analysis [8].

Sediment Sample

The sediments were collected into plastic bags and kept in the oven to ensure dryness. Dried samples were then homogenized by grinding using the Agate Mortar and pestle. Homogeneity of the samples was further ensured by making each sample to undergo traditional quartering technique by making each sample to go through several sub-divisions. The grinded samples were then kept in sealed bottles awaiting analysis procedures. 1 gram of each sample were weighted into beakers and moistened with distilled water. 5ml of Nitric acid was then added to the sample in the beaker after which 10ml of Hydrofluoric acid was then added. The resulting solution was then placed on a sand bath at about 60^0C in a vacuum cupboard until dryness was achieved. In some cases, fresh additions of the reagents were necessary for complete loss of silica.The reason for the addition of distilled water and nitric acid is to soften the matrix and to reduce a likely vigorous reaction between the HF and the sample. The dried sample were then recovered from the vacuum cupboard and made into solution by adding concentrated Hydrochloric acid and distilled water 1:1 (v/v). It was ensured that all samples were taken up into solution and kept in labelled plastic bottled and ready for analysis [8].

3 Results and Discussion

The mean concenrations of heavy metals analyzed in Wastewater and sediment samples are presented in table i. For Lead (Pb), it has an average concentration of 0.832 ± 0.0002 (ppm) in Wastewater sample and average concentration of 1733.031 ± 0.0012 (ppm) in the sediment. When compared with World Health Organization WHO (2008) guidelines for portable water, the value obtained for Wastewater sample is found to be more than 83 times the acceptable limit for Pb in drinking water i.e. (0.01ppm) [9]. For the sediment sample, the value is over 4 times when compared with USEPA (2008) guidelines acceptable limit for Pb in soil i.e. (400ppm) [10]. This value is lower than the value of <0.01 – 0.32ppm reported by UNEP/OCHA (2010) in Abare village, but within the range of <0.01 – 1.10 ppm reported in Bagega village [7]. In case of the sediment sample, the average value obtained by the present study agreed with the range of <100 -2360mg/kg reported by UNEP/OCHA (2010) for sediment in Abare village [7]. The elevated levels of Pb found on these samples should be properly addressed, as these facts underscore the great risks which any ongoing build-up of heavy metals in the environment portends for human health and wellbeing. This can be done by shifting the processing of the gold outside the villages as a first step, thus preventing further deposition of more contaminants on these sites. Some form of remediation of the sites should be done particularly in respect of Pb [11].

For mercury (Hg), it has an average concentration of 7.278 ± 0.0027(ppm) in Wastewater sample and average concentration of 2.540 ± 0.0007(ppm) in the sediment. When compared with World Health Organization WHO (2008) guidelines for portable water, the value obtained for Wastewater and sediment samples are several times more than the acceptable limit for Hg in drinking water i.e. (0.01ppm) [9].

Table i: Concentrations of Heavy Metals Analyzed.

Metals	Concentration (ppm)	
	Wastewater	Sediment
Lead (Pb)	0.832 ± 0.0002	1733.031 ± 0.0012
Mercury (Hg)	7.278 ± 0.0027	2.540 ± 0.0007
Cadmium (Cd)	0.004 ± 0.0002	0.005 ± 0.0001
Chromium(Cr)	0.0001 ± 0.0006	2.277 ± 0.0004
Copper (Cu)	0.062 ± 0.0002	45.908 ± 0.0007
Iron (Fe)	7.770 ± 0.0011	1024.459 ± 0.0013

Key: Results were presented as mean ± standard deviation of triplicate analysis.

This value is lower than the value of 0.002 – 0.009ppm reported by Cobbina *et al.,* (2013) in Water Sources of Small Scale Gold Mining area of Datuku in the Talensi-Nabdam District of Ghana [12]. But the pattern of the concentration obtained by this study agreed with average values of 0.212 ± 0.149(ppm) for sediment and 1.48 ± 0.256(ppm) for Wastewater reported by Boamponsem(2010) for Hg in the streams of Tarkwa gold mining area of Ghana [2]. Mining activities may have probably released extremely high levels of Hg into the environment, which were rain washed into water system. The relatively high levels of Hg could also be due to anthropogenic inputs, both point and non-point sources, as sample sites are closed to the processing sites, and direct and indirect discharge of mine waste may be another contributing factor to the elevated levels of Hg in the water samples, which may have also entered the waterways through wet and dry deposition from air or through rain.

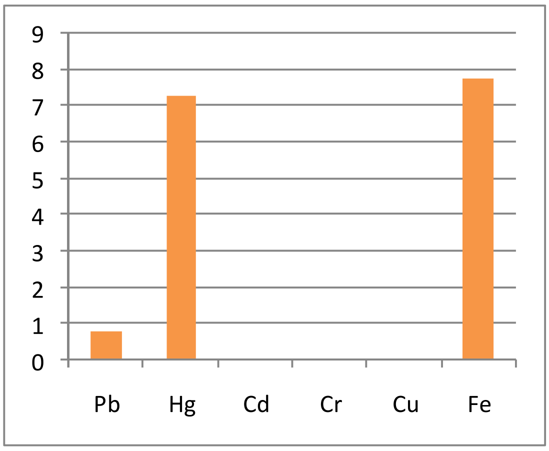

Fig.1: Variation of heavy metals in the Wastewater sample

For Cadmium (Cd), it has an average concentration of 0.004 ± 0.0002 (ppm) in Wastewater sample and average concentration of 0.005 ± 0.0001 (ppm) in the sediment. When compared with World Health Organization WHO (2008) guidelines for portable water i.e. (0.003ppm) [9], the value obtained for Wastewater is a bit higher, and sediment sample is several times lower than the maximum allowable concentration of Cd in soil i.e. (0.3ppm) (Adegoke *et al.,* 2009) [13].

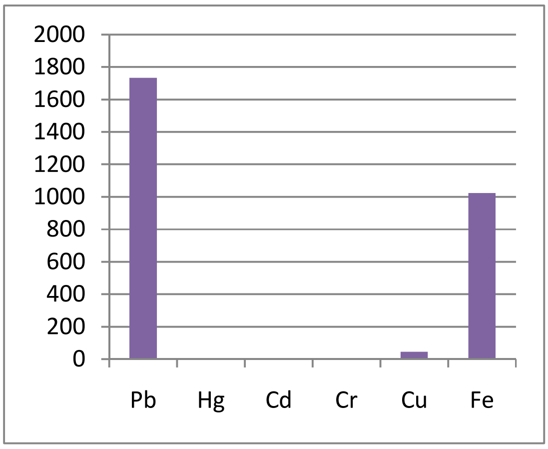

Fig.2 Variation of the heavy metals in the sediment sample

This value fall within the range of <0.005 – 0.008ppm reported by Cobbina *et al.,* (2013) in Water Sources of Small Scale Gold Mining area of Datuku in the Talensi-Nabdam District of Ghana [12]. But is lower than the concentration of 0.658 ± 0.584(ppm) for sediment and 1.11 ± 0.361(ppm) for Wastewater reported by Boamponsem (2010) for Hg in the streams of Tarkwa gold mining area of Ghana [2]. The main sources of cadmium are industrial activities. However, the presence of Cadmium in some of the water sources in the study area could be caused by seepage from the parent rock. The use of cadmium containing products such as batteries, plastics and mining tools are also sources of cadmium in water bodies. Cadmium causes adverse health effects such as kidney damage, bronchitis, osteomalacia (soft bones) at very low exposure levels (Adegoke *et al.,* 2009) [13].

For Chromium (Cr), it has an average concentration of 0.0001 ± 0.0006(ppm) in Wastewater sample and average concentration of 2.277 ± 0.0004(ppm) in the sediment. When compared with World Health Organization WHO(2008) guidelines for portable water i.e. (0.005 ppm) [9], the value obtained for Wastewater is lower, and sediment sample is several times lower than the maximum allowable concentration of Cr in soil i.e. (100 ppm) (Adegoke *et al.,* 2009) [13]. This value is lower than 16.73ppm reported by Tsafe *et al.,* (2012) in soil around Yargalma area, Zamfara State [14], but is higher than the concentration of 0.045 - 0.299 ppm for soil in Dareta village, reported by Udiba *et al.,* (2013) [15]. Cr is not acutely toxic to humans. However, Cr (+6) is more toxic than Cr (+3) because of its high rate of absorption through intestinal tracts. In the natural environment, Cr (+6) is likely to be reduced to Cr (+3), thereby reducing the toxic impact of chromium discharges (Rasheed *et al.,* 2012).

For Copper (Cu), it has an average concentration of 0.062 ± 0.0002(ppm) in Wastewater sample and average concentration of 45.908 ± 0.0007 (ppm) in the sediment. When compared with World Health Organization WHO(2004) guidelines for portable water i.e. (2ppm), the value obtained for Wastewater is much lower [17], and sediment sample is close to the maximum allowable concentration of Cu in soil i.e. (50ppm) (Adegoke *et al.,* 2009) [13]. This value is higher than 1.13ppm reported by Tsafe *et al.,* (2012) in soil around Yargalma area, Zamfara State [14]. But the pattern of the concentration obtained by this study agreed with average values of 13.0 ± 4.40(ppm) for sediment and 3.66 ± 1.11(ppm) for Wastewater reported by Boamponsem (2010) for Cu in the streams of Tarkwa gold mining area of Ghana [2]. Contamination of soil with Cu has health hazards implication as the excessive concentration of Cu could bring about anaemia, infections, thinning of bones, thyroid gland dysfunction, heart disease and nervous systems problems [13].

For Iron (Fe), it has an average concentration of 7.770 ± 0.0011 (ppm) in Wastewater sample and average concentration of 1024.459 ± 0.0013 (ppm) in the sediment. When compared with World Health Organization WHO (2004) guidelines for portable water i.e. (0.3ppm), the values of Fe obtained by this study are several times higher than that limit [17]. The value obtained by the present study is also higher than 195.25ppm reported by Tsafe *et al.*, (2012) in soil around Yargalma area, Zamfara State [14]. But the value of Fe in Wastewater agreed with the range of 0.018 – 19.41ppm reported by Cobbina *et al.,* (2013) in Water Sources of Small Scale Gold Mining area of Datuku in the Talensi-Nabdam District of Ghana [12].

Iron is ubiquitous in the earth's crust and an essential element in human nutrition. No health based guideline value is proposed for iron. However, at levels above 0.3mg/litre, iron stains laundry and plumbing fixtures [12]. The ingestion of Fe in large quantities results in a condition known as heamochromatosis (normal regulatory mechanism do not operate effectively), where in tissue damage results from Fe accumulation. General symptoms include abdominal pain, fatigue, bronzing of skin color, joint pains, loss of body hair, weight loss and lack of energy [16].

Statistical analysis: Tests for significant difference between means were carried out using independent groups t-test between means. The t-statistic at the 0.05 critical alpha level shows, there is signicant difference between the concentrations of all the elements in the Wastewater and sediment samples i.e. p = 0.0000 for Pb, Hg, Cr,Cu and Fe respectively. While for Cd p = 0.0015 which also shows significant difference between the concentrations of Cd in Wastewater and the sediment.

Fig 1 and 2 represent the variation in the concentration of the elements in the Wastewater and sediment samples. As can be seen from fig. 1 the concentration of the elements in the Wastewater are of the order Fe > Hg > Pb > Cu > Cd > Cr. i.e Fe has the highest concentration with the Cr having the least concentration. For fig. 2 which represent the concentration of the elements in sediment, the concentration is of the order Pb > Fe > Cu > Hg > Cd > Cr. i.e Pb has the highest concentration with the Cr having the least concentration.

In general, the concentrations of the elements in the sediment sample are higher than that of the water except for Hg, and this might be due to the fact that metals can be either transported with the water or suspended sediment stored within the riverbed bottom sediment. Also, suspended sediments and metallic chemical solids are stored in riverbed sediment after they aggregate to form large denser particles that settle at the bottom of the water. In addition, the high concentrations could also be due to the inherent mineralogy of the ores of the study area.

4 Conclusions and Recommendations

4.1 Conclusion

The results of this study have generally shown high levels of all the examined elements in the Wastewater and sediment samples. Direct and indirect discharge of mine waste may be a contributing factor to the high levels of these metals. High concentrations of most of the heavy metals observed in Wastewater may have a detrimental effect on the health of the inhabitants of the communities that use the river and surface water directly without treatment for domestic purposes.

This research may serve as a reference for future studies on the assessment of the levels of toxic metals in the study area. It is envisaged that the results of this study will enrich the discussion and understanding of the effects of mining activities on the environment as well as the health implications of people. It is recommended that, there should be formulation and enforcement of a directive to prevent any form of farming activities on the contaminated land and relocation of the processing sites out of the sensitive areas, and the enforcement of other environmental protection regulations to stop the ongoing buildup of these metals. Findings from this study will be of immense help to researchers and environmental regulators in developing countries.

4.2 Recommendations

In view of the result obtained from this study, the following recommendations are hereby suggested.

1. Given the reality of extreme poverty in Zamfara State, stopping mining operations without an alternative source of income is not realistic. Focus should instead be placed on informing about and implementing safer practices; enacting stronger regulation; and establishing areas outside of villages where ore could be securely stored and safely processed without posing significant threats to human health and the environment.
2. Given the scope and complexity of the lead pollution crisis in Zamfara State, and the need for many actors to be working together closely and sharing information regularly, the importance of coordination for the response to this emergency cannot be understated.
3. National and international experience and expertise in safer mining practices should be drawn upon.
4. Grinders used for the processing of ore should not be used for the processing of food.
5. Children should not be allowed to play on former ore processing sites. They should wash their hands before eating to avoid contaminating the food with lead soil.
6. Sacks used for transporting ore, and mortar and pestles used for crushing ore, should not be used for the transport and processing of food.
7. Grains and any other food items should not be dried or stored on the ground where lead dust may be present.
8. Assess other villages for possible contamination where suspected and/or confirmed mining and/or ore processing

activities have taken/are taking place should be assessed immediately for possible lead pollution and poisoning.
9. Measures should be taken by Federal, State and local authorities to prevent further ore processing activities from taking place at sensitive sites, such as water sources from which humans and livestock drink.
10. All polluted villages should be remediated in the nearest possible future.

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