DETERMINATION OF PHYSICOCHEMICAL PROPERTIES AND HEAVY METAL CONTENTS IN WATER, SEDIMENT AND FISH IN WATER AND FOOD CROPS IN, ZAMFARA STATE, NIGERIA

BY

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DECLARATION

I hereby declare that work in this thesis entitled **"DETERMINATION OF PHYSICOCHEMICAL PROPERTIES AND HEAVY METAL CONTENTS IN WATER, SEDIMENT AND FISH IN WATER AND FOOD CROPS IN, ZAMFARA STATE, NIGERIA"**has been performed by me in the Department of Chemistry under the supervision of Prof. E. B. Agbaji, Prof. V. O. Ajibola and Prof. C. E. Gimba. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis has been previously presented for another degree or diploma at this or any other Institution.

Moses SUNDAY	Sign	Date

CERTIFICATION

This thesis entitled **"DETERMINATION OF PHYSICOCHEMICAL PROPERTIES AND HEAVY METAL CONTENTS IN WATER, SEDIMENT AND FISH IN WATER AND FOOD CROPS IN, ZAMFARA STATE, NIGERIA"** by Moses SUNDAY meets the regulations governing the award of the degree of Doctor of Philosophy (Analytical Chemistry) of Ahmadu Bello University Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

TO

My parents: Eld. and Mrs. Sunday Akamo

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ABBREVIATION

AAS	**Atomic Absorption Spectrometry**
ANOVA	**Analysis of Variance**
AR	**Analytical Reagent**
ATSDR	**Agency for Toxic Substances and Diseases Registry**
CF	**Contamination Factor**
FAO	**Food and Agricultural Organisation**
FEPA	**Federal Environmental Protection Agency**
PLI	**Pollution Load Index**
WHO	**World Health Organization**
USEPA	**United State Environmental Protection Agency**
MSF	**Medecins San Frontiers**
SAWQG	**South African Water Quality Guidelines**
CDC	**Centre for Disease Control**
LGA	**Local Government Area**

ABSTRACT

The physicochemical properties of water of the three major dams and rivers in Zamfara State were analyzed using standard analytical methods. The concentrations of heavy metals in the sediments, fish and food crops were also examined. The result revealed marked variations and non-uniform distribution of all the physicochemical parameters from one season to another for two years of study. pH, temperature, EC, TDS, TSS, alkalinity, DO, BOD, COD, Cl, SO_4, PO_4 and hardness have values that fall below the USEPA standard limit for drinking water with exception of turbidity (88.67 mg/l).Analysis of variance revealed that there were significant difference ($P < 0.05$) between the parameters based on locations and seasons. The concentration of heavy metals in the crops (tomatoes and cassava) grown around the vicinity of the dams and rivers determined using atomic absorption spectrometry (AAS) revealed, a spatial and non-uniform distribution in the concentration of the heavy metals (Zn, Cd, Cr, Pb and Hg) in the water, sediments, fish, and food crops in all six locations studied. The concentration of heavy metal determined in water, sediment, fish and food crops were generally high during the dry season with exception of Hg which recorded its highest concentration in year 2015. Zn and Cr levels in the water, sediment, fish and food crops were within international safe limits while Cd (0.1022 mg/l), Pb (0.2104 mg/l) and Hg (1.8818 mg/l) levels were far above (0.01, 0.01 and 0.001mg/l) USEPA safe limits respectively for drinking water. Two major indices such as contamination factor (CF) and pollution load index (PLI) were used for determining the contamination level of water, sediment, tomatoes, cassava and fish samples. The result revealed a high contamination factor for Cd, Pb and Hg across all the six locations and a general overall pollution load across all the locations. The direct effect of heavy metal was observed during the histological assessment of fish tissues such as gills, liver and skin. All gills showed common abnormalities in the Tilapia fish (*Orechromis mossambicus*)inhabited in all the six locations. Most common are desquamation

of lamellar epithelium, hypertrophy of epithelial cells, lifting up of lamellar epithelium, intraepithelial oedema, aneurysm, hyperplasia, and haemorrhage in the gill filament. Histology of liverrevealed the presence of heterogeneous parenchyma characterized by vacuolization, foci of necrosis, hypertrophy ofnuclei and degenerated hepatocytes. Histological changes of the skin were mostly at the level of the epidermis, without major changes in the dermis and hypodermis; picnotic nuclei in the matrix layer of the epidermis are the most severe lesion recorded.

A four step sequential extraction was used to determine the chemical association of the metals (Zn, Cd, Cr, Pb and Hg). Major sedimentary phases in the sediments showed differences in the distribution of each metal among those phases. Of all the five elements studied, Cd (14.739- 39.931%) and Pb (0.105- 9.832%) appeared to be the most readily solubilized, thus making these elements the most potentially bioavailable.The evidence of pathological alterations in gills, livers and skin of *Orechromis mossambicus* appeared to be a useful bio-marker to assess the impact of metal pollution in water on the health of fish and higher levels of Cr, Cd, Zn, Pb and Hg in the fish are worrying as it may cause health related problems in the consumers of fish in the study area.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Environmental pollution by toxic heavy metals does not only elicit concern in the metropolitan cities but also in remote and rural communities where anthropogenic activities are taking place. Contamination of the environment usually result from industrial activities, such as mining, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticides application, and generation of municipal waste (Olaofe*et al*, 2004). Gold mining and processing have been the main sources of heavy metal contamination in the environment (Duruibe *et al*., 2007; Boamponsem *et al*., 2010; Girigisu *et al*., 2012). The uncontrolled dissemination of waste effluents to large water bodies has negatively affected both water quality and aquatic life (Abdulrahman*et al*., 2008). During the processing of the ores for gold, poisonous substances such as oxides and sulphides of heavy metals are released into the environment (Boamponsem *et al*., 2010).Hence**,** most of the water sources, particularly in Zamfara State, are gradually becoming polluted due to the addition of these foreign materials from the enviroment.

Food and Agricultural Organization (FAO) of U.S.A revealed that in African countries, particularly Nigeria, water related diseases had been interfering with basic human development (FAO, 2007).Different aquatic organisms often respond to external contamination in different ways, where the quantity and form of the element in water, sediment, or food will determine the degree of accumulation (Abdulrahman*et al*., 2008; Olaoye and Onilude (2009).Certain environmental conditions such as salinity, pH, and water hardness can play an important factor in heavy metals accumulationup to toxic concentrations in living organisms and cause ecological damage (Garba *et al*., 2010). Thus, heavy metals

acquired through the food chain as a result of pollution are potential chemical hazards that threaten consumers (Olaofe *et al*., 2004).

A study by Umeh *et al.* (2004) revealed that 48% of the people in Katsina-Ala Local Government Area of Benue State are affected by urinary *Schistosomiasis*, due to increase in water pollution. Garba *et al*. (2010) reported a mean arsenic concentration of 0.34 mg/l in drinking water from hand dug wells, boreholes and taps of Karaye Logal Government Area, Kano state. The arsenic levels are of serious concern to regulatory agencies because they by far exceed the upper band of 0.01 mg/l recommended by WHO (2008). Nwidu *et al*.(2009) reported that quality of water and prevalent water related diseases in hospitals were casually related to contamination of rivers.

1.2Statement of the Research Problem

The government of Zamfara State constructed dams in order to provide good water for the teaming population. However, the dream thatthese dams would provide clean and safe water in the State is being threatened by metal pollutants and carcinogenic organic compounds. There have been gold mining activities in Zamfara State, northern Nigeria, for decades, but it was not widespread or profitable until 2009 (MSF, 2012). In March-April 2010, Médecins Sans Frontières (MSF) informed the Zamfara state Ministry of Health of an increasing number of childhood deaths and illnesses in seven villages of Anka and Bukkuyum LGAs.

From the time the Lead poisoning incidence was reported to the state authority:

It has been estimated that at least 10,000 people of whom 2,000 are children under 5 years of agefrom the seven villages in the State are in acute danger of death or severe illnesses.

There is also an increasingly active artisanal mining industry, which digs up rocks by hand, breaks them into pebbles with hammers, grinds the pebbles to sand with flour mills, and

extracts gold from the sand using sluicing, panning, and Mercury amalgamation and in some cases, cyanidation (MSF, 2012).

In theState, gold bearing deposits contain problematic concentrations of lead;hence mining activities leads to the release of lead.

The crushing of pebbles into sand in dry-running flour mills produces enormous amounts of dust which sometimes containshigh amount of lead. Lead can enter the body through the lungs or the digestive tract (MSF, 2012).

1.3Justification of the Study

In March 2010, an unusually high number of deaths, primarily among children under age 5 in Bukkuyum and Anka Local Government Areas (LGAs) of Zamfara State, was reported by Médecins Sans Frontières (MSF). Field work by MSF focused on five villages in Anka (LGA), which are Abare, Sunke, Kirsa, Baggega and Dareta. From the five villages investigated, four had been confirmed as lead contaminated and only one was remediated (Dareta). Further study by *Roddiger et al*.(2010) on blood samples taken from the people revealed that the increased mortality was as a result of acute lead poisoning, determined to be caused by massive environmental contamination from artisanal mining and processing of gold found in lead-rich ore. The grinding of the ore into fine particles resulted in extensive dispersal of lead dust in the villages concerned, including within family compounds. Ingestion and inhalation of the fine lead particles was determined to be the major reason for high blood lead levels in victims' bodies (MSF report, 2010).

A personal survey of these villages found that livestock were drinking from contaminated ponds, rivers, and crops were found to be growing in contaminated soil near affected wells, ponds and rivers. Therefore, until complete remediation of polluted villages take place, and as long as gold/ore processing continue in sensitive areas – home compounds and villages, wells, ponds and rivers used for drinking water by humans and livestocks

remain in continuing health risk. Hence, it is essential that a thorough assessment on quality parameters of water from rivers and dams in the State be carried out.

1.4 Aim

The aim of the research was to determine physicochemical properties of water and heavy metal concentration in water, sediment, and fish (*Oreochromis mossambicus)*from the three major dams (Gusau, Bakolori and Dangulbi dams), and three selected rivers in Anka LGA (Bagega, Sunke and Abare) as well as food crops (tomatoes and cassava) from the surroundings in Zamfara State.

1.5 Objectives of the Study

The aim of the research work will be achieved through the following specific objectives:

(i) Determination of physico-chemical parameters (pH, temperature, conductivity, total dissolved solids, total suspended solid, alkalinity, hardness, dissolved oxygen, chloride, turbidity, sulphate, phosphate, chemical oxygen demand and biochemical oxygen) of the water from the dams and rivers.

(ii) Microbiological assessment (Total Bacterial and Coliform Count) of water from dams and rivers will be determined.

(iii) Determination of the concentrations of Pb, Hg, Cd, Zn, Cr in water, sediment, fish and food crops (cassava, and tomatoes) samples that are commonly found in and around all the three dams and rivers.

(iv) Sequential extraction of the metals in the sediments from the dams and rivers will be determined.

(v) Proximate composition and histopthalogical analysis of the fish will also be determined.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Quality Parameters

2.1.1 pH

pH measures the level of acidity or alkalinity of the water sample. The pH is indicated by the concentration of hydrogen ion present (Edward, 1980). It is expressed on a scale of 0-14 where 7 is neutral, below 7 is acidic and above 7 is basic. Practically, every phase of water treatment such as softening, precipitation, coagulation, disinfection and corrosion are pH dependent (ALPHA, 1999). Natural water has pH values in the range 4 to 9 and most are slightly basic due to the presence of bicarbonate and carbonates of alkali and alkaline earth metals (ALPHA, 1999). High or low pH values in a river have been reported to affect aquatic life and alter toxicity of other pollutant in one form or the other (DWAF, 1996c). Low pH values in a river for examples impair recreational uses of water and effect aquatic life. A decrease in pH values could also decrease the solubility of certain essential element such as selenium, while at the same time low pH increases the solubility of many other element such as Al, B, Cu, Cd, Hg, Mn and Fe (DWAF, 1996c).

2.1.2 Temperature

The temperature of water is not the main issue when considering it as physical parameter, butits effect on other properties e.g. changing solubility of gases.Water temperature may cause the differences in metal deposition in various organs. Higher temperatures promote accumulation of cadmium especially in the most burdened organs: kidneys and liver (Yang and Chen, 1996). Increased accumulation of metals by fish at higher temperatures probably results from higher metabolic rate, including higher rate of metal uptake and binding.Cool water is generally more palatable than warm water, and temperature will impact on the acceptability of a number of other inorganic constituents and chemical

contaminants that may affect taste. High water temperature enhances the growth of microorganisms and may increase taste, odour, colour and corrosion problems (WHO, 2008). The effect of temperature, and especially changes in temperature, on living organisms can be critical. Temperature controls the solubility of gases in water, and the reaction rate of chemicals, the toxicity of ammonia, and of chemotherapeutics to fish. Temperature is the most important physical variable affecting the metabolic rate of fish and is therefore one of the most important water quality attributes in aquaculture (WHO, 2008).

2.1.3 Electrical conductivity

This is a quantitative measure of the ability of water to conduct electric current. It can also be defined as a numerical expression of the ability of an aqueous solution to carry an electric current (ASTM, 2004). Electrical conductivity is influenced by the presence of dissolved salts such as sodium chloride and potassium chloride which produce ion that migrate in solution and then generate electric current.Conductivity does not have direct impact on human health. It is determined for several purposes such as determination of mineralization rate (existence of minerals such as potassium, calcium, and sodium) and estimating the amount of chemical reagents used to treat this water (Kavcar *et al*., 2009; Cidu *et al*., 2011; Muhammad *et al.,* 2011; and Khan *et al*., 2013). High conductivity may lead to lowering the aesthetic value of the water by giving mineral taste to the water. For the industrial and agricultural activity, conductivity of water is critical to monitor. Water with high conductivity may cause corrosion of metal surface of equipment such as boiler. It is also applicable to home appliances such as water heater system and faucets. Food-plant and habitat-forming plant species are also eliminated by excessive conductivity (Khan *et al*., 2013 and Kavcar *et al*., 2009).

2.1.4 Dissolved oxygen

It is a measure of the oxygen content in water. Different life forms in water need oxygen for survival. Water low in dissolved oxygen has an unpleasant smell while waters high in dissolved oxygen are good for drinking purposes(Iqbal *et al*., 2004). Several factors determine the DO levels in water including water temperature, which has inverse relationship with DO, photosynthesis by green algae, salinity and pollution resulting from both natural and anthropogenic activities (Iqbal *et al*., 2004; IEPA, 2001). Organic wastes and other nutrient inputs from sewage and industrial discharges, agricultural and urban runoff can result in decreased oxygen levels. Nutrient input often leads to excessive algal growth; when the algae die, the organic matter is decomposed by bacteria, a process which consumes a great deal of oxygen that could lead to oxygen sag (Aiyesanmi *et al*., 2006). A high DO level in a community water supply is good because it makes drinking water taste better. However, high DO levels speed up corrosion in water pipes.

2.1.5 Biological oxygen demand

It is the amount of oxygen used by microorganism per unit volume of water at a given time. Biological oxygen demand (BOD) measure the amount of oxygen requires by bacteria for breaking down to simpler substances the decomposable organic matter present in any water,

Waste-water or treated effluent. It is also taken as a measure of the concentration of organic matter present in any water. The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD values (Ademoroti, 1996).Natural sources of organic matter include plant decay and leaf fall. However, plant growth and decay may be unnaturally accelerated when nutrients and sunlight are overly abundant due to human influence. If there is a large quantity of organic waste in the water supply, there will also be a lot of bacteria present working to decompose this waste (Keith *et al*., 1997). Oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need

to live. In this case, the demand for oxygen will be high (due to all the bacteria) so the BOD level will be high. As the waste is consumed or dispersed through the water, BOD levels will begin to decline. When BOD levels are high, dissolved oxygen (DO) levels decrease because the bacteria are consuming the oxygen that is available in the water. Since less dissolved oxygen is available in the water, fish and other aquatic organisms may not survive.

2.1.6 Chemical oxygen demand

The chemical oxygen demand (COD) is the amount of oxygen consumed to completely chemically oxidize the organic water constituents to inorganic end products. COD is an important, rapidly measured variable for the approximate determination of the organic matter content of water samples. Some water samples may contain substances that are difficult to oxidize (Harrafi *et al*, 2012).

2.1.7 Chlorine

The chloride content in water is another important factor for water quality analysis (Ademorati, 1996). Excess chlorides in water are usually taken as index of pollution. The mining, sewage water and industrial effluents are rich in chloride and hence the discharge of these wastes result in high chloride level in the rivers (Hasalam, 1991).Chloride is a ubiquitous aqueous anion in all natural waters, the concentrations varying very widely and reaching a maximum in sea water. Natural levels in rivers and other fresh waters are usually in the range 15 - 35 mg/L Cl^- and much below the permissible drinking water standard of < 250 mg/L (IEPA, 2001; USEPA, 2002; EUDWS, 1998; WHO, 2003). Chloride has little effect on fish health or behaviour and is not considered a problem in inland waters (SAWQG, 1996).

2.1.8 Alkalinity

The presence of hydroxides, carbonate and bicarbonate in natural water cause alkalinity. Alkalinity is defined by Ademorati, (1996) as a measure of the ability of water

samples to neutralize strong acids to an arbitrary pH or an indicator end-point.When natural waters contain weak acids, alkalinity is usually determined as well as pH in water quality assessment. Alkalinity, the concentration of bases in water is composed mainly of bicarbonate, carbonate and hydroxyl ions (WHO, 2006). Alkalinity is affected by variations in flow regimes and its natural unevenness is linked to the presence or absence of carbonate rock (Dladla, 2009). The change in alkalinity depends on carbonates and bicarbonates, which in turn depend upon release of CO_2. Change in carbonates and bicarbonates also depend upon release of CO_2 through respiration of living organisms (Verma *et al*., 2013).

2.1.9 Total suspended solid

These are discrete particles that can be measured by filtering thesample through appropriate filters. The magnitude of these solids depends on the typeof filter (paper or sintered glass) used, the pore size, the physical nature and the size of the particles (ASTM, 2004, APHA, 1999). Increase in suspended solids in water is proportional to the increase in the extent of pollution and also account for odour and colour (Golterman, 1978). The materials deposited on the filter are the principal factors affectingseparation of suspended solid from dissolved solid.

2.1.10 Total dissolved solid

Total dissolved solids are due to soluble materials. This refers to the portion of total solid that pass through the filter and is expressed in mg/l (APHA, 1999). Water with high dissolved solid is generally of inferior palatability and may induce an unfavourable physiological reaction in the consumer (ASTM, 2004; APHA, 1999). High concentration of dissolved solid in water is also responsible for hardness, turbidity, odour, taste, colour and alkalinity (ASTM, 2004). The maximum permissible concentration of TDS is 500mg/L in potable water.

2.1.11 Turbidity

Turbidity:is a measure of the loss of transparency of a solution.Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis(Kavcar *et al*., 2009). It is also related to the content of diseases causing organisms in water, which may come from soil runoff. The presence of colloidal solid gives water a cloudy appearance which reduces its transparency.The standard recommended maximum turbidity limit, set by WHO and NDWQS, for drinking water is 5 nephelometric turbidity units (NTU) (Kavcar *et al*., 2009; Cidu *et al*., 2011; Muhammad *et al*., 2011).

2.1.12 Water hardness

Hardness of water is a phenomenon which occurs when soap does not lather easily with water and scales are produced in pipes and boilers/kettles. Hardness is caused by metallic salt (ion) of calcium and magnesium and sometimes iron. These salts are usually in the form of bicarbonate, sulphates and chlorides (ALPHA, 1999). Water hardness could be temporary or permanent. Temporary hardness is caused by dissolved calcium and magnesium bicarbonates. It can be removed by boiling. Permanent hardness is caused by sulphate and chloride of calcium and magnesium and it cannot be removed by boiling but by addition of sodium carbonate or ion exchange methods. Water hardness is usually expressed as $mgl^{-1}CaCO_3$.

2.2 Water Quality Challenges

Several studies have shown that the effects of human activities like agricultural runoffs, sewage and industrial effluents contaminate freshwater resources (Jaji *et al*., 2007; Dladla, 2009; Ogleni and Topal, 2011; Al-Anzi, 2012). The effects of human activities on water quality differ in magnitude from one place to another. Changes in the physical,

chemical, and biological characteristics of water negatively affect both human and ecosystem health (Wagner *et al*., 2013).

2.2.1 Agricultural use of fertilizer and runoff

Agricultural activities around the world contribute significantly to water-pollutant loads (Wagner *et al*., 2013). Agricultural activities are among the most frequently cited sources for degradation and pollution of fresh water systems (Mustapha *et al*., 2013). Hoff (2013) carried a study to establish the source and magnitude of pollution in Kranji Reservoir in Singapore. The report findings indicated that there were high levels for nutrients and bacterial concentration in the downstream from an intensive cropping vegetable production operation and it is a major contributor to non-point source of pollution in the reservoir. Nyakungu *et al*. (2013) investigated the impacts of human activities along Manyame River and its tributaries (Mukuvisi, Marimba, Ruwa and Nyatsime rivers) in Zimbabwe. The report established that the contamination is associated with agricultural activities among other sources.

2.2.2 Environmental impacts of Mining activities

Artisan mining is an important economic sector in many developing countries. However, limited resources and training, and the availability of cheap, but potentially hazardous methods of extraction and processing of minerals can cause significant threats to both miners and the local environment (Bitala, 2008; Armah *et al*., 2010). Such a scenario is being experienced in mining locations in Zamfara State.During peak mining periods, up to 5000 people invade the mining areas from outside the State. This has devastating effects on health and environment. Surface waters in the proximity to mining industries are at a great risk of contamination due to waste discharges from mining activities (UNEP, 2010). Mining industries require different amounts of water based on their operations. The end products of mines come with lot of wastewater that end up being discharged into open water courses

(Johnston *et al*., 2008; Caruso *et al*., 2012) investigated the impacts of mining on water quality in the Caucasus Mountains in Georgia. Concentrations of manganese, iron and nickel were detected from public water supplies. High concentrations of Iron and manganese were detected on rivers downstream the mining industrial discharges. Nganje *et al*. (2010) studied the influence of mine drainage on water quality along river Nyaba in Nigeria. Results showed that the river water quality was polluted due to the presence of heavy metals such as manganese, nickel and chromium whose values were above WHO maximum permissible limits.

2.3Heavy Metal Toxicity

Artisan gold mining is a dangerous activity as the heavy metals, mainly Hg, Pb, Cd and As are released to the environment. According to the United States Agency for Toxic Substances and Disease Registry (ATSDR, 1999) As, Pb and Hg top the priority list of hazardous substances. The first two are major metals in gold-sulphide deposits, where they occur as minerals mainly in arsenopyrite (FeAsS) and galena (PbS), respectively. Under natural conditions, they are relatively stable. However, once mining has taken place, the minerals are broken down due to exposure to oxygen and water(Harada *et al*., 1997).Mercury as a pollutant in artisan mining is due mainly to gold processing, when mercury is used to amalgamate gold. Cadmium, which is another common toxic metal, occupying position seven in the priority list of hazardous substances (ATSDR, 1999), generally occurs as an isometric trace element in sphalerite. Cadmium levels are likely to be quite low. The main problem for identification of heavy metal poisoning is that typical symptoms of poisoning are often masked by microbial and parasitic infections, malnutrition and poor living conditions and medical care (Harada, 1997).

2.4 Heavy Metals and their Sources

Heavy metals are conventionally defined as elements with metallic properties and an atomic number >20(ATSDR, 1999). The most common heavy metal contaminants are Cd, Cr, Cu, Hg, Pb, Zn and As. Metals are natural components in soil (Lasat, 2000). Some of these metals are micronutrients necessary for plant growth, such as Zn, Cu, Mn, Ni, and Co, while others have unknown biological function, such as Cd, Pb, and Hg (Gaur *et al*., 2004). Metal pollution has harmful effect on biological systems and are non-biodegradable. Toxic heavy metals such as Pb, Co, Cd can be differentiated from other pollutants, since they cannot be biodegraded but can be accumulated in living organisms, thus causing various diseases and disorders even in relatively lower concentrations (Pehlivan *et al*., 2009).

2.4.1 Cadmium

Cadmium is widely distributed in the Earth's Crust at an average concentration of about 0.1mg/kg and is commonly found in association with zinc (Cole *et al*., 1999). The atmospheric fall-out of cadmium to fresh and marine waters also represents a major input of cadmium at the global level (Nriagu and Pacyna, 1988). Cadmium is produced as a byproduct of zinc and lead refining. Cadmium has chemical similarity to zinc, an essential micronutrient for plants, animals and humans. Cadmium is bio-persistent but has few toxicological properties and once absorbed by an organism, remains resident for many years (Cole *et al*., 1999). The significant use of cadmium is in nickel/cadmium batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Cd is known to be toxic even at low concentrations and is also regarded as a probable carcinogen. Severe exposure to Cd may result in pulmonary effects such as bronchiolitis, emphysema, and alveolitis (Kabata, 2011). Cd can also result in bone fracture, kidney dysfunction, hypertension and even cancer (Cao *et al*.,

2010). Arthritis, diabetes, anaemia, cardiovascular disease, cirrhosis, reduced fertility, headaches and strokes are some of its odd long term effects.

2.4.2 Chromium

Chromium occurs ubiquitously in nature with natural levels in uncontaminated waters ranging from fractions of microgram to a few 1 micrograms per little. Sea water contain less than 1µg/l of chromium (USEPA, 2003), but the exact chemical forms in which chromium is present in the oceans and surface water is unclear. Theoretically, chromium can persist in the hexavalent state Cr (VI) in water with low organic matter content. In the trivalent form Cr (III), chromium will form insoluble compounds at the natural pH of water, unless protected by complex formation. Regulations are currently being implemented worldwide to decrease the use of antifouling treatments to prevent the leakage of various metals into the marine environment (Mance *et al*., 1984). Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. Breathing high levels of chromium (VI) may cause asthma and shortness of breath. Long term exposure may cause damage to the liver and kidneys (Ogwuegbu, 2005).Mance *et al*. (1984) reviewed data on the toxicity of chromium to saltwater organisms. The authors reported acute toxicity to be variable. Fish appeared to be considerably less sensitive than invertebrates, although the data on fish larvae indicated that these forms were sensitive to chromium contamination.

2.4.3 Lead

Lead occurs as galena and is associated with gold mineralization, thus during ore crushing and panning lead is released into the environment. It eventually finds its way into the sediments and surface and underground water. Lead does not dissolve, but water, air and sunlight change its minerals and compounds (Kabata- Pendics, 2011). It sticks to soil particles and enters underground water or drinking water only if the water is acidic or soft. Exposure to Pb takes place mostly through drinking water, breathing polluted air or dust, and

eating contaminated food, for example, food grown on soil with high Pb content (Khan *et al*., 2013). Pb is regarded as a human mutagen and probable carcinogen (Ogwuegbu, 2005). It induces renal tumours, and also disturbs the normal functioning of kidneys, joints, reproductive systems (Khan *et al*., 2013). Lead is toxic even at very low levels of exposure. Even the lowest doses can impair the nervous system and affect foetus, infants and young children, resulting in lowering of IQ (UN, 1993). It may also cause cancer and, thus is classified as a possible human carcinogen. Low level Pb exposure leads to encephalopathy, inschaemic heart disease, abnormalities in children, testicular atrophy, anaemia and interstitial nephritis (UN, 1993). In the US, the Environmental Protection Agency (USEPA, 2003) requires that Pb in air should not exceed $1.5\mu gm^{-3}$ and the amount in drinking water is limited to $15\mu gL^{-1}$ (ATSDR, 1993).

2.4.4 Mercury

Mercury exists in both inorganic and organic compounds. Methylation of inorganic mercury into organic mercury occurs in micro-organisms under anaerobic conditions, for example, in underwater sediments. Organic mercury is highly poisonous and is easily absorbed by the gastric and intestinal organs, and it is carried by blood into the brain, liver, kidney and even foetus (Cao *et al*., 2010). For centuries, mercury has been used in the amalgamation of gold (Au). It is estimated that about 1.32 kg of Hg is lost for every 1kg of Au produced (Harada, 1997). About 40% of this loss occurs during the initial concentration and amalgamation stage of Au. The lost Hg is released directly into the soil, streams and rivers, initially as inorganic Hg, which later converts into organic Hg. This is then taken up into the food chain, mainly by fish and other aquatic life (Cao *et al*., 2010). The remaining 60% Hg is released directly into the air when the Hg–Au amalgam is heated during the purification process and is often inhaled. Mercury is a very volatile element, thus dangerous

levels are readily obtained in air. Safety standards require that Hg vapour should not exceed $0.1 mgm^{-3}$ in air (Kabata-Pendics, 2011).

Mercury, once taken in, is accumulated into the human body and attacks the central nervous system, resulting in numbness and unsteadiness in the legs and hands, awkward movements, tiredness, ringing in the ears, narrowing of the field of vision, loss of hearing, slurred speech, loss of sense of smell and taste and forgetfulness (Podsiki, 2008). Mercury poisoning may lead to a disease known as Minamata. (UN, 1993). It was caused by eating large quantities of fish or shellfish, contaminated by industrial discharges of mercury compounds into Minamata Bay. Harada (1997) noted that 200 mgL^{-1} of Hg in blood and 50 mgg^{-1} in hair are the provisionally established standards and anyone with higher concentrations is considered to be at risk of poisoning. The allowable level of methyl-mercury in fish is 0.3 $mgkg^{-1}$. The acute ingestion of inorganic Hg potentially causes gastrointestinal disorders, diarrhoea, and haemorrhage (Podsiki, 2008). Repeated and prolonged exposure may seriously affect the kidneys, liver and skin.

2.4.5 Zinc

Water is polluted with zinc, due to the presence of large quantities present in wastewater of industrial plants. Zinc may also increase the acidity of waters. Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to bio magnify up the food chain. Water-soluble zinc compounds that are in soils can contaminate groundwater (Bowen, 1979). Excessive intake of Zn and Cu may cause non-carcinogenic effects on human health, even though they are essential to human life (Nolan, 2003). Zn may cause impairment of growth and reproduction (Winde *et al*., 2010).

2.5 Indicators for Heavy Metal Pollution in Aquatic Environment

The pollution of coastal or estuarine areas by trace metals can be studied by the analysis of trace metals in water, food crops, sediments and organism in the aquatic environment (Adeyeye, 1993; Ipinmoroti and Oshodi, 1993).

2.5.1 Fish

Fish assimilate metals from food and the surrounding water. The uptake of metals from solution may occur across the body surface particularly the gills or across the gastro-intestinal wall after drinking(Ipinmoroti and Oshodi, 1993). Fishes are considerably territorial and are therefore representative of the environment in which they are sampled. Fish has been used as an indicator organism for heavy metal pollution especially Pb and their possible unfitness for human consumption from a toxicological point of view (Adeyeye, 1993;Wildianarko *et al.*, 2000; Rashed, 2001; Van der Oost *et al.*, 2003).

Histopatholoigcal changes in animals tissues are powerful indicators of prior exposure to environment stressors and are net result of adverse biochemical and physiological changes in an organism **(**Malik *et al*., 2012). For filed assessment behavioral studies, histopathology is often the easiest method of assessing both short and long term toxic effects. Histopatholoigcal biomarkers can be indicators of the effects on organisms of various anthropogenic pollutants and are a reflection of the overall health of the entire population in the ecosystem. Well-documented lesions based on experimental data in liver, kidney, gill, ovary, skeleton system and skin have been used as biomarkers (Reddy *et al*., 2010; Butchiram et al., 2013; Akpolih, 2013).Therefore, histopathology is the gold standard when defining toxicological effects and its evaluation remains an important part of the assessment of the adverse effects of xenobiotics on the whole organism.

2.5.2 Water

Several workers have reported the use of water as an indicator for metal pollution of oceans, coastal areas, estuaries, rivers, and lakes (Chang *et al*., 2009; Garba *et al*., 2010; Olaoye *et al*., 2009).The values or concentrations attributed to water quality parameters can be used to describe the pollution status of the source, its biotic status or to predict the likelihood or otherwise of particular organisms being present (SAWQG, 1996; Aiyesanmi *et al*., 2006). The menace of water-borne diseases and epidemics still looms large on the horizon of developing countries as a result of lack of accessibility to good quality water (Packham, 1996; WHO, 2002). Polluted water has been the cause of all such cases, in which the major sources of pollution are domestic and municipal wastes from urban and industrial activities and runoff from farmland (Apina, 1999; Baig *et al*., 2010).

2.5.3 Sediments

Sediments are significant in the assessment of the quality of aquatic systems. This is due to the fact that natural fresh water lakes have been the centers of important cultural developments since the earliest days of civilizations. Sediments act both as historical records of man's effects on the marine environment, particularly the effect of intense biological and chemical activity the sediment-water interface and as a wealth of mineral resources. Sediment is extremely important in the aquatic environment since they can act as trace element "trap" (Guerozoin *et al.,* 1990) and have thus been used in assessing metal pollution in aquatic environments by many research workers (Kakulu and Osibanjo, 1988; Guerozoin *et al.,* 1990; Asaolu *et al.,* 1997; Nwajei and Gagophen, 2000).

2.5.4 Food crops

Heavy metals are found naturally in the earth, and become concentrated as a result of human activities such as industrial production, mining, agriculture and transportation (Noor-ul *et al*., 2015; Bassey *et al*., 2014). These metals have positive and negative roles on human life (Noor- *et al*., 2015, Colak *et al*., 2005; Oktem *et al*., 2005). For instance heavy metal

such as copper, chromium, cobalt and zinc are essential micronutrients for higher animals and for plant growth (Manohara *et al*., 2014) Studies have revealed that fruits and leafy vegetables are vulnerable to heavy metal contamination from soil, waste water and air pollution (Manohara *et al*., 2014). Heavy metals such as Cd, Cu, Pb, Cr, Zn, Ni, As, Co and Hg cannot be degraded or destroyed and can be accumulated in living tissue through the food chain, causing various diseases and disorders (Manohara *et al*., 2014). Fruits, vegetables and other foods are among pathways by which heavy metals enter the human tissues leading to deterioration of health (Noor-ul *et al*., 2015).

2.6 Chemical Fractionation of Metals in Sediment

Metals exist in several different forms and are associated with a range of components in soil and sediments. To assess the environmental impact of polluted sediments, information on total metal concentrations alone is not sufficient for an understanding of the environmental behavior of heavy metals present in different chemical form in sediments (Stecko and Bendell –Young, 2000; Bendell – Young *et al*, 2002). Studies on the distribution and separation of heavy metals in sediments can provide not only information on the degree of pollution, but especially the actual environmental impact of metal bioavailability as well as their origin (Rauret *et al*, 1988; Lopez-Gonzales *et al*, 2006). The most labile are metals associated with water soluble ions, exchangeable and carbonate that can be easily remobilized by changes in environmental conditions such as pH, salinity etc. (Perez *et al*, 1991). Metals in reducible fraction can be released in the system only with a pH decrease, and also if sediments change from oxic to anoxic conditions. This may change depending upon the surrounding physical and geochemical conditions (Tessier *et al*., 1979; Wong *et al*., 2007). Metals associated with residual fractions usually form part of the crystalline structure of minerals, remain relatively stable and inert, and they are not easily released into the mobile

and bioavailable phases (Tessier *et al.*, 1979; Lopez Gonzales *et al.*, 2005; Wong *et al.*, 2007).

Therefore, an understanding of the mobility, transport rates, paths and sinks of sedimentary particles and associated contaminants is necessary for predicting both the fate of substances that have been introduced into the rivers and any risk associated with their presence.

CHAPTER THREE

3.0 MATERIALS AND METHODS

All the chemicals and reagents used were of analytical grade (AR). Distilled deionized water was used throughout the research work.

3.1 Description of the Sampling Area

Zamfara State is located in the North Western Zone of Nigeria between Latitude 11^0 40′ E and Longitudes 70^0 25′ E at an altitude of 420m. The state inherited three major dams from the former Sokoto State in the quest to provide potable water for the teeming population. The dams are located in Gusau LGA (Gusau dam), Maradun LGA (Bakolori dam), and Maru LGA (Dangulbi dam). The dams are considered for investigation as a result of lead poisoning epidemic that struck the State sometimes around year 2010. These dams became very necessary to investigate because mining activities are still going on across the State in which water from the dams are used in the mining processes and more so because livestock are seen drinking from the dams and plants are sited growing around the vicinity of the mining areas (Plate 3.1).Three rivers were selected for investigation following the recommendation of a joint team of US Center for Diseaase control and prevention (CDC), World Health Organization (WHO) and Medecins Sans Frontieres (MSF). The recommendations are:

i. That a thorough contamination assessment be carried out on all the source of water in the local government areas where lead poisoning was reported since their investigations was limited to remediation of home compounds, wells and ponds directly used for the mining activities.

ii. That food pathways be investigated since livestock were sighted drinking from contaminated ponds and rivers used for mining activities. Also food crops grown around the vicinity of the mining areas (MSF, 2010).



Plate 3.1: Mining activities around Farmland

The choice of the selected rivers in Anka was based on the report by MSF that villages such as Abare, Sunke and Bagega are contaminated with lead poisoning coming from extensive gold mining in those villages.

Figures 3.1 – 3.4 shows the map of the sampling dams and rivers.

3.2Sampling and Sample Preservation

A two-liter polythene bottle used for the collection of water sample was thoroughly washed with detergent solution, rinsed with distilled water and then leached with 10% HNO_3 and 1:1 HCI for 48 hours. The bottle was then rinsed with distilled water and allowed to drain to dryness.

3.2.1 Water

The water samples were collected for dry and wet season in the month of February and July respectively by dipping a two litre polythene bottle below the water surface at a depth of one meter. The sample water was collected at three different points, five meters away from each other to form a composite sample. At each sampling locations, the sampling bottles were rinsed three times with the water before collection of the sample. The samples were preserved by acidifying with 2 ml of concentrated HNO_3 in order to achieve a pH of 2 and prevent metal adsorption onto the inner surface of the container(APHA, 2005). All the samples were returned to the laboratory and analysis was carried out immediately.

3.2.2 Sediment

The sediment samples were collected for dry and wet season in the month of February and July respectively. About 1 kg of the sediment samples was collected at three different points in a location, five meters away from each other to form a composite sample. Sediment samples were collected using a plastic spoon by scooping the top layer sediments and then stored in a pre-cleaned 1000ml polyethylene container, labelled and transported to the laboratory for storage in freezers awaiting analysis. Samples were air dried in the laboratory and crumbs found

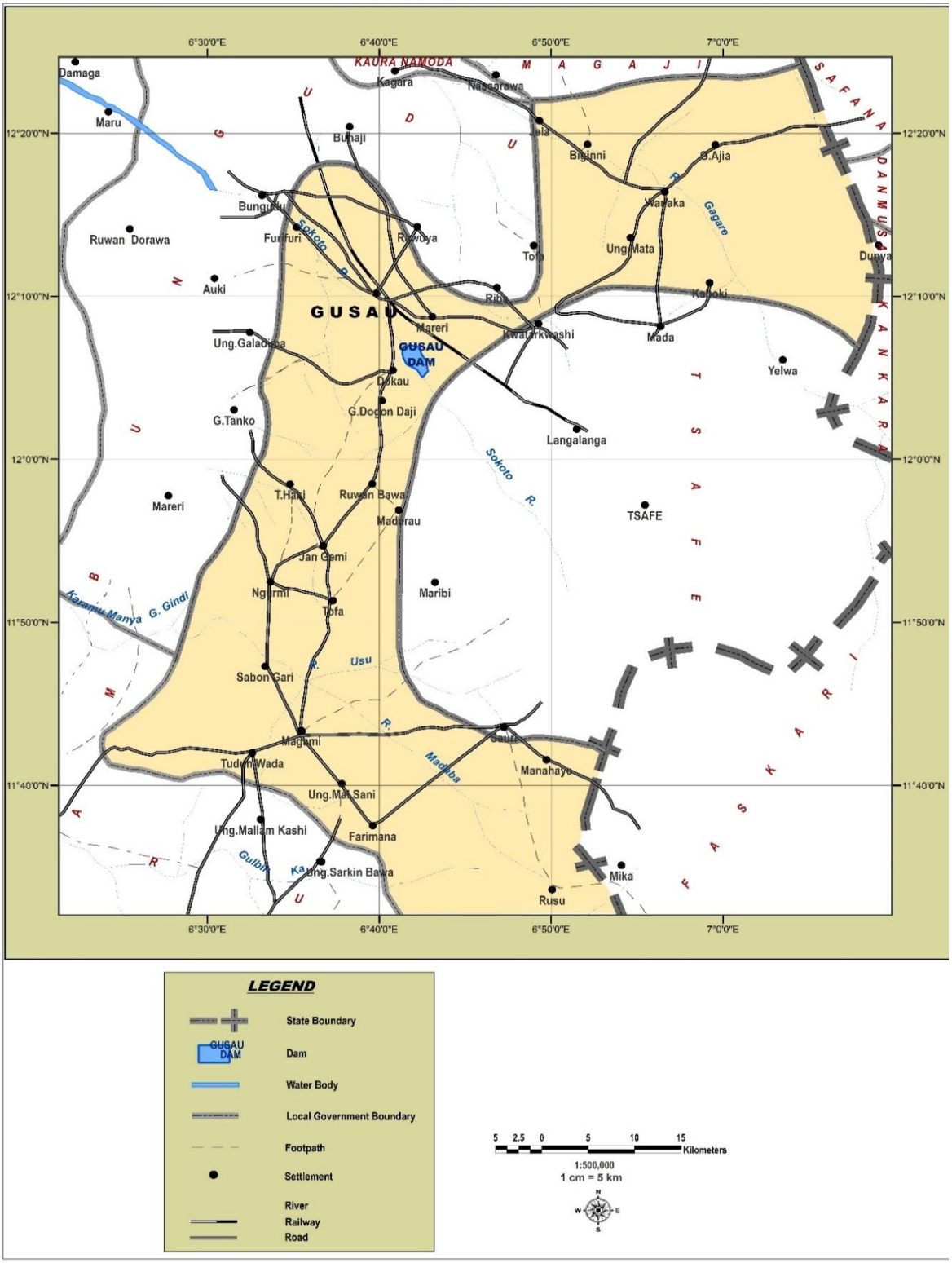


Fig 3.1 Gusau Dam in Gusau LGA Map

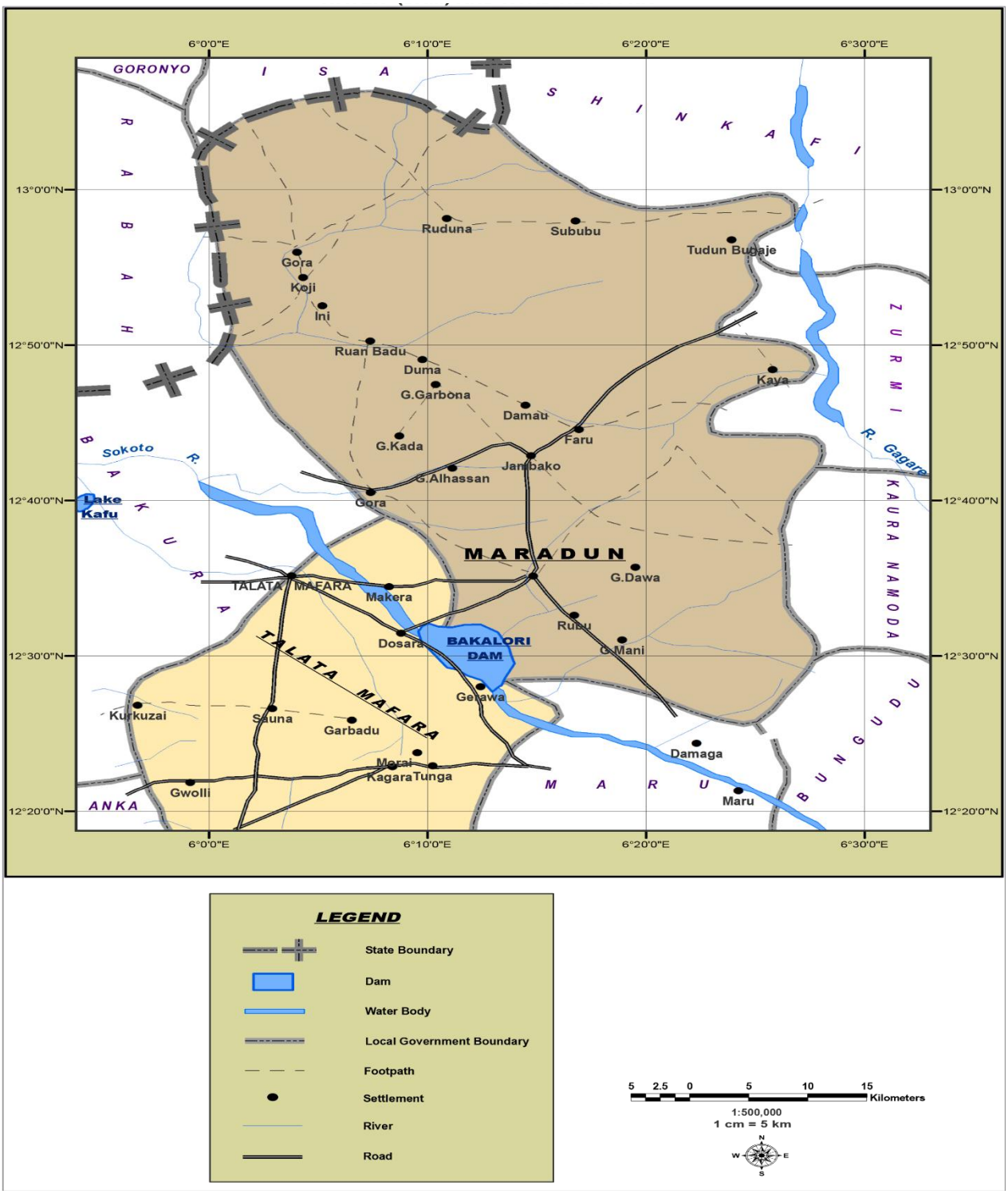


Fig. 3.2: **Bakolori Dam in Maradun LGA Map**



Fig. 3.3: **Dangulbi Dam in Maru LGAMap**

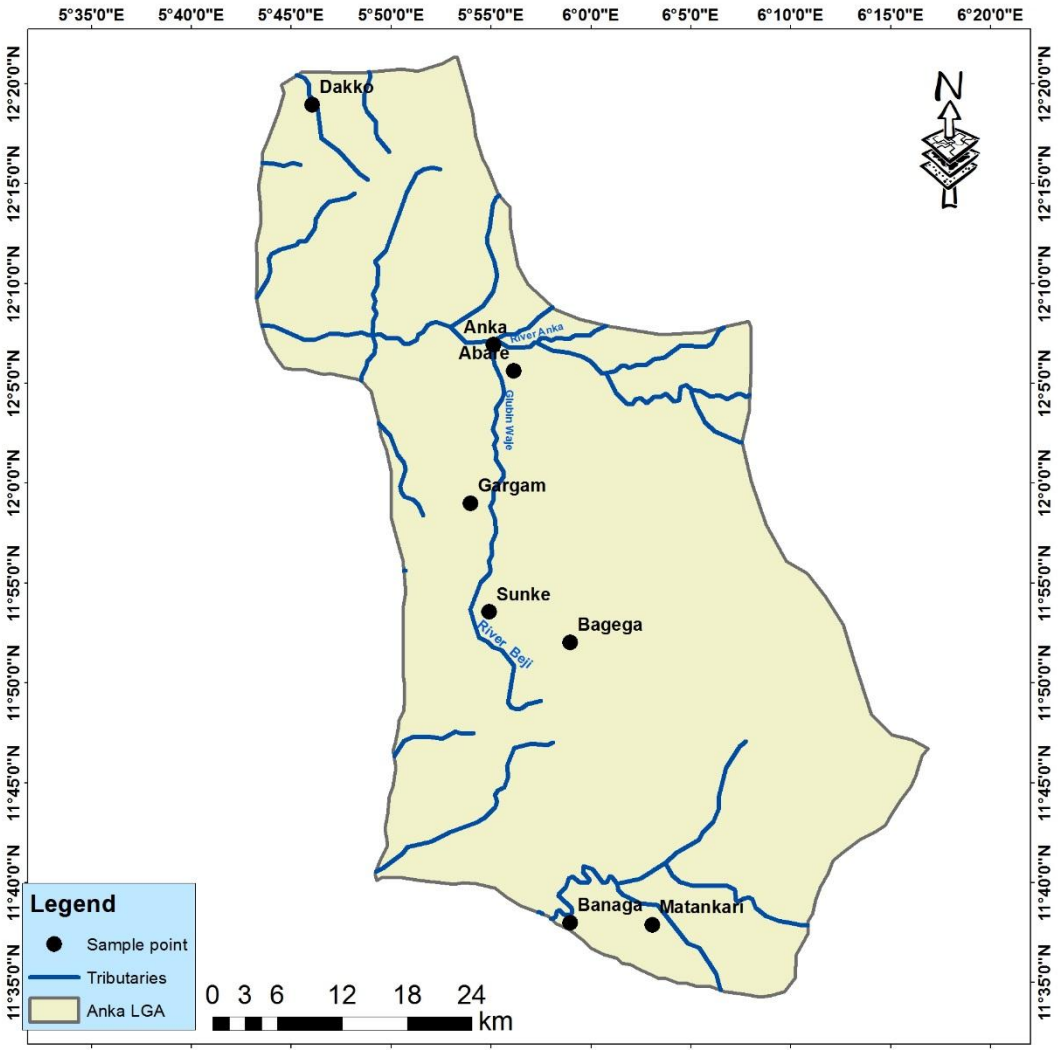


Fig. 3.4: Bagega, Sunke and Abare Rivers in Anka LGA Map

in the sediment were removed. Sediments were also sieved through a 2 mm sieve to remove coarse particles.

3.2.3 Food crops

Two healthy plants samples each of (tomatoes and cassava) were randomly collected from three different points, five meters away from each other on the farmlands in the sampling locations to form composite sample. At each of the sampling locations, about 2 kg each of cassava and tomatoes (fresh weight) samples were collected and thoroughly washed with distilled water to remove surface sand. In the laboratory, the cuticles of the cassava were removed with a stainless steel knife and the edible parts (cortex) were cut into pieces and put into apre-cleaned polyethylene container for refrigeration. The samples were then oven dried at 85 + 1^{o}C to constant weight. The dried samples were grounded into powdery form and labeled.

3.2.4 Fish

Twelve pieces of Tilapia*(Orechromis mossambicus)* fish samples of 28 cm average length and 52 g average weight, three from each of the sixsampling locations was collected by a local fisherman.The fish samples were rinsed with distilled water immediately to remove any adhering contaminants and were stored in a frozen pre-cleaned polythene bags. The fishes were immediately transported to a laboratory where they are dissected and parts removed for histopthalogical analysis and digestion for heavy metal determination.

3.3 Laboratory Analysis

Metals in water, sediment, fish and crop samples were analyzed by Atomic absorption Spectrometry (HG – AAS, ICE 3000AA01122804v1.30 Series).

3.3.1 Water

A well mixedacid preserved water sample of about (100 ml), was transferred into beaker (250 ml). Concentrated HNO_3(5 ml) was added and heated and evaporated on a hot plate until the volume reduced to about 20 ml. Heating and addition of concentrated HNO_3 continued until digestion was completed as indicated by a light colour, clear solution(APHA, 2005). The content was then transferred to pre-cleaned plastic bottle (100ml), cooled and diluted to mark with distilled water. A blank water sample (distilled de-ionized water) was digested as detailed above. Portions of this solution were used for heavy metals determination.

3.3.2 Physicochemical properties

Temperature was measured with the aid of a digital thermometer. Measurements of both the water temperature and the ambient temperature were measured and values recorded in degrees Celsius.

3.3.3 pH, TDS and EC

The pH and total dissolved solids (TDS) and electrical conductivity (EC) of the water samples were measured with HANNA HI 9810 pH-TDS meter. The meter was standardized with a buffer solution (i.e. buffer 7 and 9). The buffer tablet was distilled in water (100ml) in a beaker (250 ml). The probe of the meter was then placed in the solution and adjusted to read 000 to standardize it. The electrode response was checked by measuring the pH of the test sample, first with distilled water and then with the sample. The system was allowed to stabilize before the final reading was made.

3.3.4 Total suspended solids (Gravimetric method)

A known amount of the water sample was filtered through a pre weighed filter paper. The filter paper was then dried between 103˚C and 105˚C(APHA, 1995). TSS was determined by using the following formula:

Calculation

$$\text{Total Suspended Solids (TSS) mg/l} = \frac{(\text{A-B}) \times 10^3}{\text{C}} \qquad 3.1$$

Where A=weight of filter plus solids (g); B=weight of filter (g);

C=volume of sample filtered (ml)

3.3.5 Turbidity Nephelometric method

Procedure

The water sample was gently agitated until air bubbles disappeared from the water sample. About 100 mlof the agitated sample was transferred into a cell and the turbidity was measured directly from the meter display. The turbidity meter (HACH 2100P) was initially calibrated with a turbidity standard reagent before any sample reading was taken. Turbidity was measured in the field with a portable Hach Turbidity Meter (APHA, 1995).

3.3.6 Dissolved oxygen

Reagent:

i. Manganese sulphate solution: $MnSO_4$. H_2O (500 g) was weighed into a beaker (1000 ml) and dissolved using distilled water. The solution was transferred quantitatively into a volumetric flask and made up to 1000 ml mark

ii. Alkaline- iodide solution: NaOH (500 g) was weighed and dissolved in a beaker with of distilled water (500 ml). This solution was cooled and transferred to a plastic bottle and allowed to stand for a few days. KI (150 g) was dissolved with

distilled water in a beaker and the supernatant of the alkali was decanted and mixed with the iodide solution and made up to 100 ml in a volumetric flask.

iii. Starch indicator: Soluble starch (2g) was mixed with boiling distilled water in another beaker. The mixture was boiled for a few minutes, then cooled and then decanted into a reagent bottle**(**APHA, 1995).

Procedure

A glass stopped bottle (300 ml) was filled with sample and stoppered without trapped air. $MnSO_4$ solution (1.0 ml) and alkaline iodide solution (1.0 ml) were added and the bottle stoppered carefully to exclude air bubbles. The bottle was inverted several times to mix content. The formed precipitate was allowed to settle and H_2SO_4 (sp. gr. 1.84, 1.5 ml) was added, re-stoppered and mixed by inverting several timed. An aliquot (25 ml) was titrated with $Na_2S_2O_3.5H_2O$ solution to a colorless end point using starch indicator.

DO was calculated using the expression:

$$\text{DO (mg/L)} = \frac{\text{T cm}^3 \text{ x } 100}{\text{Volume (ml) of aliquot}} \qquad 3.2$$

Where T =volume of titrant used.

3.3.7 Biochemical oxygen demand (BOD_5)

Procedure

A glass stoppered bottle (300 ml) was filled with the sample (25 ml) and distilled water (25 ml) and was stoppered without trapped air(APHA, 2005). The bottle was incubated at 20^{o}C for five days. DO was then determined as in section 3.3.6 above. BOD was calculated using the expression,

$$BOD_5\,(\text{mg/L}) = \frac{D_1 - D_2}{P} \qquad 3.3$$

Where D_1 = DO of diluted sample before incubation; D_2= DO of diluted sample after 5 days of incubation; P= Fraction of sample used

3.3.8 Chemical oxygen demand

Reagent:

i. Standard Poatassium Dichromate reagent (Digestion solution): $K_2Cr_2O_7$ (4.913 g) was added to $HgSO_4$ (33.3 g) and conc. H_2SO_4 (sp. gr. 1.84, 167 ml) into a 1000 ml volumetric flask and when it was cooled to room temperature, water was added to make up to mark.

ii. Sulphuric acid reagent: $AgSO_4$ (5.5 g) was added to 1000 ml volumertric flask and conc. H_2SO_4 (500 ml) was carefully added and allowed to stand for 24 hours.

iii. Standard Ferrous Ammonium Sulphate Solution: Ferrous ammonium sulphate crystals (39.2 g) was dissolved in 1000ml volumetric flask and made up to mark with distilled water.

Procedure

An aliquot (2.5 ml)of the sample was placed in a reflux flask and potassium dichromate reagent (1.5 ml) was added. Thereafter, concentrated sulphuric acid reagent (3.5 ml) was carefully added to the solution mixture to form an acid layer. The flask was capped and inverted several times in order to mix the solution completely. It was then placed on a heating mantle and gently refluxed at 150^0C for 2 hours and was then cooled to room temperature. Thereafter, the solution mixture was titrated against ferrous ammonium sulphate solution using 3 to 4 drops of ferroin indicator. The titration became complete when the colour changed from bluish green to reddish brown (APHA, 2005). Blank solution was also prepared. COD was calculated using the expression,

$$\text{COD (mg/L)} = \frac{(A - B) \times M \times 8 \times 1000}{\text{Sample volume ml}} \qquad 3.4$$

Where A= vol. of ferrous ammonium sulphate solution for blank

B= vol. of ferrous ammonium sulphate solution for sample

M= molar conc. (mol/l) of ferrous ammonium sulphate solution

3.3.9 Total alkalinity (Titration method)

Procedure

Total alkalinity of water, usually due to the bicarbonate, carbonate and hydroxide components was determined by titrating aliquot of the water sample against standard H_2SO_4(0.02 mol/l) using a mixed indicator, bromocresol green-methyl red (APHA, 1995).

An alliquot (100ml) of the water sample was measured into volumetric flask (250ml) after which few drops of the mixed indicator was added. The solution in the volumetric flask was then titrated against solution of sulphuric acid (0.02 mol/l) until the colour change from blue to red. A blank titration was carried out using distilled water (100ml). Total alkalinity (as mg/L $CaCO_3$) was calculated using the average liter value.

$$\text{Total Alkalinity (as mg } CaCO_3\text{/L)} = \frac{\text{Titre (ml) x Molarity X 50.00}}{\text{Volume titrated (ml) X 1}} \qquad 3.5$$

3.3.10 Total water hardness

Accurate titrations were made without the bulk and fragility of conventional burette. The titration body is constructed of precision-moulded, heavy-duty, chemical and impact-resistant acetic plastic. Accuracy is rated at ±1% for a titration of more than 100 digits. Titrating solutions were packaged in disposable polyethylene plastic containers with Teflon covered neoprene seals and polyethylene releasable closures to cover the cartridge. Each cartridge contains approximately 13ml of titrating solution, sufficient for 50 – 100 average titrations.

About (100ml) of the water sample was pipette and transferred into a flask (250ml). Buffer solution (1.0 ml) was added and the flask was swirled for thorough mixing. The content of one manver hardness indicator powder pillow was added to the solution in the flask and swirl for mixing. The solution was titrated with EDTA which showed colour change from red to blue. Total hardness was calculated as:

$$\text{Total hardness} = \frac{\text{Titre x A x 1000}}{\text{Volume of sample}} \qquad 3.6$$

Where A = mg $CaCO_3$ equivalent to 1.00ml of EDTA titrant.

3.3.11 Chloride

Determination of chloride was performed using the titrimetric method of APHA/AWWA/WPCF (1995). A pinch of pure $CaCO_3$ was added to the solution obtained at the end of methyl orange alkalinity determination, so that the red or pink colour vanishes. K_2CO_4(1.5 ml) indicator solution was added and titrated against $AgNO_3$(0.02 mol/l)until a permanent pink tinge persisted in the white precipitate. The whole process was repeated for five times to meet concordant readings. The volume of burette was recorded as V ml. Strength of the chloride ion was calculated using:

$$\text{Strength of Cl ions (mg/L)} = \frac{0.02 \times V \times 35.5 \times 1000}{100} \quad 3.7$$

3.3.12Sulphate

Sulphate in water samples was done using Turbidimetric method: the water sample (100 ml) was measured and transferred quantitatively into Erlenmeyer flask (250 ml). A conditioning reagent (5 ml) was then added and the mixture was thoroughly mixed using a magnetic stirrer. The absorbance was measured and the corresponding SO_4^{2-} concentration determined by extrapolation from the calibration curve(Ademoroti, 1996).

3.3.13 Phosphate

The excessive colour in the sample was removed by shaking (500ml) portion with of activated carbon (0.2g) in an Erlenmeyer flask for 5 minutes. The solution was then filtered. The pH of the sample was between 4 and 10, hence there was no need of pH adjustment. 100ml of sample was measured and transferred into conical flask (250ml). The sample was acidified with H_2SO_4 to methyl orange (pH 3.0 – 4.4), then boiled gently for 90 minutes and cooled. The solution was then neutralized with NaOH (6 mol/l) until phenolphthalein colour in the solution became faint pink tinge. The solution (20 ml) was then pipetted into a volumetric flask (50ml) and vanadate-molybdate reagent (10ml) added and diluted to mark with distilled water. A blank (distilled water) of the same volume with the sample was

substituted for the sample solution. After 10minutes the vanadate-molybdate reagent (10ml) was added, the absorbance of the sample was then determined against the blank at 470nm(Ademoroti, 1996).

Calculation:

$$Mg/l\ PO_4^{3-} = \frac{\text{Reading from curve} \times 1000 \times D}{\text{Sample (ml)}} \quad 3.8$$

Where D = dilution factor.

3.4. Bacteriological Analysis of water

3.4.1 Total bacterial count

The pour plate method was used for the enumeration of total bacterial count of the water samples. Following vigorous agitation from the water in the bottles, ten-fold dilutions (10^1, 10^2 and 10^3) of the samples were made and volumes of 1ml of the appropriate dilutions were introduced into each of the labeled sterile petri dishes. Subsequent to this was the addition of 20ml melted nutrient agar at 45^0C. The Plates while kept flat on the bench were swirled to allow proper mixing of the sample and distribution of bacterial colonies. The plates were then left undisturbed until the agar has set and incubated at 37^0C for 24 hours in an inverted position. Plates having between 30 and 300 colonies were selected for counting and the total plate count was obtained by multiplying the number of colonies counted by the dilution factor. It was recorded in colony forming units per ml (cfu/ml) of the original sample. Bacteriological counts were done in duplicates.

3.4.2 MPN Determination

The standard multiple tube or most probable number (MPN) technique as suggested by APHA (1988) and modified by Olutiola *et al.* (2000) was used. The water sample (100ml) was transferred to presumptive media by using a sterile transfer device. At this point the tubes were incubated inspection for positive reaction followed at 24 and 48 hours. A Durham tube was used to collect gas. The presence of coliforms in the gas positive tube was confirmed by

using brilliant green lactose bile broth. An extent of the confirmed coliform number in 100ml of original sample was determined using Mccrady table.

3.5 Sediment

Approximately (5.0 g) of dried and sieved sediment sample was weighed into a beaker (100 ml). Nitric/perchloric acid (10 ml) in the (2:1) was added to the sample. This sample was then digested at 105 + 1°C. This was followed by the addition of HCl and distilled water (1:1) to the digested sample and the mixture was transferred to the digester again for 30 min. The digestate was then removed from the digester and allowed to cool to room temperature. The content was filtered using Whatman filter paper No. 42, then transferred into 100 ml plastic bottles and diluted to mark. Blank solution was handled as detailed for the samples. Portions of this solution were used for heavy metals determination(Adelakan *et al*., 2011).

3.5.1 Chemical Fractionation of Metals in Sediments

Selected sediments samples were analyzed for chemical partitioning using a five step sequential extraction method described by Tessier *et al*. (1979) and Li *et al*. (1995). The same quality control scheme was adopted in the sequential extraction. The concentrations of Zn, Cr, Cd, and Pb were determined in the four fractions. The sequential extraction was carried out using (1.0g) of powder sample weighed into a glass centrifuge (60 ml) and the following fractions were obtained. The heavy metals in the soluble fraction were determined in the saturation extract of the soil samples.

3.5.1.1 Water soluble fractions

Approximately (1.0 g) of air dried sediment sample was weighed into a polythene container (60 ml); water (10 ml) was added and shaken for 1 hour. The soil coolloids was then centrifuged a Baird and TatLock authobench centrifuging machine at 4000 rpm for 20 min.

The supernatant was decanted and filtered through Whatman No.42 filter paper into a volumetric flask (50 ml), then made up to the mark with water.

3.5.1.2 Exchangeable fraction

To the residual soil sample from F1, (10 ml) of $MgCl_2$(1.0 mol/l)at pH 7 for one hour with continuous agitation using magnetic stirrer.

3.5.1.3 Carbonate –bound fraction

To the residue obtained above. An aliquot (8 ml) sodium acetate (10mol/l) (pH = 5, adjusted with acetic acid) was added. Continuous agitation was maintained for 5 hours.

3.5.1.4 Residual fraction

The residue from above step was digested with a 5:1 mixture of hydrofluoric and per chloric acids. The sediment was first digested in a platinum crucible with a solution of concentrated $HClO_4$ (2ml) and HF (10ml) to near dryness; subsequently a second addition of $HClO_4$ (1ml) and HF (10ml) was made and again the mixture was evaporated to near dryness. Finally, $HClO_4$ (1ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in HCl (12 mol/l) and diluted to 25ml. The resulting solution was then analyzed by flame atomic absorption spectrophotometry for metal using standard addition technique.

3.6 Food Crops

About (1g) of grounded tomatoes and cassava sample was weighed into beaker (100 ml). Concentrated HNO_3 (5 ml) and perchloric acid (2 ml) was added and heated in a fume cupboard to almost dryness. Then, distilled water (10 ml) was added and the solution was properly stirred and filtered with whatman filter paper No. 42. The filtrate of each digestate was then transferred into bottles (50 ml) and made up to mark with distilled water (APHA, 2005). Blank samples were prepared in the same procedure with distilled water.

3.7 Fish

Dry weight fish sample (5 g) was put into a beaker (50 ml) with HNO_3(5 ml) and H_2SO_4(5 ml). When the fish stopped reacting with HNO_3 and H_2SO_4, the beaker was then placed on a hot plate and heated at 60°C for 30 min. After allowing the beaker to cool, HNO_3(10 ml) was added and returned to the hot plate to be heated slowly to 120°C. The temperature was increased to 150°C, and the beaker was removed from the hot plate when the samples turned black. The sample was then allowed to cool before adding H_2O_2(20 ml) until the sample was clear. The content of the beaker was transferred into a volumetric flask (50 ml) and diluted to the mark with distilled water(Tuzen, 2003). All the steps were performed in the fume cupboard.

3.8 Proximate Composition

3.8.1 Moisture content

The moisture content of the fish was determined using an air oven as described by AOAC (1990). A known weight of the fish sample was weighed, as w_1 into a dry petri dish and transferred into oven at a temperature of 105^0C for 6 hours. The petri dish was removed just from the oven and placed in a desiccator. After cooling, it was weighed as w_2, the heating, cooling and weighing were repeated until a constant weight was obtained. The percentage moisture content was calculated as

$$\%\text{Moisture content} = (W_1 - W_2) \times \frac{100}{W_1} \qquad 3.9$$

3.8.2 Ash content

The ash content was determined by using Pearson (1976) method. Weight of the fish sample was weighed, as W_1 into a dry, clean crucible (W_0) and transferred into a muffle furnace. The temperature of the furnace was increased gradually until it reached 550^0C and maintained at 550^0C. The ashing was completed when there was no black speck in the sample. The percentage ash content was calculated as

$$\%\text{Ash Content} = (W_2 - W_0) \times \frac{100}{W_1} \quad 3.10$$

3.8.3 Crude fat content

The fat content was determined using Soxhlet apparatus as described in AOAC (1990). A known weight (W_1) of the fish sample was put into thimble, (the thimble was weighed). The thimble with sample (W_2) was inserted into the Soxhlet apparatus and extraction under reflux was carried out with petroleum ether (40-60^0C) for 5 hours. At the end of extraction, the thimble with its content was dried in an oven for about 30 minutes at 60^0C to evaporate the solvent. The thimble was rapidly transferred and was cooled in a desiccator, the weight of the thimble with its content was determined as (W_3). The fat extracted from a given quantity of the sample was then calculated as:

$$\text{Fat (\%) w/w} = \frac{(W_2 - W_3) \times 100}{W_2 - W_1} \quad 3.11$$

3.8.4 Protein content

The crude protein was determined by using microkjeldahl method as described by Pearson (1976). A known weight of the fish sample was weighed into a long necked Kjedahl flask along with concentrated nitrogen free sulphuric acid (10 ml). The flask was gently swirled and clamped in an inclined position and heated on a Bunsen burner. The heating continued strongly until a clear solution was obtained. The digestion lasted between 3 to 5 hours. The clear hot solution obtained was allowed to cool after which the solution was

diluted with distilled water in a standard flask (100 ml). The distillation of the resulting solution was carried out.

Then 2% boric acid (25 ml) was pipette into a conical flask (100 ml), 2 drops of mixed indicator (screened methyl red) was added and placed at receiving end of the distillation flask. The conical flask was placed in such a way that the delivery tube just touched the boric acid level inside the flask (Pearson, 1976). 40% NaOH solution was used to liberated ammonia outof the digest during the distillation. The liberated ammonia was trapped in the boric acid solution. A blank sample was prepared as described above. The distillate was titrated with a standardized HC1 solution (0.10 mol/l). The Colour changed from blue to golden yellow. The bank solution was titrated as well.

$$\% \text{ Nitrogen} = \frac{\text{Titre Value} \times M \times 0.0014}{\text{Weight of Sample}} \qquad 3.12$$

$$\% \text{ Crude protein} = \% \text{ Nitrogen} \times 6.25$$

3.8.5 Fibre content

The crude fibre content was determined as described by Pearson (1976). A known weight (W_1) of the fish sample was extracted with petroleum ether, after which the extracted sample was air dried and transferred to a dry conical flask. About (200 ml) of H_2SO_4(0.127 mol/l)was added and brought to boiling point. Boiling was carried out for further 30 minutes, maintaining a constant volume and rotating the flask every few minutes in order to mix the content and remove particles from the sides. At the end of the 30 minutes boiling period, the acid mixture was allowed to stand for about 1 minute and immediately poured into a Buchner funnel. The suction was adjusted so that the filtration of the bulk (200 ml) was completed within 10 minutes. The insoluble matter was washed with boiling water until it was free from acid. The insoluble matter was now boiled with (200 ml) of NaOH (0.313 mol/l), this was boiled for 30 minutes, after the alkali digestion, the solution was allowed to stand for 1 minute and then filtered immediately through a filter paper.The insoluble material was

transferred into the filter paper by means of boiling distilled water then with 1% HC1 solution and finally with boiling distilled water until it was free from acid. It was then washed with alcohols two times and three times with ether. The insoluble matter was transferred to a dried, weighed rmined (W_3) and % fibre was calculated as.

$$\text{Fibre content \%} = \frac{(W_2 - W_3)}{W_1} \times 100 \qquad 3.13$$

3.8.6 Carbohydrate content by difference

Carbohydrate content= 100 – (% moisture + ash + % crude protein + % crude fat + % crude fiber). Addition of all of moisture, crude protein, crude fat and crude fiber subtracted from 100% gives the carbohydrate by difference.

3.9 Histopathological Analysis

The gills, skin and liver tissues with a diameter of 5 mm of six fishes, one from each location were fixed in sera (60% ethanol +30% formalin + 10% acetic acid) for about 3-4 hours. The fixed tissues were dehydrated at room temperature, embedded in paraffin, sectioned at 4- 5 mm by using a microtome (MICROM GmbH, Walldorf, Germany) and stained with haematoxylin and eosin (Bernet *et al*., 1999). The stained samples were then examined under a light microscope (Vickers Ltd, England) and photographed by using the Moticam 1000 camera (Motic, China).

3.10 Preparation of Working Solutions for AAS

Stock solutions for the determination of heavy metals were prepared from high purity standard solutions and appropriate volumes were diluted to obtain solution used to plot the calibration curves (Appendix LXX – LXXIII). Calibration standard for each of the metals were prepared to give concentration within the linear range of the metal. Dilution formula C1V1 = C2V2 was used to calibrate the required calibration standard concentration. Where C1 and C2 are concentrations of the stock and calibration standards respectively. V1 and V2

are the volume of stock standard required to make the desired concentration C2 of given volume (V2) of the calibration standard. The preparations were as follows:

3.10.1 Lead solution

The working standards were prepared by diluting 0.2, 0.4, 0.6, 0.8, and 1.0 mlof stock solution with distilled water in a volumetric flask(100 ml) to give 2.0, 4.0, 6.0, 8.0 and 10.0mg/l respectively.

3.10.2 Cadmium solution

The working standards were prepared by first diluting 1 ml of the stock solution appropriately to give solution of cadmium (10 mg/ml). From this solution 0.2, 4.0, 0.6, 0.8 and 1.0 mlwere taken in to different volumetric flasks (100 ml) and diluted to mark with distilled water to give 0.02, 0.04, 0.06, 0.08, 0.1 mg/l solutions of cadmium respectively.

3.10.3 Chromium solution

The working standards were prepared by diluting 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the stock solutions in volumetric flasks (100 ml) and made to mark with distilled water to give 2.0, 4.0, 6.0, 8.0 and 10.0 mg/l of Cr respectively.

3.10.4 Zinc solution

Working standards of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2mg/l were prepared by diluting 0.2, 0.4, 0.6, 0.8 1.0 and 1.2 ml in a volumetric flask (100 ml) respectively.

3.10.5 Mercury solution:

Aliquort 10 ml of the stock solution was diluted with 90 ml of distilled water in a volumetric flask to give 100mg/L. the working standards were prepared by diluting 0.5, 1.0, 1.5, 2.0 and 2.5 ml involumetric flask (100 ml) to give 0.5, 1.0, 1.5, 2.0 and 2.5 mg/l respectively.

3.10.6 Preparation of stock solution

I. Cadmium solution: was prepared by dissolving $Cd(NO_3)_2.4H_2O$ (0.274g) in concentrated HNO_3(5 ml). The Solution was made up to 1 litre with distilled deionized water in a volumetric flask giving 1000 mg/L

II. Lead solution: This was prepared by dissolving $Pb(NO_3)_2$ (1.5985 g) in distilled deionized water and making up to 1 litre giving 1000mg/L

III. Zinc solution: This was prepared by dissolving ZnO (1.2444g) in water (5 ml) adding concentrated HNO_3 (25 ml) and making up to 1 litre with distilled deionized water giving 1000mg/L

IV. Mercury solution: It was prepared by dissolving $HgCl_2$ (0.068g) in concentrated HNO_3(5 ml). The solution was made up to 500 ml with distilled deionized water in a volumetric flask giving 100mg/L

V. Chromium solution: This was prepared by dissolving $K_2Cr_2O_7$ (2.828g) in distilled deionized water and making up to 1 litre giving 1000mg/L

3.11 Validation of Analytical Method

Determination of a certified reference material is a common means of establishing accuracy of a routine analytical method. This followed quality control procedures established by Glier (1996).A quadruple set of certified reference standard solution of each metal to be analyzed was run. A certified reference standard was purchased as follows:

i. PL01050100: Lead (II) nitrate in nitric acid(250 ml) with concentration of 5.0 mol/L

ii. ME01110500: Mercury (II) nitrate monohydrate in nitric acid (250 ml) with concentration of 5.0 mol/L

iii. ZI01260500: Zinc nitrate in nitric acid (250 ml) with concentration of 5.0 mol/l

iv. CR02220500: Chromium (III) nitrate in nitric acid (250ml) with concentration of 5.0 mol/L

v. CA00410500: Cadmium (II) nitrate in nitric acid(250 ml) with concentration of 5.0 mol/L

Preparations:

i. Solution of lead (4.0 ml) was pipetted from the 250 ml standard reference stock into a volumetric flask (50 ml) and made up to the mark with distilled water to prepare 0.4 mol/l lead stand solution.

ii. Solution of zinc (4.0 ml) was pipetted from the 250 ml standard reference stock into a volumetric flask (50 ml) and made up to the mark with distilled water to prepare 0.4 mol/l zinc standard solution

iii. Solution of cadmium (6.0 ml) was pipetted from the 250 ml standard reference stock into a volumetric flask (50 ml) and made up to the mark with distilled water to prepare 0.6 mol/L cadmium standard solution

iv. A solution of chromium (6.0 ml) was pipetted from the 250 ml standard reference stock into a volumetric flask (50 ml) and made up to the mark with distilled water to prepare 0.6 mol/l chromium standard solution

v. Solution of mecurry (40 ml) was pipetted from the 250 ml standard reference stock into a volumetric flask (50 ml) and made up to the mark with distilled water to prepare 4.0 mol/l mercury standard solutions.

3.12 Methods for Estimating Pollutant Impact

A number of geochemical parameters have been put forward for quantifying the degree of metal enrichment in sediments and water bodies (Ridgway and Shimmield, 2002). Various authors (Salomons and Förstner 1984; Hakanson 1980) have proposed pollution impact scales (or ranges) to convert the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity. The proposed pollution impact scales are discussed below:

3.12.1 Contamination factor (CF)

The Contamination factor (CF) is the ratio obtained by dividing the concentration of each metal in the sediment, water and fish samples by the background level.

$$CF = \frac{\text{Concentration of metal in sample}}{\text{Concentration of metal in background}} \quad 3.14$$

In this study, the WHO (2004) guidelines values for drinking water quality were selected as background level for the calculation of contamination factors of the water samples (Appendix LXIX). For soil/sediment samples, however, the world shale value (Bhupander *et al*., 2011) was used as background metal levels.The contamination levels may be classified based on their intensities on a scale ranging from 1 to 6 (0= none, 1= none to medium, 2= moderate, 3= moderately to strong, 4= strongly polluted, 5=strong to very strong, 6=very strong) (Bhuiyan *et al*., 2010 and Harikumar and Jisha, 2010). The CF value of 6 indicates that the metal concentration is 100 times greater than what would be expected in the world average shale as reported by Wedepohl (1995).

3.12.2 Pollution Load Index (PLI)

The pollution load index (PLI) was proposed by Tomlinson *et al* (1980) for detecting pollution which permits a comparison of pollution levels between sites and at different times. The PLI was obtained as a concentration factor of each heavy metal with respect to the background value in the samples. According to Angula (1996) the PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken.

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times CF_4 ... \times CF_n} \quad 3.15$$

Where CF_1 to CF_n indicate the contamination factors calculated for the first sample to the n^{th} one. A PLI value close to one indicates heavy metal loads near the background level, while values above one indicate sample pollution (Bhupander *et al*., 2011; Angula, 1996).

3.13Statistical Analysis

Descriptive statistics (such as mean and standard deviation) were performed on all the data. A two way ANOVA was used to compare means of the different parameters measured for two seasons (wet and dry) and for two years (2014 and 2015). Duncan multiple Range Test was used to separate means where significant. Means were considered significantly different at $P< 0.05$. Correlation analysis was also conducted on the data at confidence level of 0.01 and 0.05. Pearson's correction was used to determine the relationship between the concentrations of different heavy metals measured in water bodies at different locations in the state. Relationships were considered significant at $P<0.01$.

Table 3.1: The Operating Conditions for AAS Analysis for Heavy metals

Element	Lamp current (mA)	Wavelength (nm)	Slit width (mm)	Gas Mixture ($2300^{o}C$)	Flow rate(L/min)	Burner height(mm)
Cd	8	228.8	1	Nitrous-acetylene	1.8	7
Cr	10	357.9	0.5	Nitrous-acetylene	2.1	9
Hg			2	Nitrous-acetylene	2.6	4
Zn	10	213.9	0.5	Nitrous-acetylene	2.0	7
Pb	5	283.3	7	Nitrous-acetylene	2.4	5

CHAPTER FOUR

4.0 RESULTS

4.1 Validation of Methodology

The percentage recoveries obtained for the metals under investigation (Zn, Cr, Cd, Pb and Hg) varied between 76.81 and 103.54%. The pattern of recovery efficiency was found to be following the decreasing order: Cr > Pb > Cd >Zn > Hg. (Table 4.1).

4.2 Water Quality Parameters

4.2.1 pH

The result for the estimation of pH is given in Table 4.2. The pH of Gusau dam was between 7.67 ± 0.03 and 7.68 ± 0.03 during the wet season of 2014 and 2015 respectively. Bakolori dam recorded pH of 7.86 ± 0.03 and 7.98 ± 0.03 during the wet season of 2014 and 2015 respectively and this was also the highest pH recorded across all the locations. Abare River showed the lowest pH value of 7.53 ± 0.03 and 7.45 ± 0.03 in 2014 and 2015 respectively.

During the dry season (Table 4.3), Bakolori dam showed a mean pH of 7.95 ± 0.21 and 7.90 ± 0.08 in 2014 and 2015 respectively. Again this is also the highest pH recorded across all the locations.The pH values in 2014 dry season were generally higher than those of 2015. Also, the pH values recorded for Bagega, Sunke and Abare Rivers in this research work are lower than those of Gusau, Bakolori and Danglubi Dams. The combined mean pH of all the water locations in year 2014 was significantly higher than those of 2015 (Appendix VI – IX).

Table 4.1 Validation of Experimental Protocols

Metal	Actual Concentration	Number of Run	Observed Concentration	% Recovery
Pb	0.4	1	0.4409	100.71
		2	0.3991	
		3	0.3731	
		4	0.3982	
			0.4028 ± 0.0120	
Zn	0.4	1	0.3847	90.19
		2	0.3658	
		3	0.3460	
		4	0.3466	
			0.3608 ± 0.1320	
Cd	0.6	1	0.5532	90.96
		2	0.5445	
		3	0.5440	
		4	0.5413	
			0.5458 ± 0.1410	
Cr	0.6	1	0.6399	103.54
		2	0.6356	
		3	0.6047	
		4	0.6947	
			0.6212 ± 0.0131	
Hg	4.0	1	3.4616	76.81
		2	3.1713	
		3	2.4220	
		4	3.234	
			3.0722 ± 0.2140	

Table 4.2: The Mean and Standard Deviation of Location and Year of the Physicochemical Parameters of Water Bodies in the Wet Season

Location	Year	pH	Temp ^{0}C	EC µs/cm	TDS mg/L	TSS mg/L	Cl mg/L	Alk. mg/L	Tur. NTU
Gusau	2014	7.67± 0.03	26.53 ± 0.06	125.00 ± 0.00	196.67 ± 5.77	102.33 ± 1.15	15.93 ± 0.12	16.70 ± 0.46	6.67 ± 0.58
dam	2015	7.68 ± 0.02	26.50 ± 0.00	123.33 ± 2.89	180.00 ± 0.00	66.53 ± 4.31	15.20 ± 0.20	15.33 ± 0.40	4.67 ± 0.58
Bakolori	2014	7.86 ± 0.01	26.60 ± 0.00	200.00 ± 0.00	300.00 ± 0.00	1.64.67 ±0.58	19.40 ± 0.17	18.27 ± 0.12	7.00 ± 0.00
dam	2015	7.98 ± 0.58	26.50 ± 0.00	211.67 ± 2.87	293.3 ± 1.55	148.33 ± 2.89	18.00 ± 0.00	16.06 ± 0.75	7.67 ± 0.58
Dangulbi	2014	7.73 ± 0.04	26.50 ± 0.00	220.00 ± 0.00	350.00 ± 0.00	186.00 ± 1.73	20.07 ± 0.11	17.30 ± 0.00	10.00 ± 0.00
dam	2015	7.74 ± 0.35	26.57 ± 0.58	206.67 ± 0.00	326.67 ± 5.77	170.67 ± 0.58	21.33 ± 0.40	19.47 ± 0.06	11.67 ± 0.58
Bagega	2014	7.60 ± 0.03	26.73 ± 0.58	231.67 ± 2.89	360.00 ± 0.00	3.85.33 ±1.15	26.70 ± 0.17	20.04 ± 0.05	72.67 ± 1.35
river	2015	7.54 ± 0.03	26.77 ± 0.06	250.00 ± 0.00	346.67 ± 5.73	406.67 ± 2.52	27.67 ± 0.29	21.93 ± 0.40	73.33 ± 1.57
Sunke	2014	7.52 ± 0.03	26.70 ± 0.00	260.00 ± 0.00	400.00 ± 0.00	430.00 ± 0.00	33.07 ± 0.11	23.47 ± 0.12	76.67 ± 0.35
river	2015	7.54 ± 0.03	26.77 ± 0.68	253.33 ± 2.89	396.67 ± 5.77	420.00 ± 0.00	36.00 ± 0.34	20.67 ± 0.12	74.33 ± 1.77
Abare	2014	7.53 ± 0.03	26.80 ± 0.00	328.33 ± 2.89	500.00 ± 0.00	573.33 ± 2.89	36.60 ± 0.00	23.54 ± 0.22	80.33 ± 1.77
river	2015	7.45 ± 0.03	26.87 ± 0.08	330.00 ± 0.00	516.67 ±5.77	573.33 ± 2.89	25.29 ± 0.35	22.33 ± 0.06	77.67 ± 1.35
Nigeria		6.5 – 8.5	35 - 40	1000	500	-	250		
range									
WHO		6.5 – 7.5	35 - 37	500	1000	-	250	200	5.0 - 25
range									

n = 3; mean ± S.D.

KEY: E.C = Electronic Conductivity; T.D.S = Total Dissolved Solids; Cl = Chlorine; Alk = Alkalinity; Tur = Turbidity

Table 4.3: Mean Standard Deviation of Location and Year of the Physicochemical Parameters of Water Bodies in the Dry Season

Location	Year	pH	Temp. ^{0}C	E C µs/cm	TDS mg/L	TSS mg/L	Cl mg/L	Alk mg/L
Gusaudam	2014	7.85 ± 0.03	26.80 ± 0.00	186.67 ± 0.09	75.53 ± 0.74	123.00 ± 1.73	16.330 ± 0.26	18.73 ± 0.29
	2015	7.80 ± 0.47	26.67 ± 0.58	156.67 ± 0.77	71.80 ± 1.11	92.00 ± 1.73	15.70 ± 0.26	16.77 ± 0.15
Bakolori dam	2014	7.95 ± 0.21	26.70 ± 0.00	200.00 ± 0.00	246.67 ± 0.34	119.00 ± 0.24	17.30 ± 1.84	18.40 ± 0.05
	2015	7.90 ± 0.08	26.57 ± 0.06	250,00 ± 0.00	300.00 ± 0.00	119.00 ± 0.74	18.73 ± 0.12	17.53 ± 0.12
Dangulbi dam	2014	7.85 ± 0.01	26.73 ± 0.58	230.00 ± 0.00	360.00 ± 0.00	184.66 ± 0.58	21.47 ± 0.58	19.23 ± 0.06
	2015	7.75 ± 0.02	27.00 ± 0.00	233.3 ± 0.87	370.00 ± 0.00	182.00 ± 0.00	20.70 ± 1.00	18.70 ± 0.10
Bagega river	2014	7.50 ± 0.01	27.00 ± 0.00	260.00 ± 0.00	400.00 ± 0.00	431.33 ± 0.58	27.67 ± 0.33	21.82 ± 0.36
	2015	7.40 ± 0.01	27.17 ± 0.15	270.00 ± 0.00	426.67 ± 057	447.33 ± 1.15	27.27 ± 0.42	21.90 ± 0.61
Sunke river	2014	7.55 ± 0.01	27.00 ± 0.00	280.00 ± 0.00	430.00 ± 0.00	470.00 ± 0.00	33.67 ± 0.12	24.47 ± 0.12
	2015	7.52 ± 0.01	27.01 ± 0.01	300.00 ± 0.00	420.00 ± 0.00	450.00 ± 0.00	37.97 ± 0.21	23.40 ± 0.01
Abare river	2014	7.50 ± 0.01	27.20 ± 0.00	350.00 ± 0.00	510.00 ± 0.00	560.00 ± 0.00	36.37 ± 0.58	22.80 ± 0.01
	2015	7.40 ± 0.03	26.73 ± 0.06	330.00 ± 0.00	520.00 ± 0.00	545.00 ± 0.00	32.67 ± 0.12	21.50 ± 0.01

KEY: E.C = Electronic Conductivity; T.D.S = Total Dissolved Solids; Cl = Chlorine; Alk = Alkalinity;

4.2.2 Temperature

The temperature (Table 4.2) recorded for Abare River varied between 26.80 ± 0.00 and 26.87 ± 0.08 during the wet season of 2014 and 2015 respectively and it's also the highest mean temperature measured across all the locations while Sunke River recorded the least mean temperature which ranged between 26.70 ± 0.00 and 26.77 ± 0.68 during the wet season of 2014 and 2015 respectively. Generally, the temperature recorded for Bagega, Sunke and Abare Rivers are slightly higher than those of the dams during wet season of 2014 and 2015. In the dry season (Table 4.3), Bakolori dam showed the lowest mean temperature of 26.70±0.08 and 26.57±0.06 in 2014 and 2015 respectively while Bagega recorded the highest mean temperature of 27.00±0.00 and 27.17±0.15 in 2014 and 2015 respectively.The mean temperature of the water bodies for Gusau and Dangulbi dams were significantly the lowest ($p < 0.05$), while that of Abare River was significantly the highest. Also the combined mean temparature of all the water locations in 2014 were higher than those of 2015 (Appendix X - XIII).

4.2.3 Electrical conductivity

The result of EC is presented in Table 4.2. Bakolori Dam showed the least EC, it varied between 125.00 ± 0.00 and 123.33 ± 2.87 µs/cm for 2014 and 2015 respectively. Abare River recorded the highest EC which varied between 328.57 ± 2.89 and 330 ± 0.00 µs/cm during the wet season of 2014 and 2015 respectively.

During the dry season (Table 4.3), the EC value for Gusau dam varied between 186.67 ± 0.09 and 156.67 ± 0.77 µs/cm during the dry season of 2014 and 2015 respectively. This represent the lowest EC recorded across all the locations while the EC value for Abare River varied between 328.33 ± 2.89 and 330 ± 0.00 µs/cm for 2014 and 2015 respectively. This equally represents the highest EC recorded across all the locations. Generally, the EC

values of dry seasons are higher than those of the wet seasons, which suggest a seasonal variation. Also the EC values from Bagega to Abare Rivers are higher than those of Gusau to Dangulbi dams.

The mean EC value for both years (2014 and 2015) for Gusau dam was significantly the lowest amongst the three dams' considred while Abare River recorded the highest mean EC value. The mean EC value for both wet and dry seasons across all the location is higher in 2015 than in 2014 (Appendix XIV – XVII).

4.2.4 Total dissolved solids

Total dissolved solids (TDS) for the water sample during the wet and dry season is presented in Table 4.2. Gusau Dam recorded the lowest TDS, it varied between 196.67 ± 5.77 and 180 ± 0.00 mg/l during wet season of 2014 and 2015 respectively. The highest TDS value was obtained in Sunke River which varied between 500 ± 0.00 and 516.67 ± 5.77 mg/l in the wet season of 2014 to 2015 respectively. There was a general decrease in the value of TDS from year 2014 to 2015.Abare River recorded the highest TDS (Table 4.3), which varied between 510 ± 0.00 and 520 ± 0.00 mg/l during the dry season of 2014 and 2015 respectively. The values of TDS recorded during the dry season are higher than those of the wet season. This suggests a seasonal variation.

The mean TDS concentration for both year 2014 and 2015 for all the dams and Bagega rivers, were significantly the lowest ($P < 0.05$). While that of Sunke and Abare Rivers are significantly the highest ($P < 0.05$). The mean TDS of all the water bodies across all the six location in 2015 are higher than those of 2014 (Appendix XVIII – XXI).

4.2.5 Total suspended solids

The result obtained for Total Suspended Solid (TSS) for all the locations is presented in Table 4.2. Abare River recorded the highest TSS value which varied between 573.33 ±

2.89 and 573.33 ± 2.89 mg/l during the wet season of 2014 and 2015 respectively while Gusau Dam recorded the lowest TSS value which varied between 102.33 ± 1.15 and 66.53 ± 4.31 mg/l. A gradual increase in the TSS value was observed from Gusau to Dangulbi dam during the west season of year 2014 and 2015.

During dry season (Table 4.3), Gusau Dam recordedthe lowest TSS level which varied between 123 ± 1.73 and 92 ± 1.73 mg/l for 2014 and 2015 respectively, while, Abare River recorded the highest value of TSS which varied between 560 ± 0.00 and 545 ± 0.00 mg/l for 2014 and 2015 respectively.Generally, the values of TSS recorded in the wet season are lower than the dry season, which also indicate the effect of seasonal variation. It was also observed that the TSS levels for rivers are higher than for the dams. The mean TSS of all the water bodies across the six locations under study in 2014 were significantly higher ($p < 0.05$) than that of 2015 (Appendix XXII - XXV).

4.2.6 Chloride

The result for chloride (Cl) is as shown in Table 4.2. Gusau dam recorded the lowest value which varied between 15.93 ± 0.12 and 15.20 ± 0.20 mg/l in 2014 and 2015 respectively. Sunke River recorded the highest value 33.07 ± 0.11 and 36.00 ± 0.00 mg/l in the wet season of 2014 and 2015 respectively. During the dry season (Table 4.3), the concentration Cl in Gusau dam varied between 16.3 ± 0.26 and 15.7 ± 0.26 mg/lfor 2014 and 2015 respectively.this is also the lowest value recorded across all locations. Sunke River also recorded the highest Cl concentration which varied between 33.67 ± 0.12 and 37.97 ± 0.21 mg/lduring the dry season of 2014 and 2015 respectively. Generally, the concentration of chlorine in Bagega, Sunke and Abare Rivers are higher than those of Gusau, Bakolori and Dangulbi dams during the wet and dry seasons of 2014 and 2015. The mean concentration of all the water bodies in 2014 was significantly higher than those of 2015(Appendix XXVI – XXIX).

4.2.7 Alkalinity

The result obtained for alkalinity in all the locations is presented in Table 4.2. The values recorded at Gusau dam for 2014 and 2015 wet season varied between 16.07 ± 0.12 and 15.20 ± 0.20 mg/l respectively which is also the lowest across all the locations. Abare River has values between 23.54 ± 0.01 and 22.33 ± 0.22 mg/l for 2014 and 2015 respectively. While in the dry season (Table 4.3), Gusau dam has values which varied between 18.73 ± 0.03 and 16.77 ± 0.15 mg/l for 2014 and 2015 respectively which is also the lowest recorded across all locations. Sunke River recorded values between 24.47 ± 0.01 and 23.40 ± 0.01 mg/l as the highest across all the locations for 2014 and 2015 respectively. Generally, the dry season recorded higher alkalinity levels than the wet season. Hence seasonal variation is established. The alkalinity levels recorded for the rivers are slightly higher than those of the dams during wet and dry season of 2014 and 2015 period. The mean alkalinity concentrations of all the water bodies in 2014 were significantly higher than that of 2015 (Appendix XXX – XXXIII).

4.2.8 Turbidity

Results for turbidity of water samples collected from all the locations is presented in Table 4.2. The turbidity values for Gusau dam varied between 6.67 ± 0.58 and 4.6 ± 0.58 NTUduring wet season of 2014 and 2015 respectively. This is also the lowest across all six locations. While the turbidity level of Abare River varied between 80.33 ± 1.77 and 77.67 ± 1.35 NTU during the wet season of 2014 and 2015 respectively. This is also the highest across all six locations.While in the dry season (Table 4.3), the turbidity values recorded for Gusau dam varied between 8.00 ± 0.00 and 7.33 ± 0.58 NTU, while Sunke River has value between 81.00 ± 0.00 and 80 ± 0.00 NTU for 2014 and 2015 respectively. Generally, the rivers recorded an increase in turbidity value than those of the dams. There is also general

increase in the values recorded for turbidity during the dry season than the wet season which also indicate seasonal variation. The mean turbidity of all the water bodies in 2014 was significantly higher than that of 2015(Appendix XXXIV –XXXVII).

4.2.9 Sulphate

At Gusau dam (Table 4.4), sulphate level varied between 9.56 ± 0.06 and 9.21 ± 0.19 mg/l during the wet season of 2014 and 2015 respectively. There is a slight decrease in the sulphate level from 2014 to 2015. A similar variation pattern was observed across all the other locations. The sulphate levels recorded for Bagega, Sunke and Abare Rivers are slightly higher than that of Gusau, Bakolori and Dangulbi Dams during the wet season. While during the dry season, there is also a slight decrease in the sulphate level from 2014 to 2015.

During the dry season, the pattern of variation that was observed in the wet was also observed across all the other locations during the dry season (Table 4.5). Generally, the sulphate levels recorded in the wet season are less than those observed in the dry season, a situation which suggests influence of seasonal variation. Statistics showed that the mean sulphate concentration of all the water bodies from the six locations in 2014 was significantly higher than that of 2015 (appendix XXXVIII – XLI).

4.2.10 Phosphate

The levels of phosphate obtained for all the locations are presented in Table 4.4. The levels of phosphate recorded at Gusau dam varied between 2.19 ± 0.15 and 2.01 ± 0.01 mg/l during the wet season of 2014 and 2015 respectively. While at Abare river phosphate level varied between 8.29 ± 0.12 and 8.06 ± 0.05 mg/l for 2014 and 2015 respectively. Again the highest level of phosphate was recorded at Abare River. Also, it was observed that the variation

Table 4.4:The Mean and Standard Deviation of Location and Year of the Physicochemical Parameters of Water Bodies in the Wet Season.

Location	Year	COD (mg/l)	BOD (mg/l)	DO (mg/l)	Hardness (mg/l)	SO_4 mg/l	PO_4 mg/l
Gusaudam	2014	198.00 ± 1.73	10.67 ± 1.10	7.67 ± 0.06	80.00 ± 0.00	9.56 ± 0.06	2.19 ± 0.15
	2015	195.33 ± 1.15	09.67 ± 0.81	7.40 ± 0.17	88.00 ± 0.00	9.21 ± 0.19	2.01 ± 0.01
Bakolori dam	2014	182.33 ± 1.15	14.40 ± 0.10	7.47 ± 0.06	84.67 ± 1.15	9.47 ± 0.12	1.82 ± 0.12
	2015	178.00 ± 1.73	12.50 ± 0.17	7.37 ± 0.06	81.00 ± 1.73	9.19 ± 0.07	1.54 ± 0.12
Dangulbi dam	2014	169.07 ± 0.58	11.37 ± 0.23	8.00 ± 0.00	90.67 ± 0.58	9.52 ± 0.03	2.78 ± 0.04
	2015	164.33 ± 1.15	10.63 ± 0.29	7.80 ± 0.17	88.33 ± 1.15	9.30 ± 0.02	2.59 ± 0.06
Bagega river	2014	241.33 ± 1.31	33.31 ± 0.34	4.03 ± 0.06	92.33 ± 0.58	14.11 ± 0.18	6.17 ± 0.12
	2015	240.00 ± 0.00	35.59 ± 0.70	2.37 ± 0.23	92.67 ± 1.15	14.20 ± 0.17	6.06 ± 0.04
Sunke river	2014	256.67 ± 1.15	25.57 ± 0.64	3.53 ± 0.12	92.33 ± 0.58	15.04 ± 0.06	7.73 ± 0.75
	2015	260.33 ± 0.58	33.47 ± 0.12	2.60 ± 0.17	92.67 ± 1.15	16.68 ± 0.64	7.25 ± 0.05
Abare river	2014	266.33 ± 0.82	33.13 ± 0.23	2.60 ± 0.17	89.17 ± 1.35	17.56 ± 0.07	8.29 ± 0.12
	2015	272.00 ± 0.46	34.53 ± 0.23	2.73 ± 0.12	89.78 ± 1.01	12.54 ± 0.29	8.06 ±0.05
Nigeria standard						100	
WHO standard						200	5

Tur = Turbidity; SO_4 = Sulphate ; PO_4 = Phosphate; COD = Chemical Oxygen Demand; BOD = Biological Oxygen Demand; TSS = Total Suspended Solid; DO = Dissolved Oxygen

Table 4.5: The Mean and Standard Deviation of Location and Year of the Physicochemical Parameters of Water bodies in the Dry Season.

Location	Year	COD mg/L	BOD mg/L	DO mg/L	Hardness mg/L	Tur NTU	SO_4 mg/L	PO_4 mg/L
Gusaudam	2014	199.67 ± 0.58	8.33 ± 0.21	7.70 ± 0.73	80.33 ± 0.58	8.00 ± 0.00	10.43 0.02	2.42 ± 0.02
	2015	182.33 ± 0.15	9.03 ± 0.26	7.30 ± 0.10	90.67 ± 0.58	7.33 ± 0.58	10.41 ± 0.12	2.14 ± 0.02
Bakolori dam	2014	194.53 ± 0.61	11.10 ± 0.88	7.67 ± 0.21	81.33 ± 0.52	8.00 ± 0.00	10.50 ± 0.02	2.20 ± 0.38
	2015	171.33 ± 0.21	11.47 ± 0.10	7.53 ± 0.06	82.67 ± 0.58	7.67 ± 0.58	10.12 ± 0.02	1.48 ± 0.17
Dangulbi dam	2014	170.43 ± 0.15	8.13 ± 0.06	8.50 ± 0.10	86.67 ± 0.57	12.00 ± 0.01	11.03 ± 0.03	2.87 ± 0.06
	2015	165.87 ± 0.06	11.70 ± 0.15	7.90 ± 0.01	91.58 ± 0.58	11.00 ± 0.01	10.96 ± 0.03	2.59 ± 0.02
Bagega river	2014	243.00 ± 0.00	26.33 ± 0.10	6.67 ± 0.06	90.00 ± 0.00	81.00 ± 1.00	24.49 ± 0.02	5.60 ± 0.05
	2015	244.50 ± 0.97	22.37 ± 0.10	6.57 ± 0.15	94.00 ± 0.09	79.66 ± 0.58	25.76 ± 2.89	6.20 ± 0.01
Sunke river	2014	270.00 ± 0.00	34.43 ± 0.11	2.83 ± 0.06	93.67 ± 0.58	81.00 ± 0.00	27.01 ± 0.17	7.51 ± 0.02
	2015	256.33 ± 0.58	26.33 ± 0.10	3.87 ± 0.06	94.00 ± 0.58	80.00 ± 0.00	27.16 ± 0.15	7.40 ± 0.01
Abare river	2014	290.00 ± 0.50	37.34± 0.06	2.76 ± 0.06	92.33 ± 0.54	88.67 ± 0.58	29.81 ± 0.01	8.76 ± 0.05
	2015	280.33 ± 0.58	33.60± 0.15	2.90 ± 0.01	97.33 ± 0.15	85.33 ± 0.58	29.13 ± 0.11	8.28 ± 0.06

n = 3; mean ± S.D.

KEY: Tur = Turbidity; SO_4 = Sulphate ; PO_4 = Phosphate; COD = Chemical Oxygen Demand; BOD = Biological Oxygen Demand; DO = Dissolved Oxygen;

pattern in Bagega, Sunke and Abare rivers are similar in such way that there was slight decrease in their level from year 2014 to 2015.

During the dry season (Table 4.5), the phosphate level at Bakolori Dam in 2014 and 2015 varied between 2.20 ± 0.38 and 1.48 ± 0.17 mg/l respectively, whileat Abare River it varied between 8.76 ± 0.05 and 8.28 ± 0.06 mg/l in 2014 and 2015 respectively. A similar variation pattern exist between Gusau, Bakolori and Dangulbi dams which showed that there was a consistent decrease in the phosphate level from year 2014 to 2015. Statistics showed that the mean phosphate concentration of all the water bodies from the six locations in 2014 was significantly higher than that of 2015 (Appendix XLII – XLV).

Generally, the levels of phosphate recorded in dry season are higher than those of the wet season, a situation which suggest seasonal variation.

4.2.11 Chemical oxygen demand

The results obtained for Chemical Oxygen Demand (COD) for all the locations are presented in Table 4.4**.** The level of COD for Dangulbi dam varied between 169.07 ± 1.15 and 164.33 ± 1.73 mg/l for 2014 and 2015 wet saeson respectively. This is also the lowest value recorded across all locations. It was observed that there was a consistent decrease in COD level from Gusau to Dangulbi dams. The COD level for Abare River varied between 266.3 ± 0.82 and 272 ± 0.46 mg/lduring the wet season of 2014 and 2015 respectively. While during the dry season (Table 4.5), the COD level for Dangulbi River varied between 170.43 ± 0.15 and 165.87 ± 0.06 mg/l for 2014 and 2015 respectively, while at Abare River the COD varied between 290 ± 0.00 and 280 ± 0.58 mg/l during the dry season of 2014 and 2015 respectively. The mean COD of all water bodies for 2014 was significantly higher ($P < 0.05$) than that of 2015 (Appendix XLVI – IXL). It was generally observed that the COD levels for

the rivers are much higher than the levels for the dams. This suggests an influence of seasonal variation on the chemical oxygen demand.

4.2.12 Biological oxygen demand

The result obtained for biological oxygen demand (BODs) for all the locations are presented in Table 4.4. The BOD of Gusau dam varied between 10.67 ± 0.64 and 9.67 ± 0.70 mg/lduring the wet season of 2014 and 2015 respectively which is also the lowest recorded across all the locations. While at Bagega River, the BOD level varied between 33.31 ± 0.34 and 35.59 ± 0.70 mg/l during the wet season of 2014 and 2015 respectively. The mean BOD of all the water bodies from Gusau dam to Abare river are significantly different (Appendix L - LIII). During the dry season (Table 4.5), there is a significant increase in the level of BOD from Gusau dam 8.33 ± 0.21 mg/l to Abare River 37.34 ± 0.06 mg/l.

4.2.13 Dissolved oxygen

The result obtained for dissolved oxygen (DO) for all locations are presented in Table 4.4. Dangulbi dam recorded the highest DO values which vary between 8.00 ± 0.00 and 7.80 ± 0.17 mg/l which is also the highest level recorded across all the locations. While at Abare River, the level further reduced from 2.60 ± 0.17 to 2.73 ± 0.12 mg/l during the wet season of the year 2014 and 2015 respectively.

While during the dry season (Table 4.5), Dangulbi dam recorded the highest level of DO which varied between 8.50 ± 0.10 and 7.90 ± 0.01 mg/l for 2014 and 2015 respectively, while at Abare River, the level of DO varied between 2.76 ± 0.06 and 2.90 ± 0.01 mg/l for 2014 and 2015 respectively. It was generally observed that the dams for both wet and dry seasons have higher DO values than those of the rivers. Seasonal variation is observed in DO

concentration, with higher values in the wet seasons, this could be due to increased aeration and continuous recharge of the water bodies as a result of rainfall(Appendix LIV – LVII).

4.2.14 Water hardness

The level of hardness at Gusau dam (Table 4.4) varied between 80 ± 0.00 and 88 ± 0.00 mg/lduring the wet season of 2014 and 2015 respectively which is also the lowest across all the locations. There is a consistent increase in the level of hardness from Gusau dam to Sunke River whose level of hardness varied between 92.33 ± 0.58 and 92.67 ± 1.15 mg/l respectively. While during the dry season (Table 4.5), the hardness level for Gusau dam varied between 80.33 ± 0.58 and 90.67 ± 0.58 mg/l for 2014 and 2015 respectively. At Abare River the hardness level varied between 92.33 ± 0.54 and 97.33 ± 0.15 mg/l for year 2014 and 2015 respectively. There was a gradual increase in the hardness level from year 2014 to 2015. It was also generally observed that the levels of hardness in the dams both in wet and dry seasons are lower than the levels in the rivers. Also the levels of hardness in the dry season are higher than in the wet season, an indication of seasonal variation effect. Statistical analysis of variance showed that the mean hardness of all six locations of the water bodies in 2014 was significantly higher ($p < 0.05$) than that of 2015 (Appendix LVIII - LXI).

4.2.15 Correlation matrix for pH and other physicochemical parameters for two wet and dry Seasons

The result of correlation matrix (Table 4.6) conducted on pH and other physicochemical parameters revealed that, a negative significant correlation ($P < 0.05$) exist between pH and other examined parameters like TDS, TSS, Alkalinity Sulphate, Turbidity and chloride. While positive significant correlations exist between alkalinity and TSS, TDS, also between turbidity, and sulphate, Alk, TSS, and TDS,while a significant negative correlation exist between alkalinity and pH.

Table 4.6: Correlation Matrix for pH and other Physicochemical Parameters for Two Wet and Dry Seasons

Correlations

	pH	EC	TDS	TSS	Alk.	SO_4	Tur.	Cl
pH	1							
EC	.281	1						
TDS	-.686**	-.068	1					
TSS	-.805**	-.167	.792**	1				
Alk	-.761**	-.188	.757**	.850**	1			
SO_4	-.627**	-.114	.528**	.592**	.476*	1		
Tur	-.894**	-.202	.774**	.854**	.900**	.637**	1	
Cl	-.765**	-.165	.798**	.833**	.894**	.600**	.907**	1
N	24	24	24	24	24	24	24	24

** Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed).

4.3 Heavy Metals in Water Samples

The results obtained for metals in water samples collected from the different locations of the Dam and Rivers for both wet and dry season are presented in Table 4.7 and 4.8.

The concentration of Zn in Gusau dam varied between 0.002 ± 0.0001 and 0.004 ± 0.0001 mg/l in the wet season of 2014 and 2015 respectively. This represents the lowest concentration recorded across all the six location. Bagega River recorded the highest concentration across all the six locations which varied between 0.0246 ± 0.0020 and 0.0252 ± 0.0020 mg/l for 2014 and 2015 respectively. While during the dry season, the lowest Zn concentration was recorded for Bakolori dam which varied between 0.0068 ± 0.0001 and 0.0266 ± 0.0010 for 2014 and 2015 respectively. Bagega River also recorded the highest Zn concentration which varied between 0.0328 ± 0.0020 mg/l and 0.0362 ± 0.0020 mg/l for 2014 and 2015 respectively. It was generally observed that the concentration of Zn in all the six locations were higher during the dry season when compared with the wet season for both years. This is a reflection of seasonal variation.

The concentration of Cd in Sunke River varied between 0.0006 ± 0.003 and 0.0044 ± 0.0002 mg/l in the wet season of 2014 and 2015 respectively. This also represents the lowest contration of Cd recorded across all the locations. The highest concentration was recorded at Bakolori dam which varied between 0.0064 ± 0.0030 and 0.0024 ± 0.0002 mg/l for 2014 and 2015 respectively. During the dry season, Dangulbi dam recorded the lowest concentration which varied between 0.0550 ± 0.0010 and 0.0140 ± 0.0050 for 2014 and 2015 respectively while Sunke River recorded the highest value which varied between 0.1022 ± 0.0030 and 0.0680 ± 0.0020 for 2014 and 2015 respectively.Generally, the concentrations of Cd in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

Table 4.7: Heavy Metal Concentrations (mg/l) of Water Samples for Two Wet Seasons

location	year	Zn	Cd	Cr	Pb	Hg
L1	2014	0.0020 ±0.0001	0.0040±0.0001	0.0210±0.0003	0.0918±0.0004	0.2638±0.0000
	2015	0.0024 ±0.0001	0.0036±0.0002	0.0262±0.0040	0.0029±0.0001	1.5532±0.0030
L2	2014	0.0060± 0.0001	0.0064±0.0003	0.0078±0.0003	0.0476±0.0020	ND
	2015	0.0066± 0.0001	0.0024±0.0002	0.0044±0.0003	0.0068±0.0001	0.5005±0.0030
L3	2014	0.0042± 0.0002	0.0024±0.0001	0.0014±0.0004	0.0126±0.0002	ND
	2015	0.0049±0.0003	0.0066±0.0005	0.0042±0.0002	0.0480±0.0020	0.5308±0.0030
L4	2014	0.0246 ±0.0020	0.0024±0.001	0.0210±0.003	0.0980±0.004	ND
	2015	0.0252 ±0.0002	0.0110±0.002	0.0236±0.004	0.0126±0.001	1.1909±0.003
L5	2014	0.0066± 0.0001	0.0006±0.003	0.0248±0.003	0.0500±0.002	0.0289±0.000
	2015	0.0068± 0.0001	0.0044±0.002	0.0288±0.003	0.1210±0.001	1.7955±0.003
L6	2014	0.0140± 0.0002	0.0058±0.001	0.0118±0.004	0.0166±0.002	ND
	2015	0.0144±0.003	0.0044±0.005	0.0144±0.002	0.0292±0.002	0.9904±0.003

Key

ND: not detected

L1	Gusau dam	L4	Bagega river
L2	Bakolori dam	L5	Sunke river
L3	Dangulbi dam	L6	Abare river

Table 4.8: Heavy Metals Concentrations (mg/l) of Water Samples for Two Dry Seasons

location	year	Zn	Cd	Cr	Pb	Hg
L1	2014	0.0244 ±0.0002	0.0904±0.0001	0.0682±0.0030	0.1376±0.0040	ND
	2015	0.0112±0.0020	0.2044±0.0020	0.0694±0.0040	0.0062±0.0001	1.5570±0.0030
L2	2014	0.0068± 0.0001	0.0740±0.0003	0.0034±0.0003	0.0876±0.0020	ND
	2015	0.0266± 0.0010	0.0744±0.0020	0.0304±0.0030	0.1314±0.0010	0.5573±0.0030
L3	2014	0.0076± 0.0002	0.0550±0.0010	0.1090±0.0040	0.0334±0.002	ND
	2015	0.0118±0.0030	0.0140±0.0050	0.1098±0.0020	0.0668±0.0020	0.8506±0.0030
L4	2014	0.0328 ±0.0020	0.0668±0.0010	0.1982±0.0030	0.1792±0.0040	ND
	2015	0.0362±0.0020	0.0862±0.0020	0.1970±0.0040	0.0584±0.0010	1.1982±0.0030
L5	2014	0.0104± 0.0010	0.1022±0.0030	0.0962±0.0030	0.1396±0.0020	ND
	2015	0.0128± 0.0010	0.0680±0.0020	0.0992±0.0030	0.2104±0.0010	1.8818±0.0030
L6	2014	0.0158± 0.0020	0.0708±0.0010	0.0806±0.0040	0.1688±0.0020	ND
	2015	0.0148±0.003	0.0708±0.0050	0.0826±0.0020	0.0792±0.002	1.7084±0.030

Key

ND: not detected

L1	Gusau dam	L4	Bagega river
L2	Bakolori dam	L5	Sunke river
L3	Dangulbi dam	L6	Abare river

The lowest concentration of Cr was recorded at Dangulbi dam which varied between 0.0014 ± 0.0004 and 0.0042 ± 0.0002 mg/l during the wet season of 2014 and 2015 respectively. While at Sunke River, the concentration of Cr was high across all the locations it varied between 0.0248 ± 0.0030 and 0.0288 ± 0.0030 mg/l for 2014 and 2015 respectively. During the dry season, Bakolori dam recorded the lowest Cr concentration which varied between 0.0034 ± 0.0003 and 0.0304 ± 0.0003 mg/l for 2014 and 2015 respectively. The highest concentration of Cr was recorded at Bagega River which varied between 0.1982 ± 0.0030 and 0.1970 ± 0.0040 mg/l for 2014 and 2015 respectively. Generally, the concentrations of Cr in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

The lowest concentration of Pb was recorded at Bakolori dam which varied between 0.0476 ± 0.0020 and 0.0068 ± 0.0001 mg/l during the wet season of 2014 and 2015 respectively. While at Bagega River, the concentration of Pb recorded was highest across all the locations it varied between 0.0980 ± 0.0040 and 0.0126 ± 0.0010 mg/l for 2014 and 2015 respectively. During the dry season, Dangulbi dam recorded the lowest Pb concentration which varied between 0.0334 ± 0.0020 and 0.0668 ± 0.0020 mg/l for 2014 and 2015 respectively. The highest concentration of Pb was recorded at Abare River which varied between 0.1688 ± 0.0020 and 0.0792 ± 0.0020 mg/l for 2014 and 2015 respectively.

It was generally observed that, the concentration of Pb in 2014 and 2015 dry seasons were higher than their corresponding wet season. This is also an indication of seasonal variation. The lowest concentration of Hg was recorded at Bakolori dam which varied between below detection and 0.5005 ± 0.0030 mg/l for 2014 and 2015 respectively. Sunke River recorded the highest value which varied between 0.0289 ± 0.0000 and 1.7955 ± 0.003 mg/l during the wet season of 2014 and 2015 respectively.

During the dry season, Bakolori dam recorded the lowest Hg concentration which varied between below detection and 0.5573 ± 0.0030 mg/l for 2014 and 2015 respectively. The highest concentration of Hg was recorded at Sunke River which varied between below detection and 1.8818 ± 0.0030 mg/l for 2014 and 2015 respectively.

It was generally observed that the three rivers recorded higher Hg concentration than the dams and that the concentration was higher in the dry seasons than their corresponding wet seasons. It was also generally observed that, the concentration of Hg was mostly below detection limit in 2014 and recorded very pronounced concentration in year 2015.

4.3.1 Correlation matrix of heavy metals concentrations (mg/l) in water samples for two wet and dry seasons

Correlation analysis showed a significant and positive relationship for Cd and Zn and Hg and Cr during the wet season and a significant positive at the ($p<0.05$) relationship for Cr and Zn in the dry season. This may explain the consistent variation of these metals in all the locations across all the seasons (Table 4.9).

4.3.2 Assessment of heavy metal pollution in water samples

The calculated heavy metals contamination factors (CF) and their pollution load indices for water samples at different locations are presented in Table 4.10. It was revealed that all the water samples analyzed had contamination factor less than one, with exception of Pb, particularly of Bagega (CF = 1.060) and Sunke river (CF = 1.7100) during the wet season. Hg recorded a far higher contamination factor (CF>>>>6) across all six location studied during the wet season. The entire water sample analyzed from all the six locations revealed very high contamination factor (CF >>6) for Cd with exception of Zn which

Table 4.9: Correlation Matrix of Heavy Metals Concentrations (mg/l) in Water Samples for Two Wet and Two Dry Seasons

	Correlations For wet					Correlations For dry				
	Zn	**Cd**	**Cr**	**Pb**	**Hg**	**Zn**	**Cd**	**Cr**	**Pb**	**Hg**
Zn	1					1				
Cd	.394*	1				-.023	1			
Cr	-.130	-.074	1			.565**	-.247	1		
Pb	-.021	-.128	-.102	1		.243	-.306	.056	1	
Hg	-.023	.280	.365*	.034	1	-.017	.233	.025	-.189	1
	36	36	36	36	36	36	36	36	36	36

*.Correlation is significant at the 0.05 level (2-tailed).**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.10: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in Water for Wet and Dry Seasons.

Location/Wet	Zn	Cd	Cr	Pb	Hg	PLI
Gusau dam	0.0004	0.3800	0.2360	0.9470	90.8500	0.3206
Bakolori dam	0.0013	0.4400	0.0610	0.5440	50.0500	0.2486
Dangulbi dam	0.0009	0.4500	0.0280	0.6060	53.0800	0.2053
Bagega river	0.0050	0.6700	0.2230	1.1060	190.9000	0.6911
Sunke river	0.0015	0.2500	0.2680	1.7100	91.2200	0.4356
Abare river	0.0028	0.5100	0.1310	0.4580	990.4000	0.6106
Dry						
Gusau dam	0.0035	14.7400	0.6880	1.4380	155.700	1.5188
Bakolori dam	0.0033	7.4200	0.1690	2.1900	557.300	1.3858
Dangulbi dam	0.0019	3.4500	1.0940	1.0020	850.600	1.4423
Bagega river	0.0395	7.6500	1.9760	2.3760	1198.200	4.4263
Sunke river	0.0023	8.5100	1.9540	3.5000	1881.800	3.0269
Abare river	0.0031	7.4400	0.8160	2.4800	1708.400	2.3944

followed this trend: Gusau Dam (14.7400)>>Sunke (8.5100)> Bagega (7.6500)>Abare (7.4400)>Dangulbi Dam (7.4200). Also it was revealed that Hg recorded a far higher contamination factor (CF>>>6) across all the six location during the dry season.

The calculated pollution load indices (PLI) for all the locations were less than 1 during the wet season and higher than 1 during the dry season particularly for Bagega (4.4263)>Sunke(3.0269) > Abare (2.3944). This might be attributed to the fact that these villages houses higher number of active mining processes.

4.4 Heavy metals in sediment samples

The results obtained for metals in sediment collected from all six locations of the dams and rivers are presented in Table 4.11 and 4.12.

The lowest concentration of Zn was recorded at Bakolori dam which varied between 0.058 ± 0.0010 and 0.044 ± 0.0010 mg/kg during the wet season of 2014 and 2015 respectively.While at Abare River, the concentration of Zn recorded was highest across all the locations, it varied between 0.299 ± 0.0020 and 0.289 ± 0.0030 mg/kg for 2014 and 2015 respectively.During the dry season, Dangulbi dam recorded the lowest Zn concentration which varied between 0.123 ± 0.0020 and 0.080 ± 0.0030 mg/l for 2014 and 2015 respectively. The highest concentration of Zn was recorded at Gusau dam which varied between 0.571 ± 0.0020 and 0.432 ± 0.0020 mg/kg for 2014 and 2015 respectively. Generally, the concentrations of Zn in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

The concentration of Cd in Bakolori dam varied between 0.022 ± 0.0030 and 0.004 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cd recorded across all the locations.

Table 4.11: Heavy Metals Concentrations (mg/kg) of Sediment Samples for Two wet Seasons

Location	year	Zn	Cd	Cr	Pb	Hg
Gusau dam	2014	0.258 ±0.002	0.034±0.001	0.209±0.003	0.469±0.004	ND
Bakolori dam	2015	0.238±0.002	0.029±0.002	0.379±0.004	1.063±0.001	1.850±0.003
Dangulbi dam	2014	0.058± 0.001	0.022±0.003	0.183±0.003	0.396±0.002	ND
Bagega river	2015	0.044± 0.001	0.004±0.002	0.144±0.003	0.261±0.001	1.801±0.003
Sunke river	2014	0.054± 0.002	0.027±0.001	0.072±0.004	0.896±0.002	ND
Abare river	2015	0.059±0.003	0.011±0.005	0.288±0.002	0.521±0.002	0.720±0.003
Wet						
Gusau dam	2014	0.227 ±0.002	0.035±0.001	0.248±0.003	0.156±0.004	ND
Bakolori dam	2015	0.217 ±0.002	0.032±0.002	0.268±0.004	1.316±0.001	0.915±0.003
Dangulbi dam	2014	0.124± 0.001	0.021±0.003	0.033±0.003	0.521±0.002	ND
Bagega river	2015	0.121± 0.001	0.023±0.002	0.157±0.003	0.115±0.001	3.834±0.003
Sunke river	2014	0.299± 0.002	0.086±0.001	0.340±0.004	1.105±0.002	ND
Abare river	2015	0.289±0.003	0.999±0.005	0.454±0.002	0.998±0.002	3.090±0.003

ND: below detection

Table 4.12: Heavy Metals Concentrations (mg/kg) of Sediment Samples for Two dry Seasons

Location	year	Zn	Cd	Cr	Pb	Hg
Gusau dam	2014	0.571 ±0.002	0.256±0.001	1.933±0.003	2.471±0.004	ND
Bakolori dam	2015	0.432±0.002	0.688±0.002	1.903±0.004	1.960±0.001	3.227±0.003
Dangulbi dam	2014	0.165± 0.001	0.944±0.003	0.545±0.003	0.450±0.002	ND
Bagega river	2015	0.111± 0.001	0.511±0.002	0.541±0.003	0.365±0.001	0.896±0.003
Sunke river	2014	0.123± 0.002	0.472±0.001	0.690±0.004	1.135±0.002	ND
Abare river	2015	0.080±0.003	0.275±0.005	0.694±0.002	0.584±0.002	2.563±0.003
Dry						
Gusau dam	2014	0.337 ±0.002	0.609±0.001	1.438±0.003	2.831±0.004	ND
Bakolori dam	2015	0.211±0.002	0.845±0.002	1.430±0.004	2.532±0.001	1.139±0.003
Dangulbi dam	2014	0.268± 0.001	0.236±0.003	0.235±0.003	0.569±0.002	ND
Bagega river	2015	0.109± 0.001	0.688±0.002	0.215±0.003	0.229±0.001	3.813±0.003
Sunke river	2014	0.433± 0.002	0.315±0.001	0.399±0.004	2.033±0.002	ND
Abare river	2015	0.363±0.003	1.315±0.005	1.411±0.002	1.413±0.002	3.430±0.003

Key

ND: not detected

The highest concentration was recorded at Abare River which varied between 0.086 ± 0.0010 and 0.999 ± 0.0050 mg/kg for 2014 and 2015 respectively. During the dry season, Dangulbi dam recorded the lowest concentration which varied between 0.472 ± 0.0010 and 0.275 ± 0.0050 mg/kg for 2014 and 2015 respectively while Abare River recorded the highest value of Cd which varied between 0.315 ± 0.0010 and 1.315 ± 0.0050 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cd in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect. The concentration of Cr in Dangulbi Dam varied between 0.072 ± 0.0040 and 0.288 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cr recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.340 ± 0.0040 and 0.454 ± 0.0020 mg/kg for 2014 and 2015 respectively.

During the dry season, Sunke river recorded the lowest concentration which varied between 0.235 ± 0.0030 and 0.215 ± 0.0030 mg/kg for 2014 and 2015 respectively while Gusau dam recorded the highest value of Cr which varied between 1.933 ± 0.0030 and 1.903 ± 0.0040 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cr in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect. The concentration of Pb in Bakolori Dam varied between 0.396 ± 0.0020 and 0.261 ± 0.001 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Pb recorded across all the locations. The highest concentration was recorded at Abare River which varied between 1.105 ± 0.0020 and 0.998 ± 0.0020 mg/kg for 2014 and 2015 respectively. During the dry season, Bakolori dam recorded the lowest concentration which varied between 0.450 ± 0.0020 and 0.365 ± 0.0010 mg/kg for 2014 and 2015 respectively while Bagega River recorded the highest value of Pb which varied between 2.831 ± 0.0040 and 2.532 ± 0.0010 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Pb in the dry seasons were higher than in the wet season, a situation which

suggests seasonal variation effect. The concentration of Hg in Dangulbi Dam varied between below detection limit and 0.720 ± 0.0030 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Hg recorded across all the locations. The highest concentration was recorded at Sunke River which varied between below detection limit and 3.834 ± 0.0030 mg/kg for 2014 and 2015 respectively.

During the dry season, Dangulbi dam recorded the lowest concentration which varied between below detection and 2.563 ± 0.0030 mg/kg for 2014 and 2015 respectively while Sunke River recorded the highest value of Hg which varied between below detection and 3.813 ± 0.0030 mg/kg for 2014 and 2015 respectively. It was generally observed that Hg concentrations are higher in the dry seasons than their corresponding wet seasons. It was also generally observed that, the concentration of Hg was mostly below detection limit in 2014 and recorded very pronounced concentration in year 2015.

4.4.1 Correlation matrix of heavy metals concentrations (mg/l) in sediment samples for two Wet and dry seasons

Correlation analysis (Table 4.13) revealed a significant positive relationship for Cr and Zn, Cr and Cd, Pb and Cd, Hg and Cd and Hg and Cr respectively during the wet seasons of year 2014 and 2015. While during the dry season it also showed a significant positive relationship for Cr and Zn, Pb and Zn, Pb and Cr and lastly Hg and Cd. This may explain the consistent variation of these metals in all the locations across all the seasons.

4.4.2 Assessment of Heavy Metal Pollution in Sediments Samples

The heavy metal contamination factor (CF) and pollution load indices (PLI) calculated for the sediment samples are presented in table 4.14. The result revealed that Pb and Hg recorded very high contamination factors in this trend:

Table 4.13: Correlation Matrix of Heavy Metals Concentrations (mg/l) in Sediment Samples for Two Wet and two dry seasons

Correlations For wet

	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.319*	1			
Cr	.636**	.624**	1		
Pb	.189	.504**	.231	1	
Hg	.125	.499**	.389*	-.177	1
	36	36	36	36	36

**.Correlation is significant at the 0.01 level (2-tailed).

*.Correlation is significant at the 0.05 level (2-tailed).

Correlations For dry

	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	-.273	1			
Cr	.422*	.251	1		
Pb	.332*	.073	.797**	1	
Hg	.066	.449**	.130	-.194	1
	36	36	36	36	36

*.Correlation is significant at the 0.05 level (2tailed).

**.Correlation is significant at the 0.01 level (2tailed).

Table 4.14: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in Sediment for Wet and Dry Seasons.

Location/Wet	Zn	Cd	Cr	Pb	Hg	PLI
Gusau dam	0.0005	1.4500	3.9650	29.7500	1151	2.5333
Bakolori dam	0.0009	1.5500	1.3650	118.2500	1183	3.0417
Dangulbi dam	0.0011	1.2000	0.8650	39.1000	0523	1.8709
Bagega river	0.0009	2.5500	0.8800	20.3500	1002	2.1125
Sunke river	0.0019	1.8000	0.6850	19.8000	1103	2.1945
Abare river	0.0025	2.4500	1.6150	37.6000	0896	3.2007
Dry						
Gusau dam	0.0007	34.4000	7.3300	30.7500	4363	7.4314
Bakolori dam	0.0010	27.5000	3.1900	78.7000	2527	7.0383
Dangulbi dam	0.0016	51.1000	11.575	62.9500	1343	9.6111
Bagega river	0.0012	57.0000	1.4900	37.4000	1362	5.5342
Sunke river	0.0028	41.3500	1.2100	51.6000	1188	6.1159
Abare river	0.0071	37.3500	3.2400	55.6500	1293	9.0908

Pb: Bakolori (118.25) >> Dangulbi (39.100) > Abare (37.600) > Gusau (29.7500) > Bagega (20.3500) > Sunke (19.800).

Hg: Bakolori (1183) > Gusau (1151) > Sunke (1103) Bagega (1002) > Abare (896) > Dangulbi Dam > (523) during the wet season. While during the dry season all the locations under study revealed very high contamination factor (CF>>>6) for all the heavy metal with exception of Zn. The calculated pollution load indices (PLI) for all the metals analyzed across all the six locations had values greater than 1 for both season.

4.4.3 Chemical fractionation of metals in sediments

The chemical partitioning of Zn, Cr, Cd, Pb and Hg in the sediments from all the dams and rivers under investigation in Zamfara state are presented in percentage starck graph in Fig. 4.1 – 4.5. The three chemical fractions that constitute the non-residual fraction considered in this work are operationally defined as water soluble (F1), exchangeable (F2) and carbonate bound (F3) while the residual fraction is defined as F4.

The percentages of Zn in different chemical fractions across all the six locations under study are presented as stack gragh in Fig. 4.1 and Appendix I. The percentage bioavailable fractions (F1 + F2 +F3) of Zn for Gusau, Bakolori Dangulbi dams, Bagega, Sunke and Abare rivers were 41.586%, 45.316%, 66.664%, 45.944%, 31.312% and 53.422% respectively. The highest percentage bioavailable Zn was recorded in the exchangeable fraction (53.359%) of Dangulbi dam. It was generally observed that the residual fraction recorded the highest percentage of Zn in Abare River. The percentage of Cd in different chemical fractions across all the six locations study are presented as bargraph in Fig. 4.2 and Appendix II.The percentage bioavailable fractions (F1 + F2 +F3) of Cd for Gusau, Bakolori Dangulbi dams, Bagega, Sunke and Abare rivers were 98.655%, 97.615%, 95.797%, 98.881%, 98.641% and 94.609% respectively.

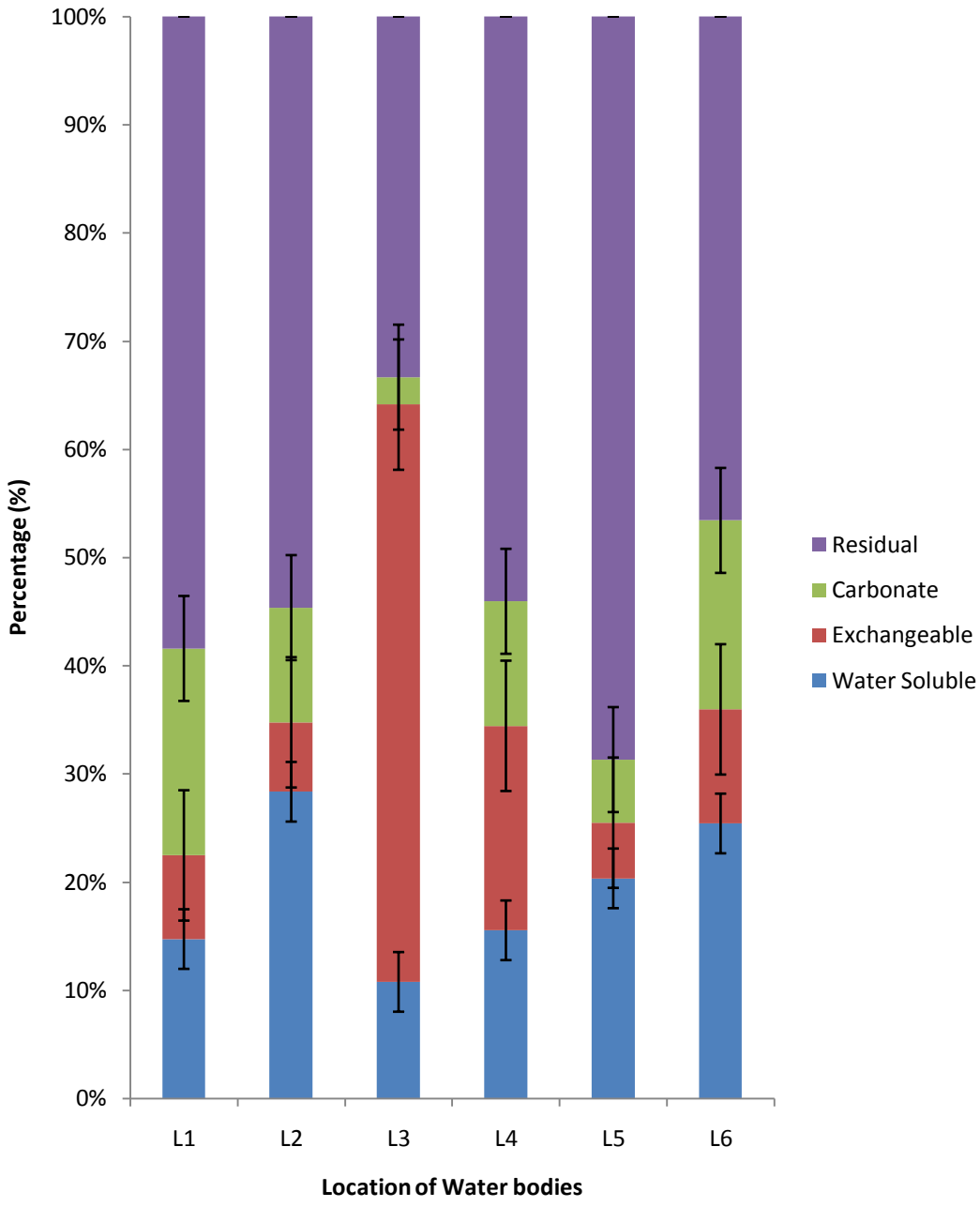


Fig 4.1: Percentage of Zn in different chemical fractions across all locations

Key:

L1	Gusau dam	L2	Bakolori dam
L3	Dangulbi dam	L4	Bagega river
L5	Sunke river	L6	Abare river

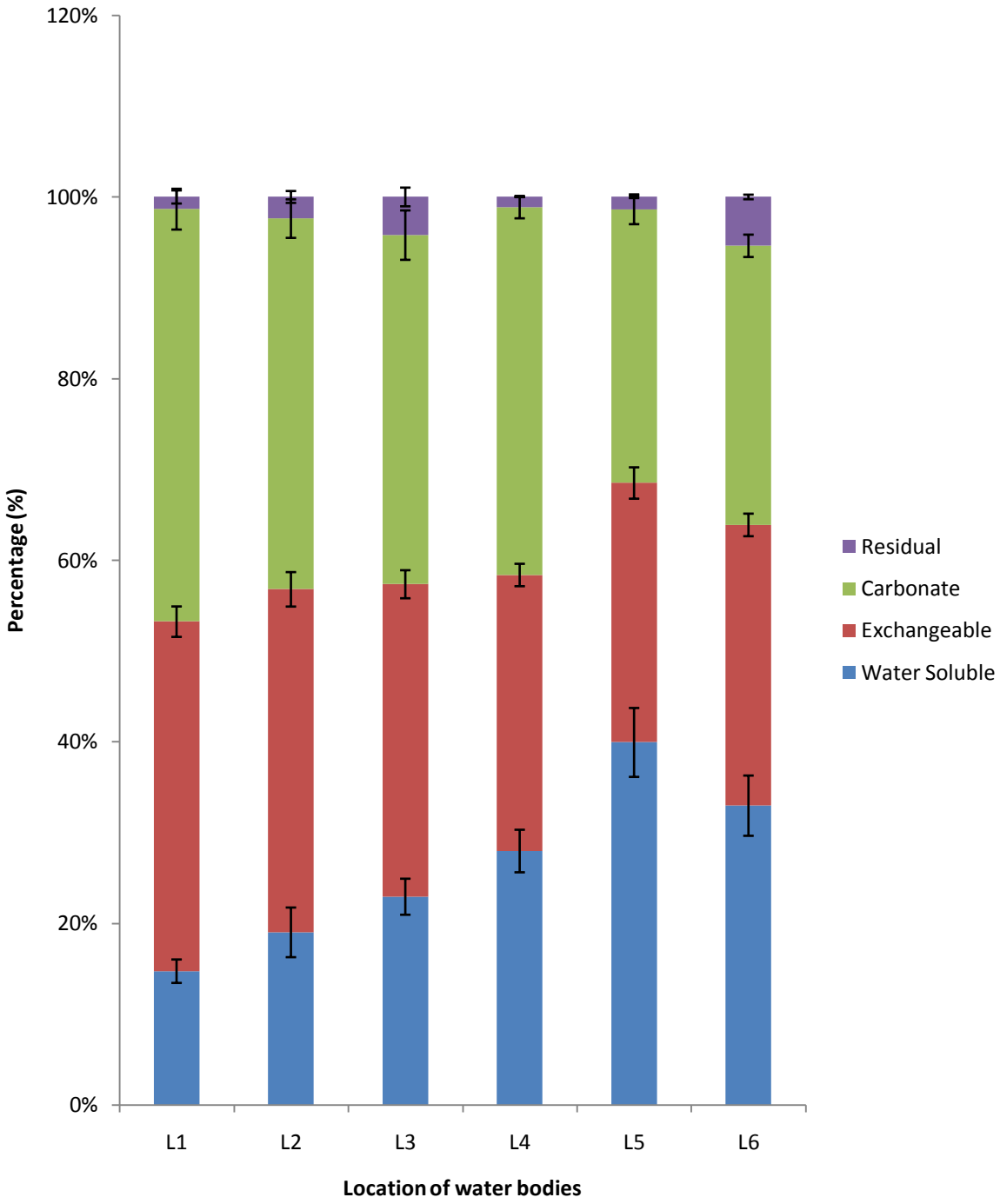


Fig 4.2: Percentage of Cd in different chemical fractions across all locations

Key:

L1	Gusau dam	L2	Bakolori dam
L3	Dangulbi dam	L4	Bagega River
L5	Sunke river	L6	Abare River

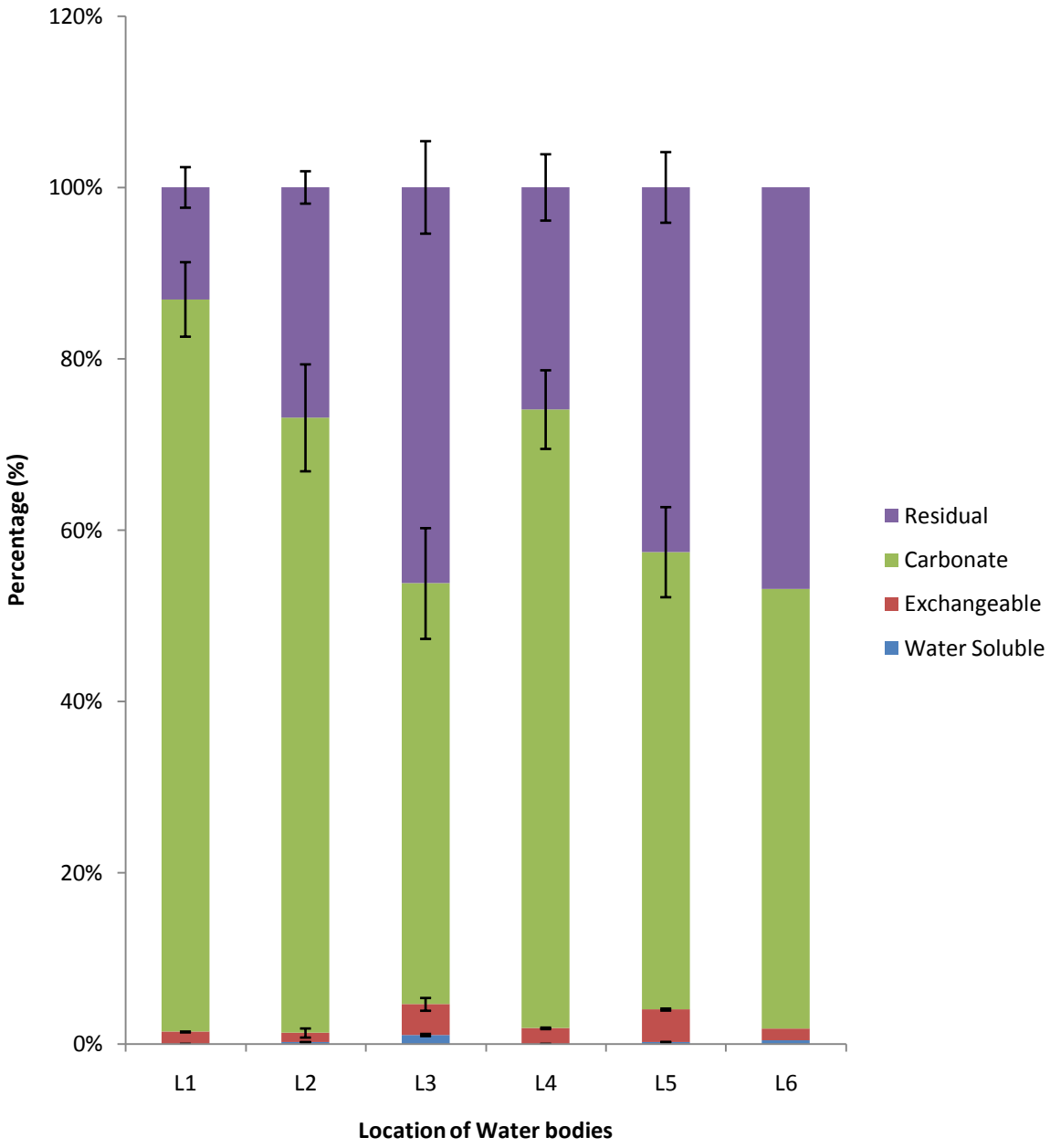


Fig 4.3: Percentage of Cr in different chemical fractions across all locations

Key:

L1	Gusau dam	L2	Bakolori dam
L3	Dangulbi dam	L4	Bagega River
L5	Sunke river	L6	Abare River

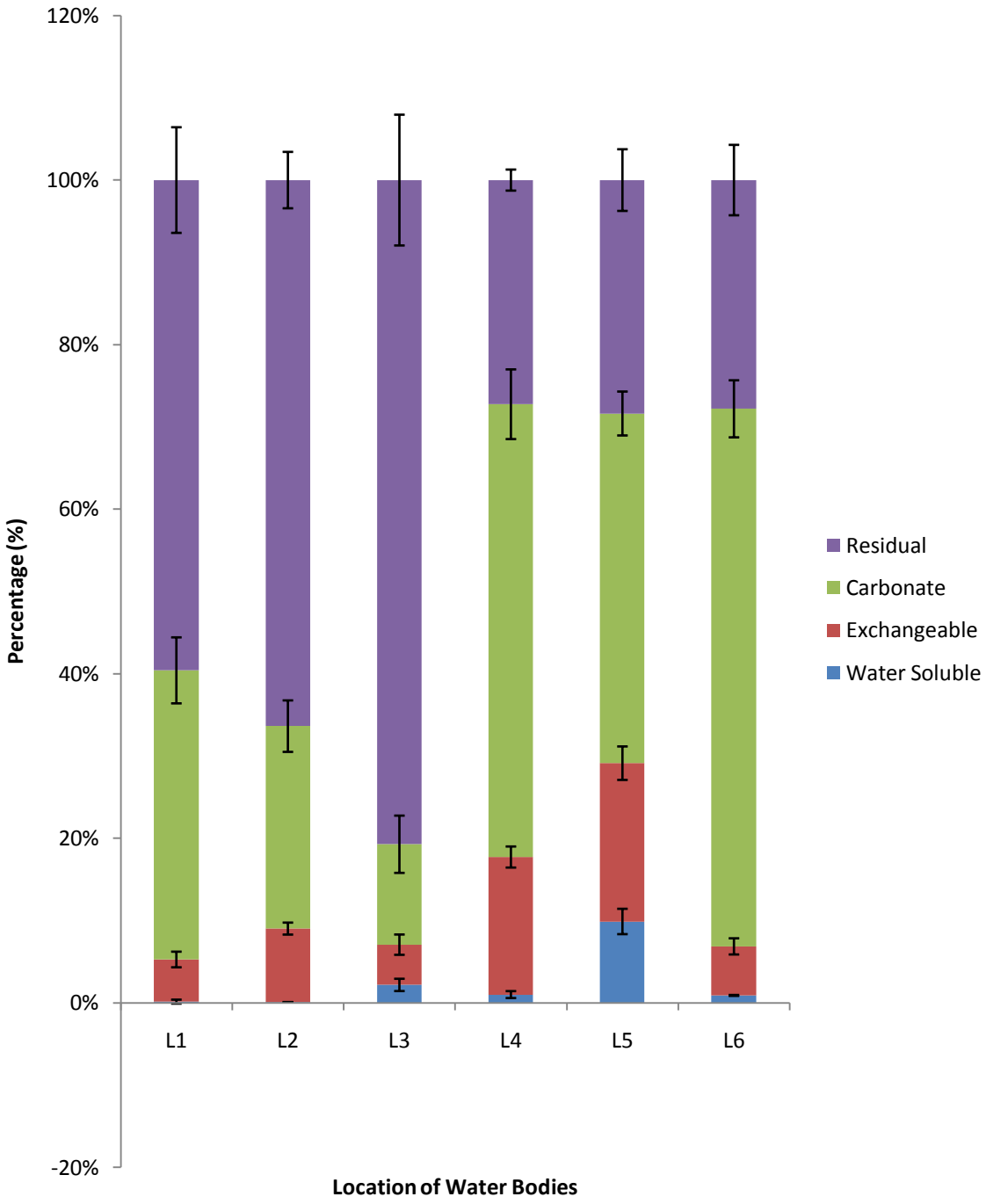


Fig 4.4: Percentage of Pb in different chemical fractions across all locations

Key:

L1	Gusau dam	L2	Bakolori dam
L3	Dangulbi dam	L4	Bagega River
L5	Sunke river	L6	Abare River

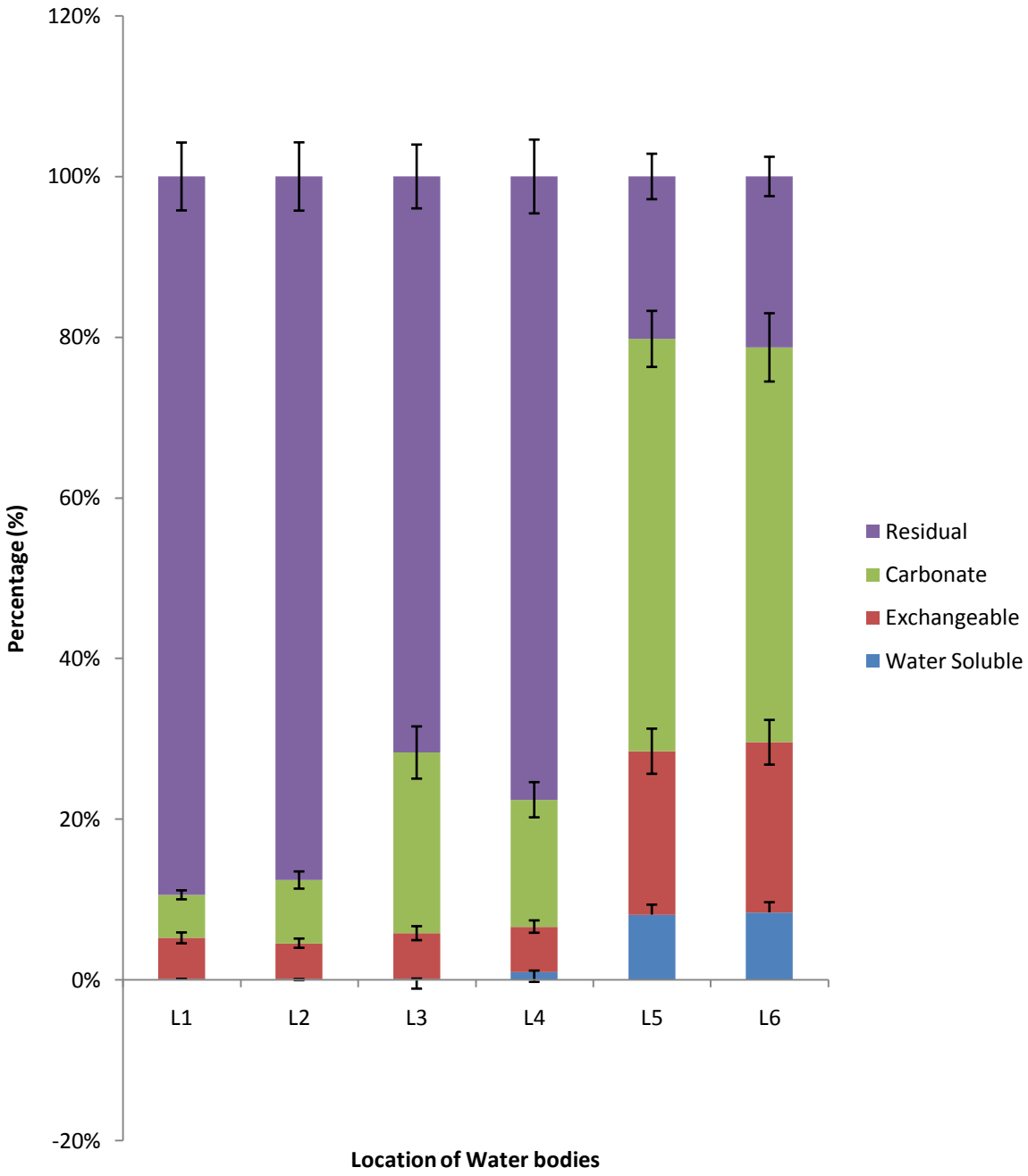


Fig 4.5: Percentage of Hg in different chemical fractions across all locations

Key:

L1	Gusau dam	L2	Bakolori dam
L3	Dangulbi dam	L4	Bagega River
L5	Sunke river	L6	Abare River

It was generally observed that the carbonate bound fraction (F3) recorded the highest percentages of Cd across all the six locations with exception of location L5 and L6 which recorded their highest percentage Cd in water soluble fraction. The residual fraction generally recorded low percentage Cd across all the locations. The percentage of Cr in different chemical fractions across all the six locations study are presented as bargraph in Fig. 4.3 and Appendix III.The percentage bioavailable fractions (F1 + F2 +F3) of Cr for Gusau, Bakolori Dangulbi dams, Bagega, Sunke and Abare rivers were 86.925%, 73.101%, 52.145%, 74.062%, 57.416% and 53.128% respectively.

It was generally observed that the carbonate bound fraction (F3) recorded high Cr percentages across all the location with exception of location L3, which recorded its highest percentage Cr in the residual fraction. The water soluble fraction F1 consistently recorded very low (below 1.5%) percentage fraction of Cr across all the six locations studied. The percentage of Pb in different chemical fractions across all the six locations study are presented as bargraph in Fig. 4.4 and Appendix IV.The percentage bioavailable fractions (F1 + F2 +F3) of Pb for Gusau, Bakolori Dangulbi dams, Bagega, Sunke and Abare rivers were 40.417%, 42.704%, 13.986%, 72.755%, 71.147% and 72.203% respectively. It was generally observed that the carbonate bound fraction (F3) recorded high Pb percentages in Bagega River (55.025%), Sunke River (42.207%) and Abare River (65.332%), while Dangulbi dam recorded the least percentage Pb (8.66%) in the exchangeable fraction. The percentage of Hg in different chemical fractions across all the six locations study are presented as bargraph in Fig. 4.5 and Appendix V.The percentage bioavailable fractions (F1 + F2 +F3) of Hg for Gusau, Bakolori Dangulbi dams, Bagega, Sunke and Abare rivers were 10.490%, 12.421%, 15.754%, 22.431%, 79.786% and 78.730% respectively. It was generally observed that predominant percentage Hg was recorded in the residual fraction across all the location with exception of Sunke (51.316%) and Abare rivers (49.145%) with high percentage Hg in the

carbonate bound fraction. Water soluble fraction generally recorded very low percentage Hg across all the locations.

4.5 Heavy Metals in Tomatoes Samples

The results obtained for metals in tomatoes samples collected from all locations around the dams and rivers in study area are presented in Table 4.15 and 4.16.The lowest concentration of Zn was recorded at Gusau dam which varied between 0.029 ± 0.0020 and 0.024 ± 0.0020 mg/kg during the wet season of 2014 and 2015 respectively. While at Abare River, the concentration of Zn recorded was the highest across all the locations, it varied between 0.128 ± 0.0020 and 0.124 ± 0.0030 mg/kg for 2014 and 2015 respectively. During the dry season, Gusau dam recorded the lowest Zn concentration which varied between 0.036 ± 0.0020 and 0.031 ± 0.0020 mg/kg for 2014 and 2015 respectively. The highest concentration of Zn was recorded at Abare River which varied between 0.420 ± 0.0020 and 0.297 ± 0.0030 mg/kg for 2014 and 2015 respectively. The lowest concentration of Zn was recorded at Gusau dam which varied between 0.029 ± 0.0020 and 0.024 ± 0.0020 mg/kg during the wet season of 2014 and 2015 respectively.

At Abare River, the concentration of Zn recorded was the highest across all the locations, it varied between 0.128 ± 0.0020 and 0.124 ± 0.0030 mg/kg for 2014 and 2015 respectively. During the dry season, Gusau dam recorded the lowest Zn concentration which varied between 0.036 ± 0.0020 and 0.031 ± 0.0020 mg/kg for 2014 and 2015 respectively. The highest concentration of Zn was recorded at Abare River which varied between 0.420 ± 0.0020 and 0.297 ± 0.0030 mg/kg for 2014 and 2015 respectively. The concentration of Cd in Gusau dam varied between 0.019 ± 0.0010 and 0.010 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cd recorded

Table 4.15: Heavy Metals Concentrations (mg/kg) of Tomatoes Samples for Two wet Seasons

location	year	Zn	Cd	Cr	Pb	Hg
L1	2014	0.029 ±0.002	0.019±0.001	0.183±0.003	0.261±0.004	0.556±0.002
	2015	0.024±0.002	0.010±0.002	0.010±0.004	0.334±0.001	1.746±0.003
L2	2014	0.039± 0.001	0.019±0.003	0.261±0.003	0.125±0.002	0.163±0.000
	2015	0.049 ± 0.001	0.012±0.002	0.012±0.003	0.396±0.001	2.202±0.003
L3	2014	0.052± 0.002	0.014±0.001	0.157±0.004	0.271±0.002	0.446±0.000
	2015	0.056±0.003	0.016±0.005	0.016±0.002	0.511±0.002	0.600±0.003
L4	2014	0.044 ±0.002	0.032±0.001	0.157±0.003	0.021±0.004	0.953±0.000
	2015	0.048±0.002	0.019±0.002	0.019±0.004	0.386±0.001	1.050±0.003
L5	2014	0.092± 0.001	0.017±0.003	0.118±0.003	0.208±0.002	ND
	2015	0.097 ±0.001	0.019±0.002	0.019±0.003	0.188±0.001	1.103±0.003
L6	2014	0.128± 0.002	0.027±0.001	0.301±0.004	0.356±0.002	ND
	2015	0.124±0.003	0.022±0.005	0.022±0.002	0.396±0.002	0.896±0.003

Key

ND: not detected

Table 4.16: Heavy Metals Concentrations (mg/kg) of Tomatoes Samples for Two dry Seasons

location	year	Zn	Cd	Cr	Pb	Hg
Gusau	2014	0.036 ±0.002	0.432±0.001	0.364±0.003	0.250±0.004	ND
	2015	0.031±0.002	0.256±0.002	0.369±0.004	0.365±0.001	4.363±0.003
Bakolori	2014	0.058± 0.001	0.216±0.003	0.324±0.003	1.074±0.002	ND
	2015	0.041± 0.001	0.334±0.002	0.314±0.003	0.500±0.001	2.527±0.003
Dangulbi	2014	0.093± 0.002	0.668±0.001	1.165±0.004	0.615±0.002	ND
	2015	0.071±0.003	0.354±0.005	1.150±0.002	0.644±0.002	1.343±0.003
Bagega	2014	0.059 ±0.002	0.668±0.001	0.199±0.003	0.354±0.004	ND
	2015	0.061±0.002	0.472±0.002	0.099±0.004	0.394±0.001	1.362±0.003
Sunke	2014	0.166± 0.001	0.729±0.003	0.126±0.003	0.511±0.002	ND
	2015	0.113 ±0.001	0.098±0.002	0.116±0.003	0.521±0.001	1.188±0.003
Abare	2014	0.420± 0.002	0.256±0.001	0.314±0.004	0.394±0.002	ND
	2015	0.293±0.003	0.491±0.005	0.334±0.002	0.719±0.002	1.293±0.003

Key

ND: Below detection

across all the locations. The highest concentration was recorded at Bagega River which varied between 0.032 ± 0.0010 and 0.019 ± 0.0020 mg/kg for 2014 and 2015 respectively.

During the dry season, Bakolori dam recorded the lowest concentration which varied between 0.216 ± 0.0030 and 0.334 ± 0.0020 mg/kg for 2014 and 2015 respectively. At Bagega River the highest value of Cd was recorded which varied between 0.668 ± 0.0010 and 0.472 ± 0.0020 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cd in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect. The concentration of Cr in Gusau Dam varied between 0.183 ± 0.0030 and 0.010 ± 0.0040 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cr recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.301 ± 0.0040 and 0.022 ± 0.0020 mg/kg for 2014 and 2015 respectively. During the dry season, Sunke River recorded the lowest concentration which varied between 0.126 ± 0.0030 and 0.116 ± 0.0030 mg/kg for 2014 and 2015 respectively while Dangulbi dam recorded the highest value of Cr which varied between 1.165 ± 0.0040 and 1.150 ± 0.0020 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cr in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

The concentration of Pb in Bagega River varied between 0.021 ± 0.0040 and 0.386 ± 0.0010 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Pb recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.356 ± 0.0020 and 0.396 ± 0.0020 mg/kg for 2014 and 2015 respectively. During the dry season, Gusau dam recorded the lowest concentration which varied between 0.250 ± 0.0040 and 0.365 ± 0.0010 mg/kg for 2014 and 2015 respectively while Bakolori dam recorded the highest value of Pb which varied between 1.074 ± 0.0020 and 0.500 ± 0.0010 mg/kg for 2014 and 2015 respectively.Generally, the

concentrations of Pb in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

The concentration of Hg in Dangulbi Dam varied between 0.466 ± 0.0000 and 0.600 ± 0.0030 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Hg recorded across all the locations. The highest concentration was recorded at Bakolori dam which varied between 0.163 ± 0.0000 and 2.202 ± 0.0030 mg/kg for 2014 and 2015 respectively. During the dry season, Sunke River recorded the lowest concentration which varied between below detection and 1.188 ± 0.0030 mg/kg for 2014 and 2015 respectively while Gusau dam recorded the highest value of Hg which varied between below detection and 4.363 ± 0.0030 mg/kg for 2014 and 2015 respectively. It was generally observed that Hg concentrations are higher in the dry seasons than their corresponding wet seasons. It was also generally observed that, the concentration of Hg was mostly below detection limit in 2014 and recorded very pronounced concentration in year 2015.

4.5.1 Correlation matrix of meavy metals concentrations (mg/kg) in tomatoes samples for two wet and dry Seasons

Correlation analysis (Table 4.17)conducted on the data to examine whether there is a relationship between the heavy metal concentrations in the tomatoes for two wet and dry seasons revealed a significant positive relationship for Cr and Cd, Cd and Zn, Hg and Pb in the wet season. A significant positive relationship for Cr and Cd, and Pb and Cr for dry season, this may explain the consistent variation of these metals in all the locations across the four seasons.

Table 4.17: Correlation matrix of Heavy Metals Concentrations (mg/kg) in Tomatoes Samples for Two Wet and Two Dry Seasons

	Correlations For wet					Correlations For dry				
	Zn	**Cd**	**Cr**	**Pb**	**Hg**	**Zn**	**Cd**	**Cr**	**Pb**	**Hg**
Zn	1					1				
Cd	.416*	1				.416*	1			
Cr	.128	.471**	1			.128	.471**	1		
Pb	.166	-.350*	-.429**	1		.166	-.350*	-.429**	1	
Hg	-.375*	-.414*	-.709**	.277	1	-.375*	-.414*	-.709**	.277	1
	36	36	36	36	36	36	36	36	36	36

*.Correlation is significant at the 0.05 level (2-tailed).

**.Correlation is significant at the 0.01 level (2-tailed).

*.Correlation is significant at the 0.05 level (2tailed).

**.Correlation is significant at the 0.01 level (2tailed)

4.5.2 Assessment of Heavy Metal Pollution in Tomatoes Samples

Contamination factor calculates for heavy metal concentration tomatoes are presented in Table 4.18. It revealed that only Hg had contamination factor (CF>>6) higher than 6 across all the location for both wet and dry seasons. The pollution load indices (PLI) for all the locations have values less than one (1) for both wet and dry season.

4.5.3 Heavy Metals in Cassava Samples

The results obtained for metals in cassava samples collected from different locations around the dams and rivers in Zamfara State are presented in Table 4.19 and 4.20.

The lowest concentration of Zn was recorded at Dangulbi dam which varied between 0.074 ± 0.0020 and 0.084 ± 0.0020 mg/kg during the wet season of 2014 and 2015 respectively. While at Gusau dam, the concentration of Zn recorded was the highest across all the locations, it varied between 0.177 ± 0.0020 and 0.197 ± 0.0020 mg/kg for 2014 and 2015 respectively. During the dry season, Dangulbi dam recorded the lowest Zn concentration which varied between 0.166 ± 0.0020 and 0.087 ± 0.0030 mg/kg for 2014 and 2015 respectively. The highest concentration of Zn was recorded at Abare River which varied between 0.380 ± 0.0020 and 0.207 ± 0.0030 mg/kg for 2014 and 2015 respectively.

The concentration of Cd in Dangulbi dam varied between 0.009 ± 0.0010 and 0.005 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cd recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.026 ± 0.0010 and 0.027 ± 0.0050 mg/kg for 2014 and 2015 respectively.

Table 4.18: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in Tomatoes for Wet and Dry Seasons.

Location/Wet	Zn	Cd	Cr	Pb	Hg	PLI
Gusau	0.0026	0.1050	0.0029	0.0383	6.1667	0.0453
Bakolori	0.0005	0.0443	0.0016	0.0164	6.0033	0.0206
Dangulbi	0.0006	0.0653	0.0018	0.0354	2.4000	0.0225
Bagega	0.0024	0.1117	0.0026	0.0368	3.0500	0.0378
Sunke	0.0013	0.0733	0.0010	0.0159	12.7800	0.0283
Abare	0.0017	1.8083	0.0057	0.0526	10.3000	0.0992
Dry						
Gusau	0.0053	1.5733	0.0132	0.1108	10.7567	0.1671
Bakolori	0.0015	2.4250	0.0054	0.0204	2.9867	0.0662
Dangulbi	0.0011	1.2450	0.0069	0.0430	8.5833	0.0915
Bagega	0.0029	2.4233	0.0143	0.1341	3.7967	0.1384
Sunke	0.0019	1.5400	0.0023	0.0199	12.7100	0.0705
Abare	4.1895	2.7166	0.0091	0.0862	11.4330	0.6328

Key

ND: Below detection

Table 4.19: Heavy Metals Concentrations (mg/kg) of Cassava Samples for Two Wet Seasons

location	year	Zn	Cd	Cr	Pb	Hg
Gusau	2014	0.177 ±0.002	0.026±0.001	0.111±0.003	0.365±0.004	ND
	2015	0.197±0.002	0.019±0.002	0.275±0.004	0.155±0.001	0.673±0.003
Bakolori	2014	0.148± 0.001	0.013±0.003	0.179±0.003	0.189±0.002	ND
	2015	0.158 ± 0.001	0.009±0.002	0.190±0.003	0.858±0.001	1.195±0.003
Dangulbi	2014	0.074± 0.002	0.009±0.001	0.190±0.004	0.219±0.002	ND
	2015	0.084±0.003	0.005±0.005	0.157±0.002	0.462±0.002	1.059±0.003
Bagega	2014	0.128 ±0.002	0.055±0.001	0.183±0.003	0.396±0.004	ND
	2015	0.122±0.002	0.005±0.002	0.183±0.004	0.281±0.001	1.112±0.003
Sunke	2014	0.130±0.001	0.026±0.003	0.248±0.003	0.271±0.002	ND
	2015	0.136±0.001	0.029±0.002	0.216±0.003	0.466±0.001	1.103±0.003
Abare	2014	0.171± 0.002	0.026±0.001	0.196±0.004	0.563±0.002	0.154±0.000
	2015	0.174±0.003	0.027±0.005	0.268±0.002	0.772±0.002	1.934±0.003

Key

ND: Below detection

Table 4.20: Heavy Metals Concentrations (mg/kg) of Cassava Samples for Two Dry Seasons

location	year	Zn	Cd	Cr	Pb	Hg
Gusau	2014	0.373 ±0.002	0.963±0.001	1.008±0.003	0.851±0.004	ND
	2015	0.183±0.002	0.806±0.002	1.018±0.004	0.744±0.001	0.874±0.003
Bakolori	2014	0.249± 0.001	0.256±0.003	0.529±0.003	0.188±0.002	ND
	2015	0.240 ± 0.001	0.197±0.002	0.548±0.003	1.636±0.001	1.900±0.003
Dangulbi	2014	0.166± 0.002	0.629±0.001	0.859±0.004	0.977±0.002	ND
	2015	0.087±0.003	0.747±0.005	0.867±0.002	1.012±0.002	1.902±0.003
Bagega	2014	0.292 ±0.002	0.924±0.001	0.970±0.003	2.545±0.004	ND
	2015	0.086±0.002	0.826±0.002	0.985±0.004	2.330±0.001	1.232±0.003
Sunke	2014	0.293± 0.001	1.081±0.003	0.711±0.003	1.669±0.002	ND
	2015	0.134 ±0.001	0.806±0.002	0.745±0.003	0.817±0.001	1.971±0.003
Abare	2014	0.380± 0.002	0.767±0.001	1.415±0.004	2.488±0.002	ND
	2015	0.207±0.003	0.806±0.005	1.405±0.002	2.612±0.002	2.839±0.003

Key

ND: Below detection

During the dry season, Bakolori dam recorded the lowest concentration which varied between 0.256 ± 0.0030 and 0.197 ± 0.0020 mg/kg for 2014 and 2015 respectively while Sunke River recorded the highest value of Cd which varied between 1.081 ± 0.0030 and 0.806 ± 0.0020 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cd in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect. The concentration of Cr in Dangulbi Dam varied between 0.190 ± 0.0030 and 0.0157 ± 0.0020 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cr recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.196 ± 0.0040 and 0.268 ± 0.0020 mg/kg for 2014 and 2015 respectively.

During the dry season, Bakolori dam recorded the lowest concentration which varied between 0.529 ± 0.0030 and 0.548 ± 0.0030 mg/kg for 2014 and 2015 respectively while Abare river dam recorded the highest value of Cr which varied between 1.415 ± 0.0040 and 1.405 ± 0.0020 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cr in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect. The concentration of Pb in Bagega River varied between 0.396 ± 0.0040 and 0.281 ± 0.0010 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Pb recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.563 ± 0.0020 and 0.772 ± 0.0020 mg/kg for 2014 and 2015 respectively. During the dry season, Gusau dam recorded the lowest concentration which varied between 0.851 ± 0.0040 and 0.744 ± 0.0010 mg/kg for 2014 and 2015 respectively while Abare River recorded the highest value of Pb which varied between 2.488 ± 0.0020 and 2.612 ± 0.0020 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Pb in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

The concentration of Hg in Gusau Dam varied between below detection limit and 0.673 ± 0.0030 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Hg recorded across all the locations. The highest concentration was recorded at Abare River which varied between 0.154 ± 0.0000 and 1.934 ± 0.0030 mg/kg for 2014 and 2015 respectively. During the dry season, Gusau dam recorded the lowest concentration which varied between below detection and 0.874 ± 0.0030 mg/kg for 2014 and 2015 respectively while Abare River recorded the highest value of Hg which varied between below detection and 2.839 ± 0.0030 mg/kg for 2014 and 2015 respectively.It was generally observed that Hg concentration are higher in the dry seasons than their corresponding wet seasons. It was also generally observed that, the concentration of Hg was mostly below detection limit in 2014 and recorded very pronounced concentration in year 2015. Summarily, the concentration of Hg was higher in the dry season than in wet season, also concentration of Zn, Cd, Cr and Pb with exception of Hg in year 2014 were higher than 2015.

4.5.4 Correlation matrix of heavy metals concentrations (mg/kg) in cassava samples for two wet and dry seasons

Correlation analysis (Table 4.21)conducted on the data to examine whether there is a relationship between the heavy metal concentrations in the cassava for two wet and dry seasons revealed a significant positive relationship for Cr and Cd, Cd and Zn, Hg and Pb in the wet season while significant positive relationship for Cr and Cd, and Pb and Cr for dry season.This explains the consistent variation of these metals in all the locations across the seasons.

Table 4.21: Correlation matrix of Heavy Metals Concentrations (mg/kg) in Cassava Samples for Two Wet and Two Dry Seasons

Correlations For wet

	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.357*	1			
Cr	.278	.138	1		
Pb	.277	.080	.052	1	
Hg	.121	-.262	.320	.646**	1
	36	36	36	36	36

*.Correlation is significant at the 0.05 level (2-tailed).

**.Correlation is significant at the 0.01 level (2-tailed).

Correlations For dry

	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.165	1			
Cr	.173	.495**	1		
Pb	.086	.328	.619**	1	
Hg	-.173	-.157	.095	.169	1
	36	36	36	36	36

**.Correlation is significant at the 0.01 level (2tailed).

4.5.5 Assessment of Heavy Metal Pollution in Cassava Samples

The calculated contamination factor (CF) for cassava samples are presented in Table 4.22. It revealed that all cassava sample analyzed had very high contamination factor (CF>>>>6) for Pb and Hg across the six locations. The contamination factor of Hg is particularly for higher than the maximum permissible limits during the dry season. Durig the dry season, the calculated contaminated factor are very high (CF>>>6) across all the locations with exception of Zn.The calculated pollution load (PLI) had values greater than one across all location for both wet and dry seasons. The pollution load indices during the dry season of all locations from Bakolori dam with PL1 value 10.0682 to Abare river with PL1 of 20.05742 are very high.

4.6 Heavy Metals in Fish Sample

The results obtained for metals in Tilapia fish (*Orechromis mosammbicus*) samples collected from all locations of the Dams and Rivers are presented in Table (4.23 - 4.24) for wet and dry respectively.The lowest concentration of Zn was recorded at Bakolori dam which varied between 0.010 ± 0.0010 and 0.010 ± 0.0040 mg/kg during the wet season of 2014 and 2015 respectively. While at Abare River, the concentration of Zn recorded was the highest across all the locations, it varied between 0.313 ± 0.0020 and 0.334 ± 0.0030 mg/kg for 2014 and 2015 respectively. During the dry season, Bakolori dam recorded the lowest Zn concentration which varied between 0.024 ± 0.0010 and 0.019 ± 0.0010 mg/kg for 2014 and 2015 respectively. The highest concentration of Zn was recorded at Abare River which varied between 0.802 ± 0.0020 and 0.447 ± 0.0030 mg/kg for 2014 and 2015 respectively. Generally, the concentrations of Zn in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

Table 4.22: Heavy Metal Contamination Factors (CF and Pollution Load Index (PLI) in Cassava for Wet and Dry Seasons.

Location/Wet	Zn	Cd	Cr	Pb	Hg	PLI
Gusau	0.0037	2.2500	1.9300	26.000	0673	3.0954
Bakolori	0.0031	1.1000	1.8450	52.3500	1195	3.2930
Dangulbi	0.0016	0.7000	1.7350	34.0500	1059	2.3335
Bagega	0.0029	3.000	1.8300	33.8500	1112	3.5876
Sunke	0.0029	2.7500	2.3200	36.8500	1103	3.7553
Abare	0.0037	2.6500	2.3200	66.7500	1044	4.3535
Dry						
Gusau	0.0056	88.4500	10.6300	79.7500	0874	12.9512
Bakolori	0.0049	22.6500	5.3850	91.2000	1902	10.0682
Dangulbi	0.0025	68.8000	8.6550	99.4500	1902	12.3297
Bagega	0.0038	87.5000	9.8300	243.7500	1232	15.7730
Sunke	0.0043	94.3500	7.4600	248.6000	1971	17.1246
Abare	0.0059	78.6500	11.0300	255.0000	2839	20.05742

Key

ND: below detection

Table 4.23: Heavy Metals Concentrations (mg/kg) of Fish Samples for Two wet Seasons

location	year	Zn	Cd	Cr	Pb	Hg
Gusau	2014	0.055 ±0.002	0.024±0.001	0.098±0.003	0.240±0.004	ND
	2015	0.057±0.002	0.198±0.002	0.261±0.004	0.198±0.001	0.887±0.003
Bakolori	2014	0.010 ± 0.001	0.014±0.003	0.092±0.003	0.177±0.002	ND
	2015	0.040 ± 0.001	0.438±0.002	0.235±0.003	0.438±0.001	0.796±0.003
Dangulbi	2014	0.021± 0.002	0.028±0.001	0.059±0.004	0.177±0.002	ND
	2015	0.028±0.003	0.448±0.005	0.072±0.002	0.448±0.002	0.476±0.003
Bagega	2014	0.011±0.002	0.021±0.002	0.137±0.002	0.188±0.002	ND
	2015	0.019± 0.002	0.188±0.001	0.216±0.003	0.178±0.002	0.567±0.003
Sunke	2014	0.045±0.001	0.024±0.003	0.196±0.003	0.302±0.001	ND
	2015	0.049±0.002	0.177±0.002	0.105±0.002	0.177±0.001	0.717±0.001
Abare	2014	0.313±0.002	0.018±0.002	0.142±0.002	0.354±0.003	ND
	2015	0.334± 0.003	0.250±0.005	0.163±0.003	0.250±0.003	0.900±0.005

Key

ND: below detection

Table 4.24: Heavy Metals Concentrations (mg/kg) of Fish Samples for Two dry Seasons

location	year	Zn	Cd	Cr	Pb	Hg
Gusau	2014	0.077 ±0.002	0.845±0.001	0.810±0.003	0.907±0.004	ND
	2015	0.075±0.002	0.201±0.002	0.850±0.004	0.479±0.001	1.176±0.003
Bakolori	2014	0.024± 0.001	0.904±0.003	0.430±0.003	0.292±0.002	ND
	2015	0.019 ± 0.001	0.538±0.002	0.433±0.003	0.677±0.001	0.871±0.003
Dangulbi	2014	0.026± 0.002	0.826±0.001	0.682±0.004	0.187±0.002	ND
	2015	0.036±0.003	0.609±0.005	0.697±0.002	0.477±0.002	0.871±0.003
Bagega	2014	0.048 ±0.002	0.432±0.001	0.694±0.003	0.605±0.004	0.219±0.002
	2015	0.017±0.002	0.275±0.002	0.681±0.004	0.792±0.001	0.581±0.003
Sunke	2014	0.088±0.001	0.550±0.003	0.390±0.003	0.615±0.002	0.876±0.003
	2015	0.066±0.001	0.511±0.002	0.397±0.003	0.828±0.001	0.839±0.003
Abare	2014	0.802± 0.002	0.963±0.001	1.300±0.004	0.386±0.002	ND
	2015	0.447±0.003	0.256±0.005	1.315±0.002	0.277±0.002	1.349±0.003

Key

ND: not detected

The concentration of Cd in Bakolori dam varied between 0.014 ± 0.0030 and 0.438 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Cd recorded across all the locations. The highest concentration was recorded at Dangulbi dam which varied between 0.028 ± 0.0010 and 0.448 ± 0.0050 mg/kg for 2014 and 2015 respectively. During the dry season, Bagega River recorded the lowest concentration which varied between 0.432 ± 0.0010 and 0.275 ± 0.0050 mg/kg for 2014 and 2015 respectively while Abare River recorded the highest value of Cd which varied between 0.963 ± 0.001 and 0.256 ± 0.005 mg/kg for 2014 and 2015 respectively.The concentration of Cr in Dangulbi Dam was the lowest it varied between 0.059 ± 0.004 and 0.072 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. The highest concentration was recorded at Abare River which varied between 0.142 ± 0.002 and 0.163 ± 0.003 mg/kg for 2014 and 2015 respectively.

During the dry season, Sunke River recorded the lowest concentration which varied between 0.390 ± 0.003 and 0.397 ± 0.003 mg/kg for 2014 and 2015 respectively while Abare River recorded the highest value of Cr which varied between 1.300 ± 0.004 and 1.314 ± 0.002 mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Cr in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect**.** The concentration of Pb in Bagega River was the lowest it varied between 0.188 ± 0.002 and 0.188 ± 0.002 mg/kg in the wet season of 2014 and 2015 respectively. The highest concentration was recorded at Abare River which varied between 0.354 ± 0.003 and 0.250 ± 0.003 mg/kg for 2014 and 2015 respectively.

During the dry season, Dangulbi dam recorded the lowest concentration which varied between 0.187 ± 0.002 and 0.477 ± 0.002 mg/kg for 2014 and 2015 respectively while Gusau dam recorded the highest value of Pb which varied between 0.907 ± 0.004 and 0.479 ± 0.001

mg/kg for 2014 and 2015 respectively.Generally, the concentrations of Pb in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect.

The concentration of Hg in Dangulbi Dam varied between below detection limit and 0.476 ± 0.0030 mg/kg in the wet season of 2014 and 2015 respectively. This also represents the lowest concentration of Hg recorded across all the locations. The highest concentration was recorded at Abare River which varied between below detection limit and 0.900 ± 0.0050 mg/kg for 2014 and 2015 respectively. During the dry season, Dangulbi dam recorded the lowest concentration which varied between below detection and 0.585 ± 0.0030 mg/kg for 2014 and 2015 respectively while Abare River recorded the highest value of Hg which varied between below detection and 1.349 ± 0.0030 mg/kg for 2014 and 2015 respectively.It was generally observed that Hg concentration are higher in the dry seasons than their corresponding wet seasons. It was also observed that, the concentration of Hg was mostly below detection limit in 2014 and recorded very pronounced concentration in year 2015.

4.6.1 Correlation matrix of heavy metals concentrations (mg/kg) in fish samples for two wet and dry seasons

Correlation analysis (Table 4.25) conducted on the data to examine whether there is a relationship between the heavy metal concentrations in the fish sample for two wet and dry seasons. The result revealed a significant positive relationship for Pb and Cd, Hg and Cd and Hg and Cr respectively for wet seasons.This explains the consistent variation of these metals in the locations in a particular season. While during the dry seasons, a significant negative relationship was established for Pb and Zn, Pb and Cr and Hg and Cd then a significant and positive relationship for Cr and Zn respectively. This explains the different sources of these metals in the environmental samples.

Table 4.25: Correlation matrix of Heavy Metals Concentrations (mg/kg) in Fish Samples for Two Wet and two dry seasons

Correlations For wet

	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	-.083	1			
Cr	.055	.266	1		
Pb	.162	.633**	.111	1	
Hg	.118	.763**	.530**	.137	1
	36	36	36	36	36

**.Correlation is significant at the 0.01 level (2-tailed).

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Correlations For dry

	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.228	1			
Cr	.823**	-.023	1		
Pb	-.334*	-.206	-.371*	1	
Hg	-.040	-.828**	.025	.082	1
	36	36	36	36	36

**.Correlation is significant at the 0.01 level (2tailed).

*.Correlation is significant at the 0.05 level (2tailed)

4.6.2 Assessment of Heavy Metal Pollution in Fish Samples

The calculated contamination factor (CF) for fish samples are presented in Table 4.26. It revealed that all the fish samples analyzed had very high contamination factor (CF>>>6) for Cd, Pb and Hg across all the location during the wet season. While during the dry season, the contamination factor (CF) were very high (CF>>>6) for all the metals with exception Zn.

The pollution load indices (PLI) for all the location had value far greater than 1. This indicates a serious overall pollution load on the fish sample in both wet and dry seasons.

4.7 Proximate Composition (%) of Fish Samples

The results of proximate composition (%) of fish samples collected from dams and rivers in Zamfara State for wet and two seasons of 2014 and 2015 respectively are presented in Table 4.27 – 4.28.

4.7.1 Moisture content

Bagega River recorded the lowest ash across all the six locations, it varied between 71.05 and 69.85% for wet and the same was also recorded in dry season for 2014 and 2015 respectively, while at Dangulbi dam, the moisture content of the fish varied between 77.71 and 77.11%, 74.18 and 74.01% for the wet and dry seasons of 2014 and 2015respectively. This also represents the highest moisture content across all the six locations investigated. Generally, the moisture content of the fish sample where generally high in the wet season than in the dry season. This suggests seasonal variation effect.

4.7.2 Ash content

The percentage ash content of the fish at Bakolori dam, recorded the lowest percentage ash content which varied between 7.02 and 6.06%, 5.94 and 4.94 % for wet and dry seasons of 2014 and 2015 respectively.

Table 4.26: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in Fish for Wet and Dry Seasons.

Location/Wet	Zn	Cd	Cr	Pb	Hg	PLI
Gusau	0.0011	11.0000	1.7950	21.9000	887	3.3621
Bakolori	0.0005	22.6000	1.6350	30.7500	796	3.4103
Dangulbi	0.0005	23.8000	0.6550	31.2500	476	2.5769
Bagega	0.0003	10.4500	1.7650	18.8000	567	2.2602
Sunke	0.0009	10.0500	1.5050	23.9500	717	2.9768
Abare	0.0065	13.4000	1.5250	30.2000	900	5.1417
Dry						
Gusau	0.0015	52.3000	8.3000	69.300	1176	8.8331
Bakolori	0.0004	72.1000	4.3150	48.4500	871	5.6278
Dangulbi	0.0006	71.7500	6.8750	33.200	585	5.6886
Bagega	0.0007	35.3500	6.8750	69.8800	400	5.3575
Sunke	0.0015	53.0500	3.9350	72.1500	857.5	7.2398
Abare	0.0124	60	13.0750	33.1500	1349	13.4801

Key

ND: below detection

Table 4.27: Proximate Composition (%) of the Fish Samples from Dams and Rivers in Zamfara State in both Wet and Dry Seasons of 2014

	Location of Water Body											
	Gusau		**Bakolori**		**Dangulbi**		**Bagega**		**Sunke**		**Abare**	
PC	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
M	76.48 ± 3.03	74.17 ± 2.90	75.69 ± 2.36	72.85 ± 3.52	77.71 ± 1.08	74.18 ± 4.37	71.05 ± 6.01	69.85 ± 4.60	72.51 ± 5.20	68.07 ±2.83	73.56±6.14	72.89 ± 6.69
A	7.32 ± 1.09	7.77 ± 0.30	7.02 ± 3.31	5.94 ± 2.08	6.30 ± 2.71	6.43 ±2.97	10.20 ± 0.20	8.76 ± 1.39	6.64 ± 2.50	6.77 ± 2.68	7.94 ± 0.86	7.35 ± 0.99
P	65.49 ± 3.30	65.84 ± 3.98	63.35 ± 4.41	63.48 ±10.73	61.74 ± 5.95	60.41 ± 7.25	60.78 ± 8.16	59.51 ± 3.45	62.23 ± 1.48	62.01 ± 7.79	60.12 ± 1.36	61.09 ± 3.47
Fa	10.28 ± 1.82	10.74 ± 2.86	8.59 ± 3.28	10.53 ± 6.48	11.67 ± 0.65	13.53 ± 4.21	11.34 ± 4.11	10.90 ± 2.73	10.30 ± 1.91	12.31 ± 5.35	11.00 ± 0.51	10.95 ± 0.79
Fi	10.30 ± 0.83	10.15 ± 1.56	9.51 ± 2.17	8.95 ± 3.70	11.22 ± 1.47	10.44 ± 2.55	10.18 ± 2.29	9.72 ± 2.99	10.64 ± 1.45	10.49 ± 2.37	9.31 ± 0.31	9.54 ± 0.53
C	6.61 ± 4.04	5.50 ± 4.77	8.79 ± 2.42	10.17 ± 4.69	9.39 ± 3.52	8.93 ± 3.90	7.48 ± 3.12	10.20 ± 3.26	10.51 ± 2.08	8.43 ± 2.95	11.29 ± 2.28	10.74 ± 4.26
OM	92.68 ± 1.10	92.23 ± 0.30	92.98 ± 3.31	94.06 ± 2.09	93.70 ± 2.71	93.30 ± 2.52	89.80 ± 0.20	91.25 ± 1.40	93.36 ± 2.50	93.23 ± 2.68	91.73 ± 0.32	92.32 ± 0.73

n = 3; mean ± S.D

KEY: PC = Proximate composition; M= Moisture; A = Ash; P = Protein; Fa = Fat; Fi = Fibre; C = Carbohydrate; OM = Organic Matter

Table 4.28: Proximate Composition (%) of the Fish Samples from Dams and Rivers in Zamfara State in both Wet and Dry Seasons of 2015

	Location of Water Body											
	Gusau		**Bakolori**		**Dangulbi**		**Bagega**		**Sunke**		**Abare**	
PC	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
M	76.45 ± 3.03	76.14 ± 2.90	74.67 ± 2.36	71.85 ± 3.52	77.11 ± 1.08	74.01 ± 4.37	71.05 ± 6.01	69.85 ± 4.60	72.51 ± 5.20	68.07 ±2.83	71.56±6.14	70.89 ± 6.69
A	6.32 ± 1.09	6.77 ± 0.30	6.06 ± 3.31	4.94 ± 2.08	6.33 ± 2.71	6.63 ±2.97	11.21 ± 0.20	9.74 ± 1.39	6.64 ± 2.50	6.77 ± 2.68	7.94 ± 0.86	7.35 ± 0.99
P	65.48 ± 3.30	65.81 ± 3.98	63.35 ± 4.41	63.48 ±10.73	61.70 ± 5.95	59.41 ± 7.25	60.78 ± 8.16	59.51 ± 3.45	62.23 ± 1.48	62.01 ± 7.79	62.12 ± 1.36	63.09 ± 3.47
Fa	11.28 ± 1.82	11.74 ± 2.86	8.59 ± 3.28	10.53 ± 6.48	11.60 ± 0.65	13.51 ± 4.21	11.34 ± 4.11	10.90 ± 2.73	10.30 ± 1.91	12.31 ± 5.35	11.00 ± 0.51	10.95 ± 0.79
Fi	10.39 ± 0.83	10.19 ± 1.56	10.51 ± 2.17	9.95 ± 3.70	10.72 ± 1.47	10.21 ± 2.55	10.18 ± 2.29	9.72 ± 2.99	10.94 ± 1.45	10.78 ± 2.37	9.31 ± 0.31	9.54 ± 0.53
C	6.45 ± 4.04	5.40 ± 4.77	8.79 ± 2.42	10.17 ± 4.69	9.39 ± 3.52	8.93 ± 3.90	7.48 ± 3.12	10.20 ± 3.26	10.21 ± 2.08	8.43 ± 2.95	11.20 ± 2.28	10.20 ± 4.26
OM	93.68 ± 1.10	93.23 ± 0.30	93.98 ± 3.31	95.06 ± 2.09	93.64 ± 2.71	93.21 ± 2.52	88.81 ± 0.20	90.22 ± 1.40	93.36 ± 2.50	91.87 ± 2.68	91.73 ± 0.32	92.32 ± 0.73

n = 3; mean ± S.D

KEY: PC = Proximate composition; M= Moisture; A = Ash; P = Protein; Fa = Fat; Fi = Fibre; C = Carbohydrate; OM = Organic Matter

At Bagega river recorded the highest ash content which varied between 10.20 and 11.21%, 8.76 and 9.74 % for wet and dry seasons respectively. Generally, the ash content of the fish sample from all the location are high in the dry season than the wet season. This also suggests seasonal variation.

4.7.3 Protein content

The percentage protein of the fish samples at Gusau dam varied between 65.49 and 65.84 for wet and dry of 2014, while it varied between 65.48 and 65.82 for wet and dry of year 2015. It also represent the highest protein content measured across all the six locations. Dangulbi dam recorded the lowest protein content which varied between 60.78 and 60.51 %, for wet and dry seasons of 2014 while in 2015 it varied between 60.70 and 59.41 %, for wet and dry seasons respectively. Generally, the % protein content for all the fish from all six locations are slightly higher in the wet seasons than in the dry seasons.

4.7.4 Fat content

The percentage fat content at Bakolori dam varied between 8.59 and 10.53 % for the wet and dry seasons of 2014 and varied between 8.59 and 10.52 % for wet and dry of 2015. It also represents the lowest recorded across all the six locations studied. At Dangulbi dam, the fat content varied between 11.67 and 13.53 % for wet and dry season of 2014 while in 2015 it varied between 11.60 and 13.51 % for wet and dry respectively. This also represents the highest fat content of all the fish in all locations under study.

4.7.5Percentage Fibre

The percentage fibre content of fish in Bakolori dam recorded the lowest percentage which varied between 9.51 and 10.51 for wet and dry in year 2014, while varied between 8.95 and 9.95 for wet and dry seasons of 2015 respectively, while at Dangulbi dam the percentage fibre content varied between 11.22 and 10.72 for wet and dry of 2014, while it

varied between 10.44 and 10.21 for wet and dry seasons of 2015 respectively. This equally represent the highest recorded across all the six locations.

4.7.6 Carbohydrate

The percentage carbohydrate content of At Gusau dam, varied between 6.61 and 5.50 for wet and dry season of 2014 and varied between 6.45 and 5.40 for 2015 respectively. This represents the lowest carbohydrate content of all the locations under study. While at Abare River, percentage carbohydrates varied between 11.29 and 10.74 for wet and dry seasons of 2014, while in 2015 it varied between 11.20 and 10.20 for wet and dry respectively. Again this represents the highest percentage carbohydrate content across all the locations under study.

4.7.7 Organic Matter

Bakolori dam recorded the highest percentage organic matter content which varied between 92.98 and 93.98 for wet and dry of 2014, while in 2015 it varied between 94.06 and 95.06 for wet and dry season of 2015 respectively, while at Bagega river the percentage organic matter content varied between 89.80 and 88.81 for wet and dry of 2014, while in 2015 it varied between 91.25 and 90.22 % for wet and dry season of 2015 respectively. This represents the lowest percentage carbohydrate content across all the six locations.

A two way ANOVA analysis of variance ($P < 0.05$) conducted on the fish showed that there is no significant difference from one location to another and on the seasons (Appendix LXII – LXVIII).

4.8 Microbiological Analysis of the Water Samples

The total bacteria counts of the water samples from all the six locations are shown in Table 4.29 for both dry and wet seasons. The total Baterial count for Gusau dam to Dangulbi dam ranged between 2.4 x 10^5 to 6.4 x 10^5 cful/ml and that of Bagega river to Abare river ranged between 6.4 x 10^5 to 7.9 x 10^5cful/ml during the dry seasons while in the wet seasons it ranged between 3.6 x 10^6 to 7.4 x 10^6cful/ml and 7.8 x10^6 to 8.87 x 10^6 cful/ml for the dams and rivers respectively.

The most probable number (MPN) determination were shown in Table 4.30 for both dry and wet seasons for water samples from all the six locations (dams and rivers) in Zamfara State. The probable number in the dry seasons for Gusau dam to Dangulbi dam ranged between 20 – 50 Coli-form per 100 ml, while for Bagega river to Abare river it ranged between 33 - 67 coli-form per 100 ml. The result further revealed that during the wet season the probable number for the dams ranged between 35-67 coli-form per 100 ml, while for the rivers it ranged between 43 – 89 Coli-form per 100 ml. The most probable number (MPN) values for the rivers are higher than that of the dams. The most probable number (MPN) for Dangulbi dam was highest amongst dams which ranged between 60 - 67 coli-form per 100 ml. This suggests that the dam has more dead material and runoffs in them. Generally, The MPN values for the wet seasons were higher than for the dry seasons

4.9 HistopathologyObservation of the Tilapia Fish (*OrechromisMosammbicus)* from all the Locations

Histopatholoigcal changes in the fish sample tissues were examined and results are as presented below.

Table 4.29: Total Bacterial Count Cful/ml of Water Samples For Dry and Wet Season

Name	Year	Dry x 10^5	Wet x10^6
Gusau dam	2014	2.4	3.6
	2015	3.2	4.5
Bakolori dam	2014	4.8	5.7
	2015	4.1	4.5
Dangulbi dam	2014	6.4	7.4
	2015	5.2	6.2
Bagega river	2014	6.4	7.8
	2015	7.4	7.9
Sunke river	2014	7.4	8.5
	2015	7.8	8.3
Abare river	2014	7.9	8.6
	2015	7.8	8.9

Table 4.30: MPN Determination Using Multiple Tube for Dry and Wet Water Sample

		MPN/100ml	
Name	**Year**	**Season**	
		Wet	**Dry**
Gusau dam	2014	35	25
	2015	42	31
Bakolori dam	2014	41	20
	2015	39	28
Dangulbi dam	2014	60	47
	2015	67	50
Bagega river	2014	45	35
	2015	43	33
Sunke river	2014	67	50
	2015	80	63
Abare river	2014	75	53
	2015	89	67

4.9.1 Histopathological observation of the gills

The gills of a fish comprise of multifunctional organs (respiration, ion regulation, acid-base balance and nitrogenous waste regulation, excretion), which constitute over 50 percent of the total surface area of the fish that make it sensitive to chemicals in water. The fish gills play an important role in maintaining ionic homeostasis in both freshwater and marine environment. Consequently, injury to gill epithelium is a common response observed in fish exposed to a variety of contaminants(Mohamed, 2009).

The results of histopathological studies are presented in Plate 4.1 – 4.6**.**The slide for Gusau dam was damaged during the processing time and could not be recovered. It was observed that all the fish gills from Gusau dam to Abare River were injured. The severity of damage to the gills depends on the concentration of the toxicants available in the different dams and rivers. The gills of Bakolori dam, Bagega to Abare River were more damaged when compared with other location of this studies. It was also observed that the sample gills of Bakolori dam and Dangulbi dam when compared with the control (Plate 4.1)**,**the lamellar epithelial cells were lifted away from the basement membrane due to penetration of fluid, this is the most common lesion, which could give rise to reduced respiratory gas exchange by increasing diffusion distance and decreasing interlamellar distance. For the gills of Bagega, Sunke and Abare River fusion of neighboring lamellae and epithelial rupture are observed. It was also observed that there was a swelling of the necrosis for all the locations except for Gusau dam, a situation which would increase diffusion of ions and water.

4.9.2 Histopathology changes of liver

In general, liver is a target organ due to its large blood supply that causes noticeable toxicant exposure and accumulation and also its clearance function and its pronounced metabolic capacity (Mohamed, 2009). The slides of fish liver for all the locations including the control are presented in Plates 4.7 – 4.13

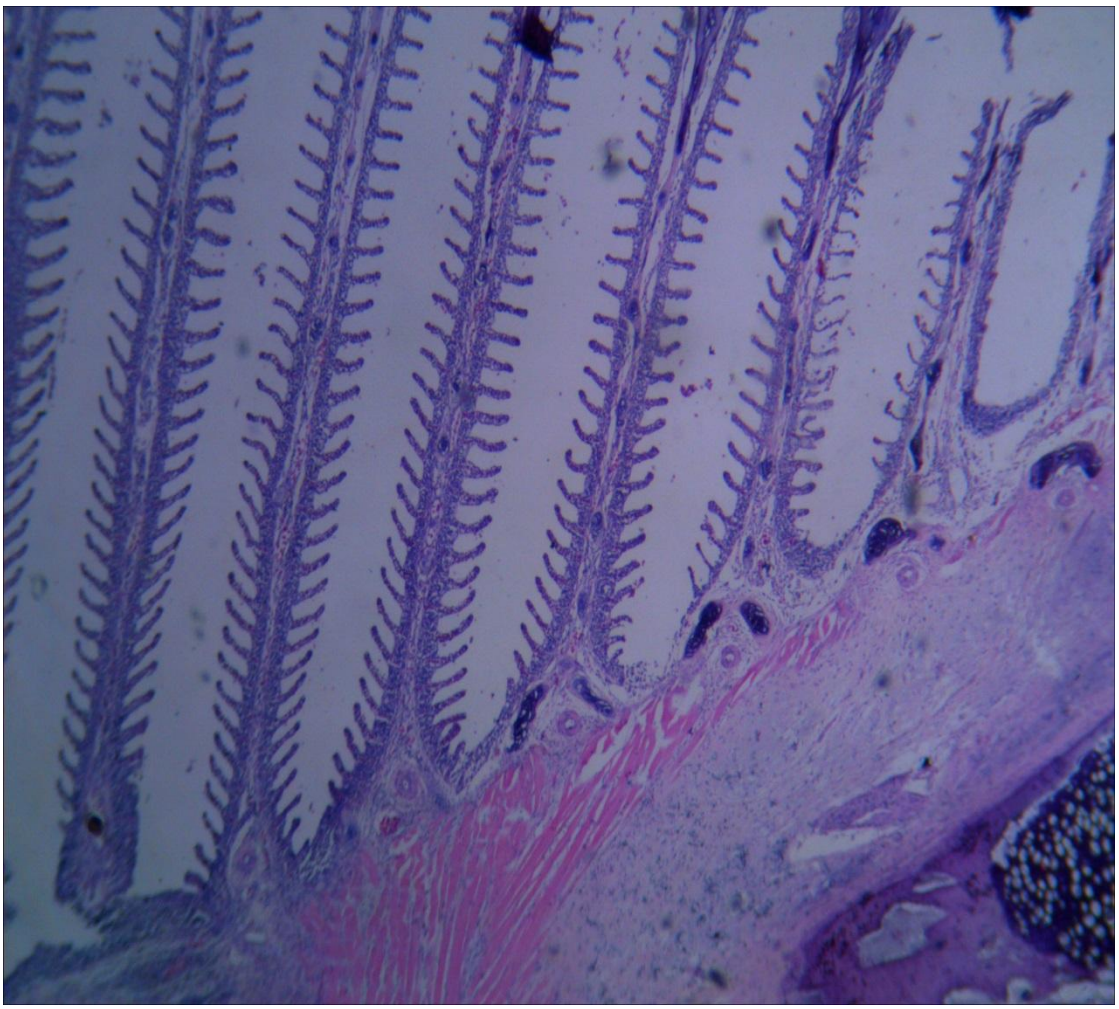


PLATE 4.1:Histopathology of Control fish gills (H&E; x40)

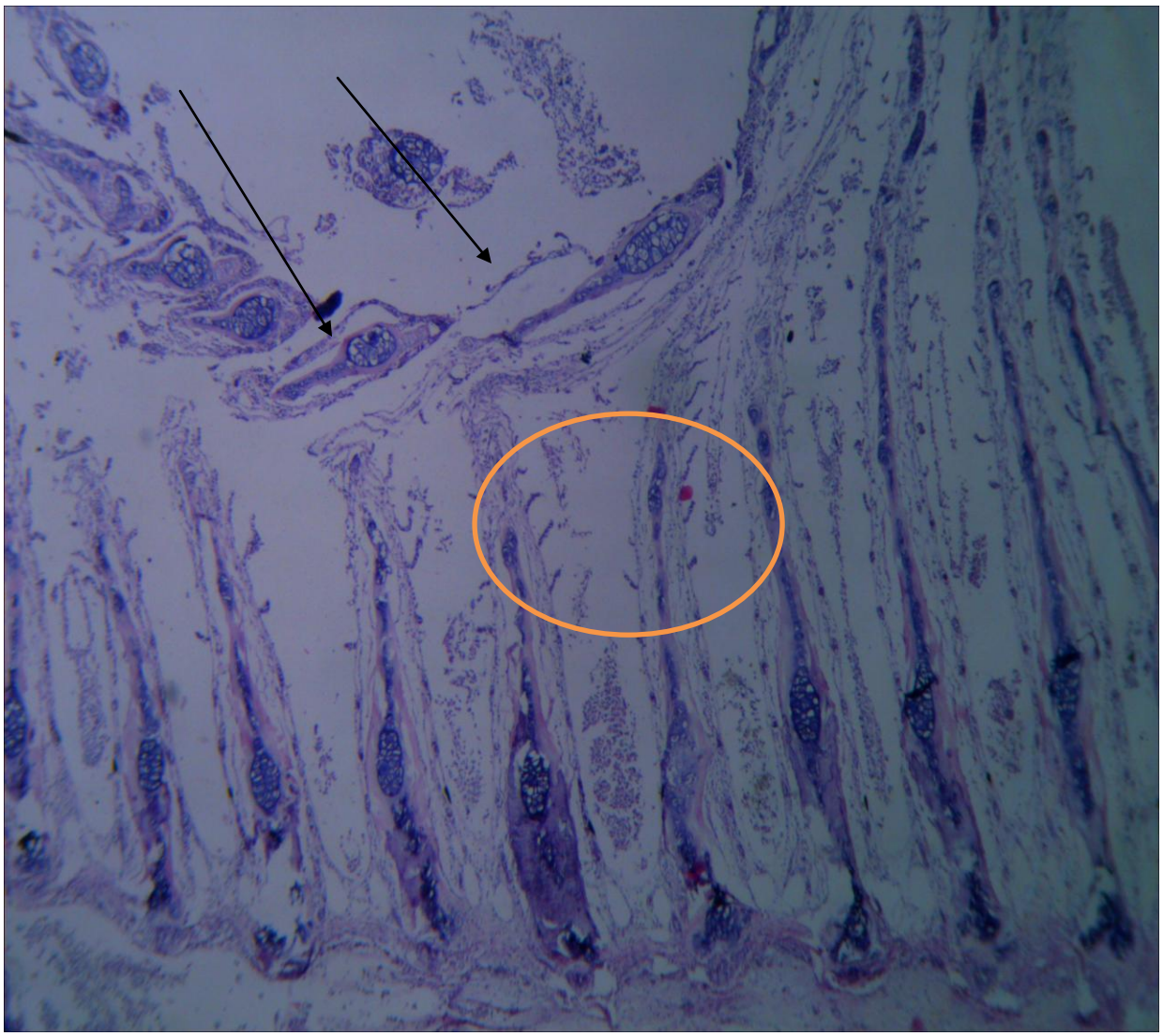


Plate 4.2: Histopathology of Bakolori dam fish gills (H & E x40) Report: Photomicrograph of section from gill showing thin and curling secondary lamellae (arrow head); desquamation and necrosis of gill epithelium (green circle)

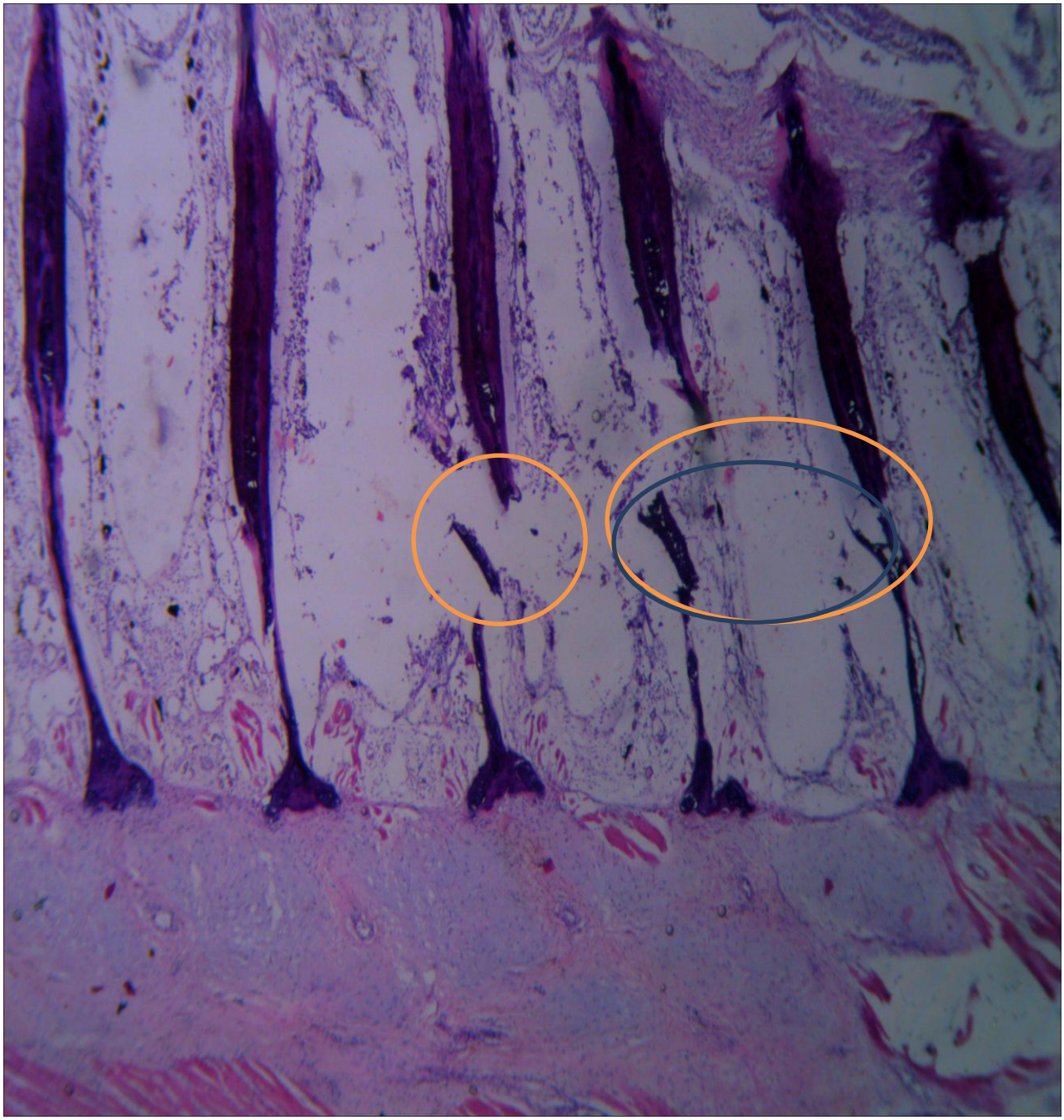


Plate 4.3:Histopathology of Dangulbi dam fish gills(H&E; x40). Report: Photomicrograph of section of gill showing disappearance of secondary lamellae, disintegration and destruction of gill epithelium (green circles).

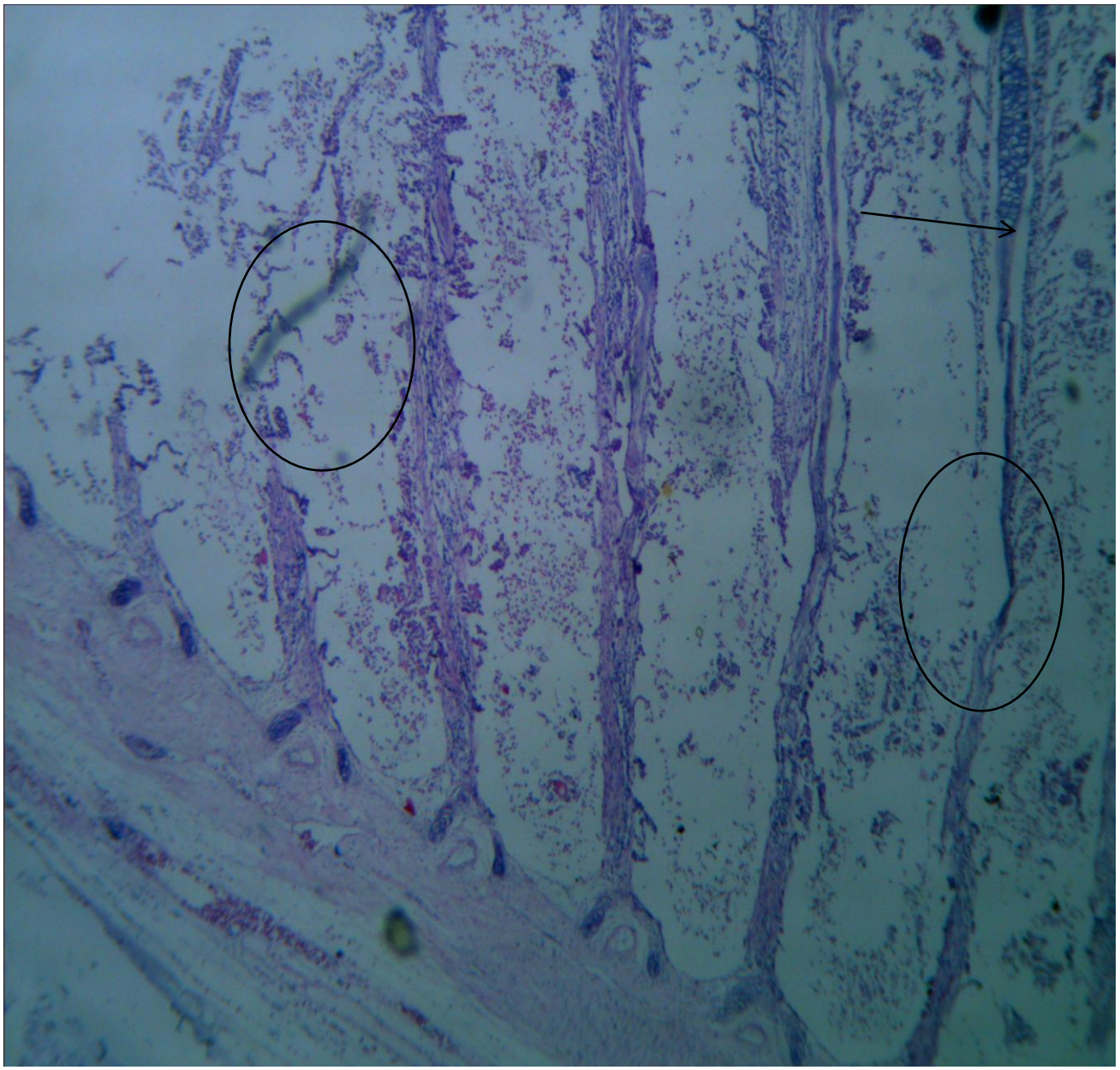


Plate 4.4:Histopathology of Bagega river fish gills(H&E; x40) Report: Photomicrograph of section of gill showing disappearance of secondary lamellae, disintegration and destruction of gill epithelium (black circles). Desquamation and necrosis of primary gill epithelial cells (black arrow)

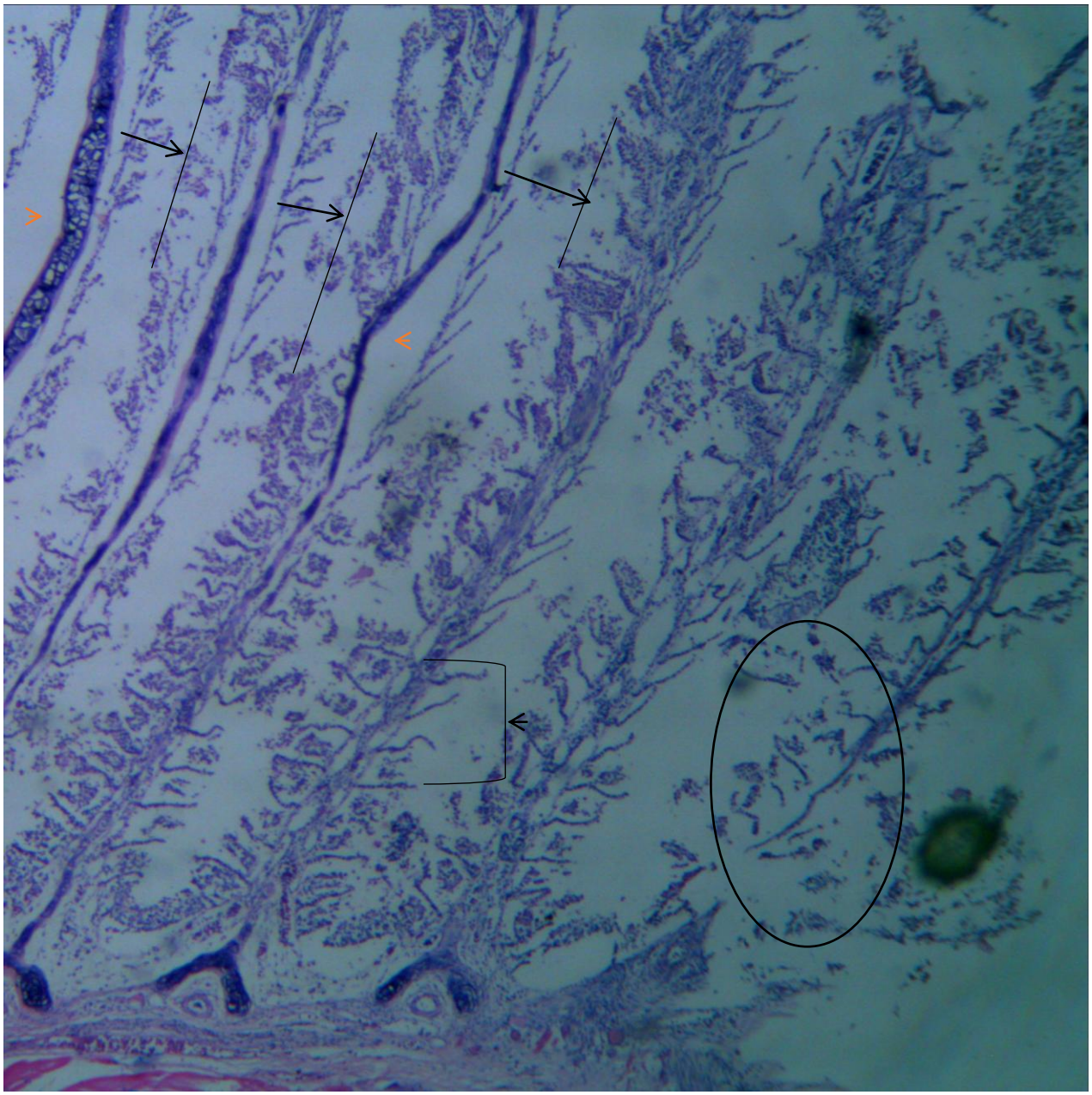


Plate 4.5:Histopathology of Sunke river fish gills (H&E; x40). Report: Photomicrograph of section from gill showing thin and curling secondary lamellae (arrow head); desquamation and necrosis of gill epithelium (arrows & bars); complete disintegration of primary gill and epithelium (black circle).

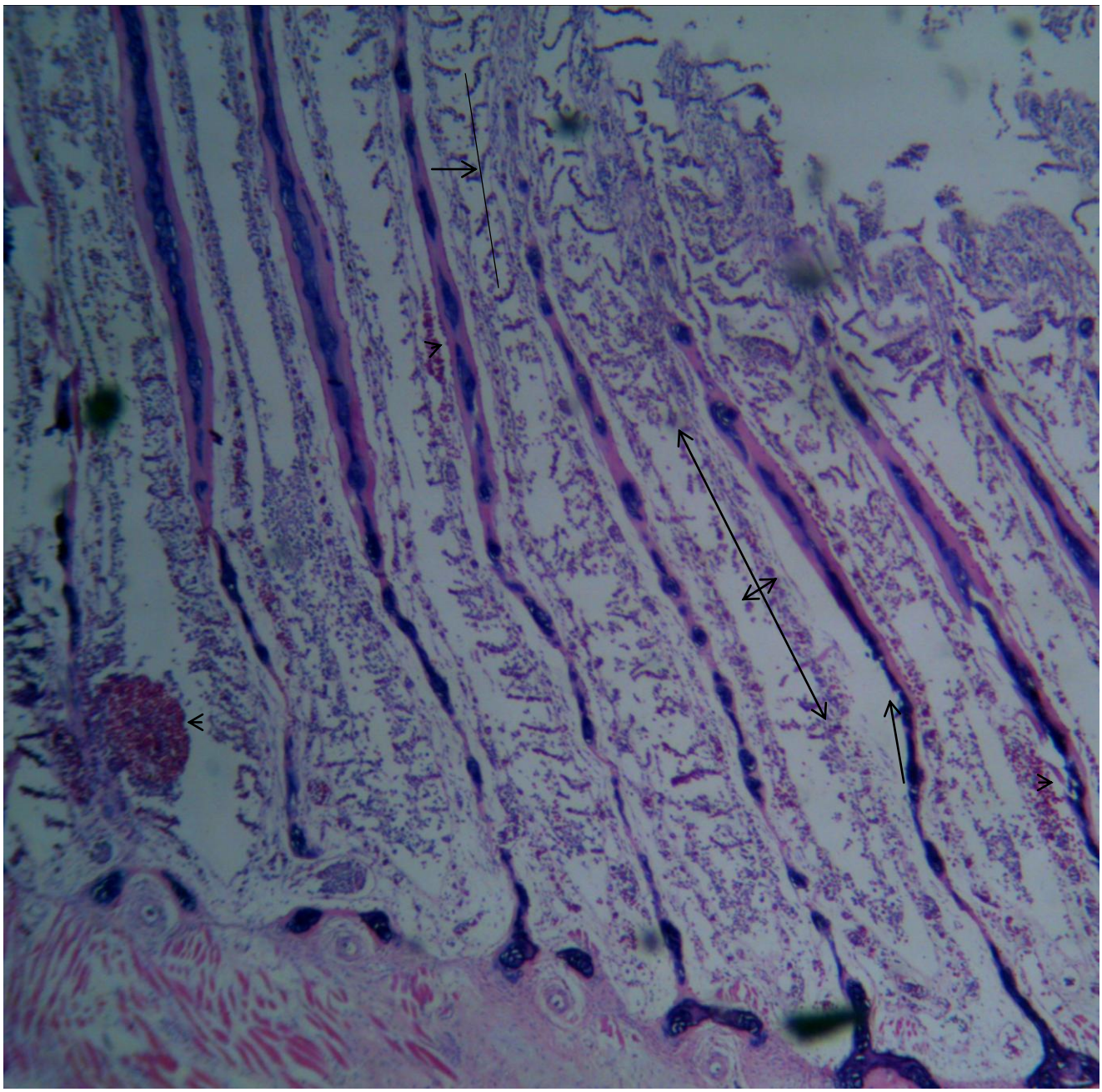


Plate 4.6: Histopathology of Abare river fish gills(H&E; x40). Report: Thinning and curling of secondary lamellae (arrow & bar); desquamation and necrosis of gill epithelial cells (cross double head arrows); oedematous changes (long arrow) and haemorrhage (arrow heads).

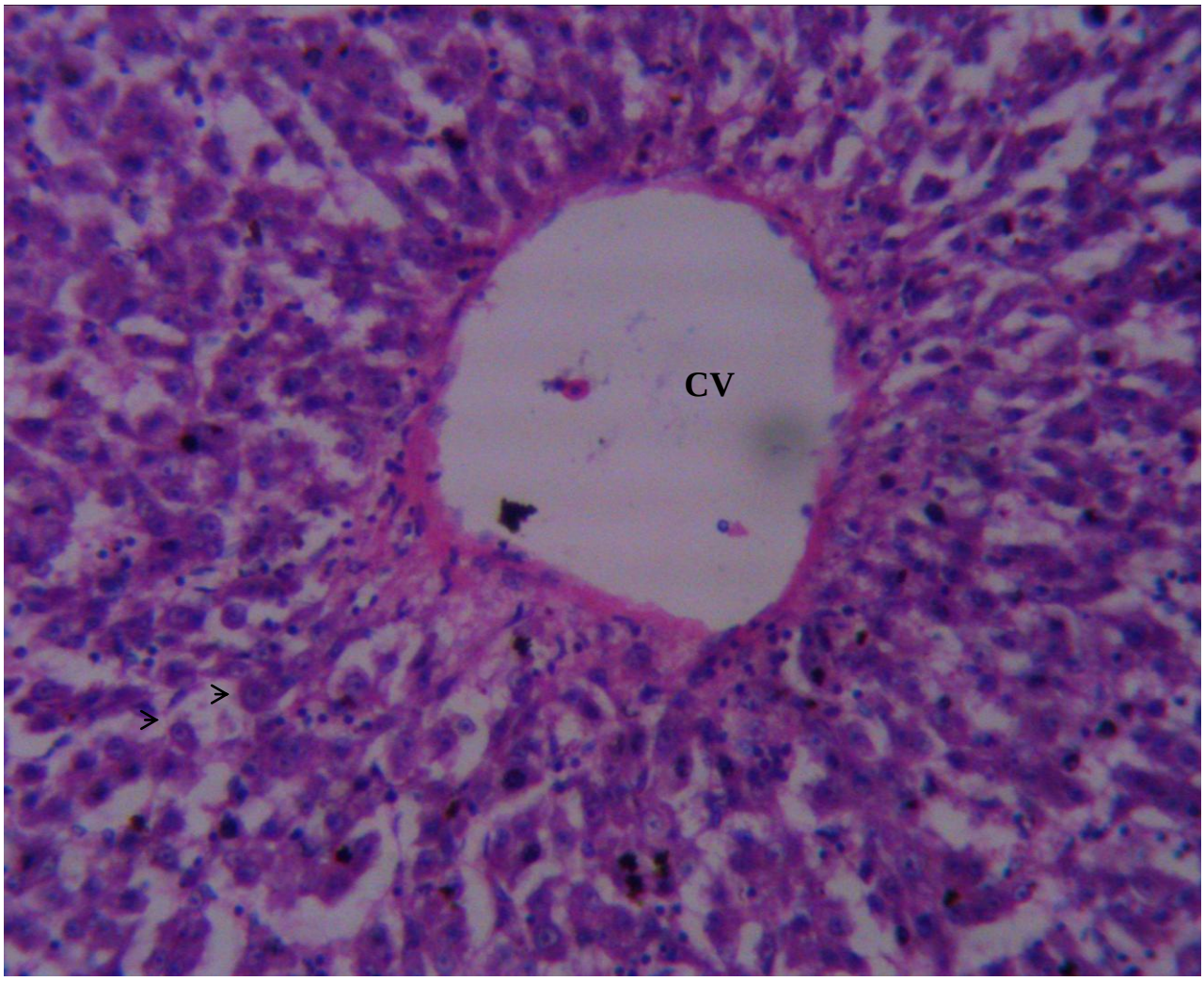


Plate 4.7:Histopathology of Control Liver (H&E; x250). Report: Photomicrograph of section from liver of *T. masonbis* showing the normal cellular pattern of the liver histo-architecture.Normal cv (central vein), hepatocytes (arrow heads)

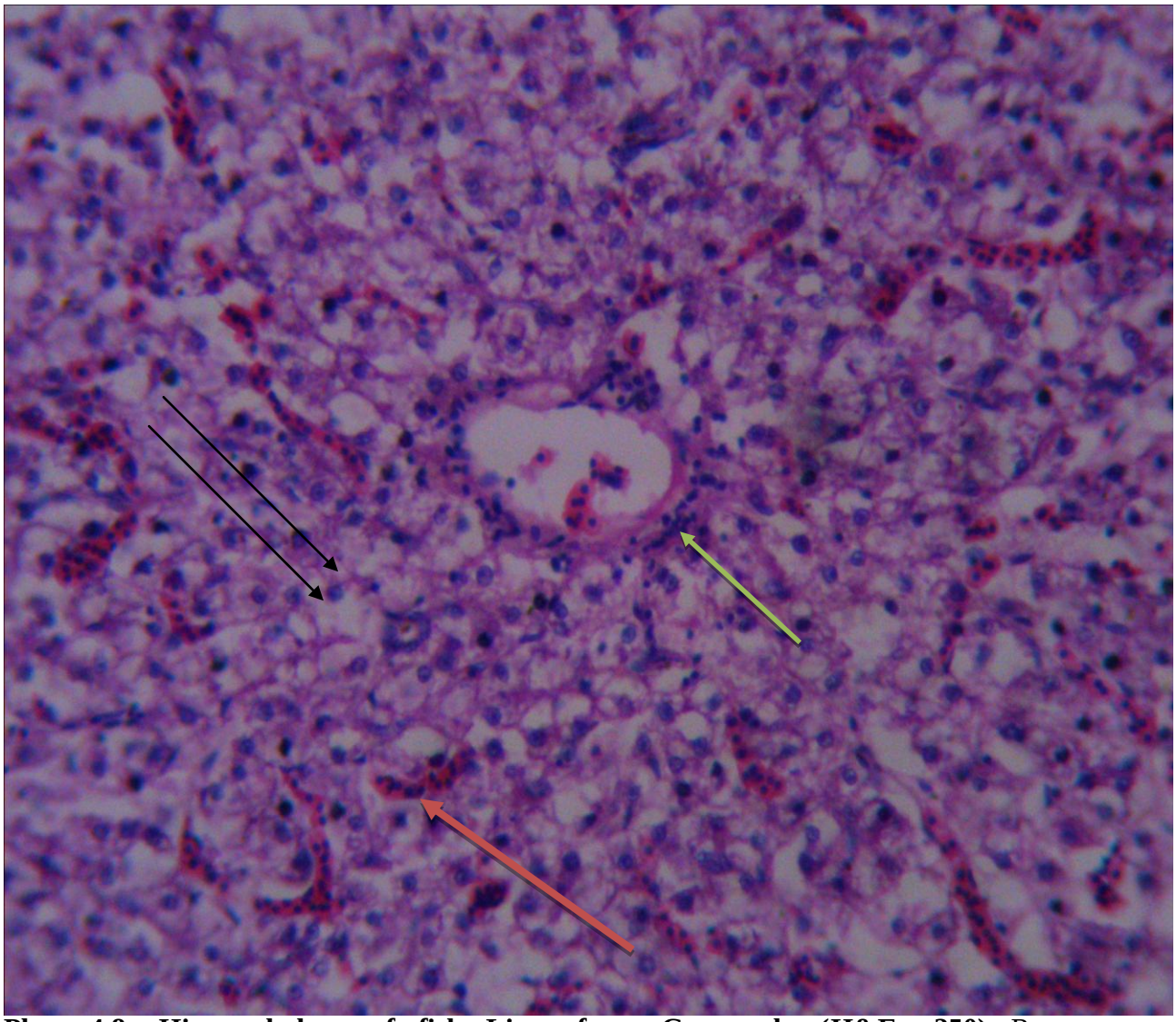


Plate 4.8: Histopathology of fish Liver from Gusau dam(H&E x250) Report: Photomicrograph of section from liver showing a distorted cellular pattern of the liver. Hepatocellular microvesicular fatty changes seen (double black arrow); necrosis of hepatocytes pyknotic nuclei- (long red arrow) and mononuclear cells infiltration (green arrow) was observed.

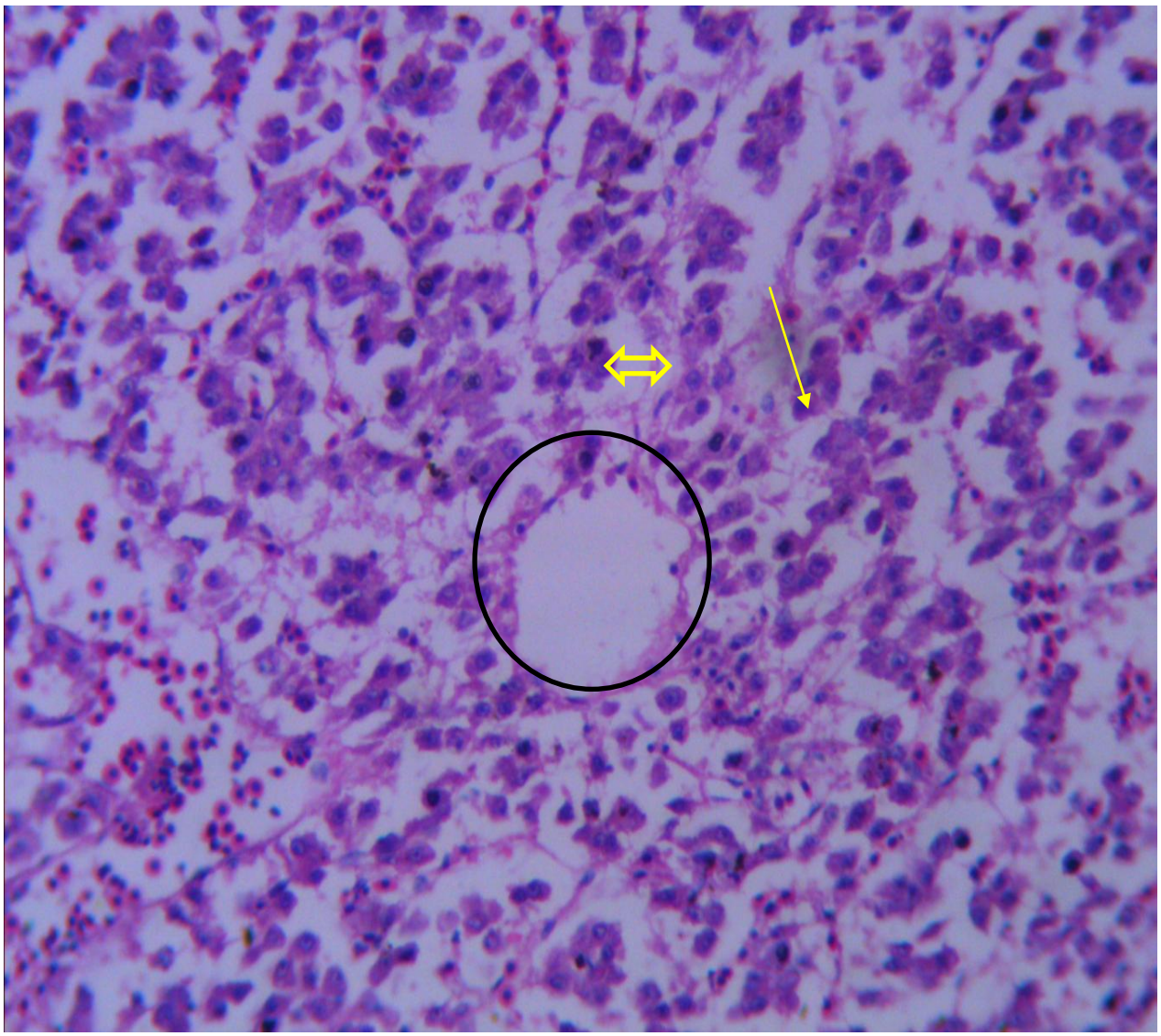


Plate 4.9:Histopathology of fish Liver from Bakolori dam(H&E x250) Report: Photomicrograph of section from liver showing a distorted cellular pattern of the liver. Hepatocellular microvesicular fatty changes seen (double yellow arrow heads); necrosis of hepatocytes pyknotic nuclei- (long arrow); and much reduced central nervous system (black circle) was observed.

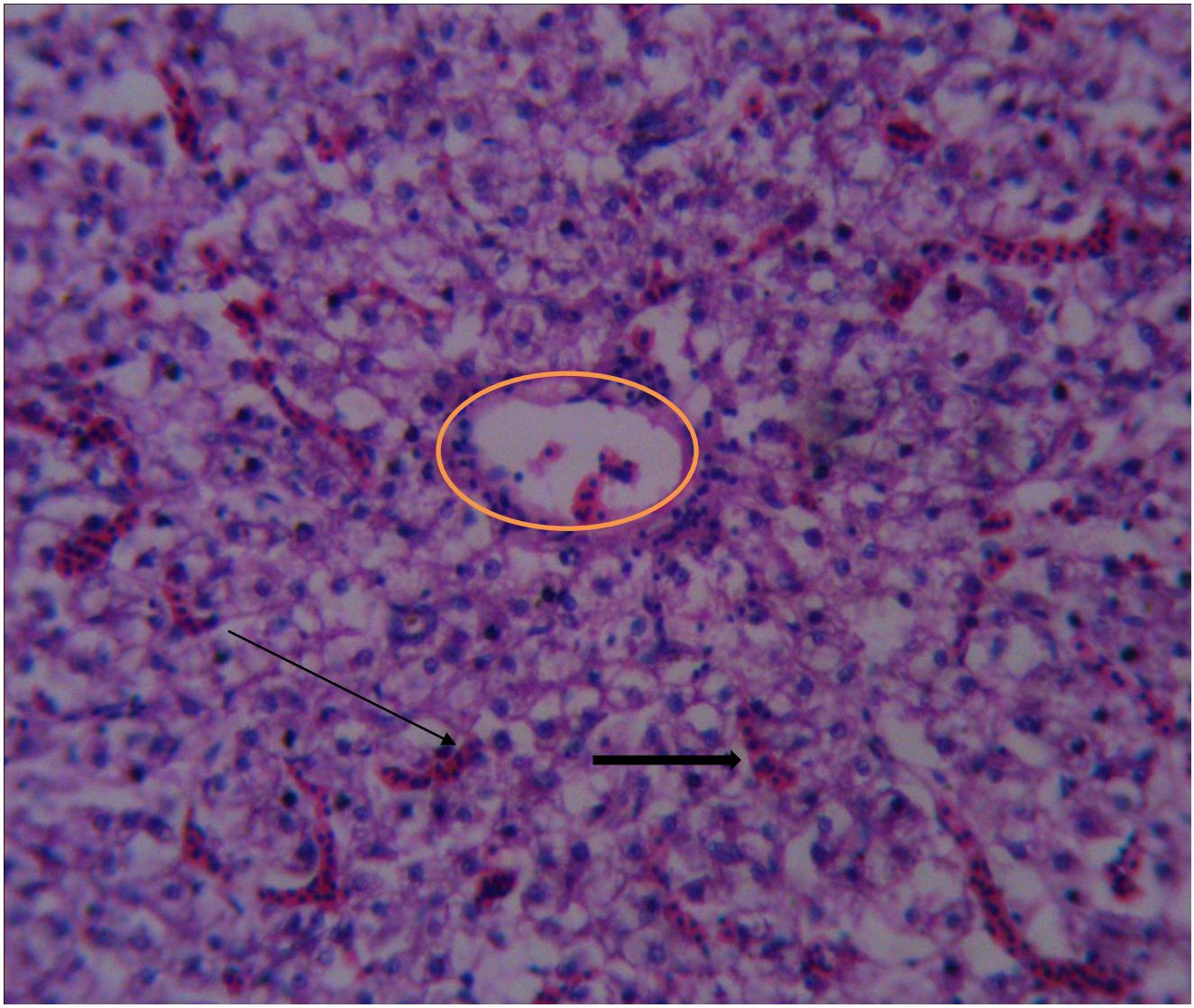


Plate 4.10:Histopathology of fish Liver from Dangulbi dam(H&E x250). Report photomicrograph of section of liver showing distorted cellular pattern of the liver with evidence of hepatocellular microvesicular fatty change in hepatocytes; necrosis of hepatocytes (pyknotic nuclei-black circles; karyolitic nuclei-black arrows) and a very reduce central nervous system (green circle).

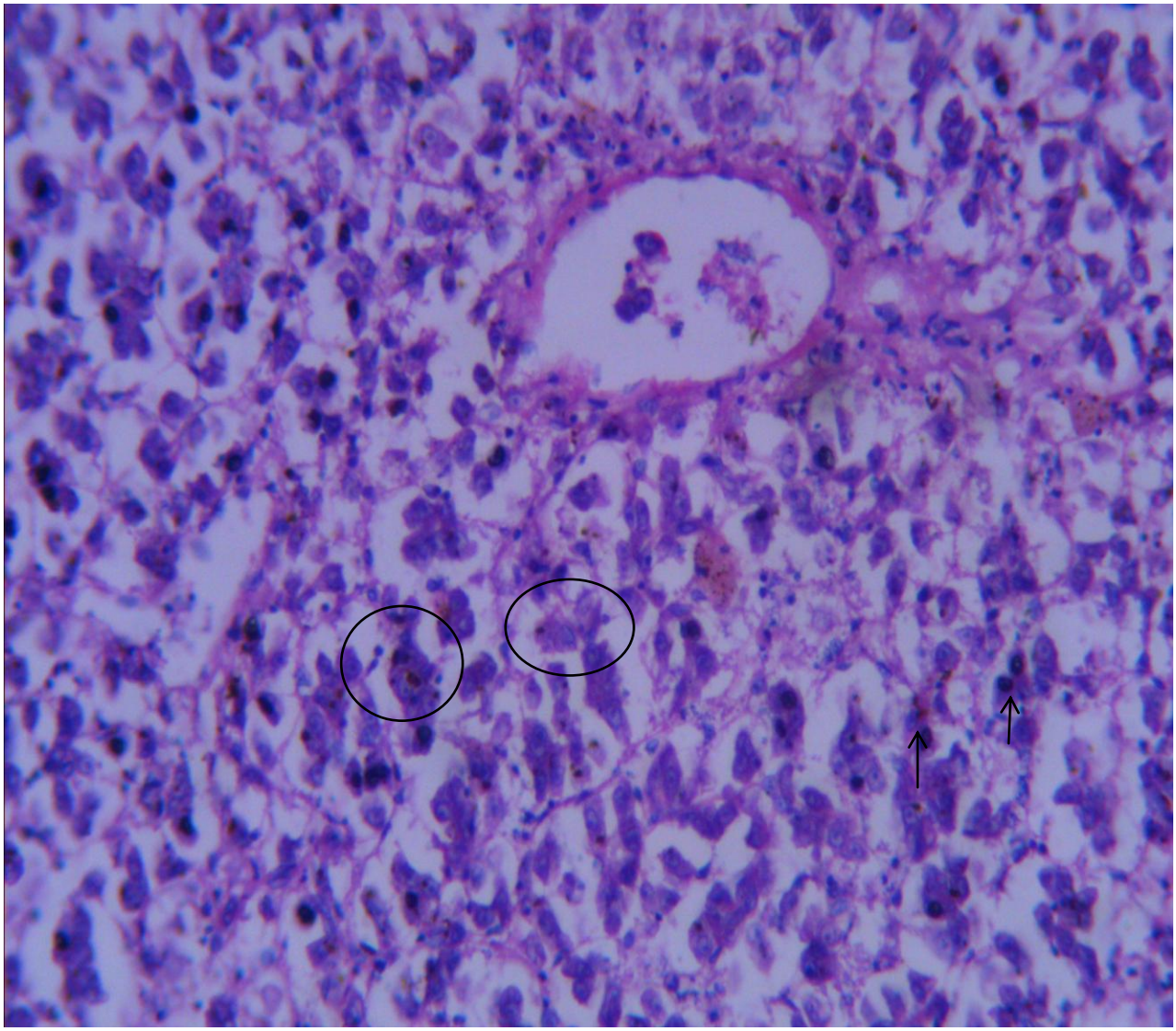


Plate 4.11: Histopathology of fish Liver from Bagega river(H&E x250) Report: photomicrograph of section of liver showing distorted cellular pattern of the liver with evidence of hepatocellular microvesicular fatty change in hepatocytes; necrosis of hepatocytes (pyknotic nuclei-black circles; karyolitic nuclei-black arrows)

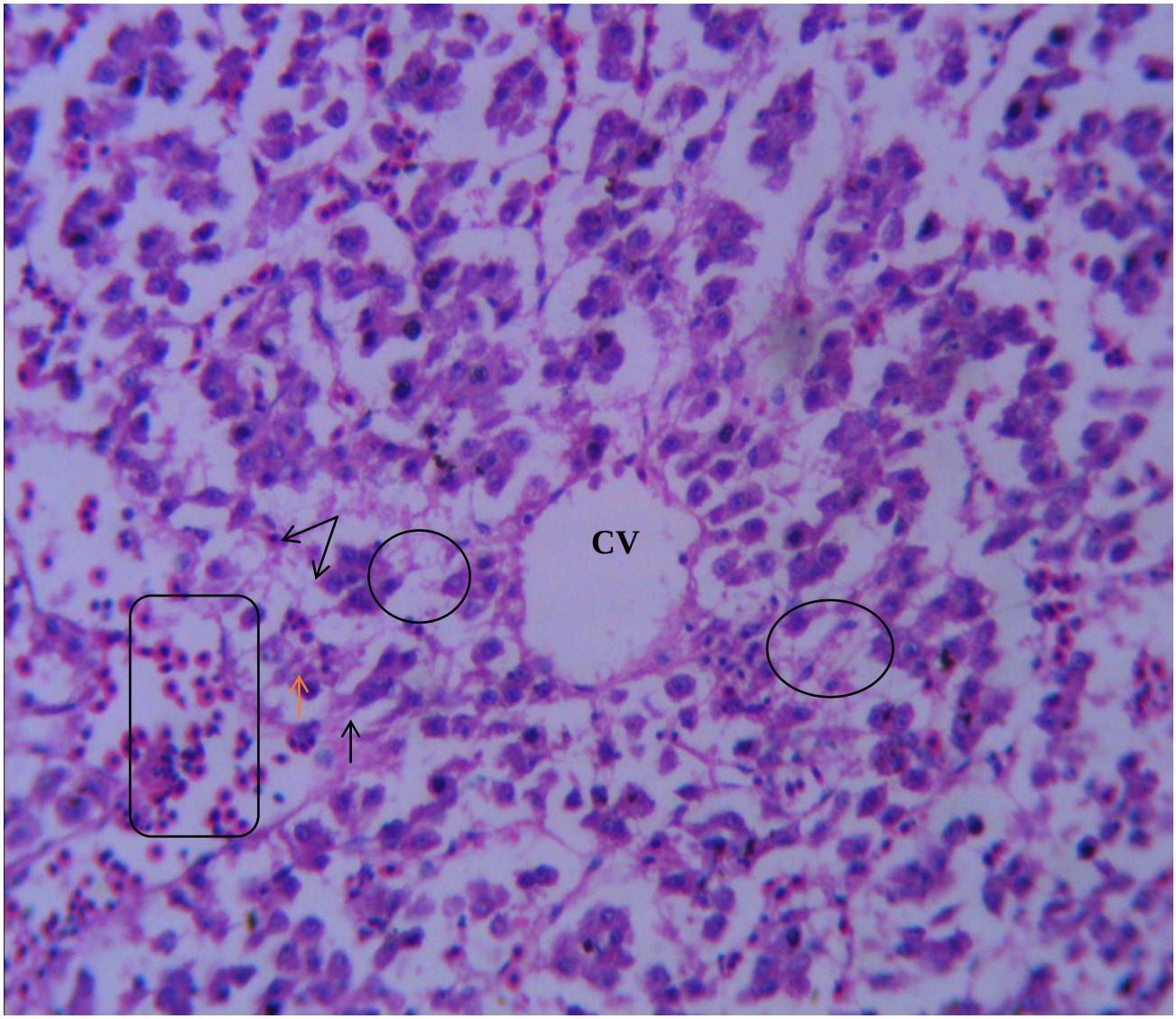


Plate 4.12: Histopathology of fish Liver from Sunke river(H&E x250) Report: Photomicrograph of fish liver section showing distortion in the cellular pattern of the liver. Hepatocellular microvesicular fatty change seen in hepatocytes (single and double black arrows); necrosis of hepatocytes (pyknotic nuclei-black circles and karyhexic nuclei-brown arrow); mononuclear immunologic cells infiltration (black rectangle).

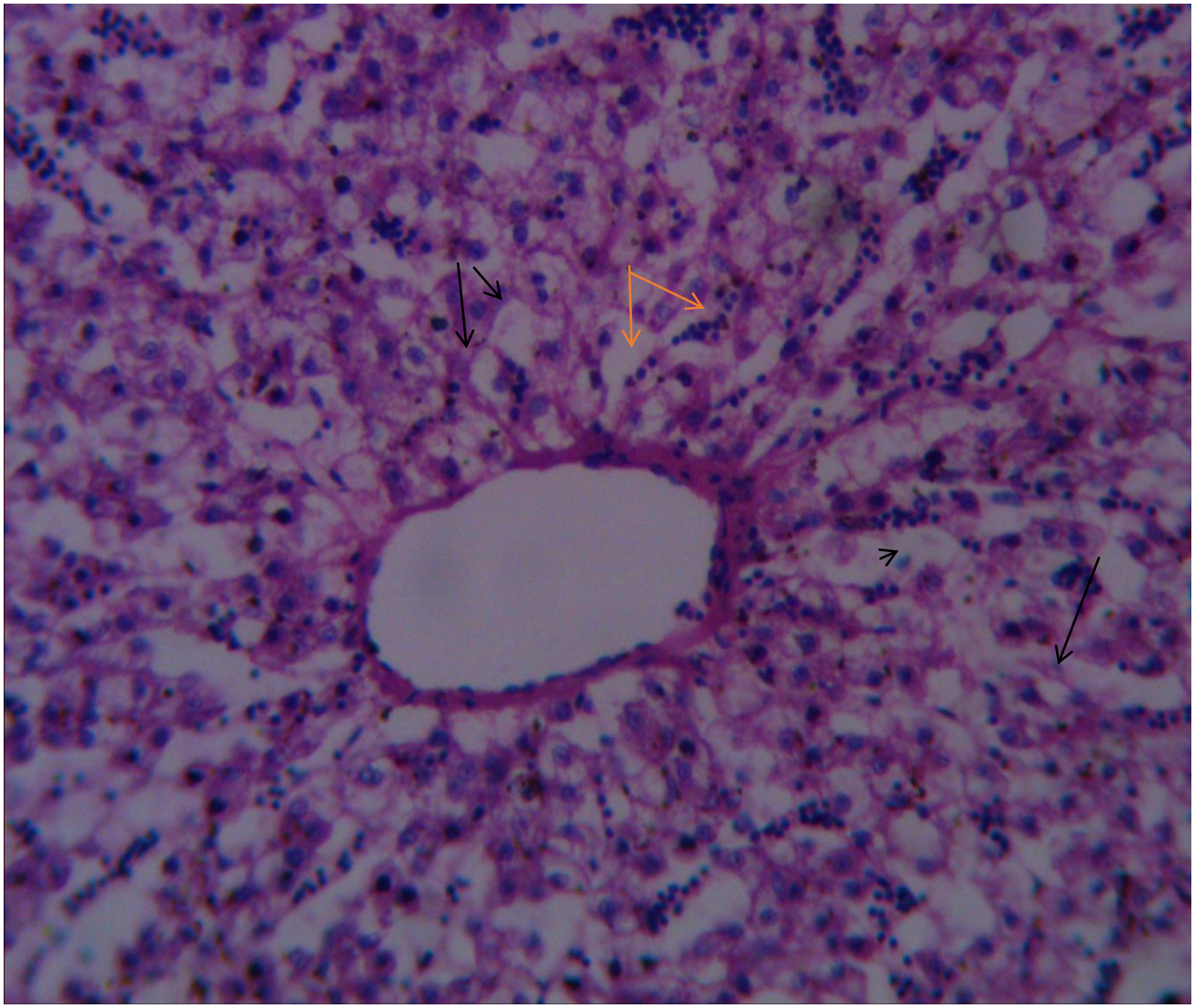


Plate 4.13: Histopathology of fish Liver from Abare river(H&E x250) Report: Photomicrograph of section from liver showing a distorted cellular pattern of the liver. Hepatocellular microvesicular fatty changes seen (double black arrow); necrosis of hepatocytes pyknotic nuclei- (long arrow); karyolitic nuclei – (arrow head) and mononuclear cells infiltration (double brown arrow) was seen.

The liver of fish samples in all the six locations show sign of abnormalities such as irregular shaped hepatocytes, cytoplasmic vacuolation and nucleus in a lateral position in the siluriform Corydoras paleatus as if they have been exposed to organophosphate pesticides. The liver of fish sample collected in Bagega, Sunke and Abare rivers shows signs of degeneration (cytoplasmic and nuclear degeneration and nuclear vacuolation) and thefocal necrosis in the liver parenchyma.

4.9.3 Histopathology Changes of Skin

The slides of fish skin for all the locations including the control are presented in Plate 4.14 - 4.19**.** The slide for Gusau dam was damaged during the processing time and could not be recovered. It was observed from the histological sections of all the fish skin from Bakolori dam, Dangulbi dam, Bagega, Sunke and Abare rivers that the infected epithelium showed epithelial hyperplasia. The epithelial cells must have been locally irritated by the suction of the contaminants from the studied dams and rivers thus causing epithelial cellular growth and excess of mucus production on the skin. From the histological sections it was also observed for Bagega, Sunke and Abare rivers that contaminants were found more onthe skin. The severity of these contaminants may have caused injury like haemorrhage, necrotic skin were increased and seen in dorso-ventral and caudal regions of the fishes.

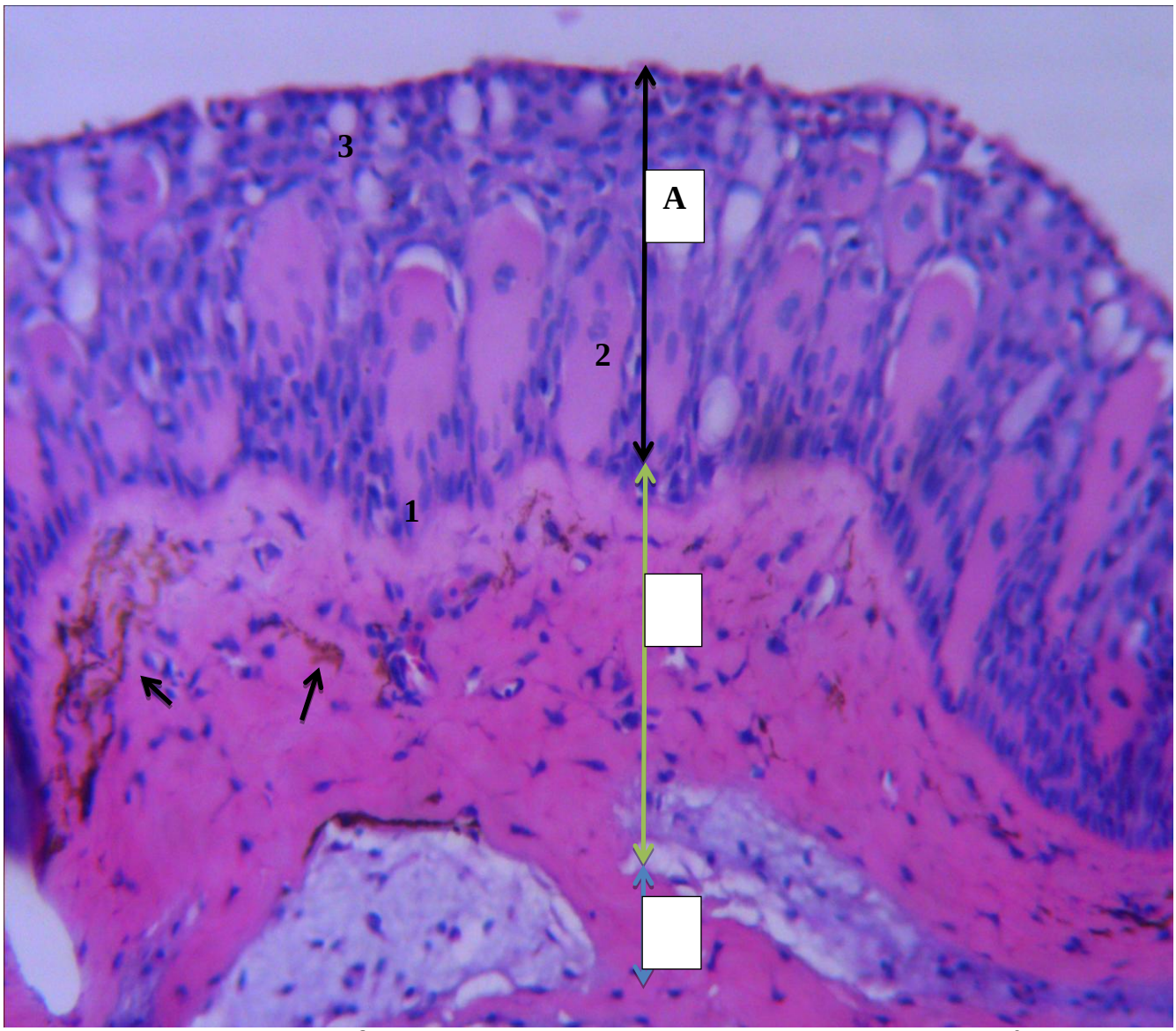


Plate 4.14:Histopathology of Control skin (H&E stain; x250). Report: section from Tilapia*(Orechromis mosambicus)*showing the normal histo-architecture of the skin and its layers. A (epidermis), B (dermis), C (hypodermis): 1-basal cells; 2- alarm cells; 3-epithelial cells.

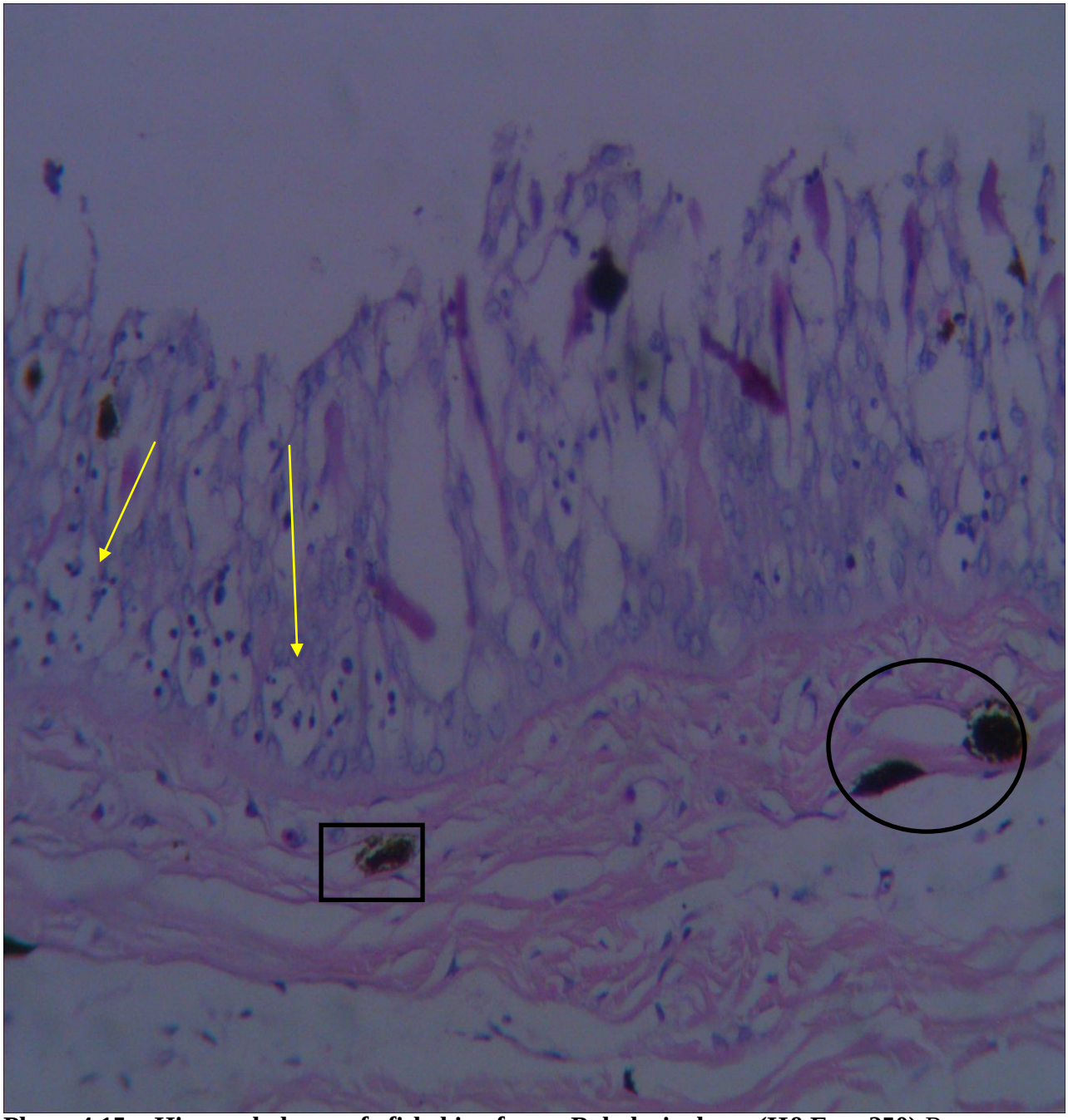


Plate 4.15: Histopathology of fishskin from Bakolori dam (H&E; x250). Report: photomicrograph from section of skin (*Orechromis masambicus*). There was massive necrosis of the epidermis characterized by pyknosis of epithelial cells (black circles); karyolysis of nuclei of alarm cells (black arrow heads); hyperplasia of mucus cells (yellow arrow); area of complete necrosis of cells (Black Square); decreased melanin secretion (yellow arrow).

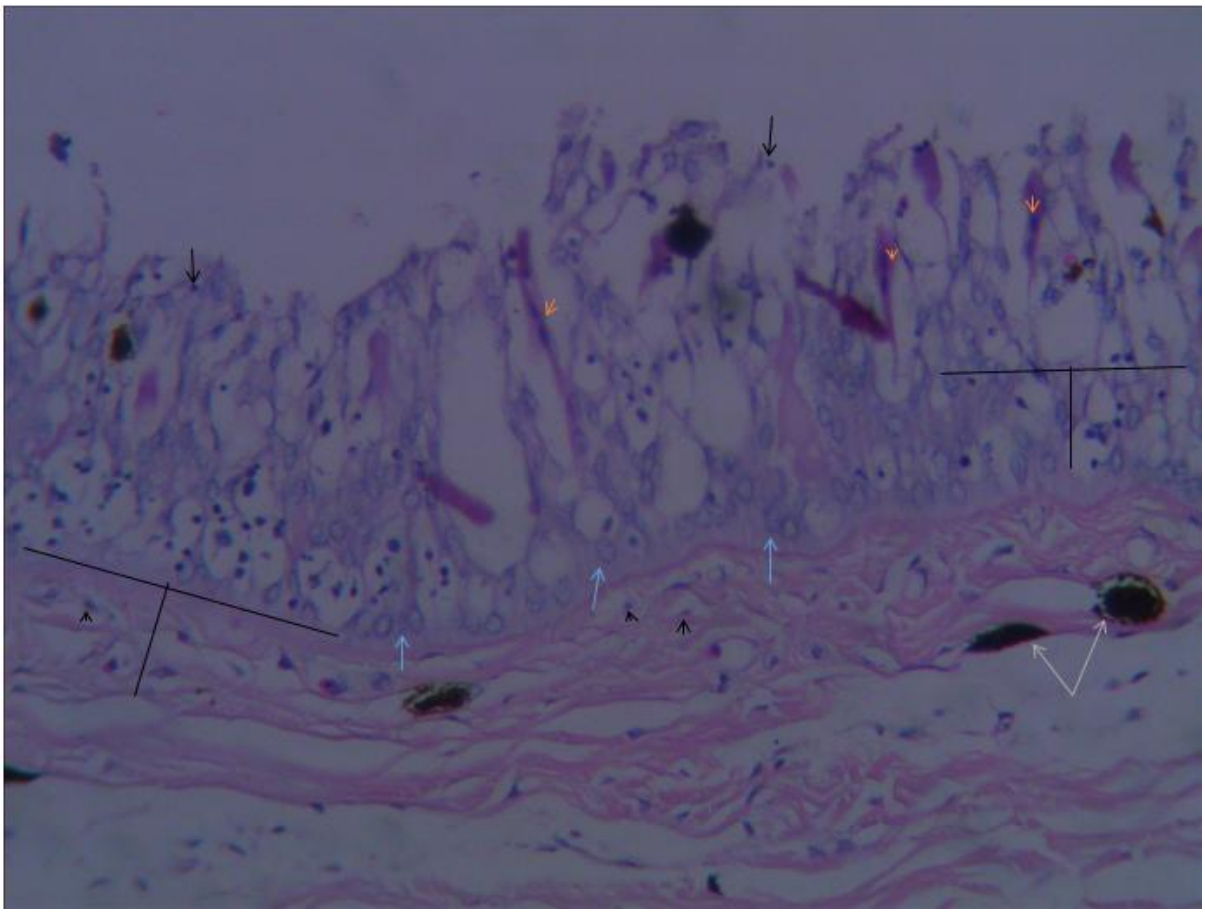


Plate 4.16: Histopathology of fishskin from Dangulbi dam (H&E; x250). Report: Photomicrograph of section from skin of *Orechromis mosambicus*showing massive destruction of the epidermis with necrosis of epithelial cells (pyknotic nuclei- black arrows); necrosis of alarm cells (pyknotic nuclei-brown arrow heads); hypertrophy of basal cells (blue arrows); hypertrophy and hyperplasia of fat cells (black T); pyknosis of cells of dermis (black arrow heads); condensation & darkening of melanin (green double arrow).

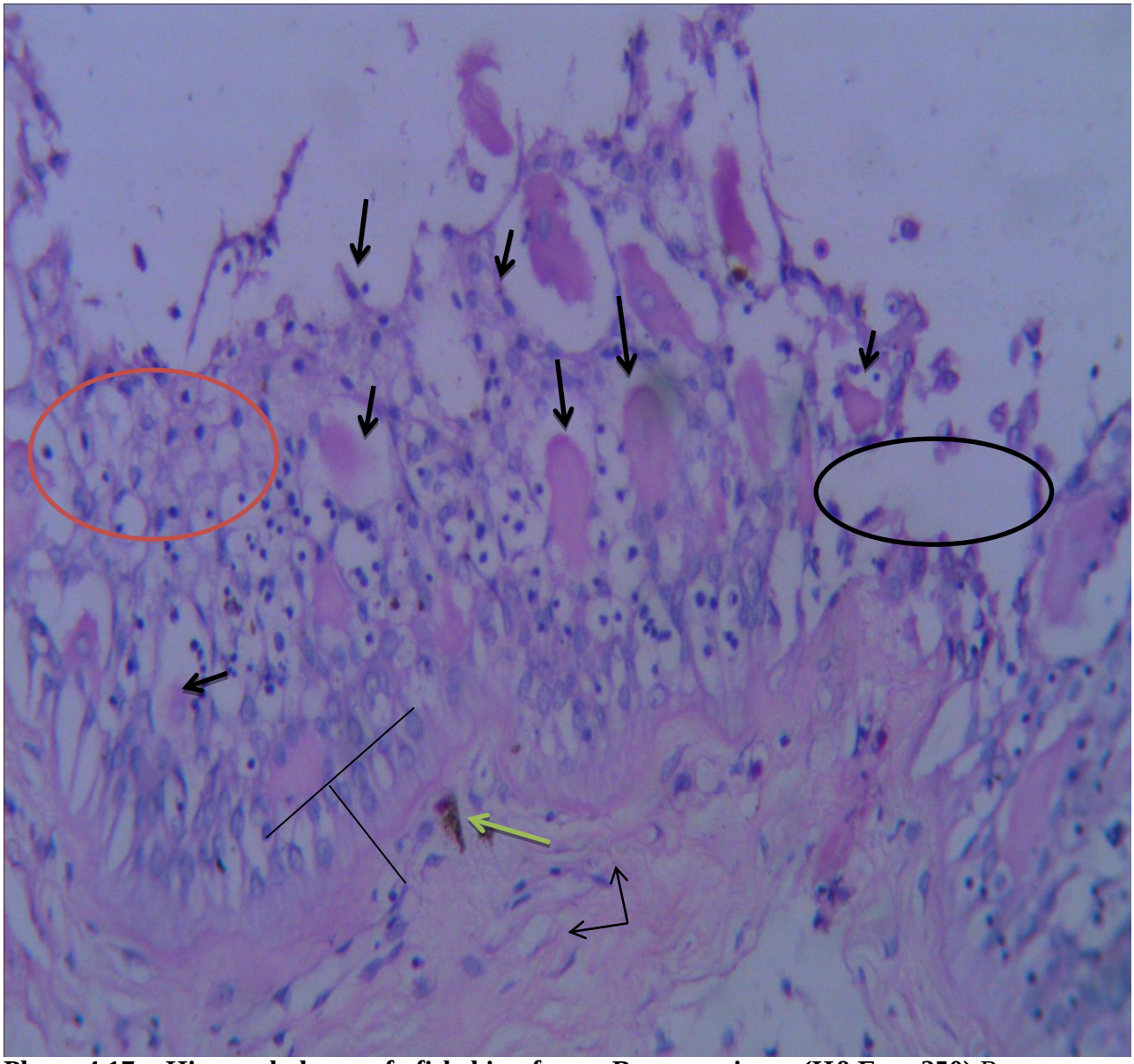


Plate 4.17: Histopathology of fishskin from Bagega river (H&E; x250). Report: photomicrograph from section of skin (*Orechromis. mosambicus*). There was massive necrosis of the epidermis characterized by pyknosis of epithelial cells (black arrows); karyolysis of nuclei of alarm cells (black arrow heads); hyperplasia of mucus cells (brown circle); area of complete necrosis of cells (black circle); decreased melanin secretion (green arrow) and pyknosis of cells in dermis (double head arrow).

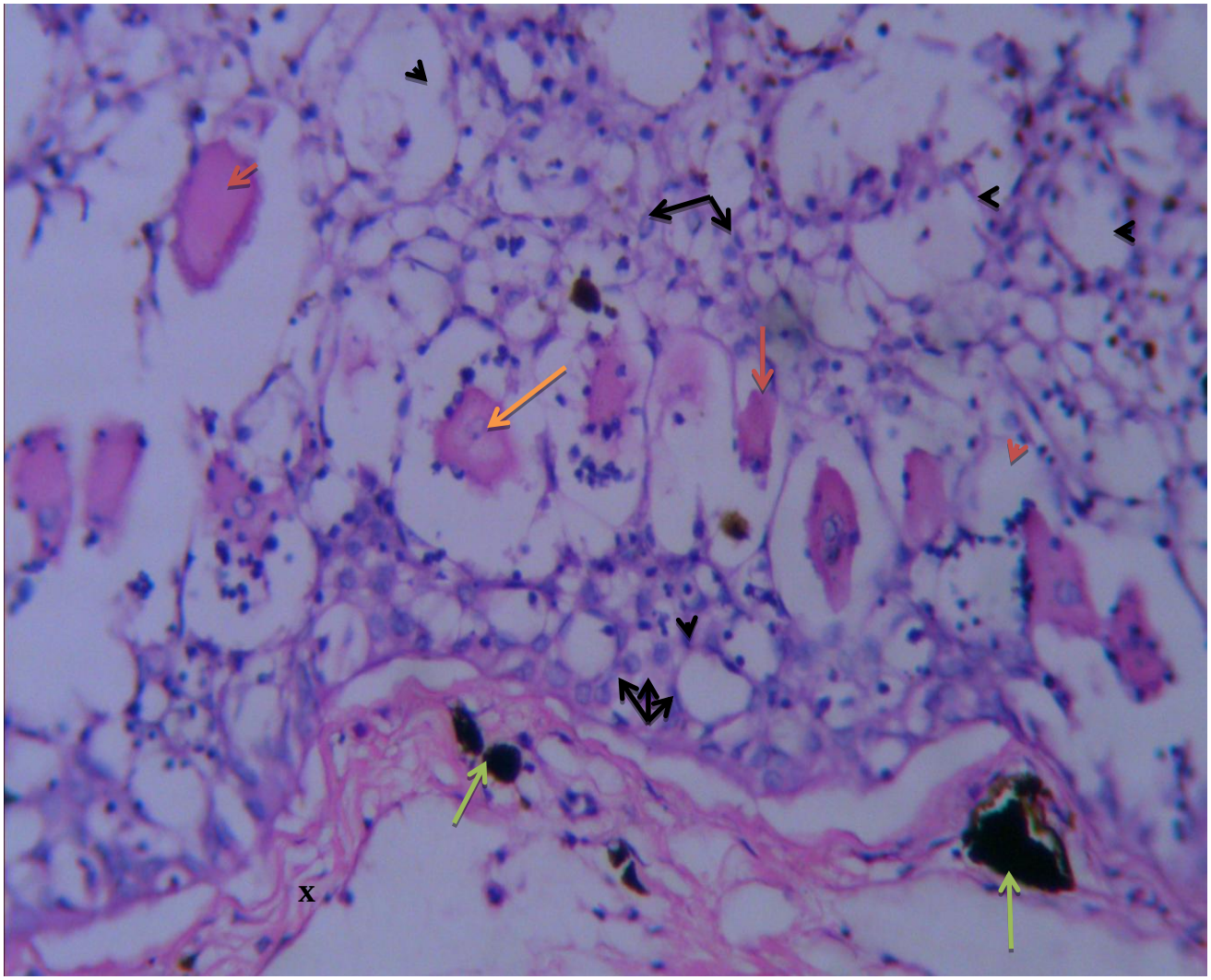


Plate 4.18:Histopathology of fishskin from Sunke river (H&E; x250). Report: micrograph section from *Orechromis mosambicus*showing destruction of the epidermis and dermis of the skin. Necrosis of epithelial cells (pyknosis of epithelial cell-double head arrow); massive vacoulation and hypertrophy of fat cells (black arrow head); hypertrophy of basal cells (triple head black arrow). Necrosis of dermis (x) and darkening/condensation of melanin (green arrow).

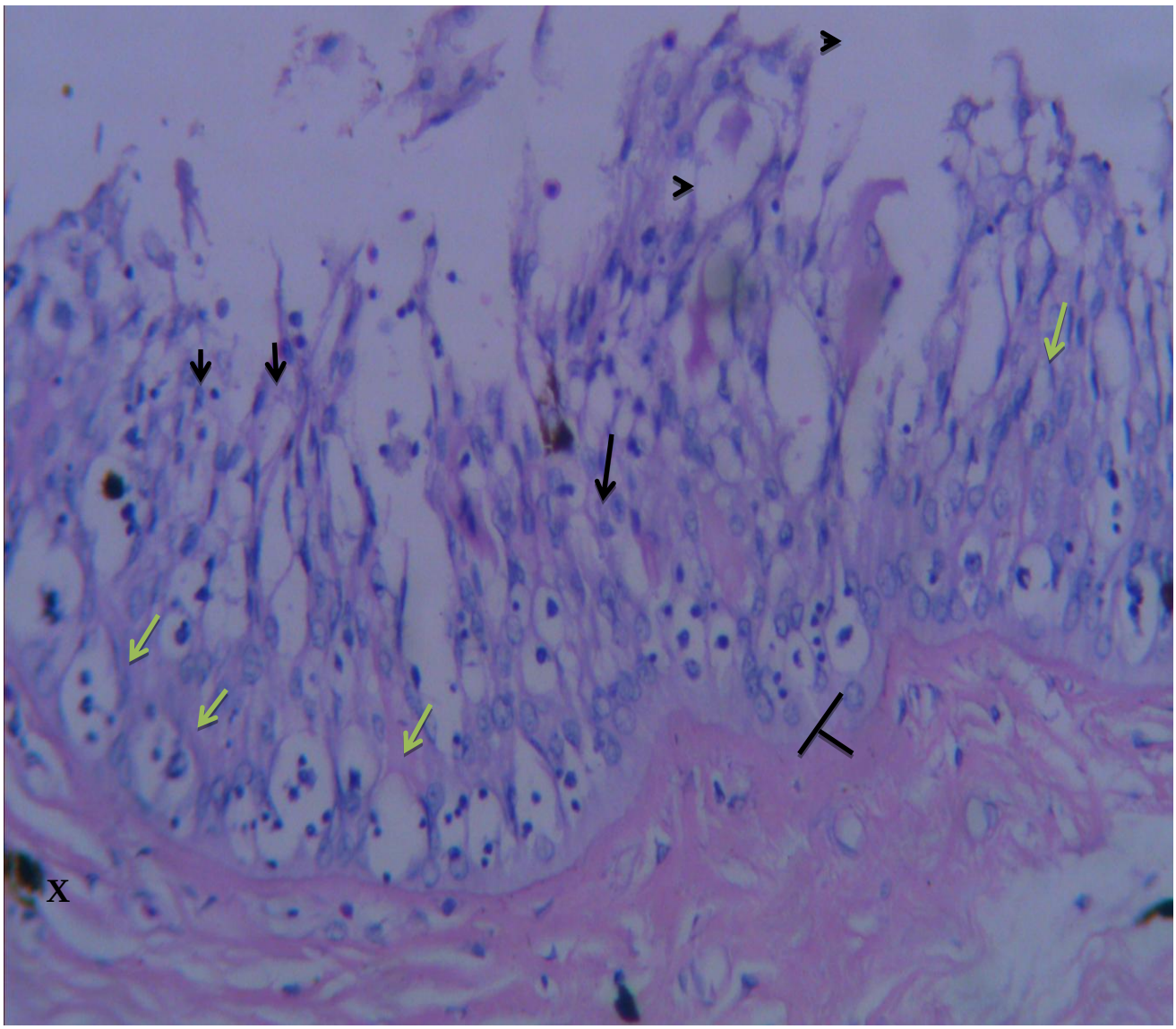


Plate 4.19: Histopathology of fishskin from Abare river (H&E; x250). Report: photomicrograph section of skin from *Orechromis mosambicus.* There is massive necrosis of epithelial cells of the epidermis; massive vacoulation and hypertrophy of fat cells (green arrows); complete necrosis of alarm cells(pyknotic basal cell) and hypertrophy of basal cells (black T). Darkened/condensed melanin (x) and necrosis of dermis; 1-2 mononuclaear cells sited (black arrow head).

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physico-Chemical Properties of Water Samples

The dams considered in this research work provide a unique productive environment that support diversity of fishes and farm irrigations which contributes to the economy of the state and the nation by extension. Physical water quality parameters varied seasonally, and amongst locations.

5.1.1 pH

The pH of all the water bodies of the six locations for the two years (2014 and 2015) tends to be alkaline; this is because it ranged between 7.57 and 7.96. Statistical analysis of variance conducted on the data revealed that there was no significant difference between the interaction of locations and year.

The pH of aquatic environment can be upset by added acid or alkali from waste water. The maximum pH value recorded in this study is lower than 8.22, and 8.1 reported in similar water bodies in Nigeria (Arimoro, *et al*., 2008; and Davies *et al*., 2006). However, values recorded in this study which ranged between 7.57 and 7.96 are comparable to the work of Adeyeye and Abulude (2005) with a pH range between 5.90 and 7.60 when studying the assessment of some surface ground water resources in Ile-Ife, Nigeria. The pH of all the locations was within the 6.0 and 9.5 WHO and USEPA standard limits for dringing water.

It is a well-known fact that pH has profound effects on water quality. It affects metals solubility (at low pH), the alkalinity and hardness of water according to Fakayode, (2005). Aquatic organisms are also affected by pH because most of their metabolic activities are dependent on pH (Fan *et al*., 2002).The lower values recorded during the wet season as against the dry season might be due to deposition of some organic matter into the water

bodies from run-off. Partial decomposition of this organic matter by bacteria and fungi has been recognized to produce various organic acids that are capable of lowering the pH of aqueous solutionFakayode, (2005). Lower wet season pH values for dam water were found to be consistent with reports from similar studies (Adefemi *et al*., 2007). Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters. Extremes of pH can affect the palatability of water but the corrosive effect on distribution systems is a more urgent problem (EPA, 2010). No health-based guideline value has been proposed for pH, however, an acceptable range for drinking water pH is from 6.5 to 9.5 (EPA, 2010; USEPA, 2002). Corrosion effects may become significant below pH 6.5, and the frequency of incrustation and scaling problems may be increased above pH 8.5.

5.1.2 Temparature

The relatively high temperature recorded in the dry season is in response to time and period of sample collection. Similar observation was reported forsome dams and surface waters within the same geographic region with the dam and riverunder investigation (Aiyesanmi *et al*., 2006; Adefemi *et al*., 2007). Cool water is generally more palatable than warm water, and temperature will impact on the acceptability of a number of other inorganic constituents and chemical contaminants that may affect taste. High water temperature enhances the growth of microorganisms and may increase taste, odour, colour and corrosion problems (WHO, 2008). The effect of temperature, and especially changes in temperature, on living organisms can be critical. Temperature controls the solubility of gases in water, and the reaction rate of chemicals and the toxicity of ammonia. Temperature is the most important physical variable affecting the metabolic rate of fish and is therefore one of the most important water quality attributes in aquaculture (WHO, 2008). The highest mean temperature value (27.20°C) recorded in this work fell within the optimal water temperatures (Target Guidelines) of 28°C - 30°C, within which maximal growth rate, efficient food

conversion, best condition of fish, resistance to disease and tolerance of toxins (metabolites and pollutants) are enhanced by South African water quality guidelines (SAWQG, 1996).

5.1.3 Electrical conductivity

It is known that electrical conductivity of water is an important parameter of water quality conductivity. Values from this study revealed that Bagega, Sunke and Abare rivers contained some appreciable amounts of dissolved ions than the dams. The values recorded in this study was however lower than 852.38 µs/cm reported by Arimoro *et al* (2008) in Warri coastal rivers. Water conductivity values measured for the dry seasons were higher than for the wet seasons. This may be attributable to excessive evaporation of water from the dam during the dry season, which might have consequently increased the concentration of dissolved salts, also when compared to the work of Fakayode (2005) who studied Alaro River in Ibadan, values obtained in this study were lower.

Generally, Abare River recorded the highest conductivity value which could be as a result of the mining activities and other mineral exploitation done using the river water since it is close to mining sites. However, the result of this study showed that they are below the 500µs/cm 1000µs/cm WHO and Nigeria recommended tolerable limits.

5.1.4 Total dissolved solid

Gusau dam recorded the lowest mean TDS amongst the dams while Abare river recorded the highest mean TDS value amongst the rivers.

TDS is most important to water quality when it concerns designated uses and has been listed by the EPA as a secondary ground water and drinking water contaminants (Akpan *et al.*, 2007). The secondary contaminant causes aesthetic, technical, and cosmetic effects. Water high in total dissolved solids may have an unpleasant taste, odour, colour and may have a laxative effect beyond the tolerance level (EPA, 2010). The TDS recorded in the dry season

is higher than the wet season; this may be due to evaporation during the dry season which caused some dehydration of aquatic animals (Marini and Piccolo, 2004). Excessive TDS can reduce water clarity, hinder photosynthesis, and lead to increased water temperatures (USEPA, 1999). However, the TDS levels recorded in this work were below the WHO guideline of 1000 mg/L for the protection of fisheries and aquatic life and for domestic water supply.

5.1.5 Total suspended solid

Gusau dam recorded the lowest mean TSS value amongst the Dams, while Abare River has the highest mean TSS value. Total suspended solids also affect water clarity. Suspended solids absorb heat from sunlight which increases water temperature and subsequently decreases levels of dissolved oxygen. Suspended solids may kill fish and other aquatic fauna by causing abrasive injuries, by clogging the gills and respiratory passages, by blanketing the stream bottom, by destroying the spawning beds and by screening out light necessary for the photosynthetic activity of aquatic plants (Chapman, 1999). Settling suspended particles may trap bacteria and bring them to the bottom of the lake or river. With excessive concentration of organic wastes, bacterial action may lead to anaerobic decomposition and anoxic condition in water. Similarly when the rate of photosynthesis is low, then oxygen concentration become low and CO_2 concentration become higher (Akpan *et al*., 2007). From the results of this study, the levels of TSS in the entire sampling locations exceeded the WHO guidelines of 50 mg/l for the protection of fisheries and aquatic life (Chapman, 1999). Higher TSS concentrations in this work may be attributed to discharges from use of the river/dam for mining, agricultural and domestic purposes (Parr *et al*. (1998); Peck and Zinke, 2006).

5.1.6 Chloride

Gusau dam recorded the lowest mean chloride concentration amongst the dams while the highest mean chloride concentration was recorded at Abare River amongst the rivers. The mean chloride concentration of Sunke, Bagega and Abare River were consistently higher than those of the dams, indicating possible pollution state of the rivers. The consistently higher values recorded during the dry season over the wet season could be as a result of concentration of this anion from excessive water evaporation from the dam and river as earlier pointed out byArimoro *et al* (2008). Excess chlorides in water are usually taken as index of pollution. The mining, sewage water and industrial effluents are rich in chloride and hence the discharge of these wastes result in high chloride level in the rivers (Gaballah *et al.*, 2005). Chloride is a ubiquitous aqueous anion in all natural waters, the concentrations varying very widely and reaching a maximum in sea water. Natural levels in rivers and other fresh waters are usually in the range 15 - 35 mg/L Cl^- similar to what was recorded in this work, and much below the permissible drinking water standard of < 250 mg/l (EPA, 2010; USEPA, 2002; WHO, 2003).

5.1.7 Alkalinity

Alkalinity serves as a pH reservoir for inorganic carbon. High values of alkalinity could indicate greater ability of the river to support algal growth and other aquatic life. Gusau dam recorded the lowest mean alkaline concentration while Abare River recorded the highest mean alkalinity concentration. The mean alkalinity concentration of all the water bodies in 2014 was significantly higher than that of 2015. Low concentrations were obtained for alkalinity across all the locations when compared with 880 mg/lreported by Fakayode (2005) from Alaro River in Ibadan. Alkalinity is one of the best measures of the sensitivity of river/dam to acid inputs (Gaballah *et al.,* 2006). The concentrations of alkalinity recorded in this work across all the locations fall below the maximum acceptable standard (WHO, 2003).

5.1.8 Turbidity

Turbidity is a measure of the ability of water to receive light and is caused by small particles in the various locations where turbidity exist. The turbidity value of all the three dams' Gusau, Bakolori and Dangulbi dams studied are low when compared to the three rivers (Bagega, Sunke and Abare rivers). Gusau dam recorded the lowest turbidity value while Abare River recorded the highest mean turbidity level. Result revealed that the rivers were quite turbid when compared to the value of 16.7 NTU reported by Arimoro *et al*. (2008) in Warri river. Mean turbidity values measured of the dams and river water samples in this work were higher than the guideline value of 5.0 NTU for drinking water (WHO, 2008; EPA, 2010). The remarkable high turbidity in this work may not be unconnected with the restrictions placed upon mining, agriculture and other human anthropogenic activities around the river and dam.

5.1.9 Sulphate

Low sulphate concentrations which ranged between 10.12 – 29.81 mg/l were recorded in the dam and river water compared to 250 mg/L guideline value for drinking water (EPA, 2010; USEPA, 2002). Sulphates or sulphuric acid products are used in the manufacture of numerous chemicals, dyes glass, paper, soaps, textile, fungicides, insecticides, astringents, and also used in mining, pulping, metal and plating industries (Winde *et al.*, 2010).Sources of sulphate in the water could be associated with soil mineralogy and contribution from anthropogenic activities. Sulphates exist in nearly all natural waters, the concentrations varying according to the nature of the terrain through which they flow. No health-based guideline is proposed for sulphate, but its presence in drinking-water can cause noticeable taste, and very high levels might cause a laxative effect especially with the presence of magnesium and sodium. Sulphate concentrations obtained in this investigation revealed seasonal variation effect since concentration recorded in the dry season is higher than those of

the wet season. Generally, the result obtained in this study for all locations were lower than the 100mg/l and 200mg/l of Nigeria and WHO (2003) tolerance limits respectively.

5.1.10 Phosphate

The mean value of phosphate in the dry season is higher than its corresponding phosphate level in the wet season. This shows a seasonal variation effects on the water bodies. Bakolori dam recorded the lowest mean phosphate level while Abare River consistently recorded the highest level of phosphate concentration.This may be supported by the mining and agricultural activities that are being done using the dams and river water in the process. Phosphate concentrations in the water bodies are very high as compared to 0.1mg/l standard guidelines (USPH). The maximum values obtained from the rivers were higher than 5.0mg/l phosphate concentration in the South Africa guidelines for drinking water.Phosphorus from where phosphate is derived occurs widely in nature in plants, in micro- organisms, in animal wastes; and large quantities of phosphate are applied as fertilizers in agriculture for which runoff from this area will often contains elevated concentrations of phosphate (SAWQG, 1996; EPA, 2010). Typical phosphate concentrations in surface waters range from 0.001 mg/L in unpolluted water to 0.30 mg/L or more in nutrient enriched waters. The significance of phosphorus in water is principally in regard to the phenomenon of eutrophication of lakes along with nitrogen as nitrate. Natural dissolved phosphates are considered to be largely non-toxic, although certain man-made organophosphates do have toxic effects. It is, however, likely that high concentrations of dissolved phosphate may lead to osmotic stress, as is the case with high nitrate concentrations (SAWQG, 1996).

5.1.11 Chemical oxygen demand

The mean COD values for wet season are significantly lower than the mean COD value for dry season. This situation indicates the effect of seasonal variation on the water

bodies. Dangulbi dam recorded the lowest COD values amongst the other dams, while Sunke and Abare River also showed very high COD level in this study. The COD values obtained for this work were higher than the one in the report of Bawa *et al*, (2007) for Lome's lagoon with COD of 110mg/l. COD levels varied significantly in all locations, especially at the rivers (244.50 – 290 mg/l), which suggest that a discharge of Quantum amount of waste into the rivers. The activities around the rivers such as mining, agricultural and domestic uses may account for the high values obtained for the rivers.The COD levels observed in this present study are in consistence with the findings of earlier researchers (Cotman *et al*., 2001), (Ahipaty and Puttaiah, 2006) who also reported many fold increase of COD in downstream which ranged between 662 and 366 mg/L than upstream in summer, and decreased to 74 and 180 mg/L in rainy season in Vrishabhavathy River, Ban-galore. Chemical Oxygen Demand (COD) is the amount of oxygen consumed to completely chemically oxidize the organic water constituents to inorganic end products. COD is an important, rapidly measured variable for the approximate determination of the organic matter content of water samples. Some water samples may contain substances that are difficult to oxidize. The least value detected at Bakolori dam (171.33 mg/l) did not exceed the WHO limit of 200 mg/L. The increasing trend in COD concentration in the six sampling locations when compared to the WHO standard limit is an indication of wastewater discharges from settlements along the River courses particularly from abattoirs, homes and mining waste into the dams and rivers, and also from surface and ground flows that carry chemicals directly from agricultural field into the dams (Keith and Plowes 1997).

5.1.12 Biological oxygen demand

Gusau dam recorded the highest mean concentration of BOD while Abare river recorded the lowest. The mean BOD concentration for the dry seasons is higher than that of wet seasons, an indication of seasonal variation effect on the water bodies. The BOD values

obtained in this work were lower than that reported by Ahmed and Tanko (2000) for Lome's Lagoon with BOD of 40 mg/l. The variations in the levels of BOD between the six sampling locations might be due the run-off from agricultural and mining activities within the area of study. Biochemical Oxygen Demand is a measure of the quantity of oxygen consumed by microorganisms during the decomposition of organic matter. Natural sources of organic matter include plant decay and leaf fall. However, plant growth and decay may be unnaturally accelerated when nutrients and sunlight are overly abundant due to human influence. If there is a large quantity of organic waste in the water supply, there will also be a lot of bacteria present working to decompose this waste. Oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need to live. In this case, the demand for oxygen will be high (due to all the bacteria) so the BOD level will be high. As the waste is consumed or dispersed through the water, BOD levels will begin to decline. When BOD levels are high, dissolved oxygen (DO) levels decrease because the bacteria are consuming the oxygen that is available in the water. Since less dissolved oxygen is available in the water, fish and other aquatic organisms may not survive. Generally, the BOD levels recorded in the entire sampling locations were higher than the EU guidelines of 3.0 to 6.0 mg/L (BOD) for the protection of fisheries and aquatic life and for domestic water supply (Chapman, 1999), (EPA, 2010).

5.1.13 Dissolved oxygen

Dissolved Oxygen (DO) is very crucial for the survival of aquatic organisms and is also used to evaluate the degree of freshness of a river or dam. Seasonal variation is observed in DO concentration, with higher values in the wet seasons, this could be due to increased aeration and continuous recharge of the water bodies as a result of rainfall, a situation which was also observed by Ayodele *et al* (2006) who reported that DO concentration of Asejire Lake attained its peak at the height of rainy season. However, the lower DO in this study

especially for the rivers compared to 4.0 – 6.0mg/l standard limits (USEPA) implies that the river are more polluted, since it is very common to find mining, domestic, agricultural, and waste discharge into the river, this may be the main reason for the high pollution of the water. Also, low DO could be as a result of high TSS, which in a broad sense reflects the pollutant burden in the aquatic system. In addition, according to Arimoro *et al*. (2008), high level of DO and suspended solids in river systems increased the BOD and COD which deplete the dissolved oxygen and this is in accord with the results obtained in this work.Several factors determine the DO levels in water including water temperature, which has inverse relationship with DO, photosynthesis by green algae, salinity and pollution resulting from both natural and anthropogenic activities (Iqbal *et al*., 2004; EPA, 2010). Nutrient input often leads to excessive algal growth; when the algae die, the organic matter is decomposed by bacteria, a process which consumes a great deal of oxygen that could lead to oxygen sag (Aiyesanmi *et al*., 2006). A high DO level in a community water supply is good because it makes drinking water taste better. However, high DO levels speed up corrosion in water pipes.In comparison with the present findings, Das *et al*. (2003) reported low DO 3.8 and 2.1 mg/L in upstream and downstream within the rainy season, which decreased to 1.7 mg/L in upstream and 1.2 mg/L in downstream within summer in Kathajodi River at Cuttack City. Singh *et al* (2005) reported that the average DO concentration of Gomti River in its Pipraghat region ranged from 0.00 to 5.4 mg/L, due to the flow of urban drains into the river, whereas Chang (2005) reported that the average DO concentrations were more than double, 7.2 ± 2.3 mg/L in upstream, than the downstream 2.4 ± 1.5 mg/L of Han River in Seoul, Korea. The ranged of DO in the six sampling locations were above the (USEPA, 1999; WHO, 2002) permissible limit of 4 mg/L and 5 mg/L. Therefore, the parameter does give cause for concern within this portion of dams and rivers.

5.1.14 Water hardness

Gusau dam recorded the lowest mean hardness concentration amongst dams, while Abare River recorded the highest mean hardness concentrations amongst all the rivers studied. Hardness in water comprises the determination of calcium and magnesium as the main constituents and their widespread abundance in rock formations often leads to very considerable hardness levels in surface waters. One of several arbitrary classifications of waters by hardness include: Soft up to 50 mg/L $CaCO_3$; Moderately Soft 51 - 100 mg/L $CaCO_3$; Slightly Hard 101 - 150 mg/L $CaCO_3$; Moderately Hard 151 - 250 mg/L $CaCO_3$; Hard 251 - 350 mg/L $CaCO_3$; Excessively Hard over 350 mg/L $CaCO_3$ (EPA, 2010).The values recorded from this work were within the moderately soft classification. Although hardness may have significant aesthetic effects, a maximum acceptable level has not been established because public acceptance of hardness may vary considerably according to the local conditions. Water supplies with hardness greater than 200 mg/l $CaCO_3$ are considered poor but have been tolerated by consumers; those in excess of 500 mg/l $CaCO_3$ are unacceptable for most domestic purposes (WHO, 2008). It has been suggested that a hardness level of 80 to 100 mg/l (as $CaCO_3$) provides an acceptable balance between corrosion and incrustation (WHO, 2008). Also, a number of ecological and analytical epidemiological investigations have suggested that there is an inverse statistical correlation between drinking water hardness and certain types of cardiovascular disease (WHO, 2008; Tuzen *et al.,* 2006). More than 15 mg $CaCO_3$/L hardness as recorded in this study is suitable for fish growth, while less than this value causes slow growth of fish and require liming for high fish production (Iqbal *et al*., 2004; Ali *et al*., 2005) Calcium and magnesium ions measured in the dam lake ranged from 13.47 - 20.26 mg/L and 5.94 - 11.74 mg/L respectively, with calcium contributing more to the hardness.

5.2 Heavy Metal Content in Water

The abnormal high contamination factor (CF) level of Hg was expected across all the locations and more for Bagega, Sunke and Abare rivers since gold processing is very active in these villages. The higher contamination factor for all the heavy metals during the dry season might be due to seasonal rainfall which dilutes some concentration of the metal concentration during the wet season. The pollution index value of the water samples across all the six location indicated that there is need for immediate intervention to ameliorate pollution particularly in the dry season.Generally, the natural sources of heavy metals in rivers and dams, Marine and Coastal water are through land, heavy fresh water inflow, agricultural waste, aquaculture discharge and river run-offs and the mechanical and chemical weathering of rocks (Ashokkumar *et al*., 2009). Correlation analysis showed a significant and positive relationship for Cd and Zn and Hg and Cr during the wet season and a significant positive at the ($p>0.05$) relationship for Cr and Zn in the dry season. Similar observation was reported on the study of heavy metals in Ureje dam in Ado-Ekiti by Adefemi *et al.* (2007) and in Kanji dam (Amoo *et al*., 2005) and other studies on surface water (Chapman, 1999; Asaolu *et al*., 1997; Karadede and Unlu, 2000). In this work, the concentration of the analysed heavy metals in mg/l was in the order of Hg> Pb >Cd > Cr > Zn.

5.2.1 Zinc

The concentration of Zn in the water samples was significantly higher at Bagega river in both wet and dry seasons, while Bakolori dam recorded the least value. Zn plays a biochemical role in the life processes of all aquatic plants and animals; therefore, they are essential in the aquatic environment in trace amounts. Zinc is used in a number of alloys including brass and bronze, batteries, fungicides and pigments. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life

(WHO, 2004). In addition, Zn is involved in a variety of enzyme systems which contribute to energy metabolism, transcription and translation. Zinc is also potentially hazardous and excessive concentrations in soil lead to phytotoxicity as it is a weed killer (Anglin-Brown *et al*., 1995; Abbasi *et al*., 1998). Zinc is used in galvanizing steel and iron products. Zinc carbonates are used as pesticides (Anglin-Brown *et al*., 1995). The concentrations of Zn in this water bodies was observed to be lower than the permissible limits of 5 mg/L in water set by (CPCB, 2010; USEPA, 2002).

5.2.2 Cadmium

Cd levels in the water samples were highest at Bagega river, while Bakolori dam recorded the least level. Higher concentration of cadmium is extremely toxic to fish population. Its effects on the growth rate have been observed even for concentrations between 0.005 and 0.01 mg/L (Green *et al*., 1986).The highest levels of Cd obtained in water samples relative to the amount in sediment in this area of study might be due to agricultural runoff, where fertilizers, pesticides and other agro-chemical are used in addition to possible release of sediment bound metal. Apart from natural sources, other probable sources of this metal in surface water include leaching from Ni-Cd based batteries (Hutton *et al*., 1999) runoff from agricultural soils where phosphate fertilizers are used (Stoeppler, 1991) and other metal wastes. The levels of cadmium in the water samples from the six sampling locations were above the (WHO, 2004) standard values of 0.01 mg/L for the survival of aquatic organism

5.2.3 Chromium

Cr levels in the water samples were highest at Bagega River, while Bakolori dam recorded the leastlevel. In aquatic environment, Cr is one of the bio-chemically active transition metals. Weathering of the earth crust is the primary and natural source of the chromium in the surface water. Though an essential trace nutrient and a vital component for

the glucose tolerance factor, chromium toxicity damages the liver, lungs and causes organ hemorrhages (Flaherty, 1995). Chromium compounds are used as pigments, mordents and dyes in the textiles and as the tanning agent in leather. Anthropogenic sources of emission of Cr in the surface waters are from municipal wastes, laundry chemicals, paints, leather, road run off due to tire wear, corrosion of bushings, brake wires, radiators (Amoo *et al*., 2005). Agricultural runoff is the main anthropogenic source of these toxic heavy metals in this portion of Lake Chad. The concentrations of Cr in water samples from the locations was found to be higher than the permissible limits of 0.1 mg/L set by (WHO, 2004).

5.2.4 Lead and mercury

The highest level of lead was recorded in Sunke River when compared with others, while Gusau dam recorded the least value. Hence, likely source of Pb in these water bodies is from mineral exploitation, soil erosion and runoff water (Winde and Stoch, 2010). Studies done elsewhere in Kenya indicate higher Pb concentration levels for example Ashraf*et al*. (2011) found mean Pb levels ranging from 0.26 – 0.99 mg/l in Lake Victoria. Also Ashraf*et al*. (2011) recorded lower and higher mean Pb levels at different sites (nd – 0.047 mg/l) in surface water of Athi river tributaries. The concentration of Pb and Hg in the water samples from this water bodies exceeded the permissible limit of 0.05 and 0.001 mg/L respectively set by (WHO, 2004; USEPA, 2002). The three rivers considered studied in this work are among the polluted sites in the report of medical expect from Ministry of Health and Medecins San Frontieres (MSF) in 2010, which reported that more than 400 children from seven villages in Zamfara State died from lead (Pb) poisoning within just six (6) months in 2010. They describe the affected children to show devastating symptoms such as "Gastro intestinal upsets, skin rashes, changes in mood; some were lethargic, some partially paralyzed, some had become blind and deaf. The worst affected were coming into the small Ministry of Health Clinic with seizures that could last for hours and would sometimes lead to coma and then

often to death". The poisoning which is primarily associated with mineral exploitation, consumption in water and food and air-based inhalation, have so far affected 3,600 children, with further expectations that 180 villages covering around 30,000 people may be affected.

5.3 Microbiological Analysis of the Water Samples

5.3.1 Bacterial count

The total bacterial count is a reflection of the general purity of the water samples analysed. In all the dams, the total plate count obtained during the wet season were generally higher than those obtained in the dry seasons attributable to influx through runoff of microorganisms originating from vegetation decay, municipal sewage, garbage, domestic and faecal waste (GCDWQ, 2006).While those obtained from the rivers were generally higher than those of dams. This situation suggests that the rivers are more polluted. Otunola *et al*. (1994) in their study on the bacteriological assessment of some selected streams reported that the total viable plate counts of twelve different samples of Mogaji streams in Ilorin, Kwara State ranged between $6.4 \times 10^6 - 2.38 \times 10^7$cful/ml.This implied that the total viable counts were consistently high at all the sites sampled for the study. The microbial values recorded in the dam and rivers water body represent high bacteria load compared to the recommended standards for drinking water (WHO, 2008; EPA, 2010; USEPA, 2002; GCDWQ, 2006). This condition constitutes a threat to end users, thus suggesting adequate disinfection process before distribution for domestic and industrial uses.

5.3.2 MPN Determination

The result of most probable number (MPN) revealed that during the wet season the probable number for the dams ranged between 35-67 coli-form per 100ml, while for the rivers it ranged between 43 – 89 Coli-form per 100ml. The most probable number (MPN) values for the river are higher than for the dams. The most probable number (MPN) for

Dangulbi dam was highest amongst the dams which ranged from 60 - 67coli-form per 100ml. This suggests that the dam has more dead material and runoffs in them. The MPN values for the wet seasons were higher than for the dry seasons; this may be due to run-offs, dead material in water and the more favourable low temperature during the Wet season. This is also in agreement with the work of Ellis and Yu (1995) which reported that faecal bacteria could enter natural water from variety of sources. Ademoroti (1996) also explained that animal slurry or sewage sludge to land with subsequent run-off would also increase bacteria counts in water.

Most aquatic bacteria are free-living and perform beneficial functions such as the decomposition of organic matter. A few species are opportunistic pathogens and cause diseases in fish, particularly under conditions of stress and immune deficiency. Symptoms of most bacterial diseases include fish not feeding well and swimming erratically. Low levels of dissolved oxygen, thermal stress, and high concentrations of nitrogenous metabolites are the principal causes which render fish susceptible to bacterial diseases (SAWQG, 1996) However, there is dearth of information in scientific literatures to show that E.coli affects the growth, reproduction, health or survival of fish. In India, for instance fish are cultured in sewage ponds, with no detrimental effects, but fish grown in wastewater harbour microorganisms, some of which are pathogenic and may infect consumers and handlers (SAWQG, 1996).

5.4 Heavy Metal Content in Sediment

The pollution load indices (PLI) calculated for all the metals analyzed have values far greater than 1. This indicates that there is serious overall load of heavy metal contamination in the entire sediment sampling site even though lead and mercury showed very high contamination factors.

Concentration of heavy metals in sediment showed spatial and temporal variation at all the locations during the study period. The relative abundance of different metals at the six locations during the study period varied with location and with season. All the metals examined except Zn were measured in relatively high concentration across all the locations during the period of investigation. The concentration of heavy metal particularly Cd, Pb and Hg recorded very high level in Dangulbi dam, Bagega, Sunke and Abare rivers. Although Bagega, Sunke and Abare rivers are locations with high risk of heavy metal contamination as established from the report of Medecins San Frontieres (MSF) in 2010. A significant positive relationship was established for Cr and Zn, Cr and Cd, Pb and Cd, Hg and Cd and Hg and Cr respectively during the wet seasons of year 2014 and 2015. While during the dry season it showed a significant and positive relationship for Cr and Zn, Pb and Zn, Pb and Cr and lastly Hg and Cd.

5.4.1 Zinc

The concentration of Zn in the sediment samples was significantly higher at Gusau dam in the wet and Abare River in the dry seasons, while Bakolori dam recorded the least level.The levels of Zn were generally low and the values were lower than the mean (0.73mg/kg) reported by Ado *et al* (2012) and much lower than 7.8 - 830mg/kg reported by Ajao *et al* (1991) and 128-308mg/kg reported by Ong and Kamaruzzaman, 2009) and 76 - 1200mg/kg in surface sediment across Stockholm (Sebastien, 2007). Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life (WHO, 2004). In addition, zinc is also potentially hazardous and excessive concentrations in soil lead to phytotoxicity as it is a weed killer (Anglin-Brown et al., 1995; Abbasi et al., 1998). The concentrations of Zn in the sediment of this water bodies was observed to be higher than the permissible limits of 123 μg/g set by (CPCB, 2010; USEPA, 2002).

5.4.2 Cadmium

The concentration of Cd in the sediment samples was significantly higher at Abare River in both wet and dry seasons, while Bakolori dam showed the least level. Cadmium is widely distributed in the Earth's crust at an average concentration of about 0.1mg/kg and is commonly found in association with Zinc. The concentrations found in marine sediment ranged from 0.02 to 1.0mg/kg (Korte, 1983).The concentration recorded in all the six locations ranged from (0.004 – 1.315mg/kg) were higher than the mean (1.15mg/kg) reported in Aderinola *et al*. (2009) and (0.1 – 0.9mg/kg) reported in Ajao *et al*, (1999). It's however, lower than the values (0.99 – 4.97mg/kg) reported for the southeast Coast of India (Ashokkumar *et al*., 2009).The levels of cadmium in the sediment samples from the six sampling locations in this work were above the (WHO, 2004) standard value of 6 μg/g.

5.4.3 Chromium

The concentration of Cr in the sediment samples was significantly higher at Abare river in both wet and dry, Gusau dam in the dry seasons, while Sunke river showed the least level. The mean value (0.62mg/kg) of Cr reported by Aderinola *et al*. (2009) is lower than the mean values recorded for Cr in all locations but higher than the mean value recorded in Bakolori dam andSunke river. Ajao *et al* (1991) reported higher values (2.9 – 113.3 mg/kg) for Cr in sediments taken from the lagoon in 1986 and 27 – 77 mg/kg was found in Stockholm surface sediment in Sweden (Sabastein, 2007). The level of Cr in all locations in this work is relatively high except for Bakolori dam and Sunke river where the concentration is relatively low during the period of study. The acute toxicity of chromium to saltwater organisms is extremely variable Mance *et al* (1984). Aderinola *et al*. (2009) reported a mean

value of 0.66mg/kg which is lower than the mean obtained for most of the locations.According to WHO guideline value for sediment, the concentration of 25 μg/g, Cr is acceptable (Radojevic *et al*., 1999). The Cr concentrations in sediment samples did exceed this limit, indicating pollution of this water bodies in the state.

5.4.4 Lead

The concentration of Pb in the sediment samples was significantly higher at Abare River in both wet and dry, and Gusau dam in the dry seasons, while Bagega River showed the leastlevel.The concentration recorded for Pb in all the location was between 0.229 – 2.831mg/kg. The mean for some locations were higher than the average (0.45mg/kg) reported by Aderinola *et al* (2009) for the Ijora section of the lagoon.The levels of lead in the analyzed sediment samples showed that the limiting value set by USEPA of 10 μg/g was exceeded. The level of Pb in the sediment samples from this water bodies might be attributed to heavy agricultural run-off which contains fertilizers, mining activities, agrochemicals and pesticides (Bassey *et al*., 2014).

5.4.5 Mercury

The concentration of Hg in the sediment samples was significantly higher at Sunke river in both wet and dry seasons, while Gusau dam showed the least level. The burning of fossil fuels is a source of mercury. The wood pulping industry, also releases significant amount of mercury to the environment. Although the use of mercury is decreasing, high concentrations are stills present in sediments associated with the mineral exploitations of Gold. Some mercury compound are been used in agriculture, principally as fungicides WHO (1989). Dissolved mercury has a strictly affinity for organic matter and suspended sediment and so can be expected to be bound to these particles in the water column and subsequently to accumulate in sediments. Once deposited in sediments, mercury can undergo methylation to

produce methyl-mercury (Cambell *et al*., 1986). This form of mercury is bioavailable and generally more toxic to aquatic organisms than the organic forms (WHO, 1989).A recent survey of contamination from historic metal mining in the swale catchment, northern England (Cambell *et al*., 1986) showed that more than 55 percent of the flood plains covering an area of nearly 30km^2 and used for agriculture, is likely to be contaminated by metals significantly above background concentrations.

5.5 Chemical Fractionation of Metals in Sediment

5.5.1 Zinc

The distribution of Zn in the four fractions obtained by the sequential extraction of sediment across all the six locations showed that Zn was mostly concentrated in the water soluble (FI) with the highest percentage of 28% in Bakolori dam and the least at Dangulbi dam (10.765%). The highest percentage concentration of Zn in the exchangeable was recorded in Dangulbi dam while Bakolori dam recorded the lowest level. The predominant percentage of Zn was mostly recorded in the residual fraction. This suggests that the greater percentage of Zn in the sediments is non-bioavailable. High percentage of total Zn have been found associated with the reducible fraction in other studies of polluted sediments, which was not determined in this present work (Fernandes, 1997; Li *et al*., 1995; Fan *et al*., 2002; Korfali and Davies 2004). Zn absorption onto these oxides has higher stability constants than onto carbonates (Rao*et al.,* 1990). Several other workers have also found Zn to be associated with exchangeable and Fe-Mn oxides (Kuo *et al*., 1983; Ramos *et al*., 1994) which is consistent with the result of this wok.

5.5.2 Cadmium

The predominant percentages of Cd were recorded in the carbonate bound fraction of Gusau dam 45.424%, Bakolori dam 40.820%, Dangulbi dam 38.446% and Bagega river

40.512%. The residual fraction generally recorded low Cd concentration across all the locations. This further suggests that a high concentration of Cd in this sediment might be easily available and can easily enter the food chain. This is in agreement with the report of Ahumada *et al.,* 1999; Narwal *et al.,* 1999 who reported that Cd is distributed more as carbonate, reducible and as residual fraction. High concentrations of Cd in carbonate bound fractions have also been reported in sediments (Rao*et al,* 1990; Korfali and Davies 2004).These result obtained in this work were in accordance with previous studies that highlighted that the potential risks caused by Cd were extremely associated with the acid-soluble fractions (Adelakan*et al*., 2011)

5.5.3 Chromium

Cr recorded the highest percentage level in the carbonate bound fraction across all the locations with exception of Dangulbi dam. The lowest percentage was generally recorded in the water soluble fraction across all the six locations. This suggests that Cr was mostly concentrated in the carbonate bound fraction (72.234%) much more than its concentration in exchangeable fraction (1.828%). The residual fraction has concentration of 171.2 mg/kg i.e. about 25.937% while water soluble has the least value. This is consistent with reports of other researchers where large proportion of Cr was found in the carbonate bound fraction and the least fraction located in the water soluble fraction (Korfali and Davies 2004; Naimo *et al*., 2005).Chromium may not be easily mobilized, this is because of the small fraction found in the exchangeable phase (F2), and hence a more severe condition might be required for their released. This result was also in aggrement with previous report that the potential risks caused by Cr were extremely associated with acid – soluble fractions (Adelakan *et al,* 2011). However, the potential ecological risks still exist and cannot be ignored even with the low percentage degree of association with the mobile fraction since environmental condition could modify this scenario (Adelakan*et al*., 2011).

5.5.4 Lead

The exchangeable fraction recorded some appreciable amount of Pb across all the locations with the highest being (16.714%) at Bagega river. The percentage of Pb distribution is in order: F3>F2>>F1. This is consistent with the results obtained by several authors (Jones and Turki, 1997; Li *et al*., 1995; Fan *et al*., 2002;Adelakan*et al*., 2011 and Wong *et al*., 2007).

5.5.5 Mercury

All three dams considered in this work and Bagega River recorded their highest percentage Hg concentration in the residual fraction while Sunke and Abare River recorded their highest percentage fractions in the carbonate bound fraction. The exchangeable also had some appreciable percentage Hg concentration across all the six locations. Water soluble fraction consistently had the lowest percentage Hg concentration across all the locations. This suggests that the mercury metal fractions were associated with the alumino–silicate minerals(Korfali and Davies *et al*., 2004; Naimo *et al*., 2005). The relative metal concentration in non-residual fraction can be used as a measure of the contribution from natural as well as anthropogenic sources, and higher percentage in these fractions indicates a high level in pollution of sediments from the sampling regions (Cao *et al*., 2014). Comparing the way the metals were bound to the different phases in the sediments,Cd and Pb appeared to be the most readily solubilized, thus making these elements the most potentially bioavailable. This may present a real threat as Cd is transferred into the food chain from soil contaminated by this metal. It is also clear that from the results and discussion so far that the metals in the sediments are bound to different fractions with different strength (Duan *et al*., 2014).

5.6 Heavy Metals Content in Food Crops (Tomatoes and Cassava)

Correlation analysis conducted to examine whether there is a relationship between the heavy metal concentrations in the tomatoes and cassava tubers for two wet and dry seasons revealed a significant positive relationship for Cr and Cd, Cd and Zn, Hg and Pb in the wet season and a significant and positive relationship for Cr and Cd, and Pb and Cr for dry season. This may explain the consistent variation of these metals in all the locations across the seasons.Concentrations of heavy metal in tomatoes and cassava in this work revealed spatial variation at all locations during the study periods. The relative abundance of different metals at the six locations during the wet and dry seasons varied with locations and with season in the tomatoes and cassava samples.

5.6.1 Zinc

All the metals investigated except Zn were measured in relatively high amount especially during the dry seasons across all the locations. This situation is expected in view of the reduction in the pollution in the wet season arising from increased dilution and water flow. Heavy metals are found naturally in the Earth, and become concentrated as a result of human activities such as industrial production, mining, agriculture and transportation (Noor-ul *et al*., 2015; Bassey *et al*., 2014). These metals have positive and negative roles in human life (Noor-ul *et al*., 2015, Colak *et al*., 2005; Oktem *et al*., 2005). For instance, heavy metal such as copper, chromium, cobalt and zinc are essential micronutrients for higher animals and for plant growth (Manohara *et al*., 2014). Studies have revealed that fruits and leafy vegetables are vulnerable to heavy metal contamination from soil, waste water and air pollution (Manohara *et al*., 2014). Zn is the least toxic among all heavy metals, and is an essential element in the human diet as it is required to maintain the proper functioning of the immune

system, normal brain activity and is fundamental in the growth and development of the foetus. Excessive Zn in the diet e.g. prolonged daily intake of Zn ranging from 150-450 mg/day is also detrimental to human health (Johnson *et al*., 2007). This was also similar to the report by Kirmani *et al*., 2011 and Bosiacki and Tyksinski, 2009, on the levels of Zn in onions, carrot, cabbage, and tomatoes above permissible levels by FAO/WHO.

5.6.2 Cadmium

Heavy metals such as Cd, Cu, Pb, Cr, Zn, Ni, As, Co and Hg cannot be degraded or destroyed and can be accumulated in living tissue through the food chain, causing various diseases and disorders (Manohara et al., 2014). Fruits, vegetables and other foods are among pathways by which heavy metals enter the human tissues leading to deterioration of health (Manohara et al., 2014). The presence and accumulation of the analyzed heavy metals in the cassava and tomatoes plants could be traced to their presence in the wastes used. Liu *et al*., 2005 opined that the soil type, root stock, mulching, irrigation, fertilization, and other cultural practices influence the water and nutrient supply to plant and affect the composition and quality attributes of the harvested parts. Although, Fe, Cu and Zn are normal nutrients required for the normal growth of plants though not required in large quantities hence their presence in the fruits could be justified. For instance heavy metal such as copper, chromium, cobalt and zinc are essential micronutrients for higher animals and for plant growth (Manohara *et al*., 2014).

5.6.3 Chromium

Studies by Sharma *et al*., (2007) indicated high Cr concentration in cassava, (1.39g/g-dw). Muchuweti *et al*.,(2006) also reported studies in non-polluted areas and recorded Cr (0.03µg/g-dw) in cassava and 2.45µg/g-dw) in cabbages with respective concentrations in soil of cauliflowers (0.016µg/g-dw) and cabbages (2.947µg/g-dw). Health effects of consuming

Cr contaminated vegetables include kidney and liver damage, skin rashes, stomach upset and ulcer, respiratory problem and lungs cancer and alteration of genetic materials. The result of this study agreed with the data reported by Liu *et al*., (2005). Also report from some researchers (Muchuweti *et al*., 2006; Sharma *et al*., 2007) demonstrated that the plants grown on wastewater-irrigated soils are contaminated with heavy metals and pose a major health concern.The accumulation of these heavy metals in the tomatoes and cassava was a manifestation of the presence of the metals in the soil due to their irrigation with waste water.

5.6.4 Lead and Mercury

The concentrationof Pb in this study was supported by the submission of *Liu et al*., 2005 who opined that the extractable Pb in both cultivated and uncultivated soils increased by increasing Pb addition to the soil. Sharma *et al*. (2007) showed that the concentrations of exhaustible metals (Zn, Cd, Pb) in the soil increased with increase in sludge application rate. This was supported by the submission of Sharma *et al*. (2007) who find a highly significant correlation between the chemical composition of irrigation water used and the soil chemical properties. The concentration of the heavy metal reported in the present study are lower than the one reported by Kakulu (1985) for Niger Delta, Okoye (1989) for Lagoon and that which was reported by Asaolu (1998) for Ondo State Coastal area.Average Pb level for this study are higher than the average value of 0.50µg/g which was obtained in a similar study along the highways of Benue State Nigeria (Adebayo and Rapheal, 2011) and also higher than 1.73µg/g in cassava tubers recorded by Nkwocha *et al* (2012) in an oil field in Bayelsa State. These values are unusually high and it is reflective of the anthropogenic activities around the locations (dams and rivers). Consumption of vegetables and tubers with high concentration would certainly result in health problems such as cognitive dysfunction, neurobehavioral disorders, hypertension and renal impairment (Peck *et al.*, 2006). The calculated contamination factor (CF) revealed that only Hg had CF values greater 6, which indicates a

serious contamination of tomatoes harvested from all the location. The pollution load index (PLI) across all the locations had PLI values less than 1. This indicates that there is no serious overall pollution load on the tomatoes samples. While in cassava sample, the calculated contamination factor (CF) for all the heavy metals with exception of Zn is very high, this showed the level of contamination of the samples. While the pollution load index (PLI) for all the location showed serious overall load of pollution on the sample.

5.7 Heavy Metal Content in Fish

Fish is widely acceptable for consumption because of its high palatability, low cholesterol and tender flesh (Ado *et al.,* 2012) and also a cheap source of protein. The demand for fresh water fishes can still be improved on, if information dissemination on the valuable nutritional composition of fishes reaches the grass route. Besides this, there is the need to raise consumer awareness to ensure that contaminated fishes are avoided. This will relieve the body of the burden of these toxic chemicals. Physicochemical properties of the water bodies across all locations favour production of fishes which conforms to standard for aquaculture (Damari*et al*., 2008).However the high concentration of non-essential heavy metals in some of the fish evaluated (*Orechromis. mossambicus)* is a source of concern. The fish sample in all the dams and river (*Orechromis mossambicus*) was analyzed for heavy metals for the period of two years (2014 and 2015) for both wet and dry seasons. The high level of heavy metals in the fish samples could probably be due to the prior exposure of these fishes to toxicants from polluted water body before swimming down to the reservoir since they are pelagic fishes. Medhi*et al*., (2012) linked the accumulation of the toxicants in the fish to the possibilities of the fish to accumulate metals and thus could serve as indicators of pollution.

5.7.1 Zinc

Zinc is known to be involved in most metabolic path-ways in humans and zinc deficiency can lead to loss of appetite, growth retardation, skin changes and immunological abnormalities (Malakootian *et al*., 2011). Fish takes up Zn directly from water, especially via mucous and gills. The concentration of Zn in fish in this work, fall below the maximum zinc level permitted for fish (50 mg/kg) according to Food Codex and WHO, 2004. The values recorded for this work are lower compared to Zn values reported for freshwater fishes in China (Du *et al*., 2012). United States environmental protection agency and the European Commission (US-EPA and EC) have not considered any standards or limits for the zinc concentrations in fish (WHO, 2008).

5.7.2 Cadmium

Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering *et al*; 1994). High concentrations of Cd have been found to lead to chronic kidney dysfunction. Cd can bio-accumulate at all levels of aquatic and terrestrial food chains (Sprague, 1986). The concentration of Cd was generally high across all the six locations especially in the dry season. The highest mean concentrations of 0.963 mg/kg in this work were recorded at Abare river. Gusau and Bakolori dams also showed very high Cd concentration of 0.845 mg/kg and 0.904 mg/kg respectively. This may have come from natural sources, run-off fromagricultural soils around the dams and rivers where phosphate fertilizers are in use, and more so, during the dry season when the volume of water of ponds and wells has reduced, miners relocate the mining processing closer to the dams and rivers where there is large volume of water, this was also in agreement to the report of (Stoeppler, 1991; Dimari *et al*., 2008).The concentrations recorded in this work are above the 0.01 mg/kg maximum permissible level for fish consumption (WHO, 2003).

5.7.3 Chromium

Chromium concentrations in normal and tolerant plants, fishes are (mgkg-1) 0.1 – 0.5 and 10.0 – 100.0 respectively (FAO, 2007). The concentration of Cr was generally high across all the six locations especially in the dry season. The highest mean concentrations of 1.313 mg/kg in this work were recorded at Abare river. Gusau and Dangulbi dams also revealed high Cr concentration of 0.850 mg/kg and 0.697 mg/kg respectively. This may have come from natural sources, run-off from agricultural soils around the dams and rivers where phosphate fertilizers are in use, and more so, during the dry season when the volume of water of ponds and wells has reduced, miners relocate the mining processing closer to the dams and rivers where there is large volume of water, this was also in agreement to the report of (Stoeppler, 1991; Dimari *et al*., 2008). High concentrations of chromium in plants have been associated with several chlorosis, necrosis and a host of other abnormalities and anatomical disorders. Chromium is necessary for the proper utilization of sugars and other carbohydrates by optimizing the production and effects of insulin. It is widely distributed in the body. The RDA is 0.05 to 2mg. sources include liver, meat, cheese, whole grain, yeast and wine. The effects of excess chromium are not known. Deficit causes impaired insulin function, hence increased insulin secretion and the risk of adult onset diabetes mellitus (Csuros and Csuros, 2002).

5.7.4 Lead

Lead is non-essential element that constitutes body burden and a great threat to life if present in substantial quantity. It is toxic even at low concentrations and has no known function in biochemical processes (Burden *et al.*, 1998). The standard level Pb was reported to be 0.5 mg/kg dry weight (FAO, 2007). Similar to Pb, Cadmium was also high value in the fishes and highest in location L6 (0.963 mg/kg). The standard permissible level of 0.05 to 5.5 mg/kg fish dry weight was reported for Cd (FAO, 1983). The concentrations of lead across all the locations are generally high when compared with the 0.01 mg/kg maximum

permissible level (NIS 554, 2007; WHO, 2003). This high concentration of lead might have come from sewage and agricultural and mining wastes discharged into the dams and rivers (El-Nagger *et al*., 2009).

5.7.5 Mercury

Mercury concentrations are high across all locations particularly Gusau dam (1.176 ± 0.003 mg/kg) and Abare river (1.349 ± 0.003 mg/kg) are alarming. The observed heavy metal concentrations in this fish are above the 0.001 mg/kg recommended limit for human consumption (Davies *et al*; 2006; Olowu *et al*, 2010; WHO, 2003). The public health implication of this work seems to show possibility of acute toxicity of the heavy metal of edible fishes consumed at these locations (Oshisanja and Oshisanya, 2009). This is more so because levels of Cd, Cr, Pb and Hg were above normal range in minimum allowable in the diet of man.

Correlation analysis was conducted to examine whether there is a relationship between the heavy metal concentrations in the fish sample for two wet and dry seasons. The result revealed a significant positive relationship for Pb and Cd, Hg and Cd and Hg and Cr respectively for wet seasons.This may explain the consistent variation of these metals in the locations in a particular season. While during the dry seasons, a significant and negative relationship was established for Pb and Zn, Pb and Cr and Hg and Cd then a significant and positive relationship for Cr and Zn respectively.This explains the different sources of these metals in the environmental samples. Generally, the concentrations of heavy metals (Zn, Cd, Cr, Pb and Hg) determined were higher in the dry seasons than in the wet seasons.This situation is expected in view of the reduction in the pollution in the wet season arising from increased dilution and water flow. This is also the trend observed for water and sediment

samples. This observation is also reported in a similar work by Asaolu and Olafe (2004) for fishes and crayfish from coastal water of Ondo State. The concentrations of the metal in the fish samples are lower than the one reported by Kakulu (1985) for Niger Delta, Okoye (1989) for Lagos lagoon and Asaolu (1998) for Ondo State Coastal area.

5.8 Proximate Composition of the Fish Samples

5.8.1 Moisture

The moisture content of the fish samples from all the locations ranged between 71.05 – 77.71% for the wet and in the dry season it ranged between 68.07 to 76.17% for year 2014 and 2015. The result showed that the percentage moisture content in the wet seasons were higher than that of the dry season. This further suggests a seasonal variation trend on the fish sample. Body composition is a good indicator for the physiological condition of fish. The percentage of water is a good indicator of its relative content of energy, proteins and lipids. The lower the percentage of water, the greater the lipid and protein contents, and the higher the energy density of the fish (Dempson *et al*., 2004; Ali *et al*., 2005). The increased value of moisture content during the wet season may be due to increase rainfall which eventually increases the volume of water on the body of the fish samples. This was also in close agreement with Davies and Davies (2009) who peg fish to be made up of 70 – 84% water. The high moisture content of the fish sample would increase the deterioration level of the fish when kept for long time. This is because the micro-organisms would be highly active with high moisture content. This is also in agreement with the observation reported by Abolude and Abdullahi (2003); Otitologbon *et al*. (1997); Balogun and Adebayo (1996). Also, moisture content range of 65.88 to 78.62 (Mazumder *et al*., 2008), 77.93 to 82.7% (Ravichandran *et al*., 2011) and 68.6 to 77.1% (Aberoumand and Pourshafi, 2010) were reported for fishes.

5.8.2 Ash

The value of the ash content for both seasons were relatively similar except Bakolori dam which recorded the lowest ash content during the dry season, while Bagega river during the wet season recorded the highest ash content of 10.20%. This result was also in agreement with Johnson, (2010) which reported that fresh water fish recorded the lowest ash and crude fibre content. The result is also comparable to the observation of Abolude and Abdullahi (2003, 2005), who studied the proximate analysis and mineral contents in components of Clarias Gariepinus.

5.8.3 Crude Protein

The crude protein values for both seasons are relatively high, although those of Gusau dam to Dangulbi dam are higher than those of Bagega River to Abare River. This is an indication that the fish sample is a good source of protein. This is also an expected outcome since fish is a good source of protein (Tidwell, 2001). The higher crude protein content in fish is important from a dietary point of view since; the quality of fish protein is very high because of its essential amino acid composition. This very studies indicate that the crude protein content of the fish from Bagega river to Abare river are relatively lower when compared to that of the dams and other literatures. This may be due to activities done using the rivers which include but no limited to mineral exploitations, gold mining, farming and so on, which releases a lot of toxic metals into the river and may lead to eventual death of fish.Protein and fat are the major nutrient in fish and their level help to define the nutritional status of a particular organism (Aberoumad and Pourshafi, 2010). The chemical composition of fish varies from one individual to another depending on age, sex, environment and season with protein level ranging from 16 to 21%, lipid from 0.1 to 25 %, ash 0.4 to 1.5%, moisture content of 60 to 80 % with extreme of 96% having been reported (Muchuweti*et al*., 2006).

Furthermore, reports also indicate that fish muscle is more digestible than other animal protein due to lower level of connective tissues (Muchuweti*et al*., 2006).

5.8.4 Crude Fat

The values of the crude fat content ranged between 8.59 to 11.67% for the wet season while it ranged between 10.53 to 13.53% for dry season respectively. The result here revealed that the values are relatively similar with the exception of Dangulbi dam which recorded the highest crude fat both in wet and dry season. The fat content value is also in close agreement with the one reported by Abolude and Abdullahi (2005) in Clarias Gariepinus fish sample and also that of Olafe *et al* (1998) for grasshopper. Fat is the major source of energy supply in foods. The concentration of the proximate components in the fish samples are within the reference value of FAO/WHO (1991) for Humans. The values we obtained for the proximate composition where within the reported ranges with higher percentage in the case of ash.

In view of the importance of fish in human diet, it is necessary that biological monitoring of the fish meant for consumption should be carried out regularly to ensure safety. WHO (1999) reported that heavy metals must be controlled in food sources in order to assure public safety.

5.9 Histopathology of the Fish (Orechromis *mosambicus*)

In the context of pollution, aquatic systems are highly at risk because of their trend for accumulation of relatively high concentrations of chemicals entering from surrounding terrestrial systems, thus, regardless of their source of entry to the environment, water bodies are frequently stores for a large variety of stressor chemicals (Reddy, 2012).Most biomarkers are narrow in their expression whereas histopathology is broad in its evaluation (Medja *et al*.,

2011). Well documented lesions based on experimental data in liver, kidney, gills, ovary, skeleton system and skin have been used as biomarkers to date (Reddy *et al*., 2010; Akpolih, 2013)**.** Therefore, histopathology is the gold standard when defining toxicological effects, biomarkers with a known histological distribution may fill the need of localizing toxic injury to distinct organs or tissues.

5.9.1 Histopathological observation of the gills

The gills of a fish comprises of multifunctional organs (respiration, ion regulation, acid-base balance and nitrogenous waste regulation, excretion), which constitute over 50 percent of the total surface area of the fish that make it sensitive to chemicals in water. The fish gills play an important role in maintaining ionic homeostasis in both freshwater and marine environment. Consequently, injury to gill epithelium is a common response observed in fish exposed to a variety of contaminants. It was observed that all the fish gills from Gusau dam to Abare riverare injured. The severity of damage to the gills depends on the concentration of the toxicants available in the different dams and rivers. The gills of Bakolori dam, Bagega, Sunke and Abare river are more damaged when compared with those of Gusau and Dangulbi dams**.** It was also observed for gills of Bakolori and Dangulbi dams when compared with the control that the lamellar epithelial cells were lifted away from the basement membrane due to a penetration of fluid, this is the most common lesion, which could give rise to reduce respiratory gas exchange by increasing diffusion distance and decreasing interlamellar distance. While for the gills of Bagega, Sunke and Abare rivers, fusion of neighboring lamellae and epithelial rupture are observed which are the direct results of pavement cell lifting and represent more severe gill damage. This was also in agreement with report of (Reddy *et al*., 2010; Au, 2004). Lamellar fusion, hyperplasia, necrosis of different lamellar is another most commonly reported responses, but is more common for metals than for organics or other pollutants, possibly since metals directly interact with ion

transport proteins and inhibit their activity (Reddy *et al*., 2010; Butchiram *et al*., 2013). It was also observed that there was a swelling of the Necrosis for all the locations except Gusau dam. Hypertrophy of the pavement cells is possibly an event associated with necrosis cell swelling. These alterations are more commonly associated with chronic exposures to metal contaminants than acutely lethal exposures (Rosety-Rodriguez *et al*., 2002).These are the gills lesions in response to a wide range of contaminants, including, petroleum compounds, organophosphates, carbonates, herbicides and heavy metals with a greater reported occurrence (Au, 2004)**.** The same changes have also been reported in the gills of the fishes exposed to organic toxicantsand metals and industrial effluent (Rosety-Rodriguez *et al*., 2002).

5.9.2 Histopathological changes of liver

In general, liver is a target organ due to its large blood supply that causes noticeable toxicant exposure and accumulation and also its clearance function and its pronounced metabolic capacity (Mohamed, 2009). Numerous categories of liver pathology are present as reliable biomarkers of toxic damage (Reddy *et al*., 2012; Deore *et al*., 2012).

The liver of fish samples in all the six locations showed sign of abnormalities such as irregular shaped hepatocytes, cytoplasmic vacuolation and nucleus in a lateral position in the siluriform *Corydoras paleatus* as if they have been exposed to organophosphate pesticides. This was similar to the report ofFunta *et al*., (2003)who reported such abnormalities in the liver of fish. The liver of fish sample collected in the rivers (Bagega, Sunke and Abare) also showed more signs of degeneration (cytoplasmic and nuclear degeneration and nuclear vacuolation) and thefocal necrosis in the liver parenchyma. This was also in close agreement with the report of Reddy *et al*., (2010)and Reddy and Baghel(2012)who observed signs ofdegeneration (cytoplasmic and nucleardegeneration and nuclear vacuolation) and thefocal necrosis in the liver parenchyma of fishesexposed to the industrial effluent. Thesealterations

have been reported as more severechanges, which are more commonly associatedwith the exposure of the fishes to contamination by various metals (Hyalij, 2012; Medhi *et al*., 2012; Golemi *et al*., 2013). Lesions including hepatocellular cytoplasmic vacuolization, leucocytes infiltrations, blood congestion necrosis and fatty infiltrations were found in the liver of catfish Clarias gariepinus treated with fenvalerate (Sakr *et al*., 2001).The same changes were reported by Teh *et al*.(2005) in the liver of 7-day-old larvae of the fish Sarcamento *Splittail*.

5.9.3 Histopathological observation of skin

Samples of the examined Tilapia fish (*Orechromis mosambicus)* skinhave shown changes only at the level of the epidermis, without major changes in the dermis and hypodermis. Picnotic nuclei in the matrix layer of the epidermis were the most severe lesion was recorded. A common feature was erosion with desquamation of epithelium, and rupture (excoriation) of parts of epidermis. The major skin change revealed was a hyperplasia of the epidermal cells including hyperplasia of mucous cells. The mucous cells of the fishes of Gusau and Bakolori dam were emptied, whereas other samples revealed a lack of this cell type, indicating an overproduction of mucous that hasexhausted the capacity of the epidermis to divide and differentiate into mucous cells. In addition, a leucocytes infiltration in the epidermis was found in Bagega riverindicating a possible inflammatory reaction, especially in parts with excoriated epidermis where lack and/or erosion of the epidermis induced a defense mechanism. Skin changes recorded in this present study were restricted to the epidermis, and there were no deeper changes in the dermis and hypodermis. The same changes have also been reported in the skins of the fishes exposed to organic toxicants**,** metals and industrial effluent (Rosety-Rodriguez *et al*., 2002). The severity of these contaminants causes injury like haemorrhage.This was similar to the report ofFunta *et al*., (2003) and (Peck and Zinke, 2006). However, the fish sample in this work showed response to the direct effects of the pollutants. Thisinformation verifies that histopathology studies are

valuable biomarkers for fieldevaluation, especially in tropic regions thatare naturally affected by variety ofenvironmental variations.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

The physicochemical parameters of the dams and the rivers water samples revealed a fresh water environment with low chemical pollutants burden. However, high turbidity and low dissolved oxygen of the river values compared with drinking water standards were recorded. Seasonal variation in most of the measured water quality parameters and heavy metal in sediment, food crops and fish samples were significant. Microbial burden of the dam and river water was high compared to the recommended standards by WHO and USEPA for drinking water, thus constituting a serious hazard to public health, as their presence is indicative of a possible presence of micro-organism associated with water-borne diseases, suggesting the need for adequate disinfection process before distribution for domestic and industrial uses.

The distribution pattern of heavy metals levels in the water, sediment, tomatoes and cassava crops and fish samples suggests contribution from anthropogenic influences which include but not limited to mining activities through runoff into the water bodies.The levels of the metals in the water bodies particularly Cd, Pb, and Hg were generally high with exception of Zn metal which should cause trepidation to both the aquatic lives and human health, hence calling for urgent regular monitoring of the dam and control of anthropogenic input into the water bodies particularly the rivers situated in the Villages.

The speciation of heavy metals with selective extracting agents gives additional information about the fundamental reactions governing the behaviour of the metals in sediments. Comparing the way the metals were bound to the different phases in the sediments, it is clear that the metals in the sediments are bound to different fractions with different strength. Anthropogenic input of Cd and Cr was primarily in the carbonate bound fraction while Inputs of Zn and Hg appear mainly in the residual form. Inputs of Pb were found in carbonate, exchangeable and water soluble fractions. The distribution of the five studied metals in the various fractions confirms their differences in mobility.

Of the five elements studied, Cd and Pb appeared to be the most readily solubilized, thus making these elements the most potentially bioavailable. This may present a real threat as Cd and Pb are transferred into the food chain from soil contaminated by these metals.

The pollution level of all the water bodied and other samples was accessed using the contamination factor (CF) and pollution load index (PLI), which revealed that all the locations under study have suffered from metal pollution particularly of Pb, Cd and Hg.

The histopathological analysis of the fish gills, liver and skin sample in this study showed responses to the direct effects of the pollutants. This information verifies that histopathology studies are valuable biomarkers for field evaluation, especially in tropical regions that are naturally affected by variety of environmental variations.

6.2Conclusion

i. The physicochemical parameters reveaved high turbidity and low dissolved oxygen particularly of the river values when compared with drinking water standards by WHO,USEPA

ii. The research also revealed a high microbial burden of the dam and river water when compared to the recommended standards by WHO and USEPA for drinking water, thus constituting a serious hazard to public health.

iii. Concentration of the metals in the water bodies particularly Cd, Pb, and Hg were generally high with exception of Zn metal which could cause trepidation to both the aquatic lives and human health, hence calling for urgent regular monitoring.

iv. From the five elements studied, Cd and Pb were the most readily solubilized, making these elements the most potentially bioavailable. This may present a real threat as Cd and Pb are transferred into the food chain from soil contaminated by these metals.

v. The information provided by this research verifies that histopathology studies are valuable biomarkers for field evaluation, especially in tropical regions that are naturally affected by variety of environmental variations.

6.3 Recommendations for further studies

It is recommended that

1. Blood specimen be collected from persons around the vicinity of the dams and rivers where mining is taking place to monitor heavy metal levels in them.
2. Heavy metal content of the dust particles above ground level should also be monitored around the state particularly the mining vicinities.
3. There is need to introduce plants and develop new ones (genetically) that can increase phytoremediation potentials so as to offer a viable remediation solution for the polluted water and farmland instead of the soil excavation that is been done to remediate polluted soils in the state.

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APPENDIX I

Sequential Extraction of Heavy Metals in the Soil at the Mining Site around the Dams and Rivers

Locations	Fractions (mg/kg) Zn								
	Water Soluble		Exchangeable		Carbonate Bound		Residual		Total
Gusau dam	23.920	**14.724**	12.560	**7.731**	31.080	**19.131**	94.900	**58.414**	162.460
Bakolori dam	47.680	**28.310**	10.800	**6.413**	17.840	**10.593**	92.100	**54.685**	168.420
Dangulbi dam	56.120	**10.765**	278.180	**53.359**	13.240	**2.540**	173.800	**33.337**	521.340
Bagega river	28.420	**15.533**	34.580	**18.900**	21.060	**11.511**	98.900	**54.056**	182.960
Sunke river	43.930	**20.333**	11.120	**5.147**	12.600	**5.832**	148.400	**68.688**	216.050
Abare river	45.820	**25.408**	19.020	**10.547**	31.500	**17.467**	84.000	**46.579**	180.340

Values in Bold form are the percentage (%) fraction.

APPENDIX II

Sequential Extraction of Heavy Metals in the Soil at the Mining Site around the Dams and Rivers

Location	Fractions (mg/kg) Cd								
	Water Soluble		Exchangeble		Carbonate Bound		Residual		Total
Gusau dam	502.520	**14.739**	1312.400	**38.492**	1548.760	**45.424**	45.850	**1.34476**	3409.530
Bakolori dam	891.940	**19.019**	1771.540	**37.776**	1914.320	**40.820**	111.850	**2.38504**	4689.650
Dangulbi dam	1760.000	**22.941**	2639.800	**34.410**	2949.460	**38.446**	322.450	**4.2031**	7671.710
Bagega river	825.260	**27.972**	896.780	**30.397**	1195.220	**40.512**	33.000	**1.11855**	2950.260
Sunke river	1265.380	**39.931**	905.320	**28.569**	955.140	**30.141**	43.050	**1.35852**	3168.890
Abare river	2673.280	**33.027**	2492.280	**30.791**	2492.280	**30.791**	436.300	**5.39032**	8094.140

APPENDIX III

Sequential Extraction of Heavy Metals in the Soil at the Mining Site around the Dams and Rivers

Locations	Fractions (mg/kg) Cr								
	Water Soluble		Exchangeble		Carbonate Bound		Residual		Total
Gusau dam	0	**0.000**	4.66	**1.406**	283.52	**85.519**	43.35	**13.076**	331.53
Bakolori dam	1.36	**0.214**	6.8	**1.068**	457.1	**71.819**	171.2	**26.899**	636.46
Dangulbi dam	0.24	**0.109**	7.64	**3.472**	104.86	**47.655**	105.3	**47.855**	220.04
Bagega river	0	**0.000**	13.32	**1.828**	526.22	**72.234**	188.95	**25.937**	728.49
Sunke river	1.76	**0.222**	30.1	**3.801**	422.8	**53.393**	337.2	**42.583**	791.86
Abare river	4.68	**0.420**	15.32	**1.375**	571.9	**51.333**	522.2	**46.872**	1114.1

APPENDIX IV

Sequential Extraction of Heavy Metals in the Soil at the Mining Site around the Dams and Rivers

Site	Fractions (mg/kg) Pb								
	Water Soluble		Exchangeble		Carbonate Bound		Residual		Total
Gusau dam	9.72	**0.158**	314.46	**5.122**	2157.16	**35.137**	3658	**59.583**	6139.34
Bakolori dam	8.24	**0.105**	892.4	**11.363**	2453.18	**31.236**	4500	**57.297**	7853.82
Dangulbi dam	9.92	**0.152**	370.4	**5.672**	1468.46	**22.485**	4681.95	**71.691**	6530.73
Bagega river	157.54	**1.016**	2591.7	**16.714**	8532.28	**55.025**	4224.75	**27.245**	15506.27
Sunke river	1454.74	**9.832**	2827.08	**19.108**	6244.72	**42.207**	4168.75	**28.176**	14795.29
Abare river	119.46	**0.912**	780.76	**5.959**	8560.28	**65.332**	3642.3	**27.798**	13102.8

APPENDIX V

Sequential Extraction of Heavy Metals in the Soil at the Mining Site around the Dams and Rivers

Location	Fractions (mg/kg) Hg								
	Water Soluble		Exchangeble		Carbonate Bound		Residual		Total
Gusau dam	0.046	**0.014**	14.833	**5.112**	17.778	**5.364**	296.689	**89.516**	329.346
Bakolori dam	0.381	**0.115**	14.795	**4.464**	25.991	**7.842**	290.269	**87.579**	331.436
Dangulbi dam	5.151	**1.554**	18.362	**5.540**	28.702	**8.660**	279.222	**84.246**	331.473
Bagega river	5.359	**1.028**	29.288	**5.618**	83.179	**15.785**	404.382	**77.569**	522.219
Sunke river	240.201	**8.145**	599.397	**20.325**	1513.340	**51.316**	596.123	**20.214**	2949.061
Abare river	266.663	**8.414**	670.522	**21.167**	1556.801	**49.145**	687.406	**21.270**	3181.392

Values in Bold form are the percentage (%) fraction**.**

APPENDIX VI

Two Way ANOVA Showing the Effect of Location and Year on the pH of Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	0.39	5	32.15	32.15	0.00*
Year	0.01	1	4.94	4.94	0.00*
Location * Year	0.01	5	0.58	0.58	0.36
Error	0.59	24			
Total	0.42	35			

* Significantly different at $P < 0.05$

APPENDIX VII

Two Way ANOVA Showing the Effect of Location and Year on the pH of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	0.63	5	0.13	5.42	0.00*
Year	0.07	1	0.07	2.99	0.10
Location * Year	0.06	5	0.01	0.49	0.78
Error	0.56	24			
Total	0.31	35			

*Significantly different at $P < 0.05$

APPENDIX VIII

Multiple range test of pH for 2014 and 2015 for all locations of water bodies in the wet and dry season

Location	pH Wet	Ph Dry
L1	7.60 ± 0.02^{a}	7.70 ± 0.06^{a}
L2	7.59 ± 0.02^{a}	7.67 ± 0.06^{a}
L3	7.60 ± 0.02^{a}	7.63 ± 0.06^{a}
L4	7.67 ± 0.02^{b}	7.92 ± 0.06^{b}
L5	7.89 ± 0.02^{c}	7.94 ± 0.06^{b}
L6	7.70 ± 0.02^{b}	7.63 ± 0.06^{a}

n=6, mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX IX: Combined Mean of pH for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	pH Wet	pH Dry
2014	7.69 ± 0.01	7.79 ± 0.04
2015	7.66 ± 0.01	7.71 ± 0.04

n = 36; mean ± S.D

APPENDIX X

Two Way ANOVA Showing the Effect of Location and Year on the Temperature of Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	0.50	5	0.10	60.27	0.00*
Year	0.10	1	0.01	6.0	0.02*
Location * Year	0.13	5	0.00	1.60	0.20
Error	0.40	24	0.00		
Total	0.57	35			

* Significantly different at $P < 0.05$

APPENDIX XI: Two Way ANOVA Showing the Effect of Location and Year on the Temperature of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	0.93	5	0.19	55.68	0.00*
Year	0.01	1	0.01	4.08	0.06
Location * Year	0.52	5	0.10	1.60	0.00*
Error	0.08	24	0.00		
Total	1.54	35			

❖ Significantly different at $P < 0.05$

APPENDIX XII

Multiple range testof Temperature for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	Temperature Wet	Temperature Dry
L1	26.52 ± 0.02[a]	26.73 ± 0.02 [b]
L2	26.60 ± 0.02 [b]	26.63 ± 0.02 [a]
L3	26.53 ± 0.02 [a]	26.87 ± 0.02 [c]
L4	26.73 ± 0.02 [c]	27.03 ± 0.02 [e]
L5	26.75 ± 0.02 [c]	27.08 ± 0.02 [e]
L6	26.83 ± 0.02 [d]	26.97 ± 0.02 [d]

* n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XIII: Combined means of Temperature for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	Temperature Wet	Temperature Dry
2014	26.64 ± 0.01	26.91 ± 0.01
2015	26.68 ± 0.01	26.87 ± 0.01

n = 2; mean ± S.D

APPENDIX XIV

Two Way ANOVA Showing the Effect of Location and Year on the EC of Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	136250.00	5	27250.00	4360	0.00*
Year	25.00	1	25.00	4	0.57
Location * Year	1025.00	5	205.00	32.80	0.00*
Error	150.00	24	6.25		
Total	2014350.00	35			

* Significantly different at $P < 0.05$

APPENDIX XV: Two Way ANOVA Showing the Effect of Location and Year on the E.C of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	87213.89	5	17442.78	149.51	0.00*
Year	2.78	1	2.78	0.02	0.88
Location * Year	9613.89	5	1922.78	16.48	0.00*
Error	2800.00	24	116.67		
Total	99630.56-	35			

*Significantly different at $P < 0.05$

APPENDIX XVI

Multiple range test of EC for 2014 and 2015 for Different Locations of Water Bodies in the Wet and Dry Season

Location	EC Wet	EC Dry
L1	124.17± 1.02 [a]	171.67 ± 4.41 [a]
L2	205.83 ± 1.02 [b]	225.00 ± 4.41 [b]
L3	213.33 ± 1.02 [c]	231.67 ± 4.41 [b]
L4	240.83 ± 1.02 [d]	265.00 ± 4.41 [c]
L5	256.67 ± 1.02 [e]	290.00 ± 4.41 [d]
L6	329.17 ± 1.02 [f]	325.00 ± 4.41 [e]

* n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XVII: Combined means of EC for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	EC Wet	E.C Dry
2014	227.50 ± 0.59	251.11 ± 2.55
2015	229.12 ± 0.59	251.67 ± 2.55

n = 36; mean ± S.D

APPENDIX XVIII

Two Way ANOVA Showing the Effect of Location and Year on the TDS of Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	338922.22	5	67784.44	225.95	0.00*
Year	544.44	1	544.44	1.82	0.19
Location * Year	145.57	5	291.11	0.97	0.46
Error	7200.00	24	300.00		
Total	348122.22	35			

* Significantly different at $P < 0.05$

APPENDIX XIX: Two Way ANOVA Showing the Effect of Location and Year on the T.D.S. of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	714742.22	5	142948.44	54.84	0.00*
Year	1860.48	1	1860.48	0.71	0.41
Location * Year	3943.76	5	788.75	0.97	0.46
Error	62564.48	24	2606.85		
Total	783110.94	35			

Significantly different at $P < 0.05$

APPENDIX XX

Multiple range test of TDS for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	TDS Wet	T.D.S. Dry
L1	188.33 ± 7.01^{a}	173.67 ± 20.8^{a}
L2	296.67 ± 7.01^{b}	273.33 ± 20.8^{b}
L3	338.33 ± 7.01^{c}	365.33 ± 20.8^{c}
L4	353.33 ± 7.01^{c}	413.33 ± 20.8^{c}
L5	398.33 ± 7.01^{c}	425.00 ± 20.8^{c}
L6	508.33 ± 7.01^{d}	515.00 ± 20.8^{d}

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XXI: Combined means of TDS for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**TDS Wet**	**TDS Dry**
2014	227.50 ± 4.08	337.03 ± 12.03
2015	229.12 ± 4.08	351.41 ± 12.03

n = 36; mean ± S.D

APPENDIX XXII

Two Way ANOVA Showing the Effect of Location and Year on the TSS in Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P – Value
Location	1040644.80	5	208128.96	1011.27	0.00*
Year	1854.74	1	1854.74	9.01	0.01*
Location * Year	3003.22	5	600.64	2.91	0.03*
Error	4939.44	24	205.81		
Total	1050442.2	35			

❖ Significantly different at $P < 0.05$

APPENDIX XXIII: Two Way ANOVA Showing the Effect of Location and Year on the TSS in Water Bodies in the Dry season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	1133450.33	5	226690.07	8285.12	0.00*
Year	373.78	1	373.78	13.66	0.01*
Location * Year	2692.22	5	538.44	19.68	0.00 *
Error	656.67	24	27.36		
Total	1137173.00	35			

Significantly different at $P < 0.05$

APPENDIX XXIV

Multiple range test of TSS for 2014 and 2015 for Different Locations of Water Bodies in the Wet and Dry Season

Location	TSS Wet	T.S.S. Dry
L1	84.43 ± 5.86[a]	107.50 ± 2.14[a]
L2	156.50± 5.86 [b]	126.17 ± 2.14[b]
L3	178.33 ± 5.86 [c]	183.33 ± 2.14[c]
L4	396.00 ± 5.86 [d]	439.50 ± 2.14[d]
L5	425.00± 5.86[e]	460.00 ± 2.14[e]
L6	558.33± 5.86 [f]	552.50 ± 2.14[f]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XXV: Combined means of TSS for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**TSS Wet**	**TSS Dry**
2014	306.94 ± 3.38	314.72 ± 1.23
2015	292.59± 3.38	308.28 ± 1.23

n = 36; mean ± S.D

APPENDIX XXVI

Two Way ANOVA Showing Effect of Location and Year on the Concentration of Cl in Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		
Total	2199.90	35			

*

* Significantly different at $P < 0.05$

APPENDIX XXVII: Two Way ANOVA Showing Effect of Location and Year on Concentration of Cl in Water Bodies in Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	2144.14	5	428.83	1341.25	0.00*
Year	0.02	1	0.02	0.06	0.82
Location * Year	52.10	5	10.60	33.15	0.00*
Error	7.67	24	0.32		
Total	2204.83	35			

* Significantly different at $P < 0.05$

APPENDIX XXVIII

Multiple range testof Cl for 2014 and 2015 for Different Locations of Water Bodies in the Wet and Dry Season

Location	Cl Wet	Cl Dry
L1	15.56 ± 7.07 [a]	16.00 ± 0.23 [a]
L2	18.70 ± 7.071 [b]	18.01 ± 0.23 [b]
L3	20.70 ± 7.07 [c]	21.08 ± 0.23 [c]
L4	27.18 ± 7.07 [d]	27.18 ± 0.23 [d]
L5	34.54 ± 7.07 [e]	35.81 ± 0.23 [f]
L6	36.00 ± 7.07 [f]	34.52 ± 0.23 [e]

n =6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XXIX: Combined means of Cl for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**Cl** **Wet**	**Cl** **Dry**
2014	35.11 ± 4.08	25.46 ± 0.13
2015	34.33 ± 4.08	25.51 ± 0.13

n = 36; mean ± S.D

APPENDIX XXX

Two Way ANOVA Showing the Effect of Location and Year on the Alkalinity of Water Bodies in the Wet Season

Source	Sum of Squares	df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

significantlydifferent at $P < 0.05$

APPENDIX XXXI: Two Way ANOVA Showing the Effect of Location and Year on the Alkalinity of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	195.98	5	39.20	518.52	0.00*
Year	7.98	1	7.98	105.58	0.00*
Location * Year	3.62	5	0.73	9.60	0.00*
Error	1.81	24	0.08		
Total	209.40	35			

❖ Significantly different at $P < 0.05$

APPENDIX XXXII: Multiple range testof Alkalinity for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	Alkalinity Wet	Alkalinity Dry
L1	15.70 ± 0.13 [a]	17.75 ± 0.11 [a]
L2	17.70 ± 0.13 [b]	17.97 ± 0.11 [a]
L3	18.38 ± 0.13 [c]	18.97 ± 0.11 [b]
L4	20.99 ± 0.13 [d]	21.86 ± 0.11 [c]
L5	22.06± 0.13 [e]	23.93 ± 0.11 [d]
L6	22.93± 0.13 [f]	22.15 ± 0.11 [c]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XXXIII: Combined means of Alkalinity for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	Alkalinity Wet	Alkalinity Dry
2014	19.78 ± 0.07	20.91 ± 0.07
2015	19.30± 0.07	19.97 ± 0.07

n = 36; mean ± S.D

APPENDIX XXXIV
Two Way ANOVA Showing the Effect of Location and Year on the Turbidity of Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

Significantly different at $P < 0.05$

APPENDIX XXXV: Two Way ANOVA Showing the Effect of Location and Year on the Turbidity of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	48998.13	5	9799.43	32070.86	0.00*
Year	14.69	1	14.69	48.09	0.00*
Location * Year	8.47	5	1.69	5.55	0.02*
Error	7.33	24	0.31		
Total	49027.64	35			

Significantly different at $P < 0.05$

APPENDIX XXXVI

Multiple range testof Turbidity for 2014 and 2015 for Different Locations of Water Bodies in the Wet and Dry Season

Location	Turbidity Wet	Turbidity Dry
L1	5.67 ± 1.76 [a]	7.67 ± 0.23 [a]
L2	7.33 ± 1.76 [a]	7.83 ± 0.23 [a]
L3	10.83 ± 1.76 [a]	11.50 ± 0.23 [b]
L4	73.00 ± 1.76 [b]	80.33 ± 0.23 [c]
L5	75.50± 1.76 [b c]	80.50± 0.23 [c]
L6	79.00± 1.76 [c]	87.00± 0.23 [d]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XXXVII: Combined means of Turbidity for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**Turbidity Wet**	**Turbidity Dry**
2014	42.22 ± 1.02	46.44 ± 0.13
2015	41.56± 1.02	45.45± 0.13

n = 36; mean ± S.

APPENDIX XXXVIII

Two Way ANOVA Showing the Effect of Location and Year on the SO_4 of Water Bodies in the Wet Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

* Significantly different at $P < 0.05$

APPENDIX XXXIX: Two Way ANOVA Showing the Effect of Location and Year on the SO_4 of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	2528.71	5	505.74	723.43	0.00*
Year	0.14	1	0.14	0.19	0.66
Location * Year	3.02	5	0.60	0.86	0.00*
Error	16.78	24	0.70		
Total	2548.64	35			

* Significantly different at $P < 0.05$

APPENDIX XL

Multiple range testof SO_4 for 2014 and 2015 for Different Locations of Water Bodies in the Wet and Dry Season

Location	SO_4 Wet	SO_4 Dry
L1	9.38 ± 0.07 [a]	10.43 ± 0.34 [a]
L2	9.33 ± 0.07 [a]	10.53 ± 0.34 [a]
L3	9.41 ± 0.07 [a]	10.10 ± 0.34 [a]
L4	14.15 ± 0.07 [b]	25.13 ± 0.34 [b]
L5	15.86± 0.07 [c]	27.08 ± 0.34 [c]
L6	18.13± 0.07 [d]	29.47 ± 0.34 [d]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XLI: Combined means of Turbidity for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**SO_4 Wet**	**SO_4 Dry**
2014	12.54 ± 0.04	18.88 ± 0.20
2015	12.88± 0.04	19.01± 0.20

* n = 36; mean ± S.D

APPENDIX XLII

Two Way ANOVA Showing the Effect of Location and Year on the PO_4 of Water Bodies in the Wet Season

Source	Sum of Squares	df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		
Total	257.96	35			

* Significantly different at $P < 0.05$

APPENDIX XLIII: Two Way ANOVA Showing Effect of Location and Year on the PO_4 of Water Bodies in the Dry Season

Significantly different at $P < 0.05$

APPENDIX XLIV

Multiple range testof PO_4 for 2014 and 2015 for Different Locations of Water Bodies in the Wet and Dry Season

Location	PO_4 Wet	PO_4 Dry
L1	2.10 ± 0.04 [b]	2.29 ± 0.47 [b]
L2	1.68 ± 0.04 [a]	1.84 ± 0.47 [a]
L3	2.68 ± 0.04 [c]	2.73 ± 0.47 [c]
L4	6.12 ± 0.34[d]	6.38 ± 0.47 [d]
L5	7.31± 0.04 [e]	7.46 ± 0.47 [e]
L6	8.17± 0.04[f]	8.52 ± 0.47 [f]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XLV: Combined means of PO_4 for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	PO_4 Wet	PO_4 Dry
2014	4.77 ± 0.02	5.05 ± 0.03
2015	4.58± 0.02	4.68± 0.03

n = 36; mean ± S.D

APPENDIX XLVI

Two Way ANOVA Showing the Effect of Location and Year on the COD of Water Bodies in the Wet Season

Source	Sum of Squares	df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

* Significantly different at $P < 0.05$

APPENDIX XLVII: Two Way ANOVA Showing the Effect of Location and Year on the COD of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	71757.48	5	14351.50	2162.00	0.00*
Year	974.48	1	974.48	146.802	0.00*
Location * Year	501.16	5	100.23	15.10	0.00*
Error	159.313	24	6.64		
Total	73392.44	35			

*Significantly different at $P < 0.05$

APPENDIX XLVIII

Multiple range testof COD for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	COD Wet	COD Dry
L1	196.67 ± 2.54[c]	191.00 ± 1.05[c]
L2	180.17± 2.54 [b]	182.93± 1.05 [b]
L3	166.70 ± 2.54 [a]	168.15 ± 1.05 [a]
L4	240.67± 2.54 [d]	244.50 ± 1.05 [d]
L5	263.00± 2.54 [e]	267.67 ± 1.05 [e]
L6	269.17± 2.54 [e]	285.17± 1.05 [e]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX XLIX: Combined means of COD for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**COD Wet**	**COD Dry**
2014	220.46 ± 1.46	220.46 ± 1.46
2015	218.33± 1.46	218.33± 1.46

n = 36; mean ± S.D

APPENDIX L

Two Way ANOVA Showing the Effect of Location and Year on the BOD of Water Bodies in the Wet Season

Source	Sum of Squares	df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

*Significantly different at $P < 0.05$

APPENDIX LI: Two Way ANOVA Showing the Effect of Location and Year on the BOD of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	3641.30	5	728.26	363.47	0.00*
Year	70.00	1	70.00	34.94	0.00*
Location * Year	61.75	5	12.35	6.16	0.01*
Error	48.08	24	2.00		
Total	3821.14	35			

*Significantly different at $P < 0.05$

APPENDIX LII

Multiple range testof BOD for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	BOD Wet	BOD Dry
L1	34.67 ± 0.21^{f}	35.47 ± 0.58^{e}
L2	26.95± 0.21 ^{e}	30.37± 0.58^{d}
L3	19.50 ± 0.21 ^{d}	21.57 ± 0.58^{c}
L4	11.94± 0.21 ^{c}	12.75 ± 0.58^{b}
L5	10.51± 0.21 ^{b}	11.28 ± 0.58^{b}
L6	7.83± 0.21 ^{a}	8.63± 0.58^{a}

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX LIII: Combined means of BOD for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**BOD Wet**	**BOD Dry**
2014	19.74 ± 0.12	21.41 ± 0.33
2015	17.40± 0.12	18.62 ± 0.33

n = 36; mean ± S.D

APPENDIX LIV

Two Way ANOVA Showing the Effect of Location and Year on the DO of Water Bodies in the Wet Season

Source	Sum of Squares	df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

significantly different at $P < 0.05$

APPENDIX LV: Two Way ANOVA Showing the Effect of Location and Year on the DO of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	182.82	5	36.56	3290.82	0.00*
Year	0.22	1	0.22	19.60	0.00*
Location * Year	4.13	5	0.83	74.38	0.00*
Error	0.27	24	0.01		
Total	187.44	35			

Significantly different at $P < 0.05$

APPENDIX LVI

Multiple range testof DO for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	DO Wet	DO Dry
L1	7.53 ± 0.05 [d]	7.50 ± 0.04[d]
L2	7.42± 0.05 [d]	7.60 ± 0.04 [d]
L3	7.90 ± 0.05 [e]	8.20 ± 0.04 [e]
L4	4.17± 0.05 [c]	6.62 ± 0.04 [c]
L5	2.95± 0.52 [b]	3.35 ± 0.04 [b]
L6	2.17± 0.52 [a]	2.33 ± 0.04 [a]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX LVII Combined means of DO for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	**DO Wet**	**DO Dry**
2014	5.19 ± 0.03	5.86 ± 0.03
2015	5.52±0.03	6.01 ± 0.03

* n = 36; mean ± S.D

APPENDIX LVIII

Two Way ANOVA Showing the Effect of Location and Year on the Hardness of Water Bodies in the Wet Season

Source	Sum of Squares	df	Mean Square	F	P - Value
Location	2176.25	5	435.25	9852.87	0.00*
Year	0.83	1	0.83	18.88	0.00*
Location * Year	21.76	5	4.35	98.53	0.00*
Error	1.06	24	0.04		

APPENDIX LIX: Two Way ANOVA Showing the Effect of Location and Year on the Hardness of Water Bodies in the Dry Season

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	763.58	5	152.71	12.11	0.00*
Year	173.36	1	173.36	13.74	0.01*
Location * Year	89.14	5	17.83	1.41	0.26*
Error	302.67	24	12.61		
Total	1328.75	35			

* Significantly different at $P < 0.05$

APPENDIX LX

Multiple range test ANOVAof Hardness for 2014 and 2015 for all Locations of Water Bodies in the Wet and Dry Season

Location	Hardness Wet	Hardness Dry
L1	84.00 ± 0.36[b]	85.50 ± 1.45[ab]
L2	82.83± 0.36 [a]	82.00 ± 1.45 [a]
L3	89.50± 0.36 [c]	89.17 ± 1.45 [bc]
L4	92.50± 0.36 [d]	92.00 ± 1.45 [cd]
L5	92.50± 0.36 [d]	94.00 ± 1.45 [d]
L6	95.50± 0.36 [e]	94.83 ± 1.45 [d]

n = 6; mean ± S.D; Values with the same Superscripts are not significantly different (P> 0.05)

APPENDIX LXI: Combined means of Hardness for all locations of Water Bodies for 2014 and 2015 in the Wet and Dry Season

Year	Hardness Wet	Hardness Dry
2014	89.17 ± 0.21	87.39 ± 0.84
2015	89.78±0.21	91.78 ± 0.84

n = 36; mean ± S.D

APPENDIX LXII

Two Way ANOVA Showing the Effect of Location of Water Body and Season on Moisture Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	205.232	5	41.05	2.14	0.10 ^{ns}
Season	42.250	1	42.25	2.20	0.15 ^{ns}
Location * Season	21.189	5	4.24	0.22	0.10 ^{ns}
Error	461.132	24	19.21		
Total	729.803	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXIII

Two Way ANOVA Showing the Effect of Location of Water Body and Season on Ash Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	40.92	5	8.18	1.97	0.12 ^{ns}
Season	1.44	1	1.44	0.35	0.56 ^{ns}
Location * Season	4.29	5	0.86	0.21	0.96 ^{ns}
Error	99.82	24	4.16		
Total	146.47	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXIV

Two Way ANOVA Showing the Effect of Location of Water Body and Season on Protein Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	128.87	5	25.77	0.77	0.58 ^{ns}
Season	1.44	1	0.47	0.14	0.91 ^{ns}
Location * Season	4.29	5	1.26	0.04	0.10 ^{ns}
Error	99.82	24	33.46		
Total	146.47	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXV

Two Way ANOVA Showing the Effect of Location of Water Body and Season on Fat Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	29.88	5	5.98	0.51	0.76 ^{ns}
Season	8.35	1	8.35	0.72	0.41 ^{ns}
Location * Season	9.15	5	1.83	0.16	0.98 ^{ns}
Error	279.92	24	11.66		
Total	327.30	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXVI

Two Way ANOVA Showing the Effect of Location of Water Body and Season on Fibre Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	11.88	5	2.38	0.54	0.74^{ns}
Season	0.86	1	0.86	0.20	0.66^{ns}
Location * Season	0.96	5	0.19	0.04	0.10^{ns}
Error	104.84	24	4.37		
Total	118.53	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXVII

Two Way ANOVA Showing the Effect of Different Water Body and Season on Carbohydrate Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	79.27	5	15.85	1.26	0.32^{ns}
Season	0.00	1	0.00	0.00	0.99^{ns}
Water Body * Season	23.06	5	4.61	0.37	0.87^{ns}
Error	302.86	24	12.62		
Total	405.20	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXVIII

Two Way ANOVA Showing the Effect of Location of Water Body and Season on Organic Matter Content of Fish Sample

Source	Sum of Squares	Df	Mean Square	F	P - Value
Location	40.79	5	8.16	2.11	0.10^{ns}
Season	1.15	1	1.15	0.30	0.60^{ns}
Water Body * Season	4.85	5	0.97	0.25	0.94^{ns}
Error	92.76	24	3.87		
Total	139.56	35			

n = 3; ns = not significant (P > 0.05)

APPENDIX LXIX

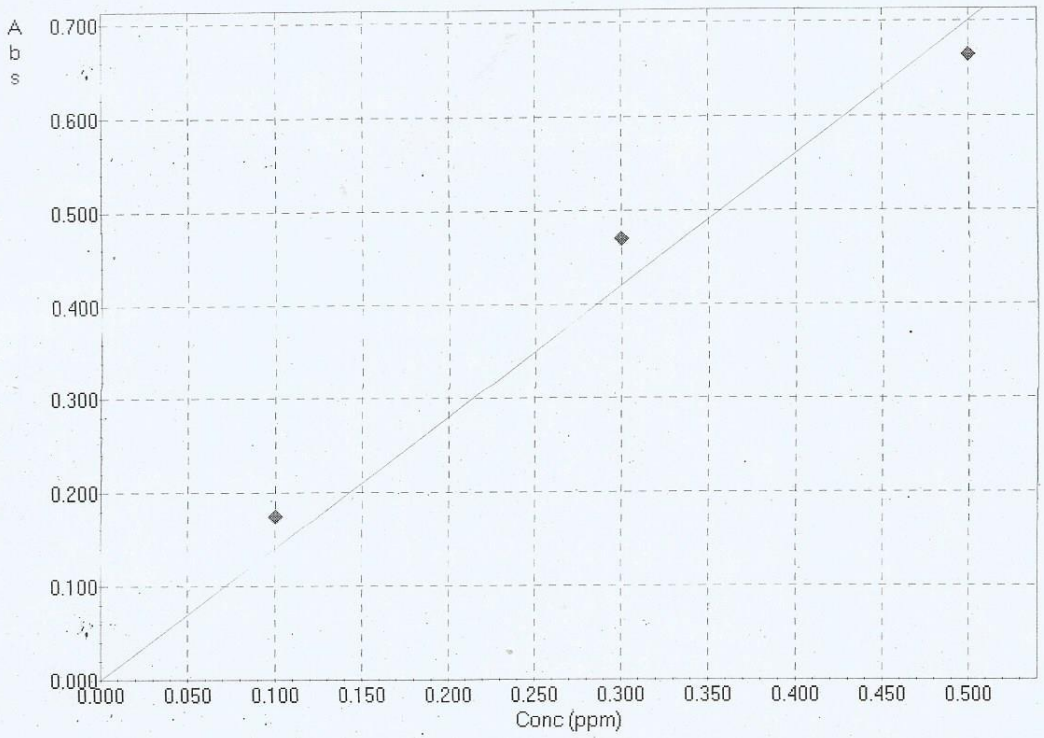
Selected Metal Concentration in Average World Shale and WHO Guidelines Values for Drinking Water Quality

Element	Water (mg/l)	Sediment (mg/kg)
Zn	5	95
Cd	0.01	0.3
Cr	0.1	100
Pb	0.01	20
Hg	0.001	0.3

(WHO, 2004) (Bhupander et al., 2011)

Appendix LXX

Calibration Curve(Element:Zn:Flame C#:01)

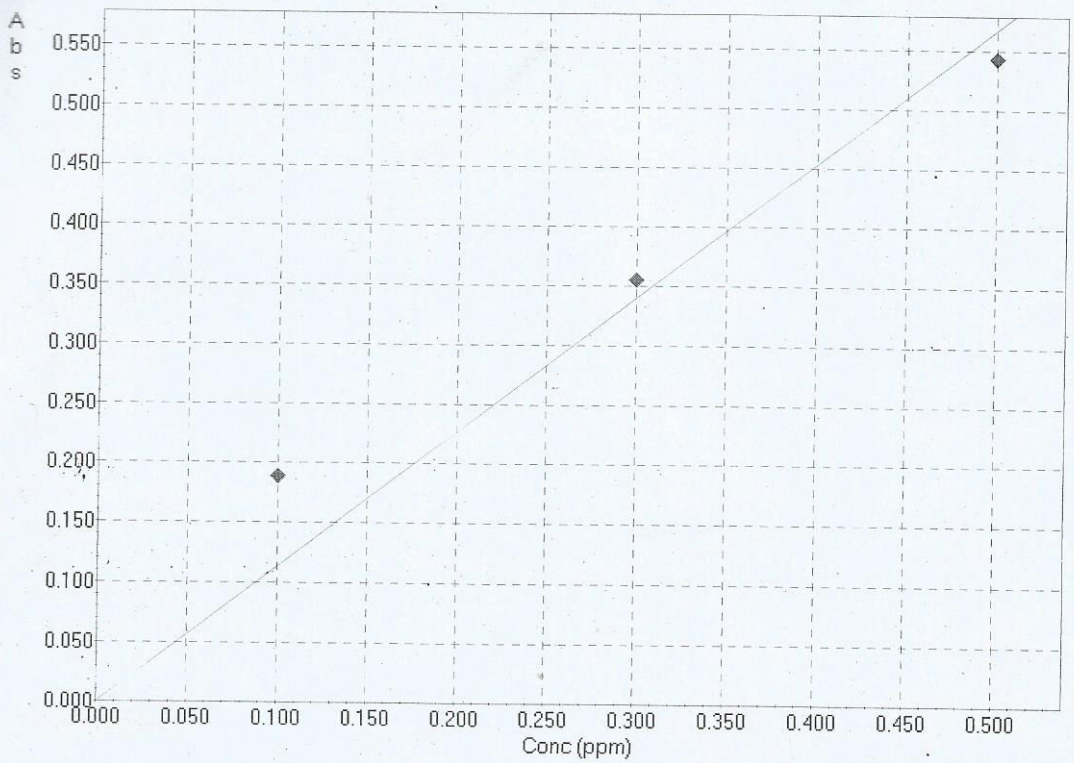


Abs=1.40124Conc+ 0 r=0.9931

CONC	ABS
0.1000	0.1741
0.3000	0.4694
0.5000	0.6644

Appendix LXXI

Calibration Curve(Element:Cd:Flame C#:01)

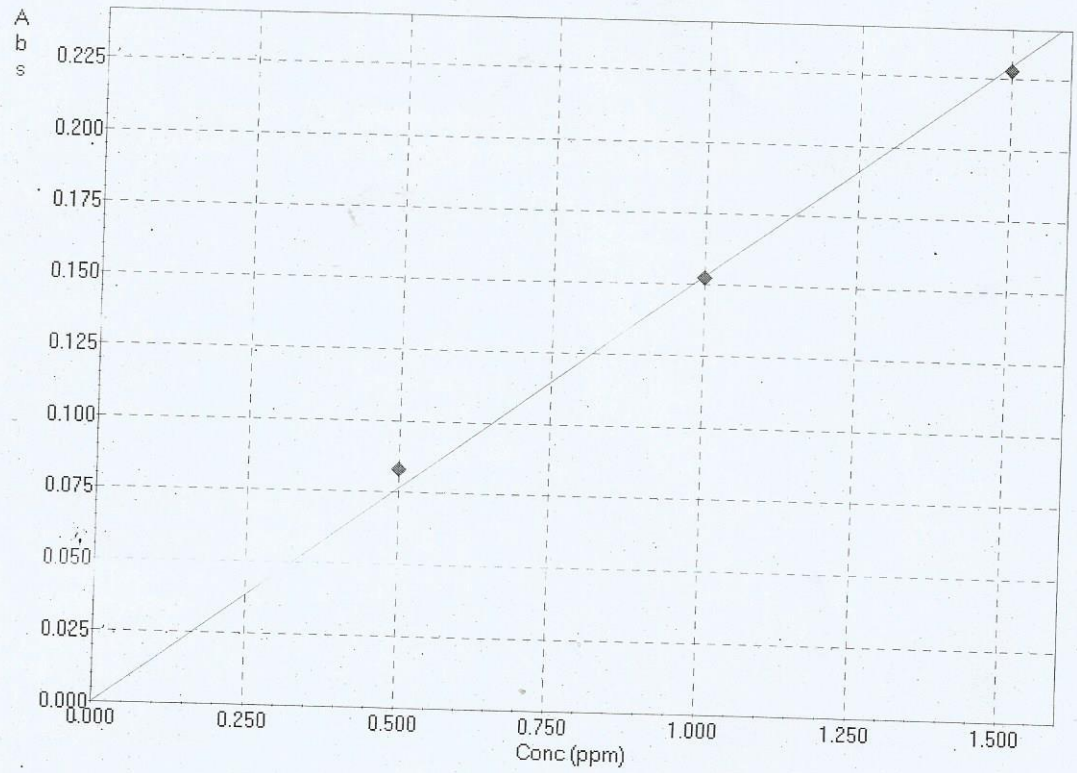


Abs=1.13367Conc+ 0 r=0.9994

CONC	ABS
0.1000	0.1883
0.3000	0.3551
0.5000	0.5429

Appendix LXXII

Calibration Curve(Element:Cr:Flame C#:01)



Abs=0.152958Conc+ 0 r=0.9997

CONC	ABS
0.5000	0.0831
1.0000	0.1523
1.5000	0.2277

Appendix LXXIII

