CONCENTRATION OF LEAD, MANGANESE AND COPPER IN RAW WATER (FROM KUBANNI, GALMA RIVERS, AND ZARIA DAM), TREATED WATER AND SOME VEGETABLE SAMPLES IN ZARIA METROPOLIS.

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DECLARATION

I hereby declare that this thesis has been written by me and it is a record of my research work, carried out under the joint supervision of Prof. Magaji Garba and Dr. Ibrahim A. Yakasai. No part of this thesis was previously presented for another degree at any university. The work of other investigators are acknowledged and referred to accordingly.

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CERTIFICATION

This thesis entitled "Concentrations of Lead, Manganese and Copper in raw water, treated water and some vegetable samples in Zaria metropolis" by AMINU MUSA meets the regulations governing the award of the degree of MASTER OF SCIENCE of AHMADU BELLO UNIVERSITY, and is approved for its contribution to science, knowledge and literary presentation.

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ABSTRACT

Population growth and industrialization of the world has dramatically increased the overall environmental load of heavy metals. The effects of pollution by heavy metals are not only an environmental problem but also a public health matter. In this study, raw water samples were collected from two sites (A and B) along river Kubanni, two sites (C and D) along river Galma and also at Zaria Dam (site E) all in Zaria, Nigeria. Vegetable samples (lettuce and tomato) were also collected from farmlands located along the banks of the rivers at sites where raw water samples were collected. Treated water samples were also collected from the public water supply in Zaria. For this purpose Zaria metropolis was divided into 8 zones (T_A-T_H). Sampling was done during the dry season (February to April 2006) and rainy season (August to October 2006). All the samples were analysed for lead, manganese and copper using the Atomic Absorption spectrophotometer (AAS).

Lead and copper were not detected in any of the raw water samples analysed. However, manganese was detected in all the raw water sample analysed. In the dry season, manganese concentrations ranged from 0.58 ± 0.28 mg/l to 2.52 ± 1.65 mg/l while in the rainy season, the concentrations ranged from 0.12 ± 0.05 mg/l to 5.36 ± 0.26 mg/l.

Lead and manganese were detected in all the vegetable samples analysed. The mean lead concentrations in the dry season ranged from 0.40 ± 0.01 mg/l to 0.80 ± 0.003 mg/l while in the rainy season the concentrations ranged from 0.38 ± 0.01 mg/l to 22.6 ± 0.07 mg/l. The mean manganese concentration in vegetable samples ranged from 0.1 ± 0.003 mg/l to 0.3 ± 0.006 mg/l in the dry season and 0.13 ± 0.007 mg/l to 0.21 ± 0.003 mg/l in the rainy season. Copper on the other hand, was only detected in samples contacted from just one site (site D) in the rainy season with concentration ranging from 9.5 ± 0.12 mg/l to 9.7 ± 1.2 mg/l.

For the analysis of treated water samples, lead and copper were not detected. However, manganess was detected in all the samples analysed with the dry season recording concentrations ranging from 0.02 ± 0.02 mg/l to 3.53 ± 0.85 mg/l while the rainy season recorded 0.00 ± 0.00 mg/l to 2.81 ± 0.31 mg/l.

TABLE OF CONTENTS

Content		Page
Title page		i
Declaration		ii
Certification		iii
Acknowledgment		iv
Abstract		v
Table of contents		vi
List of Appendices		ix
List of Figures		x
List of Maps		xi
List of Tables		xii
Chapter 1:	Introduction	1
1.1	Causes of pollution	1
1.2	Water pollution	3
1.2.1	Types of water pollution	4
1.2.2	Water pollutants	4
1.2.3	Effects of water pollutants	6
1.3	Statement of problem	6
1.4	Justification for the study	7
1.5	Objectives of the study	7
Chapter 2:	Literature review	9
2.1	Heavy metals and pollution	9
2.2	Toxicity and adverse health effect of heavy metals	11
2.3	Lead	13

2.3.1 Sources of exposure to lead 13

2.3.2 Target tissues for lead 13

2.3.3 Signs and symptoms of lead toxicity 14

2.4 Manganese 15

2.4.1 Sources of exposure to manganese 15

2.4.2 Target tissue for manganese 16

2.4.3 Signs and symptoms of manganese toxicity 17

2.5 Copper 17

2.5.1 Sources of exposure to copper 18

2.5.2 Target tissues for copper 18

2.5.3 Signs and symbols of copper toxicity 18

2.6 Theory of atomic absorption spectrophotometry 19

Chapter 3: **M**aterials and Methods 21

3.1 Materials 21

3.1.1 Chemicals and Reagents 21

3.1.2 Equipment and Glassware 21

3.1.3 Instrumentation 22

3.2 Methods 23

3.2.1 Description of study area 23

3.2.2 Sampling points for treated water 25

3.2.3 Sampling points for raw water 25

3.2.4 Sample collection and preservation 27

3.2.5 Collection of raw water samples 27

3.2.6 Collection of treated water samples 28

3.2.7 Collection of vegetable crop samples 28

3.3 Analysis of samples 28

3.3.1 Preparation of stock solution 28

3.3.2 Preparation of calibration curve 29

3.3.3 Pretreatment and analysis of lead, manganese and copper in water 29

3.3.4 Pretreatment and analysis of lead, manganese and copper in vegetable samples 29

Chapter 4: Results 31

4.1 Concentration of lead, manganese, and copper in raw water sample 31

4.2 Concentration of lead, manganese, and copper in treated water sample 31

4.3 Concentration of lead, manganese and copper in vegetable samples 31

4.4 Seasonal variation in the mean levels of lead, manganese and copper in samples analysed 37

4.5 Mean pH values in raw and treated water 38

Chapter 5: Discussion and Conclusion 41

5.1 Concentration of lead, manganese, and copper in raw water samples 41

5.2 Concentrations of lead, manganese and copper in treated water samples 43

5.3 Concentrations of lead, manganese and copper in vegetable samples 46

5.3.1 Concentration of lead in vegetable samples 46

5.3.2 Concentration of manganese in vegetable sample 47

5.3.3 Concentration of copper in vegetable samples 49

5.4 Mean pH values of raw and treated water sample 50

5.5 Conclusion 51

5.6 Recommendations 52

References 54

LIST OF APPENDICES

Appendix		Page
I:	AAS calibration of concentration vs absorbance for lead	57
II:	AAS calibration of concentration vs absorbance for manganese	58
III:	AAS calibration of concentration vs absorbance for copper	59
IV:	Mean concentrations of lead, manganese and copper (mg/l $\pm$ s.e.m) in raw water samples	60
V:	Mean concentrations of lead, manganese and copper (mg/l $\pm$ s.e.m) in treated water samples	61
VI:	Concentrations of lead in vegetable samples	62
VII:	Concentrations of manganese in vegetable samples	63
VIII:	Concentrations of copper in vegetable samples	64

LIST OF FIGURES

Figures		Page
1.	Mean concentrations of lead, manganese and copper in raw water Samples	32
2.	Mean concentrations of lead, manganese and copper in treated water samples	33
3.	Mean concentrations of lead in the vegetable samples	34
4.	Mean concentrations of manganese in the vegetable samples	35
5.	Mean concentrations of copper in the vegetable samples	36

LIST OF MAPS

Map		Page
1	Zaria and Environs	24
2	Sampling sites for raw water	26

LIST OF TABLES

Table		Page
1.	Water quality guidelines for heavy metals and threshold values leading to crop damages	12
2.	Seasonal variations in the mean concentration of manganese in raw water samples	37
3.	Seasonal variations in the mean concentration of manganese in treated water samples	38
4.	Mean pH values for raw water samples	39
5.	Mean pH values for treated water samples	40

INTRODUCTION

CHAPTER ONE

An essentially accurate definition of pollution is “too much of something in the wrong place”. Thus any chemical can become a “pollutant” if it is present at high concentration. Nonetheless some chemicals can be selected as being of high priority for control in the environment because, they are frequently found there, are capable of exerting adverse effects at low concentrations, they remain unchanged in the aquatic environment for long periods or because they biomagnify in food chains. Often the priority chemicals selected display more then one of these characteristics (Harrison, 1993).

Pollutants are numerous and includes; gases, such as sulphur dioxide and nitrogen oxides, particulate matter such as smoke particles, pesticides and radioactive isotopes in the atmosphere and water ways, sewage, organic chemicals, and phosphates in water, solid waste on land, excessive heating (thermal pollution) of rivers and lakes and many other toxic metals such as zinc, copper, lead, mercury etc.

In some cases, the environmental levels of most of the pollutant are largely due to natural sources while in others the levels are largely produced by man’s activities. Even when natural sources are more important on a global scale, man generated pollutants may be more important in urban and industrial areas where the adverse effects of pollution are more severe.

1.1 Causes of Pollution

One of the factors that affect the degradation of the environment is population growth. The development of thousands of chemical compounds to restore and enhance the soil fertility and to protect many of the domesticated species, has enabled man to expand his

food producing capacity significantly. These activities together with the birth of modern medicine have resulted in an explosive growth of population with inevitable consequences. A study conducted by the SCEP (Study of Critical Environmental Problems) group points out that the demand for minerals, energy and space are exponentially increasing at a rate of 5 to 6 percent per year and if this trend continues, the next doubling of population will increase the environmental impact six fold.

The increased demand for energy has resulted in the extensive burning of coal and other fossil fuels. When coal and other fossil fuels are burnt or processed, a variety of pollutants are emitted in to the atmosphere. These include, particulates, trace elements, a variety of hydrocarbons, and sulphur and nitrogen compounds. Probably the most important pollutant emitted by coal combustion is sulphur (IV) oxide (SO_2). Sulphur (IV) oxide is oxidized to H_2SO_4 and some of the H_2SO_4 in turn reacts with trace elements emitted alongside SO_2 or other substances present in the atmosphere to form submicron-size sulphate compounds. Recent studies indicate that it is the 'mist' containing H_2SO_4 and metallic, and not SO_2 gas itself that is the major ingredient in sulphur pollution. Another environmental problem of great concern, which is related to sulphur in fossil fuels, is acid rain. The environmental effect of acid rain probably include increased leaching of nutrients such as calcium from soil, changes in metabolic rates of organisms which depend on acid or base catalysts, and corrosion of basic materials such as limestone and marble (Okeniyi, 2000).

Coupled with rapid population growth, other factors such as urbanization, rapid industrial development, mining, agricultural activities etc have resulted in huge accumulation of wastes and pollutants. These pollutants, which in most cases contain heavy metals, may end up in water bodies such as river, lakes, streams etc, thereby polluting them. These

water bodies which are used extensively for irrigation of crops could lead to the introduction of these heavy metals in to the food chain if they are taken up by the crops. N.I. Dike and co-workers in a study conducted between January and April 2003 observed very high levels of Pb, Cu, Fe and Cd in River Jakara in Kano. On the other hand, high levels of the same metals were reported in vegetable crops cultivated along the banks of River Kaduna (Ojeka and Achi, 2004).

The industrialization of the world has dramatically increased the overall environmental load of heavy metals to the point that our societies are dependent upon them for proper functioning. Industry and commercial processes have actively mined, refined, manufactured, burned and manipulated heavy metal compounds, for a number of reasons. Today heavy metals are abundant in our drinking water, air and soil due to our increased use of these compounds.

Other causes of pollution include sewage and fertilizers which contains nutrients such as nitrates and phosphates. In excess level, nutrients stimulate growth of aquatic plants and algae. Excessive growth of these types of organisms clogs our waterways, use up dissolved oxygen as they decompose, and this in turn affects the respiratory ability of fish and other invertebrates in the water.

1.2 Water Pollution

Comprising over 70 % of the earth's surface, water is undoubtedly the most precious natural resource on our planet. Its many uses include drinking and other domestic uses, industrial cooling, power generation, irrigation, transportation and water disposal. In the chemical process industry water is used as a reaction medium, a solvent, a scrubbing medium, and a heat transfer agent.

Although humans recognize that water is essential for life, we disregard it by polluting our rivers, lakes and oceans. Subsequently, we are slowly but surely harming our planet to the point where organisms are dying at a very alarming rate.

1.2.1 *Types of Water Pollution*

Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. When it is unfit for its intended use, water is considered polluted. Two types of water pollution exist, point source and non-point source pollution.

Point source pollution: point sources of pollution occur when harmful substances are emitted directly in to the water body. This is best illustrated by the oil spillage into the sea that occurs as a result of oil drilling activities.

Non point source pollution: A non point sources delivers pollutants indirectly through environmental changes. An example of these types of water pollution is when fertilizer from a cultivated field is carried in to a stream by rain, in the form of run-off which in turn affects aquatic life.

The technology exists for point source pollution to be monitored and regulated, although political factors many complicate matters. Non point sources account for a majority of the contaminants in streams and lakes.

1.2.2 *Water Pollutants*

The problem of water pollution due to discharge of domestic and industrial waste into aquatic system has already become a serious problem in the country. The rivers and lakes near urban centers emit disgusting odours and fish are being killed in millions along sea coasts in the Niger Delta. The origin of these problems must be attributed to many sources and types of pollutants. Some of these pollutants may have indirect effects whilst

substances normally not considered as pollutants may become so under special circumstances. These water pollutants may be classified into eight categories as described below:

Oxygen Demanding Wastes: Dissolved oxygen is consumed in their breakdown by microorganism**,** thus exerting a demand on the availability of dissolved oxygen.

Disease Causing Agent: Water is a potential carrier pathogenic microorganisms from sewage and municipal wastes.

Synthetic Organic Compound: An example is the pesticides. These compounds are not biodegradable, are accumulative toxic poisons and may reach objectionable levels in water.

Plant Nutrients: Nitrogen and phosphorus are essential for plant and animals' growth and metabolism. When present in water bodies in large concentrations, an excess algal growth, known as "algal broom" appears over the water. This reduces light penetration and restricts atmospheric reoxygenating of the water.

Inorganic Chemicals and Minerals: Example includes inorganic salts, mineral acids metal, and their compounds. These pollutants enter water bodies from municipal and industrial wastes and mine run-off. Most of these substances, particularly the heavy metals are toxic and capable of building up in the food chain

Radioactive Substances: These can enter humans through food and water, and get accumulated in blood and certain vital organs like thyroid gland, liver, bones and muscular tissues. Radium (a waste product of Uranium ore mining) is considered to be a hazard in drinking water.

Thermal Discharge: Used coolant water from power plants and industries is usually discharged directly in to water bodies. This could result in increase in temperature of the

water bodies with a consequent decrease in oxygen saturation percentage and also accelerates the lowering of dissolved oxygen levels.

Oil: Oil and oil wastes enter rivers and other water bodies from several sources like industrial effluents, oil refineries and storage tanks, automobile wastes oil, petrochemical plants. All these make a significant contribution to the pollution of the aquatic environments.

1.2.3 *Effects of Water Pollutants*

- Drop in the level of Dissolve Oxygen leading to deoxygenating of the aquatic system.
- Municipal wastes and sewage introduce pathogenic microorganisms into drinking water, which can cause diseases such as typhoid fever.
- Synthetic organic chemicals e.g. pesticides are not biodegradable and thus accumulate to toxic levels in the environment.
- Heavy metals tend to bioaccumulate and toxic concentrations can build up in the food chains.
- Human activities that cause increase in water temperature can result in decreased oxygen saturation percentage and thus lowering of Dissolved oxygen levels.
- Oil slick on the surfaces of water can prevent oxygen transfer from the atmosphere leading to very low dissolved oxygen levels.

1.3 Statement of Problem

Human beings have been exposed to heavy metals for an immeasurable amount of time. Rapid increase in populations, coupled with other factors such as urbanization, rapid industrial development, mining, agriculture etc, result in huge accumulation of wastes and pollutants which end up in water bodies such as rivers, streams and lakes thereby polluting them (Dike *et al*, 2004). Heavy metals are also present in virtually every area of

modern consumerism such as rivers construction materials, cosmetics, medicines, processed food, fuel sources, personal care products, etc. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment. Heavy metals toxicity represents an uncommon, yet clinically significant medical condition. If unrecognized or inappropriately treated, heavy metal toxicity can result in significant morbidity and mortality (Ferner, 2005).

1.4 Justification for the Study

Zaria like any other urban area in Nigeria, is experiencing an upsurge in pollution due to population growth, municipal waste disposal, exhaust emissions, agricultural activities, industrial and commercial process. The products and effluents from such processes may end up in the water bodies, thus contributing to the heavy metal contamination of such water bodies in Zaria. Also, food crops that are irrigated using these water bodies may also take up some of these metals. Thus, introducing these metals into the food chain where they tend to bioaccumulate.

Due to the toxicity and health hazards of heavy metals, this study is aimed at investigating the levels of Lead (Pb), Manganese (Mn) and Copper (Cu) in raw and treated water samples as well as some vegetable crops.

1.5 Objectives of the Study

This study is aimed at determining the levels of Lead, Manganese and Copper in raw water samples from rivers Kubanni and Galma, and their respective tributaries as well as concentration of these elements in some vegetable crops cultivated along the banks of these rivers. Also raw and treated water samples will be collected from Zaria Dam as well as from other parts of Zaria metropolis to determine the concentration of the elements in them.

The objectives of the study are to:

(i) Determine the level of Pb, Mn and Cu in raw water samples from rivers Kubanni and Galma, and compare with levels in the vegetable crops cultivated along their banks.

(ii) Determine the level of the metals in raw water samples from Zaria Dam and compare with the levels to be determined from treated water samples around Zaria metropolis.

(iii) Compare the levels of Pb, Mn and Cu in raw and treated water with W.H.O limits for safe drinking water and also compare the levels in the vegetable crops with FAO threshold values for crops.

(iv) Compare the levels of Pb, Mn and Cu obtained in the dry season to that obtained in the rainy season and determine the seasonal variation if any.

Chapter 2 LITERATURE REVIEW

2.1 Heavy Metals and Pollution

Heavy metals are defined as metals having density greater than 5 g/cm^3 and these include transition metals and higher atomic weight metals of group III to V of the period table. These metallic chemical elements having relatively high densities are toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Ti), and lead (Pb).

Heavy metals are natural components of the earth's crust. The core of the earth is a vast reserve of metallic substances while the earth's crust is about a quarter metals. Heavy metals cannot be degraded or destroyed. To a small extent they enter out bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, manganese) are essential to maintain the metabolism of the human body. However, at higher concentration they can lead to poisoning. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and are stored faster than they are metabolized or excreted.

Pollution of the ecosystem by toxic metals as a result of man's activities poses a serious problem because they are not degradable and persistent in the ecosystem. Human beings have been exposed to heavy metals for an immeasurable amount of time. The industrialization of the world has dramatically increased the overall environmental 'load' of heavy metals to a point that out societies are dependent upon them for proper functioning. Industrial and commercial processes have actively mined, refined, manufactured, burned and manipulated heavy metal compounds for a number of reasons.

Advancement in technology has lead to high levels of industrialization leading to the discharge of effluent containing heavy metals in our environment. Various activities of man in recent years have increased the quantity and distribution of heavy metals in the atmosphere, land and water bodies. The extent of this wide spread but generally diffused contamination has caused concern about its possible hazards on plants, animals and humans (Warren, 1981).

In municipal sewage, the metallic contents are often absorbed on the sewage solids or sewage sludge. When the sludge is disposed off to farm land, the metallic contents are taken up by plants in amounts which may have unpleasant effects on the fruits they produce as they may be rendered unsuitable for human consumption. High levels of Pb, Cu, Fe and Cd were reported in river Jakara in Kano state which receives industrial and municipal wastes, and is used for irrigating farmlands (Dike *et al* 2004). This may have adverse effect on the growth of the plants. The grasses produced on the farmlands are readily consumed by grazing animals. These grazing animals as well as the food crops serve as food for man. In effect, the heavy metals are passed on to man by food chain and the cumulative effects of these metals, most of which are toxic are generally adverse.

Pollution of streams and rivers flowing through agricultural areas where pesticides, fungicides, etc may have been applied; and industrial districts where there may have been metals waste deposits, all these present varied and difficult problems due to drainage into our different water bodies. Between 1984 and 1986, the National Inorganic and Radionuclide Survey (NIRS) collected data from 989 U.S community public water systems (PWSs) served by ground water in 49 states and found that 68 % of the ground water PWSs reported detectable level of manganese. Supplemental survey data from

PWSs supplied by surface waters in five states reported occurrence ranges similar to those of ground water PWSs (U.S EPA, 2004).

Heavy metals occur in the air as solid particulate matter. Lead for example gets into air during smelting process in industries producing the metal and also by motorized vehicle during exhaust emission.

Lead in the form of tetra-ethyl lead [$Pb(C_2H_5)_4$], is the most common additive to petrol to raise its octane number, the other co-additives are halogen carrier e.g. $FeCl_3$. Upon combustion of the petrol in the engine, the organic lead is oxidized to lead oxide thus;

$$2Pb\ (C_2H_5)_4 + 27O_2 \rightarrow 2PbO + 16CO_2 + 20H_2O$$

The lead oxide formed reacts with the halogen carriers to form lead halide particles which escapes into the air through the vehicle exhaust pipes. Humans, animals, vegetation and soil are the ultimate recipients of the lead particulate.

Automobile exhaust constitutes, 75 – 80 % of the gross air pollution in Nigeria while the remaining comes from dust arising from untarred roads, smoke and gases from the industries and the burning of bush and refuse. The lead level in super Grade petrol in Nigerian is the range of 210 – 520 mg/ litre (Ademoroti, 1986).

2.2 Toxicity and Adverse Health Effect of Heavy Metals

Heavy metals contribute to a variety of adverse heath effects. There exists over 20 different heavy metals that can impact human health and each will produce different behavioral, physiological and cognitive changes in an exposed individual. The degree to which a system, organ, tissue or cell is a affected by a heavy metal toxin depends on the toxin itself and the individuals degree of exposure to the toxin. The accumulation of the

heavy metal toxin within the body leads to a decline in the mental, cognitive and physical health of the individual.

While it does not appear that we are going to naturalize the threat of heavy metal toxicity in our communities nor decrease our utilization of the many commercial goods that they help produce, we can take steps to understand this threat and put into action policies of prevention and treatment that may help to lessen the negative impact that these agents have on human health. Thus, to this end, various organization and agencies such as the W.H.O, U.S.E.P.A, Federal Environment Protection Agency (FEPA) to mention but a few, have set guidelines for drinking water quality. Recommended maximum concentrations of heavy metals in food crops have also been given by the Food and Agriculture Organization (FAO). The tolerance limits for some heavy metals in drinking water and food crops is presented in Table 1.

Table 1 Water Quality Guidelines for Heavy Metals and Threshold Values Leading to Crop Damage (Mg/L)

Element	A	B	C
	WHO drinking Water guideline	FEPA drinking water guideline	FAO recommended max. conc. for crops
Arsenic	0.01	0.05	0.1
Cadmium	0.003	0.01	0.01
Chromium	0.05	0.05	0.1
Copper	2.0	1.5	0.2
Iron	0.3	<0.3	5.0
Manganese	0.5	<0.5	0.2
Mercury	0.001	0.0001	-
Nickel	0.02	-	0.2
Lead	0.01	< 0.05	5.0
Zinc	3.0	15.0	2.0

Sources: A => WHO (1993), B => FEPA (1998), C => Cited by Pescod (1992)

The metals of interest in this study are lead (Pb), manganese (Mn), and copper (Cu). The specific sources of exposure where these metals tend to be deposited and the adverse health effects of each metal are identified below.

2.3 Lead

Lead is one of the most significant toxins of the heavy metals. It is among the most recycled nonferrous metals and its secondary production has therefore grown steadily inspite of declining lead prices. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries.

2.3.1 *Sources of Exposure to Lead*

Human exposure to lead occurs primarily through drinking water, air borne lead – containing particulates and lead based paints. Several industrial processes create lead dust or fumes resulting in its presence in the air. Mining, smelting and manufacturing processes, the burning of fossil fuels (especially lead – based gasoline) and municipal waste and incorrect removal of lead-based paints results in air borne lead concentration. After lead is air borne for a period of ten days, it falls to the ground and becomes distributed in soils and water sources (fresh and salt water, surface and well water, and drinking water). However the primary source of lead in drinking water is from lead-based plumbing material (U.S EPA, 1989). The corrosion of such materials will lead to increased concentrations of lead in municipal drinking water. Lead from water and air borne sources have been shown to accumulate in agricultural areas leading to increased concentration in agricultural produce and farm animals (ATSDR, 1993).

2.3.2 *Target Tissues for Lead*

Lead can be found in organic and inorganic forms. Inorganic forms of lead typically affect the CNS, peripheral nervous system, hematopoietic, renal, gastrointestinal,

cardiovascular, and reproductive systems. Organic lead toxicities tend to predominantly affect the CNS. The Inorganic leads are absorbed through ingestion or inhalation, whereas organic lead salts are absorbed through the Skin. Children absorb lead much more efficiently than adults do after exposure and ingested lead is more readily absorbed in fasting individuals (U.S. EPA 1986). Over 90 % of inhaled lead is absorbed directly into the blood, after lead is absorbed into the body it circulates in the blood stream and distributes primarily in the soft tissues (kidneys, brain and muscles) and bone. Adults distribute about 95 % of their total body lead to their bones while children distribute about 73 % of their total body lead to their bones (U.S. EPA 1986a).

2.3.3 *Signs and Symptoms of Lead Toxicity*

High concentrations of lead can cause irreversible brain damage (encephalopathy), seizure, coma and death if not treated immediately (U.S. EPA 1986). Neuropsychological impairment can result from exposure to moderate levels lead. Evidence suggests that lead may cause fatigue, irritability, memory problems, a reduction in sensory and motor times, decision making impairment and lapses in concentration (Elhe and Mckee, 1990). At blood concentrations above 70 mcg/dL, lead has been shown to cause anemia characterized by a reduction in haemoglobin levels and erythropoiesis (Goyer 1980; U.S EPA 1986). Occupationally exposed individuals tend to have higher blood pressures than normal controls (Harlon *et al.*, 1985; Landis and Flagel, 1988) and are at an increased risk for cardiovascular disease, myocardial infarction and stroke (U.S. EPA, 1990). Kidney disease, both acute and chronic nephropathy is a characteristic of lead toxicity (Goyer, 1988). Kidney impairment can be seen in morphological changes in the kidney epithelium, increases in excretion rates of many different compounds, reduction in glomerular filtration rate, progressive glomerular arterial and arteriolar sclerosis and plasma albumin ratio (Goyer 1988). Other symptoms of lead toxicity include

gastrointestinal disturbances, weight loss, immunosuppression and slight liver impairment (U.S. EPA, 1986a; ATSDR, 1993).

Children are susceptible to the most damaging effects of lead toxicity. Prenatal and postnatal developments are compromised significantly by the presence of lead in the body. At blood lead concentrations of 80 – 100 mcg/dl, severe encephalopathy occurs. Those children who survive lead-induced encephalopathy typically suffer permanent brain damage marked by mental retardation, and numerous behavioural impairments (U.S EPA 1986a).

2.4 Manganese

Manganese is a naturally occurring element that can be found ubiquitously in the air, soil and water. Manganese is also an essential nutrient for humans and animals. Adverse health effects can be caused by inadequate intake or over exposure (U.S. EPA, 2004). Manganese is principally used in the manufacture of iron and steel alloys, manganese compounds, and as an ingredient in various products e.g. batteries, glass etc (ATSDR, 2000).

2.4.1 *Sources of Exposure to Manganese*

Food is the most important source of exposure to manganese in the general population (ATSDR, 2000). Manganese is found in many food including nuts, fruits, grains, legumes, tea, leafy vegetable, infant formulas, and some meat and fish. Heavy tea drinkers may have a higher manganese intake than the general population. An average cup of tea may contain 0.4 - 1.3 mg manganese (ATSDR, 2000). Infant formula contains 50 – 300 ng/l manganese (Collipp *et al* 1983), compared to human milk which contains approximately 3.5 – 15 ng/l manganese (ATSDR, 2000). Given the high content of milk-

based formula, the under exposure of infants to manganese appears less probable than their over exposure (Davidson *et al*, 1989).

Manganese compounds may be present in the atmosphere as suspended particulates resulting from industrial emissions, soil erosion, volcanic emissions, application of manganese- containing pesticides, and the burning of MMT (Methylcyclopentadienyl Manganese tricarbonyl) containing gasoline. Because particle size is small, atmospheric manganese distribution can be widespread. These particles will eventually settle into surface water or into soils.

The primary source for surface and ground water releases are industrial facility effluent discharge, Landfill and soil leaching, and underground injection (U.S. EPA, 2004).

2.4.2 *Target Tissue for Manganese*

Studies show that significant difference exist in the amount of manganese that are absorbed across different exposure routes, with inhaled manganese being absorbed more rapidly and to a greater extent than ingested manganese (U.S. EPA, 2004).

Manganese is present in all tissues of the body, the highest levels usually being found in the liver, kidney, pancreas, and adrenals. Intermediate concentrations occur in the brain, heart and lungs (ATSDR, 2000), with accumulation preferential in certain regions of the brain, infants and young animals (Kontur and Fechter, 1988). The lowest concentrations of manganese are observed in bone and fat. Some data suggests that a tissue rich in mitochondria (e.g. liver, kidney and pancreas) contains higher levels of manganese.

Manganese retention may be greater for young animals and infants due to the fact that the biliary system, the primary route of excretion, is not completely developed in human infants.

2.4.3 *Signs and Symptoms of Manganese Toxicity*

Manganese is essential to the proper functioning of both humans and animals as it is required by many cellular enzymes (e.g. manganese superoxide dismutase, pyruvate carboxylase) and can serve to activate many others (e.g. kinases, decarboxylases, transferases, hydrolases, etc) (U.S. EPA, 2004).

Although manganese is an essential nutrient at low doses, chronic exposure to high doses may be harmful. The health effects from over-exposure to manganese are dependent on the route of exposure, the chemical form, the age at exposure, and an individual's nutritional status. Irrespective of the exposure route, the nervous system has been determined to be the primary target.

The syndrome known as ''Manganism'' is caused by exposure to very high levels of manganese dusts or fumes and is characterized by a Parkinson-like syndrome including weakness, anorexia, muscle pain, apathy, slow speech, monotonous tone of voice, emotionless ''mask-like'' facial expression, and slow clumsy movement of the limbs (U.S. EPA, 2004).

Male workers afflicted with clinically identifiable symptoms of manganism also have loss of libido and impotence from occupational exposure to manganese for 1 – 21 year (Emara *et al* 1971). Impaired fertility, as measured by fewer children/married couple, has been observed in male workers exposed for 1-19years to manganese dust. At levels that did not produce obvious manganism (U.S. EPA, 2004).

2.5 Copper

Copper occurs naturally in elemental form and as a component of many different compounds. Because of its high electrical conductivity, copper is used extensively in the

manufacturing of electrical equipment and different metallic alloys. The most toxic form of copper is thought to be that in the divalent cupric (Cu^{2+}).

2.5.1 *Sources of Exposure to Copper*

Copper is released into the environment primarily through mining, sewage treatment plants, solid waste disposal, welding and electroplating processes, electrical wiring materials, plumbing supplies and agricultural processes (ATSDR, 1990a). It is present in the air and water due to natural discharges like volcanic eruptions and wind brown dust. Drinking water sources become contaminated with copper primarily because of its use in many different types of plumbing supplies. It is a common component of fungicides and algaecides and agricultural use of copper for these purposes can result in its presence in soil, ground water, farm animals and many forms of produce (ATSDR 1990a).

2.5.2 *Target Tissues for Copper*

Absorption of copper occurs through the lungs, gastrointestinal tract and skin (U.S EPA, 1987). The degree to which copper is absorbed in the gastrointestinal tract largely depends upon its chemical state and the presence of other compound like zinc (U.SAF, 1990). Once absorbed, copper is distributed primarily to the liver, kidneys, spleen, heart, lungs, stomach, intestines, nails and hair. Individual with copper toxicity show an abnormally high level of copper in the liver, kidney, brain, eyes and bones (ATSDR, 1990a).

2.5.3 *Signs and Symptoms of Copper Toxicity*

Copper is an essential element in the human diet, but in high doses it can produce numerous physiological and behavioral disturbances. Acute toxicity of ingested copper is characterized by abdominal pain, diarrhea, vomiting, tachycardia and metallic taste in the mouth. Prolonged ingestion can cause cirrhosis and other debilitating liver conditions

(Mueller-Hoecker *et al.,* 1989). Inhaled copper dust or fumes can produce eye and respiratory tract irritation, headaches, vertigo, drowsiness, chills, fever, aching muscle and discolouration of the skin and hair in humans (U.S.A.F, 1990).

Copper toxicity has been characterized in patients with Wilson's disease, a genetic disorder that cause an abnormal accumulation of copper in body tissue. Wilson' disease is fatal unless treated in time. Manifestation of Wilson's disease includes brain damage and progressive demyelination, psychiatric disturbances, haemolytic anaemia, cirrhosis of the liver motor dysfunction and corneal opacities (ATSDR, 1990a; Goyer, 1991a; U.S EPA, 1987).

2.6 Theory of Atomic Absorption Spectrophotometry

Atomic Absorption Spectrophotometry (AAS) is a classical technique for the determination of metals that are dissolved or suspended in a solution. The solution can be pure water, dilute or concentrated acids or organic solvents. The metals can be Alkalis, Alkaline earth's, transition metals, heavy metals, semi-metals and even some refractory metals.

The basic method is quite simple and fairly rapid: allowing trace metals in the fractional parts per million (PPM) range and major components in the percentage to be determined accurately and precisely.

Atomic Absorption Spectrophotometry is the measurement of optical radiation by atoms in the gaseous state and it is based on the ability of "excited" atom of an element to absorb energy from wavelengths of light of the same frequency as the elements. The grounds state atoms in vapour state are first produced by spraying solution containing metallic elements into a flame of specific characteristics. The ground state atoms in the flame are excited by passing resonance radiation of the same frequency as the element

from an external light source through the flame. This creates a decrease in the initial signal energy, and this difference is proportional to the concentration.

Each element has its own series of specific resonance wavelengths. These wavelengths will have specific characteristics for sensitivity, noise and linearity. Sensitivity and noise will determine the limit of detection for that element. Linearity will define the range in which the calibration curve will be accurate.

The optical system is set up with a hallow cathode lamp for the element of interest (Analyte), with appropriate slit and wavelengths selected for this element. A solution of a known concentration of the analyte (standard) is aspirated and the absorbance reading noted. An unknown sample is aspirated, the absorbance reading is ratioed to the standard and a sample concentration is interpolated from the intensity of the reading.

Chapter 3 MATERIALS AND METHODS

3.1 Materials

3.1.1 *Chemicals and Reagents*

All experiments were performed with analytical grade chemicals obtained from British Drug House (BDH) and Riedel de Haën. Glass distilled water was used throughout the study.

Trioxonitate (V) acid (HNO_3)

Perchloric acid ($HClO_4$)

Tetraoxosulphate (VI) acid (H_2SO_4)

Lead nitrate [$Pb(NO_3)_2$]

Manganese Sulphate ($MnSO_4.4H_2O$)

Copper sulphate ($CuSO_4.5H_2O$)

Deionised distilled water

3.1.2 *Equipment and Glassware*

Analytical balance

Oven BS, Model OV-330 Gallenkamp, England

Hot plate, Model HL 054, Gallen kamp, England

Pestle and mortar

Dessicator

Volumetric flask; 50, 100, 250, 1000 ml

Beakers; 50, 250, 500, 1000 ml

Measuring cylinder; 50, 100 ml

Pipette; 10, 25 ml

pH paper

Aluminum foil and whatamm filter paper (diameter size-11 cm).

Conical flasks

Polyethylene sample bottles

Polyethylene bags

Test tubes and test tube holders

3.1.3 *Instrumentation*

The SHIMAZU 650 model Atomic Absorption Spectrophotometer (AAS) was used for this study. The following conditions were used for each of the metals analysed.

Lead:

Lamp: Lead Hollow cathode

Lamp current: 10mA

Wavelength: 217.0 nm

Band pass: 0.5 nm

Stochiometric fuel flow: 0.9 – 1.2 $L.min^{-1}$

Flame type: Air/Acetylene

Manganese:

Lamp: Manganese Hollow cathode

Lamp current: 7.0 mA

Wavelength: 279.5 nm

Band pass: 0.20 nm

Stochiometric fuel flow: 0.9 – 1.2 $L.min^{-1}$

Flame type: Air/Acetylene

Copper:

Lamp: Copper Hollow cathode

Lamp current: 4.0 mA

Wavelength: 324.8 nm

Band pass: 0.4 nm

Stochiometric fuel flow: 0.9 – 1.2 $L.min^{-1}$

Flame type: Air/Acetylene

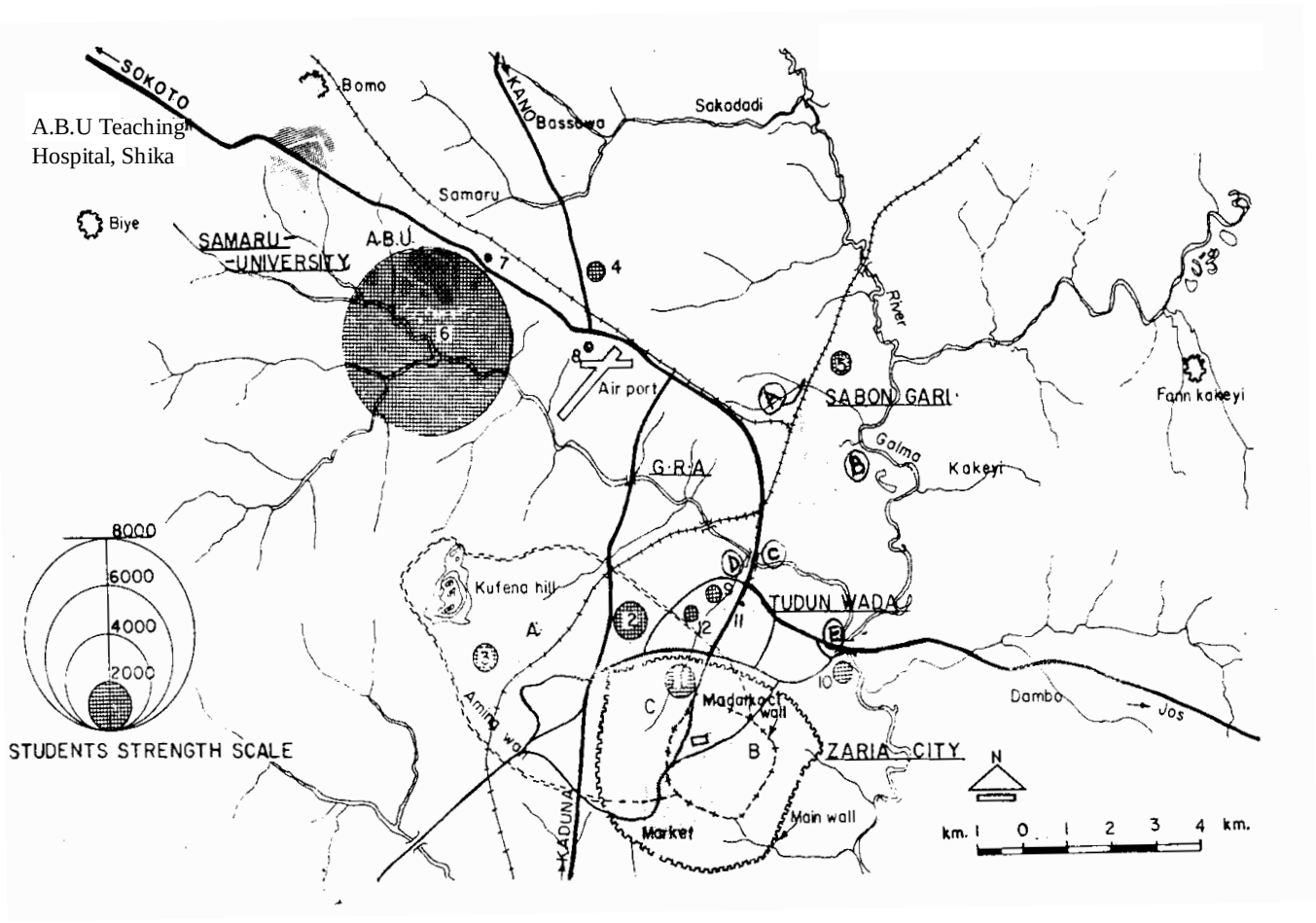
3.2 Methods

3.2.1 *Description of Study Area*

The study area is Zaria metropolis in Kaduna State of Nigerian (MAP 1). Zaria is located approximately 70km to the north of Kaduna which is the state capital. Zaria is known for its many Institutions of higher learning (e.g. A.B.U, NCAT, NITT, F.C.E to mention but a few), this attracts a lot of people to the city.

This has led to a steady increase in population and consequently to an increase in domestic and municipal waste which in most cases are not properly disposed of. In addition, a large number of automobiles, increasing agricultural activities, commercial and industrial activities, have all led to the possibilities of emission of heavy metals into the environment in Zaria.

Rivers Kubanni and Galma are the major water ways in Zaria. River Galma flows from somewhere around Zaria Dam through several rural communities including Galma village and finally linking the river Kaduna. River Kubanni on the other hand flows from the upper part of Samaru around Tudun muntsira and Unguwan Maigamo villages, through some rural communities and then through the densely populated urban areas of Tudun Jukun, Tudun wada and Sabon Gari, where it has some of its major tributaries.



Map 1: Zaria and Environs

Finally, the river Kubanni drains into the river Galma at a confluence just before the bridge on the old Jos road.

3.2.2 *Sampling Points for Treated Water*

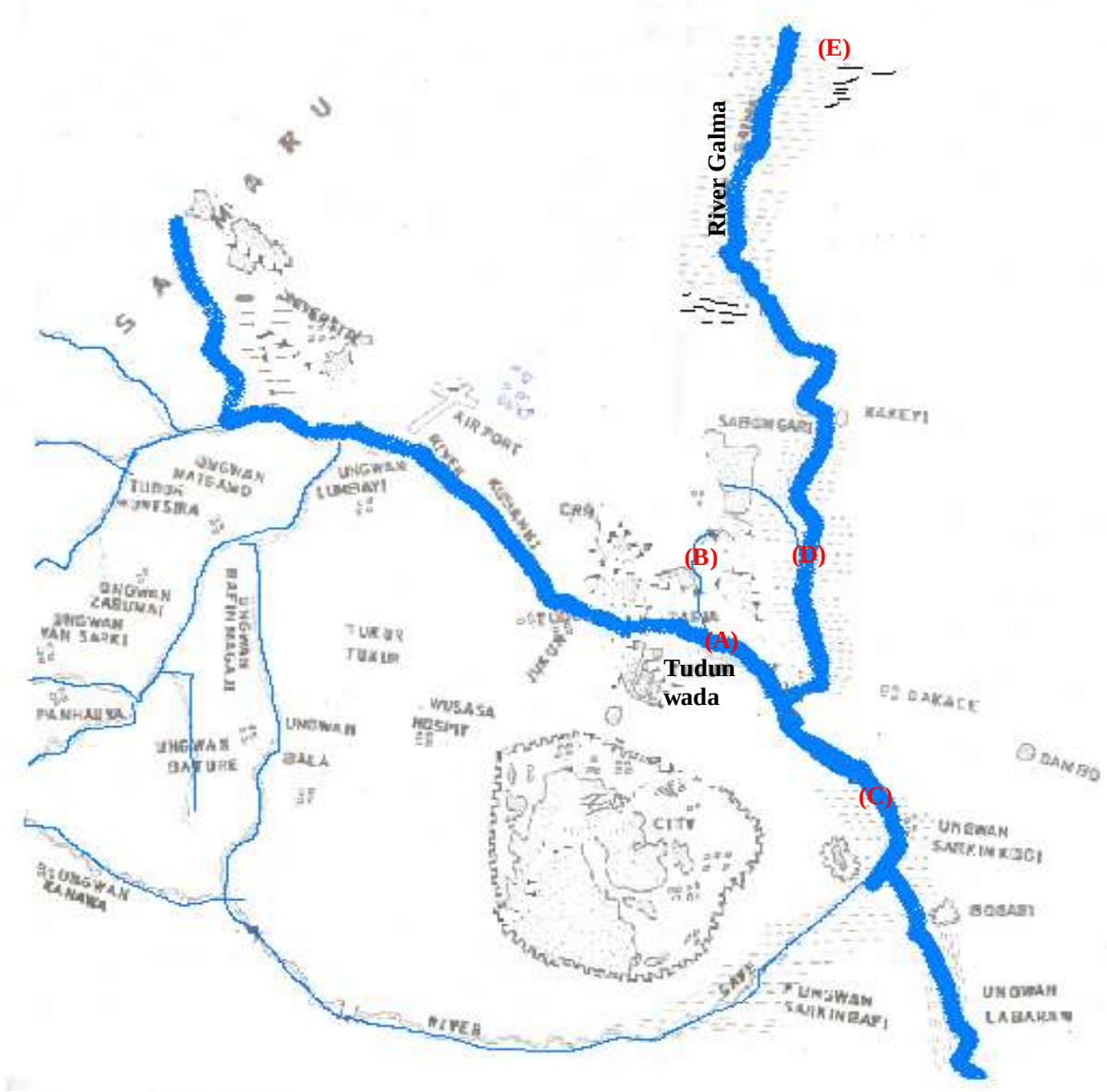
For the purpose of analysis of treated water, Zaria metropolis was divided into 8 Zones, from where samples from public water supply were collected (Scheme 1).

3.2.3 *Sampling Points for Raw Water*

For the analysis of raw water, 2 points along river Kubanni (A and B) and 2 points along river Galma (C and D) were selected. Also one point at Zaria Dam (E) was selected for collection of untreated (raw) water. These points are shown on MAP 2.

Scheme 1: Sampling Points For Treated Water

ZONE CODE	AREA
TA	Zaria water treatment plant
TB	Palladan/Hanwa/G.R.A
TC	Tudun wada/ Gyallesu
TD	Magume/ Tudun jukun
TE	Zaria city
TF	Sabon Gari/ Mucchia- cikaji
TG	Wusasa/ Dan- Magaji
TH	Samaru



Map 2: Sampling sites for raw water

3.2.4 *Sample Collection and Preservation*

Water samples were collected following the standard procedure described by DWAF (1992). The application of standard randomized controlled trial sampling was also extended to this study to achieve an optional level of success in sample collection.

At the collection site, the following parameters were recorded; name of sample, time and date of collection, place of collection and pH. Samples were collected between the months of February to April 2006 (Dry season) and, August to October 2006 (Rainy Season).

3.2.5 *Collection of Raw Water Samples*

Polyethylene bottles were used for collection of the samples. The containers were thoroughly washed with detergent, rinsed with water and then with distilled water before soaking in 5 % HNO_3 for 24 hours, container were finally rinsed with double distilled water before being used for sampling.

Two litres (2 L) of the raw water samples were collected in the container from the banks of the rivers where the water is used for irrigation at each of the demarcated sampling sites. The sample was then acidified with 1 - 2 ml of concentrated HNO_3 to get a pH 2.2 to 2.8 Water samples were kept cooled in ice packs en route to the laboratory and stored under refrigeration to stabilize the metal before analysis.

Samples were collected every month (February - April and August-October) at each of the demarcated sites.

3.2.6 *Collection of Treated Water Samples*

For collection of treated water samples, three (3) tap points were selected in each zone every month the samples were taken. The polyethylene bottles used were treated as earlier described.

The tap was allowed to run for 1 minute, then two liters (2 L) were collected into the container from each of the selected taps in every zone. The sample was immediately acidified with concentrated HNO_3 to preserve it. The samples were kept in ice packs en route the laboratory and stored under refrigeration prior to analysis.

3.2.7 *Collection of Vegetable Crop Samples*

Vegetables samples (lettuce and tomato) were purchased directly from farmers at farmlands closest to river banks at sites demarcated for sampling of raw water. Request was made for vegetable stalks from different areas of the farm. The vegetable samples were placed in polyethylene bags, labelled and taken to the laboratory.

3.3 Analysis of Samples

3.3.1 *Preparation of Stock Solution*

Stock solutions of the metals under study (i.e. Pb, Mn, and Cu) were prepared as follows:

Lead: 1.598 g of lead nitrates [$Pb(NO_3)_2$] was weighed and dissolved in 100 ml of deionised water. 5 ml of concentrated nitric acid (HNO_3) was added and the solution made up to a mark in a 1000 ml volumetric flask to give a 1000 mg/l solution.

***Manganese*:** 0.406 g of manganese Sulphate ($MnSO_4.4H_2O$) was weighed and dissolved in 100 ml of deionised water containing 1ml concentrated H_2SO_4. The solution was stirred and made up to mark in a 1000 ml volumetric flask to give a 100 mg/l solution.

Copper: 0.393 g of $CuSO_4.5H_2O$ was weighed and dissolved in 100 ml of deionied water. The solution was made to mark in a 1 litre volumetric flask to give a 100 mg/l solution.

3.3.2 *Preparation of Calibration Curve*

Five working standard solutions were prepared from the stock solutions for each of the metals by successive serial dilutions. Each of the standard solutions was aspirated into the flame of the AAS and the absorbance recorded in each case. A plot of the concentration against the corresponding absorbance gave the calibration curve for each of the metals (Appendices I, II and III).

3.3.3 *Pretreatment and Analysis Lead, Manganese and Copper in Water*

The open-beaker digestion (OBD) method using HNO_3 as described in LPFWA (2004) and as reported by Dike *et al* (2004) was employed for the chemical analysis of water samples.

Procedure: 50 ml of the water samples was measured into a 100 ml beaker and 10 ml of HNO_3 was added. The beaker with the content was placed on a hot plate and digested till brown fumes of HNO_3 escaped. Heating was continued till content have reduced to 10 ml volume. The content was then washed into a 50 ml volumetric flask and made up to mark. The digest obtained was used for the determination of Pb, Mn and Cu.

3.3.4 *Pretreatment and Analysis of Lead, Manganese and Copper in Vegetable Samples*

The plant samples were thoroughly rinsed with tap water and then with double-distilled water to remove any attached soil particles. Then cut into small portions and placed in a large crucible where they were oven-dried at 60 ^oC overnight. The dried plants were ground into fine particles using a clean mortar and pestle.

The triacid method of digestion as described in LPFWA (2004) was employed here. The acids used were Nitric acid (HNO_3), perchloric acid ($HClO_4$) and concentrated sulphuric acid (H_2SO_4) in the ratio 65 : 8 : 2 respectively.

Procedure: 0.2 g of the powdered plant samples were weighed into a 100 ml glass beaker. 30 ml of the acid mix was added and the content swirled then placed on a hot plate. The beaker was heated till brown fumes of nitric acid go off. Heating was continued till the content of the beaker reduced to about 5 ml volume. The contents were allowed to cool and a little amount of distilled water was added and the beaker swirled. The content was then poured into a 50 ml volumetric flask and made up to mark. The digest was then used for the determination of Pb, Mn, and Cu.

Chapter 4 RESULTS

The data generated were statistically analyzed using mean, standard error of the mean and student paired t-test, P values greater than 0.05 were considered to be statistically significant.

4.1 Concentration of Lead, Manganese, and Copper in Raw Water Sample

The results obtained for the levels of the each metals in raw water from five (5) sampling sites (two each from River Kubanni and river Galma, and one from Zaria Dam), are shown in Figure 1a and 1b. Figure 1a shows the mean levels of the metal in the dry season while 1b show the mean levels in the rainy season. The results were compared with the WHO limits for each of the metals in drinking water.

4.2 Concentration of Lead, Manganese, and Copper in Treated Water Sample

The levels of the metals analysed in six of the eight (8) sampling zones in both dry and raining season are shown in Figure 2a and 2b respectively. No samples were obtained from zones T_D and T_H. The results are mean of triplicate samples for each of the three (3) months in both season (i.e. February to March for dry season and August to October for raining season). The results were compared with W.H.O limits for each of the metals in drinking water.

4.3 Concentration of Lead, Manganese and Copper in Vegetable Samples

The mean levels of the each of the metals in the two vegetable samples analysed (Tomato and Lettuce) are shown in Figures 3a, 3b, 4a, 4b, 5a and 5b. The results obtained were compared to FAO recommended threshold for crops.

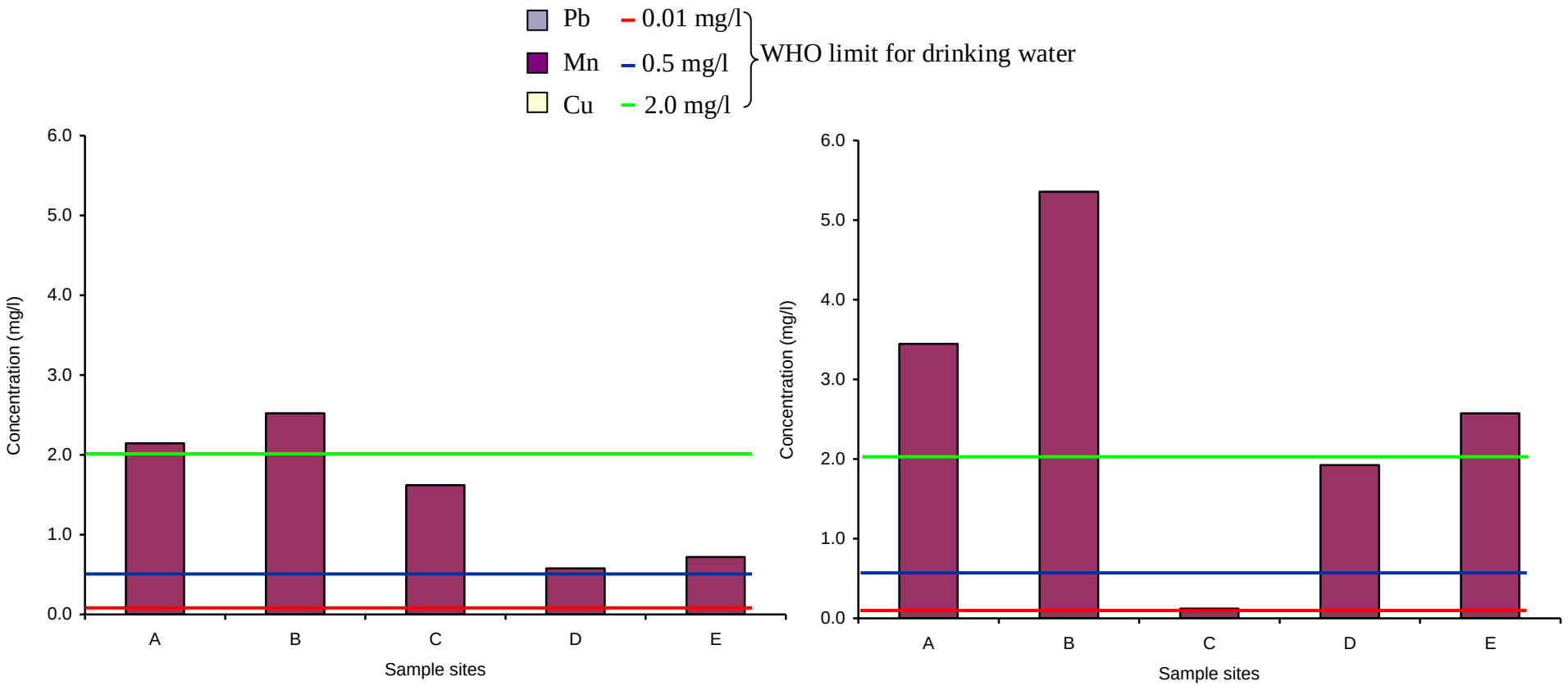


Fig. 1a: Mean concentration (mg/l) of lead, manganese and coppe in raw water samples (dry season)

Fig. 1b: Mean concentration (mg/l) of lead, manganese and copper in raw water samples (rainy season)

Seasonal variations: not significant at $p < 0.05$ at all the sites

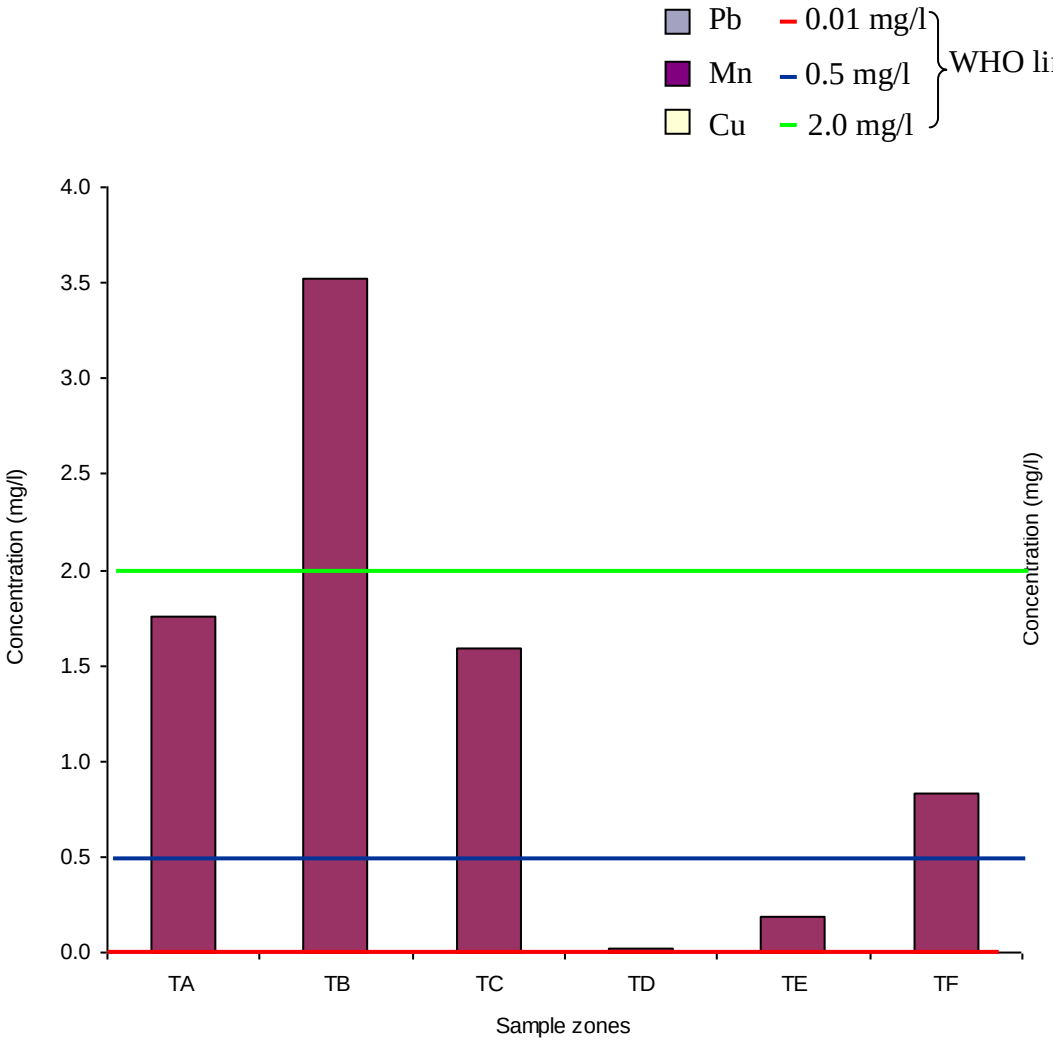


Fig. 2a: Mean concentration (mg/l) of lead, manganese and copper in treated water samples (dry season)

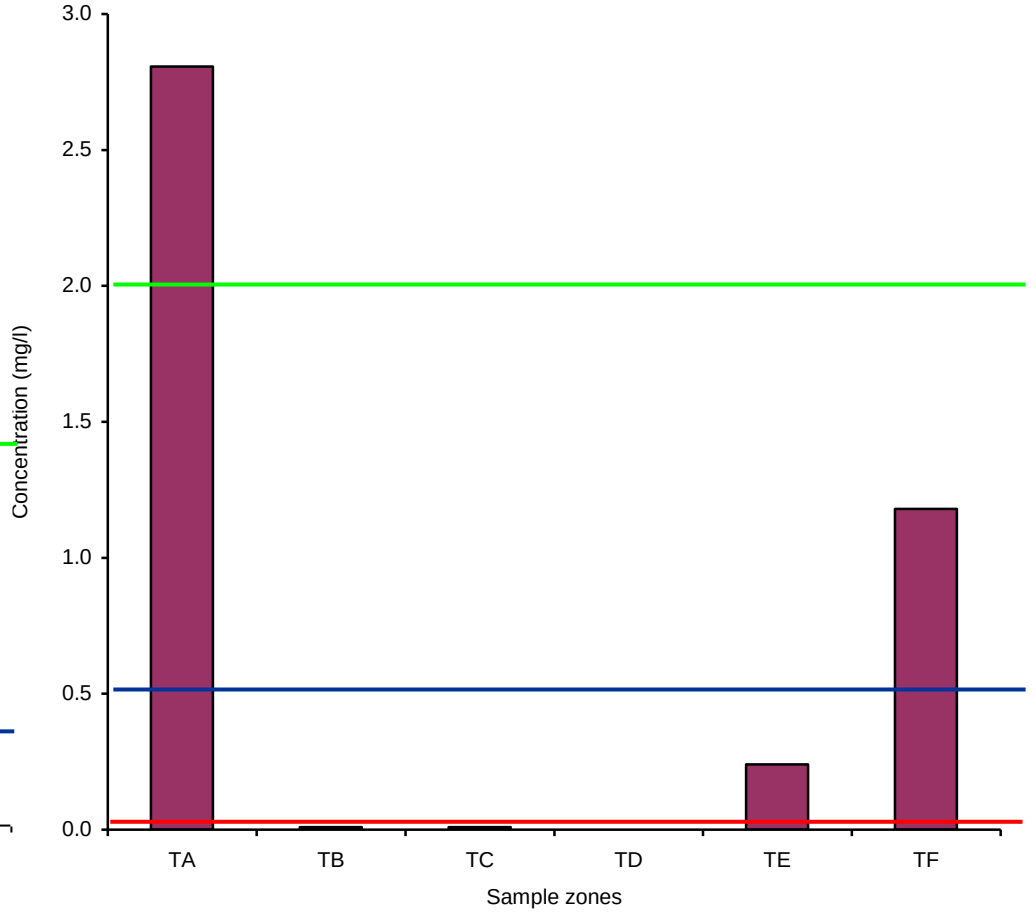


Fig. 2b: Mean concentration (mg/l) of lead, manganese and copper in treated water samples (rainy season)

Seasonal variations: significant at $p < 0.05$ only at zone T_B

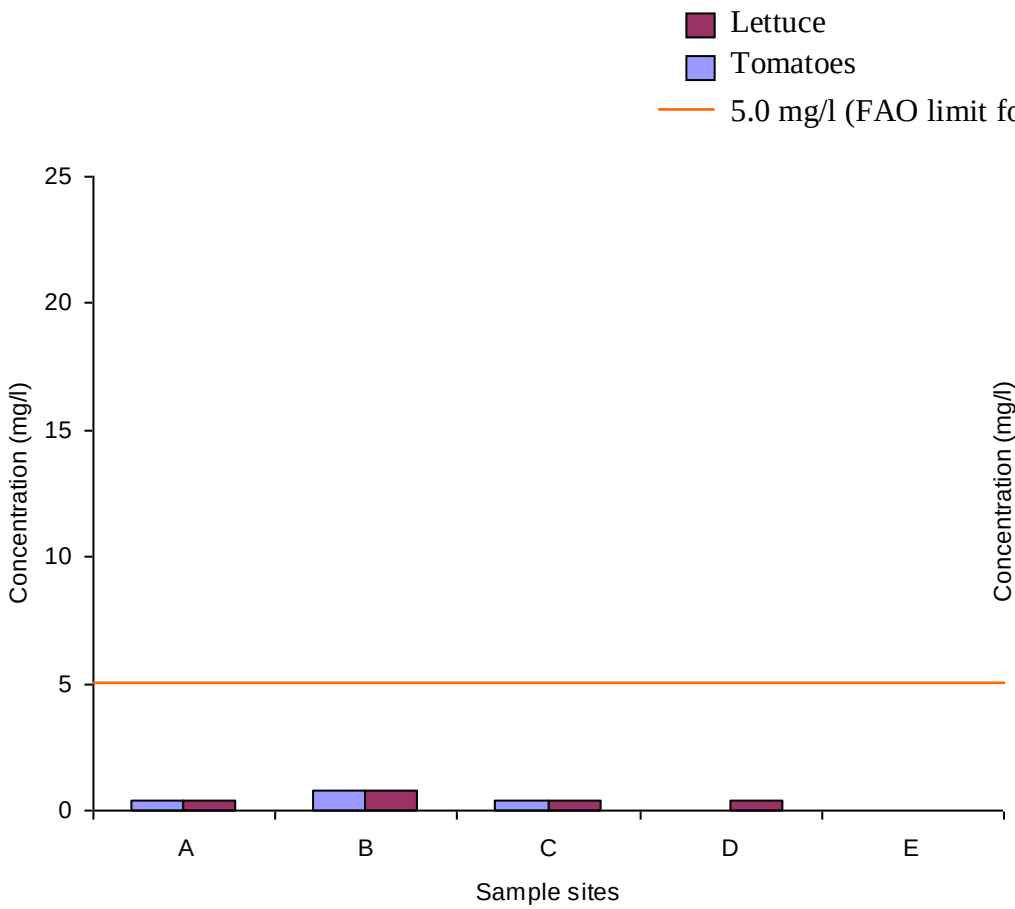


Fig 3a: Mean concentrations (mg/l) of lead in vegetable samples (dry season)

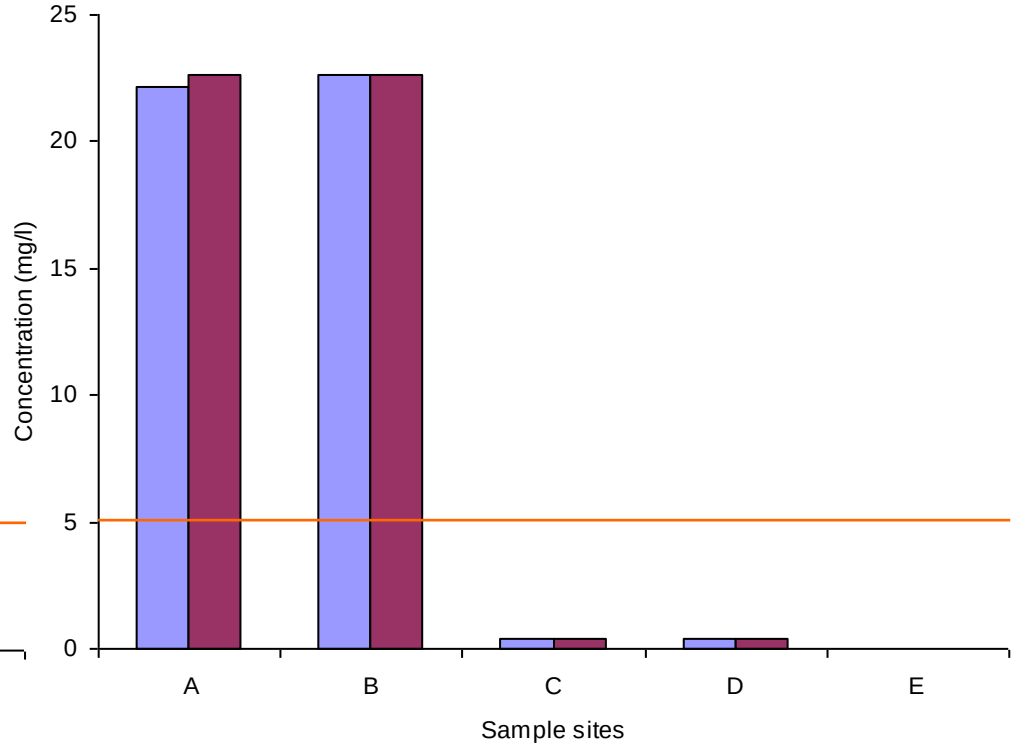


Fig 3b: Mean concentrations (mg/l) of lead in vegetable samples (rainy season)

Seasonal variations: significant at $p < 0.05$ only at sites A and B

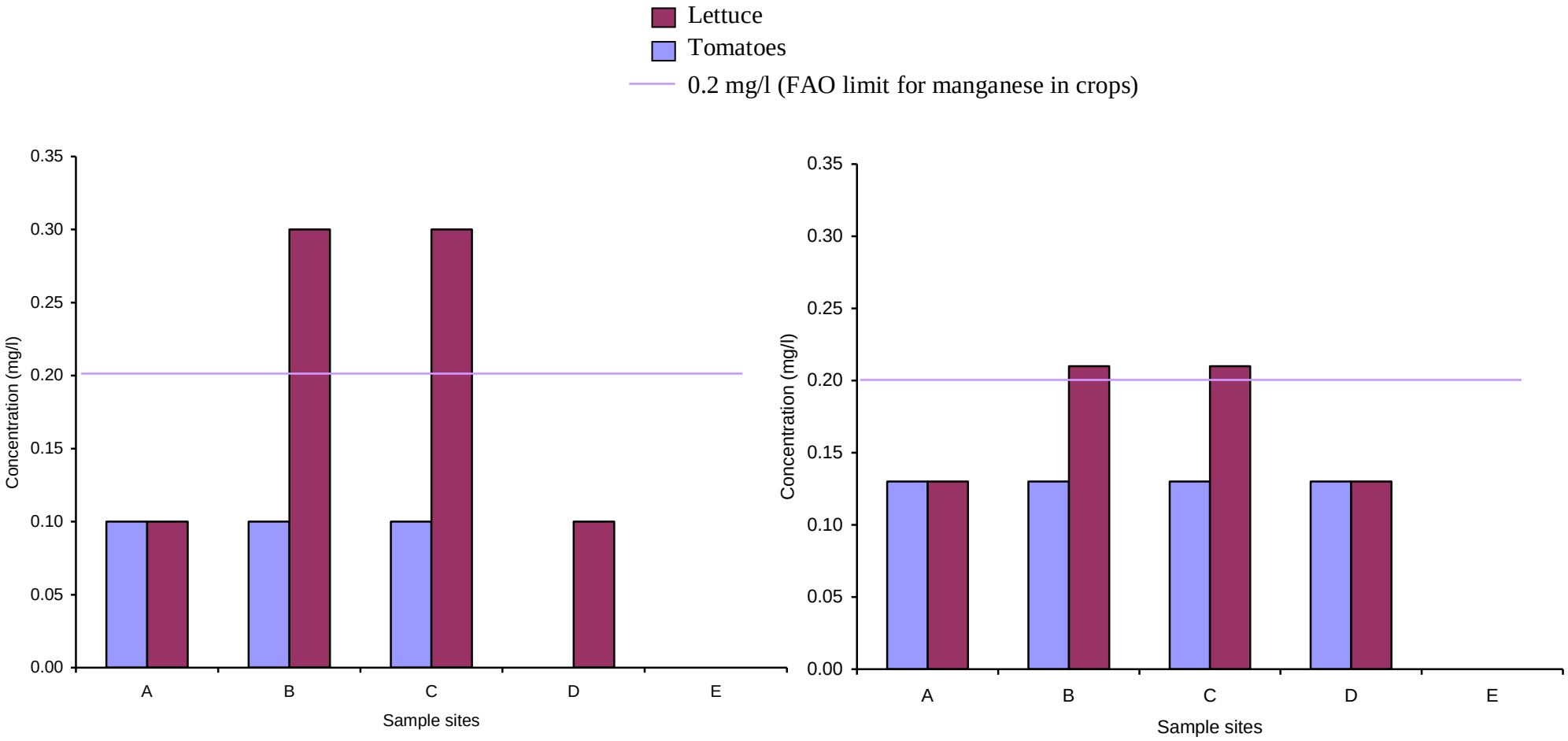


Fig 4a: Mean concentrations (mg/l) of manganese in vegetable samples (dry season)

Fig 4b: Mean concentrations (mg/l) of manganese in vegetable samples (rainy season)

Seasonal variations: not significant at $p < 0.05$ at all the sites

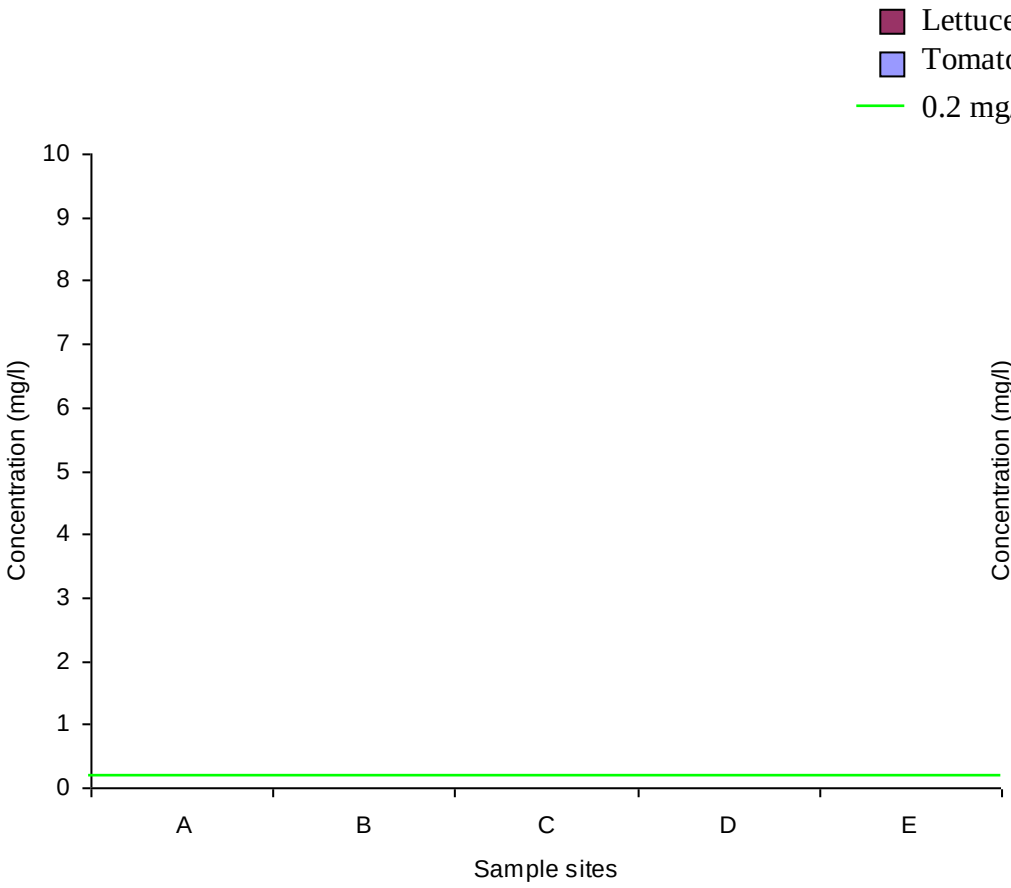


Fig 5a: Mean concentrations (mg/l) of copper in vegetable samples (dry season)

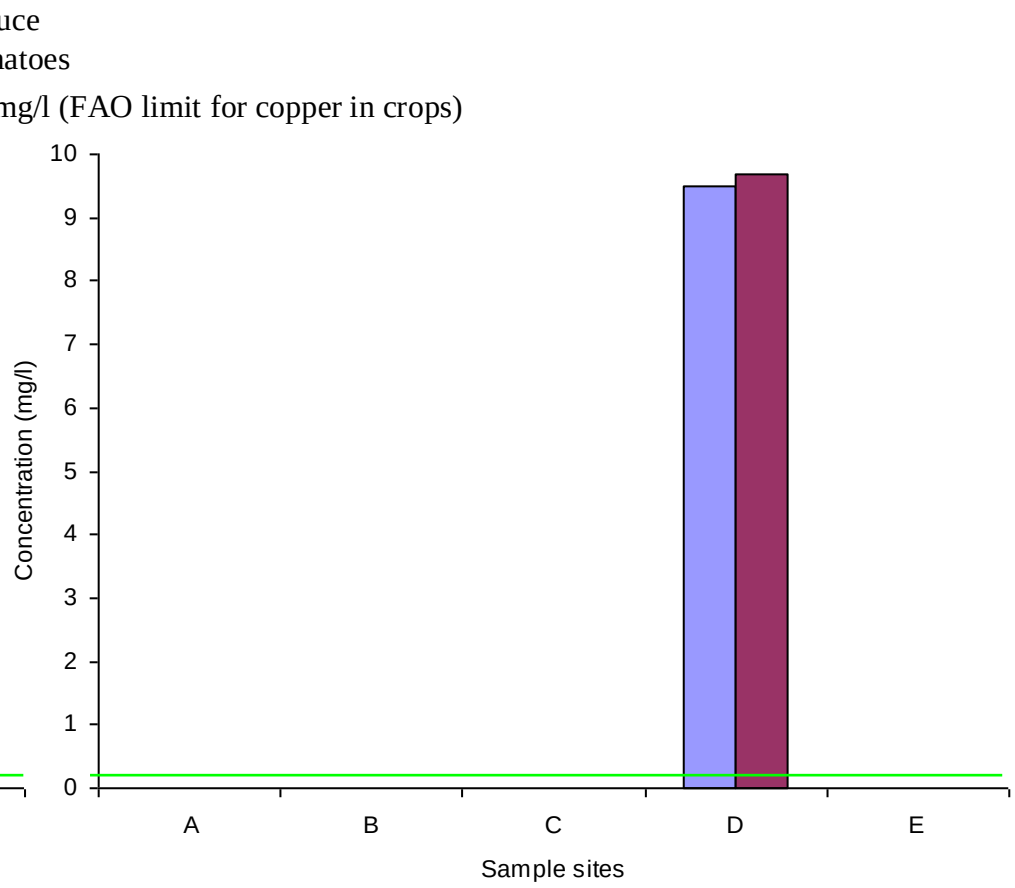


Fig 5b: Mean concentrations (mg/l) of copper in vegetable samples (rainy season)

Seasonal variations: significant at $p < 0.05$ only at sites D

4.4 Seasonal Variation in the Mean Levels of Lead, Manganese and Copper in Samples Analysed

The seasonal variation in the mean levels of the metals between the dry and rainy season was determined using the student paired t-test. The results for the raw water and treated water are shown in Tables 2 and 3 respectively. Because only manganese was detected in both raw and treated water samples, the results reflected only variations in manganese concentration between the seasons.

Table 2: Seasonal variations in the mean concentration of manganese in raw water samples

Sampling site	Mean concentration (mg/l $\pm$ SEM)		Paired Student t-test value
	Dry season	Rainy season	
A	2.14 $\pm$ 1.19	3.45 $\pm$ 0.20	1.077*
B	2.52 $\pm$ 1.65	5.36 $\pm$ 0.26	1.700*
C	1.62 $\pm$ 0.98	0.12 $\pm$ 0.05	1.400*
D	0.58 $\pm$ 0.28	1.93 $\pm$ 0.89	0.930*
E	0.72 $\pm$ 0.47	2.57 $\pm$ 1.07	0.970*

* Not significant at $P < 0.05$

Table 3: Seasonal variations in the mean concentration of manganese in treated water samples

Sampling zones	Mean concentration (mg/l ± SEM)		Paired Student t-test value
	Dry season	Rainy season	
T_A	1.76 ± 0.89	2.81 ± 0.31	1.11*
T_B	3.53 ± 0.85	0.01 ± 0.01	4.14
T_C	1.59 ± 1.37	0.01 ± 0.01	1.152*
T_D	0.02 ± 0.02	0.00 ± 0.00	1.0*
T_E	0.19 ± 0.10	0.24 ± 0.21	0.207*
T_F	0.83 ± 0.78	1.18 ± 1.07	0.263*

* Not significant at $P < 0.05$

4.5 Mean pH Values In Raw And Treated Water

The mean pH vales taken at the point of collection of both raw and treated water sample are shown in Tables 4 and 5 respectively.

Table 4: Mean pH values for raw water samples

Sampling sites	Mean concentration (mg/l ± SEM)	
	Dry season	Rainy season
A	8.3 ± 0.06	6.3 ± 0.07
B	8.0 ± 0.03	6.8 ± 0.08
C	8.6 ± 0.03	7.1 ± 0.09
D	8.7 ± 0.09	6.4 ± 0.03
E	8.4 ±0.03	6.5 ± 0.03

Table 5: Mean pH Values for treated water samples

Sampling zones	Mean concentration (mg/l ± SEM)	
	Dry season	Rainy season
T_A	6.9 ± 0.03	6.9 ± 0.03
T_B	6.7 ± 0.07	6.4 ± 0.03
T_C	6.8 ± 0.06	6.7 ± 0.03
T_D	6.5 ± 0.18	6.3 ± 0.07
T_E	7.3 ± 0.07	6.8 ± 0.03
T_F	7.1 ± 0.03	6.4 ± 0.10

Chapter 5 DISCUSSION AND CONCLUSION

5.1 Concentration of Lead, Manganese, and Copper in Raw Water Samples

The result obtained from the analysis of all the raw water samples collected from river Kubanni, river Galma and at Zaria Dam, revealed that lead and copper were not detect in both dry and rainy season. However, manganese was detected in all the samples analyzed in both season. In the dry season, the mean manganese concentration was lowest at site D (0.58 $\pm$ 0.28 mg/L) and highest at site B (2.52 $\pm$ 1.65 mg/L). This indicates that all the samples analyzed contain manganese above the 0.5 mg/l WHO desirable limit for drinking water and also the FAO recommended limit for crops (< 0.2 mg/l). In the rainy season however, the lowest mean manganese concentration was recorded at site C (0.12 $\pm$ 0.05 mg/L), while site B still recorded the highest (5.36 $\pm$ 0.26 mg/L). Thus, with the exception of samples collected at site C, all the other sites (A, B, D and E) contain mean concentration of manganese above the WHO guideline for drinking water. (0.5 mg/L) and also the FAO recommended limit for crops (< 0.2 mg/l).

A comparison of the results between the two seasons revealed that a general increase in the mean manganese concentration was observed in the rainy season relative to the dry season. The only exception was at site C where a reduction in the rainy season (0.12 $\pm$ 0.26 mg/L) was observed relative to the dry season (1.62 $\pm$ 0.98 mg/L). However, the variations observed between the two seasons were not statistically significant at all the sampling sites. The relatively higher values observed during the rainy season could most probably be due to rain water washing manganese from the soil and municipal drainages into rivers Kubanni and Galma and also into Zaria dam. In contrast, during the dry season most parts of rivers Kubanni and Galma were dried up and there was little or no washing of municipal drainages into the major tributaries that serve these rivers. Another

possible reason for the variations observed could be the slightly acidic pH value (6.3 - 6.5) observed in the rainy season compared to the slightly alkaline pH value (8.3 - 8.7) observed in the dry season. This is because water acidity is known to influence solubility and availability of metals (Awofolu *et al.,* 2005). The high concentration of manganese observed in this study which were above both the WHO drinking water guideline and FAO recommended limit for crops, suggests that the water from river Kubanni and river Galma, and also at Zaria Dam may not be suitable for domestic activity and for irrigation. But due to the persistent shortage of clean and safe drinking water faced by most parts of Zaria metropolis, some communities, especially those living close to these rivers use this water for domestic purposes. Also, farms located along the banks of these rivers are irrigated using the water.

The above findings raise serious concerns relating to environmental and public health issues caused by the effects of manganese. The accumulation of Manganese may cause hepatic encephalopathy (Layrargues *et al.* 1998) manganese is a known mutagen (Beckman *et al.* 1985). Moreover the chronic ingestion of manganese in drinking water is associated with neurologic damage (Kondakis *et al.,* 1989). Exposure to very high levels of manganese causes "manganism", a syndrome characterized by Parkinson-like symptoms (USEPA 2004).

The possible sources of these high levels of manganese in the raw water samples could be; the fact that manganese is the most abundant metal on the earth's surface, making up approximately 0.1% of the earth's crust. Some of this manganese can leach from the soil into the water depending on the acidity of the soil and water. Manganese compounds are used in products such as batteries, glass etc. these are usually discarded in refuse dumps where they become part of the organic manure used by most of the farmers, as a result,

some manganese could be washed into the rivers by rainwater. Other manganese compounds are used in fertilizers, fungicides and pesticides for agricultural purposes, these may eventually end up in the rivers.

Manganese compounds may be present in the atmosphere as suspended particles resulting from the burning of MMT (Methylcyclopentadienyl Manganese tricarbonyl) containing gasoline. Zaria is experiencing an increase in vehicular traffic and usage of gasoline powered generators due to power outages. This could result in high levels of compounds of manganese suspended in the atmosphere over Zaria. Because particle size is small, atmospheric manganese distribution can be widespread. These particles will eventually settle into surface water or soils.

5.2 Concentrations of Lead, Manganese and Copper in Treated Water Samples

The results obtained from the analysis of treated water samples from six of the eight sampling Zones, revealed that lead and Copper were not detected in both dry and rainy seasons. However, manganese was detected in 91.67 % of all the samples analysed from both seasons. In the dry season, manganese was detected in all the samples analysed with 66.67 % of the samples containing manganese above the 0.5 mg/l WHO guideline for drinking water. The lowest mean manganese concentration was recorded at zone T_D (0.02 $\pm$ 0.02 mg/L) while the highest (3.53 $\pm$ 0.85 mg/L) was recorded at zone T_B. Interestingly, the level of manganese observed in this particular zone was higher than that recorded at zone T_A (1.76 $\pm$ 0.89 mg/L) which is the water treatment plant at Zaria Dam. It is expected that as the water is distributed from the treatment plant to various parts of Zaria metropolis, the concentration of manganese in the water will drop due to diffusion. This was generally observed across all the zones except at zone T_B where the concentration increased. This could be attributed to the breakages observed on two of the

major supply pipes to this zone during the sampling period. As a result manganese could easily leach from the soil through the pipes into the water supply system within the zone.

In the rainy season, manganese was detected in 83.3 % of the samples analysed, with 33.3 % having manganese above 0.5 mg/L WHO guideline for drinking water. The lowest mean manganese concentration (0.00 mg/L) was recorded at zone T_D, while the highest (2.81 $\pm$ 0.31 mg/L) was recorded at zone T_A (i.e. the water treatment plant at Zaria Dam). These results indicate a general decrease in the concentration of manganese across all the zones as water was pumped from zone T_A to various parts of Zaria metropolis. This is consistent with the expected trend due to diffusion.

A comparison of the results between the two seasons shows a higher level of manganese at T_A during the rainy season relative to the dry season. This could most likely be due to higher concentration of manganese in the raw water from Zaria dam in the rainy season (2.57 $\pm$ 1.07 mg/L) relative to the dry season. At zone T_B where the highest concentration of manganese (3.53 ± 0.85 mg/L) was recorded during the dry seasons, a drastic decrease (0.01 mg/l) was observed in the rainy season. This may be due to the fact that the breakages observed in the dry season on the two major supply pipes in this zone were repaired, thus preventing the leaching of manganese into the water supply system. Zone T_D consistently recorded the lowest concentration of manganese, with 0.02mg/l being recorded in the dry season and 0.00mg/l in the rainy season. It can therefore be concluded that zone T_D (Magume/Tudun-Jukun) has the safest drinking water with respect to manganese. Although variations in the concentrations of manganese were observed between the two seasons in each of the sampling zones, the variations were however not statistically significant at the $p < 0.05$. The only exception was observed in zone T_B,

where the result of the paired student t-test (4.14) suggests a very significant statistical variation at $p < 0.05$.

The primary source of manganese in the public water supply in Zaria metropolis could most definitely be linked to the raw water source (i.e. Zaria Dam). As discussed earlier, analysis of the raw water samples from Zaria Dam revealed high levels of manganese above the 0.5mg/l WHO guidelines for drinking water. Another source could be as a result of the breakages on both major and minor supply pipelines. This could result in the leaching of manganese from the soil into the water supply system.

The fact that lead and copper were not detected in the public water supply system in Zaria metropolis could also be linked to the raw water source from Zaria Dam. This is because the two metals were not detected in the raw water from Zaria Dam. However, the primary source of lead and copper in public water supply is due to the use of these two metals as plumbing materials. The corrosion of such materials (especially with acidic water) may result in increased concentrations of lead and copper in municipal drinking water. However, in this study it was observed that most of the plumbing materials used in Zaria metropolis are made of plastic. But even in areas where the plumbing is done with lead or copper materials, these metals could not corrode into the water because the pH is within the range 6.3 - 7.3. Thus, the water is not acidic enough to cause corrosion of the plumbing material.

Chronic exposure to such high doses of manganese may be harmful. The health effects from over exposure to manganese include hepatic encephalopathy, neurologic damage, and impaired fertility amongst other things. Infants fed on infant formular are especially at high risk. This is because infant formulars contain 50 – 300 ng/l manganese (Collipp *et al*., 1983), compared to human milk which contains 3.5 – 15 ng/l (ATSDR, 2000). Given

the high manganese content of infant formulars, if prepared with water high in manganese (such as the samples analysed); the infant may be exposed to manganese toxicity. Heavy tea drinkers may also be at a special risk. This is because an average cup of tea may contain 0.4 – 1.3 mg manganese (ATSDR, 2000). If the tea is prepared with water containing high content of manganese, the individual may be exposed to manganese toxicity.

5.3 Concentrations of Lead, Manganese and Copper in Vegetable Samples

Results on the analysis of vegetable samples collected from farmland located at sampling sites for raw water samples along the banks of river Kubanni and river Galma revealed that; lead and manganese were detected in samples collected at all the site in both dry and rainy seasons. However, copper was only detected at one site and only in the rainy season. Samples were not collected from site E (Zaria Dam), because no irrigation farming is done at this particular site. The two vegetables selected for this study are tomatoes and lettuce.

5.3.1 *Concentration of Lead in Vegetable Samples*

Lead was detected in all the samples analyzed. In the dry season, both the tomato and lettuce samples took up the same amount of lead. Sites A, C and D recorded 0.40 ± 0.01 mg/L of lead in the samples, while site B recorded 0.80 ± 0.003 mg/L but all these values are far below the 5 mg/l recommended threshold value for lead in crops. Thus, all the samples anaylsed in dry season can be said to be safe for consumption with regards to lead.

In the rainy season, a dramatic increase in concentration of lead in samples collected at sites A and B along river Kubanni was observed. At site A, tomato recorded 22.2 $\pm$ 0.4

mg/L of lead while lettuce recorded 22.6 $\pm$ 0.07 mg/L. At site B, both tomato and lettuce recorded 22.60 mg/l of lead. These values are much higher than the 5 mg/l recommended threshold value for lead. Thus, vegetables from these two sites may be considered unsafe for consumption. Such high concentrations of lead can cause irreversible brain damage (encephalopathy), seizure, coma and death if not treated immediately (U.S. EPA 1986). Children are especially more susceptible to the damaging effect of lead toxicity. At sites C and D along river Galma, both tomato and lettuce samples recorded very low levels of lead (0.38 $\pm$ 0.01 mg/L). This is much lower than the 5 mg/l recommended threshold value for lead. Thus, samples from these sites can be considered safe for consumption.

Seasonal variations in the concentration of lead were only statistically significant (at $p < 0.05$) in samples collected from sites A and B along river Kubanni. A similar high concentration of lead was obtained in vegetable samples cultivated along the banks river Kaduna (Ojeka and Achi 2004).

Though lead was not detected in the raw water used in irrigating these vegetable samples, the presence of lead in the vegetables could be due in part to uptake from the soil. Another reason could be the organic manure used by the farmers. This manure is usually obtained from refuse dumps where items containing lead compounds such as batteries, lead based paint containers, ceramic etc. are discharge. Airborne lead particles from burning of gasoline containing tetraethyl lead fall to the ground and become distributed in the soil. This could be another possible reason for the presence of lead in the vegetable samples.

5.3.2 *Concentration of Manganese in Vegetable Sample*

Manganese was detected in all the vegetable samples analysed in both rainy and dry seasons. In the dry season, the tomato samples recorded 0.1mg/l $\pm$ 0.003 of manganese at

all the sampling sites, except at site D where no tomato samples were available. This value is below the 0.20 mg/l recommended threshold values for manganese. Thus, the tomato samples analysed during the dry season can be considered to be safe for consumption. The lettuce samples at sites A and D also recorded a mean manganese concentration of 0.10 $\pm$ 0.003 mg/L. However, lettuce samples at sites B and C had manganese concentration of 0.30 $\pm$ 0.006 mg/L which is above the recommended threshold. Lettuce from these sites can be considered unsafe for consumption. This also seem to indicate that the lettuce plant tend to take up more manganese than the tomato plant.

In the rainy season, a similar trend to that seen in the dry season was observed. Tomato samples from all the sampling sites had mean manganese concentrations of 0.13 $\pm$ 0.007 mg/L. This is below the recommended threshold value (0.20 mg/L). Thus, the tomato samples can be considered safe for consumption. The lettuce samples at sites A and D also had mean manganese concentrations of 0.13 mg/L. However, lettuce samples at sites B and C had mean manganese concentrations of 0.21 $\pm$ 0.003 mg/L. This is just above the recommended threshold value (0.20 mg/L). Thus, these particular samples may lead to the manifestations of manganese toxicity if consumed over a long period of time. As was observed in the dry season, lettuce samples at sites B and C tend to take up more manganese than the tomato samples.

No statistically significant variations in the concentration of manganese in samples analysed was observed between the two seasons at $p < 0.05$. The fact that manganese was detected in all the samples analysed is not surprising. This is because results obtained from the analysis of the raw water used in irrigating these vegetables revealed very high levels of manganese. Also manganese occurs naturally in the soil from where the

vegetables could table up the metal. Also atmospheric particles of manganese from the burning of gasoline and the use of manganese containing pesticides could contribute to the contamination of the vegetables by the metal.

5.3.3 *Concentration of Copper in Vegetable Samples*

As with the analysis of raw and treated water, copper was not detected in any of the vegetable samples in the dry season. In the rainy season also, copper was not detected in any of the samples at all the sites except at site D. Both Lettuce and tomato samples collected from this site showed excessively high levels of copper above 0.20 mg/L recommended threshold (9.50 ± 0.12 mg/L for tomato and 9.7 ± 0.12 mg/L for lettuce). This is quite surprising considering the fact that copper was not detected in the water used in irrigating these vegetables. The plants could not have taken up the metal from the soil because sample taken from the same site during the dry season showed no traces of copper. Also samples taken from all the other sites in both dry and rainy season showed no traces of copper, indicating that the soil in Zaria may not be rich in copper. Since copper is a common component of fungicides and algaecides, agricultural use of copper for these purposes can result in its presence in soil. It is very likely that the farmers at site D used such chemical during the rainy season which may be the reason for such high levels of copper at this site but not at the other sites. Another possible explanation could be that the organic manure have been sourced from refuse dumps were copper products were discarded. Similar high levels of copper were detect in vegetable samples cultivated along river Kaduna (Ojeka and Achi, 2004) and vegetables along Tyume river within the eastern cape province of south Africa (Awofolu *et al*. 2005).

Because of such high levels of copper in samples collected from site D, it can be concluded that these samples are unsafe for consumption with respect to copper. The

health effects of acute toxicity of ingested copper are abdominal pain, diarrhea, vomiting, tachycardia and metallic taste in the mouth. Continued ingestion of copper can cause cirrhosis and other debilitating liver conditions. Individuals with Wilson's disease are at a particular risk since they accumulate abnormally high levels of copper in body tissues.

5.4 Mean pH Values of Raw and Treated Water Sample

Portable water should have a pH range of 6.5 – 8.5. In the dry season, sites C and D along river Galma recorded mean pH values of 8.6 and 8.7 respectively. This is outside the recommended range. Site E where raw water samples from Zaria dam were collected recorded mean pH of 6.5, which is within the range. It was observed that all the pH values obtained from raw water sample in the dry season were in the alkaline region.

In the rainy season, sites A and D recorded mean pH of 6.3 and 6.4 respectively. This is outside the recommended range. As in the dry season, raw water samples from site E (Zaria Dam) fell within the recommended range, recording mean pH of 6.5. All the raw water samples collected in the rainy season recorded pH values within the acidic region, except at site C with pH of 7.1. This acid pH values could be due to acid rain in the rainy season.

For treated water samples collected during the dry season, pH values ranging from 6.5 to 7.3 were recorded. This means that treated water samples from all the zones had pH values within the recommended range. In the rainy season however, samples from zone T_B, T_D and T_F recorded mean pH of 6.4, 6.3 and 6.4 respectively. These values are outside the recommended range. Zone T_A (water treatment plant at Zaria dam) recorded pH value of 6.9 in both dry and rainy season. This is within the recommended range and thus has passed the test.

The implication of having the pH of public water supply outside the recommended range could be serious. This is because; acidity or alkalinity of water either naturally or from added chemicals may promote the corrosion of plumbing systems and fixtures. It the plumbing system is made using lead or copper materials, individuals consuming the water may be exposed to the toxic effects of these metals.

5.5 Conclusion

The health effects of the consumption of heavy metal contaminated drinking water and food can not be over emphasized. The results from this study suggests that 90 % of the sites from where raw water samples were collected had manganese above the WHO guidelines for drinking water and the FAO recommended threshold for crops. This makes the water from these sites unfit for these purposes. This high level of manganese could be directly detrimental to the health of people in Zaria if the water is used for drinking, in view of the persistent shortage of clean and safe drinking water experienced by residents.

There could also be indirect detrimental health effects to residents since water from river Kubanni and Galma are used to irrigate near by farmlands. Metals from the rivers water could be a contributing source to the levels in the vegetables. This assumption was supported by the detection of manganese in all the vegetable samples analyzed, there was no statistically significant variation at $p < 0.05$ between the dry and rainy seasons in the levels of manganese seen in raw water and vegetable samples. All the zone demarcated for the sampling of treated water showed the presence of manganese (with 66.67 % of the zones in the dry season and 33.3 % in the rainy season having manganese above 0.50 mg/L). Zone TD (Magume/Tudun-jukun) recorded the lowest levels of manganese and can thus be considered to be the zone with the safest public water supply. Lead and copper were not detected in all the water samples analyzed.

Lead and manganese were detected in all the vegetable samples analyzed. Most of the vegetable samples were found to be safe for consumption except for a few that contained these metals above the recommended thresholds. Copper however, was detected only at site D during the rainy season. With a few exceptions (sites A and B for lead, and site D for copper) there were no significant variations at $p < 0.05$ in the levels of the metals in the vegetable sample between the dry season and the rainy season.

Form the results obtained in this study it can be concluded that manganese is the major contaminant among the three metals analyzed,

5.6 Recommendations

Due to the essential role played by water in supporting human, plant and animal life it also has, if contaminated, a great potential for transmitting a wide variety of diseases and illnesses. As a result, strategies must be developed for the protection and proper management of water resources in Zaria and its environs. Priority must be give to the avoidance of contamination of the surface water bodies in Zaria because they serve as sources for providing public water supply and also for irrigation. This can be done through effective municipal waste disposal, reduction in the burning of fossil/fuels by using alternative energy sources, proper and effective use of agricultural chemicals to avoid run-off into the water bodies etc. Water protection is always cheaper than expensive water-body restoration and water treatment.

The old Zaria water works should be rehabilitated and modernized by way of construction of new overhead tanks and the replacement of the distribution pipes. This is because the existing once are old and rusty as a results have over the years become a

reservoir for heavy metal contamination. The water laboratory should be revitalized to ensure proper in-house quality control before water is pumped to the consumers.

Periodic analysis of water and food samples should be carried out regularly to monitor the heavy metal levels as changes occur in the environment. Also, further studies should involve *in vivo* studies on the resident in Zaria to determine the level of these metals in their bodies as this will give an indication of the health problem we are facing.

Finally, the legislative arm of government should with immediate effect review existing laws and where necessary enact new ones to check the degradation of water quality in Nigeria. Regulatory bodies like NAFDAC should ensure enforcement of such laws.

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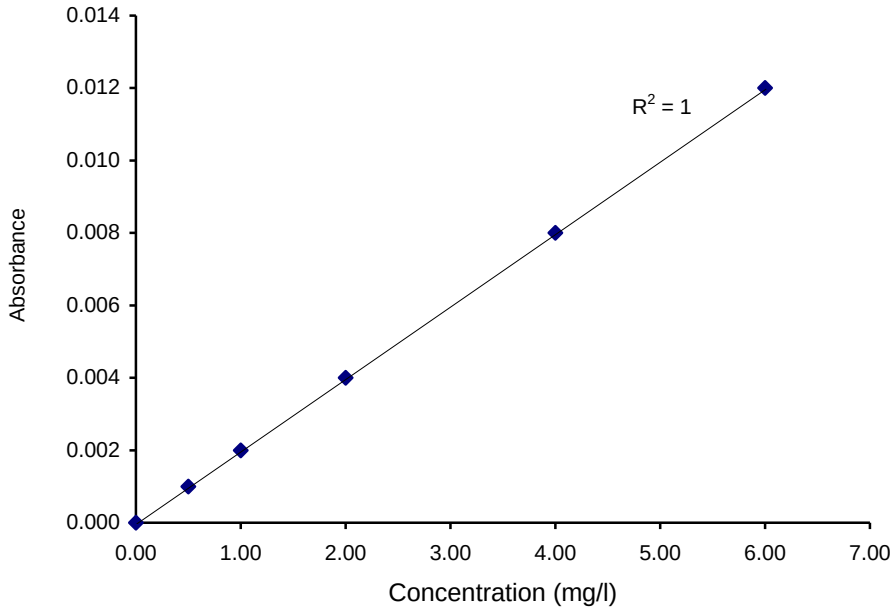
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Appendix I: AAS Calibration of Concentration vs Absorbance for lead

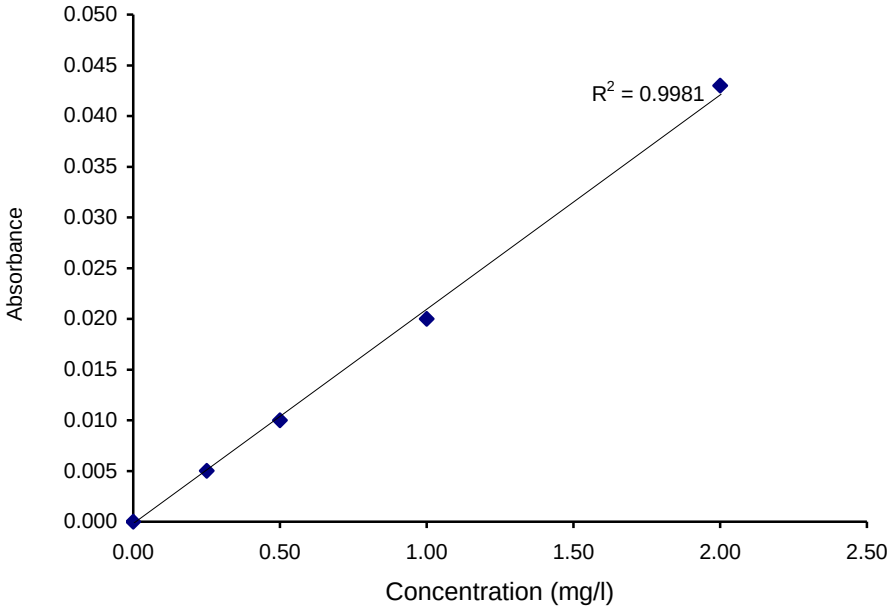
Concentration (mg/l)	Absorbance
0.5	0.001
1.0	0.002
2.0	0.004
4.0	0.008
6.0	0.012



AAS Calibration Curve of Absorbance vs Concentration (mg/l) of Lead

Appendix II: AAS Calibration of Concentration vs Absorbance for Manganese

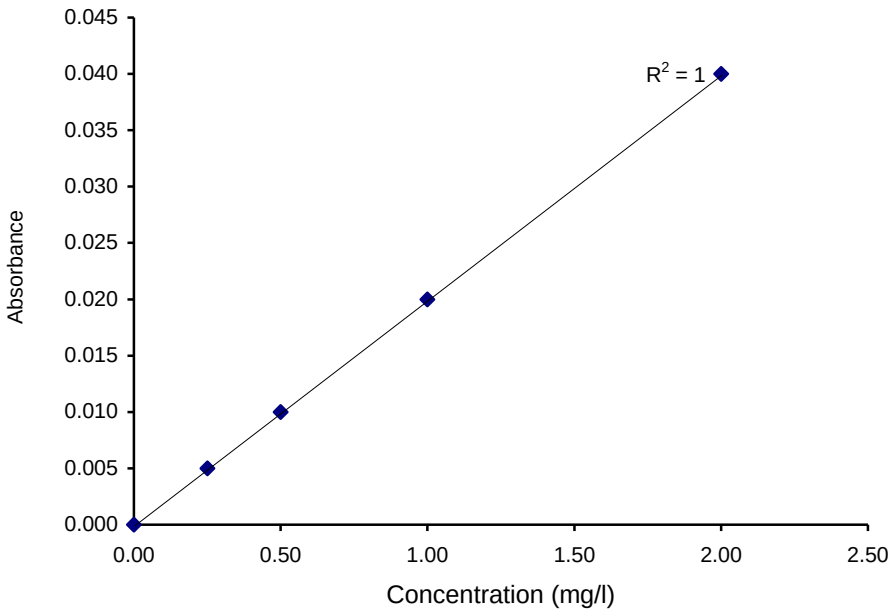
Concentration (mg/l)	Absorbance
0.25	0.005
0.50	0.010
1.00	0.020
2.00	0.045



AAS Calibration Curve of Absorbance vs Concentration (mg/l) of Manganese

Appendix III: AAS Calibration of concentration vs Absorbance for Copper

Concentration (mg/l)	Absorbance
0.25	0.005
0.50	0.010
1.00	0.020
2.00	0.040



AAS Calibration Curve of Absorbance vs Concentration (mg/l) of Copper

Appendix IV: Mean Concentrations of Lead, Manganese and Copper (Mg/L ± S.E.M) in Raw Water Samples

(DRY SEASON: FEB – APRIL 2006)

Metal	Sampling sites				
	A	B	C	D	E
Pb	0.00	0.00	0.00	0.00	0.00
Mn	2.144 ± 1.188	2.521 ± 1.646	1.621 ± 0.962	0.577 ± 0.278	0.721 ± 0.467
Cu	0.00	0.00	0.00	0.00	0.00

(*RAINY SEASON: AUGUST – OCTOBER 2006*)

Metal	Sampling sites				
	A	B	C	D	E
Pb	0.00	0.00	0.00	0.00	0.00
Mn	3.447 ± 0.203	5.357 ± 0.260	0.122 ± 0.0465	1.925 ± 0.886	2.573 ± 1.069
Cu	0.00	0.00	0.00	0.00	0.00

Appendix V: Mean Concentrations of Lead, Manganese and Copper (Mg/L ± S.E.M) in Treated Water Samples

(DRY SEASON: FEB – APRIL 2006)

Metal	Sampling Zones					
	T_A	T_B	T_C	T_D	T_E	T_F
Pb	0.00	0.00	0.00	0.00	0.00	0.00
Mn	1.76 ± 0.89	3.526 ± 0.848	1.59 ± 1.37	0.02 ± 0.02	0.192 ± 0.10	0.83 ± 0.78
Cu	0.00	0.00	0.00	0.00	0.00	0.00

(*RAINY SEASON: AUGUST – OCTOBER 2006*)

Metal	Sampling Zones					
	T_A	T_B	T_C	T_D	T_E	T_F
Pb	0.00	0.00	0.00	0.00	0.00	0.00
Mn	2.809 ± 0.308	0.01 ± 0.01	0.01 ± 0.01	0.00	0.24 ± 0.21	1.18 ± 1.07
Cu	0.00	0.00	0.00	0.00	0.00	0.00

Appendix VI: Concentrations of Lead in Vegetable Samples

Sample site	Dry season	Rainy season
A	(T) 0.4 ± 0.01 (L) 0.4 ± 0.01	(T) 22.20 ± 0.4 (L) 22.6 ± 0.07
B	(T) 0.8 ± 0.003 (L) 0.8 ± 0.003	(T) 22.6 ± 0.07 (L) 22.6 ± 0.07
C	(T) 0.4 ± 0.01 (L) 0.4 ± 0.01	(T) 0.38 ± 0.01 (L) 0.38 ± 0.01
D	(L) 0.4 ± 0.01	(T) 0.38 ± 0.01 (L) 0.38 ± 0.01
E	-	-

T = Tomatoes; L = Lettuce

Appendix VII: Concentrations of Manganese in Vegetable Samples

Sample site	Dry season	Rainy season
A	(T) 0.1 ± 0.003 (L) 0.1 ± 0.003	(T) 0.13 ± 0.007 (L) 0.13 ± 0.007
B	(T) 0.1 ± 0.003 (L) 0.3 ± 0.006	(T) 0.13 ± 0.007 (L) 0.21 ± 0.003
C	(T) 0.1 ± 0.003 (L) 0.3 ± 0.006	(T) 0.13 ± 0.007 (L) 0.21 ± 0.003
D	(L) 0.1 ± 0.003	(T) 0.13 ± 0.007 (L) 0.13 ± 0.007
E	-	-

T = Tomatoes; L = Lettuce

Appendix VIII: Concentrations of Copper in Vegetable Samples

Sample site	Dry season	Rainy season
A	(T) 0.00 (L) 0.00	(T) 0.00 (L) 0.00
B	(T) 0.00 (L) 0.00	(T) 0.00 (L) 0.00
C	(T) 0.00 (L) 0.00	(T) 0.00 (L) 0.00
D	(L) 0.00	(T) 9.5 $\pm$ 0.12 (L) 9.7 $\pm$ 0.12
E	-	-

T = Tomatoes; L = Lettuce