

**ASSESSMENT AND DISTRIBUTION OF TRACE ELEMENTS IN SOILS AND
VEGETABLES CULTIVATED ALONG THE BANK OF RIVER NGADDA AND
ALAU DAM IN MAIDUGURI, BORNO STATE**

BY

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P15SCP9009

DEPARTMENT OF PHYSICS

AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA

JULY, 2016

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DECLARATION

I declare that the work in this project report entitled **Assessment and Distribution of Trace Elements in Soils and Vegetables Cultivated Along the Bank of River Ngadda and Alau Dam in Maiduguri, Borno State** was carried out by me in the Department of Physics Ahmadu Bello University, Zaria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this project report was previously presented for another degree or diploma at this or any other Institution

BUKAR, Paul Hena

CERTIFICATION

This project report entitled **ASSESSMENT AND DISTRIBUTION OF TRACE ELEMENTS IN SOILS AND VEGETABLES CULTIVATED ALONG THE BANK OF RIVER NGADDA AND ALAU DAM IN MAIDUGURI, BORNO STATE**, by **PAUL HENA BUKAR** meets the regulation governing the award of Doctor of Philosophy of Science Degree in Physics of the Ahmadu Bello University and is approved for the contribution to knowledge and literary presentation

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ABSTRACT

The levels of trace elements and their distribution in Soil, sediments water and vegetables namely Amaranthus (*Amaranthus tricolor*), Guinea Sorrel (*Hibiscus sabdariffa*), Okro (*Abelmechus esculentum*), Lettuce (*Lactuca sativa*), Tomato (*lycopersicon esculentum*), Ben Oil (*Moringa oleifera*) and Water leaf (*Talinum tringulare*) samples collected from farmlands along the banks of river Ngadda and Alau dam was determined using the complimentary techniques of Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectrophotometry (AAS). The aim of the work was to find the extent to which the above named vegetables cultivated during dry season otherwise referred to as fadama farming along the bank of river Ngadda and Alau Dam through irrigation had bio-accumulated trace elements, the possible sources of these metal toxicants, to establish whether the soils, sediments and water of river Ngadda and Alau dam used in irrigating the vegetables were accumulated with metal toxicants and to determine the correlation between the metals toxicants in soil and sediments samples viz a viz the vegetables collected from the different sites. Pearson correlation analysis of soil samples showed that forty five elements had positive correlation coefficients ($r \geq 0.5$) at significant difference value $p \leq 0.05$ and five had ($r \geq - 0.5$) at $p \leq 0.05$. For sediments samples ninety six had ($r \geq 0.5$) at $p \leq 0.05$ and nine elements had ($r \geq - 0.5$) at $p \leq 0.05$. Assessment of the concentrations of the metal pollutants in vegetable samples showed that those elements that had high concentrations in soil samples had corresponding high concentration in the vegetable samples collected at the same site. For example concentration of Aluminum in soil sample at site one (S1) was 34470 ± 241 ppm and the concentration of Aluminum in Amaranthus at site one (A1) was 1023 ± 426 ppm; Fe in soil sample at site one was (S1)

was 10420 ± 240 ppm, Fe in Amaranthus at site one (A1) was 640 ± 54 ppm; Zn in soil (S1) was 54 ± 3 ppm, Fe in amaranthus (A1) was 22 ± 2 ppm. At site two, concentration of Zn in soil samples (S2) was 24 ± 3 ppm Zn in amaranthus samples at site two (A2) was 36 ± 3 ppm. At site three Fe in soil samples (S3) was 9982 ± 294 ppm, Fe in amaranthis samples from site three (A3) 558 ± 37 ppm, Zn in soil samples at site three (S3) was 46 ± 5 ppm, Zn in amaranthus samples (A3) was 85 ± 4 ppm;. At site four the concentration of Fe in soil samples (S4) was 9529 ± 229 ppm while Fe concentration in amaranthus samples at site four (A4) was 655 ± 40 , while Cr in soil samples at site four (S4) was 29 ± 3 ppm, Cr concentration in amaranthus samples at site four (A4) was 88 ± 21 ppm. This suggests that there was a linear correlation between the concentrations of elements in the soil and some of the vegetables cultivated on the soil. The cluster analysis using WARD's procedure on soil data produced a dendrogram consisting of two clusters S1, S4, S5, S10, S11, and S14 with similarity at 96.5%; and S2, S6, S8, S9, S12, S13, and S0 with similarity at 90.86% with an outlier S3 while that of sediment produced two clusters SS1, SS4, SS5, SS6, and SS9 with similarity at 89.07%; and SS3, and SS10, with similarity at 70.54% with SS2 as outlier. For water samples data the cluster dendrogram produced three clusters H1, H2, H3, H9 and H13 with similarity at 96.2%; H4, H10, H11 and H12, with similarity at 78.6% and H5, H6, H7 and H8.with similarity at 78.5%. The trace elements Co, Cr, Mn, Zn and Fe in most of the vegetables samples investigated had bio-accumulated concentrations above the WHO/FAO maximum permissible limits (MPL) and the elements Cd, Co, Cr, Fe, Ni and Pb in water samples were above the recommended safe limit for continuous irrigation purposes. Thus the water required elaborate purification for portability and is unsafe for continuous irrigation purposes

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LIST OF ABBREVIATIONS AND ACRONYMS

- AAS: Atomic Absorption Spectrometry
- ANOVA: Analysis of Variance
- BDL: Below Detection Limit
- CA: Cluster Analysis
- CF; Contamination Factor
- EEC: European Economic Community
- EPA: Environment Protection Agency
- eV: Electron Volt
- FAO: Food and Agricultural Organization
- GPS: Global Positioning System
- HPGe: High purity Germanium detector
- HREEs: Heavy Rare Earth Elements
- IAEA: International Atomic Energy Agency
- i.e: that is
- INAA: Instrumental Neutron Activation Analysis
- LREEs; Light Rare Earth Elements
- MAC: Maximum Allowable Concentration
- MCA: Multi Channel Analyzer
- MNSR; Miniature Neutron Source Reactor
- MPL: Maximum Permissible Limit
- NAA: Neutron Activation Analysis
- NaI(Tl): Thallium-activated Sodium iodide detector

NIRR-1: Nigeria Research Reactor-1

NPS: Non-Point Source

NIST: National Institute of Technology

PGNAA: Prompt Gamma Neutron Activation Analysis

PS: Point Source

ppm: parts per million

REEs: Rare Earth Elements

SRM: Standard Reference Material

USEPA: United State Environmental Protection Agency

WHO: World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study.

The environment basically consists of land, water, and air and these three are in constant interaction with each other. In recent years attention has been focused on the contamination of the environment because of the negative consequences being imposed, on living organism on regular basis, by it. Pollution of the environment is the introduction by man or nature, either directly or indirectly of substances or energy form into the environment resulting in hazard to human health, harm to living resources and ecosystem, damage to amenities or interferences with other legitimate users of the environment (EEC,1997). Heavy metals are elements that have a relative high density 5.0 and above) and are toxic or poisonous if ingested even at low concentration. Heavy metal pollution refers to when the quantities of these elements in a medium are higher than the maximum allowable concentrations (MAC) and this is potentially harmful to biological organisms at such a location.

In Nigeria environmental issues tops agenda at both national and international levels and this has occurred as a result of environmental degradation, deterioration and underdevelopment (Ekweozor and Agbozu, 2001). In advanced countries environmental monitoring agencies are more effective and environmental laws are strictly followed hence environmental quality monitoring is compulsory, for example, monitoring of the quality of water resources is done on a regular basis (Robson and Neal, 1997; USEPA, 2000 Neal and Robson, 2000). In developing countries, Nigeria inclusive, the case is quite the

opposite, environmental laws are rarely observed and industrial growth and its associated environmental problem such as soil, plant and air contamination is fast increasing (Fakayode and Onianwa, 2002, Fakayode, 2005)..

The contamination of the environment with heavy metals is one of the challenges that constitute Nigeria's environmental problem. Heavy metals are the major pollutants of the environment because these metals are indestructible and most of them have toxic effects on living organism when permissible concentration levels are exceeded (Mmolawa *et al*, 2011). The release of heavy metals into the environment is basically by two methods, anthropogenic (i.e. man-made) and natural phenomenon.

The natural activities that release heavy metals into the environment include;

- (i) Weathering, when rocks undergo weathering, they form part of the soil and also cation of heavy metals may find their way into surface and ground water hence causing water pollution.(Al-Juboury, 2009)
- (ii) Wind, where windstorm is predominant, heavy metals can be transported in a particulate form from one place to another therefore aiding in the spread of these heavy metal pollutants (Lomniczi *et al*, 2007)

The anthropogenic (man-made) activities include;

- (i) Industrial and agricultural processes: With increase agricultural and industrial activities, most of the water sources are becoming contaminated (Khares and Singh, 2002), and the topsoil will have some metals introduced in it.

- (ii) Vehicular exhaust emission; metals from vehicle emissions are released into the atmosphere and are subsequently deposited into the surrounding soil, vegetation, and water bodies or can be leached from the road sides during rains to surrounding water bodies causing fresh water to be polluted (Mmolawa *et al*, 2011)
- (iii) Waste disposal and application of science and technology; The indiscriminate dumping of waste is another source of heavy metals in the environment and the application of science and technology in an attempt to explore and exploit natural resources lead to the creation of waste that are disposed into the environment which may introduce heavy metals into the environment (Sykes, 1997)

As a matter of fact as the population of the world increases and its economies continue to grow, all the three components of the environment, namely land, water, and air are affected in one way or the other depending on the activities and the type of waste generated and disposed off in the environment. The increase in industrial and population growth at large scale causes a corresponding increase in waste generation and hence increase challenges in the waste management, thus the fresh, clean, and safe natural environment before is now polluted and pose health hazard to, plants, animals and human beings.

The problem of waste management always begin with increasing in waste generation due to growth of cities and continuous urban development which pose a major environmental hazard because of the difficulties in disposal (Asonye *et al*, 2007). The generation of solid waste has become an increasing environmental problem everywhere in

the world, particularly in the developing countries. The fast expansion of urban, agricultural and industrial activities spurred by rapid population growth and the change in consumer habits has produced vast amount of solid waste. This has been compounded with the absence of properly designed solid waste disposal facilities and dumpsites.

Reports showed that industrial and domestic effluents constitute largest sources of heavy metals which contribute to the steady increasing metallic contaminant in aquatic and terrestrial environment in most part of the world (Jibrin and Adewuyi, 2008; Ayodele, *et al*, 1991, Oshodi and Ipinmoroti, 1990). It has been observed that many pollutants are continuously discharged into the soils on a daily basis through land waste disposal, input from the atmosphere, metals from vehicular exhaust emissions and irrigation by municipal waste water (Uwah *et al*, 2009).

Soil, water and sediments are the major sinks for heavy metals, therefore landfills and waste dumpsites which characterize urban settlements are among the major contributors in polluting river and stream around them. Rain washout accompanied by leaching channeled these metals substances into the rivers or stream. Studies in the distribution of heavy metals in water bodies reveal that the levels of heavy metals in the bottom sediments are usually higher than in the water columns which show that sediments act as a sink for heavy metal (Atta *et al*, 1997, Adeniyi and Yusuf, 2007, Chyne-Eng *et al*, 1987, Olowu *et al*, 2010), sediments therefore are known to form the major repository of heavy metals in aquatic system because both allochthonous and autochthonous influences could also make a concentration of heavy metals in the water high enough to be of ecological significances

(Atta *et al*, 1997, Kakulu and Osibanjo, 1998, Benedict *et al*, 1991, Adeniyi and Yusuf, 2007 and Olowu, *et al*, 2010).

It has been observed that heavy metal contamination of stream and river water is a worldwide environmental problem as trace amount of heavy metals are always present in fresh waters from the weathering of rocks and soils (Muwanga, 1997, Babel and Opiso, 2007, Samarghandi *et al*, 2007; Igwe *et al*, 2008,). But the occurrences of enhanced concentration of heavy metals especially in sediments may be an indication of human induced perturbation rather than natural environment through geological weathering (Davies *et al*, 1991; Binning and Baird, 2001; Eja *et al*, 2003).

The specific problem associated with heavy metals in the environment is their accumulation through food chain and persisted in nature (Dimari *et al*, 2008). Recently water quality monitoring has become a matter of concern in stream and river water system affected by careless disposal of urban effluents, runoff, atmospheric deposition, and domestic and industrial effluent discharges which are the major sources of aquatic pollution (Wasswa, 1997, Linnik and Zubenko, 2000, Campbell, 2001; Lwangu *et al*, 2003 and Lominczi *et al*, 2007, Sekabira *et al*, 2010)

Maiduguri is the capital of Borno State in North Eastern Nigeria and river Ngadda around which the study is centered transcends the state capital dividing the town into almost two equal parts thus having three bridges across it and linking the two parts of the city, namely Gwange Ward bridge, Lagos Street bridge and Custom bridge. There is therefore a lot of vehicular movement on the named bridges on a daily basis which means a lot of exhaust emissions occur on and around the bridges along the road. These in turn end

up in the river during rain or windstorm. In addition to these sources, Maiduguri town being a state capital has some activities that generate solid waste from domestic, public institutions, and small scale industries, such activities, which led to waste generations, are assumed to occur on a daily basis. This waste may not be properly disposed, for example there are many auto mechanic maintenance centers, metal welding activities and so on, having their workshops distributed all over the metropolis at strategic places whereby a lot of their activities may release heavy metals into the environment e.g car accumulator battery services and metal works in form of car body maintenance, metal weldings which are sources of disposing heavy metals into the environment and can be washed into the river during rainy season or transported by wind in particulate form into the river as windstorm is a characteristic of such a desert environment and these metals can accumulate in the sediment of the river overtime.

Some public institutions like the State Specialist Hospital and the Central Monday Market are situated just some few meters away from the river hence wastes generated from these places may be dumped into the drainages which could be easily washed into the river or can be eroded from the surface into the river during rainy season. The University of Maiduguri Teaching Hospital which is situated along Bama road may have some of its drainages washed into river Ngadda around Lagos Street Bridge which may be transported to other points down the stream. The custom market is situated just by the bank of river Ngadda, and it is located by the custom bridge and bounded on one side by the bank of the river. The proximity will suggest that substantial amount of the waste generated in the market can easily be disposed or washed into the river or waste dumpsites leached during

rainy season into the river or the wind blowing it into the river all these contribute in polluting the river. One of the study areas which is Jere where a lot of irrigation farming takes place is located some few meters after the custom market downside of river Ngadda.

There are also the processes of reclaiming part of the river as land especially between Custom bridge and Gwange Bridge as heaps of solid waste dumps are conspicuously seen dumped by side of the river of which part of it may be washed into the river during rainy season. Some of the people living near the river may also dispose some of their domestic waste directly or indirectly into the river since environmental laws are not stringently enforced in most developing countries. These nefarious activities are assumed to have adverse effect on the quality of water and sediment of the river since these wastes from the metropolis coupled with the city storm water is known to contain toxic heavy metals which can cause pollution (Cheng *et al*, 2005; Singh *et al*, 2004)

The river Ngadda has a lot of irrigation farming activities taking place along its bank especially from custom bridge beside the custom market down to Jere area where the river has just come out of the municipal council and the water is suspected to have received point source (PS) and non-point source (NPS) pollution from the municipal. This could have polluted the water of the river which was used in irrigating the soil and taken up by the plant and hence polluting the crop themselves as sediments near urban areas commonly contain high levels of contaminants (Cook and Wells, 1996, Lamberson *et al*, 1992) which constitute a major environmental problem faced by many anthropogenically impacted aquatic environments (Shuhaimi, 2008)

Pollution of plants is of two major effects, firstly, pollutants may have direct or indirect phytotoxic impacts on the plants themselves leading to decline in crop yields and threatening our food supply, secondly the plants may act as a vehicle for transferring pollutants into food chain (Uwah *et al*, 2009), which human population depend on. Food and water are known to be the main sources of our essential metals and these are also the medium through which we are exposed to various toxic metals. Studies have shown that heavy metals are easily accumulated in the edible parts of leafy vegetables as compared to grains or fruits crops (Mapanda *et al*, 2005, Arora Monu, *et al*, 2008)

Therefore, this work which intends to investigate the extent to which *Amaranthus* (*Amaranthus tricolor*), Guinea Sorrel (*Hibiscus sabdariffa*), Okro (*Abelmechus esculentum*), Lettuce (*Lactuca sativa*), Tomato (*Lycopersicum esculentum*), Ben oil (*Moringa oleifera*), and Water leaf (*Talinum triangulare*) cultivated during dry season and sustained with irrigation water from river Ngadda and Alau Dam are bio-accumulated with metal toxicants is of significance as it will provide useful information to the public living in that area about the status of the vegetables being consumed which were cultivated through irrigation during the dry seasons along the bank of river Ngada and Alau Dam with a view of assessing the health implication associated with the consumption of these vegetables since many people in the metropolis utilized the vegetables supplied from these farming areas as being observed by the number people who patronizes these vegetables in the market located at Custom Area.

The study will also correlate the levels of these metal toxicants in the vegetables with that in the soil of the farm lands so as to ascertain the quality of the soil and water viz a viz

the quality of the vegetables cultivated in the area of study. This will give us an idea of the possibility of the risk and possible health effects that could be associated with the consumption of these vegetables by the people due to the accumulation of toxic metals in their body from continuous consumption of these vegetables and also the contribution of the soil if the soils are contaminated with metal toxicants. This is supported by studies carried out by Nirmal Kumal, et al in 2007 who observed that many people are at risk of adverse health effects from consuming common market vegetables cultivated in contaminated soil of which often the condition of the soil is unknown or undocumented therefore exposure to toxic level can occur.

1.2 Statement of Research Problem.

Over a long period, heavy metals along with other metals and minerals have been released to the environment from industrial activities, indiscriminate waste disposal, vehicle exhaust emission and agricultural processes. Water has been observed to be the major sink for these sources of pollutants. The level of heavy metals in aquatic environment has been of much concern during the last decade due to the adverse effects of some metals on living organism in food chain and human health (Huong *et al*, 2007).. Also in the study carried out by (Yousel *et al*, 1994) indicated that the transport of metals through sediment is a very slow process since the sediment possesses high metal retaining capacity, therefore analysis of bottom sediments has been used to determine the extent and source of trace metals and other contaminants

It has also been observed that the migration of people in the last few decades from rural areas to the urban areas in the country due to uneven distribution of social amenities has led to an increase in urban population and the subsequent environmental adverse effects due to increase in the waste generated. In Maiduguri, the Borno State capital, the visible heaps of solid waste dump observed by the side of river Ngadda due to people's quest to reclaim part of the river as land for infrastructural development is an indication of increase in population. The dumping of the municipal wastes in the river or by the river bank as landfill or disposal site is believed to have some negative effects on the quality of water and sediments of river Ngadda. Now since the river passes through the Maiduguri town, during rainy season some of these wastes are washed into the stream by erosion and during dry season, wind blow some of the particles into the river. Another important factor is the windstorm that precedes the commencement of the rainy season. This is so strong that it carries along with it so much waste particles of which a lot of them end up in the river.

It is also interesting to know that river Ngadda is one of the main sources of water used by the populace apart from the pipe borne water supplied by Alau Dam and some boreholes owned by a few well to do individuals. The proximity of the people to the river encourages a lot of irrigation farming along the river bank especially around the Shukwari axis of Jere Local Government Area north of Maiduguri Municipal Area. Also the long period of dry season usually experienced by that part of Nigeria makes irrigation farming very lucrative as it serves as a means of economic empowerment. The food security policy

of the government also encourages a lot of dry season farming which are mainly vegetables cultivation by using water from river Ngadda through irrigation.

It is therefore paramount to assess the composition and the distribution of metal toxicants in the soil used in cultivating vegetables sustained via irrigation with water from river Ngadda and Alau Dam. In this regard, the research work intends to investigate the concentration levels of trace elements in some vegetables that are cultivated on farm lands along the bank of river Ngadda and Alau Dam through irrigation with the water from river Ngadda and Alau Dam and compare them with set standard as the World Health Organization (WHO) has set the acceptable limit of these metals in different food forms.

Therefore this research work will attempt to answer the following statements of questions

- 1 To what levels are the soils, sediments and water of river Ngadda and Alau Dam used in irrigating vegetables accumulated with metals toxicants?
- 2 To what extent are the vegetables cultivated during dry season along the bank of river Ngada and Alau Dam through irrigation been bio-accumulated with metal toxicants?
- 3 Are the metal toxicants in vegetables cultivated with water from river Ngada and Alau Dam during dry season has their major sources from the municipal activities?
- 4 Is there some degree of correlation between the level of metals toxicants in the vegetables and the soil used in cultivating these vegetables?

1.3 Justification.

It is a known fact that as socio-economic activities increases in any society, there is the tendency of that environment to be polluted with heavy metals. There are thirty five metals that concern us because of occupational or residential exposure; twenty three of these are heavy metals (Nirmal Kumar *et al*, 2007). Nigeria has over the years experienced a rapid rate of urbanization due to uneven distribution of social amenities. People moved into the cities from the rural areas in search of the chance of a better life (Adebayo *et al*, 2007) also in Nigeria there are few sanitary landfill sites. The waste dump sites are usually haphazardly located without careful consideration of environment and public health (Agunwamba, 2007). Recently, heavy metal concentration has received much attention with regard to accumulation in soils, uptake by plants and contamination of water (Samali and Shinggu, 2007). Pollution of plants is of concern for two major reasons, firstly pollutants may have direct or indirect phytotoxic impact on the plants themselves, leading to a decline in crop yield and threatening our food supplies and secondly, the plants may act as vehicle for transferring metal pollutant into the food chain. For example Cadmium is readily accumulated in plants via metal uptake mechanism (absorption) and may get to levels which are adverse to the plants themselves, consequently posing a significant threat to animals and humans that consume the plants (Radojevic and Bashkin, 1999, Uwah *et al*, 2009). The main sources of metal pollutants to vegetable crops are their growth media (soil, air, nutrients solution) from which these metal toxicants are taken up by the roots or foliage (Lokeshwari, 2006)

In most developing countries Nigeria inclusive, the use of polluted water in the immediate surroundings of big cities for irrigation system to sustain growth of vegetables

is a common practice. Although this water is considered to be a rich source of organic matter and plants nutrients, it also contain sufficient amount of soluble salts and toxicants like Fe, Mn, Cu, Zn, Pb, Ni, Sn, Hg, Cr, As, Al.,. When such water is used for irrigation of crops and sustained for a long period, these toxicants may accumulate in soil and be toxic to the plants and also cause deterioration of the soil (Kirkhan, 1983). Studies also reveal that the presence of toxic heavy metals like Fe, Pb, and Hg reduces soil fertility and agricultural output (Lokhande and Kelkar, 1999); and that treated sewage water also contain variable amount of heavy metals such as Pb, Ni, Cd, Cu, Hg, Zn, and Cr (Sharma *et al*, 2004), which have the potential to contaminate crops growing under such irrigation ecosystem.

Heavy metals in aquatic environment are of major concern because of their toxicity and threat to plant and animal life (Dimari *et al*, 2008). Many researchers have shown that some common vegetables are capable of accumulating high levels of metals from the soil (Garcia *et al*, 1981, Khan and Frankland, 1983, Xiong 1998, Cobb *et al*, 2001). Distribution of heavy metals in plant body depends upon availability and concentration of as well as particular plant species and its population (Punz and Seighardt, 1993). Some of the metal pollutants in the waste are absorbed into the surface of fine grained particles which settle and form polluted sediments at the bottom of waters. The polluted sediments pose recontamination of overlying water through the release of pollutant from the sediments. Several studies have reported the accumulation of heavy metals in the tissues of aquatic biota from contaminated area (Asuquo *et al*, 2004).

It is worthy to note that these heavy metals accumulate in the river and the soil unnoticed unlike the build up of solid waste from the municipal dumpsites that are conspicuously seen being piled up therefore, to account for the build up of these toxicants in the water, sediment and the soil, an experimental investigation should be undertaken to ascertain the occurrence and abundance, of these metal pollutants and the possible health effects these pollutants pose to man as a component of the pollution web. In this study it is believed that long-term rain-washout and continuous erosion from the roadsides, municipal dumpsites, auto mechanic centers, market places, and medical institutions situated all over the town may have led to accumulation of toxic metals in the water and sediments of river Ngadda because of its strategic position in the state capital, therefore the use of the water for irrigation purposes may contribute in the accumulation of heavy metals in the soil and therefore been transferred to the plants in the course of absorption of nutrients. This work intends to determine the concentration levels of some trace metals in vegetables that are obtained from farmlands at various sites along the bank of river Nggada and Alau Dam which are cultivated through irrigation with the water from river Ngadda and Alau Dam and to investigate the source of these pollutants in the vegetables if discovered to have some and to compare the pollutants concentration in vegetables cultivated along river Ngadda with the ones cultivated around Alau Dam where the water has not transcends the municipal council and get mixed up with city storm and runoff from the Municipal dumpsites. The method to be employed for the analysis which is the nuclear analytical technique of instrumental neutron activation analysis (INAA) is adequate for the purpose of this investigation because:-

- (i) The process is non-destructive as the sample is not changed in any manner by chemical manipulation or the introduction of any material prior to irradiation
- (ii) INAA give an accurate results for large, bulk samples without having to dissolve or digest the sample
- (iii) It measures the total amount of an element in a material without regard to chemical or physical form (liquids, solids, suspensions, slurries or gases).

The technique also has some advantages over other chemical analysis among which include the followings: -

- Since neutrons activate the nucleus of an atom and do not interact with the electron shell, the method detects the total elemental content, regardless of oxidation state, chemical form or physical location and also since neutrons have no charge it will pass through most materials without difficulty therefore, the middle of the sample becomes just as activated as the outer surface.
- The sample is not permanently damaged by NAA; therefore, the sample can be saved and even be subjected to further analysis at a later time.
- NAA is a multi-element analytical technique in that many elements can be analyzed simultaneously in a given sample.
- In this study, the element of interest can be adequately measured by NAA

Also from literature available, this technique has not been employed in the study area for the same purpose and it is one of the reliable means for environmental studies.

Also since, the build up of heavy metals in the environment is a gradual process; there is the need for continuous investigation from time to time. Based on the above mentioned reasons, this research work which intends to investigate the accumulation of heavy and trace metals in vegetables that are grown along the bank of river Ngadda and Alau Dam by irrigation is worth doing. The results will also be used as source of information to the people of the possible health implications or otherwise that could be associated with the consumption of fresh vegetables cultivated in the study area.

1.4 Aim and Objectives.

Vegetables are popular in human diet for the vitamins and the minerals they supply (Oladele and Aborisade, 2009). The cultivation of vegetables especially during dry season is a worthwhile venture because in addition to being source of food, it serves as source of income. Because of the above reason the type of water to be used for the irrigation is always of less concern to the farmers, therefore, all sorts of available water is usually utilized. This sometimes makes it possible to use contaminated water which may contain heavy metals. These heavy metals can be absorbed by the plants and if the plants or their parts are consumed by human beings, some of these metals are ingested and if accumulated to toxic levels can cause damage to some of the organs like the nervous system and the kidney and other metabolic disruption (Mihael *et al*, 2007). Therefore, the need to assess the levels of heavy metals in vegetables viz a viz their cultivation soil and water bodies used for their irrigation is imperative so as to ascertain their contamination level and if possible avoid their utilization in order to prevent the transfer of their contaminants to

human being through food chain or direct ingestion and hence prevent their accumulation and consequently their effect on human being

This work therefore is aimed at assessing the level of bio-accumulation of metal pollutants in some vegetables cultivated during dry season with water from river Ngadda and Alau Dam with the following objectives:-

- (i) Assess the extent of metal accumulation in the soil used for the cultivation of the vegetables.
- (ii) Determine the extent to which the water and sediments of river Ngadda and Alau Dam are polluted with metal toxicants.
- (iii) Determine the occurrence and level of metal contaminants in the vegetables *Amaranthus* (*Amaranthus tricolor*), Guinea Sorrel (*Hibiscus sabdariffa*), Okro (*Abelmoschus esculentum*), Lettuce (*Lactuca sativa*), Tomato (*Lycopersicon esculentum*) and Ben oil (*Moringa oleifera*), Water leaf (*Talinum triangulare*) that were grown along the bank of river Ngadda and Alau Dam through irrigation.
- (iv) Determine the extent of possible threat to human health those metal toxicants in the vegetables pose to human being as compared to the standard set by World Health Organization (WHO).
- (v) Provide additional value of information through the use of INAA in characterization of the study area.

The results obtained from the investigation of the levels of metal toxicants in the soils and the sediments from river Ngadda and Alau Dam will be correlated to determine the degree

of their relationship and the possible sources of these metal toxicants. Also the suitability or otherwise of the vegetables for human consumption will be established by comparing the values for the levels of the metal toxicants in the vegetables and that of the World Health Organization (WHO). This will help to provide information to the public of the suitability of the consumption of these vegetables or otherwise as most of the vegetables consumed during dry season by the populace in the metropolis come from the farms of the study area.

1.5. Scope of the Study.

The study is limited to samples obtained from farm lands around Alau Dam, river Ngadda and Gongulon farming areas with emphasis to Shukwari area of Jere Local Government Area of Borno State, Nigeria. The study is to mainly investigate the levels of heavy metals bio-accumulation by some vegetables that are grown on farmlands along the bank of river Ngadda, and Alau Dam through irrigation during dry season. The sediments of the river, the soil on which the vegetables are cultivated and the water used for the irrigation will also be investigated to determine their extent of pollution with metal toxicants. The study is also limited to application of INAA and AAS technique for analysis of the metal pollutants. Other techniques will not be employed for the study due to reasons earlier mentioned

1.6 Description of Sampling Locations.

Maiduguri is the capital of Borno State and a commercial nerve center in the Northeastern region of northern Nigeria. It lies between latitude $11^{\circ} 15' N$ to $11^{\circ} 52' N$ and longitude $13^{\circ} 05' E$ to $13^{\circ} 14' E$ at an altitude of 345m above sea level. This area is known

for its dryness, with Sudan type of climate, Savanna or Tropical grassland vegetation, light annual rainfall of about 864mm (34inches) and the temperature ranging from (22°C – 31°C). The minimum occur during harmmattan, with mean of the daily maximum exceeding 40°C between March and May between the onset of the rain in June (Adeleke and Leong, 1978).

River Ngadda originates from rivers Yedzaram and Gadambole which met at a conluent at Sambisa both in Nigeria and flows as river Ngadda into Alau Dam and stretches down across Maiduguri Metropolis then empties into Lake Chad. The river Ngadda flows from Alau Dam down through the Maiduguri Municipal Council to Shukwari in Jere local government area of Borno State. In this area vegetables are cultivated through irrigation system using water from the river. The water at Shukwari is suspected to have mixed up with waste water from the Municipal Council and may be contaminated with different pollutants. The Shukwari area is also believed to be susceptible to accumulation of pollutant as it is the area that the river Ngadda has just come out of the Maiduguri Municipal Council downstream in the direction of the flow of the river. The area of study is located on sheet 90 North West on scale 1:50,000 Nigerian survey topographical maps.

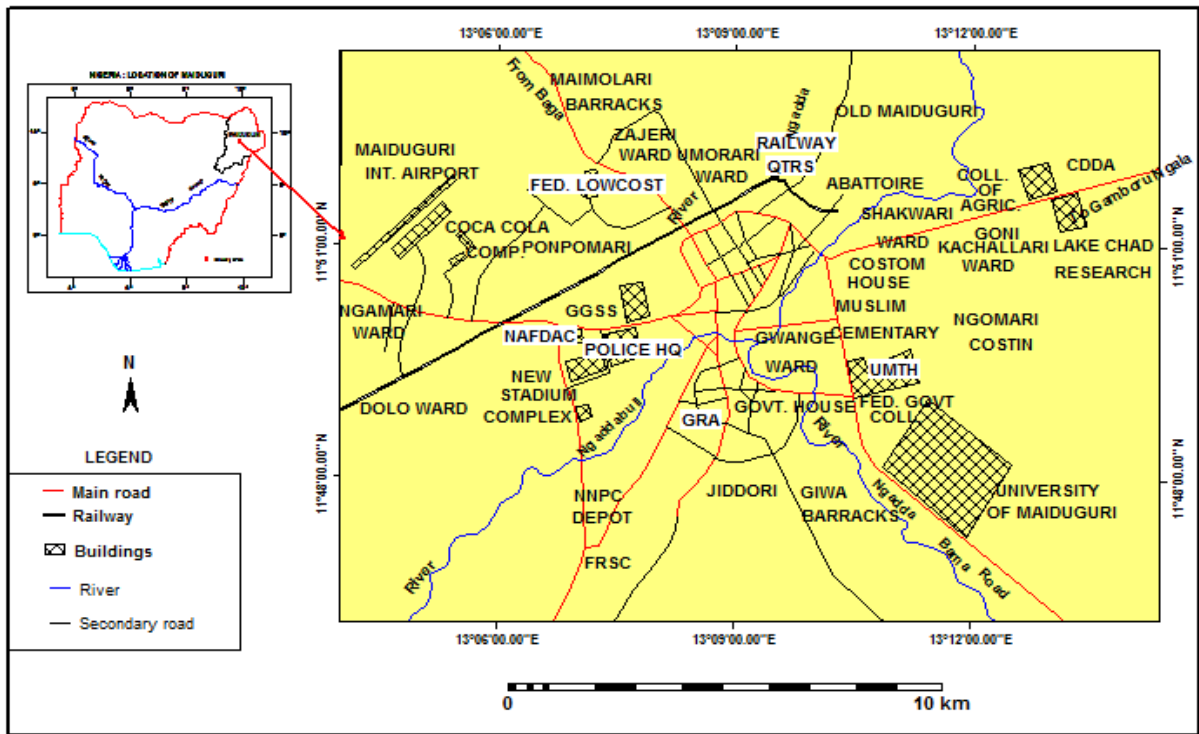


FIGURE 1 : MAIDUGURI TOWNSHIP MAP

Source : Adapted from Ministry of Land and Survey, Borno State, 2012

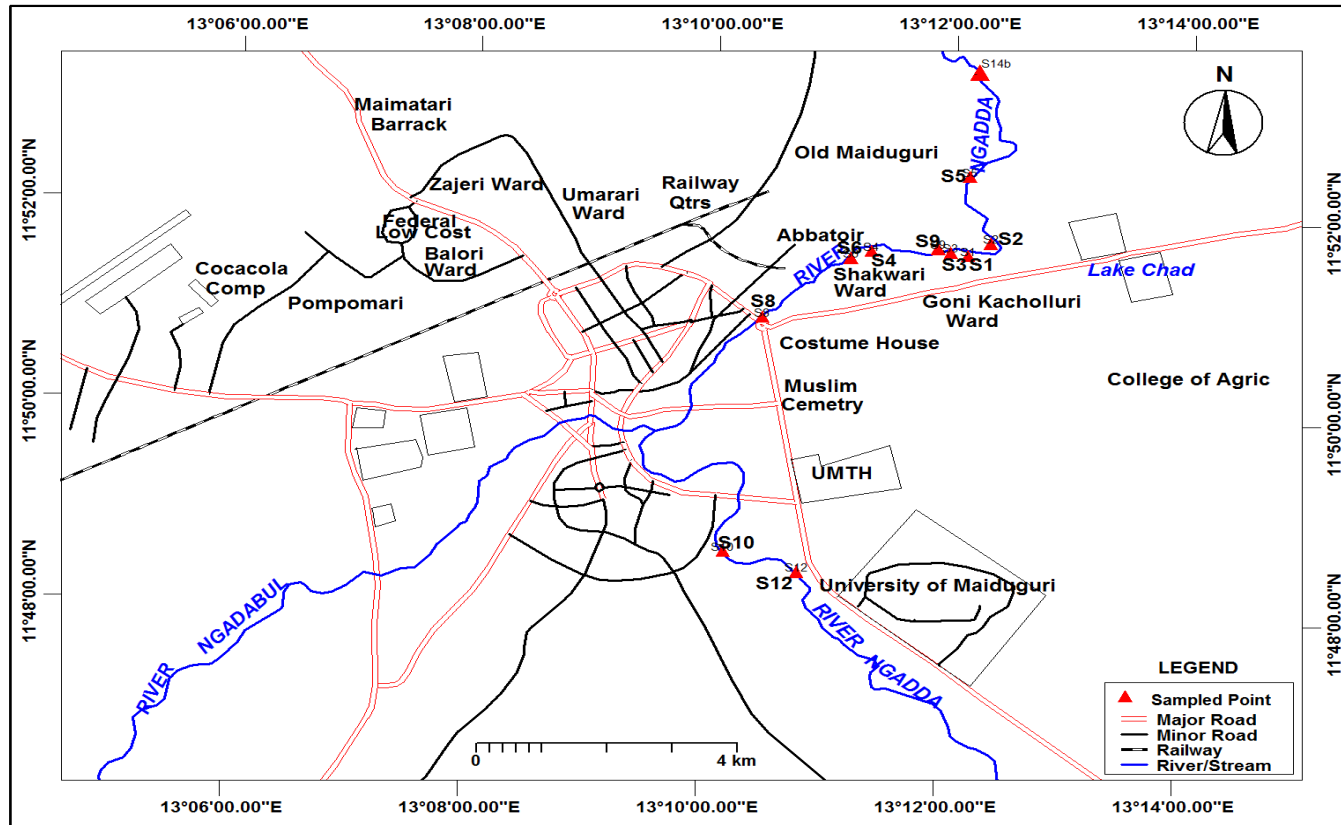


FIG. 1b: MAIDUGURI TOWNSHIP MAP SHOWING THE SAMPLING POINTS

Source: Adapted and modified from Maiduguri Township map

CHAPTER TWO

LITERATURE REVIEW

2.1.1 An Overview of Environmental Pollution with Metals

An environment can be referred to as polluted when it is carrying constituent above its natural carrying capacity i.e it is impaired by either anthropogenic or natural contaminants and either does not support a human use like serving as drinking water and/or undergoes a marked shift in its ability to support its constituent biotic communities (Asonye *et al*, 2007). An environment usually becomes polluted due to human (anthropogenic) activities or natural activities. One of the anthropogenic activities that help in impairing the environment is the creation of waste that is disposed into the environment and this situation is compounded by the growth of cities and the massing of people and their industrial and disposal needs (Asonye *et al*, 2007; Dan'azumi and Bichi, 2010). Other human activities that may result to environmental pollution include agriculture, irrigation, urbanization, landfills, mining, fire, oil exploration, and industrialization. The natural phenomena that aid in polluting the environment include volcanoes; algal blooms, windstorms, earthquakes and rain washout. All these cause major changes in soil and water quality and the ecological status of the environment.

The sources of surface water pollution are generally grouped into two categories based on their origin; Point Source (PS) pollution and Non-point source (NPS) pollution. Point source (PS) pollution referred to contamination that enters a waterway as discrete conveyance such as pipe or ditch. Examples of such source in this category include discharge from a sewage treatment plant, a factory or a city storm drain (Poppe and Hurst,

1997). NPS pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often a cumulative effect of small amounts of contaminants gathered from a huge area. Such as contaminated storm water washed off from parking lots, roads, and highways, called urban runoff. However, if this runoff is channeled into storm drain systems and discharge through pipes to local surface water it is then a point source.

2.1.2. Some Major Sources of Environmental Pollution with Metals.

Metals have many sources from which they can be deposited on the soil or flow into the water body. These sources can be grouped according to their origin as:-

- (i) Natural occurrences: metals are found throughout the earth in rocks, soil and are introduced into the environment through natural processes (weathering, erosion, windstorm, and rain washout).
- (ii) Industrial sources: industrial processes particularly that concern with the mining and processing of metal ores, the finishing of and plating of metals and the manufacture of metal objects. Also metallic compounds which are widely used in many industries as pigments in paints and dye manufacture are sources of heavy metals.
- (iii) Domestic wastewater; domestic wastewater contains substantial quantities of metals. The prevalence of heavy metals in domestic formulations such as cosmetics or cleansing agents is frequently over looked but contributes to heavy metal accumulation in the environment.

- (iv) Agricultural sources; agricultural discharge contain residual of pesticides and fertilizer which contain heavy metals.
- (v) Atmospheric pollution: acid rain contains trace metals as well as suspended particulate matter. If this is input into water body or soil will cause pollution

2.2.1 Vehicular Emission as Sources of Metal Pollutants of the Environment.

Transportation activities are known to contribute to the pollution of soil and water bodies especially those within urban settlement where a lot of vehicular activities take place. This is because vehicle exhausts are known to emit some heavy metals such as Cd, Cr, Pb, Zn, Fe, and Cu so that soils, plants and even residents along roads with heavy traffic loads are subjected to increasing levels of contamination with heavy metals (Ghrefat and Yusuf, 2006). Infact, motor vehicles and sewage systems constitute some of the major sources that release Zn, Cu, Pb, Fe, Cd, and Cr trace metals directly into the urban environment (Fatoki, 1996, Fatoki and Ayodele, 1991, Sorme and Lagerkvist, 2002). Hence roadside soils often show a high degree of contamination that can be attributed to motor vehicles.

An investigation carried out by (Pagoto *et al*, 2001; Pagoto *et al*, 2010 and Joshi *et al*, 2010) showed that the concentration of the metals Pb, Cu, Zn, Cd, and Ni decreases rapidly within 10 to 50m from roads that have a lot of vehicular activities Also according to the result obtained by (Panek and Zawodhy, 1993), pollution of roadside soils and plants by combustion of leaded petrol products is localized and usually limited to a belt of several

meters wide on either side of the road and that for similar topography and vegetation, the level of pollution decreases with the distances from the road.

In 2005 Odiyo, *et al* investigated the concentration of Cu, Zn, Cr, Pb, Cd, in soil, vegetation, and water bodies within Thohoyandou Peri-Urban town in South Africa and the result showed that the concentrations decreases with distance away from the road in the order $Pb > Zn > Cr > Cu > Cd$ thus indicating their main source was motor traffic and in 2011, Mmolawa *et al* reported concentration of Pt, Pd, Rd in roadside soil samples from Botswana in the range of 12.80 ug/g to 34.46 ug/g which is in agreement with the findings reported by Morton *et al*, 2009). These metals when deposited by the road side can then be eroded into a nearby river during rainy season or can be carried by the wind into the river during windstorm, thus contributing to the level of pollution of the water in the river.

Soil and sediment are generally known to be an important sink for heavy metals. The uptake of these heavy metals by plants is an avenue for their entry into the human food chain with harmful effect on health (Joyede *et al*, 2006). Vegetables accumulate heavy metals in their edible and non-edible parts; therefore the intake of vegetable is an important path of heavy metal toxicity to human being hence food safety issues and potential health risk make this as one of the most serious environmental concerns (Cui *et al*, 2004).

2.2.2. Industrialization as Sources of Metal Pollutants of the Environment.

The increase in industrialization has cause an increase in challenges for waste management and disposal worldwide. The consequence of this is that the ecological setting which was before clean and safe is now becoming increasingly hazardous to both plants

and animals and pose health implications to human being through food chain. Industrial waste disposal and management is an economic venture therefore, industrialist, if not strictly monitored through law enforcement may choose the cheap method of managing their waste by disposing them directly in nearby streams or in nearby bush which may eventually get eroded into nearby streams. Industrial chemical technology and engineering processes make use of different chemicals to obtain the required products. The utilization of the finished products either in homes, schools, hospitals, may be the source of releasing metal pollutants in the environment. Also at expiration of some of these products, their disposal constitutes the release of metal pollutant in the environment whether direct or indirectly and these may increase the level of environmental metal pollution. In most cities such as Maiduguri where this study was conducted, industries even at small or medium scale level e.g foundries, metal works, auto mechanic centres and so on generate wastes that in long term accumulate to constitute serious environmental pollution.

2.2.3 Urbanization as Sources of Metal Pollutants of the Environment.

The rate of industrialization coupled with consequent increase in urbanization has exacerbated pollution effect on the environment. This is because the process of urbanization has some considerable impacts. Firstly, hydrological impact both in terms of controlling rate of erosion, delivery of pollutants to rivers and in terms of influencing the nature of runoff and other hydrological characteristics (Goudie, 1990); secondly, waste generation both in terms of controlling the source of waste generation and the content of the waste generated in addition to the volume of waste generated on a daily basis and also the siting of effective and safe dumpsites.

Water and soil pollution are of great consequence because both terrestrial and aquatic life may be poisoned due to presence of some hazardous substances, this will distort the water and soil quality, and may add odor to water and deteriorate soil quality therefore significantly hinders economic activities. There are some activities that have been documented to have impacted negatively in some Nigerian soil and surface water (Awode *et al*, 2008) especially oil exploration in the Niger Delta region (Kakulu and Osibanjo, 1998; Iheyen 2001; Davies *et al*, 2006;, Chukwujindu *et al*, 2007; Asuquo *et al*, 2007; Arimoro *et al*, 2008). Of particular interest to us are the heavy metals because among very toxic elements are heavy metals, this is due to their non- biodegradable and persistence in nature

In natural aquatic ecosystem, metals occur in low concentrations normally at the nano to microgram per liter level. This has occurred as a result of natural weathering of the underlying sediment. In recent times, however, the occurrence of metal contaminants especially the heavy metal are in excess natural loads and has become a problem of increasing concern. This situation has arisen as a result of the rapid growth of population, increased urbanization, and expansion of industrial activities, exploration and exploitation of natural resources. The generation of metal pollutants cannot be completely avoided because as stated earlier on they are interlinked with socio-economic development of the society either in transportation, industrialization, urbanization or in their day to day household utilization and or general utilization

2.3.1 River and Sediment Pollution with Heavy Metals.

River pollution is an environmental problem in the developing countries due to lack of stringent measures as adopted in the developed nations for water quality requirements to control river pollution. Wastewater treatment is not given the necessary priority it deserves and therefore industrial waste and domestic sewage are discharge into receiving water bodies without adequate treatment or not at all. This is validated by the investigation carried out by (Dada, 1997 and Bichi, 2000) in which they independently investigated the effluent discharged by most of the industries situated in Challawa Industrial Estate Kano, Nigeria and discovered that the effluents were not treated to standard before discharging them into the river. The river water and sediments analysis showed excessive amount of heavy metals such as lead, chromium and Iron which are mostly toxicants.

In a similar vein an investigation carried out on the level of contamination of the sediments from river Ngadda, in Maiduguri Metropolis by Akan *et al*, in 2011 showed that the concentration of the metals Cu, Pb, Fe, Ni, Co, Mn, Cd, As, Zn, and Cr, were all above USEPA and WHO (2004) guideline and maximum permissible limit (MPL) values and that the concentration varies with depth. The variations of these heavy metals with depth of the sediment of river Ngadda ascertain the accumulation of metal pollutants with time in sediments. This is further confirmed by findings of (Akoto *et al*, 2008; Alloway, 1995). These results stressed the need for time to time investigation of the environment so as to be able to monitor the rate of bio-accumulation with heavy metals. In the current area of study that is the river Ngadda and Alau Dam irrigation farms, river Ngadda transcend Maiduguri Metropolis and just like many urban centers in developing countries, the metropolis is characterize by poor land-use planning, lack of proper sewage water and waste disposal

systems as well as high traffic congestion therefore the water of the river is likely to be contaminated with metal toxicants and will therefore be investigated for the level of heavy metal content

In 2004, Moshood, *et al*, investigated the distribution of heavy metals in surface water and sediments of Ogunpa River, in Ibadan area, southwestern Nigeria and reported that the average concentrations of Lead, Zinc and Copper are about double of that of the mean composition of world rivers (MCWR), while average Cadmium concentrations is in the order of ten times that of the MCWR. This is an indication of contamination of the water of Ogunpa drainage relative to the MCWR. In (2010) Sekabira, *et al*, investigated the concentration of some heavy metals in Nakivubo channelized stream in Kampala city of Uganda and reported that the level of heavy metals exceeded the WHO (2008) limit for most of the sites. An assessment carried out by Akoteyon *et al*, in (2011) on water samples obtained from wells situated around land fill site in a typical suburban settlement in Alimosho, Lagos, Nigeria observed that the concentration of Lead, Copper, Iron and Zinc exceeded the WHO maximum permissible limit in good number of well water samples.

2.4.1 Absorption of Heavy Metals by Plants.

In many developing countries, the use of polluted water in the immediate environment of big cities for growing of vegetables is a common practice. Although these waters are considered to be rich source of organic matter and plant nutrients, it also contain sufficient amount of soluble salts and heavy metals. The use of such water in irrigation for a long period may accumulate and contaminate the soil with heavy metals and when such

soil is used for cultivation of crops these heavy metals can be absorbed by the roots of the vegetables and transported to the various parts of the plant to toxic levels as vegetables are known to accumulate heavy metals in their edible and non-edible parts. Intavangse and Dean in (2006) study the absorption of metals by some vegetables and discovered that lettuce and radish were found to be more responsible than other vegetables for the accumulation of heavy metals in human through the edible portion. The basic reason why the use of polluted water for irrigation/farming activities is of great concern is because water has unique chemical properties due to its polarities and hydrogen bonds which makes it to be able to dissolve, absorb, adsorb or suspend many different compounds (WHO 2007).

An investigation carried out by; Uwah *et al*, in (2009) of the levels of some agricultural pollutants in soils and water leaf (*Talinum triangulare*) obtained from Alau dam and Gongulom dry season farming area in Maiduguri, Nigeria showed that the concentration of heavy metals As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Co, in the soil and the named vegetable plant above has Fe, and Cr above USEPA and WHO (2004) guideline and maximum permissible limit (MPL) while for Alau dam farming area Fe, Ni, Cr Pb, and As are above USEPA and WHO maximum limit.

2.5.1 Transfer of Heavy Metals by Plants to Man.

It is a known fact that food and water are the main sources of essential metals and these are also the media through which human being are exposed to various toxic metals (Mapanda. 2005) and some investigations have shown that most common vegetables are

capable of accumulating high levels of metals from the soil (Gracia *et al*, 1981; Khan and Frankland, 1983; Xuong, 1998 and Cobb *et al*, 2001). Investigation also showed that in the process of transfer of heavy metals from soil to plants, heavy metals are easily accumulated in the edible parts of leafy vegetables as compared to grains and fruits crops (Mapanda *et al*, 2005), therefore the continuous consumption of the vegetables cultivated with contaminated water will transfer some of the metal toxicants from the vegetables to human body especially the internal organs.

2.6.1: Review of Sampling Techniques, Sample Preparation and Analytical Methodology

Some similar investigations were carried out in various places at various time of which some few of them will be considered in this investigation so as to help in establishing the reasons as to why some of sampling techniques, sample preparation, and analytical methodology were adapted in this study. The work carried out in 2009 by Uwah *et al*, to investigate the levels of some agricultural pollutants in soils and water leaf (*Talinum triangulare*) obtained in Maiduguri, Nigeria, the leaves and top or surface soil (0 – 10cm) samples were collected from the vegetable farms of Alau Dam and Gongulon, irrigated with the Alau dam water, sewage water and available wastewater. Samples were collected for some years and then homogenized. During each collection, samples were randomly collected from different plots, put into pre-cleaned polythene bags and transported to the laboratory. During sample preparation, soil and sliced vegetable samples were dried in an oven at 105°C for 24 hours. A portion (1g) of each samples were placed in 50 ml Teflon beakers and then digested with 10 ml of HNO₃-HClO₄-HF to near dryness at 80 – 90°C on a hot plate. The digests were filtered into a 50 ml volumetric flask using whatman N^o 42

filter paper. The concentration levels of the various elements in ppm is as follows; As (1.066 ± 0.29); Cd (0.096 ± 0.01); Cr (93.50 ± 2.58); Cu (1.23 ± 0.03); Fe (5.66 ± 0.29); Mn (8.63 ± 0.35); Ni (4.89 ± 0.09); Pb (3.95 ± 0.04); Zn (0.40 ± 0.04) and Co (3.99 ± 0.26) in the leaf of *Tallinum triangulare* while in the soil As (4.84 ± 0.04); Cd (0.81 ± 0.06); Cr (76.18 ± 5.49); Cu (3.78 ± 0.29); Fe (60.20 ± 0.70); Mn (15.12 ± 0.26); Ni (20.80 ± 0.44); Pb (3.59 ± 0.08); Zn (16.72 ± 0.16) and Co (11.43 ± 0.16) were determined using an SP 1900 Pye Unicam Atomic Absorption Spectrophotometer (AAS) equipped with an air-acetylene burner. The mean values for six determinations per sample were recorded and the data obtained were subjected to statistical tests of significance using student t-test ($p < 0.05$) to assess pair's results in the *Tallinum triangulare* and soil samples that is to assess significant variation in the concentration levels of the heavy metals in vegetable as well as in soil. The result obtained for statistical test using the student t-test showed significant difference ($p < 0.05$) among most of the metals concentration levels in the *Talinum triangulere* and soil samples obtained in the two sample areas of Alau dam and Gongulon.

In the study carried out in 2010 by Akan *et al*, to investigate heavy metals in sediments from river Ngadda, Maiduguri Metropolis, Borno State, Nigeria, sediment samples were collected from river Ngadda starting from Alau Dam Bridge down to down to Shukwari Area. The collection were done randomly but targeted the three bridges namely Lagos bridge, Gwange bridge and Custom bridge which link the north and the south part of the Metropolis and city storm discharge points. At each sampling point, sediments were collected using Van-Veen grab sampler at different depth. Sediment

samples were then preserved in plastic bags and transported to the laboratory. The samples were oven-dried at (80 – 100) °C. The dry samples were gently crushed and sieved to collect the < 63 µm grain size. Two grams of each sediment sample were weighed into a pre-weighed dry crucible. The crucibles were covered and placed in a muffle furnace and then the temperature gradually increased to 2 hours (Radojevic and Bashkin, 1999). The samples were cooled to room temperature in desiccators. The ash samples were placed into acid-washed glass beakers. Sediment samples were digested by the addition of 10 ml of 0.25 M HNO₃ heated to dryness and thereafter 10 ml 0.25 M HNO₃ and 3 ml of HClO₃ were added. The solution was then heated in a fume chamber. Sample solutions were obtained by leaching the residues with 4.0 ml of HCl and thereafter filtered and diluted with distilled water to 100 ml mark (Radojevic and Bashkin, 1999). Blank solutions were handled as detailed for the samples. All samples and blanks were stored in plastic containers. Determination of metals of interest was made directly on each final solution using Perkin-Elmer Analyst 300 Atomic Absorption Spectrophotometer (AAS). The concentrations of the various elements in ppm was as follows; Cr (45.14 ± 0.02); Pb (71.23 ± 0.11); Cu (51.32 ± 0.01); Fe (58.34 ± 1.01); Ni (39.45 ± 1.41); Co (28.34 ± 0.21); Mn (154.34 ± 0.10); Cd (19.34 ± 0.08); As (40.67 ± 0.76) and Zn (163.45 ± 0.06). Data obtained are presented as mean and standard deviation and were subjected to Pearson's correlation analysis, while one-way analysis of variance (ANOVA) (P < 0.05) was used to assess whether heavy metals varied significantly between sampling depths and points. The (ANOVA) results show that there was significant variation in the levels of heavy metals from the different points

In the study “assessment of heavy metal pollution in soils along major roadside areas in Botswana” carried out by Mmolawa *et al*, in (2011), soils were randomly collected along major roadsides avoiding areas with obvious signs of disturbance such as animal burrowing and landfills. The distance between sampling sites were chosen to be about 50 or 100 km, depending on proximity of major settlements. All soils were sampled at the surface (0 to 10 cm in depth) using hand-driven stainless steel augers. Each location for all sample sites was determined using a global positioning system. The samples were air dried to constant weight and then sieved through a 500µm stainless steel mesh wire. Samples of 0.5g were digested in 20 ml of freshly prepared aqua regia (1:3 HNO₃ . HCl) on a hot plate for 3hours, then evaporated and analyzed for metal concentration. Standard reference was prepared using stock solution from SAARCHN and MERCH and was used to have a check on the accuracy of the results. The total concentration of the metal of interest in filtrate was then determined using a flame atomic absorption spectrometer (Varian Spectra 220 FS0) at specified wavelength using air acetylene flame. The mean results obtained in ppm are as follows; Al (34.6); Co (0.02); Cu (0.08); Fe (87.00); Mn (0.51); Ni (0.48); Pb (0.21) and Zn (0.14). Analysis of variance was employed to determine whether group of variables have the same mean which showed that no significant effect on variation between group means of the heavy metals at different zones except for copper ($p < 0.001$), Manganese ($p < 0.003$), and zinc ($p < 0.05$), this suggest that there is some degree of input of these (Cu, Mn, and Zn) metals between sites. Inter-elemental association was also evaluated by spearman’s rank correlation coefficient ρ and the results indicated that some elemental pairs such as Al/Mn ($r= 0.5$; $P < 0.001$), Cu/Mn ($r = 0.81$; $p < 0.0001$), and Cu/Pb ($r =$

0.65; $p < 0.0001$) have strong correlation with each other while Al/Ni ($r = 0.34$, $p < 0.05$) and Al/Zn ($r = 0.35$, $p < 0.05$) are moderately significant whereas the rest of the element pairs show no significant correlation with each other. Agglomeration schedule of cluster analysis (CA) was performed on data using nearest neighbor linkage and Euclidean distance as a measure of proximity between samples. The hierarchical cluster analysis using nearest neighbor was used to establish the significant relationship between the variables which indicate significance ($p < 0.05$).

An investigation carried on ‘‘Heavy metal assessment and water quality values in urban stream and rain water a case study of Nakivubo Stream in Kampala Uganda’’ was conducted by Sekabira *et al* in (2010). In order to assess the heavy metals, stream water samples were collected over one year period along the Nakivubo drainage system and Watindo Stream as described by Muwanga in 1997. The samples were taken from the middle of the stream careful to avoid contamination using sample bottles. Sampling bottles were washed with dilute nitric acid, rinsed with deionized water and again washed three times with the stream water before they were filled. For heavy metal analysis, a 500 ml bottle of linear polythene was used to collect water samples, filtered (using $0.45\mu\text{m}$ pore size) and three drops of concentrated nitric acid added for preservation. All were stored in a box and transported to laboratory for analysis. Other physico-chemical characteristics such as dissolved oxygen, electrical conductivity, Heavy metal elements were then analyzed by direct aspiration of the sample solution into a Perkin Elmer model 2380 flame atomic absorption spectrophotometer AAS after calibration with suitable elemental standards at close intervals. The result for the mean concentration of the elements studied

in Nakivo stream in Kampala Uganda in ppm was Zn (59 ± 9); Mn (1035 ± 650); Fe (1450 ± 550); Pb (129 ± 70); Cd (9 ± 4) and Cu (44 ± 15) while that of Watindo stream in Kampala, Uganda was Zn 924 ± 5 ; Mn (165 ± 135); Fe (460 ± 100); Pb (106 ± 47); Cd (4 ± 2) and Cu (14 ± 0). For the collection of the rain water, a modified bulk sampler consisting of a polythene funnel with 20.8 cm opening connected to a 5L polythene conical flask was used. The funnels and conical flasks were wrapped in an aluminum foil to avoid algal growth on the bulk precipitate and placed 1.5m above the ground (Nyangababo *et al*, 2005). The bulk precipitation collected in one month was poured in one flask and mixed thoroughly to homogenize the precipitate from the different flask. Duplicate samples of 500 ml were collected and transported to the laboratory in an ice box at 4°C and the precipitate was first filtered through a 0.45 µm filter and preserved with nitric acid. Heavy metal elements were then analyzed by direct aspiration of the sample solution into a Perkin Elmer model 2380 flame atomic absorption spectrophotometer (AAS) after calibration with suitable elemental standards at close intervals. Analysis of variance (ANOVA) was used to determine whether groups of variables have the same means on data that are continuous or normally distributed and with homogeneous variance. The two way ANOVA indicate that sites show no significant effect on variations between groups of means of the heavy metals at different stream sections however, the mean heavy metal concentrations of elements within sites differed significantly at different stream sections, upstream ($p < 0.001$); midstream ($p < 0.001$) and downstream ($p < 0.001$), at $p = 0.05$. Pearson correlation coefficient analysis was employed to analyze and establish inter-metal relationship and physico-chemical characteristic of the stream water. The elemental pairs

Pd/Cd ($r = 0.56$); Pb/Zn ($r = 0.50$); Cd/Mn ($r = 0.52$) and Mn/Fe ($r = 0.56$) were significantly correlated with each other

2.7.1 Nigeria Research Reactor-1 (NIRR-1).

The Nigeria Research Reactor-1 (NIRR-1) used for the analysis was acquired for an extensive soil fertility mapping project of the different arable lands in Nigeria aimed at improving food production Jonah, *et al*, 2006, and like all miniature neutron source reactor (MNSR) facilities, NIRR-1 is specifically designed for neutron activation analysis (NAA) of which in its instrumental form (INAA) has some unique feature such as multi-element capability, rapidity, reproducibility of results, complementarities to other methods, freedom from analytical blank and independence of chemical state of elements.

2.7.2 Neutron Activation Analysis.

Neutron activation analysis (NAA) is a quantitative and qualitative method of high efficiency for the precise determination of a number of main-components and trace elements in different types of samples. Neutron activation analysis, based on the nuclear reaction between neutrons and target nuclei, is a useful method for the simultaneous determination of about 25-30 major, minor, and trace elements of geological, environmental, biological samples in part per billion to part per million range without or with chemical separation.

In NAA, samples are activated by neutrons, and during irradiation the naturally occurring stable isotopes of most elements that constitute either rock/mineral samples, or biological samples are transformed into radioactive isotopes by neutron capture. Then the activated nucleus decays according to a characteristic half-life; some nuclides emit particles only, but most nuclides emit gamma-quanta, too, with specific energies. The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma-ray lines in the spectra using gamma-ray detector and special electronic accessories. As the irradiated samples contain radio nuclides of different half-lives different isotopes can be determined at various time intervals. During NAA the neutrons get into interaction with the nucleus, therefore, the chemical composition and crystal structure of the substance under analysis will have no effect on the result only in exceptional cases.

2.7.3 Principles of Neutron Activation Analysis.

In the process of NAA the neutrons interact with the stable isotopes of the target element converting them to radioactive ones. The so-called compound nucleus emits gamma rays promptly with extremely short half lives in the order of milliseconds and these can be measured during irradiation through a technique called prompt gamma neutron activation analysis (PGNAA) but in most cases the radioactive isotopes decay and emit beta particles accompanied by gamma quanta of characteristic energies and the radiation can be used both to identify and accurately quantify the elements of the sample.

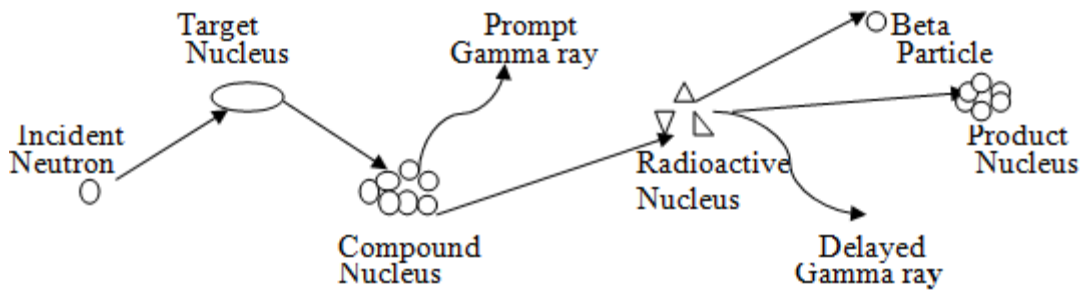


Fig 2a: The process of neutron capture by a target nucleus followed by the emission of gamma rays

In a nuclear reaction form it can be represented as

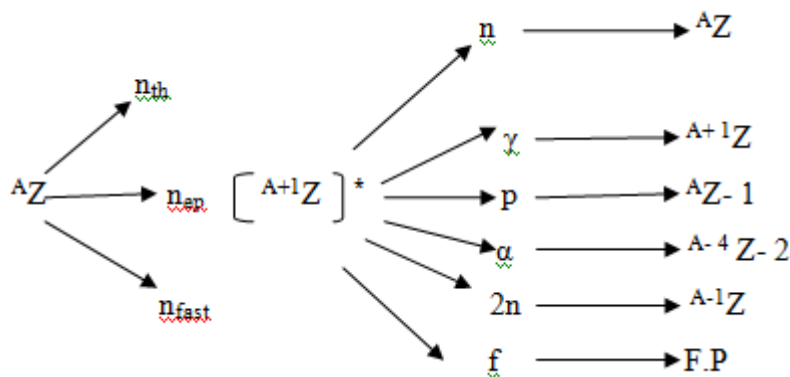


Fig 2b: Neutron – induced reactions

The activity (A) of the isotopes depends on time. During irradiation the activity of the radioactive isotope produced grows according to a saturation characteristic governed by a saturation factor: $S = 1 - e^{-\lambda t_i}$ and subsequent to the irradiation the isotope decays according to the exponential law: $D = e^{-\lambda t_d}$

where t_i is the time of irradiation; t_d is the time of decay; λ is decay constant.

Hence, during irradiation, activity is

$$A = (\phi_{th}, \sigma_{th}) \frac{m \cdot f \cdot I \cdot N_{AV}}{A_{rel}} (1 - e^{-\lambda t_i}) \quad (2.1)$$

and subsequent to irradiation

$$A = (\varphi_{th}, \sigma_{th}) \frac{m \cdot f_i \cdot N_{AV}}{A_{rel}} (e^{-\lambda t d}) \quad (2.2)$$

Where, φ_{th} = conventional thermal neutron flux (in cm^2)

σ_{th} = effective thermal neutron cross- section in (cm^2)

N_{AV} = Avogadro's number

f_i = isotopic abundance

m = the mass of the irradiated element

A_{rel} = relative atomic mass of target element

2.7.4 Reaction Rates.

Reaction rate of particles travelling through a material with nuclei of that material is parameterized by the reaction cross section $\sigma(E)$ which is the property of the material and the neutron flux spectrum $\varphi(E)$, which is related to the density of the particles travelling through the material and their speed

$$\varphi(v) = v n(v), \quad (\text{TrKov, 2005}) \quad (2.3)$$

where $\varphi(v)$ is the neutron flux per unit of velocity interval and $n(v)$ is the neutron density per unit of velocity interval

Expressed in terms of the kinetic energy of the incident particles, which is related to the speed v by the relation $E = \frac{1}{2} mv^2$ (where m is the particle mass), from equation (2.1) and

(2.2) the reaction rate A is proportional to φ , σ , m , f_i , N_{AV} . Hence the reaction rate A per nucleus capturing a neutron is given by

$$A = K \int_0^{\infty} \sigma(E) \varphi(E) dE \quad (2.4)$$

where σ = cross-section (in cm^2) at neutron energy E (in eV)

ϕ = neutron flux for energy between E and $E + dE$

$\text{cm}^{-2}\text{s}^{-1}\text{eV}^{-1}$)

In terms of speed the equivalent expression for the reaction rate can be written as

$$A = K \int_0^{\infty} \sigma(v)v \cdot n(v)dv \quad (2.5)$$

where $\sigma(v)$ is the cross section at neutron velocity v and $n(v)$ is the neutron density per unit of velocity interval

In nuclear reactors the integral in equation (2.4) is usually replaced by the sum of two integrals, separating the thermal part up to energy E_{cd} (corresponding to neutron speed v_{cd}) and epithermal part:

$$A = K \left[\int_0^{E_{cd}} \sigma_{th}(E)\phi_{th}(E) dE + \int_{E_{cd}}^{\infty} \sigma_{epi}(E)\phi_{epi}(E) dE \right] \quad (2.6)$$

where ϕ_{th} = conventional thermal neutron flux (in cm^2)

σ_{th} = effective thermal neutron cross- section in (cm^2)

ϕ_{epi} = conventional epithermal neutron flux (in $\text{cm}^{-2}\text{s}^{-1}\text{eV}^{-1}$)

σ_{epi} = effective epithermal neutron cross-section(in cm^2).

The contribution of thermal neutrons to reaction rate, expressed in “neutron speed” domain is given by:

$$A_t = K \int_0^{v_{cd}} \sigma(v)v \cdot n(v)dv \quad (2.7)$$

For a $1/v$ absorber, the cross section is

$$\sigma(v) = \sigma_0 \frac{v_0}{v} \quad (2.8)$$

where v_0 is thermal neutron speed 2200m/s by definition

σ_0 is cross section at neutron speed v_0

substituting equation (2.8) in (2.7)

$$A_t = K \sigma_0 v_0 \int_0^{v_{cd}} n(v) dv = K \sigma_0 v_0 N_t \quad (2.9)$$

Where N_t is the total thermal neutron density

Note that the reaction rate is proportional to the total thermal neutron density and is independent of the neutron speed distribution $n(v)$;

In the energy domain the equivalent expression for the thermal reaction rate is

$$A_t = K \int_0^{E_{cd}} \sigma(E) \phi(E) dE \quad (2.10)$$

Assuming that the thermal neutron flux has Maxwellian distribution

$$\phi(E) = E e^{-E/kT} \quad (2.11)$$

Where k is the Boltzmann constant, T is the temperature. The thermal reaction rate is then

$$A_t = K \int_0^{E_{cd}} \sigma(E) E e^{-E/kT} dE \quad (2.12)$$

For a $1/v$ absorber

$$A_t = K \sigma_0 \sqrt{E_0} \int_0^{E_{cd}} \sqrt{E} e^{-E/kT} dE \quad (2.13)$$

The average thermal cross section σ_{th} is define by

$$\sigma_{th} = \frac{\int \sigma(E) \phi(E) dE}{\int \phi(E) dE} \quad (2.14)$$

2.7.5 Radioactivity Induced by Neutron Activation Process.

The rate of radioactive atoms formed during nuclear activation process can be expressed mathematically as

$$\frac{dN_y}{dt} = N_x \phi \sigma \quad (\text{Michel, 1998}) \quad (2.15)$$

Where N_x is the number of target atoms, N_y the number of radioactive atoms formed, ϕ is the neutron flux ($\text{ncm}^{-2}/\text{sec}$) or charged particles and σ the activation cross-section.

The decay rate of the radionuclide formed due to neutrons or charged particles' hitting the target is

$$\frac{dN_y}{dt} \text{ decay} = -N_y \lambda_y \quad (2.16)$$

Where λ_y is the decay constant of the radionuclide formed and the negative sign indicate decrease of the number of target atoms with time.

Now the net rate of production of radionuclide is given by the equation.

$$\frac{dN_y}{dt} = N_x \phi \sigma - N_y \lambda_y \quad (2.17)$$

Integrating equation (2.17) gives

$$N_y = \frac{N_x \phi \sigma}{\lambda_y} \left[1 - e^{-\lambda_y t} \right] + N_{y_0} e^{-\lambda_y t} \quad : N_{y_0} e^{-\lambda_y t} \text{ is number of radioactive atom at } t=0 \quad (2.18)$$

Since $t = 0$, $N_{y_0} = 0$

$$N_y = \frac{N_x \phi \sigma}{\lambda_y} \left[1 - e^{-\lambda_y t} \right] \quad (2.19)$$

The activity A_t of the radioactive nuclide *Y at time t is given in terms of number of decays per second which implies

$$A_t = N_y \lambda_y \quad (2.20)$$

and

$$A_t = N_x \phi \sigma [1 - e^{-\lambda_y t}] \quad (2.21)$$

When time of irradiation is taken to be infinite i.e. $t \rightarrow \infty$ the term in the bracket of equation (2.21) become one (unity).

Therefore

$$A_{t\infty} = N_x \phi \sigma \quad (2.22)$$

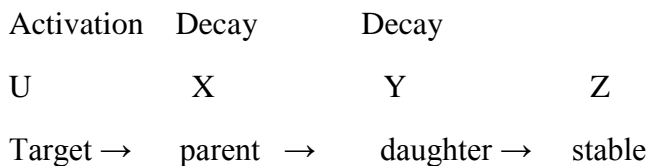
The activity $A_{t\infty}$ is referred to as the saturation activity (A_{sat}) and the expression $[1 - e^{-\lambda_y t}]$ is called the fractional saturation.

Equation (2.21) may then be written as

$$A_t = A_{sat} [1 - e^{-\lambda_y t}] \quad (2.23)$$

The optimum activation time depends on the flux of irradiating particles, the decay rate (on half-life of the radionuclide formed) and the sensitivity of the analysis required).

For decays that occurs in more than one stage



Let the initial number of target nuclei be denoted by N_0 , the number of parent and daughter nuclei after time t by N_p and N_d respectively and their respective decay constant by λ_p and λ_d . Then the net rate of production of radionuclide from parent nuclides is

$$\frac{dN_p}{dt} = N_0 \phi \sigma - \lambda_p N_p \quad (2.24)$$

$$\frac{dN_p}{dt} = N_p \lambda_p - N_d \lambda_d \quad (2.25)$$

Integrating equation (2.25) gives

$$N_p = \frac{N_0 \phi \sigma}{\lambda_p} [1 - e^{-\lambda_p t}] \quad (2.26)$$

Putting (2.26) into (2.25) to have

$$\frac{dN_p}{dt} = N_0 \phi \sigma [1 - e^{-\lambda_p t}] - \lambda_d N_d \quad (2.27)$$

Solving equation (2.27) for $t = 0$, $N_d = 0$

$$N_d = \frac{N_0 \phi \sigma}{\lambda_p} \left[1 + \frac{\lambda_d}{\lambda_p - \lambda_d} e^{-\lambda_p t} - \frac{\lambda_p}{\lambda_p - \lambda_d} e^{-\lambda_d t} \right] \quad (2.28)$$

this equation is used if daughter nuclide is easily distinguish from the other nuclide than parent.

The intensity of the measured gamma in radioactivity is proportional to the activity. The measured parameter is the total energy peak area (N_p) at a particular energy given by

$$N_p = A \cdot f_\gamma \cdot \epsilon_\gamma \cdot t_m$$

ϵ_γ = the efficiency of the semiconductor detector which varies with gamma energy

f_γ = the emission probability of a gamma photon at a given energy

t_m = the measuring time

The basic activation equation is given by

$$A = Nf\sigma \left(1 - e^{-\frac{0.693}{t_{1/2}} t} \right) \quad (2.29)$$

A = activity of product nuclide (disintegration per sec.)

N = atoms of target elements

f = flux neutrons (neutrons per cm^2 -s)

σ = cross-section of the target nuclide (cm^2)

$t_{1/2}$ = half life of the induced radioactive nuclide

t = time of irradiation

This equation can be used to calculate the number of atoms of an unknown target element by measuring the radioactivity of the product.

If the neutron fluxes ϕ , neutron captures cross section σ , absolute detector efficiency ϵ , and absolute gamma-ray abundance I_γ are known, the number of atoms n of isotope A_Z in the sample can be calculated directly

2.7.6 Activity Measurement in Neutron Activation Processes.

Assume the sample has been activated in the reactor. At the instant when the activation has been terminated ($t_c = 0$) the activity of the sample is given by the following expression`

$$A_0 = \frac{\sigma m \phi S N A}{W A} \quad (2.30)$$

where

A_0 = the number of disintegration per second of the element in the sample at $t_c = 0$ when irradiation stops and counting begins

σ = the cross section to the reaction in cm^2

$m =$ the mass of the target element in grams

$N_A =$ Avogadro's number 6.023×10^{23} molecules/mole

$\phi =$ the neutron flux expressed in neutrons/cm/s

$\alpha =$ fraction of the target isotope in the sample

$S = 1 - e^{-\lambda t}$ is the saturation factor, t is time spent under neutron irradiation

$W_A =$ gram atomic weight of the element. and

After irradiation the sample is transferred to the detector, a spectrum is accumulated for a counting time t_c long enough to get a reasonable value for the counts in the photo peak.

The time is usually at least one half-life and the number of disintegrations, N_d that occurred during counting time t_c can be determined using the equation

$$N_d = \frac{\sum p - \sum B}{G \epsilon_p f} \quad (2.31)$$

$\sum p =$ the sum of the counts under the photo peak

$\sum B =$ the background for the same counting period under the photo peak

$G = A/2\pi r$

where $A =$ the area of detector in cm^2

$r =$ the distance from the source to the detector in cm

$\epsilon_p =$ the intrinsic peak efficiency for the gamma ray energy and the detector size used

$f =$ the decay fraction of the unknown activity, which is the fraction of the total disintegration in which the measured gamma is emitted

The number of radioactive nuclei N_o (of the isotope being detected) that existed in the sample before counting started can be calculated from the equation

$$N_d = N_o (1 - e^{-\lambda t_c}) \quad (2.32)$$

Where t_c is the time during which the gamma rays from the sample were counted.

2.7.7 Relative Method of Instrumental Neutron Activation Analysis (INAA).

The method is based on the simultaneous irradiation of the sample with comparator standards of known quantities of the elements in question in identical positions, followed by measuring the induced activities intensities of both the standard and the sample in a well known geometrical position. The sample and the standard activities are related by the equation

$$\frac{A_{sam}}{A_{std}} = \frac{\phi\omega\epsilon IN_A(1-e^{-\lambda t_{irr}})_{sam}(e^{-\lambda t_d})_{sam}(1-e^{-\lambda t_c})_{sam}}{\phi\omega\epsilon IN_A(1-e^{-\lambda t_{irr}})_{std}(e^{-\lambda t_d})_{std}(1-e^{-\lambda t_c})_{std}} \quad (2.33)$$

where A_{sam} is activity of the unknown sample, A_{std} is activity of the standard

When the standard is irradiated and counted under similar conditions as the sample, the common parameters cancelled out then the mass of the element in the sample relative to the standard comparator is calculated using the equation.

$$\frac{A_{sam}}{A_{std}} = \frac{m_{sam} (e^{-\lambda t_d})_{sam}}{m_{std} (e^{-\lambda t_d})_{std}} \quad (2.34)$$

where A_{sam} = activity of sample

A_{std} = activity of standard

m_{sam} = mass of element in the sample

m_{std} = mass of element in standard

λ = decay constant for the isotope.

t_d = decay time

when performing short irradiations, the irradiation, decay, and counting times are usually fixed the same for all samples and standards such that the time dependent factors cancel.

Therefore the above equation in terms of concentrations of elements in sample and standard can be written as

$$C_{sam} = C_{std} \frac{W_{std} A_{sam}}{W_{sam} A_{std}} \quad (2.35)$$

Where C_{sam} = concentration of the element in the sample

- C_{std} = concentration of the element in the standard
 W_{sam} = weight of the sample
 W_{std} = weight of standard

2.7.8 The Single Comparator Method of NAA (k_o -NAA)

The single comparator method of NAA also known as K_o -NAA is a method for multi-element analysis of samples of materials which is based on the co-irradiation of sample matrix with a single element (comparator) usually a thin foil of gold instead of using standards prepared from known weights of elements to be determined and also experimentally determined composite nuclear constants called K_o -factors.

The K_o -NAA technique generally uses input parameters such as (i) the epithermal flux shape factor (α), (ii) sub-cadmium-to-epithermal neutron flux ratio (f), (iii) modified spectral index $r(\alpha) \sqrt{T_n / T_o}$, (iv) Westcott's $g(T_o)$ factor (v) the full energy peak detection efficiency ϵ_γ and (vi) nuclear data on Q_o (ratio of resonance integral (I_o) to thermal neutron cross section (σ_o) and K_o . The K_o -factors have been defined as independent of neutron fluence rate parameters as well as of spectrometer characteristics. According to Frans de Corte and his co-researchers' approach, the irradiation parameter $(1 + Q_o(\alpha))/f$ and the detection efficiency ϵ are separated in the expression of the equation of the k-factor

$$k_i = \frac{(M_\alpha) \cdot i_{cal} \gamma_{comp} \cdot \epsilon_{comp} \theta_{comp} \sigma_{effcomp}}{M_{ical} \gamma_{ical} \epsilon_{ical} \theta_{ical} (\sigma_{eff})_{ical}} \quad (2.36)$$

which resulted at the definition of the k_o - factor

$$k_o = \frac{1}{k'} \cdot \frac{1 + Q_{ocomp}(\alpha)/f \cdot \epsilon_{comp}}{1 + Q_{ocal}(\alpha)/f \cdot \epsilon_{comp}} = \frac{M_{comp}}{\theta_{comp} \sigma_{ocomp} \gamma_{comp}} \cdot \frac{\theta_{cal} \sigma_{oca} \gamma_{cal}}{M_{cal}} \quad (2.37)$$

$$m_{x(unk)} = m_{x(comp)} \frac{1 + Q_{o,comp}(\alpha)/f \cdot \epsilon_{comp}}{1 + Q_{o,cal}(\alpha)/f \cdot \epsilon_{comp}} \cdot \frac{\left(\frac{N_p/t_m}{(1 - e^{-\lambda t_i})e^{-\lambda t_d} (1 - e^{-\lambda t_m})^m} \right)_{unk}}{\left(\frac{N_p/t_m}{(1 - e^{-\lambda t_i})e^{-\lambda t_d} (1 - e^{-\lambda t_m})^m} \right)_{comp}} \cdot \frac{1}{k_o} \quad (2.38)$$

The concentration of the element can be determined as

$$C_{sam} = \frac{\left[\frac{N_p/t_m}{SDCW} \right]_{sam}}{\left[\frac{N_p/t_m}{SDCW} \right]_{comp}} \frac{1}{k_o(comp(x))} \frac{G_{th,comp}f + G_{spi,comp} Q_{o,comp}(\alpha) \epsilon_{p,comp}}{G_{th,x}f + G_{spi,x} Q_{o,x}(\alpha) \epsilon_{p,x}} \quad (2.39)$$

2.7.9 Measurement of Gamma ray Count Rate.

Measurement of the induced activities is usually obtained from the gamma ray spectra of the induced radio nuclides. Gamma rays from radioactive isotopes have unique discrete energies and on striking a suitable detector, they are converted to an electrical signal that is processed as a count in an energy spectrum. The accumulation of gamma counts at a particular energy generates a curve, the area of which is proportional to the radioactivity of the characteristic radio nuclides. On comparing the net area count with standards make it possible to determine abundance of a particular element or elements. The energies of the delayed gamma rays which are used to identify component samples can be measured through the following equation

$$R = \epsilon I_{\gamma} A \quad (2.40)$$

(NSRCPEP, 2000).

$$R = A \varepsilon I_{\gamma} n \phi \sigma \left(\frac{1 - e^{-\lambda t_i}}{\lambda} \right) e^{-\lambda t_d} (1 - e^{-\lambda t_c}) \quad (2.41)$$

- R = measurement gamma-ray count rate (cps)
A = absolute activity of isotope ^{A+1}Z sample
 ε = absolute detector efficiency
 I_{γ} = absolute gamma ray abundance
n = number of atoms of isotope AZ in sample
 ϕ = neutron flux (neutron – $\text{Cm}^{-2}\text{s}^{-1}$)
 σ = neutron capture cross-section (cm^2) for isotope AZ
 λ = radioactive decay constant (s^{-1}) for isotope ^{A+1}Z
 t_i = irradiation time (s)
 t_d = decay time (s)
 t_c = counting time (s)

2.7.9 Instrumentation for Gamma Rays.

The instrumentation used to measure gamma rays from radioactive samples generally consists of a semiconductor detector, associated electronics, and a computer-based, multichannel analyzer (MCA). The semi conductor detector used for this work is a Hyper pure Germanium (HPGe) type. The detectors are connected to a multichannel analyzer (MCA) by an appropriate electronic system (preamplifier, spectroscopy amplifier, etc). The most important parameters of the detectors are efficiency and the resolution.

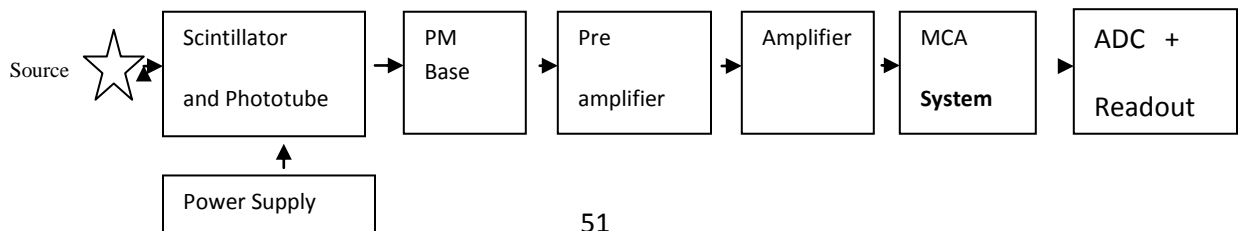


Fig 3 Electronics and interconnection for activity count.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sampling Apparatus

| | |
|--------------------------------------|-----------------------------|
| Plastic Bottles | Conductivity meter |
| Polyethene bags | Nitric Acid (Analar Grade). |
| Stainless Steel Auger (hand driven). | Masking Tape |
| pH meter (JENWAY 3505). | Cellotape |
| | Sample Bottles |
| | Thermometer |

Global Positioning System (GPS)

Device

Hand gloves

Vials

3.2 Preparation Apparatus

Pipette

Oven (Daiham Labtech.LDO-060E)

Agate Mortar and Pestle

Sieve (200 μm) pore size

Analytical Balance (Mettler 240)

Forceps

Vacuum Blower

Cotton Wool

3.3 Analysis Equipment

Neutron Source from (NIRR-!)

HPGe detector

Pre-amplifier

Amplifier

Analog-Digital Converter

Multichannel Analyzer

Computer

AtomicAbsorption pectrophotometer

3.3.1 Measurement of Gamma Rays Emitted From the Irradiated Samples

The usual objective of the measurements by spectrometers is the determination of the number and energy of the photons emitted by the source. The peak location and the peak area in the spectra have to be determined. The peak location is a measure of the gamma energy, while the peak area is proportional to the photon emission rate. For the energy measurement the pulse height scale must be calibrated with standard sources emitting photons of known energies. In order to calculate the activities, the full-energy-peak efficiencies of the source-detector system have to be determined by using sources of

known activities. For the determination of the peak areas the background under the peak interval has to be subtracted. The net count (N_p) results from

$$N_p = N_{int} - N_B \quad (3.1)$$

(N_{int} is the integral count under the peak and N_B refers to the background count).

The peak area can also be calculated by computer programs which fit an analytical function to the peak. Some of the spectral interferences that usually occur with neutron reaction and normally occur due to threshold nuclear reaction were taken into consideration when performing this experiment. The nuclides involved were as presented in Table 3.1 in line with nuclear data results.

Table 3.1: Nuclear Parameters of Elements of Interest

| Element | Product(n, γ) reaction | Half- Life | Gamma(γ) Energy (KeV) | Abundance(I) (%) | Possible interference |
|-------------------|-----------------------------------|------------|-----------------------------------|----------------------|---|
| ²³ Na | ²⁴ Na | 15.0 h | 1368 | 100 | ²⁴ Mg (n,p) ²⁴ Na, ²⁷ Al (n, α) ²⁴ Na |
| ²⁶ Mg | ²⁷ Mg | 9.45min | 843 | 71 | ²⁷ Al (n,p) ²⁷ Mg; ³⁰ Si (n, α) ²⁷ Mg |
| ²⁷ Al | ²⁸ Al | 2.31min | 1779 | 100 | ²⁸ Si (n, p) ²⁷ Al; ³¹ P (n, α) ²⁸ Al |
| ⁴¹ K | ⁴² K | 12.5h | 1525 | 19 | |
| ⁴⁸ Ca | ⁴⁹ Ca | 8.8min | 3084 | 92 | |
| ⁴⁵ Sc | ⁴⁶ Sc | 83.9d | 889 | 99 | ⁴⁶ Ti (n,p) ⁴⁶ Sc |
| ⁵⁰ Ti | ⁵¹ Ti | 5.8min | 320 | 93 | |
| ⁵¹ V | ⁵² V | 3.75min | 1434 | 100 | |
| ⁵⁰ Cr | ⁵¹ Cr | 27.8d | 320 | 10 | |
| ⁵⁵ Mn | ⁵⁶ Mn | 2.58h | 846 | 98 | ⁵⁶ Fe (n,p) ⁵⁶ Mn |
| ⁵⁸ Fe | ⁵⁹ Fe | 44.5d | 1099 | 56 | |
| ⁵⁷ Co | ⁵⁸ Co | 70.82d | 811 | 99 | |
| ⁷⁵ As | ⁷⁶ As | 26.3h | 559 | 44 | |
| ⁸¹ Br | ⁸² Br | 35.3h | 554 | 70 | |
| ⁸⁵ Rb | ⁸⁶ Rb | 18.7d | 1076 | 8 | |
| ¹²¹ Sb | ¹²² Sb | 67.1h | 564 | 69 | |
| ¹³³ Cs | ¹³⁴ Cs | 749d | 563 | 8 | |
| ¹³⁸ Ba | ¹³⁹ Ba | 84min | 166 | 22 | |
| ¹³⁹ La | ¹⁴⁰ La | 40.2h | 487 | 20 | |
| ¹⁵² Sm | ¹⁵³ Sm | 46..2h | 69 | 4.8 | |
| ¹⁵¹ Eu | ¹⁵² Eu | 9.32h | 122 | 7 | |
| ¹⁶⁴ Dy | ¹⁶⁵ Dy | 2.33h | 94 | 3 | |
| ¹⁷⁶ Lu | ¹⁷⁷ Lu | 6.7d | 208 | 11 | |
| ¹⁸⁰ Hf | ¹⁸¹ Hf | 42.3d | 482 | 80 | |
| ¹⁸¹ Ta | ¹⁸² Ta | 115d | 1221 | 27 | |
| ²³² Th | ²³³ Pa | 27.0d | 312 | 36 | |
| ²³⁸ U | ²³⁹ U | 23.47min | 75 | 50 | |
| ⁶⁴ Zn | ⁶⁵ Zn | 243.9d | 1115 | 50 | |

Online Nuclear Data: <http://www.naa-online.net/practical/ko-data>

3.3.2 Detection Limits in Instrumental Neutron Activation Analysis (INAA).

Detection limit is the smallest amounts of analyte that can be determined in a specimen and can vary from element to element. Some element become very radioactive, and can be determined at very low levels (sub part per billion). Usually the detection limit depends upon the ‘other’ elements in the sample – the matrix. If an element in the sample becomes radioactive besides the element of interest, the background noise may be too high to determine the desired element at low level. However, the signal- to- noise ratio will improve with time if the element of interest has a long half-life compared to the element(s) producing the noise.

Radiochemical separation may be employed when one or more elements in the sample become highly radioactive that it ‘interferes’ with the detection of the element of interest. This interference usually produces high detection limits for elements to be determined. To improve detection, the element(s) of interest is chemically separated from the matrix-after the irradiation, but prior to counting, for NIRR-1 the limit of detection was determined for some elements by (Jonah *et al*, in 2006) most of which were equally analyzed in this work. The gamma ray measurements were carried out using a horizontal dip-stick High- Purity Germanium (HPGe) detector with a relative efficiency of 10% at 1332.5 KeV gamma ray line. The certified reference material IAEA-soil 7 was used to determine the calibration factors except Au, Cl, Cu, and In for which standard were prepared in-house. For short irradiation regimes designated with irradiation procedure S1, first round of count source-detector geometry of 5cm was used while for the second count designated with irradiation procedure S2, source-detector geometry of 1cm was used for

counting the irradiated samples as indicated in Table 3.2a. For the long irradiation designated with L the source-detector geometry was 1cm. The neutron flux of 5×10^{11} n/cm² s was used for biological materials analyzed using NIRR-1. Table 3.2b shows the values of nuclear data and limit of detection for the elements of interest using the above measurement conditions.

Table: 3.2a: Irradiation and Measuring Regimes for NIRR-1

| Neutron flux irradiation channel | Procedure | T _{irr} | T _d | T _m | Activation Products |
|---|-----------|------------------|----------------|----------------|--|
| 1x10 ¹¹ n/cm ² s/outer irradiation channels (B4, A2) | S1 | 2min | 2– 15min | 10min | ²⁸ Al, ²⁵ Mg, ³⁸ Cl, ⁴⁹ Ca, ⁶⁶ Cu, ⁵¹ Ti, ⁵² V, ^{116m} In |
| 5x10 ¹¹ n/cm ² s/outer irradiation channels (B1.B2,A3,A1) | S2 | | 3 – 4h | 10min | ²⁴ Na, ⁴² K, ¹⁶⁵ Dy, ⁵⁶ Mn, ^{152m} Eu |
| | L1 | 6h | 4 – 5d | 30min | ²⁴ Na, ⁴¹ K, ⁷⁶ As, ⁸⁸ Br, ¹⁴¹ La, ¹⁵³ Sm, ¹⁹⁸ Au, ²³⁹ Np(U), ⁷² Ga, ¹²² Sb |
| | L2 | | 10 -15d | 60min | ⁴⁶ Sc, ¹⁴¹ Ce, ⁶⁰ Co, ⁵⁸ Cr, ¹³⁴ Cs, ¹⁵² Eu, ¹⁷⁷ Lu, ¹⁵¹ Ba, ⁸⁸ Rb, ¹⁸⁸ Ta, ¹⁶⁰ Tb, ¹⁷⁵ Yb, ²³³ Pa(Th), ⁶⁵ Zn, ⁵⁹ Fe, ¹⁸⁸ Hf |

Source: Jonah, *et al* (2006): Standardization of NIRR – Irradiation and counting facilities for INAA

Table 3.2b: Limits of Detection for NIRR-1

| Target Isotope | Limit of Detection (LOD) ppm | Target Isotope | Limit of Detection (LOD) ppm |
|----------------|------------------------------|----------------|------------------------------|
| Au | 0.02 | V | 15 |
| Sm, Lu | 0.1 | Al | 17 |
| Sc, La | 0.2 | Cr | 23 |
| In, Sb | 0.5 | Rb | 30 |
| Eu | 0.6 | Na | 40 |
| Dy | 0.7 | Zn | 120 |
| Mn, Yb | 0.9 | Cu | 172 |
| Ga, Ta | 1.0 | Ba | 264 |
| Tb, Hb | 1.1 | Fe | 829 |
| As, Th | 1.2 | K | 2400 |
| U | 1.5 | Ti | 2500 |
| Cs | 1.7 | Cl | 2900 |

| | | | |
|---------------|------------|-----------|-------------|
| Br, Co | 3.0 | Ca | 6600 |
| Ce | 14 | Mg | 7250 |

Condition: HPGe-detector, with efficiency of 10% at 1332.5 KeV and neutron flux of $5 \times 10^{11} \text{n/cm}^2 \text{ s}$

Source: Source: Jonah, *et al*, (2006): Standardization of NIRR – Irradiation and counting facilities for INAA

3.4.1 Atomic Absorption Spectrometry (AAS)

This is an analytical technique used to determine the presence of and concentration of metal ions in liquid samples. The instrument used for this determination of metal ions and their concentration is known as Atomic Absorption Spectrophotometer.

3.4.2 Theory of AAS

The energy level at which an atom exists is referred to as its state. Under normal conditions, atoms exist in their most stable state called ground state. Although it is difficult to measure the precise energy state for an atom, the changes in its energy relative to its ground state can be measured. Certain process can change the energy state of an atom. For example, adding thermal energy can cause an atom to increase to a higher energy state called excited state.

The laws of quantum mechanics suggest that atoms increase in their energy levels directly from one state to another without going through intermediates a process known as transition. The transition from one state to another requires some form of energy input ΔE ($\Delta E = E_2 - E_1 : E = \frac{hc}{\lambda}$) which is absorbed by the atom. When this energy absorption takes place in the presence of ultraviolet light, some of that light will be absorbed and this occurs at a specific wavelength. Hence each element in the periodic table will have a specific ΔE that will absorb specific wavelength of UV light. The relationship between the energy transition and the wavelength λ can be describe as

$$\Delta E = \frac{hc}{\lambda} \text{ where } h \text{ is Planck's constant.}$$

Atomic absorption uses this relationship to determine the presence of a specific element based on absorption in a specific wavelength.

The absorption spectroscopy and the atomic emission spectroscopy are used to determine the concentration of an element in solution form. For atomic absorption spectroscopy, absorbance = $-\log(I_t/I_0)$: I_t = transmitted radiation, I_0 = incident radiation while for atomic emission spectroscopy, transmission = $-\log(I_0/I_t)$: I_0 = intensity of radiation that reach the detector in the absence of sample, I_t = intensity of the radiation that reaches the detector in the presence of sample. The linear relationship between absorbance and concentration of an absorbing species is given as Absorbance = $\epsilon \cdot c \cdot d$ where ϵ is the wavelength-dependent molar absorptivity coefficient

. Specific lamp is used to generate light for a target metal. The lamp is aligned such that the beam crosses the hottest path of the flame and travel into a detector. The detector then measures the intensity of light as absorption which is shown on readout by a data system. The measure of the absorbance of a particular metal ion curve is then constructed. The absorbance value of a standard are plotted against concentration to give a required calibration curve. The concentration of the metal of interest is then obtained from the calibration curve by extrapolation

3.4.3 Principle of Atomic Absorption Spectrometer

The sample is atomized at a very high temperature (2500°C – 3000°C) so that they can only absorb the energy of light at discrete energy levels according to the excitations of electrons. When this light is absorbed it is missing from the continuous spectra of the

electromagnetic radiation; a black line appears in the absorption spectrum of the atom and no vibration or rotation energy levels that would widen the lines. As a result of absorption, the intensity of light decreases, this is proportional to the number of the examined atoms being present. That makes very sensitive quantitative measurements possible.

To produce the proper monochromatic light necessary for the AAS, hollow cathode lamps are used which are made up of the metal under investigation (or its alloy) that means that different lamps are used for the determination of each element. The anode is made of tungsten and the electrodes are surrounded by noble gases. At high voltage the cathode produces electrons that speeding up in the electric field cause the ionization of noble gas atoms. These high-speed noble gas ions bombard the cathode and therefore sputtering occurs, dislodging atoms from the surface of cathode. These free atoms are excited by the high-speed electrons and then emit the line spectrum characteristic of the particular element.

3.4.4. Instrumentation for Atomic Absorption Spectrometer

In atomic absorption Spectrophotometry only very small number of the atoms in the flame is actually present in an excited state at any given instant. Thus there are a large percentage of atoms that are in the ground state and available to be excited by some other means, such as a beam of light from a light source. Atomic absorption takes advantage of this fact and uses a light beam to excite these ground state atoms in the flame. Thus atomic absorption spectrometry measured the absorbed light by these ground state atoms and relates it to concentration. Figure 4 show the arrangement for the connection of atomic absorption spectrometry.

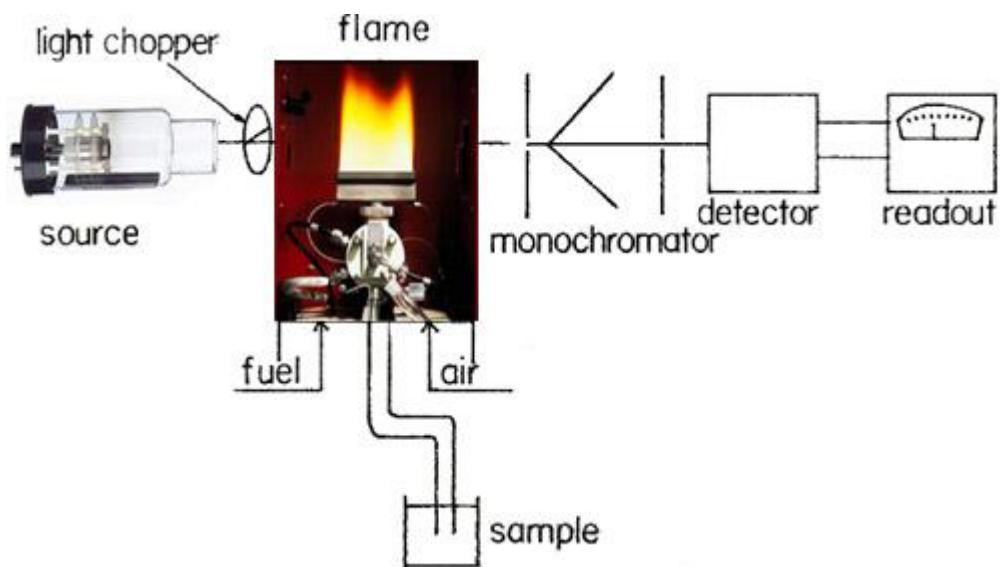


Fig.4: Schematic diagram of Atomic Absorption Spectrometry.

The light source, called a hollow cathode tube is a lamp that emits exactly the wavelength required for the analysis (without the use of monochromator). The light is directed at the flame containing the sample, which is aspirated by the same method as flame photometry. The flame is typically wide giving a reasonable long path-length for detecting small concentrations of atoms in the flame. The light beam then enters the monochromator, which is tuned to a wavelength that is absorbed by the sample. The detector measures the light intensity, which after adjusting for the blank, is output to the readout

3.5.1 Sampling and Sample Preparation for Vegetable Samples

Fresh vegetable leaves of Amaranthus (*Amaranthus tricolor*), Guinea Sorrel (*Hibiscus sabdariffa*), Okro (*Abelmechus esculentum*), Lettuce (*Lactuca sativa*), Tomato (*Lycopersicon esculentum*), Ben oil (*Moringa oleifera*), and water leaf (*Talinum triangulare*) cultivated through irrigation during dry season at various sites in various

farms along the bank of river Ngadda, Alau Dam and Gongulon farming areas were collected in the dry season between the months of January to June. These vegetables were collected directly on the farms with the permission of farm owners. It is worthy to note that the farms cultivated during dry season through irrigation were normally separated into roughly few square meters such that distribution of water flow from the main pipe were made with ease. Because of the above mentioned reason, on each plot of farm, samples were collected at five different positions; four at a point near the edges and one at the centre and this constitute a site. The edible parts of the vegetables were hand- picked and kept in a clean black polyethylene bags and then adequately labeled for easy identification. During each collection, samples were collected from different plots of farm lands but from the same area using ordinate obtained from Global Positioning System (GPS) to maintain consistency in the sample collection position. The fresh vegetables were then taken to herbarium laboratory in Biology Department of Ahmadu Bello University, Zaria for identification. They were then taken to laboratory where they were thoroughly washed with running tap water and properly rinsed with double distilled water to remove any airborne pollutants. The moisture and water droplets were removed with the help of blotting papers. The vegetables were then air dried and oven dried at low temperature and there after grounded and sieved to required particle size using a sieve that were pre-cleaned. The sample was then put in a sample bottle, labeled and caped. The samples were then taken to Centre for Energy Research Training (CERT) Ahmadu Bello University, Zaria for possible further preparation and analysis. The codes assigned to the samples for easy identification during and after irradiation is as represented in Table 3.3.

Table 3.3: Field Identification Codes for Vegetable Samples

| Personal/CERT Code | Name of Vegetable | Description of Site |
|--------------------------------|--|--|
| A1, B1, C1, D1, F1, H1, | A = Amaranthus (<i>Amaranthus tricolor</i>) B = Lettuce (<i>Lactuca sativa</i>) C = Okro (<i>Abelmechus esculentum</i>) D= GuineaSorrel (<i>Hibiscus sabdariffa</i>) E = Tomato (<i>Lycopersicon esculentum</i>) F = Water leaf (<i>Talinum Triangulare</i>) H= Moringa oleifera (<i>Moringa oleifera</i>) | Gongulon farming site, after old Maiduguri |
| A2, B2, C2, D2, F2 | A = Amaranthus (<i>Amaranthus tricolor</i>) B = Lettuce (<i>Lactuca sativa</i>) C = Okro (<i>Abelmechus esculentum</i>) D = Guinea Sorrel (<i>Hibiscus sabdariffa</i>) F = Water leaf (<i>Talinum Triangulare</i>) | Jere farming site, behind College of Agriculture |
| A3, B3, C3, D3, F3, H3 | A = Amaranthus (<i>Amaranthus tricolor</i>) B = Lettuce (<i>Lactuca sativa</i>) C = Okro (<i>Abelmechus esculentum</i>) D = Guinea Sorrel (<i>Hibiscus sabdariffa</i>) F = Water leaf (<i>Talinum Triangulare</i>) H = Moringa oleifera (<i>Moringa oleifera</i>) | Farming site by the Abattoir |
| A4, B4, C4, D4, H4 | A = Amaranthus (<i>Amaranthus tricolor</i>) B = Lettuce (<i>Lactuca sativa</i>) C = Okro (<i>Abelmechus esculentum</i>) D = Guinea Sorre (<i>Hibiscus sabdariffa</i>) H = Moringa oleifera (<i>Moringa oleifera</i>) | Shukwari/Gomboru farming site |
| C5, D5, E5 | C = Okro (<i>Abelmechus esculentum</i>) D = Guinea Sorrel (<i>Hibiscus sabdariffa</i>) E = Tomato (<i>Lycopersicon esculentum</i>) | Alau Dam farming site near water treatment discharge point just by the outlet of the Dam |
| C6, D6, E6 | C = Okro (<i>Abelmechus esculentum</i>) | Alau Dam farming site near the |

D = Guinea Sorrel (*Hibiscus sabdariffa*) main water body
E = Tomato (*Lycopersicon esculentum*)

3.5.2 Sampling and Sample Preparation for Soil Samples

Soil samples were collected on the farms where vegetables were cultivated and specifically on the same plots and in the same procedure of collecting the vegetables, i.e. where the vegetables were collected, the soil samples were collected close to it. Surface scrapping of the soil were carried out at each point of collection so as to prevent accommodation of extraneous materials along with the samples collected, and thereafter soils (0 – 20cm) were collected at five different points, four near the edges of the plots and one at the centre of the plot to constitute a homogenate sampling point. Hand driven auger was used to collect the soil samples throughout the sampling period. The soils were kept in a pre-clean black polyethylene bags and well-labeled for identification before they were transported to the laboratory. The soil samples were then allowed to dry under ambient temperature and thereafter oven dried at 70 – 80 °C. Agate mortar and pestle previously properly cleaned with dilute HCl were used to ground the soil and then sieved through a 200 µm stainless steel mesh wire. The soils were packed in sample bottles and taken to the laboratory at Centre for Energy Research and Training, Ahmadu Bello University Zaria for further preparation for neutron activation analysis. The codes assigned to the samples for easy identification during and after irradiation is as indicated in the Table 3.4

Table 3.4: Field Identification Codes for Soil Samples

| Personal/CERT Code | Description of Site |
|---------------------------|---|
| S1 | Gongulon farming site, off old Maiduguri |
| S2 | Jere farming site, behind College of Agriculture on right flank of River Ngadda |
| S3 | Jere farming site behind College of Agriculture, on left flank of River Ngadda |
| S4 | Farming site by abattoir on the right flank of River Ngadda |
| S5 | Farming site by the Abattoir on the left flank of River Ngadda |
| S6 | Farming site by Shukwari Ward |
| S8 | Farming site by Gomboru Market, downside |
| S9 | Farming site, adjacent Gomboru market |
| S10 | Farm site between Custom bridge and Lagos bridge |
| S11 | Farm site around Galtimari area |
| S12 | Farm site off Giwa barrack, downside of Alau Dam |
| S13 | Farm site around Alau Dam, near water treatment discharge point |
| S14 | Farm site around Alau Dam, near the main water body |
| S0 | Control site, off Alau Jere, an isolated area |

3.5.3 Sampling and Sample Preparation for Sediment Samples.

Sediment samples were collected at various points around the irrigated farmlands i.e around the points where pipe were laid down and generators were fixed when irrigation is to take place The sediments were collected by gently scooping the sediments with clean plastic containers into a clean black polyethylene bags The sediments samples were then

properly sealed and adequately labeled and transported to laboratory where they were first exposed to stream of air to reduce the moisture content and thereafter oven dried at 70°C - 80°C for several hours. Samples were grounded using pestle and agate mortar that were previously cleaned with dilute acid and sieved through a 200µm stainless steel mesh wire. These were packed in sample bottles and taken to Centre for Energy Research and Training, Ahmadu Bello University Zaria for further preparation for neutron activation analysis. The codes assigned to the samples for easy identification during and after irradiation is as indicated in Table 3.5.

Table 3.5: Field Identification Codes for Sediment Samples

| Personal/CERT Code | Description of Site |
|---------------------------|--|
| SS1 | Sediment at Gongulon stream point, off old Maiduguri |
| SS2 | Sediment at Jere stream point before College of Agriculture |
| SS3 | Sediment of the stream by the Abattoir |
| SS4 | Sediment of the stream by Shukwari Ward |
| SS5 | Sediment of the stream by Gomboru Market, at Custom Area |
| SS6 | Sediment of the stream between Custom and Lagos bridge |
| SS8 | Sediment of the stream around Galtimari area |
| SS9 | Sediment around Alau Dam, near water treatment discharge point |
| SS10 | Sediment at Alau Dam, near the main water body |

3.5.4. Sampling and Sample Preparation for Water Samples.

Samples were collected from Alau Dam, and at various points along the bank of river Ngadda where farming activities are carried out at the time of sampling. The water samples were collected using a 1.5 litre polyethylene bottles from the body of the stream at various irrigation points near where suction side of the pump were used to draw the water used for

irrigation. Each container to be used for sampling the water was washed and rinsed with the water at the sampling point three or four times before collection. The water used in rinsing the bottles was disposed outside the water body so that it does not mix with the water to be sampled. The sample bottle was held by the base and plunged below the surface. It was then turned slowly upward and the mouth was directed towards the water current where there was current or else moved slowly away from the hand. Precaution was taken to avoid contact with the bank or stream bed. The bottles were filled to the top and Analar grade Concentrated HCl was added in the ratio of 1ml: 1litre and then tightly sealed with the cap. A baseline sample was collected at point before the stream transcends the Metropolis. Samples were adequately labeled and stored in a cooler containing ice blocks and then transported to National Research Institute for Chemical Technology, Zaria for further preparation and analysis. The codes assigned to the samples for easy identification during and after irradiation was as indicated in Table 3.6

Table 3. 6: Field Identification Codes for Water Samples

| Personal/NARICT Code | Description Site |
|----------------------|--|
| H1 | Gongulon stream point, off old Maiduguri |
| H2 | Jere stream point, before College of Agriculture |
| H3 | Stream point behind College of Agriculture, |
| H4 | Stream point by the Abattoir |
| H5 | Stream point by Shukwari Ward |
| H6 | Stream point by Gomboru Market, downside of the market |
| H7 | Stream point, adjacent Gomboru market |
| H8 | Stream point by Custom bridge |
| H9 | Stream point between Custom bridge and Lagos bridge |
| H10 | Stream point by new G.R.A |
| H11 | Downside of Alau Dam |
| H12 | Alau Dam treatment plant discharge point |
| H13 | Alau Dam main water body |

3.6.1 Sample Preparation for Neutron Irradiation.

Polyethene bags were sterilized by putting them in dilute acid solution for twenty four (24) hours and then rinsed with bi-distilled water. In the same manner forceps and spatulas to be used were sterilized. An analytical weighing balance METLER 240 was checked to ensure that its centre of gravity was at the right position suggesting that it is in good order before connecting to the power source and putting the power on. Sterilized hand gloves was put on and a sterilized forceps was used to pick a new uncontaminated filter paper which was placed on top of the analytical weighing balance and the sterilized polyethene bag was put on the top of the filter paper to avoid it being contaminated by any previously weighed material and the reading was adjusted to zero setting. The bag was then removed from the balance and 200–250g of the vegetable sample which is the recommended quantity for biological sample was put inside the bag and it was weighed again to reaffirm the weight. The polythene bag containing the sample was then blown with a sealer blower and then gently heated with the warm air from the blower after which it was sealed up by folding it with forceps. It was then put inside a vial and some cotton wool was placed on top of the sample to suck away any leak of the sample. The vial was then capped and sealed with cellotape. Standard Reference Material (SRM) NIST 1573a (tomato leaves) which is a direct representative of the vegetable sample was prepared and put in the same type of vial and underwent the same preparation protocol with that of the sample and then irradiated simultaneously.

For the soil and sediment samples, the same procedure of sterilization of the equipment to be used as container and for measuring the sample was carried out. The sample of interest and the standard must also be of the same matrix because if the element in the sample becomes radioactive besides the element of interest, the background noise

may be too high to determine the desired element at low level. The equipment underwent the same setting of the centre of gravity, weighing of the empty polyethene bags were done followed by weighing (150 –200)g of the soil or sediment sample which is the recommended quantity for geological sample was put inside the polyethene and then blown with the sealer blower so that the warm air from the blower gently heat up the polyethene and then it was sealed up by folding it with the sterilized forceps. A filter paper was put on top of the balance before the polyethene containing the soil or sediment sample was put on top so as to avoid contamination of the sample with that which was weighed previously and the sample was weighed. The sample was then put in another sterilized polyethene bag and then put inside a vial after which cotton wool was put on top of the sample to suck away any leak that may occur from the sample. The vial was then covered properly before sealing it with a cellotape. Standard reference material (SRM) NIST 1633b (coal fly ash) which is a direct representative of geological nature was also prepared as the unknown samples and put in the same type of vial with that of the sample and then irradiated simultaneously.

CHAPTER FOUR

RESULTS

4.1.1 Quality Control of the Neutron Activation Analysis Data

In assessing quality for neutron activation analysis, there is the necessary condition that needs to be adhered to in order to make the result acceptable in line with the laid down standard. In the relative method of analysis, sample of interest and standard were irradiated simultaneously under the same condition i.e the standard were subjected to the same condition of irradiation and counting/measurement as the unknown sample under investigation. For soil and sediment samples the standard used was coal fly ash (NIST 1633b) while for the biological samples the standard used was tomato leave (NIST 1573a). The sample and the standard must have the same matrix, geometry for irradiation position and composition because if an element in the sample becomes radioactive besides the element of interest, the background noise may be too high to determine the desired element at low level. Tables 4.7 and 4.8 show standard values and the ones obtained from this work as an index of quality assurance in terms of the equipment capability, the adherence to the experimental procedures like samples preparation and the experimental know-how of analyst

The concentration of elements in geological and biological samples obtained from Alau Dam and at various sites along the bank of river Ngadda in Maiduguri, Borno State were determined using neutron activation analysis (NAA) technique. Relative method was employed for the determination process, that is, the samples were irradiated together with standard reference materials under the same scheme of irradiation and counting for the technique.

Table 4.1: Quality Control of Data Obtained with NIST 1573a (Tomato Leaves)

| Element | Certified value | This work | Variance (error) % |
|----------------|------------------------|------------------|---------------------------|
| Al | 59800 ± 12 | 59800 ± 17 | - |
| As | 0.112 ± 0.004 | BDL | - |
| Ba | 63 | BDL | - |
| Br | 1300 | 1276 ± 5 | 0.0184 |
| Ca | 50500 ± 0.09 | 50500 ± 1162 | - |
| Co | 0.57 ± 0.02 | 1.25 ± 0.07 | 1.19 |
| Cr | 1.99 ± 0.06 | BDL | - |
| Cs | 0.053 | BDL | - |
| Cu | 4.70 ± 0.14 | BDL | - |
| Fe | 368 ± 7 | 455 ± 60 | 0.236 |
| K | 27000 ± 0.05 | 30110 ± 1927 | 0.115 |
| La | 2.3 | 2.57 ± 0.22 | 0.117 |
| Mn | 246 ± 8 | 246 ± 1 | - |
| Element | Certified value | This work | Variance (error) % |
| Rb | 14.89 ± 0.27 | BDL | - |
| Sb | 16000 ± 0.0075 | BDL | - |
| Se | 101.2 ± 2.6 | 10500 ± 1806 | 0.4046 |
| Sm | 16.100 ± 0.06 | 0.26100 ± 31797 | 0.052 |
| Tb | 50.12 | BDL ± 6 | - 0.10 |
| Cs | 10.035 | BDL | - 0.045 |
| Dy | 10.835 ± 0.01 | 0.87 ± 0.045 | 0.005 |
| Zn | 30.9 ± 0.7 | 25.6 ± 6.2 | 0.171 |

Table 4.2: Quality Control of Data Obtained with NIST 1633b (Coal fly ash)

| | | | |
|----|--------------|--------------|-------|
| Eu | 4.1 | 4.8 | 0.17 |
| Fe | 77800 ± 548 | 77800 ± 0.23 | - |
| Hf | 6.8 | 8.6 ± 0.5 | 0.26 |
| K | 19500 ± 0.03 | 19320 ± 270 | 0.009 |
| La | 94 | 90.2 ± 0.2 | 0.040 |
| Mg | 4820 ± 0.008 | 4820 ± 665 | - |
| Mn | 131.8 ± 1.7 | 132 ± 1 | 0.001 |
| Na | 2010 | 1879±6 | 0.065 |
| Rb | 140 | 118 ± 8 | 0.157 |
| Sb | 6 | 7.3 ± 0.1 | 0.216 |
| Sc | 41 | 39.6 ± 0.2 | 0.034 |
| Th | 25.7 ± 1.3 | 26.3 ± 0.4 | 0.023 |
| U | 8.79±0.36 | 12.3 ± 0.4 | 0.399 |
| V | 295.7 ± 3.6 | 296 ± 9 | 0.001 |
| Yb | 7.6 | 10.6 ± 0.3 | 0.394 |
| Zn | 210 | 270 ± 12 | 0.285 |

The values (result) obtained in this study for the reference standard was compared with certified values as shown in Tables 4.1 and 4.2. The table clearly show that majority of the elements investigated were in excellent agreement with the certified (literature) values of the standard with maximum variance error of 0.46 in As, 0.39 in U, and Yb and 0.28 in Zn for geological samples and maximum deviation error of 0.40 in Sc, 0.23 in Fe, 0.19 in Co and 0.17 in Zn for biological samples. It was also observed that the accuracy recorded varied with either geological or biological matrix, for example excellent agreement was recorded for Al, Ca, Dy, and Mg in geological standard reference material (coal fly ash) while excellent agreement was recorded in Al, Ca, Cl, Mg and Mn in biological standard reference material (tomato leaves). However, there were discrepancies in the elements As, Yb, Hf, for geological sample and Fe, Co, Zn, La and K for biological sample. These discrepancies could be due to high concentrations of the elements in question

Having established the quality of the result obtained for standard materials of similar matrices with the samples under investigation, the results of the analyses of the sample under investigation namely soil, sediment, and water are hereby presented in Tables 4.3a, 4.3b; 4.4a, 4.4b and 4.5 respectively while the result for the elements determined in vegetable samples were presented in Tables 4.17 to 4.29. The result for water were obtained using Atomic Absorption Spectrophotometer hence the equipment was standardized for each element of interest before running the sample and the result is as presented in Table 4.5.

Table 4.3a: Concentration of Elements in Soil Samples Determined by INAA

| Sam-ple | Al | As | Ba | Br | Ca | Cr | Cs | Co | Dy | Eu | Fe | Hf | K | La | Lu |
|---------|------------|-----------|---------|-----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|------------|
| S1 | 34470±241 | 0.5±0.10 | 976±42 | BDL | 3010±587 | 35±3.0 | 2.4±0.4 | 3.2±0.3 | 4.6±0.3 | 1.2±0.2 | 10420±240 | 54±1.0 | 32590±036 | 63.1±0.3 | - |
| S2 | 32520±293 | BDL | 686±31 | 0.16±0.05 | 1982±484 | 29±2.0 | BDL | 4.04±0.2 | 4.6±0.3 | 0.9±0.1 | 10150±213 | 28.56±0.3 | 22650±861 | 5.1±0.1 | 0.46±0.02 |
| S3 | 3150±504 | 0.89±0.19 | 876±34 | 5.02±0.29 | BDL | 47±3.0 | BDL | 3.8±0.3 | 4.9±0.4 | 1.34±0.2 | 9982±294 | 53.4±0.5 | 31790±699 | 62.1±0.3 | 0.74±0.03 |
| S4 | 29550±355 | 0.6±0.20 | 297±35 | 1.9±0.30 | BDL | 29±3.0 | BDL | 2.8±0.3 | 4.3±0.3 | 1.0±0.1 | 9529±229 | 49.0±0.5 | 35020±420 | 43.7±0.2 | 0.74±0.03 |
| S5 | 43830±307 | 0.63±0.02 | 1145±41 | 0.57±0.08 | 3856±702 | 35±3.0 | BDL | 3.8±0.3 | 5.3±0.3 | 1.57±0.2 | 10540±211 | 56±1.0 | 38680±774 | 54.4±0.3 | 0.86±0.03 |
| S6 | 40950±450 | BDL | 813±37 | BDL | 2523±595 | 24±2.0 | BDL | 5.0±0.3 | 4.8±0.3 | BDL | 12240±208 | 33.3±0.4 | 13830±221 | 31.70±0.2 | 2.0±0.10 |
| S8 | 27760±389 | BDL | 916±37 | BDL | BDL | 42±3.0 | 1.7±0.3 | 4.8±0.3 | 3.3±0.3 | 1.3±0.2 | 13210±238 | 43.6±0.5 | BDL | 53.6±0.3 | 0.66±0.02 |
| S9 | 33780±1262 | BDL | 851±37 | 0.5±0.10 | 5080±965 | 43±3.0 | BDL | 3.3±0.4 | 6.4±0.4 | BDL | 994±023 | 62±1.0 | 29920±419 | 72±0.3 | 0.84±0.03 |
| S10 | 28970±464 | 1.0±0.20 | 721±37 | 0.4±0.10 | 2881±671 | 16±2.0 | 1.3±0.3 | 2.7±0.3 | 3.1±0.3 | BDL | 6771±182 | 18.9±0.3 | 29210±672 | 25.7±0.2 | 0.32±0.02 |
| S11 | 30680±153 | BDL | 421±25 | BDL | BDL | 18±2.0 | 1.0±0.3 | 1.6±0.3 | 4.3±0.4 | BDL | 3894±183 | 21.6±0.4 | 13130±118 | 28.0±0.1 | 0.36±0.02 |
| S12 | 43390±694 | BDL | 801±34 | 1.6±s0.20 | 3318±956 | 22±2.0 | 1.63±0.4 | 3.0±0.3 | 4.1±0.6 | 1.2±0.1 | 8668±191 | 36.0±0.4 | 22923±263 | 38.6±0.2 | 2.03±0.08 |
| S13 | 34290±377 | 0.46±0.12 | 1074±34 | 2.7±0.30 | BDL | 31.4±2.2 | BDL | 2.61±0.2 | 4.07±0.3 | 0.94±0.9 | 8766±210 | 37.7±0.4 | 29490±116 | 37.1±0.2 | 0.60±0.03 |
| S14 | 41290±289 | | 869±36 | - | BDL | 29±2.0 | 1.8±0.3 | 5.3±0.4 | 4.5±0.4 | | 13520±230 | 4.14±0.0 | 27810±014 | 36.7±0.2 | 2.01±0.09 |
| S0 | 35430±283 | BDL | 680±33 | BDL | BDL | 32±0.2 | 1.6±0.2 | 3.2±0.2 | 4.8±0.3 | 1.14±0.1 | 9678±174 | 38.1±0.4 | 22430±270 | 39.5±0.2 | 2.287±0.09 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.3b Concentration of Elements in Soil Samples Determined by INAA

| Sam- ple | Mg | Mn | Na | Rb | Sb | Sc | Sm | Ta | Ti | Th | U | V | Yb | Zn |
|-------------|-----------|------------|---------|-------|-----------|-----------|-----------|----------|----------|-----------|----------|---------|----------|---------|
| S1 | 2414±652 | 228..5±1.4 | 4377±09 | 107±6 | BDL | 4.56±0.05 | 8.14±0.03 | 2.4±0.2 | 2243±278 | 38.2±0.3 | 4.8±0.3 | 22±2 | 4.1±0.2 | 54±6 |
| S2 | BDL | 230±1.0 | 3023±01 | 81±4 | BDL | 3.9±0.10 | 0.95±0.01 | 1.5±0.2 | 3024±194 | 16.1±0.2 | 0.9±0.1 | 22±2 | 2.8±0.1 | 24±7 |
| S3 | BDL | 342±2.0 | 4438±13 | BDL | 0.26±0.06 | 4.36±0.05 | 8.55±0.04 | 1.89±0.2 | 2754±248 | 30.64±0.3 | 5.2±0.3 | 23.6±3 | 3.94±0.1 | 46.56±5 |
| S4 | BDL | 184±1.0 | 4616±09 | 109±5 | BDL | 3.81±0.05 | 5.72±0.03 | 2.61±0.3 | 2731±254 | 21.2±0.3 | 4.93±0.0 | 16.8±2 | 4.79±0.2 | 145±7 |
| S5 | BDL | 224±2.0 | 4807±01 | 129±6 | BDL | 5.51±0.06 | 7.89±0.04 | BDL | BDL | 37.0±0.3 | 6.29±0.3 | 26.5±3 | 4.65±0.1 | 38.3±5 |
| S6 | 5161±1372 | 329±2.0 | 1966±06 | 86±4 | 1.25±0.04 | 3.98±0.05 | 5.92±0.03 | 1.16±0.1 | 2834±210 | 15.5±0.2 | 3.3±0.3 | 26.3±3 | 3.4±0.1 | 42.05±6 |
| S8 | BDL | 199.8±1.4 | 3887±12 | 124±1 | 0.18±0.04 | 5.0±0.10 | BDL | 2.42±0.2 | 2857±209 | 23.1±0.3 | 4.3±0.3 | 18±3 | 5.17±0.2 | BDL |
| S9 | 4948±1262 | 447.2±2.2 | 3992±08 | 106±5 | BDL | 4.42±0.06 | 9.34±0.04 | 2.5±0.2 | 5725±361 | 38.03±0.4 | 6.2±0.3 | 26±3 | 6.1±0.2 | 39±6 |
| S10 | 2266±580 | 189±2.0 | 3730±15 | 92±5 | 0.38±0.05 | 2.22±0.04 | 3.78±0.03 | 1.17±0.2 | 1872±266 | 8.23±0.2 | 2.8±0.2 | 14.16±2 | 2.13±0.2 | 142±7 |
| S11 | BDL | 213±2.0 | 1773±04 | 39±4 | BDL | 1.73±0.03 | 3.91±0.02 | BDL | 3484±244 | 15.23±0.3 | 2.26±0.2 | 15.3±2 | 2.79±0.1 | 51±8 |
| S12 | BDL | 183±2.0 | 3855±08 | 98±5 | 14.2±3.50 | 4.26±0.04 | 7.3±0.04 | BDL | 3048±372 | 19.3±0.2 | 4.8±0.3 | 27±3 | 3.9±0.2 | BDL |
| S13 | BDL | 152±1.0 | 5231±10 | 111±5 | 0.13±0.04 | 4.01±0.05 | 5.04±0.03 | 1.8±0.2 | BDL | 16.8±0.2 | 4.4±0.3 | 22±3. | 4.0±0.1 | 21.8±4 |
| S14 | 2715±795 | 348±2.0 | 4144±08 | BDL | | 4.60±0.06 | 6.9±0.30 | 1.4±0.2 | 3259±231 | 20.9±0.2 | 3.7±0.3 | 29±2 | 4.1±0.2 | 23±5 |
| S0 | BDL | 211±2.0 | 2801±06 | 87±6 | BDL | 4.19±0.05 | 7.01±0.03 | 1.4±0.1 | 3687±202 | 21.5±0.2 | 4.0±0.2 | 28±2 | 4.6±0.2 | 72±6 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.4a: Concentration of Elements in Sediment Samples Determined by INAA

| Sam- ple | Al | As | Ba | Br | Ca | Cr | Cs | Co | Dy | Eu | Fe | Hf | K | La | Lu |
|-------------|-----------|-----|--------|---------|----------|---------|----------|---------|----------|----------|-----------|----------|-----------|-----------|-----------|
| SS1 | 42850±514 | BDL | 898±40 | 1.5±0.9 | BDL | 31±2 | 1.7±0.2 | 4.2±0.3 | 5.3±0.3 | BDL | 1127±214 | 26.4±0.4 | 28280±339 | 34.6±0.2 | 1.4±0.1 |
| SS2 | 4914±064 | BDL | 965±38 | BDL | 2152±602 | 35±2 | 1.9±0.3 | 5.7±0.2 | 5.8±0.4 | 1.1±0.1 | 13530±203 | 31.3±0.4 | 29730±297 | 38.8±0.2 | 1.881±0.1 |
| SS3 | 26460±318 | BDL | 709±33 | BDL | 2179±545 | 27±2 | BDL | 1.8±0.2 | 3.0±0.3 | BDL | 6015±168 | 36.3±0.4 | 23470±258 | 28.05±0.1 | 1.69±0.0 |
| SS4 | 34970±035 | BDL | 859±41 | BDL | BDL | 26±2 | BDL | 2.6±0.3 | 6.3±0.4 | 1.1±0.1 | 7098±185 | 52.9±0.5 | 28080±281 | 44.3±0.2 | 2.15±0.1 |
| SS5 | 35640±463 | BDL | 900±35 | BDL | 2785±657 | 2.0±0 | 1.1±0.2 | 2.6±0.2 | 4.0±0.3 | BDL | 6874±171 | 30.2±0.4 | 29880±298 | 29.4±0.2 | 1.87±0.1 |
| SS6 | 39120±313 | BDL | 818±40 | BDL | 4123±721 | 21±2 | 1.14±0.0 | 3.6±0.1 | 5.0±0.3 | 1.05±0.1 | 8753±162 | 32±4.0 | 27960±004 | 28±3.0 | 1.65±0.0 |
| SS8 | 31750±254 | BDL | 805±40 | BDL | 2374±548 | 44±2 | 1.11±0.0 | 3.0±0.2 | 16.1±0.6 | 1.36±0.0 | 9210±182 | 10.0±0.5 | 25990±005 | 103.3±0.3 | 5.1±0.2 |
| SS9 | 34820±313 | BDL | 716±37 | 2.3±0.6 | 1957±552 | 26.92±2 | 1.1±0.2 | 1.8±0.2 | 4.4±0.3 | BDL | 5949±196 | 47.7±0.5 | 27680±276 | 34.4±0.2 | 2.3±0.1 |
| SS10 | 30680±368 | BDL | 803±32 | | 2244±572 | 17±2 | 1.1±0.2 | 1.9±0.2 | BDL | | 5238±152 | 26.1±0.3 | 13500±189 | 11.7±0.1 | 1.23±0.1 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.4b Concentration of Elements in Sediment samples Determined by INAA

| Sam-ple | Mg | Mn | Na | Rb | Sb | Sc | Sm | Ta | Ti | Th | U | V | Yb | Zn |
|---------|----------|----------|--------|--------|-----------|-----------|-----------|----------|----------|-----------|----------|--------|-----------|----------|
| SS1 | BDL | 201±02 | 4117±8 | 102±5 | BDL | 3.77±0.05 | 6.13±0.03 | BDL | 2496±217 | 16.8±0.3 | 2.5±0.3 | 27±4 | 3.0±0.2 | 118±07 |
| SS2 | BDL | 219±18 | 4587±9 | 107±5 | BDL | 4.74±0.06 | 7.12±0.04 | 1.5±0.1 | 3216±264 | 20.2±0.2 | 3.9±0.3 | 23±4 | 4.1±0.2 | 110±07 |
| SS3 | BDL | 156±01 | 2929±6 | 68.3±3 | BDL | 2.52±0.04 | 4.91±0.03 | 1.22±0.1 | 2234±188 | 18.3±0.3 | 3.2±0.3 | 13.2±0 | 2.7±0.2 | 66.89±01 |
| SS4 | BDL | 220±02 | 3736±7 | 97±5 | BDL | 3.24±0.04 | 7.36±0.03 | 1.8±0.2 | 3403±265 | 23.4±0.3 | 4.1±0.3 | 21±2 | 4.3±0.2 | 68±06 |
| SS5 | BDL | 157.2±01 | 4574±9 | 106±5 | BDL | 2.68±0.04 | 5.25±0.03 | BDL | BDL | 16.7±0.2 | 2.99±0.3 | 21±3 | 3.3±0.2 | BDL |
| SS6 | 300±084 | 218±02 | 4238±5 | 92±5 | 0.45±0.03 | 3.01±0.05 | 5.29±0.01 | 1.46±0.0 | 2534±195 | 17.79±0.0 | 3.50±0.0 | 21±2 | 3.69±0.0 | 175±03 |
| SS8 | 3327±968 | 408±02 | 3354±6 | 83±8 | 0.34±0.06 | 4.39±0.03 | 17.3±1.70 | 2.6±0.1 | 6001±276 | 71±1.0 | 10.4±0.0 | 31±2 | 10.32±0.0 | 155±03 |
| SS9 | 3527±854 | 235±02 | 3401±7 | 76±4 | BDL | 2.79±0.04 | 6.03±0.03 | 1.1±0.1 | 4105±246 | 25.4±0.3 | 4.0±0.3 | 19±3 | 4.1±0.2 | 396±12 |
| S10 | 1207±469 | 160±01 | 1604±5 | 93±4 | BDL | 2.23±0.03 | 3.65±0.02 | 1.2±0.1 | 3107±224 | 21.1±0.2 | 2.7±0.3 | 18±3 | 2.8±0.1 | BDL |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.5: Concentration of Element in Water Samples Determined by AAS

| Sample | Fe | Mn | Zn | Ni | Cd | Pb | Co | Cr | Al | Cu |
|--------|--------|-------|--------|-------|-------|-------|-------|-------|-------|-------|
| H1 | 4.680 | 0.065 | 0.591 | 0.005 | 0.009 | 0.386 | 0.133 | 0.081 | 2.226 | 0.021 |
| H2 | 2.840 | 0.050 | 1.155 | 0.085 | 0.010 | 0.074 | 0.307 | 0.050 | 1.419 | 0.025 |
| H3 | 2.437 | 0.026 | 0.293 | 0.066 | 0.026 | 0.074 | 0.066 | 0.121 | 1.226 | 0.026 |
| H4 | 1.409 | 0.039 | 0.317 | 0.172 | 0.026 | 0.475 | 0.326 | 0.086 | 0.774 | 0.024 |
| H5 | 3.820 | 0.048 | 3.375 | 0.286 | 0.025 | 0.445 | 0.066 | 0.076 | 1.677 | 0.032 |
| H6 | 6.594 | 0.084 | 0.976 | 0.191 | 0.011 | 0.297 | ND | 0.015 | 2.548 | 0.035 |
| H7 | 10.480 | 0.107 | 1.260 | 0.077 | 0.020 | 0.371 | 0.024 | 0.136 | 3.355 | 0.034 |
| H8 | 9.939 | 0.107 | s1.283 | 0.085 | 0.013 | 0.134 | 0.048 | 0.091 | 1.613 | 0.039 |
| H9 | 3.034 | 0.047 | 0.636 | 0.040 | 0.015 | 0.134 | 0.271 | 0.058 | 0.677 | 0.020 |
| H10 | 6.049 | 0.072 | 0.401 | 0.217 | 0.033 | 0.387 | 0.392 | 0.035 | 1.774 | 0.019 |
| H11 | 11.900 | 0.077 | 0.428 | 0.172 | 0.015 | 0.400 | 0.368 | 0.020 | 0.710 | 0.018 |
| H12 | 0.323 | 0.003 | 0.006 | 0.024 | 0.023 | 0.297 | ND | 0.030 | 0.903 | 0.014 |
| H13 | 0.134 | 0.013 | 0.010 | 0.371 | 0.044 | 0.134 | 0.211 | 0.078 | 0.258 | 0.017 |

ND: Not Detectable

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

4.1.2 Data Handling and Treatment

With the current advancement in instrumentation it is possible to have multi-element determination in a single experiment with high degree of accuracy and effectively reproducible. However, appropriate statistical analysis techniques are required for the evaluation and or interpretation of the results for it to be meaningful (Oladipo, 1987). Fortunately, there are well established techniques of simple descriptive statistics and multi-variate analysis that can be used to evaluate the results obtained. Therefore, in this work simple descriptive statistics will be employed to evaluate the relationships between the elements that exist in the study area, the extent to which trace, minor and major elements have polluted the environment in the study area and the possible sources of these elements in the study area that have effect on the environment.

4.1.3 Assessment of Data for Correlation

Correlation is the relatedness of a variable i.e the degree to which two or more variables is related and changes together and correlation coefficient is a number or function indicating the degree of correlation between two variables. The essence of subjecting the various concentrations of elements obtained from the various sites to Pearson correlation analysis are to determine the degree of input of the elements between sites and inter-elemental association from the various sites. In this work attention will be given to inter-elemental association from the various sites for those elements with coefficient of correlation at $p \leq 0.05$ for the basic reason of determining the distribution and association value at 95% confidence level. The Pearson correlations analysis data treatment were performed on both soil and sediment samples results obtained from the INAA analysis.

Table 4.6: Correlation (Pearson) of Soil Samples Data

| | Al | As | Ba | Br | Ca | Cr | Cs | Co | Cu | Eu | Fe | Hf | K | La | Lu | Mg | Mn | Na | Rb | Sb | Sc | Sm | Ta | Ti | Th | U | V | Zn | Yb | | |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--|--|
| Al | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| As | .232 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ba | .163 | .096 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Br | .166 | .994 | .106 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ca | .401 | -.258 | .338 | -.292 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cr | -.400 | .008 | .445 | .052 | .155 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cs | .208 | .313 | .049 | .270 | -.100 | -.307 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | |
| Co | .123 | .499 | .401 | .490 | -.005 | .335 | .031 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | |
| Cu | .093 | -.006 | .170 | .003 | .449 | .297 | -.431 | .096 | 1.000 | | | | | | | | | | | | | | | | | | | | | | |
| Eu | .239 | 1.000 | .102 | .994 | -.262 | .010 | .319 | .507 | -.003 | 1.000 | | | | | | | | | | | | | | | | | | | | | |
| Fe | .092 | .369 | .283 | .371 | -.390 | .061 | .234 | .711 | -.363 | .380 | 1.000 | | | | | | | | | | | | | | | | | | | | |
| Hf | -.239 | -.602 | .266 | -.575 | .366 | .545 | -.321 | -.118 | .513 | -.596 | -.208 | 1.000 | | | | | | | | | | | | | | | | | | | |
| K | -.014 | .092 | .160 | .125 | .306 | .138 | -.273 | -.238 | .398 | .085 | -.171 | .303 | 1.000 | | | | | | | | | | | | | | | | | | |
| La | -.232 | -.087 | .397 | -.060 | .243 | .605 | .065 | .055 | .457 | -.084 | -.145 | .751 | .262 | 1.000 | | | | | | | | | | | | | | | | | |
| Lu | .063 | -.061 | .231 | -.086 | .221 | .137 | .520 | -.073 | .041 | -.059 | .119 | .271 | .211 | .342 | 1.000 | | | | | | | | | | | | | | | | |
| Mg | .256 | .218 | .148 | .183 | .524 | .108 | -.030 | .350 | .396 | .206 | -.179 | -.018 | .011 | .207 | .184 | 1.000 | | | | | | | | | | | | | | | |
| Mn | -.149 | .337 | .163 | .347 | .317 | .462 | -.236 | .465 | .699 | .332 | -.199 | .158 | .074 | .423 | -.064 | .708 | 1.000 | | | | | | | | | | | | | | |
| Na | -.063 | .119 | .400 | .167 | .054 | .279 | -.094 | -.114 | .166 | .120 | .060 | .386 | .801 | .430 | .172 | -.221 | -.109 | 1.000 | | | | | | | | | | | | | |
| Rb | .481 | -.581 | .127 | -.621 | .444 | -.227 | -.068 | -.272 | .071 | -.576 | -.151 | .470 | .146 | .089 | .163 | -.026 | -.424 | .234 | 1.000 | | | | | | | | | | | | |
| Sb | .314 | .968 | .095 | .967 | -.186 | -.042 | .372 | .470 | -.038 | .970 | .359 | -.613 | .060 | -.109 | -.081 | .184 | .286 | .104 | -.550 | 1.000 | | | | | | | | | | | |
| Sc | .223 | .162 | .586 | .176 | .182 | .317 | -.023 | .530 | .496 | .178 | .443 | .488 | .313 | .486 | .169 | .010 | .234 | .530 | .258 | .175 | 1.000 | | | | | | | | | | |
| Sm | -.093 | .124 | .447 | .156 | .369 | .766 | -.034 | .219 | .311 | .123 | -.034 | .481 | .234 | .778 | .247 | .335 | .485 | .296 | -.163 | .157 | .303 | 1.000 | | | | | | | | | |
| Ta | -.338 | -.012 | -.109 | .003 | -.164 | .184 | -.045 | .076 | .233 | -.014 | -.011 | .349 | .240 | .335 | .297 | .230 | .243 | .366 | .132 | -.126 | .259 | -.034 | 1.000 | | | | | | | | |
| Ti | -.143 | .106 | -.408 | .090 | .112 | .117 | .140 | .143 | .301 | .107 | -.361 | .013 | -.398 | .177 | -.083 | .408 | .607 | -.470 | -.281 | .132 | -.143 | .120 | .256 | 1.000 | | | | | | | |
| Th | -.057 | -.062 | .446 | -.051 | .401 | .574 | -.022 | .107 | .709 | -.054 | -.104 | .770 | .442 | .839 | .466 | .143 | .438 | .451 | .161 | -.098 | .671 | .619 | .282 | .095 | 1.000 | | | | | | |
| U | .004 | -.080 | .416 | -.045 | .307 | .431 | -.097 | -.008 | .484 | -.076 | -.113 | .729 | .482 | .882 | .136 | .090 | .257 | .642 | .287 | -.056 | .619 | .699 | .201 | -.078 | .762 | 1.000 | | | | | |
| V | .271 | .369 | .646 | .380 | .247 | .553 | .010 | .754 | .313 | .382 | .417 | .162 | -.140 | .357 | -.022 | .266 | .477 | .077 | -.145 | .437 | .658 | .586 | -.149 | .140 | .397 | .360 | 1.000 | | | | |
| Zn | -.309 | -.164 | -.438 | -.173 | -.057 | .063 | -.080 | -.214 | -.417 | -.180 | -.093 | .025 | .127 | .006 | .008 | .046 | -.189 | .019 | .067 | -.252 | -.488 | .062 | .199 | -.034 | -.224 | -.056 | -.520 | 1.000 | | | |
| Yb | .100 | .014 | .201 | .025 | .127 | .327 | -.072 | .150 | .605 | .026 | -.099 | .645 | .188 | .737 | .029 | .116 | .359 | .426 | .328 | .003 | .695 | .389 | .473 | .285 | .704 | .780 | .396 | -.227 | 1.000 | | |

Table 4.7: Correlation (Pearson) of Sediment Samples Data

| | Al | Ba | Ca | Fe | K | Mn | Na | Rb | Ti | Zn | La | Cr | V | Hf | Dy | Eu | Lu | Sc | Sm | Th | U | Yb | Ta | Cs | Co |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Al | 1.000 | | | | | | | | | | | | | | | | | | | | | | | | |
| Ba | -.292 | 1.000 | | | | | | | | | | | | | | | | | | | | | | | |
| Ca | -.137 | -.226 | 1.000 | | | | | | | | | | | | | | | | | | | | | | |
| Fe | -.777 | .239 | .508 | 1.000 | | | | | | | | | | | | | | | | | | | | | |
| K | -.086 | .933 | -.039 | .213 | 1.000 | | | | | | | | | | | | | | | | | | | | |
| Mn | -.011 | -.084 | .060 | .297 | -.173 | 1.000 | | | | | | | | | | | | | | | | | | | |
| Na | -.129 | .877 | .158 | .237 | .959 | -.280 | 1.000 | | | | | | | | | | | | | | | | | | |
| Rb | -.081 | .965 | -.190 | .113 | .985 | -.185 | .928 | 1.000 | | | | | | | | | | | | | | | | | |
| Ti | -.165 | -.178 | -.137 | .298 | -.347 | .897 | -.458 | -.327 | 1.000 | | | | | | | | | | | | | | | | |
| Zn | .036 | -.118 | .235 | .193 | -.168 | .602 | -.106 | -.187 | .683 | 1.000 | | | | | | | | | | | | | | | |
| La | -.027 | -.126 | -.036 | .236 | -.237 | .967 | -.373 | -.234 | .849 | .397 | 1.000 | | | | | | | | | | | | | | |
| Cr | -.322 | -.110 | -.265 | .205 | -.381 | .704 | -.438 | -.313 | .910 | .678 | .656 | 1.000 | | | | | | | | | | | | | |
| V | .152 | .421 | -.177 | .019 | .323 | .775 | .213 | .361 | .588 | .477 | .725 | .490 | 1.000 | | | | | | | | | | | | |
| Hf | -.011 | .021 | -.351 | -.069 | .108 | -.640 | .035 | .110 | -.394 | -.431 | -.625 | -.380 | -.662 | 1.000 | | | | | | | | | | | |
| Dy | -.025 | .395 | .217 | .051 | .567 | -.603 | .596 | .514 | -.839 | -.786 | -.514 | -.893 | -.339 | .256 | 1.000 | | | | | | | | | | |
| Eu | -.369 | .643 | -.119 | .373 | .687 | -.328 | .582 | .662 | -.422 | -.687 | -.239 | -.498 | -.138 | .439 | .762 | 1.000 | | | | | | | | | |
| Lu | .085 | .307 | .365 | .010 | .509 | -.511 | .571 | .440 | -.817 | -.688 | -.437 | -.900 | -.259 | .066 | .970 | .616 | 1.000 | | | | | | | | |
| Sc | -.119 | .461 | .202 | .160 | .619 | -.562 | .630 | .562 | -.780 | -.772 | -.478 | -.845 | -.316 | .293 | .990 | .839 | .939 | 1.000 | | | | | | | |
| Sm | .013 | .378 | .294 | .052 | .550 | -.477 | .586 | .491 | -.779 | -.731 | -.385 | -.857 | -.212 | .068 | .980 | .695 | .991 | .961 | 1.000 | | | | | | |
| Th | -.245 | -.111 | .040 | .312 | -.234 | .420 | -.196 | -.230 | .686 | .884 | .235 | .765 | .210 | -.084 | -.831 | -.540 | -.837 | -.781 | -.857 | 1.000 | | | | | |
| U | .098 | .366 | .297 | .019 | .558 | -.424 | .583 | .495 | -.752 | -.702 | -.338 | -.865 | -.155 | .042 | .966 | .670 | .989 | .943 | .994 | -.863 | 1.000 | | | | |
| Yb | .043 | .329 | .339 | .089 | .526 | -.421 | .552 | .452 | -.738 | -.713 | -.332 | -.863 | -.208 | .073 | .970 | .694 | .987 | .954 | .993 | -.850 | .995 | 1.000 | | | |
| Ta | -.052 | .806 | .037 | .235 | .899 | -.043 | .820 | .865 | -.339 | -.388 | -.021 | -.476 | .353 | -.035 | .714 | .787 | .688 | .758 | .744 | -.527 | .764 | .744 | 1.000 | | |
| Cs | .379 | -.659 | .381 | .032 | -.410 | .121 | -.453 | -.522 | -.007 | -.183 | .176 | -.338 | -.313 | .151 | .125 | -.037 | .192 | .103 | .145 | -.276 | .195 | .248 | -.140 | 1.000 | |
| Co | -.210 | .142 | -.343 | .147 | .186 | -.385 | .029 | .180 | -.309 | -.761 | -.243 | -.403 | -.458 | .754 | .506 | .787 | .319 | .568 | .384 | -.471 | .360 | .406 | .313 | .291 | 1.000 |

4.2.1 Soil Samples Data Correlation:

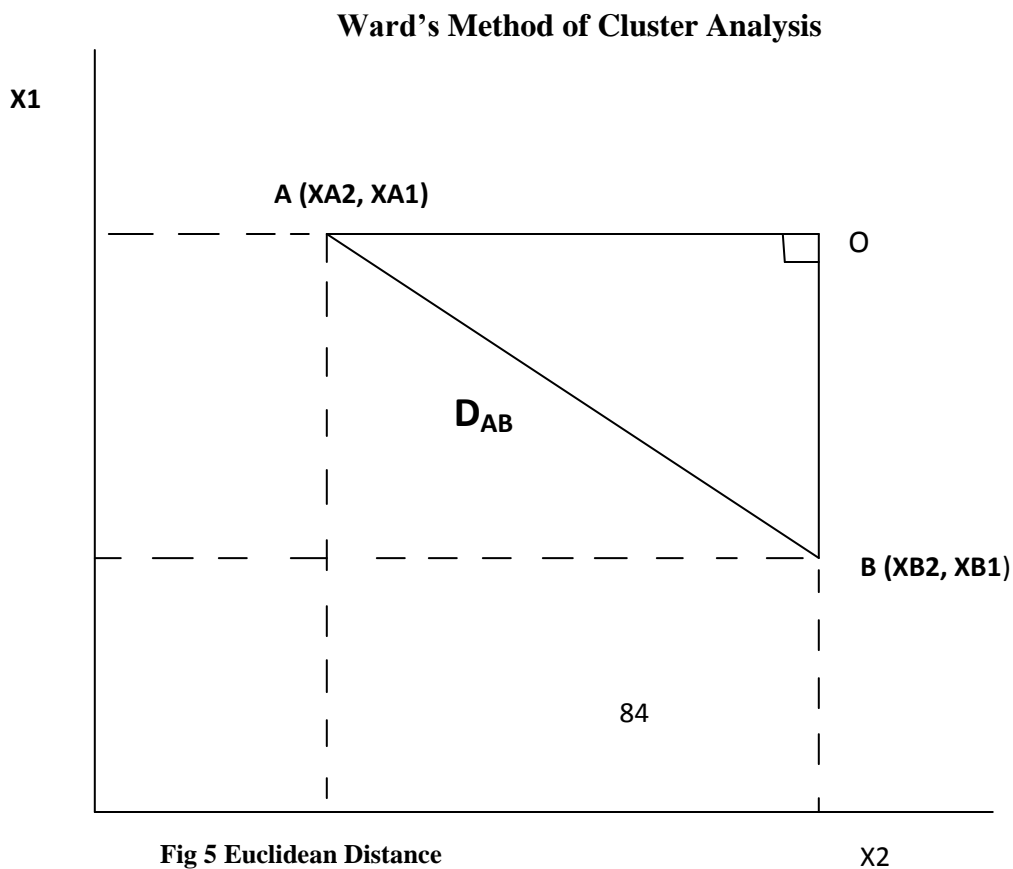
Table 4.6 shows the correlation coefficient between elements in the soil samples obtained at the various sites. The inter-elemental association for these elements in some sites had positive correlation coefficients indicating the nature of the relatedness of the variables in association i.e common association and variation while some has negative correlation coefficients indicating common association but opposite variation. The positively correlated coefficients inter-elemental association that has ($r \geq 0.5$) and those elements that indicate significant difference at $p \leq 0.05$ consist of forty five elements while those that had negative correlation coefficient ($r \geq - 0.5$) consist of five elements as indicated in Table 4.6. Thiis means that the various elements in the various sites were only fairly distributed which could be attributed to the fact that some sites may be at or near point source (PS) pollution from the municipal which enhances accumulation of the elements

4.2.2 Sediment Samples Data Correlation:

Table 4.7 shows the correlation coefficient between elements of the sediment samples at the various sites. The inter-elemental association for these elements in some sites had positive correlation coefficients while some had negative correlation coefficients. The positively correlated coefficients inter-elemental association that has ($r \geq 0.5$), and those elements that indicate significant difference at $p \leq 0.05$ consist of ninety six elements while those that had negative correlation coefficients ($r \geq - 0.5$) consist of nine elements as indicated in Table 4.7. This shows the elements are well distributed which could be attributed to dilution due to the aquatic environment.

4.2.3 Cluster Analysis Treatment of Data

This is the assignment of a set of observation into subsets called clusters so that observations in the same cluster are similar in some sense. The data obtained was normalized and a technique of cluster analysis using one of the hierarchical agglomerative procedures ‘Ward’s method’ operating a distance matrix calculated from squared mean Euclidean distance was run to produce the cluster (Oladipo, 1987). The clustering measures the similarity in composition between samples by comparing every sample with the other samples and those that are found to be very similar in chemical composition will then subsequently be found in the same cluster while dissimilar ones will be found in different cluster. Among the various distance functions that can be used in clustering, in this work the Euclidean distance is employed as it is adequate to meet an objective of this study



In Ward's method of clustering, if two samples in two sites are represented by A and B and were characterized by two elements X1 and X2 as in fig 5 then their pattern vectors are given by

$$\vec{X}_A = (XA_2, XA_1) \text{ and } \vec{X}_B = (XB_2, XB_1)$$

$$D_{AB}^2 = (OA)^2 + (OB)^2$$

$$D_{AB}^2 = (XA_2 - XB_2)^2 + (XA_1 - XB_1)^2$$

$$D_{AB}^2 = \sum_{j=1}^2 (XA_i - XB_j)^2$$

This can be represented as an n- dimensional Euclidean distance

$$D_{AB} = \sqrt{\sum_{j=1}^n (XA_i - XB_j)^2}$$

The Ward's method of clustering commence with the number of cluster equal to the number of samples and fuses together until only one cluster remains. The criteria for linking clusters are minimization of the error sum of squares (Oladipo 1987, 1992) as

$$SS = \sum_{\text{clusters}(A)} \sum [L_{ij} - L_{ij(s)}]^2 \text{ samples}(i) \text{ elements}(j) \text{ (Oladipo, 1987, 1992)}$$

where $L_{ij}(A)$ = mean value of j for cluster say (A) to which i is assigned. WARD's method calculates the increase in SS with both joining samples to clusters and merging clusters. The step involving the smallest increase in SS would lead to fusion of samples to cluster or

cluster to cluster. The basic disadvantage of Ward's method is that once a sample has been assigned to a cluster, it remains frozen in that position.

Another option is to construct a distance matrix for the element in the various sites where the number in the i^{th} row, j^{th} column is the distance between the i^{th} and j^{th} element. Then, as clustering progresses, rows and columns are merged as the clusters are merged and the distance updated. If the distance between two clusters are A and B then,

The maximum distance between elements of each cluster is

$$\max. \{d(X_2, X_1) : X_2 \in A, X_1 \in B\}$$

The minimum distance between elements of each cluster is

$$\min. \{d(X_2, X_1) : X_2 \in A, X_1 \in B\}$$

The mean distance between elements of each cluster by Unweighted Pair-Group Method using Arithmetic Averages (UPGMA) is given by

$$\frac{1}{|A| \cdot |B|} \sum_{X_2 \in A} \sum_{X_1 \in B} d(X_1, X_2).$$

In this work, twenty four chemical elements Al, Ba, Br, Cr, Co, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Rb, Sc, Sm, Ta, Ti, Th, U, Yb, V, and Zn .in fourteen soil samples were determined using neutron activation analysis. The soil data obtained from the different sites along the bank of river Ngadda and Alau Dam farming areas were subjected to multivariate cluster analysis technique using Ward's method as a measure of similarity in concentration between samples. Hierarchical clustering procedure was employed which determines the similarity coefficients in the clustering as a measure of the minimum

distance between clusters (Oladipo 1987, Ewa, 2004.). The resulting hierarchical treatment is displayed in form of a dendrogram as shown in Figure 6. It can be seen from Figure 6 that the samples have broken into two major groups with an outlier. For convenience, the groups have been labeled as cluster I and II and the clusters produced represent the similarity in origin of the sources of the variables in the samples that were grouped together as clusters. Sample S3 in this treatment came up as an outlier to the identified groups. Further observation of Figure 6 revealed that the first cluster constitutes samples S1, S4, S5, S10, S11, and S14 which suggests that the content of the samples i.e the elements in the samples have common or similar sources and it can be observed from the dendrogram that the similarity is about 96.5%, the second cluster consists of samples S2, S6, S8, S9, S12, S13, and S0 which suggested that the contents of these samples which are the elements have similarity at about 90.86% in their sources while S3 is an outlier meaning it does not belong to either cluster I or cluster II. The outlier could be associated with low value of the elemental concentration of Al in the row for S3 in Table 4.3a which is in agreement with the fact that outliers show disproportionate effect in multivariate analysis and do not tend to cluster at some levels with their sub-groups (Yarzac *et al*, 1980).

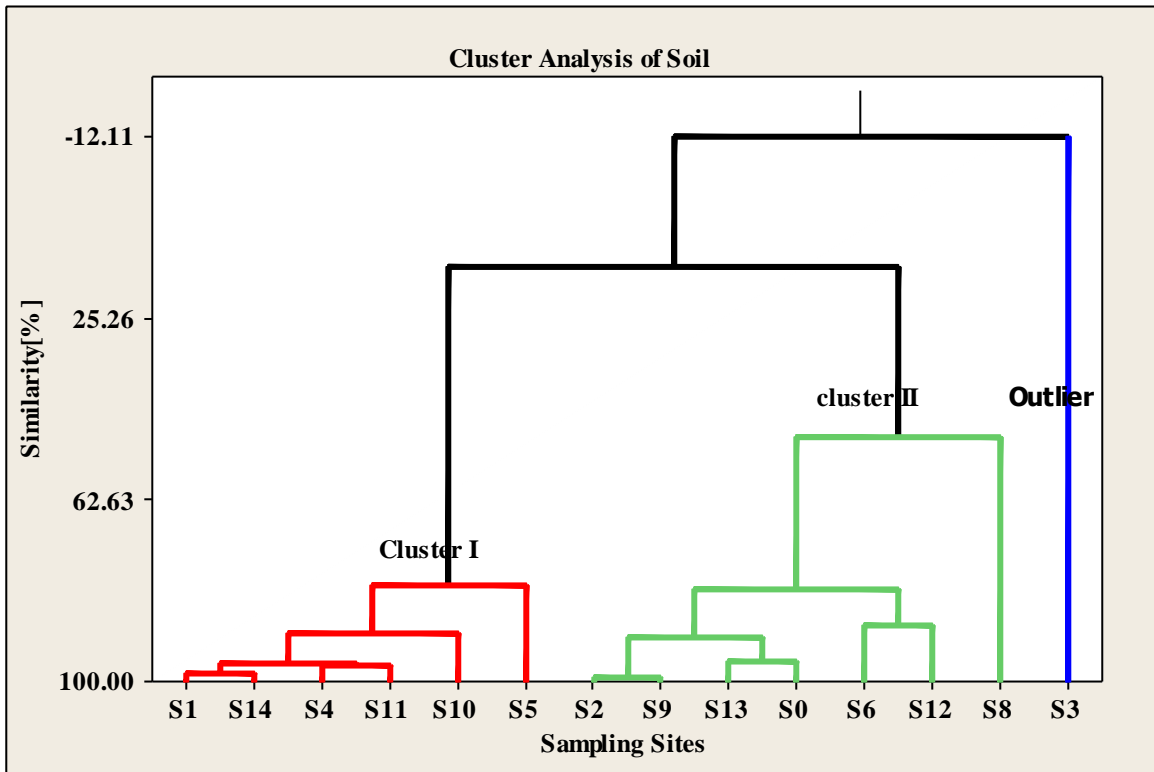


Fig 6 Cluster Analysis of Soil Samples Data

The composition of the soil cluster groups is as shown in Table 4.8. This is obtained when the element concentrations were normalized by their respective mean values. If the result of the normalized values is plotted against the element, the structure of the dendrogram is as displayed in Figure 7.

Table 4.8: Mean and standard deviation of element concentration in the soil clusters

| Element | Group I n = 8 | Group II n = 5 | Overall Mean |
|---------|------------------|-------------------|--------------|
| Al | 0.997 ± 0.15 | 0.994 ± 0.14 | 0.996 ± 0.15 |
| Ba | 0.994 ± 0.29 | 0.996 ± 0.24 | 0.995 ± 0.27 |
| Br | 0.995 ± 0.66 | BDL | - |
| Cr | 0.994 ± 0.27 | 1.00 ± 0.54 | 0.997 ± 0.41 |
| Co | 1.045 ± 0.26 | 0.994 ± 0.34 | 1.02 ± 0.30 |
| Dy | 1.06 ± 0.14 | 1.04 ± 0.05 | 1.05 ± 0.12 |
| Eu | 0.994 ± 0.18 | 0.980 ± 0.14 | 0.987 ± 0.16 |
| Fe | 0.991 ± 0.37 | 0.992 ± 0.34 | 0.992 ± 0.36 |
| Hf | 0.993 ± 0.31 | 0.998 ± 0.50 | 0.996 ± 0.41 |
| K | 0.994 ± 0.24 | 0.997 ± 0.24 | 0.996 ± 0.24 |
| La | 0.991 ± 0.33 | 0.996 ± 0.49 | 0.995 ± 0.41 |
| Lu | 1.04 ± 0.59 | 0.996 ± 0.71 | 0.998 ± 0.65 |
| Mn | 1.03 ± 0.38 | 0.994 ± 0.23 | 1.012 ± 0.31 |
| Na | 0.995 ± 0.23 | 0.994 ± 0.27 | 0.995 ± 0.25 |
| Rb | 0.996 ± 0.12 | 0.99 ± 0.36 | 0.993 ± 0.20 |
| Sc | 0.998 ± 0.21 | 0.996 ± 0.29 | 0.997 ± 0.25 |
| Sm | 0.994 ± 0.26 | 0.997 ± 0.53 | 0.996 ± 0.40 |
| Ta | 0.003 ± 0.31 | 0.997 ± 0.25 | 0.995 ± 0.28 |
| Ti | 0.998 ± 0.41 | 0.994 ± 0.2 | 0.996 ± 0.31 |
| Th | 0.995 ± 0.45 | 0.99 ± 0.14 | 0.993 ± 0.30 |
| U | 1.006 ± 0.25 | 0.992 ± 0.41 | 0.999 ± 0.33 |
| Yb | 0.988 ± 0.27 | 0.995 ± 0.21 | 0.991 ± 0.34 |
| V | 0.006 ± 0.20 | 0.98 ± 0.23 | 0.996 ± 0.22 |
| Zn | 0.994 ± 69.00 | 0.99 ± 0.47 | 0.992 ± 0.58 |

n: is the number of samples in the cluster

BDL : Below Detection Limit

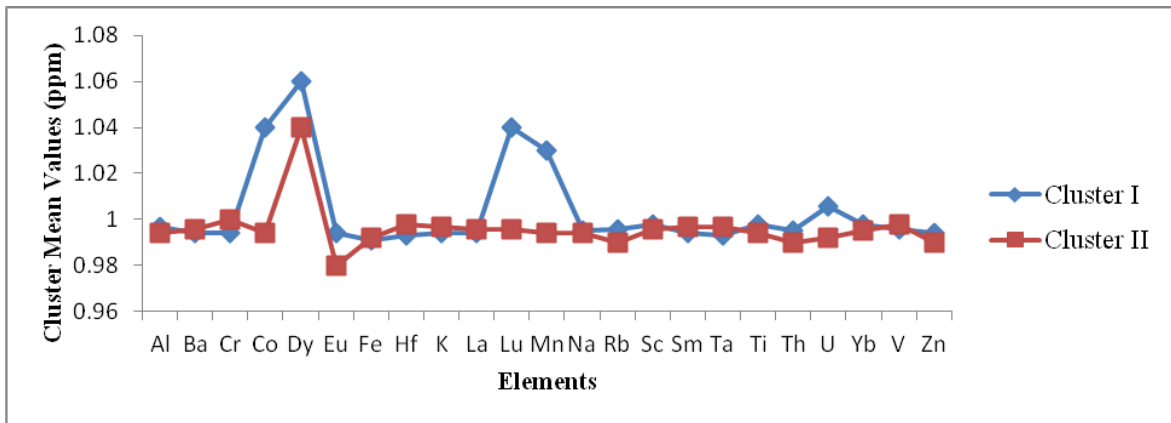


Fig 7 Normalized Concentration Profiles of Soil Samples Data

From Figure 7 it can be seen that, the deviating elements which hitherto are responsible for the separation of the samples into the two groups (groups I and group II) are Lu, Mn and slightly U from group I and slightly Eu from group II. This deviation of the different elements i.e the content of the two clusters could be due to enhanced deposition and or accumulation of these elements in the soil from different phenomenon such as natural activities like wind storms which transport some of these elements in particulate form from one point to the other since the study area is close to desert area, it may be due to effect of erosion from rain water during rainy season, it could be as a result of farming activities such as continuous application of chemical fertilizers that contain some of these elements, and may be due to landfill processes with solid waste from the Metropolis for land reclamation. It can also be seen that two of the rare earth elements (REEs) Dy and Lu constitute part of the variations in the content of the cluster structure. These elements belong to the higher atomic number and masses REE with predominance in the silicate rather than the metal or sulphide, therefore, their enhanced concentration is in agreement with the fact that the area of study is predominantly sandy which is associated with silicates. The slight variation in Cr can be attributed to some of the activities that take place

around the study area such as the presence of abattoir near the custom market by the side of river Ngadda, the washout from the heaps of solid waste dump which are generated from the market and at various points along the bank of river Ngadda.

The sediment data obtained from the different areas in river Ngadda and Alau Dam were subjected to multivariate cluster analysis technique using Ward's method as a measure of similarity in concentration between samples. Hierarchical clustering procedure was employed so as to determine the similarity coefficients in the clustering as a measure of the minimum distance between clusters. The resulting hierarchical treatment is displayed in form of a dendrogram as shown in Figure 8 and it can be observed from Figure 8 that the samples have broken into two major groups with an outlier. For convenience, the the groups have been labeled as cluster I and II with the clusters produced representing the similarity in origin of the sources of the variables in the samples that were grouped together as clusters. Sample SS2 in this treatment came up as an outlier to the identified groups. Further observation of Figure 8 revealed that the first cluster constitutes samples SS1, SS4, SS5, SS6, SS8, and SS9 which suggests that the content of the samples i.e the elements in the samples have common or similar sources at 89.07%, similarly, the second cluster consists of samples SS3 and SS10 which suggested that the contents of these samples which are the elements have similarity in their sources at 70.54% , while SS2 is an outlier meaning it does not belong to either cluster I or cluster II. The outlier could be associated with low value of the elemental concentration of Al in SS2 Table 4.10a which is in agreement with the fact that outliers show disproportionate effect in multivariate analysis and do not tend to cluster at some levels with their sub-groups (Yarab *et al*, 1980)

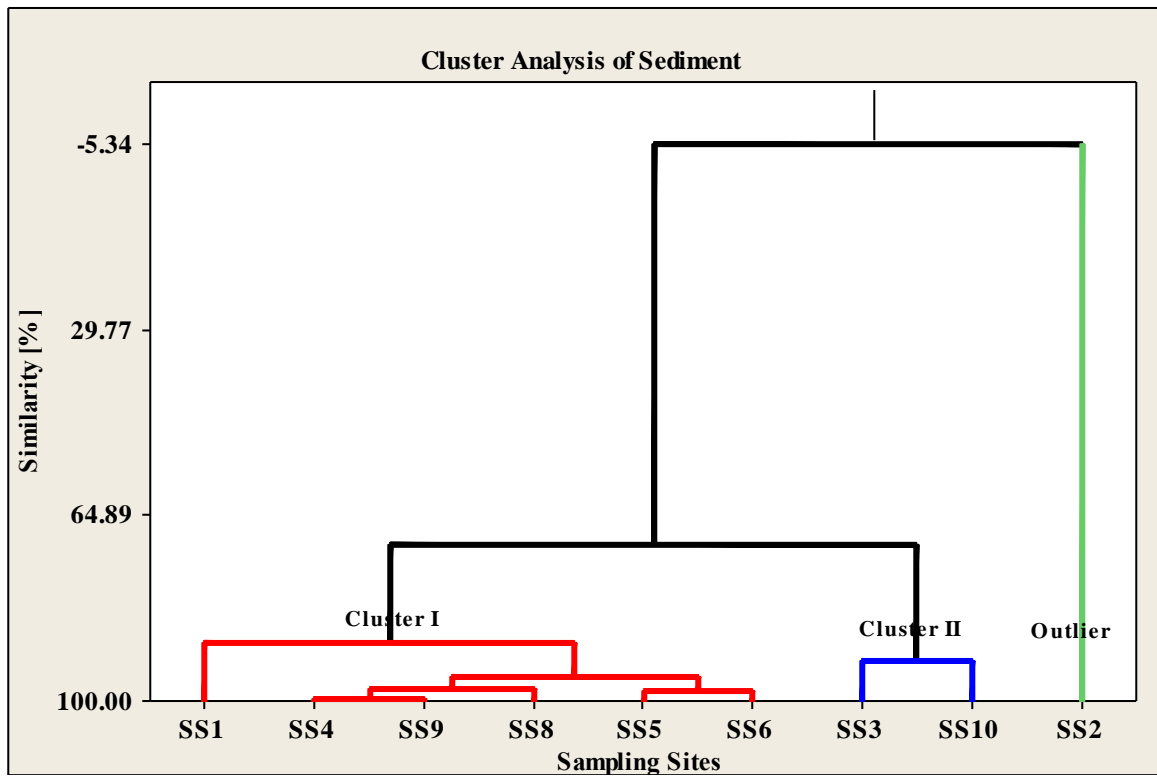


Fig 8 Cluster Analysis of Sediment Samples Data

The composition of the sediment cluster groups is as shown in Table 4.9. This is obtained when the element concentrations were normalized by their respective mean values. If the result of the normalized values is plotted against the element, the structure of the dendrogram is as displayed in Figure 9.

Table 4.9: Mean and standard deviation of element concentration in the sediment clusters
Mean of each element in the cluster, with the number constituting each cluster

| Element | Group I n = 6 | Group II n = 2 | Overall Mean |
|---------|------------------|-------------------|--------------|
| Al | 0.991 ± 0.09 | 1.000 ± 0.07 | 0.996 ± 0.01 |
| Ba | 1.00 ± 0.07 | 1.000 ± 0.06 | 1.000 ± 0.00 |
| Ca | 0.998 ± 0.24 | 0.995 ± 0.01 | 0.997 ± 0.00 |
| Cr | 0.840 ± 0.42 | 1.000 ± 0.23 | 0.920 ± 0.08 |
| Co | 0.998 ± 0.26 | 0.995 ± 0.02 | 0.997 ± 0.01 |
| Cs | 0.998 ± 0.19 | BDL | - |
| Dy | 0.996 ± 0.61 | BDL | - |
| Eu | 0.996 ± 0.11 | BDL | - |
| Fe | 0.995 ± 0.41 | 0.995 ± 0.06 | 0.995 ± 0.01 |
| Hf | 1.030 ± 0.44 | 1.000 ± 0.16 | 1.015 ± 0.02 |
| K | 0.995 ± 0.43 | 1.000 ± 0.27 | 0.998 ± 0.01 |
| La | 0.999 ± 0.57 | BDL | - |
| Lu | 0.996 ± 0.51 | 1.000 ± 0.16 | 0.998 ± 0.02 |
| Mg | 9,690 ± 0.43 | BDL | - |
| Mn | 0.965 ± 0.11 | 1.000 ± 0.01 | 0.993 ± 0.01 |
| Na | 0.993 ± 0.11 | 1.000 ± 0.29 | 0.997 ± 0.01 |
| Rb | 0.997 ± 0.11 | 1.000 ± 0.15 | 0.999 ± 0.01 |
| Sc | 0.996 ± 0.17 | 1.010 ± 0.05 | 1.003 ± 0.01 |
| Sm | 0.790 ± 0.10 | 1.000 ± 0.15 | 0.895 ± 0.10 |
| Ta | 0.977 ± 0.31 | 0.995 ± 0.01 | 0.986 ± 0.01 |
| Ti | 0.996 ± 0.34 | 1.000 ± 0.16 | 0.998 ± 0.01 |
| Th | 1.000 ± 0.18 | 1.000 ± 0.07 | 1.000 ± 0.01 |
| U | 1.000 ± 0.52 | 1.000 ± 0.05 | 1.000 ± 0.01 |
| Yb | 1.140 ± 0.51 | 1.000 ± 0.02 | 1.070 ± 0.07 |
| V | 1.000 ± 0.19 | 1.000 ± 0.15 | 1.000 ± 0.01 |
| Zn | 1.000 ± 0.61 | BDL | - |

n is the number of samples in the cluster.

BDL : Below Detection Limit

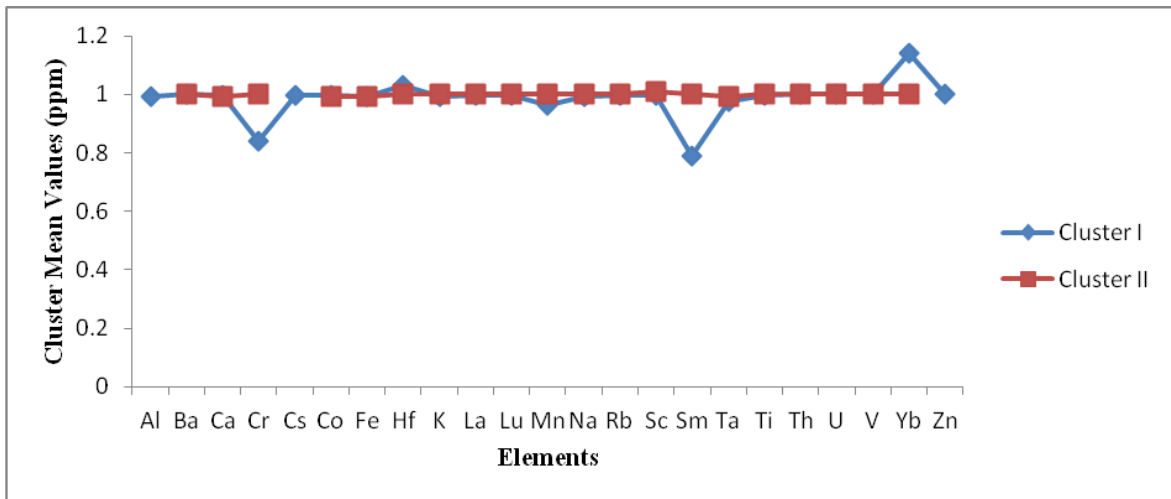


Fig 9: Normalized Concentration Profiles of Sediment Samples Data.

From Figure 9 it can be seen that, the deviating elements which basically are responsible for the separation of the samples into the two groups (groups I and group II) are Cr, Sm, and Yb and are content of the samples from group I. The enhanced presence of Cr could be due to the human activities around the bank of river Ngadda such as the presence of abattoir, waste dump along the bank of the river and so on

The water data obtained from the different points in river Ngadda and Alau Dam farming areas were subjected to multivariate cluster analysis technique using Ward's method as a measure of similarity in concentration between samples. Hierarchical clustering procedure was employed so as to determine the similarity coefficients in the clustering as a measure of the minimum distance between clusters (Oladipo, 1987, Ewa, 2004.). The resulting hierarchical treatment is displayed in form of a dendrogram as shown in Figure. 10. It can be seen from the Figure that the samples have broken into three major groups. For convenience, the the groups have been labeled as cluster I, II and III with the clusters produced representing the similarity in origin of the sources of the variables in the

samples that were grouped together as clusters. Further observation of Figure 10 revealed that the first cluster constitutes samples H1, H2, H3, H9 and H13 which suggested that the contents of these samples which are the elements have similarity in their sources at about 96.18% as it can be observed from dendrogram, the second cluster consists of samples H4, H10, H11, and H12 at similarity level of about 78.56% while the third cluster is made up of samples H5, H6, H7, H8, and H8 at similarity level of about 75.54%. This suggests that the content of the samples which are the elements in the various clusters have some degree of relationship either in concentration and or sources.

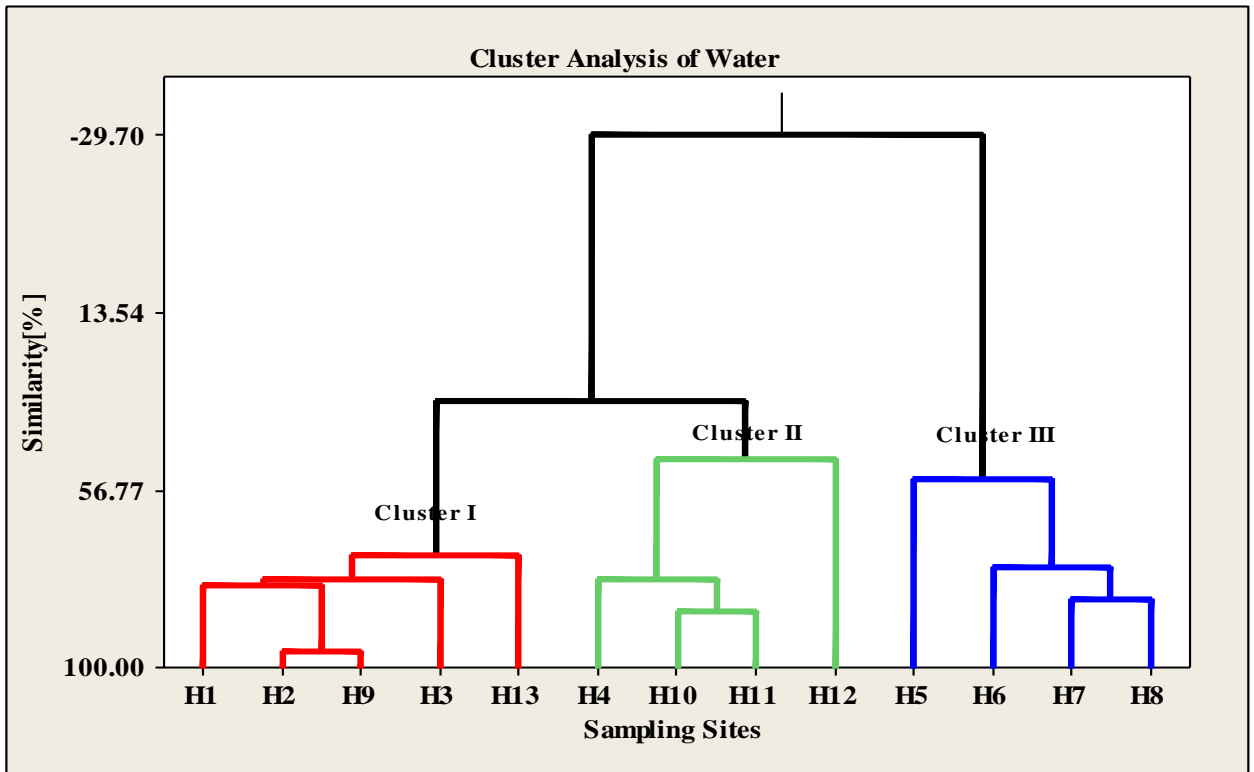


Figure 10: Cluster Analysis of Water Samples Data

The composition of the water cluster groups is as shown in Table 4.10. This is obtained when the element concentrations were normalized by their respective mean values. If the result of the normalized values were plotted against the element, the structure of the dendrogram is as displayed in Figure 11.

Table 4.10: Mean and standard deviation of element concentration in the water clusters
Mean of each element in the cluster, with the number constituting each cluster

| Element | Group I n = 3 | Group II n = 7 | Group III n = 3 | Overall Mean |
|---------|------------------|-------------------|--------------------|---------------|
| Fe | 0.969 ± 0.111 | 1.000 ± 0.652 | 1.000 ± 0.076 | 0.989 ± 0.014 |
| Mn | 1.008 ± 0.106 | 1.001 ± 0.546 | 0.999 ± 0.143 | 1.002 ± 0.003 |
| Zn | 1.001 ± 0.364 | 1.000 ± 0.334 | 1.000 ± 0.401 | 1.000 ± 0.004 |
| Ni | 0.997 ± 0.682 | 0.999 ± 0.829 | 1.003 ± 0.386 | 0.999 ± 0.002 |
| Cd | 1.004 ± 0.617 | 0.999 ± 0.407 | 1.002 ± 0.182 | 1.001 ± 0.002 |
| Pb | 0.999 ± 0.117 | 0.999 ± 0.683 | 0.999 ± 0.396 | 0.999 ± 0.000 |
| Co | 1.000 ± 0.494 | 0.999 ± 0.511 | 0.999 ± 0.070 | 0.999 ± 0.004 |
| Cr | 0.993 ± 0.538 | 1.000 ± 0.377 | 0.979 ± 0.581 | 0.997 ± 0.003 |
| Cu | 1.002 ± 0.282 | 1.000 ± 0.238 | 0.983 ± 0.317 | 0.995 ± 0.008 |
| AL | 0.999 ± 0.145 | 0.996 ± 0.450 | 1.000 ± 0.580 | 0.998 ± 0.001 |

n = number of cluster

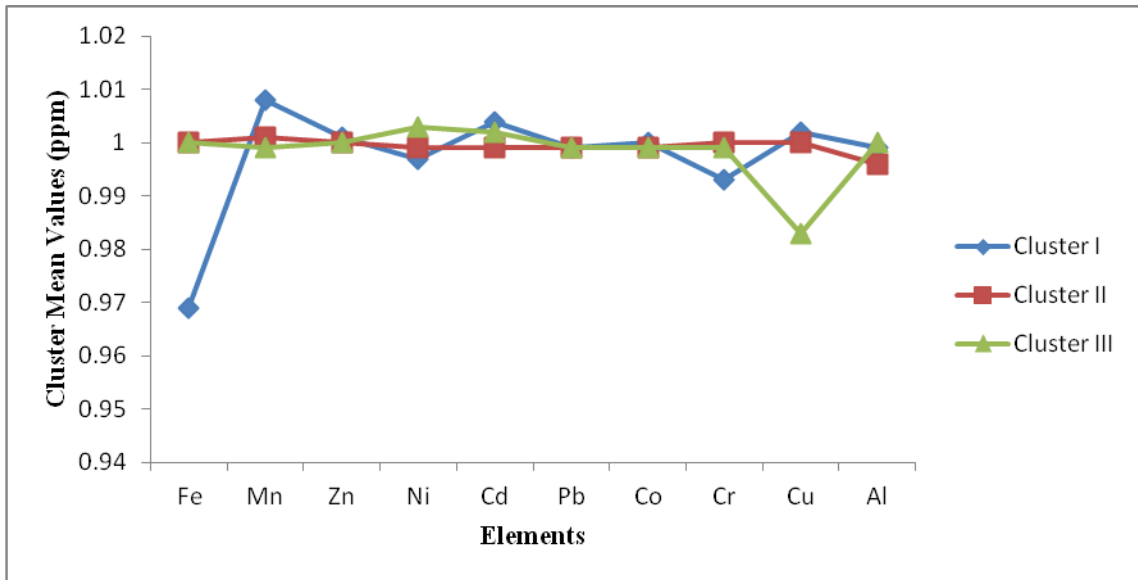


Fig 11: Normalized Concentration Profile of Water Samples Data.

It can be clearly seen from Figure 11 that, the elements responsible for the discrimination among the sampling points are Fe, Mn, Cr and Cu. The concentration of Mn as presented in Figure 11 was enhanced which can be attributed to activities by human being in the application and utilization of materials equipment and appliances containing the element. Fe, Cu and Cr seem to be lower in concentration which could be due to the fact that they might have settled in the water sediment.

4.3.1 Contamination Factor of Soil Samples

The level of contamination of soil by metal is expressed in terms of contamination factor and is evaluated using the formula in equation (4.1) (Mmolawa, *et al*, 2011)

$$CF = \frac{C_m \text{ sample}}{C_m \text{ background}} \quad (4.1)$$

where C_m sample is the concentration of a given metal in the sample, C_m background is the concentration of the given metal in the background sample i.e So values from Table 4.3a and 4.3b . The calculated contamination factor values for the various elements determined in this study is as presented in Tables 4.11a and 4.11b and the range of values that is used to evaluate the state of deterioration of the soil is as presented by the key stated below Table 4.11b

Table 4.11a: Contamination Factor of Soil in Study Area

| Samples | Al | Ba | Cr | Cs | Co | Dy | Eu | Fe | Hf | K | La | Lu |
|---------|--------------|--------------|---------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------|--------------|--------------|
| S1 | 0.973 | 1.435 | 10.940 | 1.5 | 1.000 | 0.958 | 1.053 | 1.077 | 1.421 | 1.453 | 1.597 | - |
| S2 | 0.918 | 1.009 | 9.063 | - | 1.263 | 0.958 | 0.784 | 1.049 | 0.750 | 1.010 | 1.291 | 0.201 |
| S3 | 0.089 | 1.288 | 14.688 | - | 1.188 | 1.021 | 1.18 | 1.031 | 1.402 | 1.417 | 1.572 | 0.324 |
| S4 | 0.834 | 0.437 | 9.063 | - | 0.875 | 0.896 | 0.877 | 0.985 | 1.286 | 1.561 | 1.106 | 0.324 |
| S5 | 1.237 | 1.684 | 10.938 | - | 1.186 | 1.104 | 1.377 | 1.089 | 1.470 | 1.724 | 1.377 | 0.376 |
| S6 | 1.156 | 1.196 | 7.500 | - | 1.563 | 1.000 | - | 1.263 | 0.874 | 0.6176 | 0.803 | 0.875 |
| S8 | 0.784 | 1.347 | 13.125 | 1.063 | 1.500 | 0.688 | 1.140 | 1.365 | 1.144 | - | 1.357 | 0.289 |
| S9 | 0.958 | 1.251 | 13.438 | - | 1.031 | 1.333 | - | 0.103 | 1.627 | 1.334 | 1.823 | 0.367 |
| S10 | 0.818 | 1.060 | 5.000 | 0.813 | 0.844 | 0.646 | - | 0.700 | 0.496 | 1.302 | 0.651 | 0.140 |
| S11 | 0.866 | 0.618 | 5.625 | 0.625 | 0.502 | 0.896 | - | 0.402 | 0.567 | 0.585 | 0.709 | 0.157 |
| S12 | 0.968 | 1.579 | 6.870 | 1.019 | 0.938 | 0.854 | 1.053 | 0.896 | 0.945 | 1.022 | 0.977 | 0.888 |
| S13 | 0.968 | 1.579 | 9.813 | - | 0.816 | 0.848 | 0.805 | 0.906 | 0.990 | 1.315 | 0.939 | 0.262 |
| S14 | 1.165 | 1.278 | 9.063 | 1.125 | 1.656 | 0.936 | - | 1.397 | 0.109 | 1.240 | 0.929 | 0.880 |

Table 4.11b: Contamination Factor of Soil in Study Area

| Samples | Mn | Na | Rb | Sc | Sm | Ta | Ti | Th | U | V | Yb | Zn |
|---------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------|--------------|--------------|--------------|--------------|
| S1 | 1.081 | 1.563 | 1.230 | 1.088 | 1.161 | 1.714 | 0.608 | 1.777 | 1.200 | 0.786 | 0.891 | 0.750 |
| S2 | 1.090 | 1.079 | 0.931 | 0.931 | 0.136 | 1.071 | 0.820 | 0.749 | 0.225 | 0.786 | 0.609 | 0.333 |
| S3 | 1.621 | 1.584 | - | 1.041 | 1.220 | 1.350 | 0.747 | 1.425 | 1.300 | 0.843 | 0.857 | 0.647 |
| S4 | 0.872 | 1.648 | 1.253 | 0.909 | 0.816 | 1.864 | 0.741 | 0.986 | 1.233 | 0.600 | 1.041 | 2.014 |
| S5 | 1.062 | 1.716 | 1.483 | 1.315 | 1.126 | - | - | 1.720 | 1.572 | 0.946 | 1.011 | 0.532 |
| S6 | 0.945 | 0.703 | 0.989 | 0.950 | 0.845 | 0.829 | 0.769 | 0.721 | 0.825 | 0.939 | 0.739 | 0.584 |
| S8 | 0.947 | 1.388 | 1.425 | 1.193 | - | 1.729 | 0.775 | 1.0774 | 1.075 | 0.643 | 1.124 | - |
| S9 | 0.212 | 1.425 | 1.218 | 1.055 | 1.332 | 1.786 | 1.553 | 1.769 | 1.550 | 0.929 | 1.326 | 0.542 |
| S10 | 0.896 | 1.332 | 1.057 | 0.530 | 0.539 | 0.836 | 0.508 | 0.383 | 0.700 | 0.506 | 0.467 | 1.972 |
| S11 | 1.009 | 0.633 | 0.448 | 0.413 | 0.558 | - | 0.945 | 0.708 | 0.565 | 0.546 | 0.607 | 0.708 |
| S12 | 0.867 | 1.376 | 1.126 | 1.017 | 1.041 | - | 0.827 | 0.898 | 1.200 | 0.964 | 0.848 | - |
| S13 | 0.720 | 1.868 | 0.126 | 0.957 | 0.719 | 1.286 | - | 0.781 | 1.100 | 0.786 | 0.870 | 0.786 |
| S14 | 1.649 | 1.148 | - | 1.098 | 0.984 | 1.000 | 0.884 | 0.972 | 0.925 | 1.036 | 0.891 | 0.319 |

where $CF < 1$ refer to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicate considerable contamination and $CF > 6$ indicate very high contamination and (-) means BDL for $C_{m, sample}$

4.3.2. Geochemical Index of Soil Samples

This is the assessing of the metal pollution in terms of enrichment classes and equation (5.2), which was used by Mmolawa, *et al* (2011), was employed here for the evaluation of the geochemical index of the various samples in the various sites. The calculated results is as presented in Tables 4.12a and 4.12b with the index of variation of the variation levels for the various elements given below Table 4.12b

$$I_{\text{geo}} = \log_2 \left[\frac{\text{Cm sample}}{1.5 \times \text{Cm background}} \right] \quad (4.2)$$

Table 4.12a: Geochemical Index of Soil in Study Area

| Samples | Al | Ba | Cr | Cs | Co | Dy | Eu | Fe | Hf | K | La | Lu |
|----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|
| S1 | -0.634 | -0.064 | 2.867 | 0.585 | -0.585 | -0.646 | -0.519 | -0.478 | 0.008 | -0.046 | 0.091 | - |
| S2 | -0.709 | -0.572 | 2.594 | - | -0.248 | -0.646 | -0.926 | -0.516 | -1.000 | -0.571 | - | -2898 |
| S3 | -0.408 | -0.219 | 3.292 | - | -0.337 | -0.555 | -0.352 | -0.540 | -0.097 | -0.082 | 0.068 | -2.213 |
| S4 | -0.847 | -1.780 | 2.594 | - | -0.778 | -0.744 | -0.774 | -0.607 | -0.222 | 0.058 | -0.439 | -2.213 |
| S5 | -0.278 | 0.167 | 2.867 | - | -0.337 | -0.447 | -0.123 | -0.462 | -0.029 | 0.201 | -0.122 | -1.996 |
| S6 | -0.376 | -0.327 | 2.322 | - | 0.059 | -0.585 | - | -0.246 | -0.779 | -1.283 | -0.902 | -0.778 |
| S8 | -0.937 | -0.155 | -3.129 | -0.497 | - | -1.126 | -0.395 | -0.136 | -0.390 | - | -0.145 | -2.378 |
| S9 | -.654 | -0.261 | 3.162 | - | -0.541 | -0.170 | - | -3.868 | 0.118 | -0.169 | 0.281 | -2.030 |
| S10 | -0.875 | -0.501 | 1.893 | -0.884 | -0.830 | -1.216 | - | -1.100 | -1596 | -0.204 | -1.205 | -3.422 |
| S11 | -0.793 | -0.277 | 1.907 | -1.263 | -1.585 | -0.744 | - | -1.898 | -1.403 | -1.358 | -1.081 | -3.252 |
| S12 | -0.292 | -0.349 | 2.196 | -0.558 | -0.678 | -0.812 | -0.511 | -0.744 | -0.667 | -0.552 | -0.618 | -0.757 |
| S13 | -0.632 | 0.073 | 2.711 | - | -0.879 | -0.823 | -0.863 | -0.738 | -3.787 | -0.190 | -0.675 | -2.515 |
| S14 | -0.634 | -0.231 | 2.594 | -0.415 | 0.143 | -0.678 | - | 1.000 | - | -0.275 | -0.585 | -0.771 |

Table 4.12b: Geochemical Index of Soil in Study Area

| Samples | Mn | Na | Rb | Sc | Sm | Ta | Ti | Th | U | V | Yb | Zn |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| S1 | -0.470 | 0.059 | -0.286 | -0.463 | -0.367 | 0.193 | -1.302 | 0.244 | -0.321 | -0.932 | -0.750 | -1.00 |
| S2 | -0.461 | -0.475 | -0.686 | -0.688 | -3.467 | -0.485 | -0.870 | -1.002 | -2.734 | -0.932 | -1.301 | -2.169 |
| S3 | 0.112 | 0.079 | - | -0.528 | -0.296 | -0.152 | -1.006 | -0.073 | -0.206 | -0.831 | -0.808 | -1.213 |
| S4 | -0.782 | 0.135 | -0.264 | -0.723 | -0.876 | 0.314 | -1.018 | -0.605 | -0.283 | -1.321 | -0.526 | 0.425 |
| S5 | -0.499 | 0.194 | -0.017 | -0.190 | -0.412 | - | - | -4.066 | 0.068 | -0.664 | -0.569 | -1.496 |
| S6 | 0.056 | -1.096 | -0.602 | -0.656 | -0.827 | -0.856 | -0.965 | -1.057 | -0.862 | -0.675 | -1.021 | -1.360 |
| S8 | -0.664 | -1.112 | -0.074 | -0.330 | - | 0.205 | -0.953 | -0.481 | -0.480 | -1.222 | -0.416 | - |
| S9 | 0.488 | -0.073 | -0.299 | -0.507 | 0.169 | 0.251 | 0.050 | -0.238 | 0.047 | -0.691 | -0.178 | -1.469 |
| S10 | -0.744 | -0.172 | -0.504 | -1.501 | -0.473 | -0.844 | -1.562 | -1.975 | -1.099 | -1.568 | -1.695 | 0.394 |
| S11 | -0.571 | -1.245 | -1.742 | -1.861 | -1.429 | - | -0.667 | -1.082 | -1.408 | -1.456 | -1.306 | -1.082 |
| S12 | -0.799 | -0.124 | -0.413 | -0.561 | -0.524 | - | -0.859 | -0.740 | -0.321 | -0.637 | -0.823 | - |
| S13 | -1.058 | 0.316 | -0.233 | -0.649 | -1.058 | -0.222 | - | -0.940 | -0.447 | -0.982 | -0.786 | -2.308 |
| S14 | 0.137 | -0.019 | - | -0.450 | -0.605 | -0.585 | -0.762 | -0.625 | -0.697 | -0.534 | -0.750 | -1.896 |

Where $I_{geo} < 0$ means unpolluted; $0 \leq I_{geo} < 1$ means unpolluted to moderately polluted; $1 \leq I_{geo} < 2$ means moderately polluted; $2 \leq I_{geo} < 3$ means moderately to strongly polluted; $3 \leq I_{geo} < 4$ means strongly polluted; $4 \leq I_{geo} < 5$ means strongly polluted; $I_{geo} \leq 5$ means very strongly polluted and (-) means BDL for C_m sample

4.4.1 Rare Earth Elements (REEs)

Rare earth elements are one of the set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides plus Scandium and Yttrium, (Connelly and Damhus, 2005). Scandium and Yttrium are considered rare earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. Rare earth elements, except scandium are heavier than iron and thus are produced by supernova nucleosynthesis or the s-process in asymptotic giant branch stars. Rare earth elements are divided into two sub-groups light rare earth elements (LREEs) and heavy rare earth elements (HREEs). The light rare earth elements consist of Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd while the heavy rare earth elements consist of Y, Tb, Dy, Ho, Er, Tm, Yb and Lu. The distinction between the groups is more to do with atomic volume and geological behavior.

4.4.2 Rare Earth Elements (REEs) in Soil Samples

There have been several attempts to establish the composition of the earth crust but most of these have not included the rare earth elements (REEs). Among the exceptions are in the work of Haskin, (1968) who used REEs values for a composite of nine chondrites for estimating the composition of the earth crust, Laul (1983) who used REEs values from NAA, Masuda *et al*, (1973) which produces REEs values for Leedeey chondrites Table 4.13. These values and others are normally employed as the normalizing standards in estimating the composition of the earth crust. The values of the Haskin *et al*, (1963) as shown in Table 4.13 have been applied in normalizing the REEs values for La, Sm, Eu, Yb, and Lu that are obtained in this work. The choice of Haskin values for the

normalization was as a result of the same analyzing procedure being employed in both cases i.e the use of neutron activation analysis.

**Table 4.13: Three Sets of Chondritic (Primordial) Abundance Used for Normalisation of REE Concentration Values
Chondritic Normalizing Values (ppm)**

| Atomic Number | Element | (a) | (b) | (c) |
|---------------|---------|--------|-------|-------|
| 39 | Y | - | 1.96 | - |
| 57 | La | 0.315 | 0.330 | 0.34 |
| 58 | Ce | 0.813 | 0.88 | 0.87 |
| 58 | Pr | - | 0.112 | 0.12 |
| 60 | Nd | 0.597 | 0.60 | 0.64 |
| 61 | Pm | - | - | - |
| 62 | Sm | 0.192 | 0.181 | 0.195 |
| 63 | Eu | 0.0772 | 0.069 | 0.073 |
| 64 | Gd | 0.259 | 0.249 | 0.26 |
| 65 | Tb | - | 0.047 | 0.047 |
| 66 | Dy | 0.235 | - | 0.33 |
| 67 | Ho | - | 0.070 | 0.078 |
| 68 | Er | 0.213 | 0.200 | 0.20 |
| 69 | Tm | - | 0.030 | 0.032 |
| 70 | Yb | 0.208 | 0.200 | 0.22 |
| 71 | Lu | 0.0323 | 0.034 | 0.034 |

Column (a) REE values for Leedey chondrites (Masuda, 1973) divided by 1.20. Analysis was made by isotope dilution

Column (b) REE values for a composites of nine chondrites (Haskin, 1963). Analysis were made by NAA

Column (c) REE values from NAA (Laul, 1983)

The normalization was achieved by dividing the concentration of the REEs of interest by the value given by Haskin (1963) of the corresponding element in Table 4.13. The results of the REEs chondrite-normalized values were plotted against the element as shown in Figure 12a for soil samples. As stated by Taylor and McClennan (1985) that

REEs are conveniently divided into two subgroups, those from La to Sm i.e lower atomic number and masses being referred to as the light rare earth elements LREEs and those from Gd to Lu i.e higher atomic numbers and masses being referred to as the heavy rare earth elements HREEs. It can be clearly seen from Figure 12a that the LREEs relative to chondrites are more abundant in the crust than the HREEs as indicated in the decrease of the trend of the plot as one moves from left to right of the graph in Figure 12a which is in agreement with other findings in the literature and it can be clearly seen from the graph in Figure 12a that the plotted position for Eu lies away from the trend defined by other REEs on chondrite-normalized abundance diagram. This departure which is peculiar to europium is called europium anomaly and occur distinctly for most of the samples.

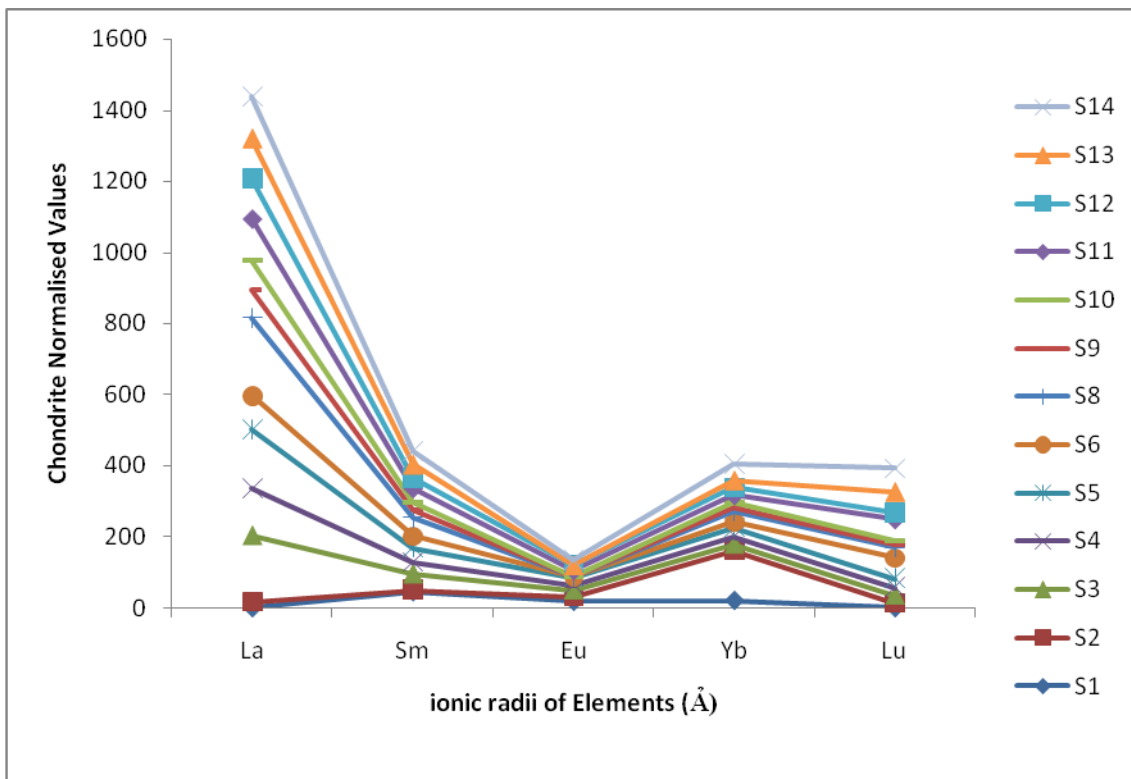


Fig 12a: Rare Earth Elements in Soil Samples

To further observed the characteristics of the REEs elements determine in the soil samples, the log values of the chondrite-normalized values were plotted against REEs element ionic radii and it can be clearly seen from the graph in Figure 12b that the plotted position for Eu only slightly lies away from the trend defined by other REEs on chondrite-normalized abundance diagram.

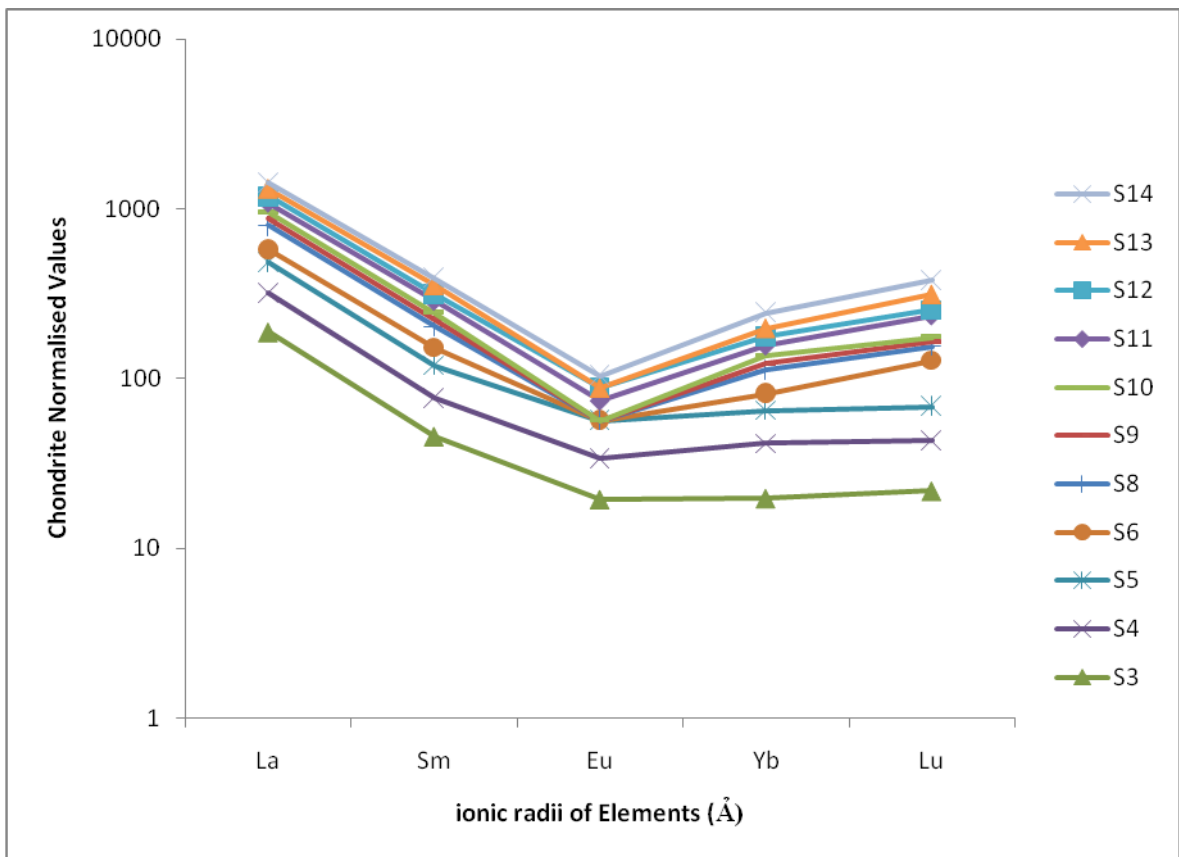


Fig 12b: Rare Earth Elements in Soil Samples

4.4.3 Rare Earth Elements in Sediments samples

The REEs determined in sediment samples were normalized using the chondrite values given by Haskin in 1963 obtained from the earth crust. It can be observed from the

graph in Figure 13a that the concentrations of the REEs in sediments follow the same pattern of distribution as that of the soil. The plot of the chondrite-normalised values versus elements showed that the abundance decreases as one moves from element of low atomic number to those of high atomic number, which means that the LREEs relative to chondrites are more abundant in the crust than the HREEs as indicated in the decrease of the trend of the plot as one moves from left to right of the graph,

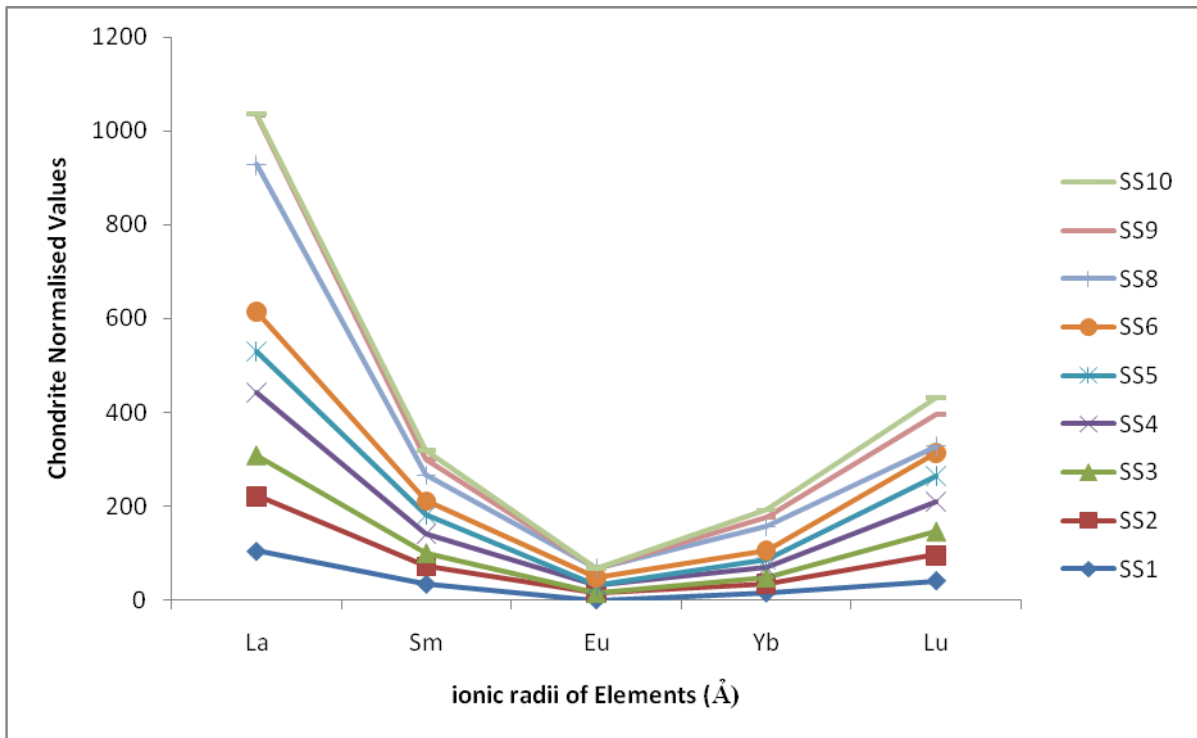


Fig 13a: Rare Earth Elements in Sediments Samples

Therefore to further observe the characteristics of the REEs determine in the sediment samples, the log values of the chondrite-normalized values were plotted against REEs Figure 13b and it can be clearly seen from the graph that the plotted position for Eu lies away from the trend defined by other REEs on chondrite - normalized abundance

diagram. This departure which is peculiar to europium is distinct for most of the samples except SS1

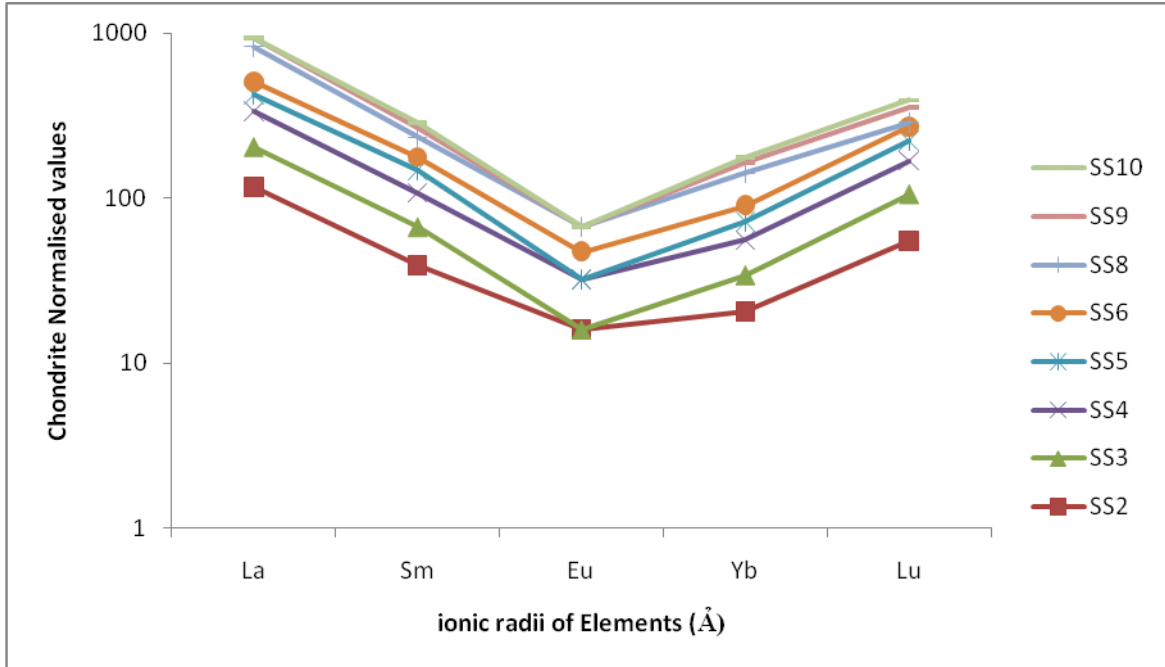


Fig 13b: Rare Earth Elements in Sediment Samples

Having established the correlation among the various elements in the soil, sediment and water from the various sites, and also the dendrogram of the cluster groups for the elements in soil, sediment and water, the concentration of the twenty four chemical elements Al, Ba, Br, Cr, Co, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Rb, Sc, Sm, Ta, Ti, Th, U, Yb, V, and Zn determined using NAA in the soil samples obtained in the fourteen sites (S0–S14) was represented graphically in the form of bar charts so as to present the variation of the various element concentrations in the different sites. Four plots were made based on the concentration of the elements determined in the soil samples for convenience purposes since the elemental concentration may vary significantly in the different sites. The same treatment was applied to the sediments and similar one to the vegetable samples.

4. 5.1 Soil Results Analysis

Table 4.14 present the ranges of concentrations of some of the elements determined in soils samples obtained in farmlands along the bank of river Nggada and Alau dam in Maiduguri Metropolis of Borno State which are extensively used for cultivation of vegetables during dry season and the maximum allowable concentrations of trace elements in Agricultural soils proposed by various countries in different years. This was done so as to to give an idea of the farming suitability of the study area viz a viz the the need for continuous monitoring of sites for agricultural purposes especially the dry season farming of the vegetable crops studied in this work and other numerous related dry season farming.

Table 4.14: Maximum Allowable Concentrations (MAC) of Trace Element in Agricultural Soils Proposed or Given in the Directives in Various Countries and Different Years (ppm DW)

| Element. | Range in this work | Austria,1977 | Poland , 1977 & 1993 | Germany, 1984 & 1992 | Russia, 1986 | U.K., 1987 | U.S., 1988 & 1993 | Euro. Comm.1986 |
|----------|--------------------|--------------|----------------------|----------------------|--------------|------------|-------------------|-----------------|
| As | 0.46 - 1.0 | 50 | 30 | 20 | 2 | 10 | 14 | - |
| B | | 100 | | 25 | | | | |
| Be | | 10 | 10 | | | | | |
| Cd | | 5 | | | | | | |
| Co | 1.6 - 5.3 | 50 | 50 | - | - | - | 20 | - |
| Cr | 3.2 - 47 | 100 | 50 - 80 | 100 & 100 | 0.05 | - | 120 & - | 50 - 150 |
| Cu | | 100 | 30-70 | 100 & 60 | 23 | 50 | 100 & 750 | 50 - 140 |
| F | | 500 | | 200 | | | | |
| Hg | | 5 | 5 | 2 & 1 | 2.1 | | 0.5 & 8 | 1- 1.5 |
| Mo | | 10 | 10 | | | | 4 | |
| Ni | | 100 | 30 -75 | 50 & 50 | 35 | 20 | 32 & 210 | 30 75 |
| Pb | | 100 | 70 -150 | 100 & 100 | 20 | 500-2000 | 60 &150 | 50-300 |
| Sb | 0.18 - 14.2 | - | 10 | - | - | - | - | - |
| Se | | 10 | 10 | 10 | | | 1.6 | |
| V | 14.16 - 29 | - | 150 | - | 150 | - | - | - |
| Zn | 21.8 - 145 | 300 | 100 - 300 | 300 | 110 | 130 | 220 | 150 - 300 |

Source: Kabata and Pandies, (2001)

For the values recommended for Agricultural soils in other countries of the World and that determined in this work displayed in Table 4.14, it can be observed that the value of chromium was far below the values recommended by the other countries except that of Russia which means that the values of chromium in the Agricultural soils investigated along the bank of River Nggada and Alau dam were within the acceptable limit. The values of Cobalt concentrations were within the acceptable limit as compared to the recommended values for other Countries. Antimony ranges of concentration values exceeded the value recommended by Poland for Agricultural soils but Vanadium concentration was within the range of the concentration limit, recommended by Poland and Russia. The ranges of Zinc concentrations determined in in this study were below the values recommended by other countries

Figures 14a –14d shows the graphical bar chart of the elements determined in the soil samples collected at various sites. The graph was plotted in four places so that the various ranges of concentration values of the same elements determine in soil samples obtained from different sites of the study area can conveniently be represented since the same element concentration values may vary significantly with different sites. It can be clearly seen from the graph in Figures 14a – 14d that the concentration of the elements presented in this bar chart ranges from tens of thousands of part per million to tens and units of part per millions in values. Tables 4.3a and 4.3b represented in Figure 14a the elements with high concentration values determined in the soil samples varies from the various sites as follows: Al (27760 ± 389 ppm to 43830 ± 307 ppm) > K (13130 ± 118 ppm to 38680 ± 774 ppm) > Fe (994 ± 23 ppm to 13520 ± 230 ppm) > Ca (1982 ± 484 ppm to 5080 ± 965 ppm) > Ba (297 ± 35 ppm to 1145 ± 41 ppm). For Figure 4b the

concentrations of the elements are in thousands of part per million with the order of concentration varying as Ti (1872 ± 266 ppm to 5725 ± 361 ppm) > Na (1773 ± 4 ppm to 5231 ± 10 ppm) > Mn (1773 ± 4 ppm to 5231 ± 10 ppm) > Rb ($.39 \pm 4$ ppm to 111 ± 5 ppm).

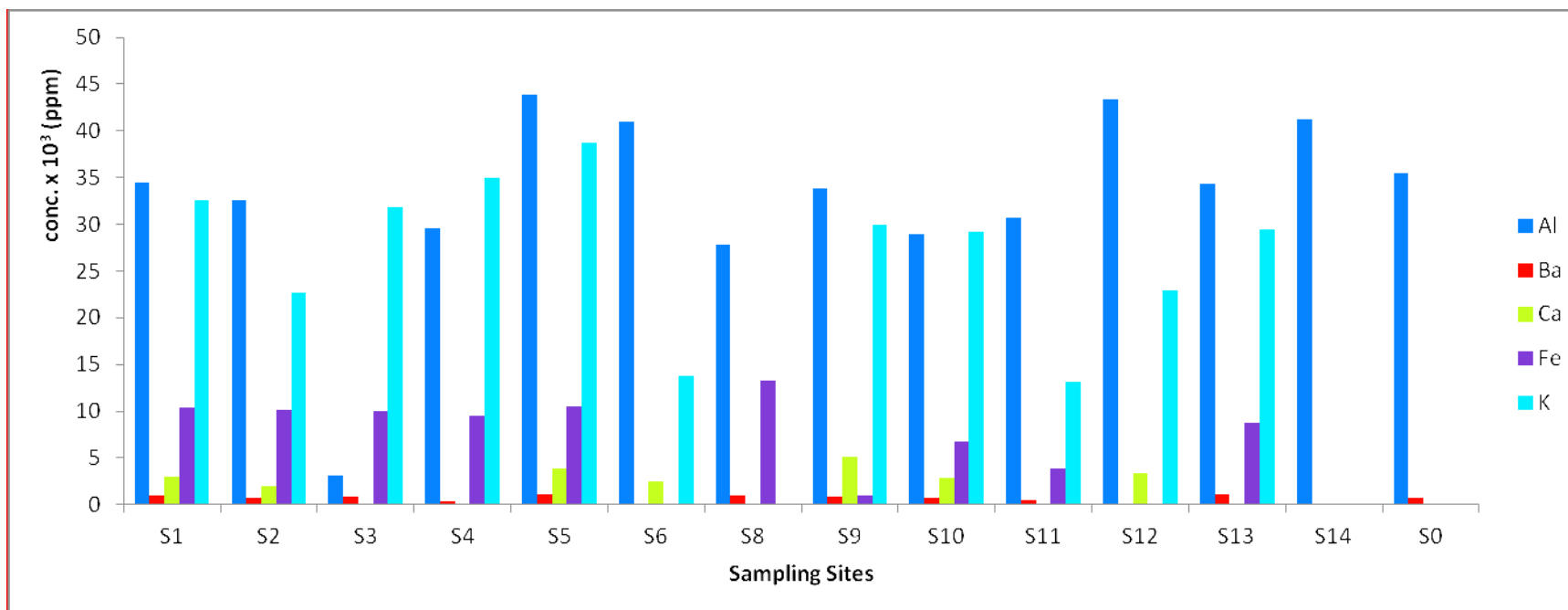


Fig 14a: Concentration of Element Determined in Soil Samples

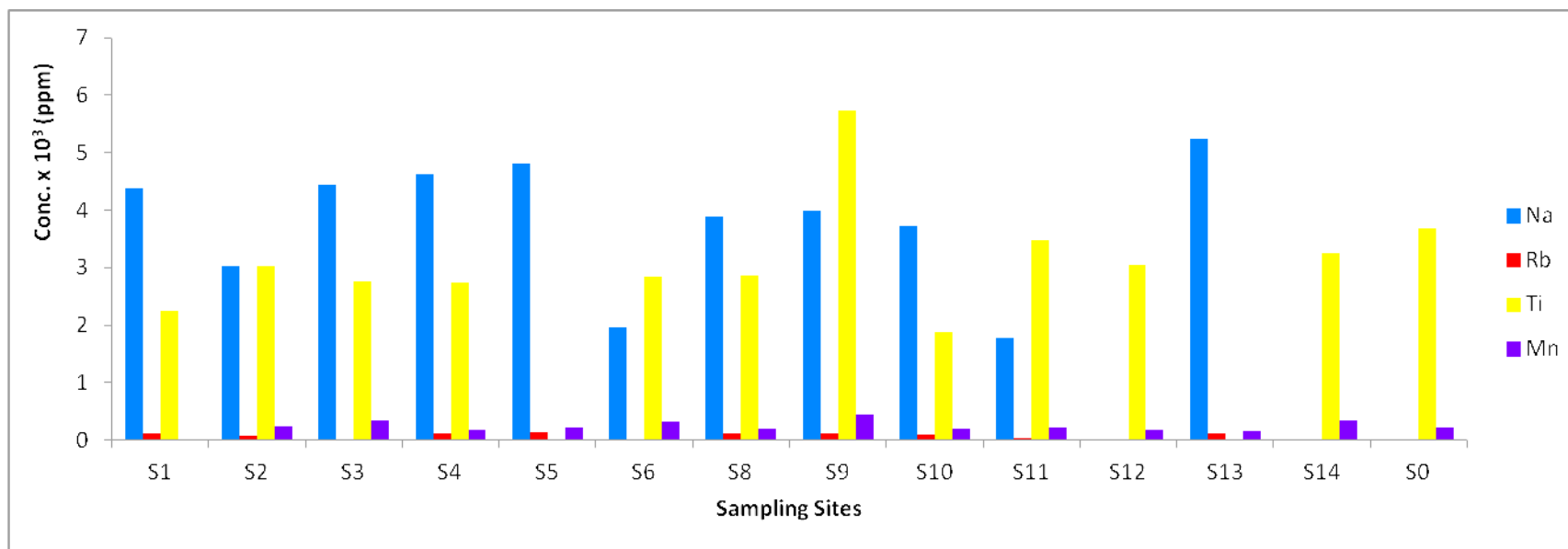


Fig 14b: Concentration of Element Determined in Soil Samples

Figure 14c show the elements whose concentrations varies in tens of part per millions with Zn (21.8 ± 4.4 ppm to 145 ± 7 ppm) > La (5.1 ± 0.1 ppm to 72 ± 0.3 ppm) > Hf (4.14 ± 0.04 ppm to 62 ± 1 ppm) > Cr (3.2 ± 0.2 ppm to 47 ± 3 ppm) > Vn (14.16 ± 2.32 ppm to 29 ± 2 ppm). It can be observed that Zn was exceptionally high in Sites four and ten. Figure 4d represent the graph of some of the rare earth elements and two other elements whose concentrations are in one of part per million with Dy (3.1 ± 0.3 ppm to 6.4 ± 0.4 ppm) > Yb ($2.13 \pm$ ppm to $6.1 \pm$ ppm) > Co (1.6 ± 0.3 ppm to 5.3 ± 0.4 ppm) > Eu (0.9 ± 0.1 ppm to 1.57 ± 0.16 ppm) > U (0.9 ± 0.1 ppm to 6.29 ± 0.29 ppm).

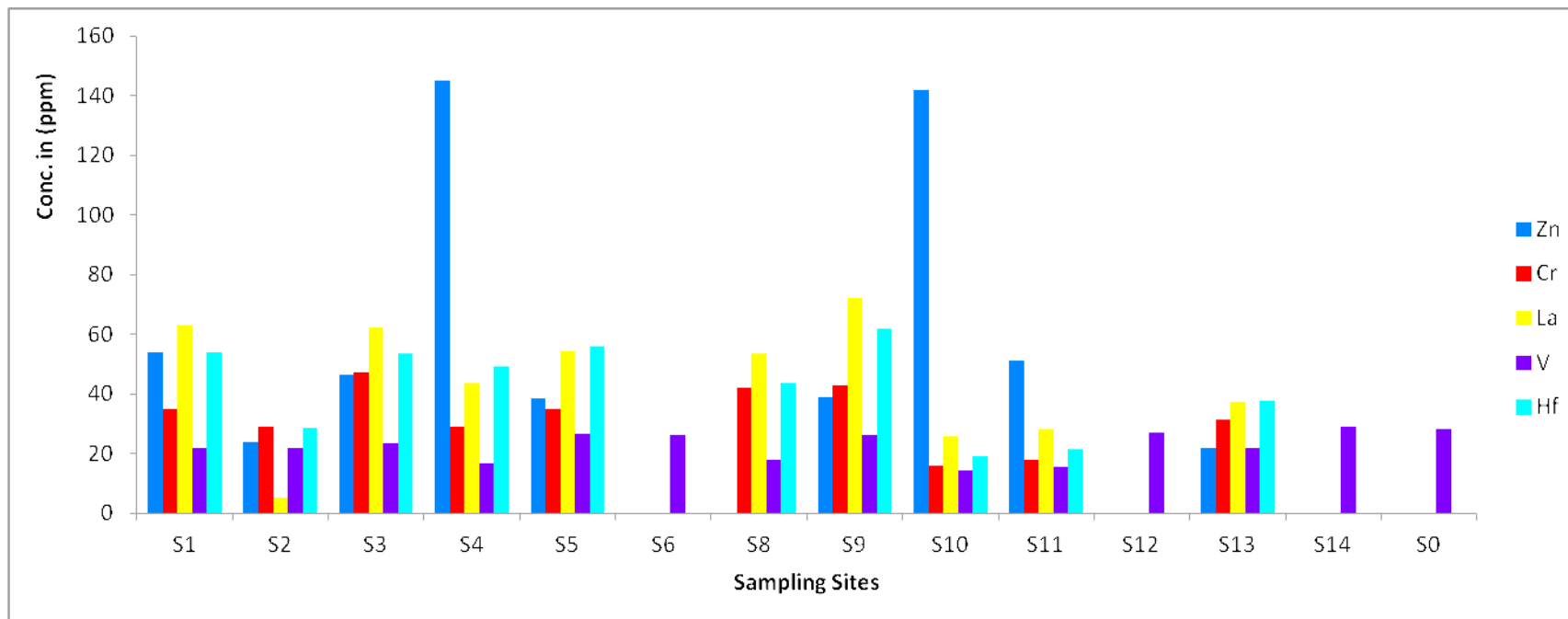


Fig 14c: Concentration of Elements Determined in Soil Samples

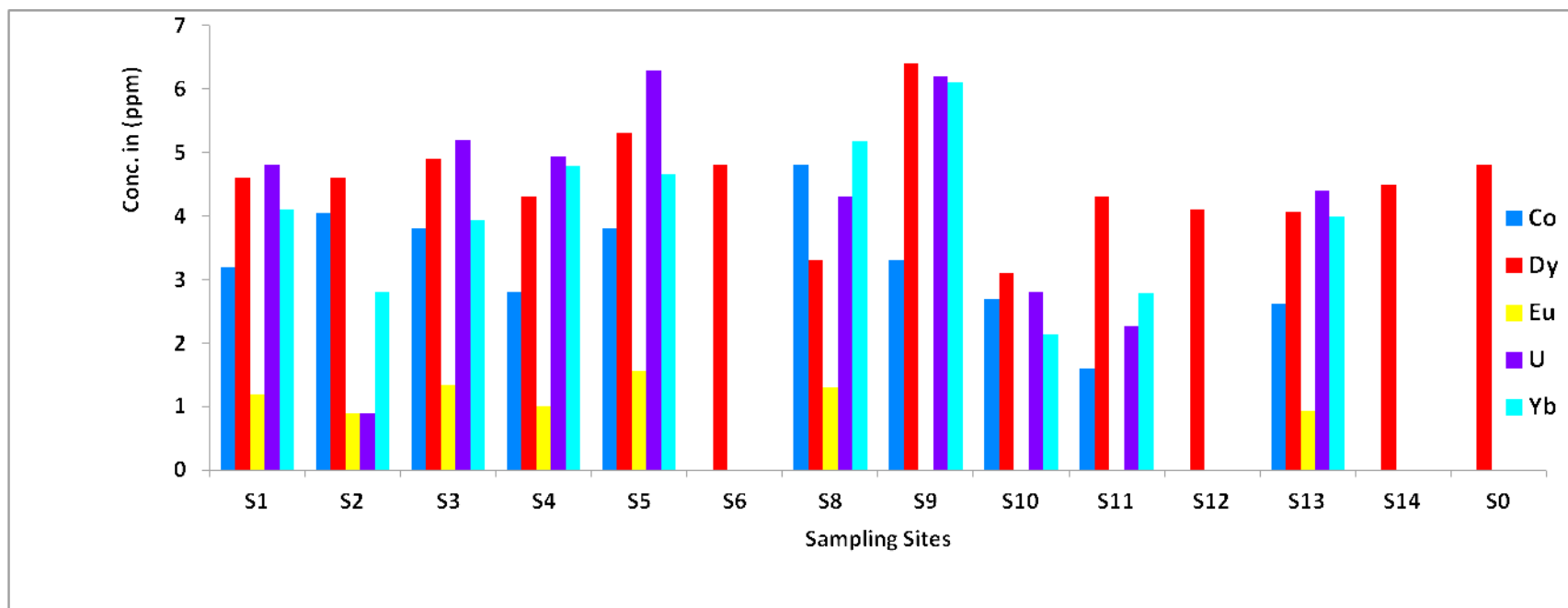


Fig 14d : Concentration of Elements Determined in Soil Samples

4. 5. 2 Sediments Result Analysis

Table 4.15 show the ranges of concentrations of the various elements determined in sediments samples obtained in river Nggada and Alau dam in Maiduguri Metropolis of Borno State of which water were extensively used for irrigation of vegetables cultivated during dry season and the ranges of concentrations of the same elements determined in the sediments of river Kubani in Zaria and some selected coastal areas in Lagos

Table 4.15: Concentrations of Elements in Sediment Samples and Other Related Works

| Elements | Range in this work | Range in Other Work *(Kubanni River) | Range in Other Work #(Selected Coastal Areas in Lagos) | Ranng in Other Work [€] (Kubani River) |
|----------|--------------------|--|---|--|
| Al | 26460 - 42850 | 35000 - 45000 | 3529 - 9650 | |
| Ba | 716 - 965 | 342 - 489 | 148 - 672 | 287.85 – 647.99 |
| Br | 1.5 - 2.3 | 1.0 – 2.2 | 2.4 - 12 | |
| Ca | 1957 - 4123 | 1000 – 8000 | 4350 - 4931 | 72.83 – 155.72 |
| Cr | 2.0 - 44 | 5 – 29.3 | 0 - 14 | 3.41 – 45.22 |
| Cs | 1.2 - 1.9 | 2 – 6.1 | 0 – 1.3 | |
| Co | 1.8 - 5.7 | 3.4 – 4.8 | 1.1 – 3.7 | 1.55 – 5.94 |
| Dy | 3.0 - 16.1 | 4.7 – 7.3 | BDL | |
| Eu | 1.1 - 1.36 | 0.7 – 1.0 | 0 – 1.64 | 0.38 – 5.10 |
| Hf | 10 - 52.9 | 15.7 – 25 | 2.5 – 14 | 0.90 – 47.42 |
| K | 13500 - 29880 | 2000 – 21000 | 2486 – 5513 | |
| La | 11.7 - 103.3 | 28.5 – 51.3 | 2 – 8.5 | |
| Lu | 1.23 - 5.1 | 0.5 – 0.8 | BDL | 0.19 -0.92 |
| Mn | 156 - 408 | 184.5 – 293.3 | 78.2 – 270.7 | |
| Na | 1604 - 4587 | 1 – 2000 | 861 – 3559 | |
| Rb | 68.3 - 107 | 100.6 | 147.6 | 68.08 – 129.30 |
| Sb | 0.34 - 0.45 | 0.2 – 2.3 | BDL | |
| Sc | 2.23 - 4.74 | 2.5 - 4.2 | 0.3 – 2.0 | 0.9 -5.60 |
| Sm | 3.65 - 17.3 | 6.7 – 53 | BDL | |
| Ta | 1.1 - 2.6 | 1.8 – 2.3 | 0 – 0.5 | 0.63 -2.30 |
| Ti | 2234 - 6001 | 2000 – 4000 | 1732 – 9892 | |
| Th | 16.7 - 25.4 | 17.4 – 29.3 | 2.1 – 4.1 | 19.27- 26.68 |
| U | 2.5 - 10.4 | 5.4 – 5.8 | 1.0 – 1.7 | 8.19 – 8.45 |
| V | 13.2 - 31 | 30.5 – 41.1 | 6.0 – 10.0 | |
| Yb | 2.7 - 10.32 | 4.5 – 6.7 | 0 – 1 | |
| Zn | 110 - 396 | 35.4 – 210 | 170.8 – 458.14 | |

*Butu and Iguisi (2013); # Omale, *et al*, (2013). [€]Ewa and Oladipo, 1992.

BDI = Below Detection Limit. (All determinations by INAA): All concentrations in ppm;

It can be clearly observed as displayed in this Table 4.15 that the elements Bromine, Calcium, Chromium, Cesium, Cobalt, Dysprosium, Europium, Hafnium, Potassium, Lanthanum, Lutetium, Manganese, Sodium, Rubidium, Antimony Scandium, Samarium, Tantalum, Titanium, Thallium, Uranium, Vanadium, Ytterbium, and Zinc determined in sediments obtained from river Ngadda and Alau dam, their water being extensively used for dry season farming had concentrations in the ranges determined by other researchers in different environment, Kubanni river in Zaria Kaduna State and selected coastal areas of Lagos state both in Nigeria. The exception was that the concentration of Aluminium obtained in this work is much higher than the values obtained in the sediments of the other river and selected coastal areas also Barium concentration ranges obtained in this study was slightly higher than the concentration ranges obtained in Kubanni River and selected coastal areas of Lagos state. The high concentration of Aluminium determined in this study could be attributed to the fact that since the river along which this study was carried out transcends the metropolis, some of the waste generated from human activities in the city which may involve materials with Aluminium content like smelting of Aluminium pots, household utensils, auto mechanical work, foundries and so on may have been disposed along the bank or eroded to the farm sites

Figures 15a–15d shows the graphical bar chart of the elements determined in the sediments samples. The graph was plotted in four places so that the various ranges of concentrations of the same elements determined in the sediment samples collected from different sites in river Ngadda and Alau dam can distinctly be separated from each other since the same element concentration values may vary significantly with different sites of collection from the river depending on where the river or dam feeder source comes from. It

can be clearly seen from the graph in Figures 15a –15d that the concentration of the elements presented in this bar chart ranges from tens of thousands of part per million to tens and units of part per million in values. The elements with high concentration values determined in sediment samples varies from the various sites as follows;: K (13500 ± 189 ppm to 42850 ± 514 ppm) > Fe (1127 ± 214 ppm to 9210 ± 182 ppm) > Ca 1957 ± 552 ppm to (4123 ± 721 ppm) > Ba (716 ± 37 ppm to 965 ± 38 ppm).

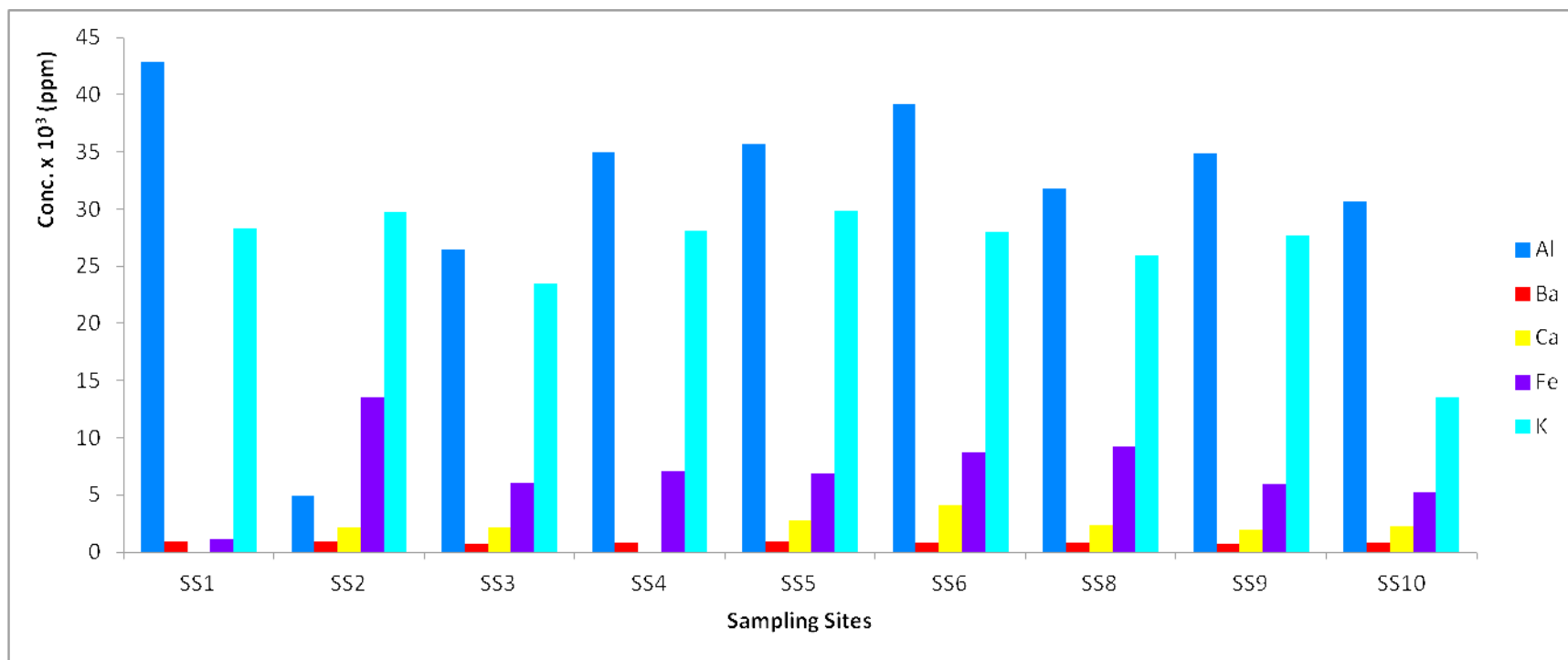


Fig 15a: Concentration of Elements Determined in Sediments Samples

Figure 15b is the bar chart of the elements having concentrations in thousands of part per million with the order of concentration range variation and as Ti (2234 ± 188 ppm to 6001 ± 276) > Na (1604 ± 5 ppm to 4587 ± 9 ppm) > Mn (156 ± 1 ppm to 408 ± 2 ppm) > Rb (68.3 ± 3.8 ppm to 107 ± 5 ppm). Figure 15c represent the graph of elements having concentrations in the order of hundreds of part per million and varies in the order Zn (110 ± 7 ppm to 396 ± 12 ppm) > La (11.7 ± 0.1 ppm to 103.3 ± 0.3 ppm) > Hf (10 ± 0.5 ppm to 52.9 ± 0.5 ppm) > Cr (2.0 ± 0.2 ppm to 44 ± 2 ppm) > V (13.2 ± 0.3 ppm to 31 ± 2 ppm) (Zn exceptionally high in site nine).

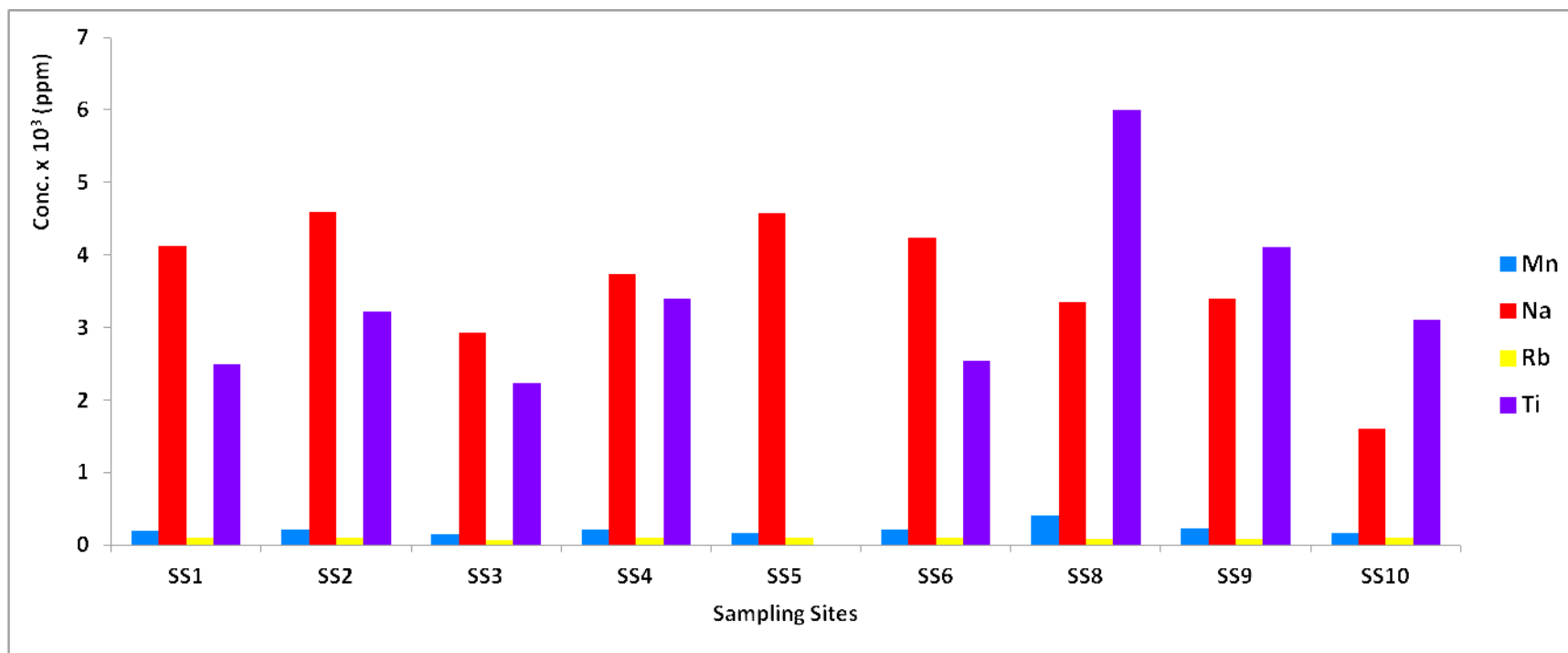


Fig 15b: Concentration of Elements Determined in Sediments Samples

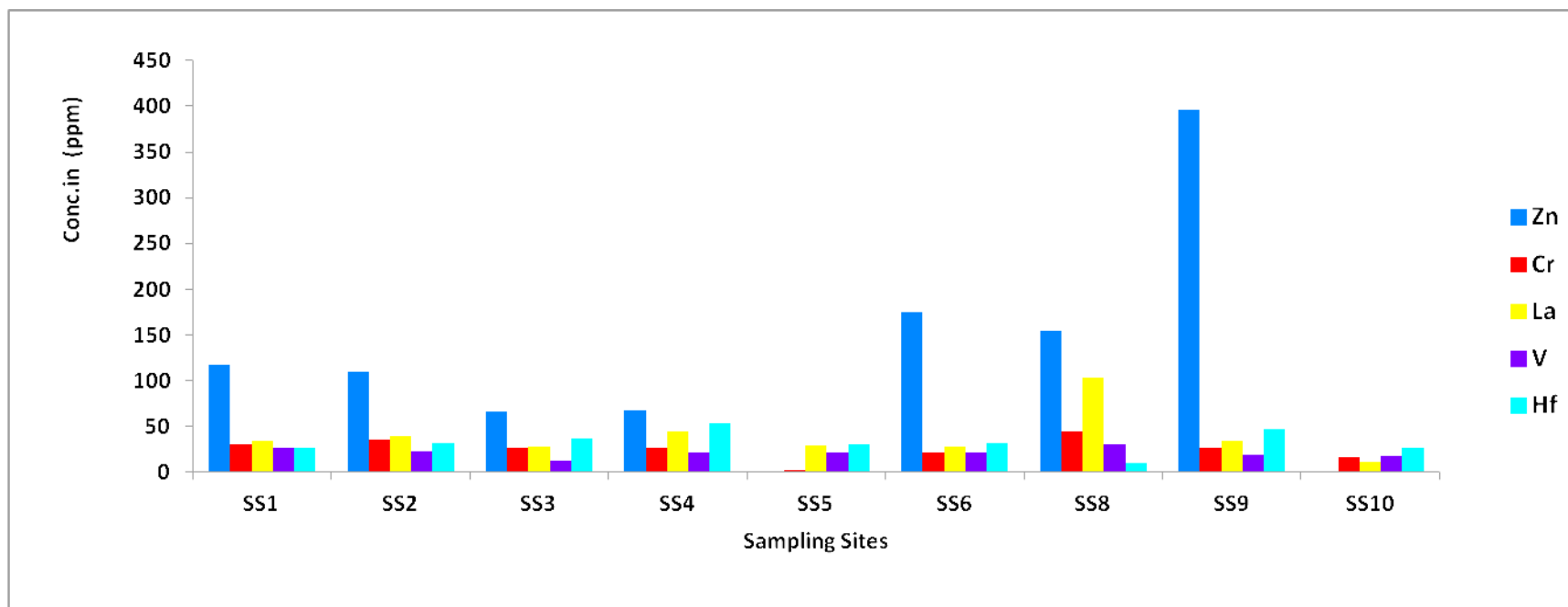


Fig 15c: Concentration of Elements Determined in Sediments Samples

Figure 15d represent the graph of some of the element with low concentration values which coincidentally constitutes some of the rare earth elements and two other trace elements and concentrations are in one of part per million with Dy ranges from $(3.0 \pm 0.3$ ppm to 16.1 ± 0.6 ppm) > Yb (2.7 ± 0.2 ppm to 10.32 ± 0.02 ppm) > Co (1.8 ± 0.2 ppm to 5.7 ± 0.2 ppm) > U (2.5 ± 0.3 ppm to 10.4 ± 0.03 ppm) > Eu (1.1 ± 0.1 ppm to 1.36 ± 0.01 ppm)

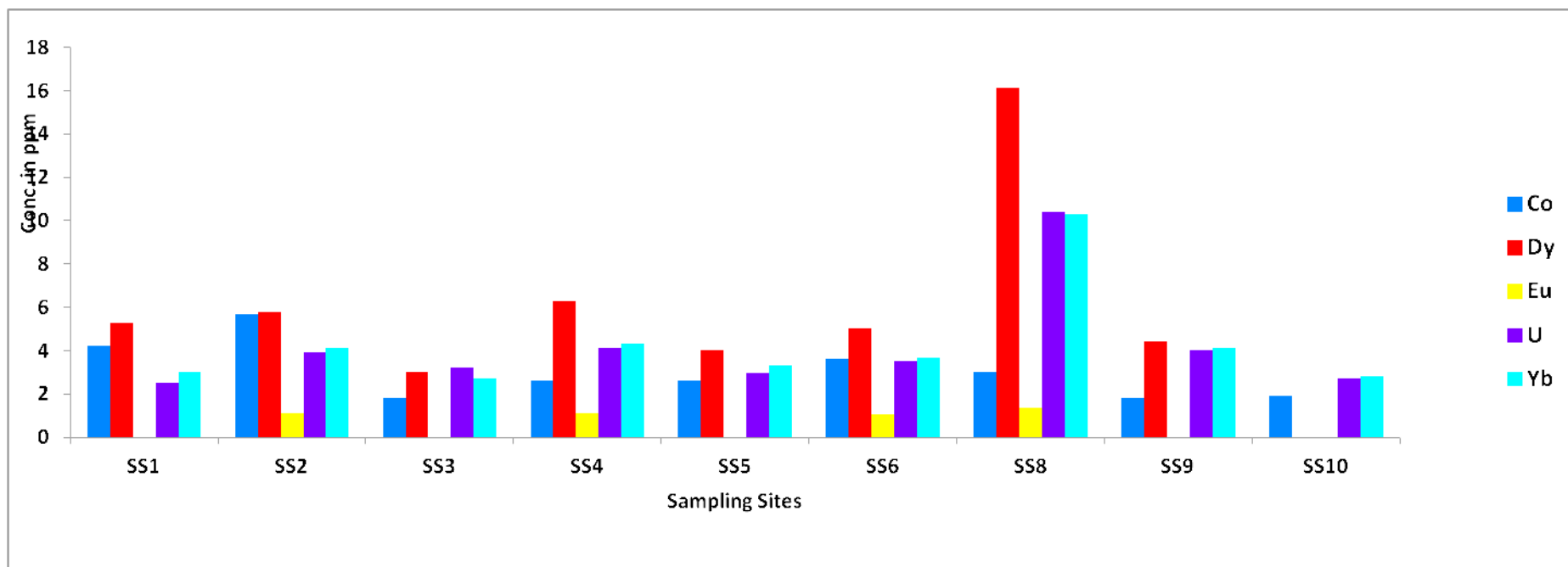


Fig 15d: Concentration of Elements Determined in Sediments Samples

4.5.3 Water Results Analysis

Table 4.16 present the range of concentrations of the various elements determined in water samples obtained from different sites in river Nggada and Alau dam in Maiduguri Metropolis of Borno State of which the water are extensively used for irrigation of vegetables cultivated during dry season along the bank of the river and the dam and the range of concentrations of the same elements recommended by some standard organizations especially the water to be used for continuous irrigation while Figures 16a to 16c shows the graphical bar chart and the linear scatter plots of the elements determined in the water samples while Figure 16d was the linear scatter plots for the water samples data. It can be clearly observed from Figure 16d that the distribution of the various elements followed similar pattern i.e the sites with high concentrations occur for the whole elements and the sites with low concentrations occur for the whole elements.

Table 4.16 Concentration of Elements in Water Samples and Recommended Values

| Element | Concentration Range in this work (ppm) | Recommended Values by different bodies (ppm) | Recommended Safe limit for Continuous Irrigation (ppm) |
|----------------|---|---|---|
| Al | 0.6774 - 3.3546 | | 5.00 [#] |
| Cd | 0.009 - 0.044 | 6* | 0.01 [#] |
| Co | 0.0241 - 0.3918 | | 0.05 [#] |
| Cr | 0.0201 - 0.1358 | 25 ⁺ | 0.10 [#] |
| Cu | 0.0143 - 0.0339 | 25* | 0.20 [#] |
| Fe | 0.3266 - 11.900 | 30 ⁺ | 5.0 [#] |
| Mn | 0.0029 - 0.1069 | 30 [#] | |
| Ni | 0.0053 - 0.3707 | 20* | 0.20 [#] |
| Pb | 0.0741 - 0.4745 | | 5.00 [#] |
| Zn | 0.006 - 3.375 | 123* | - |

*(WHO 2004), ⁺ (USEPA 1999), [#] (USEPA 2000)

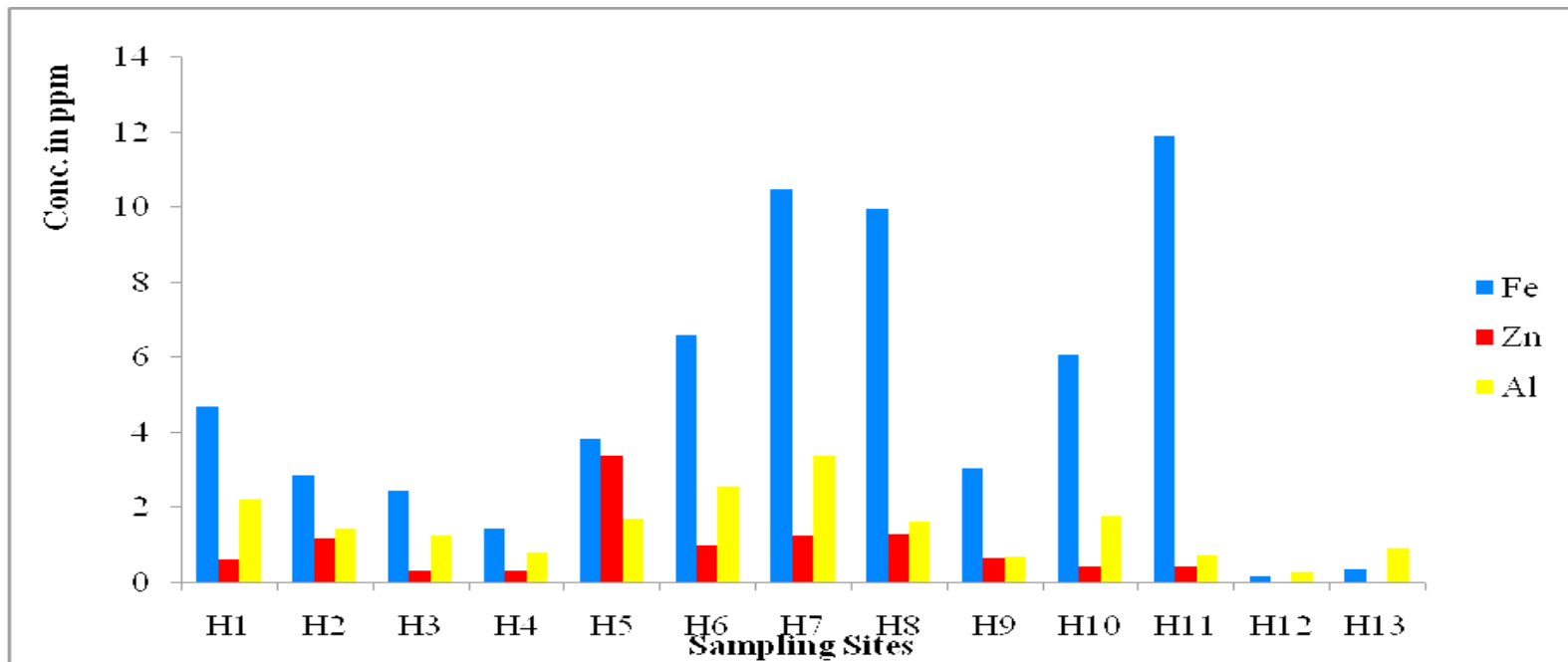


Fig 16a: Concentrations of Elements Determined in Water Samples

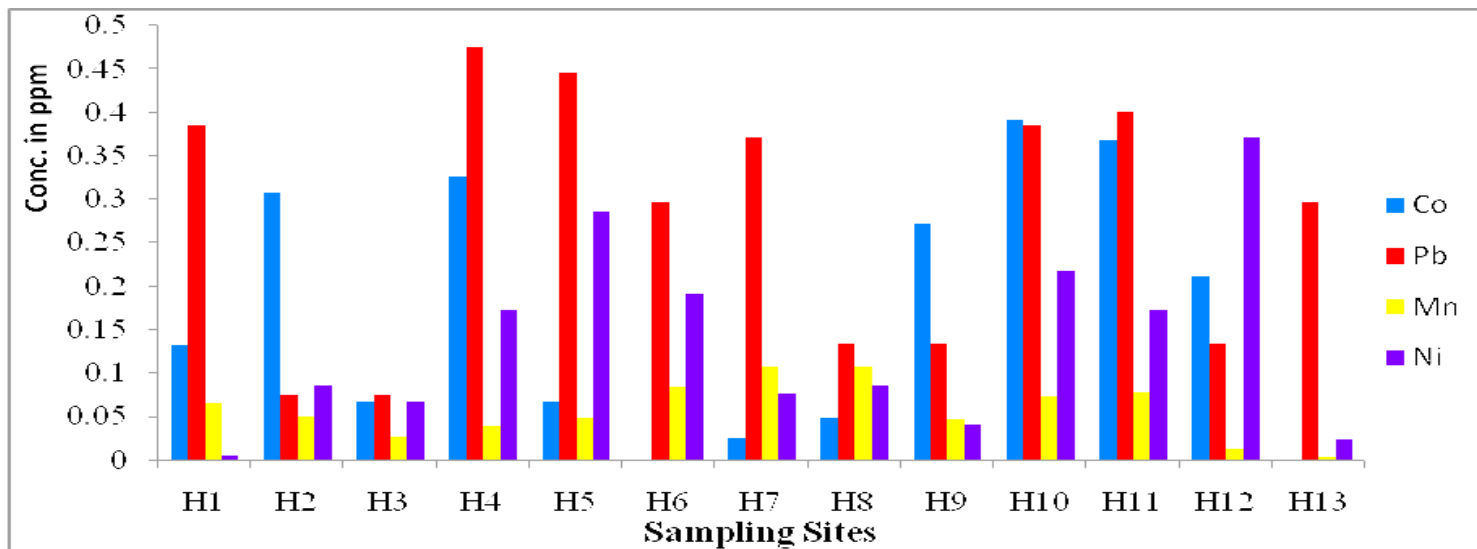


Fig 16b: Concentrations of Elements Determined in Water Samples

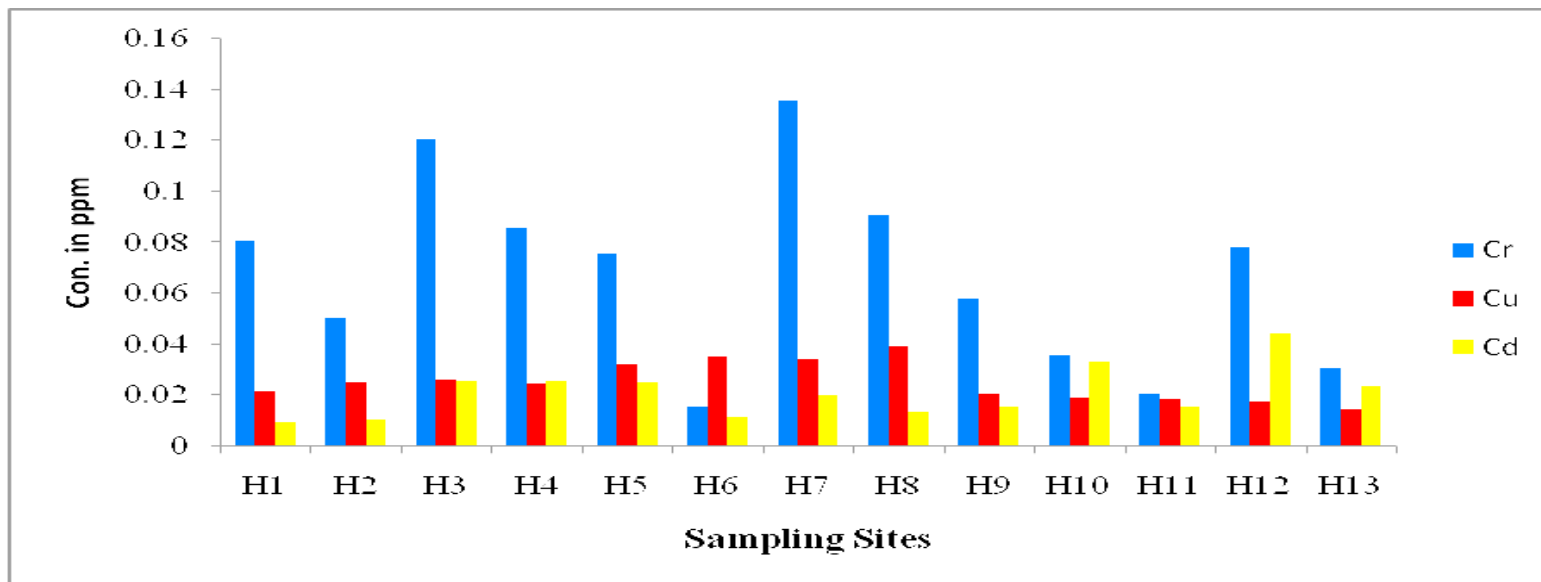
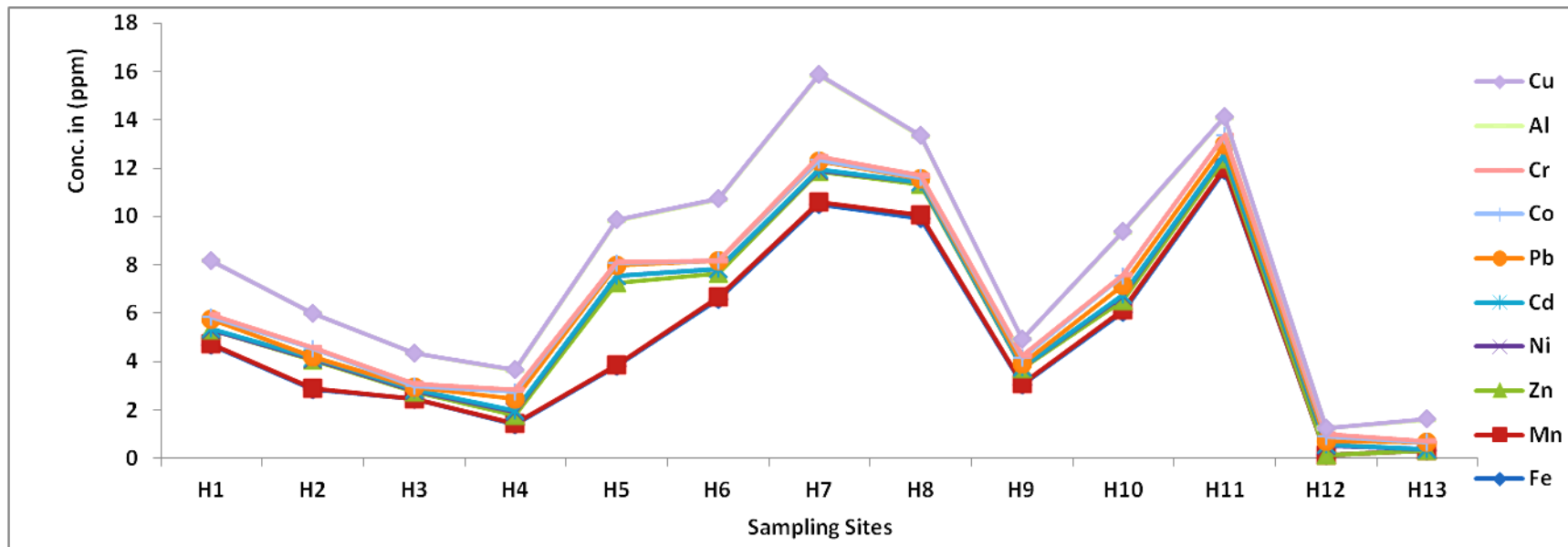


Fig 16c: Concentrations of Elements Determined in Water Samples



p

Fig. 16d: Concentrations of Elements Determined in Water Samples

4.5.4 Vegetable Result Analysis

The vegetable samples collected from farmlands along the bank of river Ngadda and Alau dam cultivated during dry season through irrigation were analyzed for elemental concentrations using neutron activation analysis (NAA). Tables 4.17 to 4.22 show the concentrations of the various elements determined in different vegetable samples collected from different sites. and Tables 4.23 to 4.29 indicate the concentrations of the various elements in the same type of vegetables collected in the various sites. These Tables 4.23 to 4.29 were presented so as to indicate which of the sites have their respective vegetables bio-accumulated with more or less of the specific element than the other and vice versa

Table 4.17 Concentration of Elements Determined in Vegetable Samples in Site 1by INAA

| Sample | Al | Ba | Br | Ca | CL | Co | Cr | Eu | Fe | Hf | K | La |
|--------|----------|---------|--------|-----------|----------|-----------|---------|------|---------|---------|-----------|-----------|
| A1 | 1023±436 | 63±03 | 25±1.0 | 43130±862 | 9390±66 | 0.31±0.04 | 1.0±0.3 | BDL | 640±54 | BDL | 41090±205 | 1.27±0.05 |
| B1 | 2983±042 | 135±14 | 11±0.2 | 9179±422 | 10130±71 | 72±11.00 | 5±1.0 | 32±5 | 1087±71 | 2.2±0.1 | 49960±300 | 2.49±0.06 |
| C1 | 518±013 | 9±02 | 5±1.0 | 12040±445 | 7106±57 | 0.11±0.03 | 1.1±0.2 | BDL | 124±30 | BDL | 16300±147 | 0.21±0.04 |
| D1 | 3369±054 | 20±02 | 21±2.0 | 9161±458 | 9690±03 | 29±4.00 | 2.6±0.3 | | 1027±53 | BDL | 50330±302 | 2.5±0.10 |
| F1 | 880±013 | 31±02 | BDL | 30000±690 | 900±23 | 12±3.00 | 82±23.0 | BDL | 361±38 | BDL | 14580±146 | 0.84±0.04 |
| H1 | 2130±030 | 16.4±03 | 17±2.0 | 16150±055 | 6018±54 | 0.40±0.04 | 8.1±0.3 | BDL | 2955±68 | BDL | 74800±299 | 1.49±0.07 |

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Sm | Th | V | Yb | Zn |
|--------|-------------|-----------|-----------|--------|-------|-----------|------------|------------|-----------|-----------|-----------|----------|
| A1 | BDL | 18180±436 | 179±1.0 | 232±1 | 16±1 | 0.2±0.03 | 0.11±0.01 | 0.15±0.05 | 0.28±0.05 | 1.5±0.40 | BDL | 22±2.0 |
| B1 | 0.005±0.001 | 4634±375 | 168±0.5 | 4441±4 | 57±3 | 4.2±0.10 | 37.1±1.40 | 0.28±0.01 | 1.1±0.10 | 3.4±0.78 | 0.12±0.03 | 42±4.0 |
| C1 | BDL | 4586±266 | 24±0.2 | 1767±4 | 12±1 | BDL | 0.03±0.004 | 0.029±0.00 | BDL | BDL | BDL | 24.0±0.1 |
| D1 | BDL | 4750±632 | 176±1.0 | 4554±5 | 21±1 | 4.6±0.10 | 27±1.00 | 0.36±0.01 | 1.04±0.06 | 4±1.00 | BDL | 36±3.0 |
| F1 | BDL | 7163±280 | 122.1±0.4 | 1596±3 | 6.2±1 | BDL | 10±1.00 | 0.09±0.01 | 28±5.00 | 1.61±0.35 | BDL | 14±2.0 |
| H1 | BDL | 18870±584 | 349±1.0 | 3052±6 | 16±1 | 0.25±0.04 | 0.17±0.01 | 0.20±0.01 | 0.60±0.05 | 2.8±0.50 | BDL | 55±3.0 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

Table 4.18: Concentration of Elements Determined in Vegetable Samples in Site 2 by INAA

| Sample | Al | Ba | Br | Ca | Cl | Co | Cr | Eu | Fe | K | La |
|--------|---------|--------|----------|-----------|----------|-----------|---------|-------------|---------|-----------|-----------|
| A2 | 1508±18 | 54±2 | 9±1.0 | 38560±762 | 7813±55 | 20±3.00 | BDL | BDL | 550±37 | 41260±206 | 1.13±0.05 |
| B2 | 1634±51 | 17±2 | 21±1.0 | 16460±609 | 19450±97 | 0.33±0.04 | 1.7±0.3 | 0.021±0.004 | 783±45 | 46860±281 | 1.6±0.10 |
| C2 | 452±19 | 10.4±2 | 5±1.0 | 10930±459 | 6750±54 | BDL | 1.0±0.2 | BDL | 219±35 | 1453±145 | 1.93±0.05 |
| D2 | 1851±20 | 17±3 | 12.1±1,5 | 14880±476 | 6018±54 | 40±4.00 | 8.6±0.3 | | 2316±65 | 49730±349 | 38±4.00 |
| F2 | 1441±43 | 40±2 | 8.9±2.7 | 15710±613 | 5388±54 | 1.04±0.02 | 31±1.0 | BDL | 3104±84 | 68330±273 | 2.15±0.06 |

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Sm | Th | V | Zn |
|--------|------|-----------|------------|--------|------|-----------|------------|------------|-----------|-----------|------|
| A2 | BDL | 13370±040 | 93.24±0.28 | 364±1 | 15±1 | 18±2.00 | 13±1.00 | 13.1±0.50 | 27±5.00 | 2.3±0.40 | 27±2 |
| B2 | BDL | 4396±426 | 170±1.00 | 3132±6 | 19±1 | 0.10±0.03 | 0.15±0.01 | 0.22±0.01 | 1.33±0.06 | BDL | 36±3 |
| C2 | BDL | 3995±340 | 22.9±0.20 | 1616±3 | 11±1 | 0.13±0.03 | 0.040±0.06 | 0.24±0.01 | 0.42±0.04 | BDL | 24±3 |
| D2 | BDL | 18670±467 | 121.4±0.50 | 2921±6 | 14±1 | BDL | 21±1.00 | BDL | 81±5.00 | 2.82±0.41 | 63±4 |
| F2 | 11±3 | BDL | 342±1.00 | 3136±6 | 48±2 | 40±3.00 | 29±1.00 | 0.264±0.00 | 1.6±0.10 | BDL | 80±4 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

Table 4.19: Concentration of Elements Determined in Vegetable Samples in Site 3 by INAA

| Sample | Al | Ba | Br | Ca | Cl | Co | Cr | Eu | Fe | K | La |
|--------|----------|------|---------|-----------|----------|-----------|---------|-------------|---------|-----------|-----------|
| A3 | 1301±029 | 40±2 | 11±1.0 | 39280±864 | 4714±47 | 0.36±0.04 | BDL | 0.027±0.007 | 502±37 | 41240±206 | 10.7±0.10 |
| B3 | 6450±213 | 10±2 | 26±1.0 | 14290±529 | 18010±90 | BDL | 1.8±0.3 | 0.023±0.006 | 349±31 | 47350±237 | 0.40±0.05 |
| C3 | 843±016 | 12±1 | 3.1±0.4 | 11500±437 | 6967±56 | BDL | 1.3±0.2 | BDL | 204±25 | 15440±140 | 0.30±0.03 |
| D3 | 932±018 | 16±2 | 10±1.0 | 28710±718 | 7102±52 | 0.15±0.03 | BDL | 0.04±0.01 | 707±47 | 17120±137 | 1.24±0.03 |
| F3 | 1412±025 | 12±2 | 14±1.0 | 16110±548 | 6052±54 | 0.41±0.04 | BDL | BDL | 2134±60 | 67790±271 | 1.2±0.10 |
| H3 | 883±017 | 37±3 | 5.1±0.6 | 30200±725 | 975±24 | BDL | 1.6±0.3 | BDL | 394±38 | 13760±138 | 1.00±0.04 |

| Sample | Mg | Mn | Na | Rb | Sb | Sc | Sm | Th | V | Yb | Zn |
|--------|-----------|-----------|----------|------------|-----------|------------|------------|-----------|---------|-----------|------|
| A3 | 19890±537 | 410±1.0 | 191±1.0 | 17.61±0.05 | 0.48±0.03 | 0.12±0.01 | 0.29±0.01 | 1.12±0.05 | BDL | BDL | 85±4 |
| B3 | 4645±395 | 116.7±0.5 | 2783±3.0 | 13±1.00 | 0.29±0.03 | 0.07±0.01 | 0.045±0.01 | 0.15±0.04 | BDL | BDL | 25±3 |
| C3 | 4773±282 | 27.8±0.2 | 1703±3.0 | 11±1.00 | 0.15±0.02 | 0.033±0.00 | 0.05±0.01 | BDL | BDL | BDL | 23±3 |
| D3 | 6403±302 | 122.8±0.4 | 19.0±0.1 | 6±1.00 | 0.29±0.03 | 0.15±0.01 | 0.149±0.00 | BDL | 1.5±0.4 | 0.10±0.02 | 26±3 |
| F3 | 19520±547 | 330±1.0 | 2749±6.0 | 14±1.00 | 0.46±0.03 | 0.15±0.01 | 0.19±0.01 | BDL | 1.6±0.5 | BDL | 70±3 |
| H3 | 7551±294 | 132.2±4.0 | 1430±3.0 | 5.4±0.50 | BDL | 11±1.00 | 0.089±0.01 | 0.25±0.04 | 1.7±0.4 | BDL | 13±2 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table4.20: Concentration of Elements Determined in Vegetable Samples in Site 4 by INAA.

| Sample | Al | Ba | Br | Ca | Cl | Co | Cr | Eu | Fe | K | La |
|--------|---------|--------|---------|-----------|----------|-----------|----------|-------------|--------|-----------|-----------|
| A4 | 1176±21 | 30±02 | 11±1.0 | 46540±884 | 12340±74 | BDL | 88±21.0 | BDL | 655±40 | 32300±194 | 1.2±0.10 |
| B4 | 1799±40 | 18±02 | 19.±1.0 | 17110±616 | 19010±95 | 0.2±0.03 | 1.3±0.2 | 0.026±0.007 | 691±44 | 48090±194 | 0.92±0.06 |
| C4 | 437±10 | 10±02 | 3.1±0.6 | 13410±443 | 7275±58 | BDL | 1.2±0.2 | 0.022±0.005 | 303±36 | 13580±149 | 0.29±0.03 |
| D4 | 1068±16 | 15±-2 | 10±1.0 | 33960±747 | 8656±61 | 0.12±0.03 | 11.3±0.4 | BDL | 395±40 | 11650±117 | 1.1±0.03 |
| H4 | 912±14 | 233±13 | 2.3±0.1 | 30930±071 | 1024±24 | 33±9.00 | BDL | BDL | 644±52 | 15130±166 | 1.34±0.04 |

| Sample | Mg | Mn | Na | Rb | Sb | Sc | Se | Sm | Th | V | Zn |
|--------|-----------|-----------|--------|------|--------|-----------|-----|-------------|-----------|------------|----------|
| A4 | 15310±429 | 72.1±0.3 | 443±2 | 18±1 | 13±2 | 15±1.00 | BDL | 0.15±0.010 | 33±5.00 | 2.3±0.50 | BDL |
| B4 | 4843±392 | 113±1.0 | 3165±3 | 19±1 | BDL | 0.16±0.01 | BDL | 0.104±0.010 | 20±3.00 | BDL | 30±3.0 |
| C4 | 4497±261 | 25.0±0.2 | 1609±3 | 12±1 | 0.26±0 | 0.04±0.01 | BDL | 0.044±0.004 | 0.18±0.04 | BDL | 27±2.0 |
| D4 | 1606±324 | 161.9±0.3 | 121±1 | 4±1 | BDL | 0.1±0.01 | BDL | 0.133±0.005 | 0.24±0.04 | 1.1±0.30 | 27.7±2.3 |
| H4 | 7262±312 | 124.3±0.4 | 1674±3 | 17±2 | 81±15 | 17±1.00 | BDL | BDL | 38±6.00 | 1.65±0..27 | 13±3.0 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

Table 4.21: Concentration of Elements Determined in Vegetable Samples in Site 5 by INAA

| Sample | Al | Ba | Br | Cl | Co | Cr | Eu | Fe | K | La |
|--------|----------|----------|---------|---------|-----------|-----|------|------------|------------|-----------|
| C5 | 47±11 | 7±0 | 7±1.0 | 6971±56 | BDL | BDL | BDL | 556±32 | 20860±146 | 0.34±0.02 |
| D5 | 1293±14 | 18±0.2 | 26±0.3 | 2648±34 | 1.08±0.05 | BDL | BDL | 664±38 | 4490±130 | BDL |
| E5 | 1067±6 | 22±0.5 | 173±1.0 | 289±5 | 1.8±0.4 | BDL | 15±1 | 470±36 | 4061700±44 | 2.7±0.3 |
| E5 | 3070±289 | 20.0±0.2 | 639±3.0 | 9.2±0.6 | BDL | BDL | | 11.3±0.500 | 18±4 | BDL |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.22: Concentration of Elements Determined in Vegetable Samples in Site 6 by INAA

| Sample | Al | Ba | Br | Ca | Cl | Cr | Eu | Fe | K | La |
|--------|---------|-----|---------|-----------|---------|---------|------------|----------|-----------|------------|
| C6 | BDL | 8±2 | 4±1.0 | 9529±619 | 7245±65 | BDL | 0.021±0.01 | 1.1±0.4 | 16500±281 | 0.203±0.03 |
| D6 | 1057±62 | BDL | 13±1.0 | 16810±723 | 6149±58 | 3.9±0.3 | BDL | 379±33.0 | 14390±245 | 1.00±0.03 |
| E6 | 417±43 | BDL | 3.7±0.7 | 7160±422 | 5219±52 | BDL | BDL | 263±30.0 | 20990±308 | 31±2.00 |

| Sample | Mg | Mn | Na | Rb | Sb | Sc | Se | Sm | Th | Zn |
|--------|----------|------------|-----------|---------|------|-------------|-----|-------------|------|------|
| C6 | 5239±613 | 22.9±0.20 | 1421±6.0 | 13±1.0 | BDL | 0.02±0.004 | BDL | 0.02±0.004 | BDL | 8±1 |
| D6 | 4660±531 | 112.2±0.40 | 107.9±1.5 | 5.4±0.6 | BDL | 0.099±0.006 | BDL | 0.106±0.004 | BDL | 17±3 |
| E6 | 4753±318 | 31.3±0.22 | 455±3.0 | 5.6±0.5 | 70±5 | | BDL | 17.4±4.600 | 13±4 | 29±3 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.23: Concentration of Elements Determined in Amaranthus in Different sites by INAA

| Sample | Al | As | Ba | Br | Ca | CL | Co | Cr | Cs | Cu | Dy | Eu | Fe | Hf | K | La |
|--------|----------|-----|------|------|-----------|----------|-----------|---------|-----|-----|----|-------------|--------|-----|-----------|-----------|
| A1 | 1023±436 | BDL | 63±3 | 25±1 | 43130±862 | 9390±66 | 0.31±0.04 | 1.0±0.3 | BDL | BDL | NA | BDL | 640±54 | BDL | 41090±205 | 1.27±0.05 |
| A2 | 1508±018 | BDL | 54±2 | 9±1 | 38560±762 | 7813±55 | 20±3.00 | BDL | BDL | BDL | NA | BDL | 550±37 | BDL | 41260±206 | 1.13±0.05 |
| A3 | 1301±029 | BDL | 40±2 | 11±1 | 39280±864 | 4714±47 | 0.36±0.04 | BDL | BDL | BDL | NA | 0.027±0.007 | 502±37 | BDL | 41240±206 | 10.7±0.10 |
| A4 | 1176±021 | BDL | 30±2 | 11±1 | 46540±884 | 12340±74 | BDL | 88±21.0 | BDL | BDL | NA | BDL | 655±40 | BDL | 32300±194 | 1.2±0.10 |

| Sam- ple | Lu | Mg | Mn | Na | Rb | Sb | Sc | Se | Sm | Ta | Ti | Th | V | Zn |
|-------------|-----|-----------|------------|-------|------------|-----------|-----------|-----|-----------|-----|----|-----------|---------|------|
| A1 | BDL | 18180±436 | 179±1.000 | 232±1 | 16±1.00 | 0.2±0.03 | 0.11±0.01 | BDL | 0.15±0.05 | BDL | NA | 0.28±0.05 | 1.5±0.4 | 22±2 |
| A2 | BDL | 13370±040 | 93.24±0.28 | 364±1 | 15±1.00 | 18±2.00 | 13±1.00 | BDL | 13.1±0.50 | BDL | NA | 27±5.00 | 2.3±0.4 | 27±2 |
| A3 | BDL | 19890±537 | 410±1.00 | 191±1 | 17.61±0.05 | 0.48±0.03 | 0.12±0.01 | BDL | 0.29±0.01 | BDL | NA | 1.12±0.05 | BDL | 85±4 |
| A4 | BDL | 15310±429 | 72.1±0.30 | 443±2 | 18±1.00 | 13±2.00 | 15±1.00 | BDL | 0.15±0.01 | BDL | NA | 33±5.00 | 2.3±0.5 | BDL |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

Table 4.24: Concentration of Elements Determined in Lettuce in Different sites by INAA

| Sample | Al | As | Ba | Br | Ca | Cl | Co | Cr | Eu | Fe | Hf | K | La |
|--------|----------|-----|--------|--------|-----------|----------|-----------|---------|-------------|---------|---------|-----------|-----------|
| B1 | 2983±042 | BDL | 135±14 | 11±0.2 | 9179±422 | 10130±71 | 72±11.00 | 5±1.0 | 32±5.000 | 1087±71 | 2.2±0.1 | 49960±300 | 2.49±0.06 |
| B2 | 1634±051 | BDL | 17±02 | 21±1.0 | 16460±609 | 19450±97 | 0.33±0.04 | 1.7±0.3 | 0.021±0.004 | 783±45 | BDL | 46860±281 | 1.6±0.10 |
| B3 | 6450±213 | BDL | 10±02 | 26±1.0 | 14290±529 | 18010±90 | BDL | 1.8±0.3 | 0.023±0.006 | 349±31 | BDL | 47350±237 | 0.40±0.05 |
| B4 | 1799±040 | BDL | 18±02 | 19±1.0 | 17110±616 | 19010±95 | 0.2±0.03 | 1.3±0.2 | 0.026±0.007 | 691±44 | BDL | 48090±194 | 0.92±0.06 |

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Sm | Th | U | V | Yb | Zn |
|--------|-------------|----------|-----------|--------|------|------------|-----------|------------|-----------|-----|----------|-----------|------|
| B1 | 0.005±0.001 | 4634±375 | 168±0.5 | 4441±4 | 57±3 | 4.2±0.1.00 | 37.1±1.40 | 0.28±0.01 | 1.1±0.10 | BDL | 3.4±0.78 | 0.12±0.03 | 42±4 |
| B2 | BDL | 4396±426 | 170±1.0 | 3132±6 | 19±1 | 0.10±0.03 | 0.15±0.01 | 0.22±0.01 | 1.33±0.06 | BDL | BDL | BDL | 36±3 |
| B3 | BDL | 4645±395 | 116.7±0.5 | 2783±3 | 13±1 | 0.29±0.03 | 0.07±0.01 | 0.045±0.01 | 0.15±0.04 | BDL | BDL | BDL | 25±3 |
| B4 | BDL | 4843±392 | 113±1.0 | 3165±3 | 19±1 | BDL | 0.16±0.01 | 0.104±0.01 | 20±3.00 | BDL | BDL | BDL | 30±3 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.25: Concentration of Elements Determined in Okro in Different sites by INAA

| Sample | Al | Ba | Br | Ca | Cl | Co | Cr | Dy | Eu | Fe | Hf | K | La |
|--------|--------|----------|---------|-----------|---------|-----------|---------|----|-------------|----------|-----|-----------|------------|
| C1 | 518±13 | 9±2.0 | 5±1.0 | 12040±445 | 7106±57 | 0.11±0.03 | 1.1±0.2 | NA | BDL | 124±30.0 | BDL | 16300±147 | 0.21±0.04 |
| C2 | 452±19 | 10.4±1.6 | 5±1.0 | 10930±459 | 6750±54 | BDL | 1.0±0.2 | NA | BDL | 219±35.0 | BDL | 1453±145 | 1.93±0.05 |
| C3 | 843±16 | 12±1.0 | 3.1±0.4 | 11500±437 | 6967±56 | BDL | 1.3±0.2 | NA | BDL | 204±25.0 | BDL | 15440±140 | 0.30±0.03 |
| C4 | 437±10 | 10±2.0 | 3.1±0.6 | 13410±443 | 7275±58 | BDL | 1.2±0.2 | NA | 0.022±0.005 | 303±36.0 | BDL | 13580±149 | 0.29±0.03 |
| C5 | 477±11 | 7±1.0 | 7±1.0 | BDL | 6971±56 | BDL | BDL | NA | BDL | 256±32.0 | BDL | 20860±146 | 0.34±0.03 |
| C6 | BDL | 8±2.0 | 4±1.0 | 9529±619 | 7245±65 | BDL | BDL | NA | 0.021±0.006 | 1.1±0.4 | BDL | 16500±281 | 0.203±0.03 |

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Sm | Ta | Ti | Th | U | V | Yb | Zn |
|--------|-----|----------|----------|---------|------|-----------|------------|-------------|-----|----|-----------|-----|-----|-----|----------|
| C1 | BDL | 4586±266 | 24±0.2 | 1767±4 | 12±1 | BDL | 0.03±0.004 | 0.029±0.004 | BDL | NA | BDL | BDL | BDL | BDL | 24.0±0.1 |
| C2 | BDL | 3995±340 | 22.9±0.2 | 1616±3 | 11±1 | 0.13±0.03 | 0.040±0.06 | 0.24±0.01 | BDL | NA | 0.42±0.04 | BDL | BDL | BDL | 24±3.0 |
| C3 | BDL | 4773±282 | 27.8±0.2 | 1703±3 | 11±1 | 0.15±0.02 | 0.033±0.00 | 0.05±0.01 | BDL | NA | BDL | BDL | BDL | BDL | 23±3.0 |
| C4 | BDL | 4497±261 | 25.0±0.2 | 1609±3 | 12±1 | 0.26±0.03 | 0.04±0.01 | 0.044±0.00 | BDL | NA | 0.18±0.04 | BDL | BDL | BDL | 8±1.0 |
| C5 | BDL | 5662±294 | 40.2±0.2 | 305±1.5 | 7±1 | | 0.05±0.01 | 0.053±0.00 | BDL | NA | BDL | BDL | BDL | BDL | 21±2.0 |
| C6 | BDL | 5239±613 | 22.9±0.2 | 1421±6 | 13±1 | BDL | 0.02±0.00 | 0.02±0.00 | BDL | NA | BDL | BDL | BDL | BDL | 8±1.0 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

Table 4.26: Concentration of Elements Determined in Guinea Sorrel in Different sites by INAA

| Sample | Al | Ba | Br | Ca | Cl | Co | Cr | Cs | Dy | Eu | Fe | Hf | K | La |
|--------|---------|------|----------|-----------|---------|-----------|----------|-----|----|-----------|---------|-----|-----------|-----------|
| D1 | 3369±54 | 20±2 | 21±2.0 | 9161±458 | 9690±03 | 29±4.00 | 2.6±0.3 | BDL | NA | | 1027±53 | BDL | 50330±302 | 2.5±0.10 |
| D2 | 1851±20 | 17±3 | 12.1±1,5 | 14880±476 | 6018±54 | 40±4.00 | 8.6±0.3 | BDL | NA | | 2316±65 | BDL | 49730±349 | 38±4.00 |
| D3 | 932±18 | 16±2 | 10±1.0 | 28710±718 | 7102±52 | 0.15±0.03 | BDL | BDL | NA | 0.04±0.01 | 707±47 | BDL | 17120±137 | 1.24±0.03 |
| D4 | 1068±16 | 15±2 | 10±1.0 | 33960±747 | 8656±61 | 0.12±0.03 | 11.3±0.4 | BDL | NA | BDL | 395±40 | BDL | 11650±117 | 1.1±0.03 |
| D5 | 1293±14 | 18±2 | 3.6±0.6 | BDL | 2648±34 | 28±5.00 | 1.0±0.3 | BDL | NA | | 464±38 | BDL | 14490±130 | 1.34±0.05 |
| D6 | 1057±62 | BDL | 13±1.0 | 16810±723 | 6149±58 | BDL | 3.9±0.3 | BDL | NA | BDL | 379±33 | BDL | 14390±245 | 1.00±0.03 |

| Sample | Mg | Mn | Na | Rb | Sb | Sc | Sm | Ti | Th | U | V | Yb | Zn |
|--------|-----------|-----------|-----------|---------|-----------|------------|-------------|----|-----------|-----|-----------|-----------|----------|
| D1 | 4750±632 | 176±1 | 4554±5.0 | 21±1.0 | 4.6±0.10 | 27±1.00 | 0.36±0.010 | NA | 1.04±0.06 | BDL | 4±1.00 | BDL | 36±3.0 |
| D2 | 18670±467 | 121.4±0.5 | 2921±6.0 | 14±1.0 | BDL | 21±1.00 | | NA | 81±5.00 | BDL | 2.82±0.41 | BDL | 63±4.0 |
| D3 | 6403±302 | 122.8±0.4 | 19.0±0.1 | 6±1.0 | 0.29±0.03 | 0.15±0.01 | 0.149±0.004 | NA | BDL | BDL | 1.5±0.40 | 0.10±0.02 | 26±3.0 |
| D4 | 1606±324 | 161.9±0.3 | 121±1.0 | 4±0.5 | BDL | 0.1±0.01 | 0.133±0.005 | NA | 0.24±0.04 | BDL | 1.1±0.30 | BDL | 27.7±2.3 |
| D5 | 5241±267 | 166.3±0.5 | 173±1.0 | 5.4±0.6 | BDL | 15±1.00 | 17.2±0.400 | NA | 36±5.00 | BDL | 2.0±0.30 | BDL | 21±3.0 |
| D6 | 4660±531 | 112.2±0.4 | 107.9±1.5 | 5.4±0.6 | BDL | 0.099±0.01 | 0.106±0.004 | NA | BDL | BDL | BDL | BDL | 17±3.0 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Se | Sm | Ta | Ti | Th | U | V | Zn |
|--------|-----|----------|-----------|-------|---------|------|-----|-----|----------|-----|----|------|-----|-----|------|
| E5 | BDL | 3070±289 | 20.0±0.2 | 639±3 | 9.2±0.6 | BDL | BDL | BDL | 11.3±0.5 | BDL | NA | 18±4 | BDL | BDL | 28±2 |
| E6 | BDL | 4753±318 | 31.3±0.22 | 455±3 | 5.6±0.5 | 70±5 | BDL | BDL | 17.4±4.6 | BDL | NA | 13±4 | BDL | BDL | 29±3 |

| Sample | Al | Ba | Br | Ca | Cl | Co | Cr | Cs | Dy | Eu | Fe | Hf | K | La |
|--------|---------|--------|---------|----------|---------|------|-------|-----|----|-----|--------|-----|-----------|------|
| E5 | 1067±61 | 224±58 | 6±1.0 | BDL | 7289±58 | 19±4 | 97±24 | BDL | NA | BDL | 470±36 | BDL | 51700±414 | 77±3 |
| E6 | 417±43 | BDL | 3.7±0.7 | 7160±422 | 5219±52 | BDL | BDL | BDL | NA | BDL | 263±30 | BDL | 20990±308 | 31±2 |

Table 4.27:
Concentration of
Elements
Determined in

Tomato in Different sites by INAA

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or $\mu\text{g g}^{-1}$

Table 4.28: Concentration of Elements Determined in Water Leaf in Different sites by INAA

| Sample | Al | As | Ba | Br | Ca | Cl | Co | Cr | Cs | Dy | Eu | Fe | K | La |
|--------|---------|-----|------|---------|-----------|---------|-----------|-------|-----|----|-----|---------|-----------|-----------|
| F1 | 880±13 | BDL | 31±2 | BDL | 30000±690 | 900±23 | 12±3 | 82±23 | BDL | NA | BDL | 361±38 | 14580±146 | 0.84±0.04 |
| F2 | 1441±43 | BDL | 40±2 | 8.9±2.7 | 15710±613 | 5388±54 | 1.04±0.02 | 31±01 | BDL | NA | BDL | 3104±84 | 68330±273 | 2.15±0.06 |
| F3 | 1412±25 | BDL | 12±2 | 14±1.0 | 16110±548 | 6052±54 | 0.41±0.04 | BDL | BDL | NA | BDL | 2134±60 | 67790±271 | 1.2±0.10 |

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Se | Sm | Ta | Ti | Th | V | Zn |
|--------|------|-----------|-----------|--------|---------|-----------|-----------|-----|------------|-----|----|---------|-----------|------|
| F1 | BDL | 7163±280 | 122.1±0.4 | 1596±3 | 6.2±0.6 | BDL | 10±1.00 | BDL | 0.09±0.01 | BDL | NA | 28±5 | 1.61±0.35 | 14±2 |
| F2 | 11±3 | BDL | 342±1 | 3136±6 | 48±2.0 | 40±3 | 29±1.00 | BDL | 0.264±0.01 | BDL | NA | 1.6±0.1 | BDL | 80±4 |
| F3 | BDL | 19520±547 | 330±1 | 2749±6 | 14±1.0 | 0.46±0.03 | 0.15±0.01 | BDL | 0.19±0.01 | BDL | NA | BDL | 1.6±0.5 | 70±3 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

Table 4.29: Concentration of Elements Determined in Moringa Oleifera in Different sites by INAA

| Sample | Lu | Mg | Mn | Na | Rb | Sb | Sc | Se | Sm | Th | V | Yb | Zn |
|--------|-----|-----------|-----------|--------|---------|-----------|-----------|-----|------------|-----------|-----------|-----|------|
| H1 | BDL | 18870±584 | 349±1.0 | 3052±6 | 16±1.0 | 0.25±0.04 | 0.17±0.01 | BDL | 0.20±0.01 | 0.60±0.05 | 2.8±0.50 | BDL | 55±3 |
| H3 | BDL | 7551±294 | 132.2±4.0 | 1430±3 | 5.4±0.5 | BDL | 11±1.00 | BDL | 0.089±0.01 | 0.25±0.04 | 1.7±0.40 | BDL | 13±2 |
| H4 | BDL | 7262±312 | 124.3±0.4 | 1674±3 | 17±2.0 | 81±15 | 17±1.00 | BDL | BDL | 38±6.00 | 1.65±0.27 | BDL | 13±3 |

BDL: Below Detection Limit

All concentrations are in part per million (ppm) or μgg^{-1}

| | Al | As | Ba | Br | Ca | Cl | Co | Cr | Cs | Dy | Fe | K | La |
|---------------|---------|-----|----------|---------|-----------|---------|-----------|---------|------|----|---------|-----------|-----------|
| Sample | | | | | | | | | | | | | |
| H1 | 2130±30 | BDL | 16.4±2.6 | 17±2.0 | 16150±55 | 6018±54 | 0.40±0.04 | 8.1±0.3 | B DL | NA | 2955±68 | 74800±299 | 1.49±0.07 |
| H3 | 883±17 | BDL | 37±3.0 | 5.1±0.6 | 30200±725 | 975±24 | BDL | 1.6±0.3 | BDL | NA | 394±38 | 13760±138 | 1.00±0.04 |
| H4 | 912±14 | BDL | 233±13 | 2.3±0.1 | 30930±71 | 1024±24 | 33±9 | BDL | BDL | NA | 644±52 | 15130±166 | 1.34±0.04 |

From the result of elemental concentration values determined in this work and displayed in Tables 4.17 to 4.22 the range of the concentration of some of the elements determined in this study were compared with the results obtained in some other works for the same types of vegetables either in the same study area or in other places in similar environment and the results were as presented in Tables 4.30 (i – x).

Table 4.30: Concentrations of Elements in Vegetable Samples compared with other works

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work) ppm | |
|------|---------|------------|----------------------------------|--------------------------------|----------|
| | | | | Alau Dam | Gongulon |
| One | Cr | Water Leaf | 82 ± 23 | 65.50 ± 0.6* | 76 ± 5* |
| Two | Cr | | 31 ± 1 | | |

(i) * (Uwah, *et al* 2009)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work) ppm | |
|------|---------|------------|----------------------------------|--------------------------------|--------------|
| | | | | Alau Dam | Gongulon |
| One | Fe | Water Leaf | 361 ± 38 | 51.02 ± 0.6* | 60.20 ± 0.7* |

(ii) * (Uwah, *et al* 2009)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work) ppm | |
|-------|---------|------------|----------------------------------|--------------------------------|--------------|
| | | | | Alau Dam | Gongulon |
| One | Zn | Water Leaf | 55 ± 3 | 13.56 ± 0.4* | 16.72 ± 0.1* |
| Three | Zn | | 70 ± 3 | | |

(iii) * (Uwah, *et al* 2009)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work) ppm | |
|-------|---------|------------|----------------------------------|--------------------------------|----------|
| | | | | Alau Dam | Gongulon |
| One | Co | Water Leaf | 12 ± 3 | 9.65 ± 0.04* | 11.43 ± |
| Two | Co | | 1.04 ± 0.02 | | 0.16 * |
| Three | Co | | 0.41 ± 0.04 | | |

(iv) * (Uwah, *et al* 2009)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work, India) ppm | |
|-------|---------|-----------|----------------------------------|---------------------------------------|----------|
| | | | | Alau Dam | Gongulon |
| Two | Fe | Spinach | 550 ± 37 | 279 – 333 [#] | |
| Three | Fe | | 502 ± 37 | | |

(v) [#] (Monu Arora *et al*, 2008)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work, India) ppm | |
|------|---------|-----------|----------------------------------|---------------------------------------|----------|
| | | | | Alau Dam | Gongulon |
| Two | Mn | Spinach | 93.24 ± 0.28 | 64 - 73 | |
| Four | Mn | | 72.1 ± 0.3 | | |

(vi) [#] (Monu Arora *et al*, 2008)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work, India) ppm | |
|-------|---------|-----------|----------------------------------|---------------------------------------|----------|
| | | | | Alau Dam | Gongulon |
| One | Zn | Spinach | 22 ± 2 | 31 - 35 [#] | |
| Two | Zn | | 27 ± 2 | | |
| Three | Zn | | 85 ± 4 | | |

(vii) [#](Monu Arora ,*et al*, 2008)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work, India) ppm |
|------|---------|-----------|----------------------------------|--|
| Five | Co | Tomato | 19 ±4 | 0.018 ^{\$} |
| Six | Co | | BDL | |

(viii) ^{\$} (Nirmal Kumar *et al*)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work, India) ppm |
|------|---------|-----------|----------------------------------|--|
| Five | Zn | Tomato | 28 ± 2 | 3.28 ^{\$} |
| Six | Zn | | 29 ± 3 | |

(ix) ^{\$} (Nirmal Kumar *et al* 2007)

| Site | Element | Vegetable | Concentration (This Work) ppm | Concentration (Other Work, India) ppm |
|-------|---------|-----------|----------------------------------|---|
| One | Zn | Okro | 22 ± 3 | 13.66 ^{\$} |
| Two | Zn | | 24 ± 3 | |
| Three | Zn | | 23 ± 1 | |
| Four | Zn | | 27 ± 2 | |
| Five | Zn | | 21 ± 2 | |

(x) ^{\$} (Nirmal Kumar *et al* 2007)

It can be observed from the results displayed in Tables 4.30(i-x) that the concentrations of some of the elements determined in vegetables investigated in this study were in good agreement with the results obtained in the same types of vegetables carried out in other works in either the same place using other techniques or in other places using other techniques. The concentration values of the various elements determined in the different types of vegetables collected from each site were graphically represented in two graphs so as to present elements with high concentration values and those with low concentration values. This was adopted for convenience purposes only since some element concentrations values were much higher than others depending on the sites where the samples were collected, the availability of the elements in the soil and the bio-accumulation capability and or the bio-absorptivity of the plants in question.

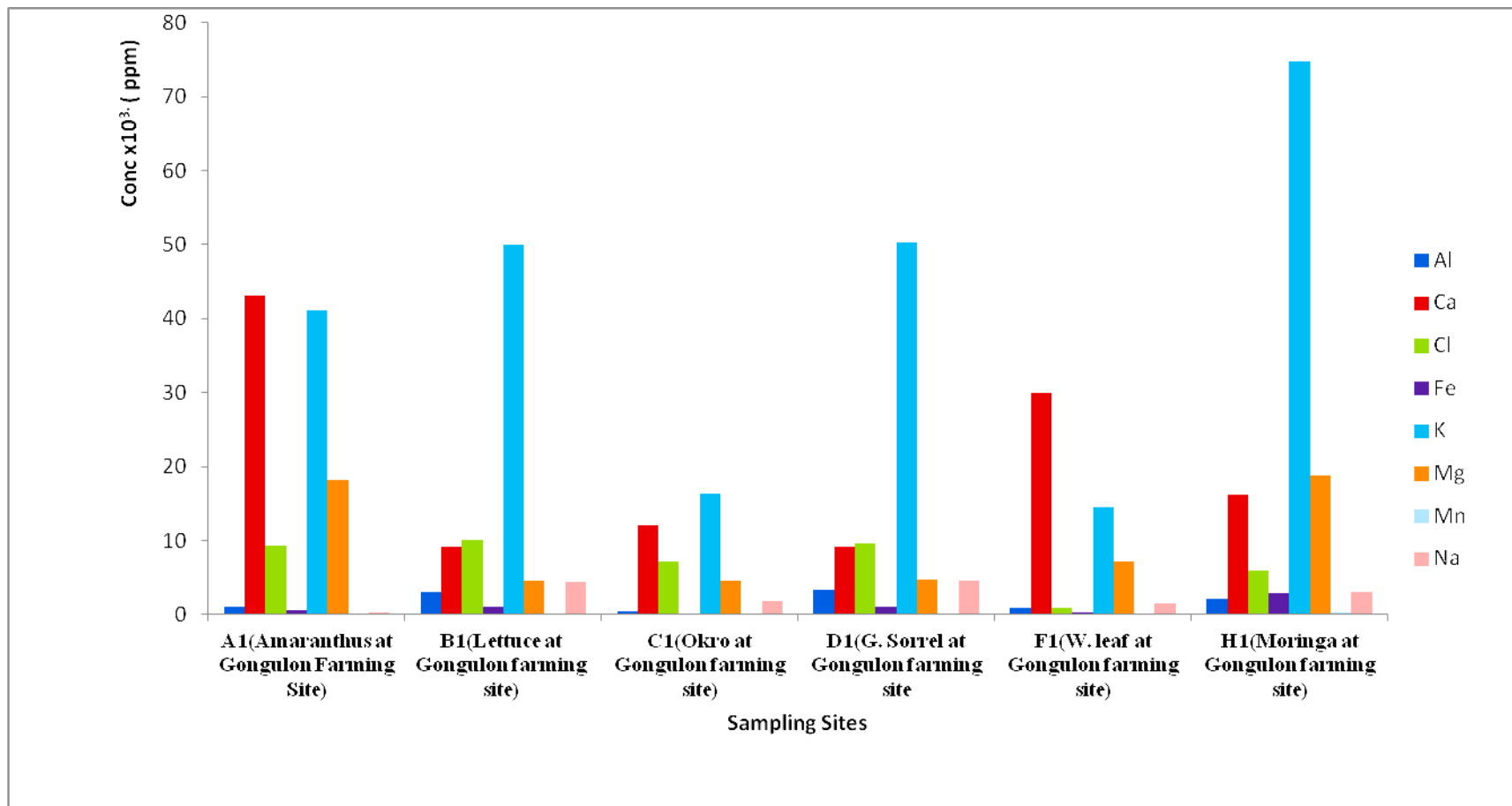


Fig 17a: Concentration of Element Determined in Different Vegetable Samples in Site 1

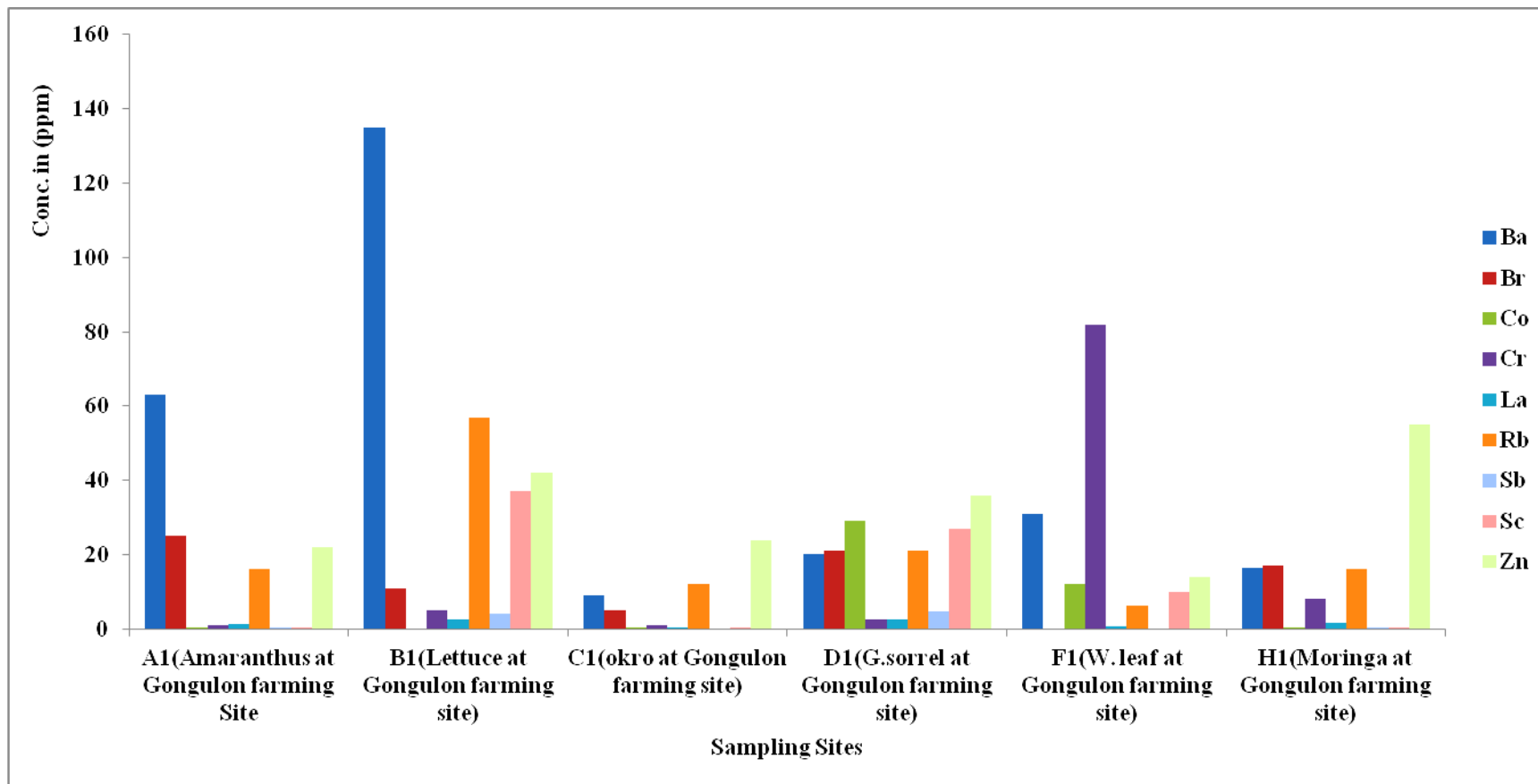


Fig 17b: Concentration of Elements Determined in Different Vegetable Samples in Site 1

Figure 17a shows the bar charts of the concentrations of some of the elements determined in the various vegetable samples obtained from site one which have relatively high concentration values and it can be clearly seen from the graph that the order in which the concentration values of the elements vary were as **K** > **Ca** > **Mg** > **Cl** > **Al** > **Na** > **Fe** > **Mn**, with highest concentration value of **K** in Moringa Oleifera (74800 ± 299) ppm followed by Guinea sorrel with concentration value of (50330 ± 302) ppm while the lowest concentration value of **Mn** was ($24. \pm 0.2$) ppm in Okro. Figure.17b shows the bar charts of some of the elements with lower concentration values determined in vegetable samples obtained from site one and it can be observed that the elements concentrations values varies from highest to lowest value as **Zn** > **Rb** > **Ba** > **Br** > **Co** > **Cr** > **Sb** > **Sc** > **La** with the highest concentration value of **Ba** (135 ± 14) ppm in lettuce followed by that of **Cr** (82 ± 23) ppm in water leaf..The other element in all the vegetables ranges from 63 ± 3 ppm in amaranthus and below in other vegetables.

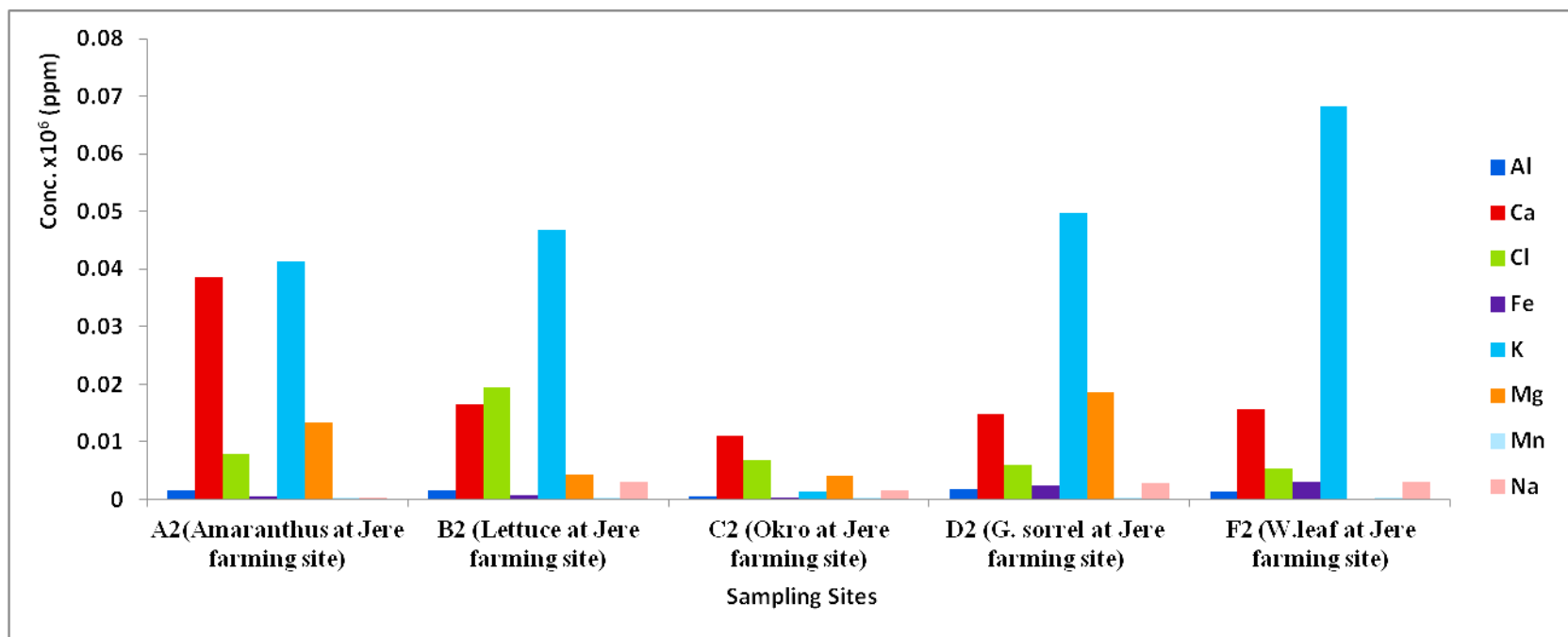


Fig 18a: Concentration of Elements Determined in Different Vegetable Samples in Site 2

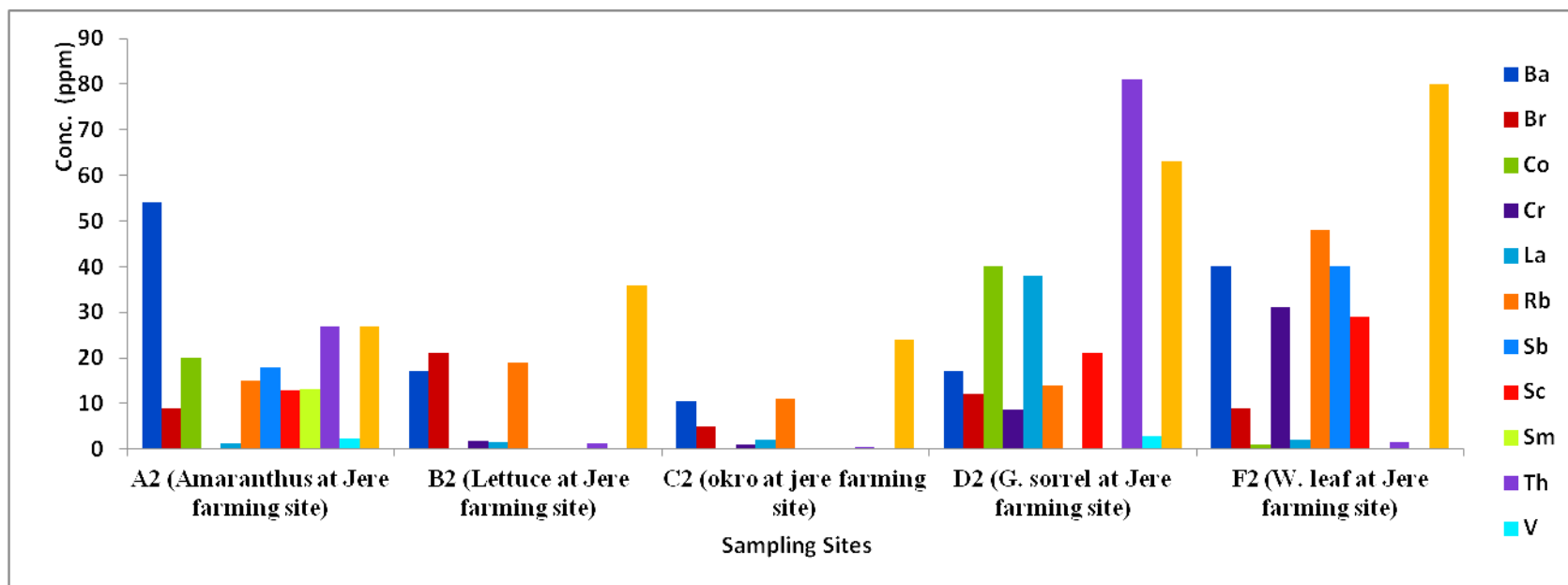


Fig 18b: Concentration of Elements Determined in Different Vegetable Samples in site 2

Figure 18a shows the concentrations of the various elements determined in the various vegetable samples obtained from site two. It can be observed from the graph displayed in Figure 18a that the concentrations of the elements with relatively high concentration values varies as **K** > **Ca** > **Mg** > **Cl** > **Al** > **Na** > **Fe** > **Mn**, with highest concentration of **K** (68330 ± 273) ppm in water leaf and **Ca** (38560 ± 762) ppm in amaranthus while the lowest concentrations of the element **Mn** (90.24 ± 0.28 ppm was determined in amranthus. Figure 18b shows the bar chart of the element with lower concentrations values determined in vegetable samples obtained from site two. It can be observed from the graph displayed in Figure 18b that the order of variations of concentration of the elements from the highest was **Zn** > **Th** > **Ba** > **Co** > **B r** > **Cr**, with highest concentration of **Zn** (80 ± 4) ppm in Morianga Oleifera, followed by that of **Ba** (54 ± 2) ppm in amaranthus, while highest concentration of **Cr** (31 ± 1) ppm in water leaf and highest concentration of **Co** (40 ± 4) ppm in Guinea sorrel.

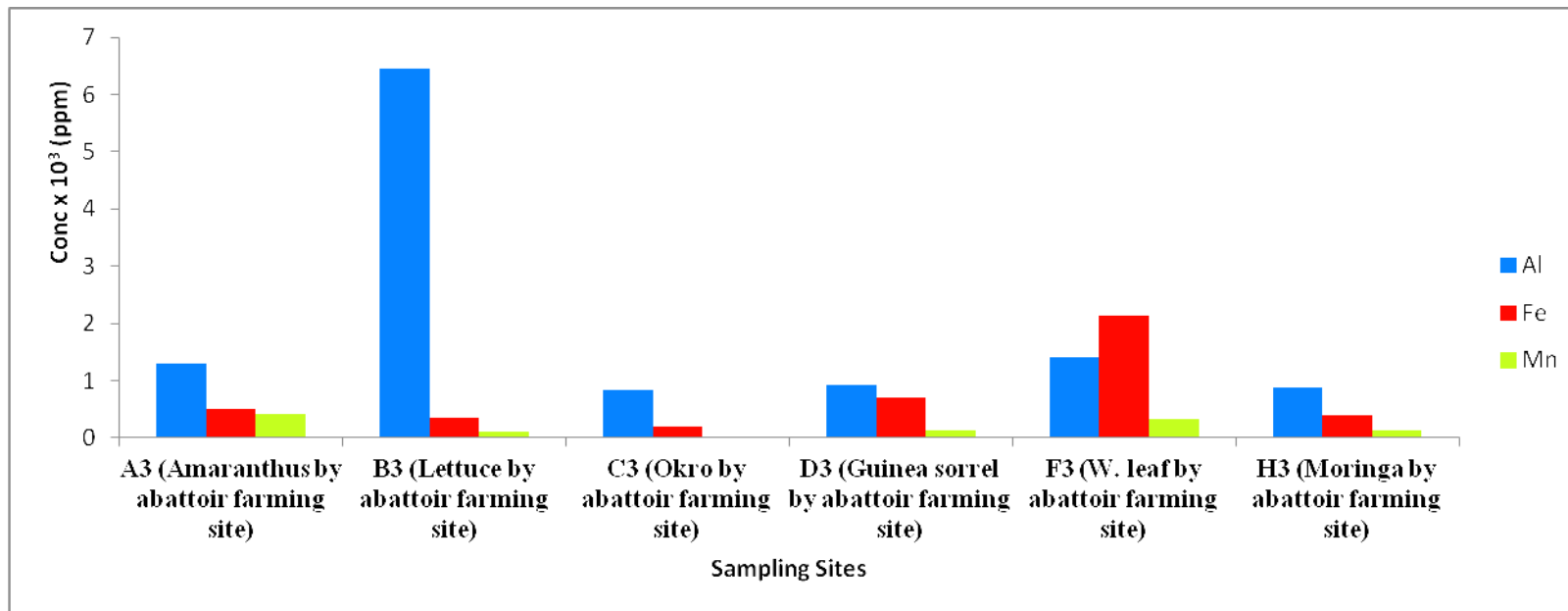


Fig 19a: Concentration of Elements Determined in Different Vegetable Samples in Site 3

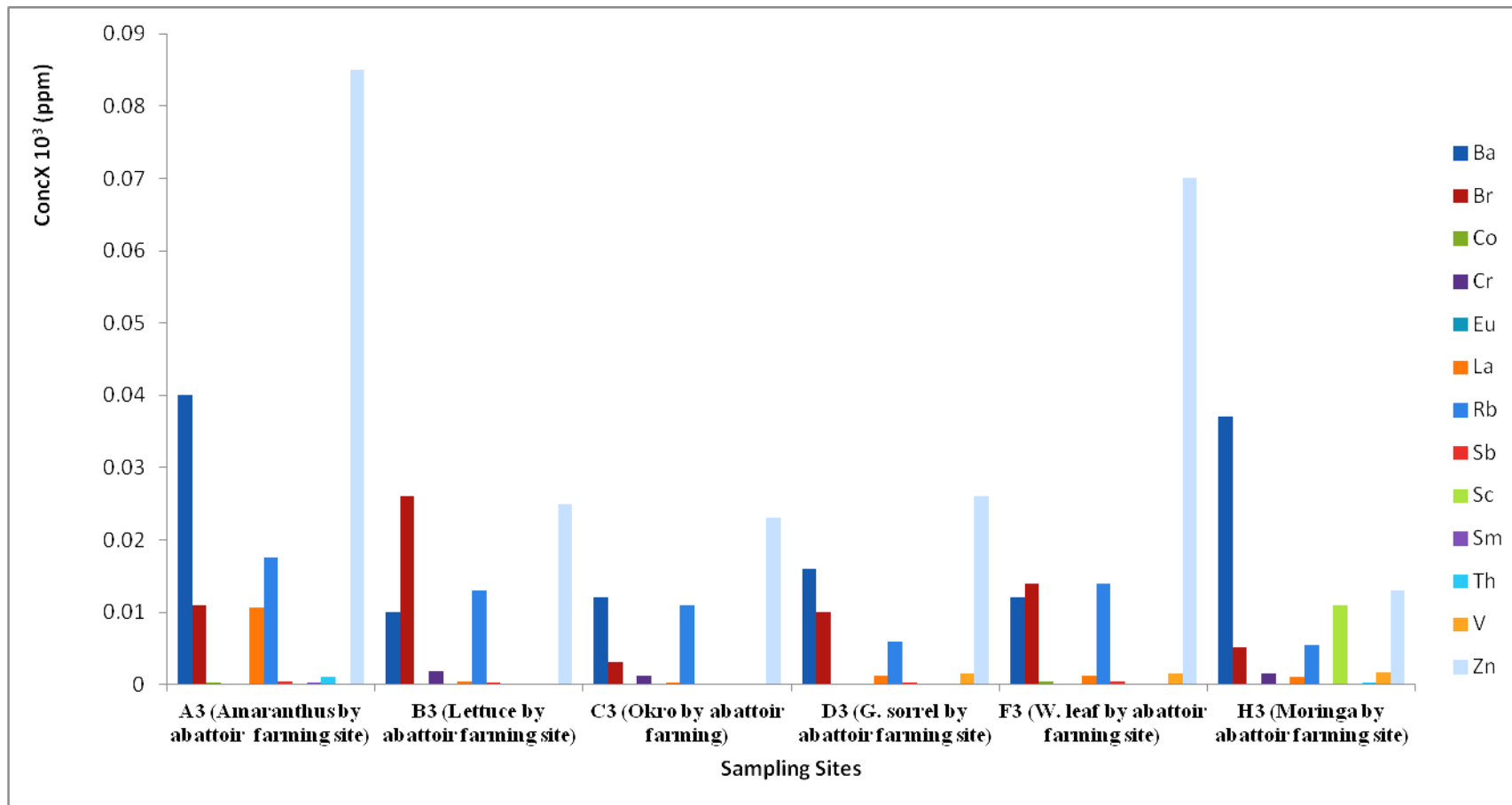


Fig 19b: Concentration of Elements Determined in Different Vegetable Samples in site 3

Figure 19a shows the bar charts of the elements with relatively high concentration values determined in vegetable samples obtained from site three. It can be observed as displayed in the graph that the order of variation of concentration values from the highest was **Al** > **Fe** > **Mn** with highest concentration value of **Al** (6450 ± 213) ppm determined in lettuce followed by **Fe** (2134 ± 60) ppm in water leaf while lowest concentration value of **Mn** (330 ± 1) in water leaf. Figure 19b shows the bar chart of the elements with lower concentration values determined in vegetables samples obtained from site three and the order of variations from the highest was **Zn** > **Ba** > **Br** > **Rb** with the highest concentration of **Zn** (85 ± 4) ppm) in amaranthus followed by (40 ± 2) ppm of **Ba** in amaranthus and that of **Sc** (11 ± 1) ppm in Morianga Oleifera. .

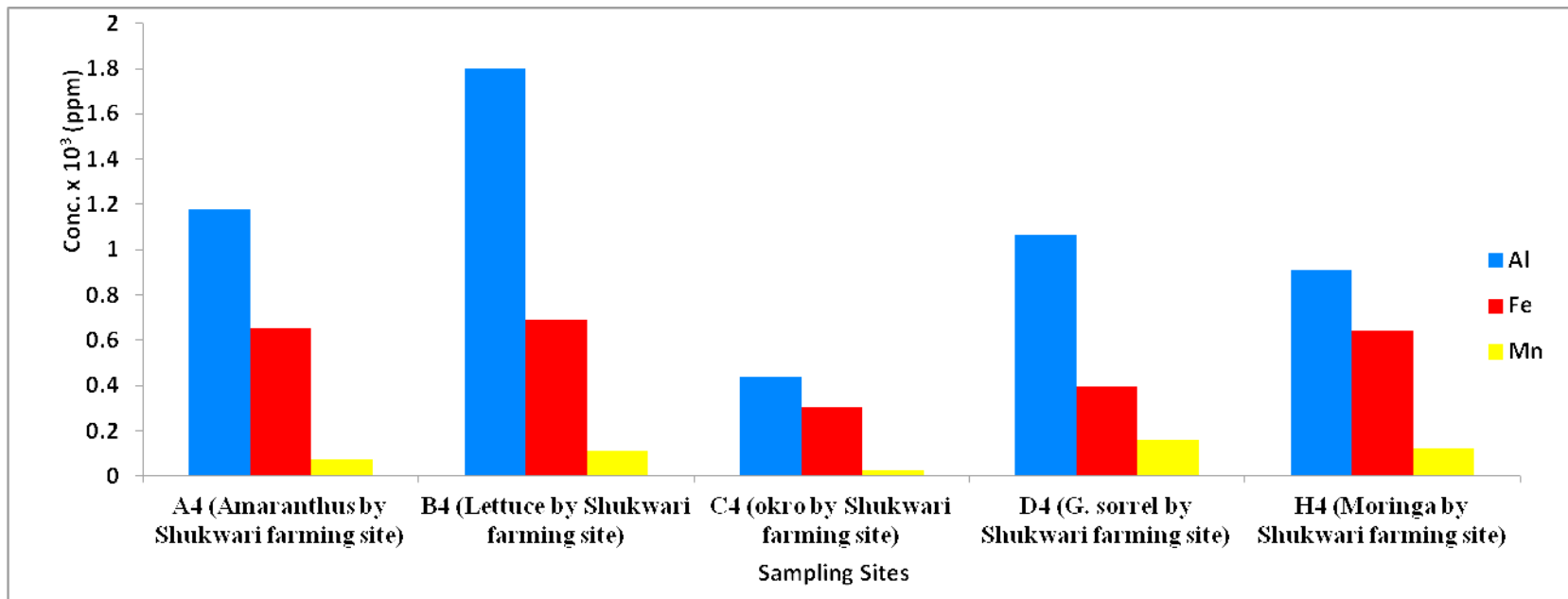


Fig 20a: Concentration of Elements Determined in Different Vegetable Samples in Site 4

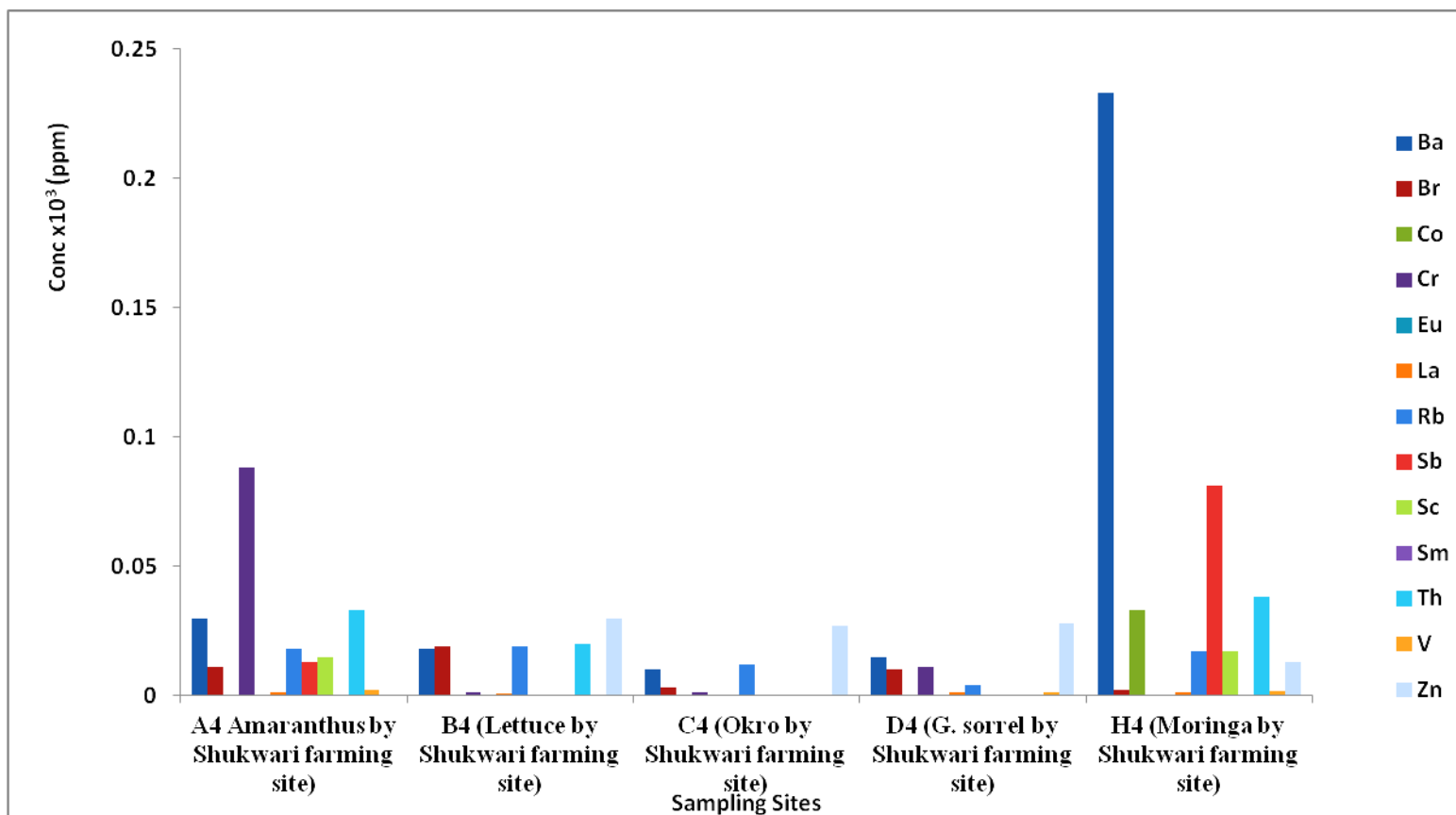


Fig 20b: Concentration of Element Determined in Different Vegetables in Site 4

Figure 20a shows the bar chart of the concentrations of the elements determined in various vegetable samples obtained from site four. It can be seen from the graph that the concentration variation of the elements from the highest indicate that **Al** > **Fe** > **Mn** with the highest concentration of **Al** (1799 ± 40) ppm in lettuce followed by that of **Fe** (691 ± 44) ppm) in lettuce and **Mn** concentration value of (161.9 ± 0.30 ppm in Guinea Sorrel. Figure 20b shows the bar chart of the concentrations of the elements with lower values determined in the vegetable samples obtained from site four and it can be clearly seen from the displayed graph that the elements varies as **Ba** > **Zn** > **Cr** > **Co** with highest concentration of **Ba** (233 ± 13) ppm in Moringa Oleifera and **Cr** concentration of (88 ± 21) ppm in amaranthus while the concentration of **Sb** was (81 ± 15) ppm in Moringa oleifera and the lowest concentration value of **Co** (0.2 ± 0.03) ppm was determined in lettuce.

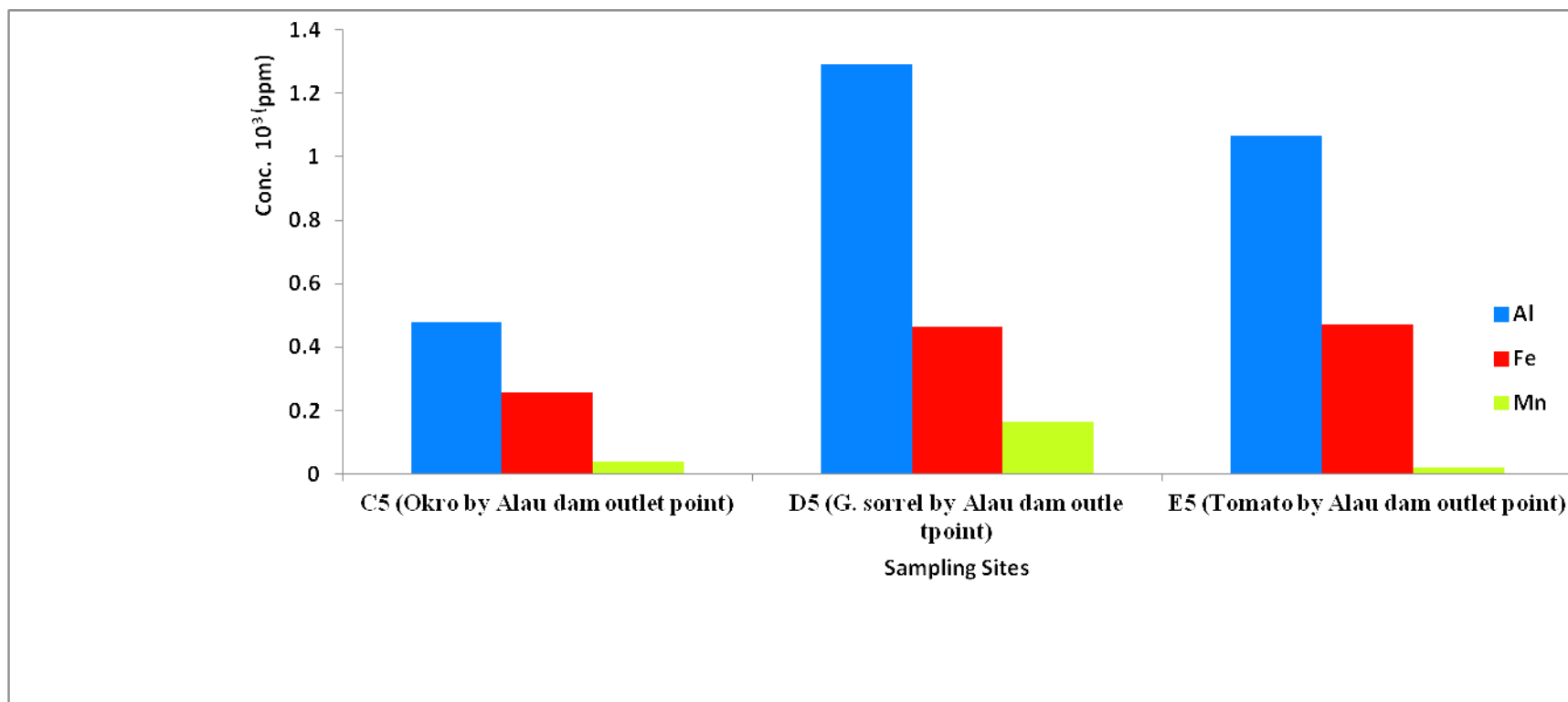


Fig 21a: Concentration of Elements Determined in Different Vegetable Samples in Site 5

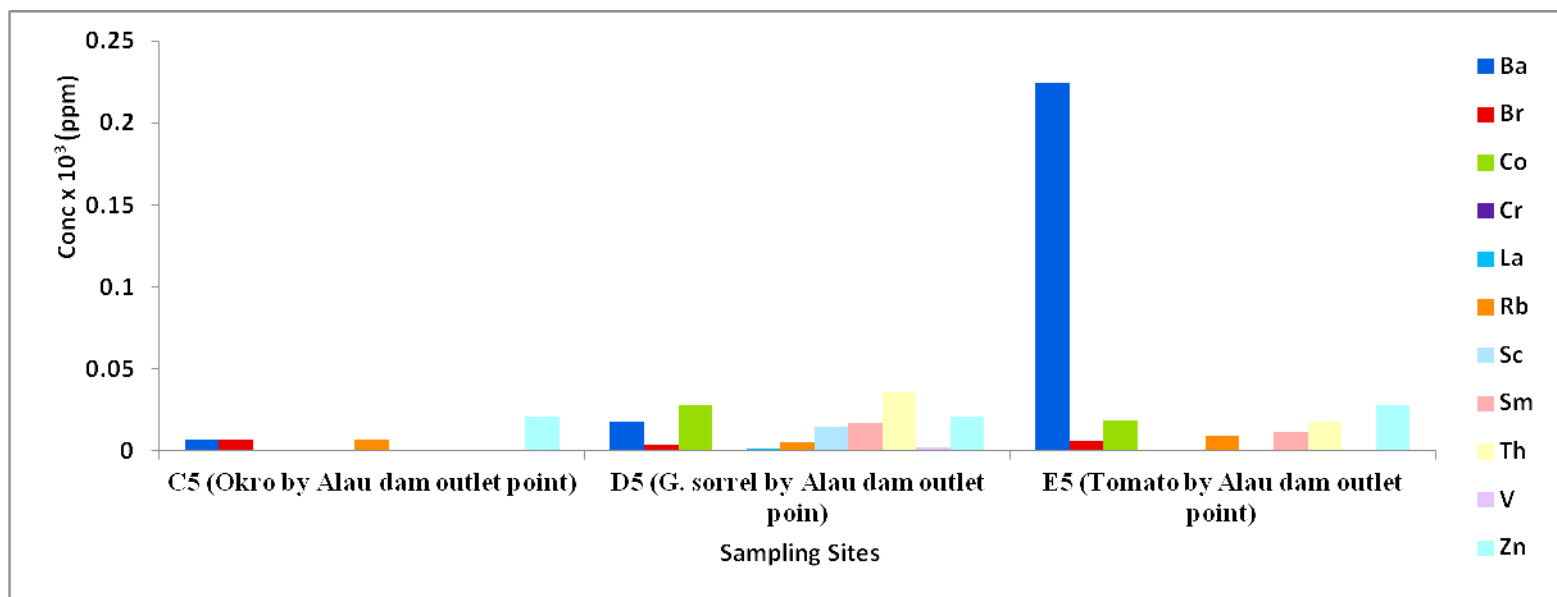


Fig 21b: Concentration of Elements Determined in Different Vegetable Samples in Site 5

Figure 21a shows the bar chart of the concentrations of the elements determined in the vegetable samples obtained from site five. From the graph it can be seen that the order of variation of the concentrations values were **Al** > **Fe** > **Mn** with the highest concentration of **Al** (1293 ± 14) ppm in Guinea Sorrel followed by (1067 ± 61) ppm of **Al** in tomatoes. **Fe** has highest concentration value of (470 ± 36) ppm in tomatoes and **Mn** has a highest concentration of (166.3 ± 0.5) ppm in Guinea sorrel and the lowest value of **Mn** (20.0 ± 0.2) ppm in tomato. Figure 21b shows the bar chart of the concentration of the various elements with low values determined in the various types of vegetable samples obtained in site five and the variation indicate that **Ba** > **Zn** > **Co** > **Th** > **Br** with highest concentration of **Ba** in tomatoes being (224 ± 58) ppm followed by (18 ± 2) ppm of **Ba** in Guinea sorrel. **Zn** has a highest value of (28 ± 2) ppm in tomatoes and **Co** has a highest value of (19 ± 4) ppm in tomatoes while **Th** has a maximum value of (36 ± 5) ppm in Guinea sorrel

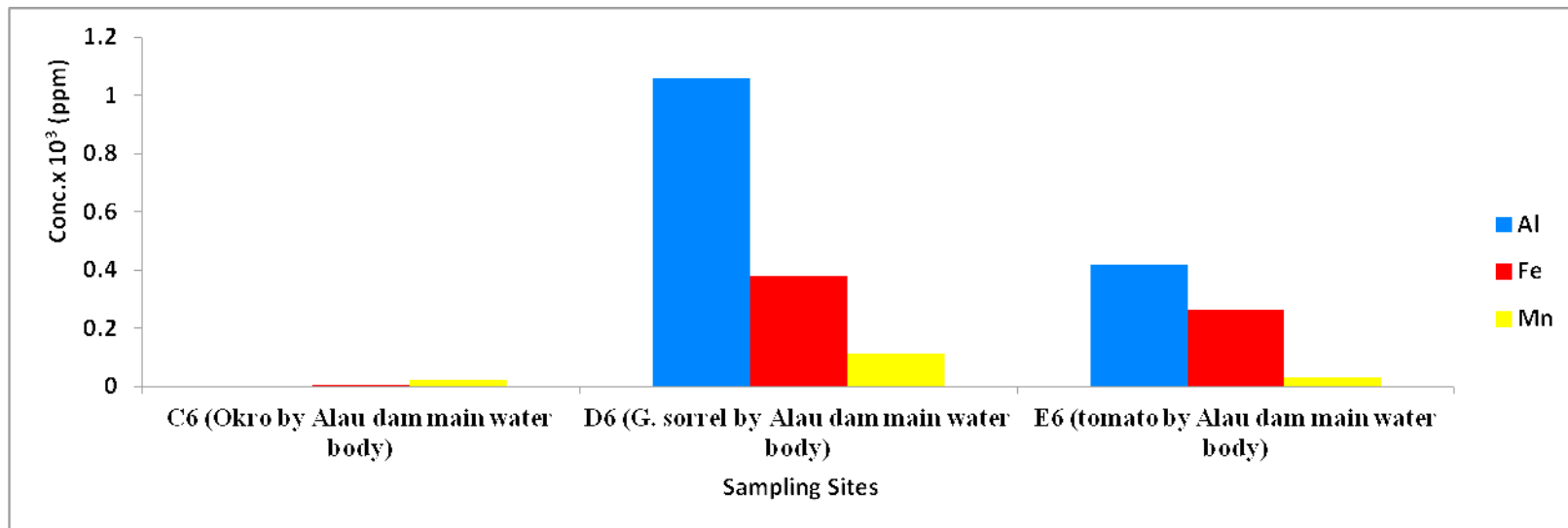


Fig 22a: Concentration of Elements Determined in Different Vegetable Samples in Site 6

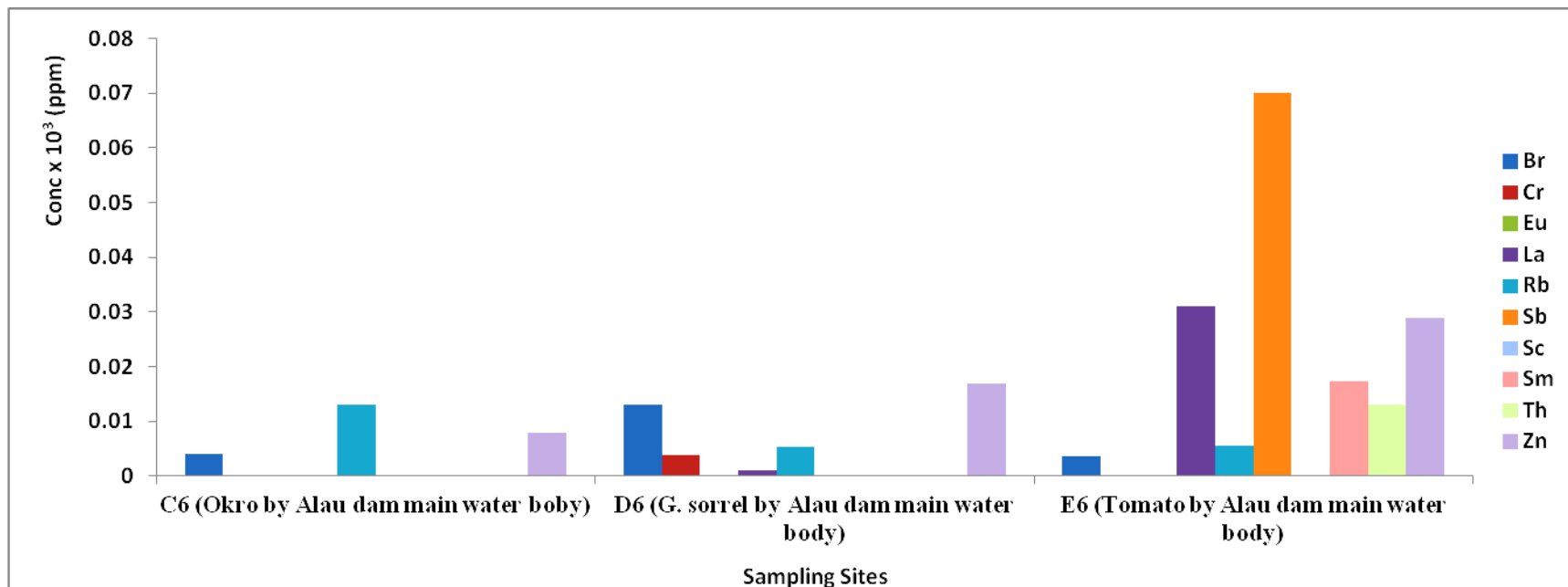


Fig 22b: Concentration of Elements Determined in Different Vegetables Samples in Site 6

Figure 22a shows the bar chart of the concentrations of the elements with relatively high values in the three types of vegetable samples obtained in site six and these elements varies in concentrations as **Al** > **Fe** > **Mn** with the highest concentration of **Al** (1057 ± 62) ppm in Guinea Sorrel followed by a concentration of **Fe** (379 ± 33) ppm in Guinea sorrel and maximum concentration of (112.2 ± 0.4) ppm of **Mn** in Guinea sorrel. Figure 22b shows the bar chart of the concentrations of the elements with low values in the three types of vegetable samples obtained in site six and the concentrations values varies as follows **Zn** > **Rb** > **La** > **Th** > **Sb** with concentration of **Sb** (70 ± 5) ppm in tomatoes and a maximum concentration of **Zn** (29 ± 3) ppm in tomatoes while the maximum concentration of **La** in tomato was (31 ± 2) ppm. **Sm**, **Th** and **Rb** have concentrations of (17.4 ± 4.6 , 13 ± 4 , and 5.6 ± 0.5) ppm respectively in tomatoes.

Having plotted the bar chart for the concentrations of the various elements in the various vegetables for the various site, the highest concentrations of the elements determined in the various vegetable samples and the lowest concentration of the elements determined in the various vegetable samples were hereby presented in Tables 4.37a to 4.43b to give an idea of how the concentration of each element were bio-accumulated in the various vegetables collected in the various sites

Table 4.31a: Elements with high Concentration values in vegetables collected at site one (Gongulon site)

| Element | Concentration (ppm) | Vegetables | Element | Concentration ppm) | Vegetables |
|---------|---------------------|------------|---------|--------------------|------------|
| Ca | (43130 ± 862) | Amaranthus | Al | 2983 ± 42 | Lettuce |
| Ba | 135 ± 14 | “ | La | 2.49 ± 0.06 | “ |
| Cl | 10130 ± 71 | “ | Na | 4441 ± 4 | “ |
| Co | 72 ± 11 | “ | Sm | 0.28 ± 0.01 | “ |
| Rb | 57 ± 3 | “ | V | 3.4 ± 0.78 | “ |
| Sc | 37.1 ± 1.4 | “ | Fe | 2955 ± 66 | Moringa |
| Cr | 82 ± 23 | Water leaf | K | 74800 ± 299 | “ |
| Th | 28 ± 5 | “ | Mg | 18870 ± 584 | “ |
| | | | Mn | 349 ± 1 | “ |
| | | | Zn | 55 ± 3 | “ |

Table 4.31b: Elements with low Concentration values in vegetables collected at site one (Gongulon Site)

| Element | Concentration ppm) | Vegetable | Element | Concentration (ppm) | Vegetables |
|---------|--------------------|------------|---------|---------------------|------------|
| Cr | 1.0 ± 0.3 | Amaranthus | Al | 518 ± 13 | Okro |
| Na | 252 ± 1 | “ | Ba | 9 ± 2 | “ |
| Th | 0.28 ± 0.05 | “ | Br | 5 ± 1 | “ |
| V | 1.5 ± 0.4 | “ | Co | 0.11 ± 0.03 | “ |
| Rb | 6.2 ± 0.6 | Water leaf | Fe | 124 ± 3 | “ |
| Zn | $(14 \pm 2$ | “ | La | 0.21 ± 0.04 | “ |
| | | “ | Mn | 24 ± 0.2 | “ |
| | | “ | Sc | 0.03 ± 0.004 | “ |
| | | “ | Sm | 0.029 ± 0.004 | “ |

Table 4.32a: Elements with high Concentration values in vegetables collected at site two (Jere site)

| Element | Concentration ppm) | Vegetables | Element | Concentration ppm) | Vegetables |
|---------|--------------------|------------|---------|--------------------|------------|
| Ca | 38560 ± 762 | Amaranthus | Al | 1851 ± 20 | G. Sorrel |
| Ba | 54 ± 2) | “ | Co | 40 ± 4 | “ |
| Sm | 13.1 ± 0.5 | “ | La | 28 ± 4 | “ |
| Cl | 19450 ± 97 | Lettuce | Mg | 18670 ± 467 | “ |
| Br | 21 ± 1) | “ | Th | 81 ± 5 | “ |
| Cr | (31 ± 1 | Water leaf | Na | 3136 ± 6 | Water leaf |
| Fe | 3104 ± 84 | “ | Rb | (48 ± 2 | “ |
| Mn | 342 ± 1 | “ | Sb | 40 ± 3 | “ |
| K | (68330 ± 273 | “ | Sc | 29 ± 1 | “ |
| | | | Zn | 80 ± 4 | “ |

Table 4.32b: Elements with low Concentration values in vegetables collected at site two (Jere site)

| Element | Concentration ppm) | Vegetables | Element | Concentration ppm) | Vegetables |
|---------|--------------------|------------|---------|--------------------|------------|
| Al | 452 ± 19 | Okro | Co | 0.33 ± 0.04 | Lettuce |
| Ba | 10.4 ± 1.6 | “ | Sm | (0.22 ± 0.01 | “ |
| Br | 5 ± 1 | “ | Sb | 0.10 ± 0.06 | “ |
| Fe | (219 ± 35 | “ | Cl | 5388 ± 54 | “ |
| Mn | 22.9 ± 0.2 | “ | Rb | 11 ± 1 | Okro |
| | | “ | Zn | 24 ± 3 | “ |

Table 4.33a: Elements with high Concentration values in vegetables collected at site three (Abattoir site)

| Element | Concentration ppm) | Vegetables | Element | Concentration (ppm) | Vegetables |
|---------|--------------------|------------|---------|---------------------|------------|
| Ba | 40 ± 2 | Amaranthus | Al | 6450 ± 213 | Lettuce |
| La | 10.7 ± 0.1 | “ | Br | 26 ± 1 | “ |
| Mg | 19890 ± 537 | ‘ | Cr | 1.8 ± 0.3 | “ |
| Mn | 410 ± 1 | “ | Na | 2783 ± 3 | “ |
| Rb | 17.61 ± 0.05 | “ | fe | 2134 ± 60 | Water leaf |
| Sb | 0.48 ± 0.03 | “ | Co | 0.41 ± 0.04 | “ |
| Sm | 0.29 ± 0.01 | “ | Sc | 11 ± 1 | Moringa |
| Th | 1.12 ± 0.05 | “ | V | 1.7 ± 0.4 | “ |
| Zn | 85 ± | “ | | | “ |

Table 4.33b: Elements with low Concentration values in vegetables collected at site three (Abattoir site)

| Element | Concentration ppm) | Vegetables | Element | Concentration ppm) | Vegetables |
|---------|--------------------|------------|---------|--------------------|------------|
| Ba | 10 ± 2 | Lettuce | Mg | 4645 ± 39 | Lettuce |
| Sm | 0.045 ± 0.007 | ‘ | Na | 19.0 ± 0.1 | G. Sorrel |
| Al | 843 ± 16 | Okro | Cl | (975 ± 24 | Moringa |
| Br | 3.1 ± 0.4 | “ | K | 13760 ± 138 | “ |
| Ca | 11500 ± 437 | “ | Rb | 5.4 ± 0.5 | “ |
| Fe | 204 ± 25 | “ | Zn | 13 ± 2 | “ |
| La | 0.30 ± 0.03 | “ | Mn | 27.8 ± 0.2 | “ |
| | | | Sc | 0.033 ± 0.004 | “ |

Table 4.34a: Elements with high Concentration values in vegetables collected at site four (Shukwari site)

| Element | Concentration ppm) | Vegetables | Element | Concentration (ppm) | Vegetables |
|---------|--------------------|------------|---------|---------------------|------------|
| Ca | 46540 ± 884 | Amaranthus | Al | 1799 ± 40) | Lettuce |
| Cr | 88 ± 21 | “ | Br | 19 ± 1 | “ |
| Mg | 15310 ± 429 | “ | Cl | 19010 ± 95 | “ |
| Sm | 0.15 ± 0.01 | “ | Fe | 691 ± 44 | “ |
| V | 2.3 ± 0.5 | “ | Na | 3165 ± 3 | “ |
| Ba | 233 ± 13 | Moringa | Rb | 19 ± 1) | “ |
| Co | 33 ± 9 | “ | Zn | 30 ± 3 | “ |
| Sb | 81 ± 15 | “ | La | 1.34 ± 0.04 | Moringa |
| Sc | 17 ± 1 | “ | Th | 38 ± 6 | “ |

Table 4.34b: Elements with low Concentration values in vegetables collected at site four (Shukwari site)

| Element | Concentration ppm) | Vegetables | Element | Concentration (ppm) | Vegetables |
|---------|--------------------|------------|---------|---------------------|------------|
| Al | 437 ± 10 | Okro | K | 11650 ± 117 | G. Sorrel |
| Ba | 10 ± 2 | “ | Mg | 1606 ± 324 | “ |
| Ca | 13410 ± 443 | “ | Na | 121 ± 1 | “ |
| Cr | 1.2 ± 0.2 | “ | Rb | 4 ± 0.4 | “ |
| Fe | 303 ± 36 | “ | Br | 2.3 ± 0.1 | “ |
| la | 0.29 ± 0.03 | “ | Zn | 13 ± 3 | “ |
| Mn | 25 ± 0.2 | “ | Sm | 0.044 ± 0.004 | Okro |
| Sc | 0.04 (0.01 | “ | Th | 0.18 ± 0.04 | “ |

Table 4.35a: Elements with high Concentration values in vegetables collected at site five (Alau dam outlet)

| Element | Concentration ppm) | Vegetables | Element | Concentration ppm) | Vegetables |
|---------|--------------------|------------|---------|--------------------|------------|
| Br | 7±1 | Okro | Ba | 224 ± 55 | Tomato |
| Mg | 5662 ± 294 | “ | Cl | 7289 ± 58 | “ |
| Al | 1293 ± 14 | G. Sorrel | Cr | 97 ± 24 | “ |
| Co | 28 ± 5 | “ | Fe | 470 ± 36 | “ |
| Mn | 166.3 ± 0.5 | “ | K | 51700 ± 414 | “ |
| Sm | 17.2 ± 0.4 | “ | La | 77 ± 3 | “ |
| Th | 36 ± 5 | “ | Na | 639 ± 3 | “ |
| Sc | 946 ± 61 | Tomato | Rb | 9.2 ± 0.6 | “ |
| Zn | 28 ± 2 | “ | | | |

Table4.35b: Elements with low Concentration values in vegetables collected at site five (Alau dam outlet)

| Element | Concentration ppm) | Vegetables | Element | Concentration ppm) | Vegetables |
|---------|--------------------|------------|---------|--------------------|------------|
| Al | 477 ± 11 | Okro | Br | 3.6 ± 0.6 | G. sorrel |
| Ba | 7 ± 1 | “ | Cl | 2648 ± 34 | “ |
| Fe | 256 ± 32 | “ | Na | 173 ± 1 | “ |
| La | 0.34 ± 0.03 | “ | Rb | 5.4 ± 0.6 | “ |
| Sc | 1.05 ± 0.02 | “ | Zn | 21 ± 3 | “ |
| Sm | 0.053 ± 0.005 | “ | Mg | 30.70 ± 239 | Tomato |
| | | | Mn | 20 ± 0.2 | “ |

Table 4.36a: Elements with high Concentration values in vegetables collected at site six (Alau dam main area)

| Element | Concentration ppm) | Vegetables | Element | Concentration pm) | Vegetables |
|---------|--------------------|------------|---------|-------------------|------------|
| Na | 1421 ± 6 | Okro | Sc | 365 ± 50 | Tomato |
| Mg | 5239 ± 613 | “ | K | 20990 ± 308 | .. |
| Cl | 7245 ± 5 | “ | La | 31 ± 2 | .. |
| Rb | 13 ± 1 | “ | Sm | 17.4 ± 4.5 | “ |
| Al | !057 ± 52 | G. sorrel | Zn | 29 ± 3 | “ |
| Ca | (16810 ± 723 | “ | Fe | 379 ± 33) | G. sorrel |
| Br | (13 ± 1 | “ | Mn | 112.2 ± 0.4 | “ |

Table 4.36b: Elements with low Concentration values in vegetables collected at site six (Alau dam main area)

| Element | Concentration(ppm) | Vegetables | Element | Concentration(ppm) | Vegetables |
|---------|--------------------|------------|---------|--------------------|------------|
| Al | 417 ± 43 | Okro | K | 14396 ± 245 | G. Sorrel |
| Fe | 1.1 ± 0.4 | “ | Mg | 4660 ± 531 | “ |
| La | 0.203 ± 0.03 | “ | Na | (107.9 ± 1.5 | “ |
| Mn | 22.9 ± 0.2 | “ | Rb | 5.4 | “ |
| Sm | 0.02 ± 0.004 | “ | Br | 3.7 ± 0.7 | Tomato |
| Zn | 8 ± 10 | “ | Ca | 7160 ± 422 | “ |

The recommended values by some standard organizations for some of the elements determined in this work were as presented in table 44

Table 4.37 World SafeLlimit ofTtrace Element in Vegetable in (ppm)

| Element | Co | Cr | Mn | Zn | Fe |
|---------|----|----|----|----|----|
|---------|----|----|----|----|----|

| | | | | | |
|------------|-------------|-------------|----------|------------|-----|
| WHO (ppm) | 0.25 | 0.05 – 0.85 | 0.3 -0.5 | 2.00 -5.0 | 0.3 |
| FAO (ppm) | 0.25 – 1.10 | 0.05 -0,08 | 2.00 | 0.6 – 5.00 | - |

CHAPTER FIVE

DISCUSSION

5.1 Discussion

The dry season farmlands along the bank of river Ngadda and Alau dam used for cultivation of vegetables during dry season through irrigation had their soils, some selected types of vegetables cultivated on the farms along the banks and sediments of both river Ngadda and Alau dam was collected and analyzed for elemental concentrations using instrumental neutron activation analysis (INAA). The results for the soil samples shows that the concentrations of the various elements determined from different sites were different as presented in Tables 4.3a and 4.3b and the range of the concentration of some of the elements determined in this study and the maximum allowable concentrations (MAC) of trace elements in Agricultural soils proposed or given in the directives in various countries and in different years were as indicated in Table 4.14. It can be clearly seen from Table 4.14 that the concentrations of Arsenic (As), Cobalt (Co), Vanadium (V) determined in the various sites in this work were below the MAC values given by the other countries while the Antimony (Sb), and Zinc (Zn) determined in the soil samples from various sites in this study are within the range of the MAC values given by other countries such as Poland (1977), Russia (1986) U.K (1970 and European Community (1986).

The result of elemental concentration values determined in some vegetables in this study are as displayed in Tables 4.17 to 4.22 and the range of the concentration of some of the elements determined in this study and those determined in the same types of vegetables in the same area or in other places using different techniques were as displayed in Tables 4.30(i – x). It can be observed from Tables 4.30 (i – x) that the concentration values of the elements Cr, Fe, Zn and Co determined in water leaf in some sites in this study were within the same range determined by Uwah, *et al*, 2009 in some sites within the same area of study using AAS technique; the concentration values of the elements Fe, Mn, and Zn determined in amaranthus in this study were in the same range determined in spinach (amaranthus) by Monu Arora *et al*, 2008 in another area of study using AAS technique; the concentration values of Co, and Zn in tomato determined in this study were within the range determined by Kumar *et al*, 2007 in another place using AAS technique while the concentration value of Zn in okro determined in this study were higher than the value determined by Kumar *et al*, (2007) in another place using AAS technique. The concentrations of the different elements determined in the various vegetables from the various sites according to those with high values and those with low values were as presented in Tables 4.31a and 4.31b at site one to Tables 4.36a and 4.36b at sites six accordingly. It can be observed that the concentrations of the various elements determined in the various vegetables have varied values at the different sites for the same type of vegetables indicating that different sources or factors may be responsible for the concentration of a particular element in the soil viz a viz the vegetables but generally those sites that have high concentrations of specific elements values in soil have high concentrations of those elements in some of the vegetables indicating positive linear

correlation between the soil and vegetables. This variation in concentrations of the same element from one vegetable to the other from the same site may be due to the differences in the bio-accumulation tendencies of the different vegetables. The values of some of the safe limits of trace elements in some of the vegetables is as presented in Table 4.37 and it can be observed that for site one, the concentration of Cobalt in lettuce, guinea sorrel and water leaf exceed the MPL recommended by WHO/FAO (2005) while the concentrations in amaranthus and moringa are within the range specified by these regulatory bodies. Cr concentration in lettuce, guinea sorrel, water leaf and moringa exceed the WHO/FAO values whereas concentrations were within the recommended limits in amaranthus and okro. Mn, Fe and Zn concentrations exceed the safe limit in all the six vegetables analysed in site one. For site two, Co concentration in amaranthus and guinea sorrel exceed the WHO/FAO recommended safe limit but within the range for lettuce and water leaf and okro. Cr concentration exceeds the WHO/FAO safe limit in lettuce and okro, guinea sorrel and water leaf and below the safe limit in amaranthus. Mn concentration exceeds WHO/FAO safe limit in amaranthus, guinea sorrel, lettuce, water leaf, and okro. Fe and Zn exceed the safe limit in all the vegetables analysed in site two. For site three, concentrations of Co exceeds the safe limit in amaranthus, guinea sorrel and water leaf but below the detection limit BDL in lettuce and okro. Cr concentrations in lettuce, okro, moringa were above WHO/FAO safe limit while concentration in amaranthus, guinea sorrel and water leaf were below detection limit. Concentrations of Mn, Fe and Zn were all above Safe limit for all the vegetables collected from site three. For site four, Co concentration in moringa was above WHO/FAO safe limit while in lettuce and guinea sorrel the concentration was within the safe limit and BDL in amaranthus and okro.

Also in the site four, Cr concentration was above WHO/FAO safe limit in amaranthus, lettuce, okro, and guinea sorrel and BDL in moringa. Concentrations of Mn, Fe, and Zn were all above the safe limit in all the vegetables obtained in site four. For site five Co concentrations in guinea sorrel and moringa were above WHO/FAO safe limit and BDL in okro, Cr concentration was above safe limit in guinea sorrel and tomato while BDL in okro. Mn, Fe, and Zn concentration were above the WHO/FAO safe limits in all the vegetables analysed in site five. For site six the concentrations of Mn, Fe, and Zn were above WHO/FAO safe limit in okro, guinea sorrel and tomato while Co concentration was BDL in okro, guinea sorrel and tomato. Cr concentration in site six was above safe limit in guinea sorrel while it was BDL in okro and tomato.

The concentration of the various elements determined in sediment samples collected from different sites in river Ngadda and Alau dam indicate some degree of variations at the various sites. The result of the elemental concentrations obtained in this study was compared with the values determined in sediment samples obtained from river Kubanni in Zaria, Kaduna state and the values obtained in sediment samples determined from selected coastal areas of Lagos in Lagos state both from Nigeria as presented in table 4.15. It can be clearly seen from Table 4.15 that among the twenty six (26) elements determined in this study and the result obtained by other researchers for sediment of Kubanni river and sediment of selected coastal areas of Lagos, twenty two (22) of the elements namely Br, Cr, Cs, Co, Dy, Eu, Hf, La, Lu, Mn, Na, Rb, Sb, Sc, Sm, Ta, Ti, Th, U, V, Yb, and Zn concentrations were within the range obtained by the other researchers while the values of Al, Ba, Ca, and K were above the values obtained by the other researchers. The excess of K observed may be due to continuous applications of fertilizers

by the farmers during cultivation of their crops on their farmlands along the bank of river Ngadda, the excess of Al may be due to disposal of waste that contain Al since the study sites were close to residents and some of these waste that were dispose by the river bank or within the town may be eroded during rainy season to the farmlands while Ca and Ba excess may be due to human activities or some natural phenomena

The water samples collected from various points in river Ngadda and Alau dam were analyzed using Atomic Absorption Spectrophotometer (AAS) and the range of the concentrations of the various elements determined in this study were compared with the values recommended by some of the world regulatory organizations and the result is as presented in Table 4.16. It can be observed from Table 4.16 that Al concentrations in all the sites were less than the tolerance limit required in water for continuous irrigation purposes while the concentration of Cd was above the tolerance limit at sites H3, H4, H5, H7, H10, H12, and H13. The concentration of Co was above the tolerance limit for continuous irrigation at sites H1, H2, H3, H4, H5, H9, H19, H11, and H13 while that of Cu were within the limit in all the sites. Concentration of Cr was above the tolerance at sites H3 and H7.while the concentration of Pb were within the limit for all the studied sites. The concentration of Fe and Ni were above the recommended tolerance limit at sites H6, H7, H8, H10,, H11 and sites H4, H5, H10, H13.respectively. This suggests that the contamination level of the water in both river Ngadda and Alau dam at the time this research was conducted may be considered to be safe for agricultural purposes for some metal pollutants but unsafe for some of the metal pollutants. The issue to consider will be in the case of bio-accumulation tendency by bio-absorption process by the various

vegetables that were being irrigated with this water which may enable the plants to accumulate metal toxicants above maximum permissible limit.

The data of the soils and the sediments samples were run for the determination of the Pearson correlation coefficient using the software SPSS version 16 the result of which were presented in Tables 4.6 and 4.7 respectively. From Table 4.6, the Pearson correlation result for the soil samples indicate that many elements were positively correlated with forty five elements having positive inter-elemental association with coefficient of correlation ($r \geq 0.5$) with significant difference at $p \leq 0.05$ while seven elements were having negative correlation coefficient ($r \geq - 0.5$) and indicating significant difference at $p \leq 0.05$. For sediments samples, the Pearson correlation of the concentration of the elements determined in the various sites is as presented in Table 4.7 and the result indicate that ninety five element were having positive correlation coefficients ($r \geq 0.5$) with significant difference at $p \leq 0.05$ while nine of the element were having negative correlation coefficients ($r \geq - 0.5$) with significant difference at $p \leq 0.05$. The above correlation results for both soil and sediment samples indicate that distribution of various elements in the study area was caused by different factors and sources.

The measure of the similarity in the elemental composition and sources of the element in soil samples obtained from the fourteen different sites was determined using statistical analysis of cluster procedure and the result obtained indicate that, soil samples from site S1, S4, S5, S10, S11 and S14 are similar in source and elemental composition while, soil samples from sites S2, S6, S8, S9, S12, S13 and S0 are similar in source and elemental composition but soil samples from site 3 has elemental composition source that

differ from the other two groups as indicated in Figure 6. For sediment samples, the measure of the similarity in elemental sources and composition for the samples obtained from nine different sites using statistical analysis of cluster procedure indicate that sediment samples from sites SS1, SS4, SS5, SS6, SS8 and SS9 are similar in source and elemental composition while sediment samples from sites SS3 and SS10 are similar in source and elemental composition but sediment samples from site SS2 has elemental composition and source that differs from the other two groups as indicated in Figure 8, Similarly, the measure of the elemental composition of the water samples from thirteen different sites using statistical analysis of cluster procedure indicate that water samples from sites H1, H2, H3, H9, and H13 are similar in source and elemental composition, water samples from sites H4, H10, H11, and H12 are similar in source and elemental composition while water samples from sites H5, H 6, H7, and H8 are similar in source and elemental composition as indicated in Figure 10 For more understanding and clarity of the similarity of the elemental compositions sources produced by the dendrograms obtained for soil, sediment and water samples, the structure of the various groups in each dendrogram were produced by normalizing the elemental concentrations with their respective mean values and the normalized values plotted against the elements thereby displaying the structure of their dendrograms. The structure of the soil samples in dendrogram shown in Figure 6 was as displayed in Figure 7. It can be clearly seen from Figure 7 that the trend displayed by the two cluster groups (cluster I and II) are similar except for difference in the mean of four elements of cluster I namely Co, Lu, Mn and U. similarly Figure 9 displayed the structure of the elemental compositions of the two cluster groups (cluster I and II) of the sediment dendrograms of Figure 8. It can be seen from the

Fig 9 that the elements Cr, Sm and Yb from cluster I have variations from the mean of the two groups, this could be due to enhanced depositions from their sources by anthropogenic means for example around the custom market there is an abattoir and centre station for Nigerian Institute of leather Research. The leather when mineral tanning process is employed chromium is used. In the same vein Figure 11 displayed the structure of the elemental compositions of the three cluster groups Cluster I, II and III) of the water dendrogram of Figure 10. It can be clearly seen from Figure 11 that only Fe of cluster I and Cu of cluster III shows variations from the mean of the three groups. These variations could be due to enhancement or deterioration from either human or natural processes

The contamination factor (CF) values for each of the elements investigated in the soil samples in the study area were calculated and presented in Table 4.11. It can clearly be seen from this table and defined by the contamination factor indices key at the bottom of table that most of the elements have (CF) values that indicate low to moderate contaminations except for chromium which has considerable to high (CF) in almost all the sites of the study area. Also the values of the geochemical indices of all the elements determined in the study area were evaluated as shown in Tables 4.12a and 4.12b. It can be observed from these tables and defined by the indices key at the bottom of the Table, that most of the elements geochemical indices suggested that the soils in the studied sites were not contaminated by the respective elements determined except for chromium which indicated moderately to strongly polluted suggesting an enhanced deposition either by human or natural processes.

The REE obtained from the soil and sediment samples were treated using Haskin values. The normalized values were plotted for both soil and sediment and both showed anomaly at the europium position which is an indication that the quality control process performed earlier on and the results obtained were correct since this anomaly serve as quality control.

CHAPTER SIX

CONCLUSION, SUMMARY AND RECOMMENDATION

6.1. Conclusion

This work determined the level of some metal pollutants in vegetable samples namely Amaranthus (*Amaranthus tricolor*), Guinea Sorrel (*Hibiscus sabdariffa*), Okro (*Abelmechus esculentum*), Lettuce (*Lactuca sativa*), Tomato (*Lycopersicon esculentum*), Ben oil (*Moringa oleifera*) and Water leaf (*Talinum triangulare*), soils samples, sediment samples and water samples that were collected from/in farmlands along the bank of river Ngadda and Alau dam. The samples were analysed using instrumental neutron activation analysis (INAA) and complimented by atomic absorption spectroscopy techniques. Soil samples result showed the maximum concentrations of Arsenic, cobalt and Vanadium determined were above MAC values, Chromium was within the range of MAC values while Zinc and Antimony were above the recommended MAC values for agricultural

purposes as recommended by other countries. Concentration of Aluminium, Cadmium, Cobalt, Chromium, Copper, Iron, Manganese, Nickel, Lead and Zinc determined in the water of river Ngadda and Alau dam used for dry season farming indicate that Cadmium, Cobalt, Chromium, Iron and Nickel concentrations exceeded the recommended values for continuous irrigation but within the value recommended by various national and international regulatory organization such as WHO, 2004, USEPA, 2000 and USEPA, 1999) for agricultural purposes. Twenty nine elements were analyzed for their elemental concentration levels for the purpose of assessing whether the vegetables had bio-accumulated metal pollutants beyond the maximum permissible limit (MPL) values provided by World Health Organization (WHO) and Food and Agricultural Organization (FAO) to provide information for the suitability of the vegetables for safe consumption in the short and long term consideration. The result obtained shows that most of the trace metals determined in the various vegetable had bio-accumulated trace elements concentration values above the safe limit provided by WHO/FAO especially on the farmlands along the bank of river Ngadda after the Maiduguri Municipal council in the direction of flow of the river which implies that the safety of these vegetables for consumption cannot be guaranteed and even the ones' that are below the safe limit there is the concern of cumulative effect for continuous consumption

.The Pearson correlation analysis result shows that forty five elements had positively correlated coefficients inter-elemental association at ($r \geq 0.5$) and indicate significant difference at $p \leq 0.05$ while five elements had negative correlation coefficient ($r \geq - 0.5$) at $p \leq 0.05$ Thiis means that the various elements in the various sites were only fairly distributed which could be attributed to the fact that some sites may be at or near

point source (PS) pollution from the municipal which enhances accumulation of the elements. The sources of these metal pollutants from different sites according to similarity were determined using cluster analysis which produces a dendrogram consisting of cluster groups at similarity of 96.5% and 90.9% respectively.

The metal pollutant concentration level of the sediment of both river Ngadda and Alau dam were determined using INAA procedure and the correlation of the elemental concentrations of the sediments collected at different points were determined using Pearson correlation procedure. The result indicates that ninety six elements had positively correlated coefficients inter-elemental association at ($r \geq 0.5$) and $p \leq 0.05$ while nine elements had negative correlation coefficients ($r \geq - 0.5$) and $p \leq 0.05$. This shows the elements are well distributed which could be attributed to dilution due to the aquatic environment. Cluster method were used to establish similarity in the sites that have common sources of the metal pollutants for the sediment samples which produces a dendrogram consisting of two cluster groups at 89.1% and 70,5% similarity respectively. Similarly the water samples elemental content cluster treatment produces three cluster groups at 96.2%, 78.6% and 76.5% similarity respectively

6.2 Summary

. From the analysis of the result of soil, vegetables, sediment, and water presented in this work, it can be observed that the concentrations of elements in the soils samples and the concentrations of elements in the vegetable samples collected from the various sites from the farmlands at the various sites varied from one site to the other. This indicates that there are different sources that are responsible for enrichment of the concentration of the

various elements at the specified sites and there are differences in level of concentration of the different elements in the different types of vegetables investigated which could be due to difference in the absorption ability of the different vegetables or the the concentration levels of the elements in the soils differ from sites to sites i. e the concentration level in the different vegetables could be either due to the level of concentrations of the element in the soil at the site of study or due to the absorption ability of the vegetables concern. The concentrations of the metal pollutants in vegetables indicates that those elements that have high concentrations in soil samples have corresponding high concentration in the vegetables, for example at site one, concentration of Aluminum in soil S1 was 34470 ± 241 ppm and in Amaranthus A1 was 1023 ± 426 ppm; Fe in soil S1 was 10420 ± 240 ppm in Amaranthus A1 was 640 ± 54 ppm; Cr in soil S1 was 35 ± 3 ppm in amaranthus A1 was 1.0 ± 0.1 ppm; Zn in soil S1 54 ± 3 ppm in amaranthus A1 22 ± 2 ppm At site two, concentration of aluminium in soil S2 was 32510 ± 293 ppm in amaranthus A2 was 1508 ± 18 ppm, Fe in soil S2 10150 ± 213 ppm in amaranthus A2 783 ± 45 . ppm Zn in soil S2 24 ± 3 ppm in amaranthus A2 was 36 ± 3 ppm. At site three, concentration of aluminium in soil S3 was 31520 ± 504 ppm and in amaranthus A3 was 1301 ± 29 ppm; Fe in soil S3 was 9982 ± 294 ppm in amaranthis A3 558 ± 37 ppm, Zn in S3 was 46 ± 5 ppm in amaranthus A3 was 85 ± 4 ppm; concentration of cobalt in S3 was 3.8 ± 3 ppm, Cobalt in amaranthus A3 was 0.36 ± 0.034 ppm at site four the concentration of aluminium in soil S4 was 29559 ± 355 , in amaranthus A4 was 1176 ± 21 ; Fe in soil S4 was 9529 ± 229 in amaranthus A4 was 655 ± 40 , Cr in soil S4 was 29 ± 3 , and Cr in amaranthus was 88 ± 21 . This suggests that there are linear correlations between the concentrations of elements in the soil and that of the vegetables cultivated on the soil. The Pearson correlation for soil samples give forty

five elements that have positive correlation coefficient of ($r \geq 0.5$) at significant level of $p \leq 0.05$) which suggest common and linear variation in concentration of the elements and five elements that have negative correlation coefficient ($r \geq -0.5$) at significant level of $p \leq 0.05$) indicating opposite linear variation in concentration of the elements. Multivariate cluster analysis of the soil samples data was carried out which produces dendrogram of the similarity in the concentration and sources of the elements. The result of the dendrogram of the sites studied in this work indicate that the area consist of two clusters I and II and an outlier. Similarly the sediment samples data were subjected to multivariate cluster analysis and two cluster groups were produced with an outlier of one sample site. The water samples collected from river Ngadda and Alau dam were analyzed for elemental concentration using Atomic Absorption Spectrometer. The data obtained were subjected to multivariate cluster analysis which produces a dendrogram consisting of three cluster groups for the whole area of study. The data obtained from the analysis of the vegetable samples were plotted using bar charts and the results indicate that for most of the sites, different vegetables bio-accumulated different concentrations of the same elements in the same site and vice versa.

6.3 Recommendation

This work which attempt to assess the distribution of trace elements in vegetables cultivated on fadama farmlands along the banks of river Ngadda and Alau dam has brought out some salient facts about bio-accumulation of metal pollutants by the vegetables/plants that are grown and consumed by the populace as revealed by the results obtained for the concentrations of the different metal pollutant determined by the INAA methods. The result further .show that most of the trace element concentrations were above maximum

permissible limit (MPL) recommended for vegetables grown on unamended soils and those within or less than the recommended values have the potential to exceed these limits considering the fact that the suspected factors responsible for the contamination of the soils are still in place. The researcher is therefore suggesting that this kind of investigation be continued periodically to ascertain the level of these metal toxicants since the accumulation of the metal pollutants concerned build up unnoticed unless laboratory investigations were conducted to ascertain the level of pollution of the soil and or the vegetables with man at the receiving end of the food chain. The single comparator NAA (K_0 -NAA) method can also be employed for such kind of investigation in the study area so that those element(s) that were not detected by the relative method can be detected thereby bringing out more elemental spectrum of the result.

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