ASSESSMENT OF SOME HEAVY METALS IN WATER AND SOME FOOD CROPS CULTIVATED ALONG RIVER KUBANNI AND GALMA, IN ZARIA, NIGERIA

BY

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(M.Sc/PHARM-SCI/10084/07-08)

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DECLARATION

I hereby declare that this research work in the project thesis entitled **ASSESSMENT OF SOME HEAVY METALS IN WATER AND SOME FOOD CROPS CULTIVATED ALONG RIVER KUBANNI AND GALMA, ZARIA,** has been performed by me in the Department of Pharmaceutical and Medicinal Chemistry, Ahmadu Bello University, Zaria,

under the joint supervision of Dr. I.A. Yakasai and Prof M.T. Odunola . The information derived from the literature has been duly acknowledged in the text and a list of reference provided. It has not been accepted in any previous publication for a higher degree elsewhere .

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CERTIFICATION

The thesis entitled '**ASSESSMENT OF SOME HEAVY METALS IN WATER AND SOME FOOD CROPS CULTIVATED ALONG RIVER KUBANNI AND GALMA, ZARIA,**' by Onalo Deborah Victoria meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research work is dedicated to my beloved husband Richard and my lovely children, Utenwu'ojo, Ojone and Ele'ojo, for their support, prayers and encouragement.

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ABSTRACT

Heavy metal contamination of food crops through irrigation is a major concern due to the potential risk involved. This study was designed to investigate the contamination of food crops grown through irrigation along River Kubanni and Galma, Zaria, with heavy metals (Pb, Cu, Mn, Cd, Cr and Fe). To achieve this, Pb, Cu, Mn, Cd, Cr and Fe concentrations in water and food crops and the transfer factor of these metals from water to food crops were determined. Samples of food crops (maize, spinach, lettuce and bitter leaf) and corresponding irrigating water were collected, water sample from Zaria water works was also collected as a control and metals assessed using Atomic Absorption Spectrophotometer. The results showed the presence Cu, Cr, Pb, Cd and Fe in all the food crops although significantly higher in lettuce compared to other food crops beyond the limits of International standard FAO/WHO. Water samples revealed low concentration of Cu and Mn, with values below the International permissible limits for water quality, WHO with exception of Pb, Cr, Fe and Cd (at some sites). Metal transfer factors from water to food crops are found significant in leafy vegetable (lettuce, spinach and bitter leaf) than maize. From this result, it was also observed that other than contamination of food crops by irrigation water, other sources of metal deposit could be responsible. Generally, heavy metal contamination of food crops grown along River Kubanni and Galma, Zaria posed a great health risk to the local population through consumption of the food crops especially lettuce.

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CHAPTER ONE

1.0 Introduction

Heavy metals contamination is a major problem of our environment and they are also one of the major contaminating agents of our food supply (Abdollatif et al., 2009; Khair et al., 2009). This problem is receiving more and more attention all over the world, in general and in developing countries in particular. The biological halflife of these heavy metals are long and have potential to accumulate in different body organs and thus produce unwanted side effects (Jarup, 2003; Sathawara et al., 2004; Ata & Modabberi, 2009).

Food safety is a major public concern worldwide. The increasing demands for food and food safety has drawn the attention of researchers to the risks associated with consumption of contaminated foodstuffs i.e pesticides, heavy metals, and or toxins in vegetables (Dmello, 2003; Abdollatif et al., 2009).

Excessive accumulation of these heavy metals in human bodies creates the problems like cardiovascular, kidney, nervous and bone diseases. It is known that serious systemic problems can develop as a result of increased accumulation of dietary heavy metals such as cadmium and lead in the human body (Oliver, 1997). Heavy metals are extremely persistent in the environment; they are non-biological and not thermo-degradable and thus their accumulation readily reaches toxic levels.

Heavy metals can impair important biochemical systems, constituting an important threat for the health of plants and animals. The adverse health effects of several chemicals have been documented.

Significant contamination of seeds, plants and plant products with toxic chemical elements due to contaminated soil and water has been observed as a result of release of these toxicants into the sea, rivers, lakes and even into irrigation channels. Afterwards, the consumption of contaminated vegetables constitutes an important route of animal and human exposure to these chemicals.

It should be realized that most of these cultivated lands are contaminated with heavy metals contributed mainly through vehicular emissions, pesticides and fertilizers, industrial effluents and other anthropogenic activities. These contaminated soils have resulted in the growth of contaminated food crops (Jackson and Alloway, 1992; Rattan et al., 2005; Sanayei et al., 2009).

The result of heavy metals contamination differed from area to area as the application of fertilizers and other human activities differ at each site. It has been studied that phosphate fertilizers are the main source of soil heavy metals pollution. This pollution is because of the presence of cadmium as an impurity in phosphate rocks. Due to this massive application of these fertilizers, there is obvious contamination of heavy metals in soil. Also most of the heavy metals are the natural constituents of earth's crust and from there, they are taken by plants and thus transferred to food chain (Zhau and Xiong, 1994).

1.1 Heavy Metals And Routes Of Exposure

Certain trace elements are essential in plant nutrition but plants growing in a polluted environment can accumulate trace elements at high concentrations causing a serious risk to human health when they are consumed.

Studies have shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils are used for crop production (Xian, 1989). Heavy metals may enter the

human body through inhalation of dust, consumption of contaminated drinking water, direct ingestion of soil and consumption of food plants grown in metal – contaminated soil (Kobata – Pendias and Pendias, 1984; Alloway, 1990).

Contamination of vegetables with heavy metals may be due to irrigation with contaminated water, the addition of fertilizers and metal-based pesticides, industrial emissions, transportation, the harvesting process and storage and/or at the point of sale.

Human beings are encouraged to consume more vegetables and fruits, which are good source of vitamins, minerals, fibers and are beneficial for health. However, these plants contain both essential and toxic metals over a wide range of concentrations.

It is well known that plant take up metals by absorbing them from contaminated soil as from deposits on parts of the plants exposed to the air from polluted environments (Khairiah et al., 2004; Chojnocka et al., 2005).

Lead and cadmium are among the most abundant heavy metals and are particularly toxic (Radwan and Salama, 2006). Excessive amount of these metals in food is associated with a number of diseases, especially of the cardiovascular, renal, nervous and skeletal systems (WHO, 1992, 1995; Steenland and Boffetta, 2000; Jarup, 2003). These heavy metals are also implicated in carcinogenesis, mutagenesis and teratogenesis (Radwan and Salama, 2006).

1.2 Water pollution and toxic chemicals

1.2.1 Water pollution

Despite the essential role played by water in supporting human life, it also has great potential for transmitting a wide variety of diseases and illness (Yakasai et al., 2004).

Due to rapid population of growth, urbanization, industrialization and exploitation of natural resources, there has been a steady increase in the quantity, quality and diversity of discharges into the aquatic environment (FAO, 1991). These discharges contain huge amount of heavy metals which adversely affect the physicochemical properties of the receiving water and consequently its biota. Industrial waste discharge into the coastal area of the United Kingdom when contained toxic heavy metals claimed several aquatic lives (Zabel, 1993). Common agents of water pollution include industrial discharges, agricultural chemicals, human sewage and animal wastes.

1.2.2 Toxic Chemicals

Municipal waste water is a source of chemical pollutants that may affect human health (Chang et al., 2002).

Surveys in the United States of America revealed that both the occurrence and the concentration of toxic pollutants in municipal waste water and sewage sludge were extremely variable and the outcomes were often influenced by industrial waste pre-treatment requirements (Chang et al., 2002; Blakeslee, 1973; Feiler, 1979 and Minear et al., 1981).

However, there are report from China that serious human health problems are related to long-term irrigation with waste water which are heavily polluted by industrial waste discharge (Chang et al., 2002).

1.3 Research Problem

Most industries still do not obey the regulations on treatment and management of effluents before discharge and these discharges contain heavy metals which still find their way to water and soil (Okoronkwo et al., 2005).

These industrial effluents may be from tanneries, and other contaminants in which when generated are channeled into drains and subsequently into the river. Consequently, the amount of pollutants and waste generated by the industrial waste pose significant stress on the vegetable crops grown on the river bank since the polluted river is used for irrigation. As a result, heavy metals may enter the vegetables thereby exposing consumers of the vegetable crop to have bioaccumulation of heavy metals with time.

Though studies have been carried out to show the level of these heavy metals in water and vegetable crops. Increased environmental population called for further assessment of the vegetable crops grown in the vicinity of the Kubani and Galma River, especially the consumable vegetables like spinach (*Spinacia oleracea*), lettuce (*Lectuca sativa* L.) bitter leaf (*Vernonia amygdalina*) and cereal like maize (*Zee mays*).

1.4 Justification

Food safety is a major public concern worldwide. The increasing demand for food and food safety has drawn the attention of researchers to the risks associated with consumption of contaminated food stuffs. According to Radwan and Salama, 2006; that heavy metals have been implicated in carcinogenesis, mutagenesis and teratogenesis. Therefore, its concentration in

consumable food should be routinely monitored so as to ensure that the FAO/WHO recommended limit of these metals are not exceeded.

Population increase is related to increase in waste generation and hence contamination. Since the population of Zaria has increased in the recent, the tendency to increased contamination is more likely. Due to this increase, various activities like agricultural farming with the use of pesticides and fertilizers, Industrial activities like the leather tanning, pollution from increased number of motor vehicles (Vehicular emission), a lot of dumping sites containing discarded rusted irons, batteries and other sources of heavy metals which are neglected around the farmland by the disposal agencies. These are equally used as organic manure in the soil for growing food crops. The need for this study to document the recent heavy metal levels in the locality.

There is concern about the possible long-term health hazards which may arise from the presence of all these sources of heavy metal, which when taken through drinking water or eaten through fresh vegetables can therefore be dangerous to human and animals. Although lots of work have been done in the area, there is need to update data. It is therefore important to assess the level of these heavy metals like lead (Pd), copper (Cu), Manganese (Mn), Cadmium (Cd), Chromium (Cr) and Iron (Fe) in raw water and food crop sample cultivated along a particular source of river, River Kubanni and Galma, as a regular basis.

1.3 Aim And Objective

The aim of this research is to assess the level of these heavy metals (Pb, Cu, Mn, Cd, Cr, and Fe) in raw water of River Kubanni and Galma and its tributaries, treated water (tap water) from the

water works at Angwan Kaya, as well as concentration of these heavy metals in some food crops cultivated along the bank of River Kubanni and Galma.

This shall be achieved through the following objectives.

(i) To assess the level of heavy metals like Pb, Cu, Mn, Cd, Cr, and Fe in raw water samples from River Kubanni and Galma and treated water sample (tap water) from water works at Angwan kaya.

(ii) To assess the level of these metals in the food crops like maize (Zee mays), spinach (*Spinacia oleracea*), lettuce (*Lectuca sativa* L.) and bitter leaf (*Vernonia amygdalina*), because they are the common consumable food that are cultivated along the river bank.

(iii) To compare the levels of these metals in raw water with WHO limits for safe drinking water and also to compare the levels of these metals obtained in the food crops with those of joint FAO/WHO limits.

(iv) To compare the level of these metals obtained in the wet season to that obtained in the dry season and determine the seasonal variation if any.

(v) To investigate the uptake of the six heavy metals through the irrigation water by the food crops.

CHAPTER TWO

2.0 Literature review

2.1 Heavy Metal Pollution

Industrial effluents and municipal waste water usually contain high amount of heavy metal such as As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn (Larsen et al., 1992; Aora et al., 1985). Their continuous use on agricultural land may results in metal accumulation in surface soil and subsequently transfers to vegetable crops (Gupta et al., 1986). Some heavy metals are essential in trace amounts, namely Cu, Zn, Fe, Mn, Mo, and Co for plants and in addition Cr, Ni, Sn for animals. As, Cd, Hg and Pb have not been known to have any function for either plants or animals (Greenland and Hayes, 1981). Higher concentration of these metals in the ecosystems may lead to an excessive accumulation of metals, becoming toxic to plants and possible danger to human health problem. A number of cases of health problems related to environmental Cd and Hg poisoning and elevated levels of Pb in the blood of infants have been reported (Singh and Steinnes, 1994). Therefore, heavy metal contamination of soil resulting from wastewater irrigation is a cause of serious concern due to the potential health impacts of consuming contaminated produce.

2.2 Sources Of Heavy Metals In Environment

Different heavy metals have different sources of origin. Metal smelters, foundries, steel mills, coal fire, power plant etc. have led to metal pollution. Other important sources of heavy metals are sewage sludge, compost refuse, fly ash and other industrial wastes (Singh, 2005). Emission of heavy metals, as particulate and gases, from volcanoes, forest fires, crusted material and

continental dust have always been a natural input to soils and ecosystems. Several processes like precipitation, gravitational setting of particulate on vegetation, ground soil and water surfaces are responsible for their transportation to greater distances from the site of their application or introduction in both terrestrial and aquatic environment (Singh, 2005).

Aquatic ecosystems, frequently contaminated with heavy metals, are known to contain dissolved metal cations. The metal toxicity is directly proportional to the concentration and availability of these substances in the environment.

Basically there are three sources of toxic metals to enter in the biosphere:

i. Use of sewage and sewage sludge in agricultural land.
ii. Industrial waste disposal and water pollutants,
iii. Air pollutants

2.2.1 Sewage And Sludge As Source Of Toxic Metals In Environment

One of the most pressing problems facing metropolitan areas today is disposal of large volumes of liquid and solid wastes generated by urban and industrial activities. The need to conserve and re-use water problem associated with water pollution resulting from discharging wastes into surface water (Singh, 2005). Sewage treatment plants effluents and sewage sludge are currently and have for many years been used to irrigate field crops and recreation areas such as parks and golf courses. The settle able solids from sewage treatment plant works are processed and sold as soil amendments and low grade fertilizers. There have been very few studies designed to evaluate the long-term consequences of applying sewage treatment plant wastes on land. One of

the potential problems associated with the long-term (decades) applications is the accumulation of toxic concentration of heavy metals (Singh, 2005).

The heavy metals concentrations in sewage sludge are related to the kinds and amounts of urban and industrial discharges into the sewage treatment systems. The composition of urban and industrial waste changes as consumer products, industrial processes and industrial activity changes (Singh, 2005).

Chang et al. (2002), found the concentration of potentially hazardous pollutants in the municipal waste water and the resulting sewage sludge varied considerably from location to location and from the same community, was subject to temporal variations due primarily to point – source discharges from industries and domestic affluent.

2.2.2 Industrial Waste Disposal and Water Pollutants as Source of Toxic Metals In Environments And Effluents.

Human communities have been polluting water since civilization begun. Rivers are polluted by adding organic waste, including human and animal excreta and fibrous agricultural waste and plants that are harvested. Rivers are frequently used as swers to discard waste. In Asian countries this is very common practice of the releasing of sewage waste into rivers. In India most of the rivers are highly polluted because of discharge of sewage and industrial effluents in rivers (Singh, 2005).

Additionally, rivers are still being polluted, not only by traitional organic wastes but also by industrial wastes, which now form the most common and hazardous pollutants. Industrial waste includes radioactive chemicals, dangerous organic chemicals, nitrates, heavy metals and oil. The

major polluting industries is the leather industries which use large amounts of chromium and other chemicals, and much of it finds its way into the meager flow of the river near the industry (Singh, 2005).

However, industry is not the only source of pollution. Sheer volume of water estimated at nearly 1 billion litres per day of mostly untreated raw sewage is a significant factor (Singh, 2005).

2.2.3 Air Pollutants as Sources Of Toxic Metals In The Environment

Air pollution can be transported hundreds of miles downwind from its origin. Since air pollutants do not recognize political boundaries, sites and communities cannot independently solve all of their air pollution problems (Singh, 2005).

Each individual breathes nearly 13,000 litres (approximately 3,400 gallons) of air everyday. Yet the air is being polluted by human activities like driving cars, burning fossil fuels, and manufacturing chemicals, and natural events such as forest fires. These add gases and particles to the air we breathe and in high enough concentrations, can have harmful effects on people and the environment. Many air pollutants such as those that form urban smog, acid rain, and some toxic compounds remain in the environment for long periods of time and can be transported to a great distances from their origin (Singh, 2005).

Toxic air pollutants are known to cause or are suspected causing cancer, adverse reproductive, developmental and central nervous system effects, and other serious health problems. Examples of toxic air pollutants include heavy metals like mercury (Hg) and lead (Pb), chemicals like polychlorinated biphenyls (PCB) and pesticides like dichlorodiphenyl-trichloroethane (DDT). Air pollutants, such as lead, mercury, PCB, and DDT, break down slowly, if at all, in the

environment and can be re-deposited many times. Additionally, they build up in the body and concentrate as they rise through food chain (Singh, 2005).

2.3 Toxicity Of Heavy Metals On Human Health

The presence of toxic metals in the environment continues to generate a lot of concern to environmental scientists, Government agencies and health practitioners (Awofolu, 2005). This is due to the health implications of their presence since they are non – essential metals that are not required for any function either by plants or animals and are usually monitored for health purposes. According to Awofolu (2005), the toxic effects of metals such as Cd, Pb, Hg, etc to man are well known. This category of metals is not required by man even in small amount (Tyter, 1981 and Borgmann, 1983).

However, metals such as Cu and Zn are classified as essential to life due to their involvement in certain physiological processes, although elevated levels of these metals were found to be toxic (Spear, 1981).

2.4 Effect Of Heavy Metals On Human Health

In the right concentrations, many metals are essential to life. In excess, these same chemicals can be poisonous. Similarly, chronic low exposures to heavy metals can have serious health effects in the long run. The main threats to human well – being are associated with; Pb, As, Cd and Hg, and it is these substances that are targeted by international legislative bodies (UNEP/GRID – EUROPE, 2003). Heavy metals required by the body in small amounts but toxic in higher concentration include; Cu, Zn and Cr.

Health effects include; Reduced growth and development particularly in children, cancer; organ damage, nervous system damage and in extreme cases death. Metals are significant to human because some of them are most important trace elements as co factor in various metabolic enzymes and constituents of cells. For example, Zn, Cu and Fe form important component of cell and co-factor in several metabolic enzymes, while organically chelated Cr^{3+} compound acts as a co-factor in insulin hormone responses controlling carbohydrate metabolism in human (Rai and Pal, 2002).

While some non-essential metals are present in all tissue and organs of man, like under normal conditions, more than 90% of Pb is retained in the skeleton. However, increased concentration of these metals can affect mineral and enzyme status of human beings. They irreversibly bind to active sites of enzymes, thereby destroying normal metabolism producing high level toxicity.

The degree to which a system, organ, tissue or cell is affected by heavy metal depends on the high level of the toxin itself and the individual's degree of exposure to the toxin. The accumulation of these heavy metals affects cognitive and physical health of the individual. Due to this toxic effect of heavy metal various organization and agencies such as the WHO, USEPA, FEPA have set guidelines for drinking water quality. Recommended maximum concentrations of heavy metals in vegetable crops have also been given by Joint FAO/WHO. The safe limits for some heavy metals in drinking water and vegetable crops is presented below

Table 2.1 Water quality guidelines for heavy metals and safe limit for Food crops

Element	**A (Mg/l)**	**B (Mg/l)**	**C (mg/kg)**
	WHO drinking water guideline	**FEPA drinking Water guideline**	**FAO/WHO JOINT recommended max. conc. For crops**
Lead	0.01	<0.05	0.3
Copper	2.00	1.50	73.3
Manganese	0.50	<1.50	500.0
Cadmium	0.003	0.01	0.2
Chromium	0.05	0.05	2.3
Iron	0.30	<0.30	425.5
Zinc	3.0	15.0	99.40
Nickel	0.02	-	67.90

Sources

A => WHO (1993)

B=> FEPA (1998)

C => FAO/WHO standard (Codex Alimentariles Commission, 2001)

2.4.1 Lead (Pb)

Lead is found as a contaminant in air, water and soils (Codex, 1995). The earth's crust contains about 15mg/kg of lead (Belilies, 1994). Lead is present in the environment in the form of metallic lead, inorganic ions and salts and organo-metallic compounds (CE, 1994).

The sources of contamination are numerous including Lead accumulators, petrol, recycling of lead batteries and combustion of industrial and household waste, lead pollution is decreasing in most parts of the world, as lead-containing chemicals, such as tetraethyl lead and tetramethyl lead used as gasoline additives to increase octane rating, are replaced by other additives (ATSDR, 1990; CODEX, 1995) and due to recycling of accumulators and batteries.

Exposure through drinking water where Lead batteries or Lead soldered pipes are still used may contribute significantly to the lead intake. The WHO Air Quality Guidelines for Europe indicate that airborne Lead contributes about 1-2% of human intake.

Lead in the soil is only poorly taken up by plant roots and is not transported away from the roots to the rest and is not transported away from the roots to the rest of the plant crop. Therefore, lead levels in the plant are to a large extent governed by air-borne lead contamination which makes leaves and leafy vegetable most vulnerable to the air-borne deposition, but also cereal grains have been shown to absorb substantial amounts of lead via the air (CCFAC, 1995).

Lead poisoning (also known as saturnism, Plumbism, Devon colic, or painter's colic) is a medical condition caused by increased levels of the metal lead in the blood. Lead may cause irreversible neurological damage as well as renal disease, cardiovascular effects, and reproductive toxicity.

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process due to accumulation, exposure and direct contact. These dangers have long been known, though the modern understanding of their full extent and the small amount of lead necessary to produce them is relatively recent, blood lead levels once considered safe are now considered hazardous, with no known threshold. Lead has also been found in some pool paint – especially those painted by lead-based expoxy paint (ATSDR, 2008).

Effects of Lead include;

- Neuropathy – such as muscle pain, weakness, tremors, twitches, spasms, or cramps.
- Encephalopathy – which, in extreme circumstances, is characterized by raised intracranial pressure, seizures, comas, or even death
- Nephropathy – which occurs because the kidneys are the main route of removal of lead from the body. Fanconi syndrome may result from acute lead poisoning while the chronic lead exposure can lead to a slowly progressive interstitial nephritis.
- Behavioural changes, such as inability to concentrate, hyperactivity, irritability, aggressiveness mood swings, or insomnia
- Cognitive problems such as memory loss
- Other associated effects such as metal taste in the mouth, chest pain, anemia, importance, and other reproductive problems.

2.4.2 Copper (Cu)

Copper is found at a concentration of 70mg/kg in the earth's crust (Beliles, 1994). Copper exists in two oxidation states: Cu (I) (Cuprous) and Cu (II) (cupric). Copper is among the most

effective of metal biochemical oxidizing agents, it is present naturally in most food stuffs in the form of copper ions or copper salt (Codex, 1995).

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities include it use for electrical equipment, construction. Such as roofing and plumbing, industrial machinery, such as heat exchangers and alloys, mining, metal production, and phosphate fertilizer production (ATSDR, 2008).

Routes of exposure of copper can be found in many kinds of food, in drinking water and in air. The absorption of copper is necessary, because copper is a trace element that is essential for human health, but too much copper can still cause eminent health problems. People that live in houses that still have copper plumbing are exposed to higher levels of copper, because copper is released into their drinking water through corrosion of pipes (ATSDR, 1990).

Toxic effect of copper can cause irritation of nose, mouth and eyes and it causes headaches, stomach aches, dizziness, vomiting and diarrhea. High uptakes of copper can cause liver and kidney damage and even death (ATSDR, 1990).

It has also been found that chronic copper poisoning can results in what is known as Wilson's Disease, a disease which is characterized by a hepatic cirrhosis, brain damage, demy elimination, renal disease, and copper deposition in the cornea (ATSDR, 1990).

2.4.3 Manganese (Mn)

Manganese is an essential element widely distributed in the environment (Codex, 1995), comprising approximately 0.1% of the earth's crust. About 90% of total manganese production is

used in steel manufacture as a deoxidizing and desulphurising additive and as an alloying constituent (Beliles, 1994). Manganese exists in two common oxidation state, as manganese (I) and manganese (IV).

The main source of exposure of manganese is in most foodstuffs. The main contributors of manganese to the diet are cereals (10-30mg/kg) as well as vegetables and fruits (0.1-5mg/kg) (Beliles, 1994; Codex, 1995). Nuts also have high content of manganese. In some countries, manganese has replaced organic lead as an additive in petrol. This will help in increasing concentrations of manganese in the environment and in foodstuffs in future. Manganese is used in steel and other alloys. It is also found in the manufacturing of glass to bleach the colour of any iron present (Saric, 1986). It is also found in pigments, glazes and other products.

Effect of manganese is mostly common in workers exposed in high levels and this involves its effects on the nervous system. These effects include behavioural changes and other nervous system effects which include movements that may become slow and clumsy. This combination of symptoms when sufficiently severe is referred to as “manganism” (ATSDR, 2008). Nervous system and reproductive effects have been observed in animals after high doses of manganese (ATSDR, 2008).

2.4.4 Cadmium (Cd)

Cadmium is a natural element in the earth’s crust. It is usually found as a mineral combined with other element such as oxygen (Cadmium oxide), chlorine (Cadmium chloride), or sulfur (Cadmium sulfate, cadmium sulfide). Cadmium occurs in the surface of the earth in all soils and rocks, including coal, (ATSDR, 2008).

Routes of exposure of cadmium is found when cadmium is emitted to soil, water, and air by non-ferrous metal mining and refining, manufacture and application of phosphate fertilizers, fossil fuel combustion, and waste incineration and disposal (ATSDR 2008). Cadmium (as oxide, chloride, and sulfate) will exist in air as particles or vapour. It can be transported long distance in the atmosphere where it will be deposited (wet or dry) onto soils and water surfaces. Highest risk of exposure is from work place which involves heating cadmium containing materials such as smelting and electroplating. The major route of exposure is through inhalation of dust and fumes or incidental ingestion from contaminated hands, food, or cigarettes (ATSDR, 2008).

Toxic effect of cadmium include:

- Damage of the lungs and even death when breathing air with high level of cadmium.
- Damage to the lungs and nasal cavity have been observed in animals exposed to cadmium
- Exposure to lower levels of cadmium for a long time can also cause bones to become fragile and break easily.
- Eating lower levels of cadmium over a long period of time can lead to a build-up of cadmium in the kidneys and this can cause kidney damage.
- Lung cancer has been found in some studies of workers exposed to cadmium in the air and studies of rats that breathed in cadmium.

The U.S. Department of Health and Human Service (DHHS) has determined that cadmium and cadmium compounds are known human carcinogens. The International Agency for Research on Cancer (IARC) has determined that cadmium is carcinogenic to humans. The Environmental Protection Agency (EPA) determined that cadmium is a human carcinogen (ATSDR, 2008).

2.4.5 Chromium (Cr)

Chromium is a naturally occurring element found in rocks, animals, plants, and soil. It can exist in several different forms. The most common forms are chromium (III) and chromium (VI). These forms of chromium are used for chrome plating, dyes and pigments, leather tanning and wood preserving.

Exposure to chromium occurs from ingesting contaminated food or drinking water or breathing contaminated workplace air. Chromium (VI) at high levels can damage the nose and cause cancer (ATSDR, 2008). Chromium (III) is an essential nutrient that helps the body use sugar, protein and fat.

Toxic effect of chromium (VI) can cause irritation to the lining of the nose, nose ulcers, runny nose, and breathing problems, such as asthma, cough, shortness of breath or wheezing.

- Sperm damage and damage to the male reproductive system have also been reported in laboratory animals exposed to chromium (VI).
- Skin contact with chromium (VI) compounds can cause skin ulcers.
- The Department of Health and Human Services (DHHS), the International Agency for Research on Cancer (IARC), and the EPA have determined that chromium (VI) compounds are known human carcinogens (ATSDR, 2008).

2.4.6 Iron

Iron is the fourth most abundant element (5%) in the earth's crust (Beliles, 1994). Iron is used for production of steel. The principal compounds of iron are ferrous, Fe (II) and Ferric, Fe (III) (Beliles, 1994). Under normal conditions the body contains about 4g of iron (Beliles, 1994).

Most of the iron in the earth crust is found combined with oxygen as iron oxide minerals such as hematite and mangnetite.

Exposure to iron occurs through its various oxide forms which are used as paint pigments (Beliles, 1994) of which some are permitted as direct food colours. The soluble salts variously used as pigments in food contact materials (Beliles, 1994). Iron contamination may also be originated from food processing equipment, containers and other utensils used for foodstuff. The iron leaching to canned food stuffs depends on storage time of the food product (Codex, 1995).

Toxic effect of iron can lead to damage DNA, proteins, lipids and other cellular components. It also lead to damage the cells in the heart, liver and even death (ATSDR, 2008). Ingestion of soluble iron salts by children in doses exceeding 0.5g of iron can give rise to severe lesions in the gastrointestinal tract, followed by metabolic acidosis, shock and toxic hepatitis (Elinder, 1986).

2.5 Heavy Metals in Food Crops

It has been reported that sewage, industrial effluents and municipal waste water contain appreciable amounts of major essential plants nutrients and therefore the futility level of soil are improved considerably under sewage irrigation of farmlands (Rajesh et al., 2004). However, studies on the water vasai creek, Maharashtra, revealed that the presences of toxic heavy metals like Pb and Hg reduce soil fertility and agricultural output (Lokhande and Kelkar, 1999). Treated sewage water also contain variable amounts of heavy metals such as Pb, Ni, Cd, Hg, Zn and Cr (Rajesh et al., 2004) which have the potential to contaminate crops growing under such irrigation.

It was reported by CCFAC (1995), that lead in the soil is only poorly taken up by plant roots and is not transported away from the roots to the rest of the plant crop. Therefore, lead levels in the plant are to a large extent governed by air – borne lead contamination which makes leaves and leaf vegetables most vulnerable to the air – borne deposition, but also cereal grains have been shown to absorb substantial amounts of lead via the air. The main sources of lead intake are food stuffs like vegetables, cereals and cereal products, fruits and fruit juices as well as wine, beverages and drinking water (Codex, 1995).

2.6 Effect Of Heavy Metals On Plants and Human Health

The effects of heavy metals on plant and human health are summarized in the table below, prepared by Ghesquiere (1999).

Table 2.2: Heavy Metals and their Effects on the Plants and Human Health

Element	Sources	Agronomic effects	Effect on health
Pb	Lead-acid batteries solder, alloys	Decrease respiration of soil organisms and inhabit plant cell growth at very high concentrations	Accumulate in skeleton, harmful for children and pregnant women
Cu	Plumbing, animal wastes, pesticides, earth's crust	Toxic to a number of plans at 0.1 to 1.0mg/l in nutrient solution	Liver cirrhosis, food main source of intake, uncertain, toxicity in humans
Mn	Industrial effluents	Toxic to a number of crops at a few tenths to a few ml/l	No convincing data of human toxicity
Cd	Washing powders as an impurity in phosphates, impurity in Zinc steel, industry, paint, plastic	Toxic to beans, beets and turnips at concentrations as low as 0.1mg/l in nutrient solutions. Risk of accumulation in plants and soils	Very harmful cumulative poison. Food chain source of intake.
Cr	Leather tanneries (about 40mg/l in surface discharge	Not generally recognized as essential growth element. Lack of knowledge on its toxicity to plants	Carcinogenic dermatitis, painful chrome ulcers. Food main source of intake
Fe	Plumbing, earth crust	Essential element of nutrition, not toxic to plants	Not a major hazard to health
Zn	Plumbing, animal wastes, pesticides	Toxic to many plants at widely varying concentration	Not a major hazard to health
Ni	Industrial effluents	Toxic to a number of plans at 0.5 to 1.0mg/l	Carcinogenic, lack of data on carcinogenicity by the oral route
As	Industrial effluents, an impurity in some detergents	Toxicity to plants varies widely	Very harmful, cumulative poison, carcinogenic, skin disease

2.7 Theory Of Atomic Absorption Spectrophotometry

Atomic Absorption Spectrophotometry (AAS) was first proposed and developed by Walsh (1955). Atomic absorption spectra are formed by the absorption of radiation of certain wavelength by atoms whose electrons are in the ground state. On absorbing this energy the atom become excited. One extent of absorption is dependent on the number of atoms in the ground state in the path of radiation beam at any one time and can thus be used as quantitative method of determining this number (Allen et al., 1989).

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

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

Atomic absorption spectrophotometry came as a necessary option to fill up the gap created by the use of flame photometry in evaluation of some metals. Atomic absorption spectroscopy is a much more accurate and sensitive method of analyzing wide range of metals (Onwuka, 2005). In the process, an atomized sample solution containing the metal is passed through the equipment, the atoms of the metals absorbs energy when the radiation contains wavelengths that can cause the electrons of the metals to undergo transition into higher energy levels. The atomized sample

absorbs the radiation, the intensity of the radiation is reduced and the reduction in intensity of the radiation is proportional to the concentration of the metal present.

In practice, the sample to be analyzed is first taken into solution using the metal ash which is subsequently atomized in a hot flame generated by a highly combustive gas mixture such as air/acetylene at temperature of 2300 ^{o} C. This breaks the metal compounds in the food sample into free metal atoms or free radicals. A radiation emanating from a cathode lamp made to pass through the free atoms will be absorbed by the atoms and the extent of this absorption is the measure of the concentration of the metal in solution. Each metal has a specific lamp, however multi-element lamps such as those for iron, zinc, calcium and magnesium is also available.

The optical system is set up with a hallow cathode lamp for the element of interest (Analyte) with appropriate slit and wavelengths selected for this element. A solution of a known concentration of the analyte (standard) is aspirated and the absorbance reading noted. An unknown sample is aspirated, the absorbance reading is ratioed to the standard and a sample concentration is interpolated from the intensity of the reading (Onwuka, 2005).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals And Reagents

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

Other reagent used include

Concentrated trioxonitrate (V) acid (HNO_3) 70% Anala R

Perchloric acid ($HClO_4$) 60%

Concentrated hycrochloric acid (HCl) 36%, AnalaR

Lead (II)nitrate ($Pb(NO_3)_2$)

Copper(II)nitrate trihydrate ($Cu(NO_3)_2$-$3H_2O$)

Manganese nitrate tetrahydrate ($Mn(NO_3)_2$-$4H_2O$)

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2$-$4H_2O$)

Chromium(III)nitrate nonahydrate ($Cr(NO_3)_3$-$9H_2O$)

Iron(III)nitrate nonahydrate ($Fe(NO_3)_3$-$9H_2O$)

3.1.2 Equipment And Glassware

Analytical balance

Oven Bs, model OV-330 Gallenkamp, England

Hot plate, Model HL054, Gallenkamp, England

Mortar and pestle

Dessicator

Volumetric Flask 50, 100, 250ml

Beakers 100, 150 and 250ml

Measuring cylinder: 10, 50 and 100ml

Filter paper: Whatman 48

Crucible

Conical flask : 100ml

Fume cupboard

Polyethylene bags

Polyethylene sample bottles

3.1.3 Instrumentation

Measurements were made using atomic absorption spectrophotometer (AAS), a SHIMAZO Model AA6800 with Autosampler ASC-6100 with the following conditions:

For lead (Pb)

Lamp :- lead hollow cathode

Lamp current low:- 8mA

Lamp current high:- 300mA

Wavelength:- 283.3nm

Slit with:- 1.0nm

Fuel Gas flow rate:-2.0L/mm

Flame type:- Air-acetylene

For copper (Cu)

Lamp:- copper hollow cathode

Lamp current low:- 10mA

Lamp current high:- 500mA

Wavelength:- 324.8nm

Slit with:- 0.5nm

Fuel Gas flow rate:-1.8L/min

Flame type:- Air-acetylene

For Manganese

Lamp: manganese hollow cathode

Lamp current low:- 10mA

Lamp current high:- 600mA

Wavelength:- 279.5 nm

Slit with:- 0.2nm

Fuel Gas flow rate:-2.0 L/min

Flame type:- Air-acetylene

For cadmium

Lamp: cadmium hollow cathode

Lamp current low:- 8mA

Lamp current high:- 100mA

Wavelength:- 228.8nm

Slit with:- 1.0nm

Fuel Gas flow rate:-1.8L/min

Flame type:- Air-acetylene

For chromium

Lamp; chromium hollow cathode

Lamp current low:- 10mA

Lamp current high:- 600mA

Wavelength:- 357.9 nm

Slit with:- 0.5nm

Fuel Gas flow rate:- 2.8 L/min

Flame type:- Air-acetylene

For iron

Lamp: iron hollow cathode

Lamp current low:- 12mA

Lamp current high:- 400mA

Wavelength:- 248.3 nm

Slit with:- 0.2nm

Fuel Gas flow rate:- 2.2 L/min

Flame type:- Air-acetylene

3.2 Method

3.2.1 Study area

The study area is in Zaria which is located in Kaduna state. Kaduna state is located in the north central part of northern Nigeria. It is bordered by Kano, Plateau, Nassarawa, FCT, Zamfara and Katsina state.

River Kubanni and Galma are located within the Sabon-Gari and Zaria local government areas of Kaduna State in Nigeria.

The Kubanni river basin, covering an area of about 130km^2 is drained by the River Kubanni. The river is seasonal, flowing only during the rains. It empties its waters into the Galma River (Ogunrambi, 1979). Most of the areas are at elevation of 670metres above sea level. It also forms part of the Galma River Basin, the river Galma joining the Kaduna River near Kaduna (Ismail, 1989).

3.2.2 Description of sampling site

There are five sampling site which are located along River Kubanni and some of its tributaries where urban agriculture is widely practiced and also another site for treated water (Tap water).

The sites were labeled A, B, C, D, E and F.

Site A: located at Kings Road, Chikaji, after NTC, Sabon-Gari. It is a tributary emptying domestic, commercial, industrial and agricultural field wastes from Chikaji area into River Galma.

Site B: located at near Sabon Gari Market, Sabon-Gari. It is another tributary of River Galma which collects effluents from Sabon-Gari main market, residential areas, ware houses and agricultural field wastes.

Site C: located at the new Kongo road bridge Sabon-Gari/Tudun Wada. It is along lower part of the River Kubanni by the bridge linking Sabon-Gari and Tudun Wada. It mainly collects wastes from domestic and agricultural fields.

Side D: located at Kwarin Dan-Goma, Tudun Wada. It serves as a sink for domestic sewage, commercial, mechanical workshop, agricultural and animal wastes.

Site E: this is where River Kubanni empties into River Galma. It is close to Old Jos Road Bridge. This point mainly receives industrial effluents, domestic and agricultural field wastes.

Site F: it is located at Angwan kaya. It is the waterworks at Angwan Kaya. This where the tap water was collected as part of the river is being used as a source of raw water before treatment.

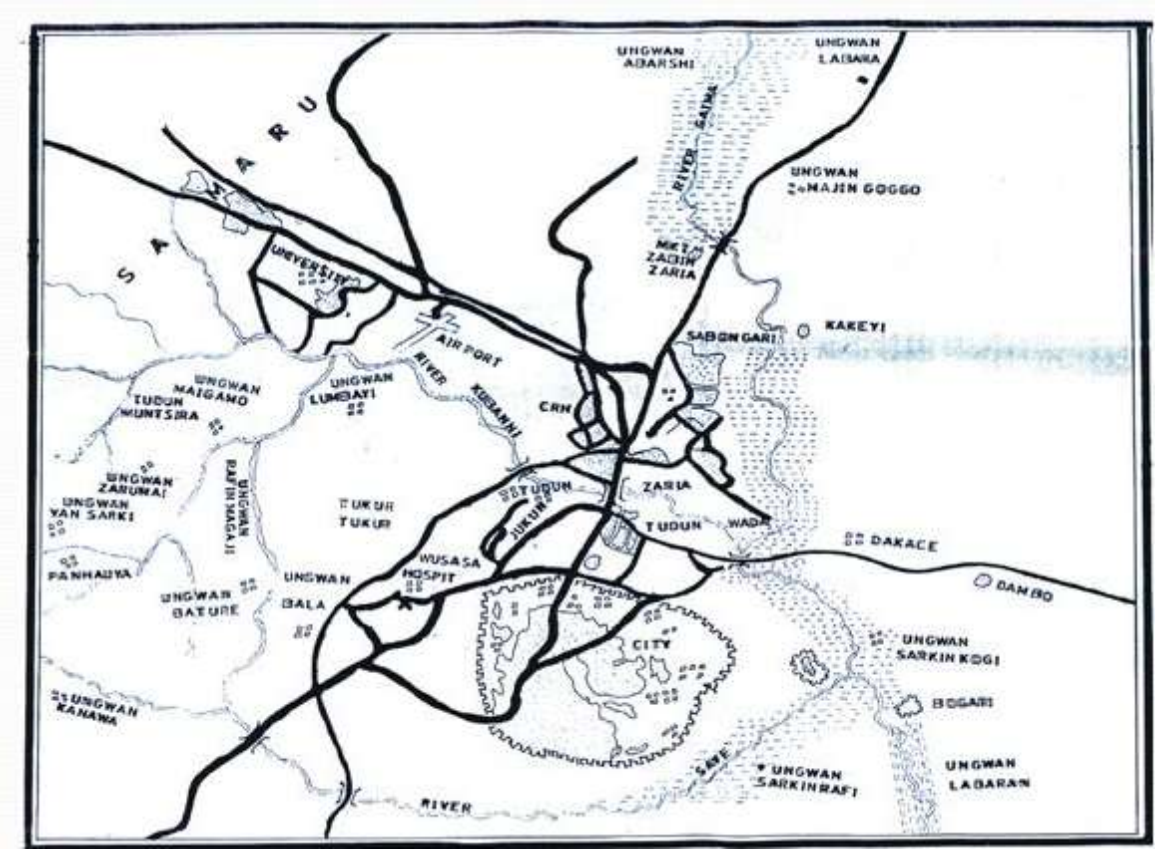


Fig 3.1 Map of Zaria and its environment

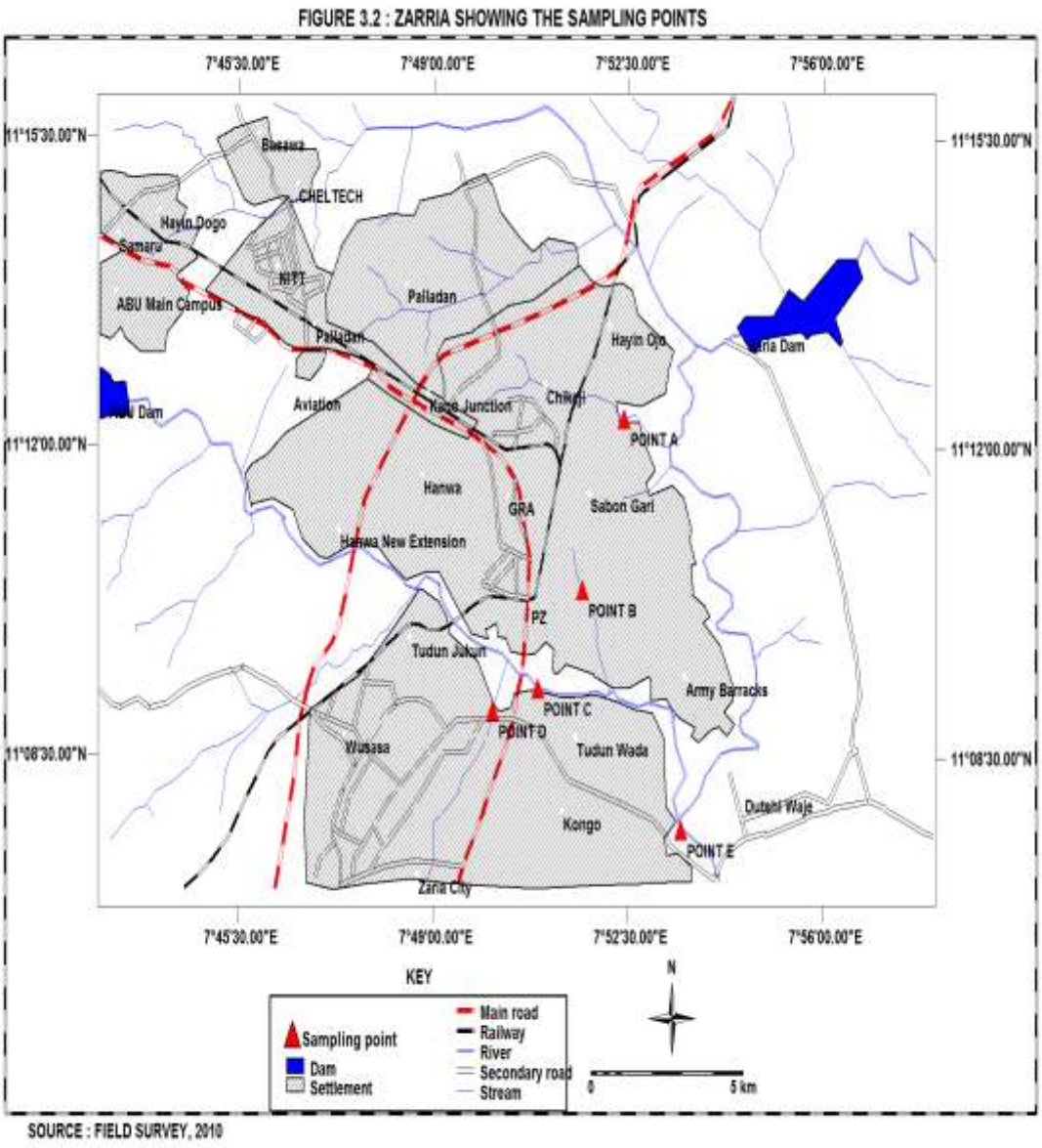


Fig 3.2. Zaria showing the sampling points

3.3 Sample collection

The study was carried out between August to October 2009 (wet season) and January to March 2010 (dry season). The application of standard randomized controlled trial sampling was also extended to this study to achieve an optional level of success in sample collection. At the collection site, the following parameters were recorded; name of sample, time and date of collection and place of collection.

3.3.1 Collection of raw water samples

Polyethylene bottles were used for collection of the samples. The containers were thoroughly washed with detergent, rinsed with water and then with distilled water before soaking in trioxonitrate (V) acid for 24 hours, containers were rinsed again with distilled water before being used for sampling.

Raw water samples were collected in the container from the banks of the Rivers where the water is used for irrigation at each of the demarcated sampling sites. The pH of the water samples were determined directly with a pH meter. The samples were then acidified with 2ml of concentrated HNO_3 to preserve the water; it was labeled and taken to the laboratory.

3.3.2 Collection of food crop samples

Food crop samples of maize (Zea mays); Spinach (*Spinacia oleracea*); Lettuce (*Lectuca sativa* L.); Bitterleaf (*Vernonia amygdalina*) were purchased directly from the farmers at the farmlands closest to the river banks at the demarcated site for sampling of raw water. The food crops were harvested freshly from different areas of the farm. The vegetable samples were placed in a brand new polyethylene bags, labeled and taken to the laboratory.

3.4 Pre-treatment and chemical analysis

3.4.1 Pre-treatment of water samples

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

Exactly 50 ml of the water samples was measured into 150ml beaker and 10ml of concentrated HNO_3 was added. The beaker with the content was placed on the hot plate and digested till brown fumes of HNO_3 escaped. Heating was continued till content have reduced to about 10ml volume. The content was then transferred into 100ml volumetric flask the volume was made up to the mark with distilled water. It was filtered with whatman 48 filter paper, and packed in to a 100ml sample bottles taken for analysis with Atomic Absorption Spectroscopy (AAS). The samples were analysed for Pb, Cu, Mn, Cd, Cr and Fe heavy metals using SHIMAZO AA 6800 Atomic Absorption Spectrophotometer (AAS) with Autosampler ASC – 6100 at NARICT Basawa, Zaria.

3.4.2 Pre-treatment of Food crop samples

The plant samples were thoroughly rinsed with tap water and then with distilled water to eliminate suspended particles. The edible parts were removed from all the samples and these were sliced and dried on a sheet of paper at room temperature to eliminate excess water. Each edible part of the sample was divided into two; one portion was freshly grounded before weighing out 1g for digestion for wet samples. The other portion were placed in a large crucible and were oven-dried at $60^{o}C$. The dried plants were grounded into fine particles using a clean

mortar and pestle. It was packed in a cleaned labeled polyethylene container with screw caps in preparation for digestion.

Procedures

The method described by AOAC (1984) was used:

1g of each sample was weighed into a pre-washed, oven dried and labeled 100ml beaker. 10 ml of concentrated trioxonitrate (V) acid was added into each beaker and allowed to soak thoroughly. 5ml of 60% $HClO_4$ was added and heated on a hot plate slowly at first between 70^{o}C to 80^{o}C, until frothing ceases. Heating was continued until HNO_3 evaporated. Then another 10ml of concentrated HNO_3 was added and heating continued until white fumes was observed. 10ml of conc. HCl was added. The digested samples were transferred into a 100ml volumetric flask and filtered with a Whatman 48 filter paper into 100ml sample bottle. The volume was made up to the mark with distilled water and taken for analysis with Atomic Absorption Spectrophotometer (AAS).

3.5 ANALYSIS OF SAMPLES

3.5.1 Preparation of Stock Solution

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

Lead: 1.60g lead (II) nitrate was accurately weighed and dissolved in deionised water and acidified with 0.5mol/L of HNO_3 and made up of 1 Litre with deionised water to obtain 1000mg/L

Copper: 3.80g Copper (II) nitrate trihydrate was weighed and dissolved in deionised water and acidified with 0.5mol/L of HNO_3 and made up of 1 litre with deionised water to obtain 1000mg/L

Manganese: 4.57g Manganese nitrate tetrahydrate was weighed and dissolved in deionised water and acidified with 0.5mol/L of HNO_3 and made up to 1 litre with deionised water to obtain 1000mg/L

Cadmium: 2.74g cadmium nitrate tetrahydrate was weighed and dissolved in deionised water and acidified with 0.5 mol/L of HNO_3 and vol. made up to 1litre to obtain 1000mg/L

Chromium: 7.70g chromium (III) nitrate nonahyddrate was weighed and dissolved in deionised water and acidified with 0.5mol/L of HNO_3 and vol made up of 1 litre with deionised water to obtain 1000mg/L.

Iron: 7.23g Iron(III) nitrate nonahydratae was weighed and dissolved in deionised water and acidified with 0.5mol/L of HNO_3 and vol. made up to 1litre with deionised water to obtain 1000mg/L.

3.5.2 Preparation of Calibration Curve

A calibration curve of absorbance against concentration for each metal ion was prepared as shown in Appendix I for Pb, Cu, Mn, Cd, Cr, Fe respectively, which yielded a good linearity. This implies that the instrument responded very well to the standard analyte of interest and therefore would respond to analyte in the samples. The calibration curves were used for the determination of metal concentrations in samples.

The actual concentration of the metal in plant sample was determined as follows:

$$\text{Amount of metal in mg/kg} = \frac{(\text{Volume used (ml)}/1000)\text{litre} \times \text{AAS reading (mg/ml)}}{\text{Weight of sample digested (kg)}}$$

3.5.3 Transfer Factor

Transfer Factor (TF) was calculated for each metal according to the following formular

$$\text{TF} = \frac{\text{Concentration of metal in plant}}{\text{Concentration of metal in water}}$$

3.6 Statistical Analysis

All data was recorded as mean ± SEM and was subjected to statistical analysis using Analysis of Variance and Pearson Correlation coefficient where applicable.

A $p<0.05$ was considered statistically significant. The statistical package for social science (SPSS) version 17 was used for all calculations and statistical analysis.

CHAPTER FOUR

RESULTS

4.1 Heavy metals in Crops

4.1.1 Levels of Pb in crops

The results of the levels of Pb ($mgkg^{-1}$) dry weight and wet weight in different crops for wet and dry seasons are presented in Figs. 4.1a and 4.1b. For maize, concentration was generally high in wet season (Site B, 97.03$mgkg^{-1}$) compare to dry season, with few exception of Sites A and C. Spinach was highest in Site A (97.71$mgkg^{-1}$) in wet season, generally high concentrations were found in wet season. The highest concentration in lettuce and bitter leaf were found in Site E (123.26$mgkg^{-1}$) and Site B (67.69$mgkg^{-1}$) respectively. Also, similar to spinach high concentrations were obtained in wet season as compared to dry seasons.

Analysis of variance (ANOVA) showed significant variation ($p < 0.05$) across the sites in all samples with exception of maize and spinach. Analysis of variation between wet and dry season revealed no significant ($p < 0.05$) for maize, spinach and lettuce across the sites with exception of bitter leaf. A correlation matrix for heavy metals in the crops across the seasons were calculated to see if some metals were interrelated with each other and the results are presented on Tables 4.1 and Table 4.2. Positive correlation were obtained between crops in both seasons, though significant ($p < 0.05$) correlation were obtained between lettuce and maize in dry season.

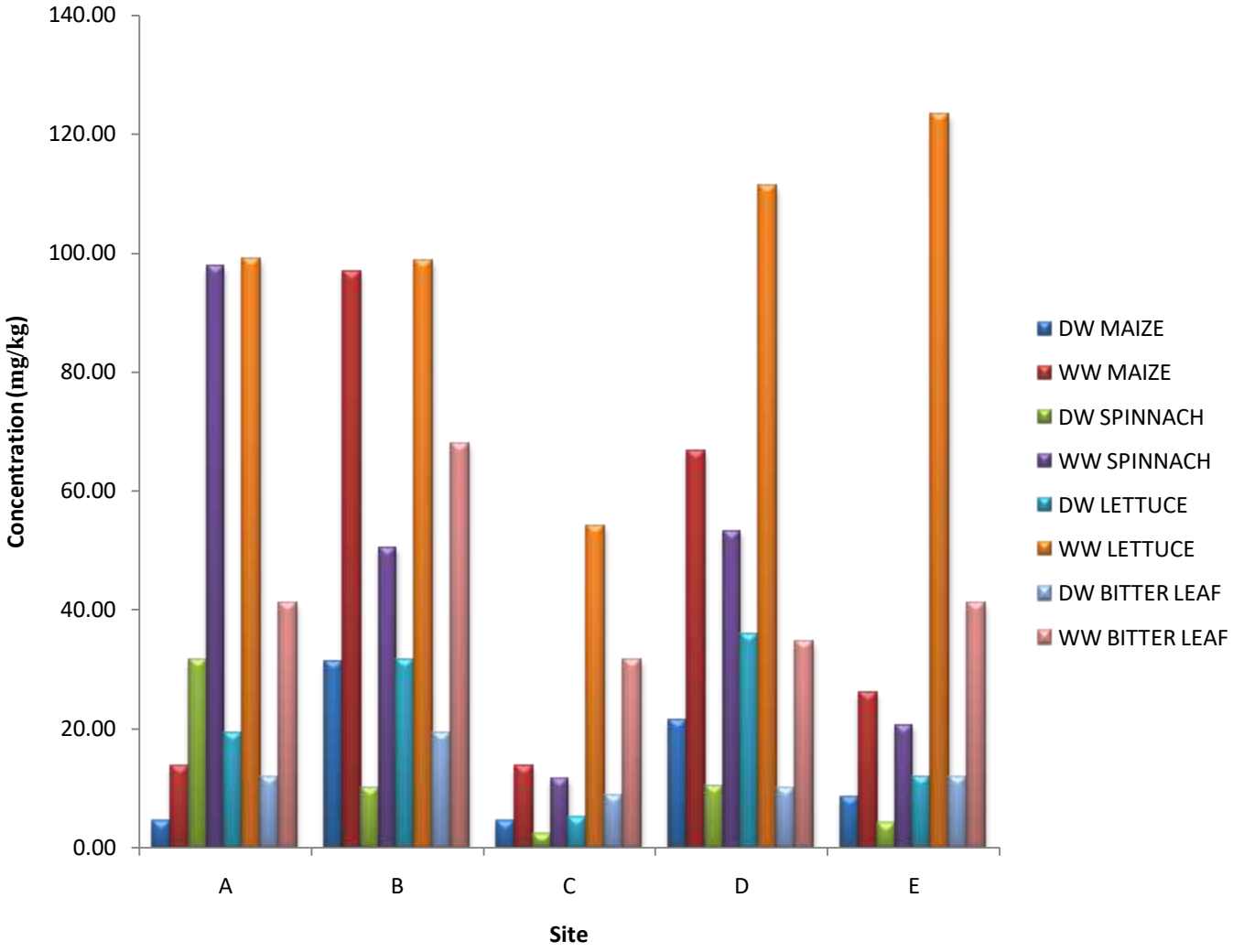


Fig. 4.1a Concentration of Pb in Irrigated Crops Across the Sites (Wet Season)

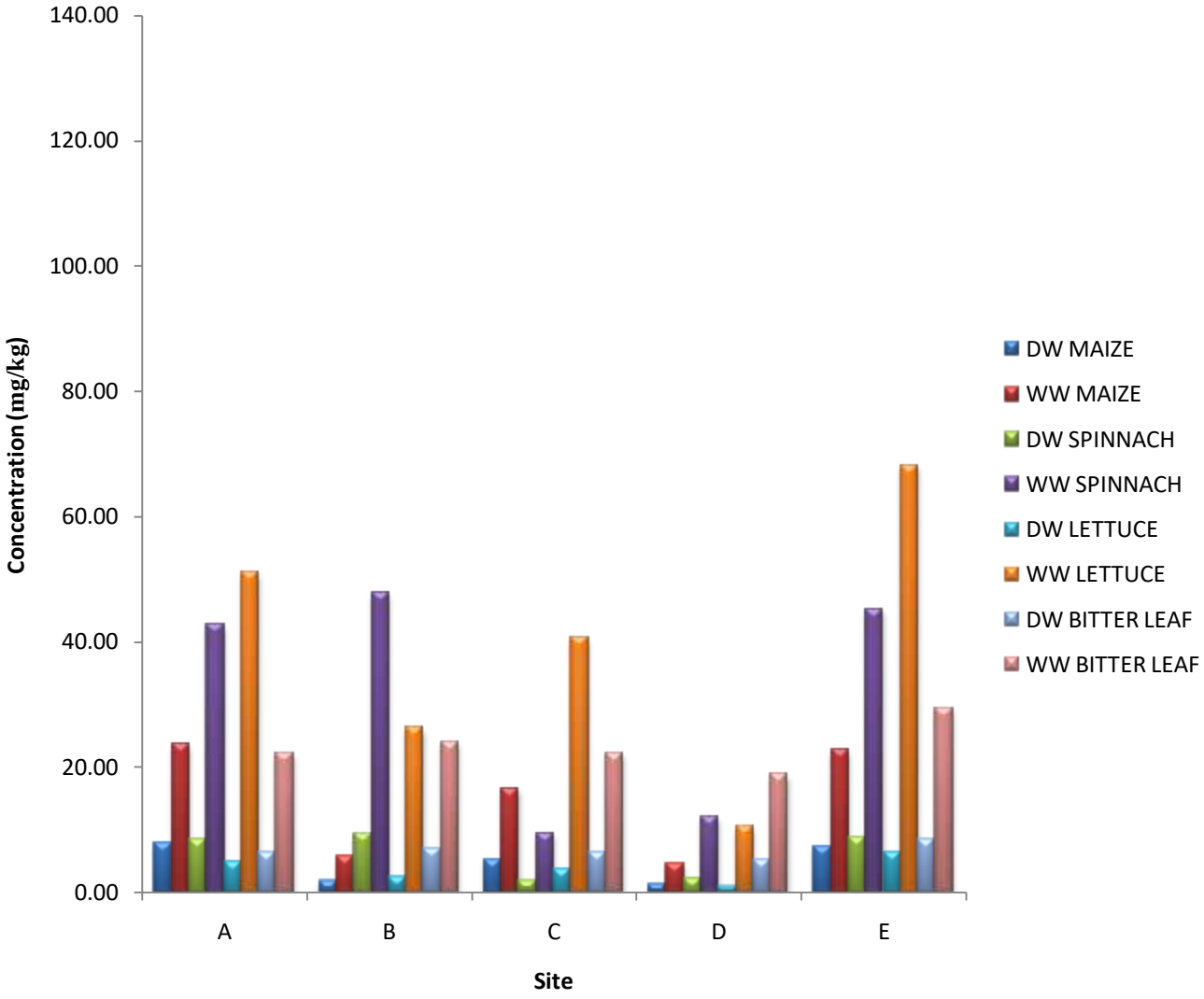


Fig. 4.1b Concentration of Pb in Irrigated Crops Across the Sites (Dry Season)

Table 4.1 Correlation matrix of Pb between different studied samples in wet season

Parameters	Pb M	Pb S	Pb L	Pb BL
Pb M	1.000			
Pb S	0.064	1.000		
Pb L	0.304	0.291	1.000	
Pb BL	0.737	0.202	0.239	1.000

M – Maize

S – Spinnach

L – Lettuce

BL – Bitter Leaf

W - Water

Table 4.2 Correlation matrix of Pb between different studied samples in dry season

	Pb M	Pb S	Pb L	Pb BL
Pb M	1.000			
Pb S	0.317	1.000		
Pb L	0.928*	0.503	1.000	
Pb BL	0.552	0.663	0.823	1.000

** Correlation is significant at the level 0.05 level.*

4.1.2 Levels of Cu in crops

The mean concentration of Cu ($mgkg^{-1}$) dry weight and wet weight in different crops for wet and dry seasons is presented in Figs. 4.2a and 4.2b. The amount of Cu in maize ranged between 6.30 (Site B) – 27.31$mgkg^{-1}$ (Site C) and 9.05 (Site A) – 16.37$mgkg^{-1}$ (Site C) in wet and dry season respectively.

Spinach ranged between 4.59 (Site C) – 40.39$mgkg^{-1}$ (Site A) and 28.40 (Site E) – 49.99$mgkg^{-1}$ (Site B) in both season respectively. Lettuce had the highest concentrations of 116.96 (Site C) and 106.08$mgkg^{-1}$ (Site B) in wet and dry season respectively. The range of 24.52 (Site C) - 38.21$mgkg^{-1}$ (Site B) and 25.87 (Site C) – 40.88$mgkg^{-1}$ (Site A) in wet and dry season respectively for Bitter leaf. Analysis of variation result showed that there were significant differences ($p < 0.05$) across the sites in all samples and between wet and dry samples across the sites. No significant variation ($p > 0.05$) was observed between wet and dry seasons for maize, spinach and lettuce across all sites with exception of bitter leaf. A relationship between Cu in the crops were analysed and shown on Table 4.4 and 4.5. Negative correlation were obtained CuM: CuS and CuBL in both season, CuS: CuL, CuL: CuBL and CuM: CuL, CuB: CuBL in wet and dry season respectively. However, others showed positive correlation.

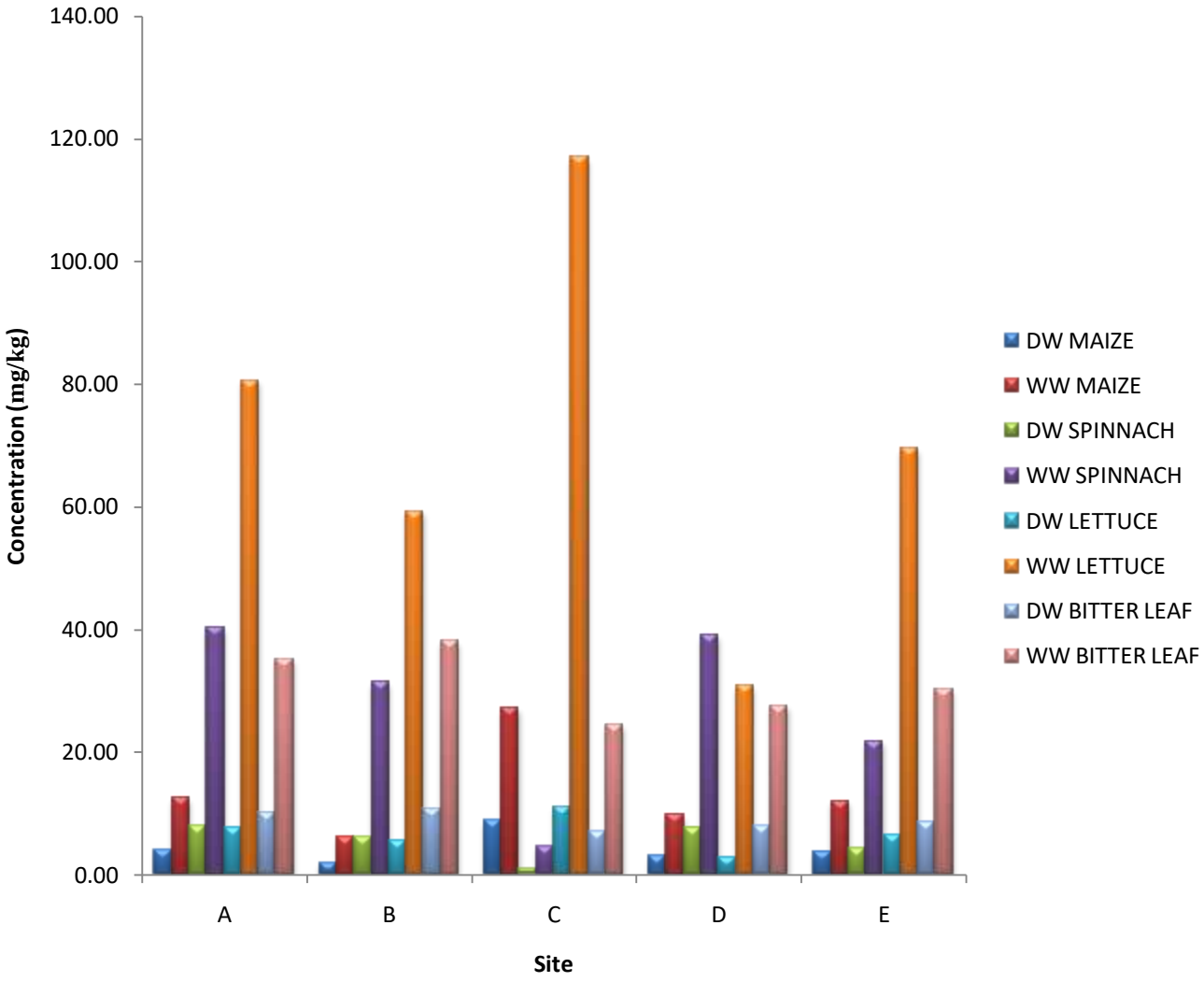


Fig. 4.2a Concentration of Cu in Irrigated Crops Across the Sites (Wet Season)

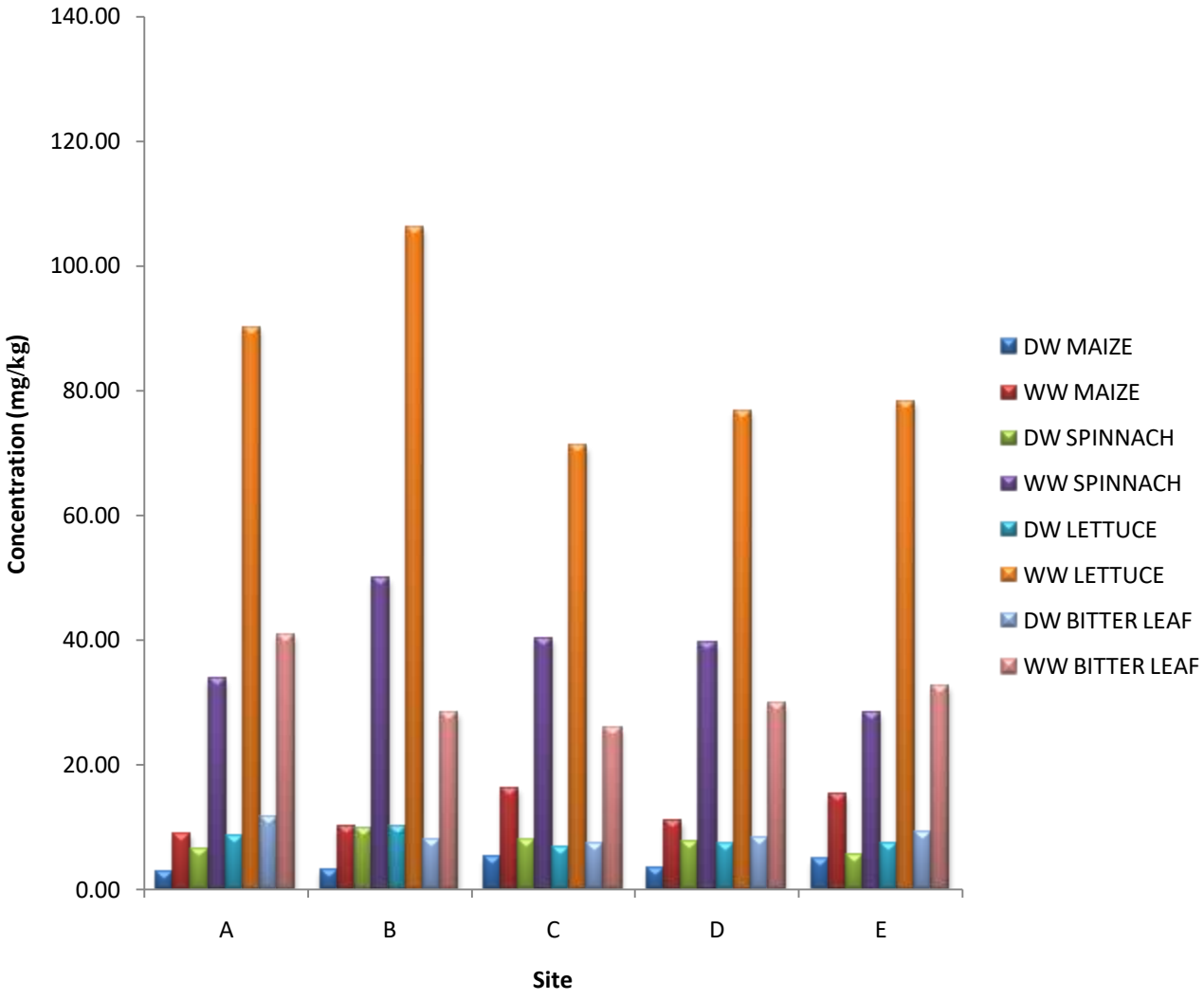


Fig.4.2b Concentration of Cu in Irrigated Crops Across the Sites (Dry Season)

Table 4.3 Correlation matrix of Cu between different studied samples in wet season

	Cu M	Cu S	Cu L	Cu BL
Cu M	1.000			
Cu S	-0.825	1.000		
Cu L	0.852	-0.772	1.000	
Cu BL	-0.734	0.599	-0.293	1.000

Table 4.4 Correlation matrix of Cu between different studied samples in dry season

	Cu M	Cu S	Cu L	Cu BL
Cu M	1.000			
Cu S	-0.323	1.000		
Cu L	-0.712	0.558	1.000	
Cu BL	-0.547	-0.550	0.216	1.000

4.1.3 Levels of Mn in crops

Mean concentration of Mn ($mgkg^{-1}$) dry weight and wet weight in different crops for wet and dry seasons is presented in Figs. 4.3a and 4.3b. The amount of Mn in maize ranged between 2.41 (Site A) – 13.33$mgkg^{-1}$ (Site C and D) and 11.29 (Site B) – 28.98$mgkg^{-1}$ (Site D) in wet and dry season respectively. Spinach ranged between 13.98 (Site A) – 58.58$mgkg^{-1}$ (Site B) and 53.56 (Site A) – 469.30$mgkg^{-1}$ (Site E) in both season respectively. Lettuce had the highest concentrations of 130.00 (Site C) and 222.94$mgkg^{-1}$ (Site C) in wet and dry season respectively. The range of 28.29 (Site E) – 100.25$mgkg^{-1}$ (Site B) and 70.19 (Site A) – 304.38$mgkg^{-1}$ (Site E) in wet and dry season respectively for bitter leaf. Higher concentration was obtained in leaf crops as compare to maize in both seasons.

Analysis of variance showed significant ($p < 0.05$) variation between wet and dry season samples across the sites. Also, significant variations ($p < 0.05$) were observed between wet and dry season for maize and spinach across all sites with exception of lettuce and bitter leaf. Correlation analysis of Mn between crops as shown on Table 4.5 and 4.6 revealed negative correlation between: MnM: MnS and MnBL (though significant), MnL: MnBL, and MnM: MnL and MnBL, MnS:MnL in wet and dry season respectively. Positive correlation was found among other crops.

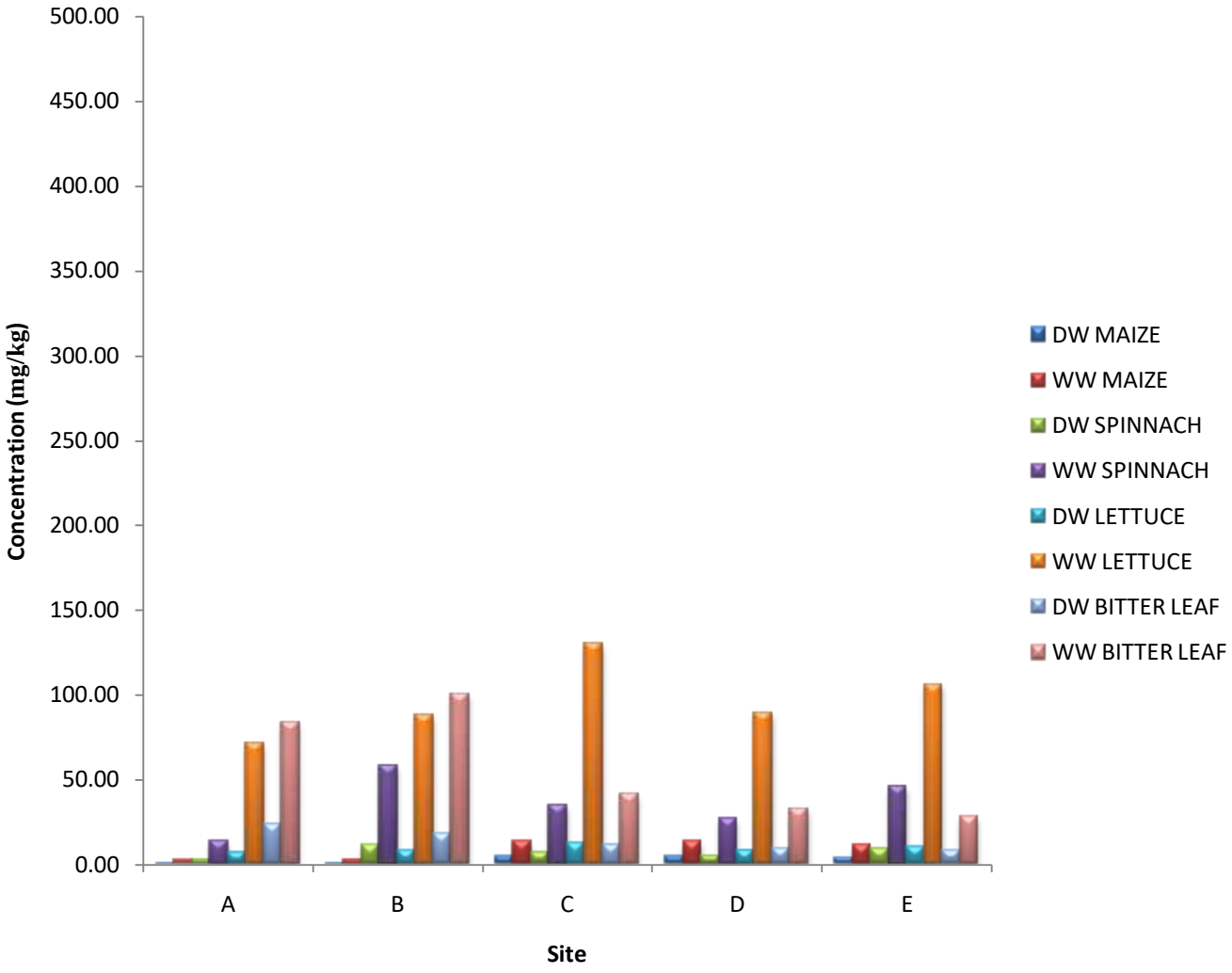


Fig. 4.3a Concentration of Mn in Irrigated Crops Across the Sites (Wet Season)

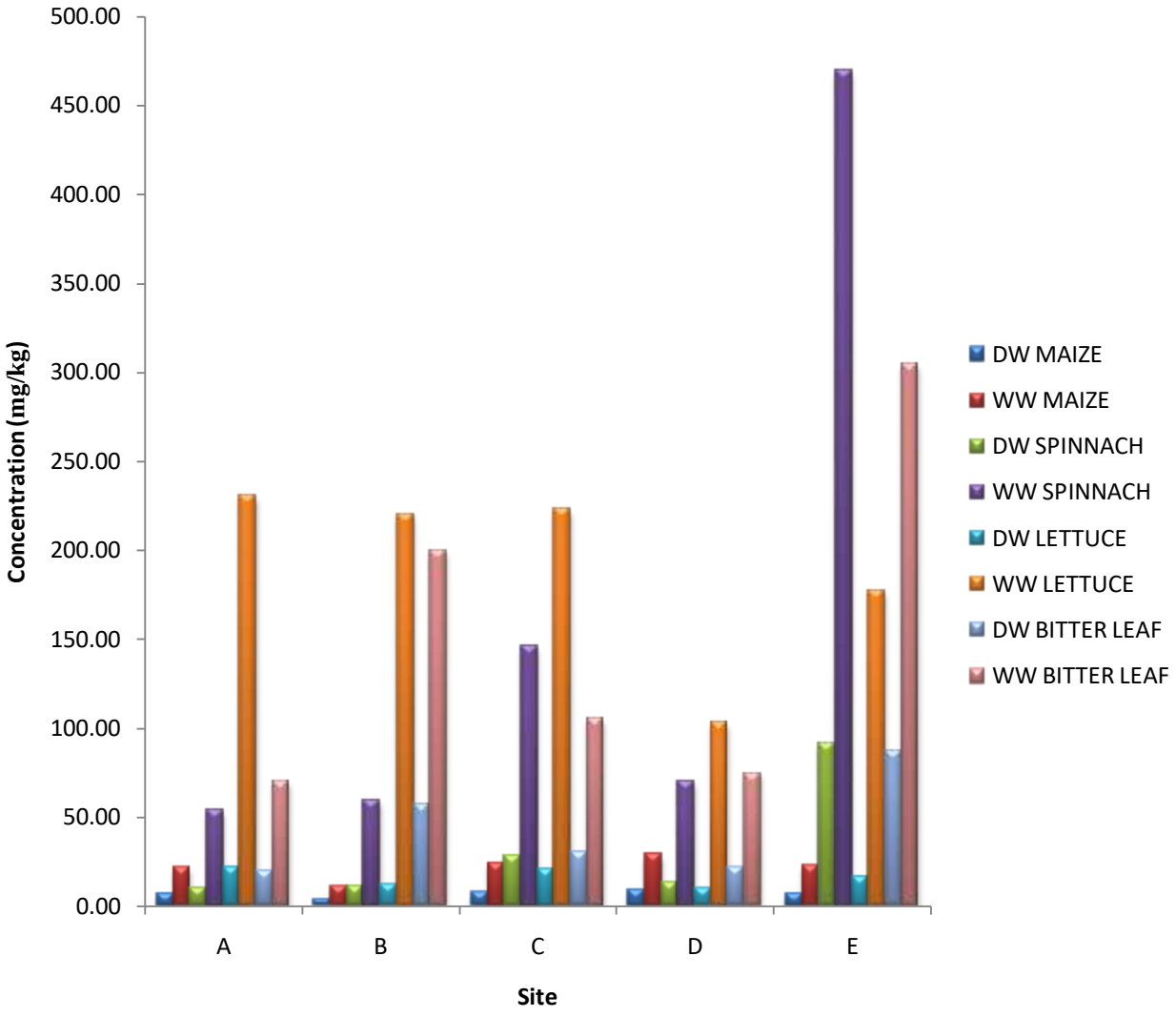


Fig. 4.3b Concentration of Mn in Irrigated Crops Across the Sites (Dry Season)

Table 4.5 Correlation matrix of Mn between different studied samples in wet season

	Mn M	Mn S	Mn L	Mn BL
Mn M	1.000			
Mn S	-0.040	1.000		
Mn L	0.726	0.308	1.000	
Mn BL	-0.940*	0.155	-0.588	1.000

** Correlation is significant at the level 0.05 level.*

Table 4.6 Correlation matrix of Mn between different studied samples in dry season

	Mn M	Mn S	Mn L	Mn BL
Mn M	1.000			
Mn S	0.139	1.000		
Mn L	-0.633	-0.109	1.000	
Mn BL	-0.399	0.824	0.061	1.000

4.1.4 Levels of Cd in crops

Mean concentration of Cd ($mgkg^{-1}$) dry weight and wet weight in different crops for wet and dry seasons is presented in Figs. 4.4a and 4.4b. The amount of Cd in maize ranged between 0.85 (Site D) – 3.13$mgkg^{-1}$ (Site E) and 0.64 (Site A) – 2.15$mgkg^{-1}$ (Site D) in wet and dry season respectively. Spinach ranged between 1.59 (Site A) – 4.86$mgkg^{-1}$ (Site E) and 0.15 (Site B) – 4.96$mgkg^{-1}$ (Site C) in both season respectively. Cadmium concentration in lettuce ranged between 3.90 (Site B) and 12.29 (Site A) in wet season specimen and between 0.63 (Site A) and 9.58$mgkg^{-1}$ (Site C) in dry season. The range was 1.12 (Site E) – 2.59$mgkg^{-1}$ (Site D) and 0.50 (Site A) – 3.30$mgkg^{-1}$ (Site C) in wet and dry season respectively for bitter leaf. Analysis of variation across the sites in all samples revealed significant variation ($p < 0.05$). Significant variation ($p < 0.05$) was also found between wet and dry season samples across the sites for both seasons with exception of spinach in dry season. No significant variation ($p < 0.05$) was observed between wet and dry seasons for all samples. Correlation analysis as shown on Tables 4.7 and 4.8, revealed negative correlation for crops in wet season. While positive correlations were obtain for Cd between crops in dry season though significant between CdS: CdL.

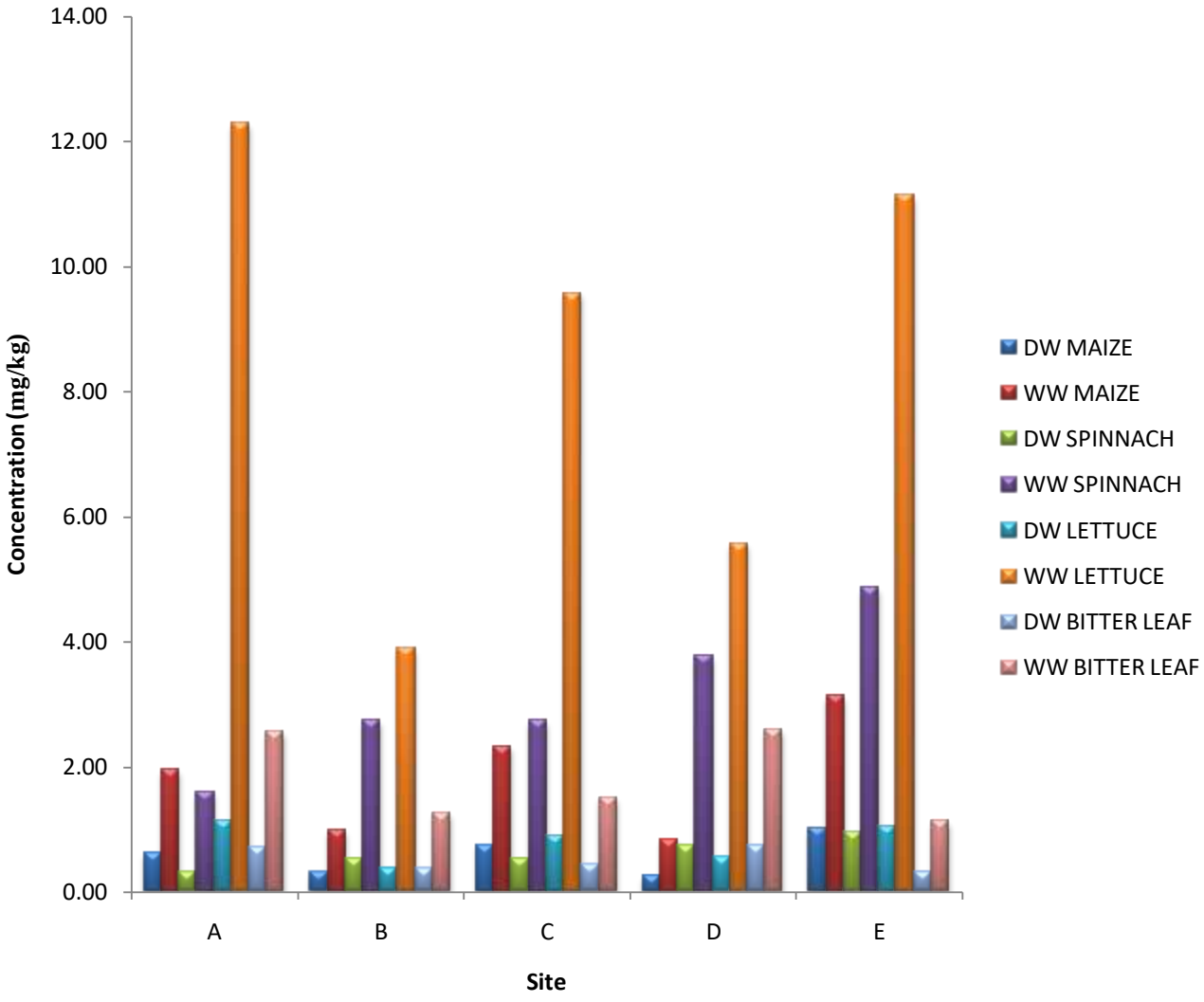


Fig. 4.4a Concentration of Cd in Irrigated Crops Across the Sites (Wet Season)

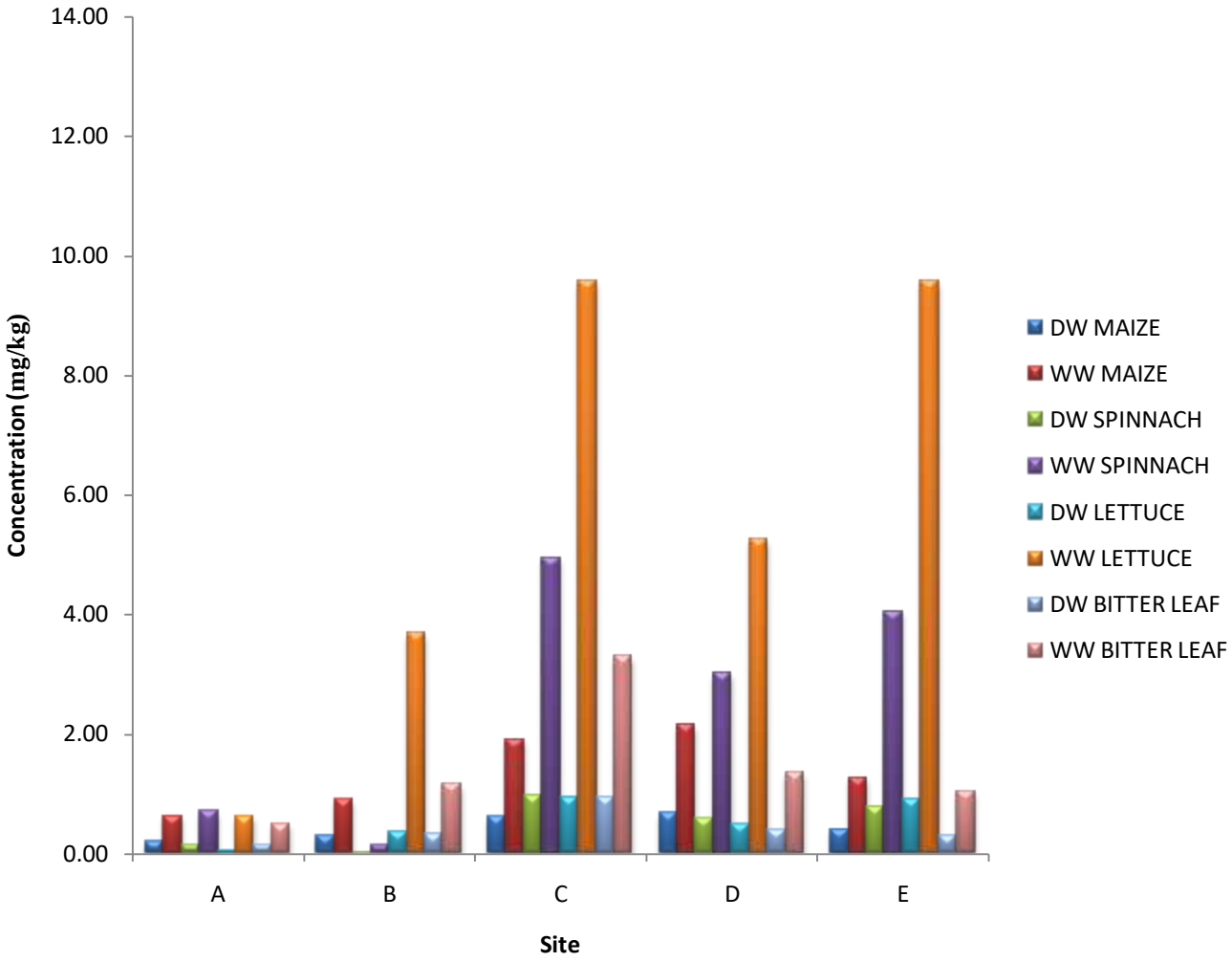


Fig.4. 4b Concentration of Cd in Irrigated Crops Across the Sites (Dry Season)

Table 4.7 Correlation matrix of Cd between different studied samples in wet season

	Cd M	Cd S	Cd L	Cd BL
Cd M	1.000			
Cd S	0.334	1.000		
Cd L	0.812	-0.102	1.000	
Cd BL	-0.459	-0.431	0.095	1.000

Table 4.8 Correlation matrix of Cd between different studied samples in dry season

	Cd M	Cd S	Cd L	Cd BL
Cd M	1.000			
Cd S	0.747	1.000		
Cd L	0.608	0.900*	1.000	
Cd BL	0.656	0.702	0.666	1.000

**Correlation is significant at the 0.05 level.*

4.1.5 Levels of Cr in crops

The concentrations of Cr in different crop samples in wet and dry season are presented in Fig. 4.5a and 4.5b respectively. The concentrations of Cr in crops ranged from 41.91 (Site B) – 123.16mgkg^{-1} (Site A) and 10.91 (Site E) – 28.08 (Site D) in maize, 8.98 (Site C) – 122.71mgkg^{-1} (Site D) and 6.43 (Site D) – 46.22mgkg^{-1} (Site A) in spinach, 80.64 (Site A) – 271.11mgkg^{-1} (Site E) and 58.69 (Site B) – 134.76mgkg^{-1} (Site A) in lettuce, and 67.62 (Site A) – 188.71 (Site E) and 1.73 (Site B) – 47.56 (Site E) in bitter leaf for wet and dry season respectively.

Analysis of variance showed significant variation ($p < 0.05$) across the sites in all samples, between wet and dry seasons across all the sites, and between wet and dry seasons for maize, spinach and lettuce across all sites with exception of bitter leaf. Higher concentrations of this metal are found across the sites in wet season with exception of lettuce.

Interrelationship of Cr among different crops as shown on Tables 4.9 and 4.10 revealed negative correlation between CrM: CrS, CrL and CrBL, and CrS: CrL in dry and wet season although positive correlation were found between CrM: CrS and CrS: CrL in wet season.

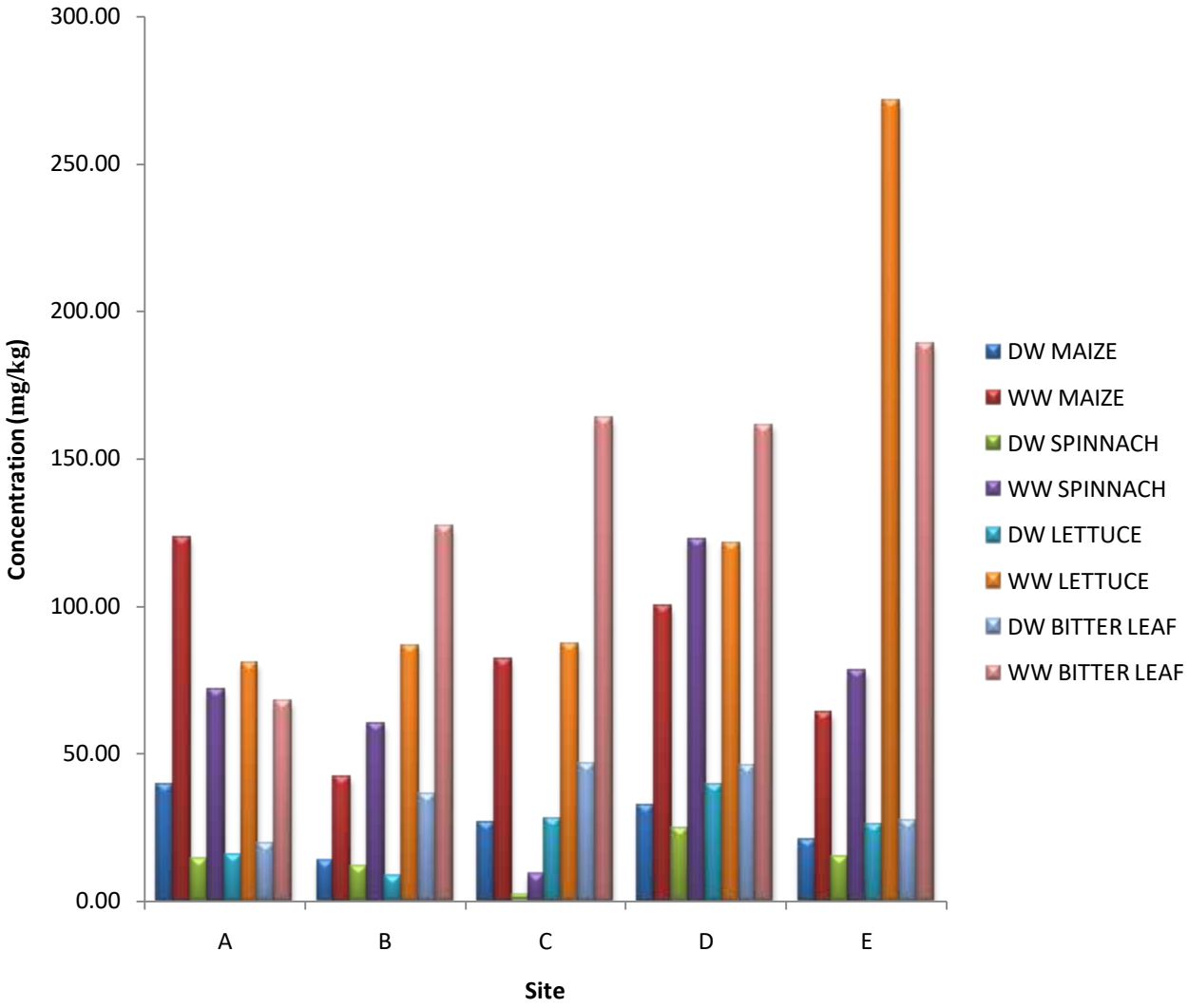


Fig.4. 5a Concentration of Cr in Irrigated Crops Across the Sites (Wet Season)

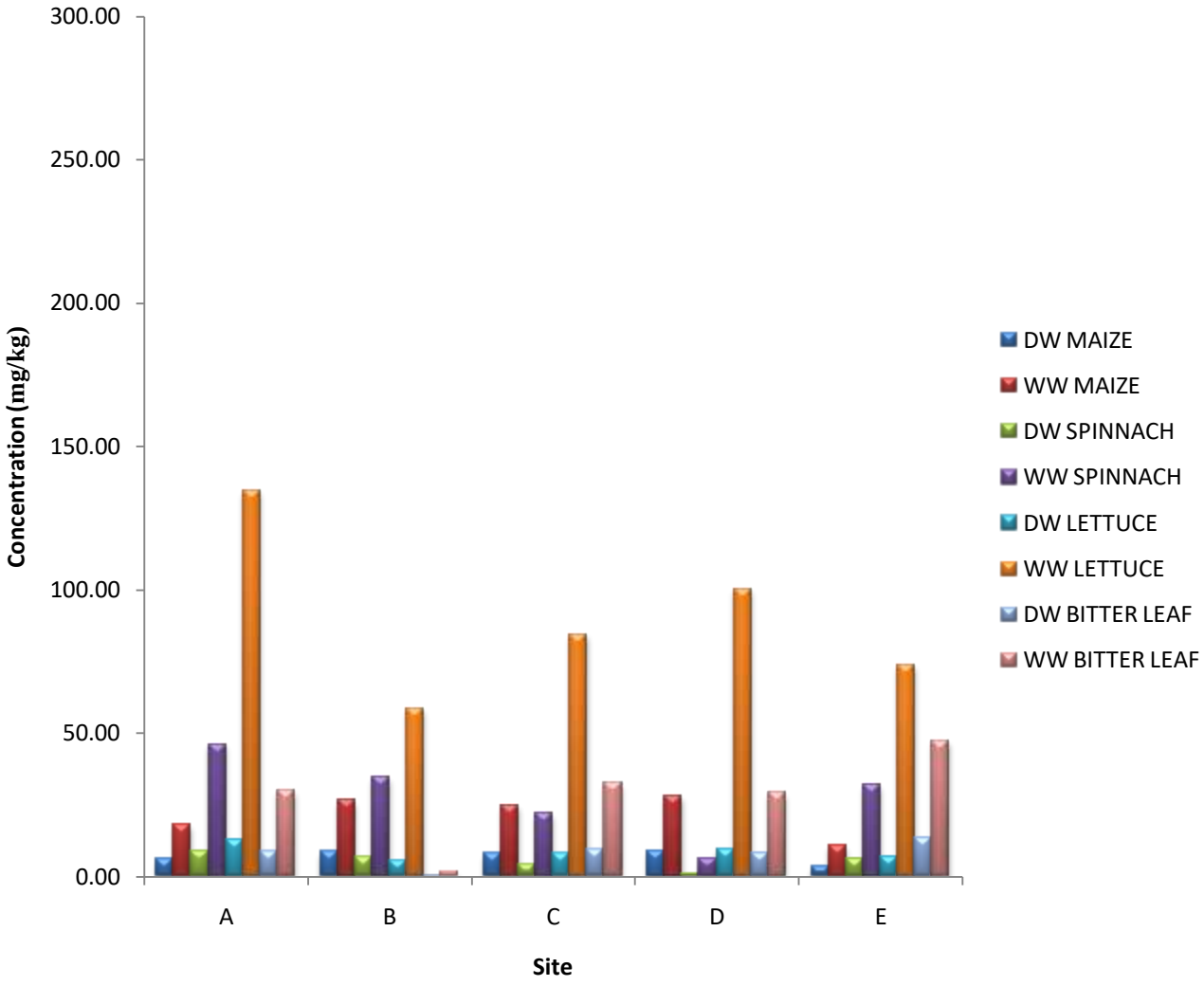


Fig.4. 5b Concentration of Cr in Irrigated Crops Across the Sites (Dry Season)

Table 4.9 Correlation matrix of Cr between different studied samples in wet season

	Cr M	Cr S	Cr L	Cr BL
Cr M	1.000			
Cr S	0.249	1.000		
Cr L	-0.296	0.275	1.000	
Cr BL	-0.504	0.011	0.648	1.000

Table 4.10 Correlation matrix of Cr between different studied samples in dry season

	Cr M	Cr S	Cr L	Cr BL
Cr M	1.000			
Cr S	-0.551	1.000		
Cr L	-0.108	0.202	1.000	
Cr BL	-0.681	-0.112	0.300	1.000

4.1.6 Levels of Fe in crops

The mean concentration of Fe ($mgkg^{-1}$) in wet and dry season are presented on Figs. 4.6a and 4.6b respectively. The ranged of 3.57 (Site D) – 137.75$mgkg^{-1}$ (Site E) and 43.84 (Site A) – 104.34$mgkg^{-1}$(Site E) was obtained in maize for both season respectively. Spinach ranged between 201.76 (Site E) – 946.59$mgkg^{-1}$ (Site D) and 554.73 (Site B) – 908.41$mgkg^{-1}$ (Site D) in both season respectively. Lettuce concentration ranged between 746.07 (Site B) – 989.63 (Site A) and 630.36 (Site E) – 954.89$mgkg^{-1}$ (Site A) in wet and dry season respectively. The range was 123.28 (Site A) – 323.69$mgkg^{-1}$ (Site D) and 181.56 (Site E) – 458.72$mgkg^{-1}$ (Site B) in wet and dry season respectively for bitter leaf. Analysis of variation across the sites in all samples revealed significant variation ($p < 0.05$). Significant variation ($p < 0.05$) was also found between wet and dry season samples across the sites for both seasons with exception of maize in wet season.

Significant variation ($p < 0.05$) was observed between wet and dry samples for all samples. As shown on Table 4.11 and 4.12 for wet and dry season respectively, correlation coefficient for Fe in the crop samples revealed negative correlation between FeM: FeS and FeBL, FeS: FeL, FeL: FeBL for wet season, and FeM: FeS, FeL and FeBL, and FeS: FeL and FeBL in dry season.

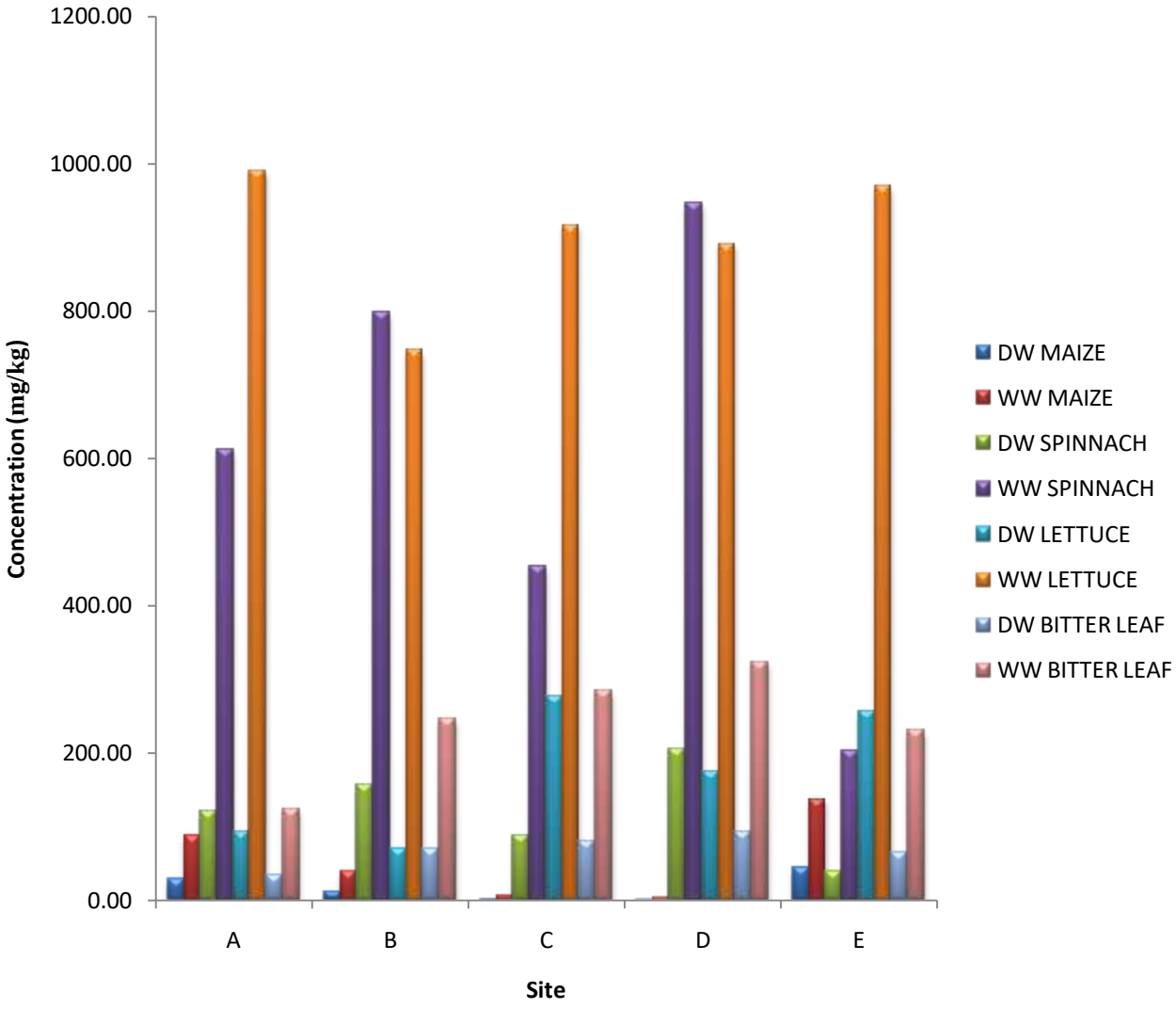


Fig. 4.6a Concentration of Fe in Irrigated Crops Across the Sites (Wet Season)

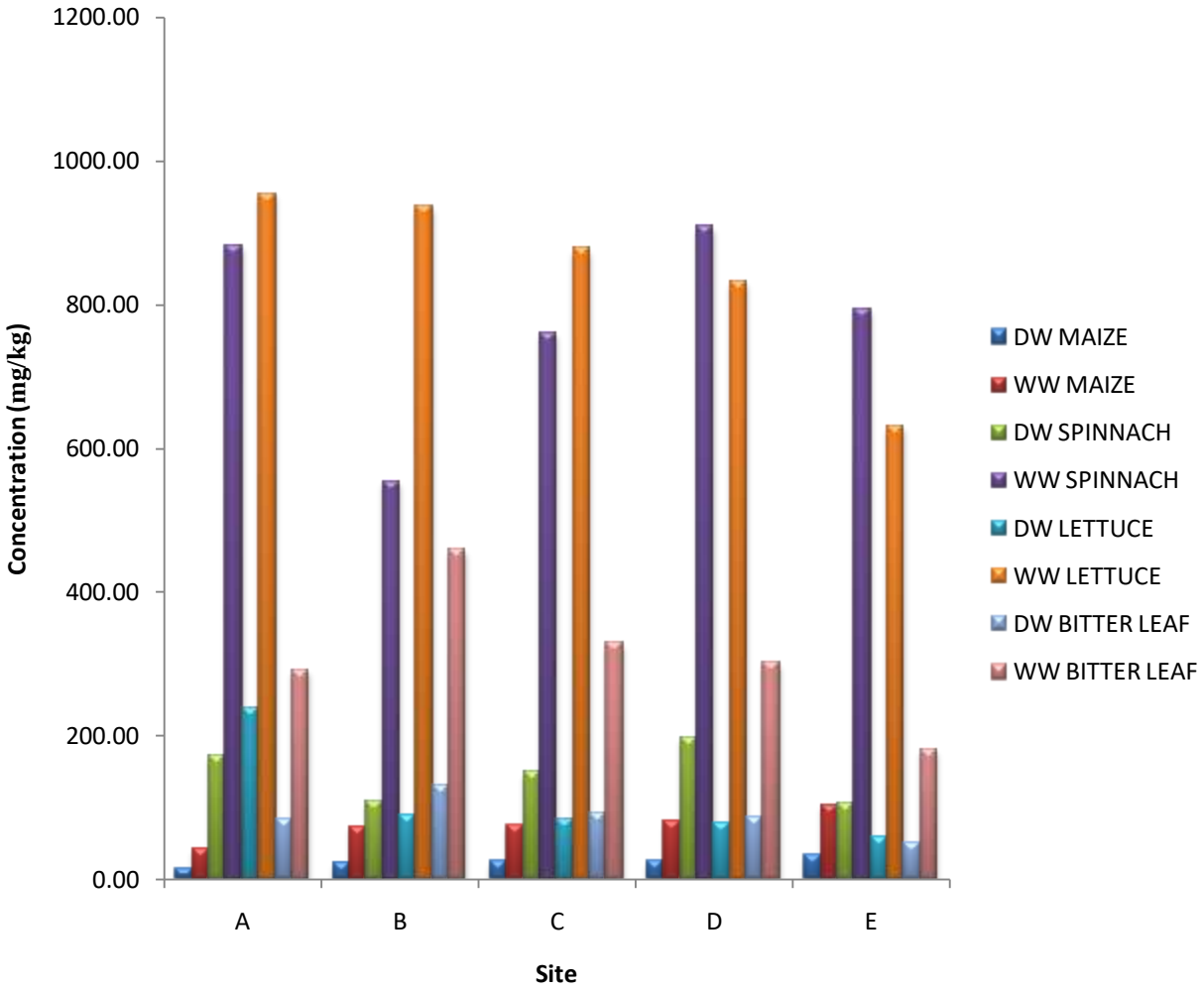


Fig. 4.6b Concentration of Fe in Irrigated Crops Across the Sites (Dry Season)

Table 4.11 Correlation matrix of Fe between different studied samples in wet season

	Fe M	Fe S	Fe L	Fe BL
Fe M	1.000			
Fe S	-0.694	1.000		
Fe L	0.483	-0.557	1.000	
Fe BL	-0.640	0.296	-0.416	1.000

Table 4.12 Correlation matrix of Fe between different studied samples in dry season

	Fe M	Fe S	Fe L	Fe BL
Fe M	1.000			
Fe S	-0.151	1.000		
Fe L	-0.881*	-0.201	1.000	
Fe BL	-0.397	-0.696	0.772	1.000

**Correlation is significant at the 0.05 level.*

4.2 Heavy Metal Content in Irrigation Water

The results of total heavy metal concentrations of surface water across the seasons are presented in Figs 4.7a and 4.7b. Pb values ranged between 0.05 (Site C) – 0.66mgl^{-1} (Site E) during the wet Season and 0.01 (Site E) – 0.08mgl^{-1}(Site B) in dry Season. Cu fluctuated between 0.01 (Site E) – 0.07mgl^{-1}(Site C) and 0.01 (Site A, B and E) – 0.03mgl^{-1} (Site C and D) across the sites in wet and dry season respectively. In the same vein, Mn concentration varied between 0.04 (Site C) – 0.07mgl^{-1} (Site E) during wet season, and 0.08 (Site B) – 0.14mgl^{-1} (Site A, C and D) during dry season. Concentration levels of Cd ranged between 0.00mgl^{-1} (Site A, C and D) - 0.03mgl^{-1} (Site E) in wet season, 0.00 (Site A and D) – 0.01mgl^{-1} (in other site) during the dry season. Cr ranged between 0.05 (Site B) – 0.83mgl^{-1} (Site C) during wet season, and 0.02 (Site C) – 0.07mgl^{-1} (Site D) during dry season. Fe values ranged between 0.39 (Site B) – 1.85mgl^{-1} (Site C) during the wet Season and 0.41 (Site E) – 2.08mgl^{-1}(Site A) in dry Season.

Concentration levels of Pb, Cu, Mn, Cd, Cr and Fe in treated water from water works ranged between 0.03 – 0.10, 0.08 – 0.01, 0.04, 0.02, 0.03, 0.01mgl^{-1} during wet and dry season respectively. High concentration of metal (same value) was observed in both seasons with exception of Pb and Cu. Also, the pattern of metal concentrations in both season showed: Fe > Cr > Pb > Mn > Cu > Cd. The seasonal concentration pattern shows that Fe had higher concentrations at all the sites in both seasons. Compared to treated water highest concentration of Cu were observed during the dry Season. Analysis of variance across the seasons showed significant differences ($p < 0.05$) for all metals except Cd. Correlation analysis as shown in Table 4.13 and 4.14 indicates significant positive correlation ($p < 0.05$) between Cd: Mn (wet season) and Fe: Mn (dry season). Among metals inter-relationships, negative correlation ($p < 0.05$) was observed.

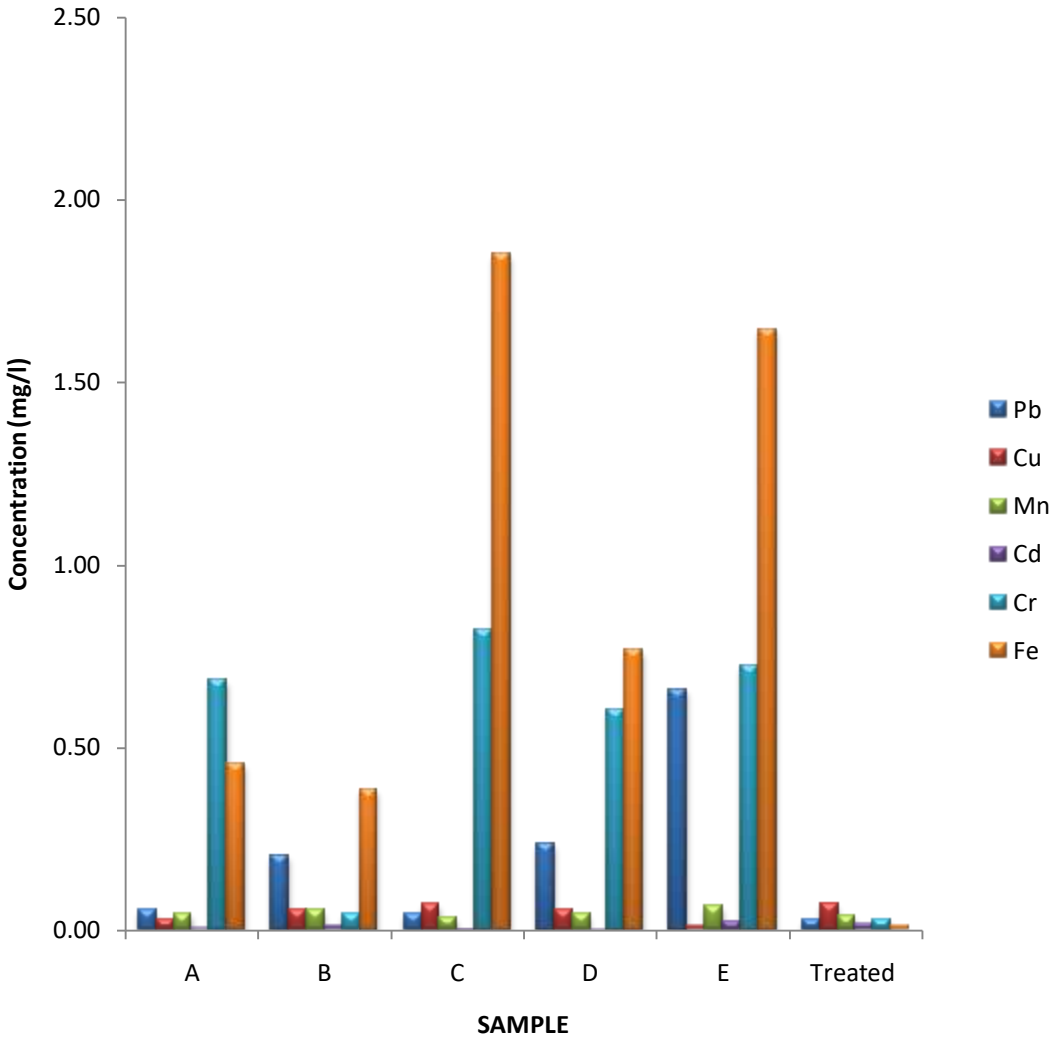


Fig.4. 7a Concentration of heavy metals in water samples across the sites (Wet Season)

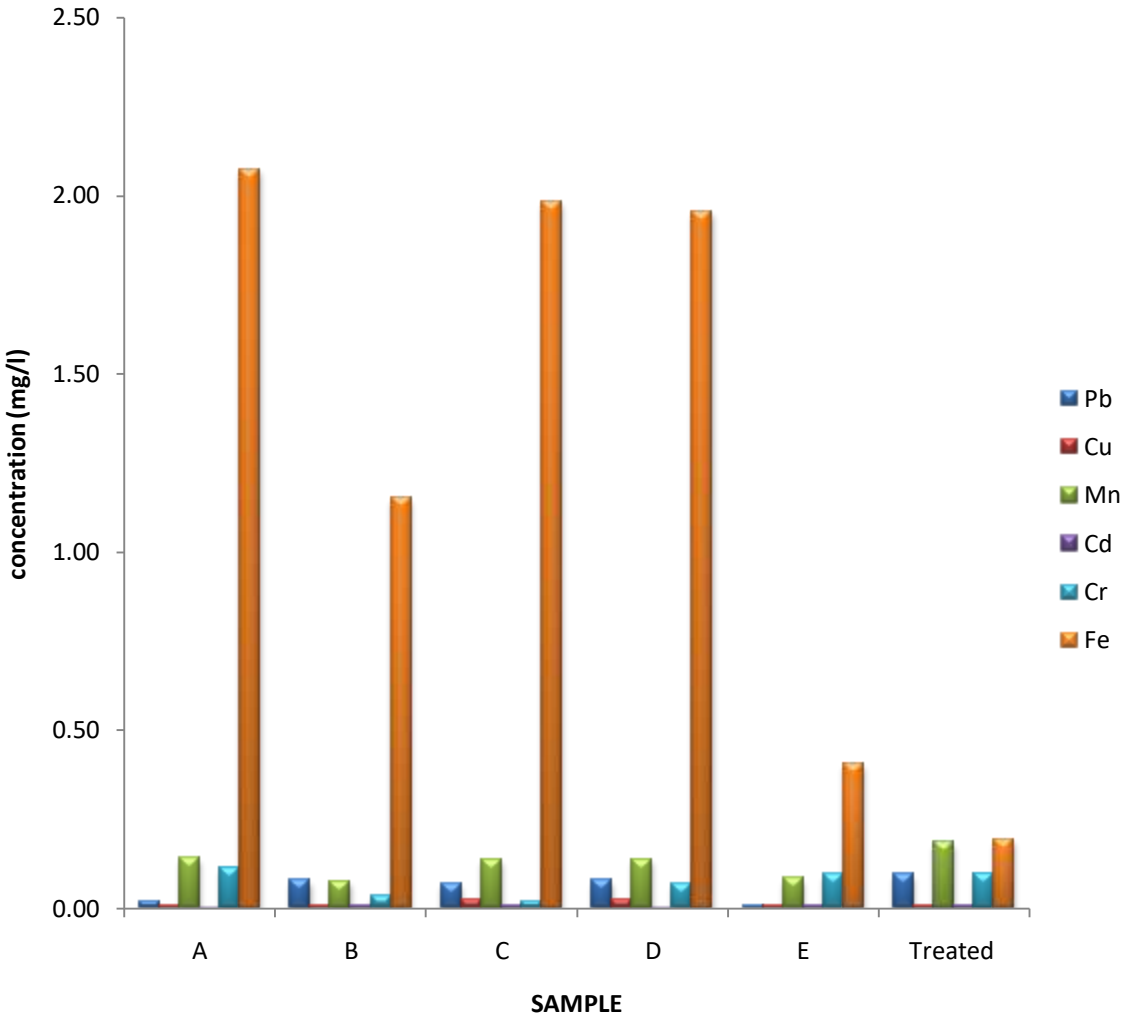


Fig.4. 7b Concentration of heavy metals in water samples across the sites (Dry Season)

Table 4.13 Correlation matrix among heavy metals in water samples in wet season

Parameters	Pb	Cu	Mn	Cd	Cr	Fe
Pb	1.000					
Cu	-0.697	1.000				
Mn	0.871	-0.716	1.000			
Cd	0.847	-0.895*	0.895*	1.000		
Cr	-0.055	-0.264	-0.345	0.013	1.000	
Fe	0.344	-0.089	-0.067	0.204	0.675	1.000

**Correlation is significant at the 0.05 level*

Table 4.14 Correlation matrix among heavy metals in water samples in dry season

Parameters	Pb	Cu	Mn	Cd	Cr	Fe
Pb	1.000					
Cu	0.614	1.000				
Mn	0.101	0.662	1.000			
Cd	0.053	-0.167	-0.662	1.000		
Cr	-0.815	-0.554	0.060	-0.554	1.000	
Fe	0.395	0.576	0.882*	-0.633	-0.148	1.000

**Correlation is significant at the 0.05 level*

4.3 Relationships Between the Heavy Metals in Crops and Water Samples

Correlation coefficients between the levels of heavy metals in crops and in water are presented in Table 4.15 and 4.16 (a-f). In wet season, significant positive ($p < 0.05$) correlations were observed between FeW: MnL (Table 4.16c), PbW: CdS (Table 4.15d), PbW: CrL (Table 4.15e), CdW: FeM and CrW: FeL (Table 4.15f) while negative significant ($p < 0.05$) correlation were observed between CrW: PbM and PbBL (Table 4.15e) and CuW: FeM (Table 4.15f). Similarly, in dry season significant positive correlation were found: FeW: PbBL (Table4.16a), CrW: CuBL (Table 4.16b), CuW: CdM (Table 4.16d) and PbW: CrM (Table 4.16e), while significant negative correlation were observed between PbW: PbM and PbL, and CuW: PbS (Table 4.16a), and FeW: MnBL (Table 4.16c).

Table 4.15a Correlation matrix between metals in water and Pb in crop samples in wet season

	Pb M	Pb S	Pb L	Pb BL
Pb W	0.043	-0.405	0.720	0.051
Cu W	0.394	-0.170	-0.679	0.038
Mn W	0.288	-0.086	0.808	0.488
Cd W	-0.156	-0.142	0.632	0.227
Cr W	-0.900*	-0.213	-0.218	-0.949*
Fe W	-0.578	-0.847	-0.349	-0.593

**Correlation is significant at the 0.05 level.*

M – Maize
S – Spinnach
L – Lettuce
BL – Bitter Leaf
W – Water

Table 4.15b Correlation matrix between metals in water and Cu in crop samples in wet season

	Cu M	Cu S	Cu L	Cu BL
Pb W	-0.345	-0.033	-0.341	-0.026
Cu W	0.299	-0.225	0.088	-0.257
Mn W	-0.654	0.232	-0.429	0.466
Cd W	-0.325	0.000	-0.057	0.306
Cr W	0.691	-0.380	0.447	-0.756
Fe W	0.755	-0.873	0.574	-0.787

Table 4.15c Correlation matrix between metals in water and Mn in crop samples in wet season

	Mn M	Mn S	Mn L	Mn BL
Pb W	0.287	0.440	0.122	-0.481
Cu W	0.180	0.091	0.281	0.154
Mn W	-0.204	0.559	-0.231	0.009
Cd W	-0.148	0.357	-0.061	-0.111
Cr W	0.601	-0.641	0.422	-0.727
Fe W	0.762	0.115	0.914*	-0.761

**Correlation is significant at the 0.05 level.*

Table 4.15d Correlation matrix between metals in water and Cd in crop samples in wet season

	Cd M	Cd S	Cd L	Cd BL
Pb W	0.493	0.894*	0.113	-0.486
Cu W	-0.655	-0.351	-0.648	0.121
Mn W	0.285	0.613	-0.024	-0.500
Cd W	0.664	0.532	0.403	-0.530
Cr W	0.638	0.141	0.772	0.254
Fe W	0.746	0.508	0.413	-0.484

**Correlation is significant at the 0.05 level.*

Table 4.15e Correlation matrix between metals in water and Cr in crop samples in wet season

	Cr M	Cr S	Cr L	Cr BL
Pb W	-0.430	0.371	0.972*	0.633
Cu W	-0.102	-0.288	-0.745	0.018
Mn W	-0.534	0.378	0.767	0.268
Cd W	0.351	0.121	0.842	0.228
Cr W	0.607	-0.139	0.279	0.224
Fe W	-0.163	-0.481	0.501	0.735

**Correlation is significant at the 0.05 level.*

Table 4.15f Correlation matrix between metals in water and Fe in crop samples in wet season

	Fe M	Fe S	Fe L	Fe BL
Pb W	0.684	-0.517	0.163	0.113
Cu W	-0.974*	0.623	-0.600	0.597
Mn W	0.761	0.343	-0.089	-0.175
Cd W	0.964*	-0.698	0.274	0.397
Cr W	0.151	-0.528	0.895*	-0.041
Fe W	0.106	-0.744	0.406	0.348

**Correlation is significant at the 0.05 level.*

Table 4.16a Correlation matrix between metals in water and Pb in crop samples in dry season

	Pb M	Pb S	Pb L	Pb BL
Pb W	-0.903*	-0.547	-0.901*	-0.656
Cu W	-0.407	-0.994*	-0.566	-0.667
Mn W	0.117	-0.725	-0.244	-0.728
Cd W	0.059	0.196	0.350	0.665
Cr W	0.573	0.506	0.487	0.251
Fe W	-0.162	-0.617	-0.508	0.895*

**Correlation is significant at the 0.05 level.*

Table 4.16b Correlation matrix between metals in water and Cu in crop samples in dry season

	Cu M	Cu S	Cu L	Cu BL
Pb W	-0.101	0.869	0.117	-0.737
Cu W	0.377	0.174	-0.692	-0.586
Mn W	-0.017	-0.197	-0.585	0.183
Cd W	0.649	0.196	0.069	-0.603
Cr W	-0.393	-0.732	0.052	0.921*
Fe W	-0.305	0.243	-0.190	0.102

**Correlation is significant at the 0.05 level.*

Table 4.16c Correlation matrix between metals in water and Mn in crop samples in dry season

	Mn M	Mn S	Mn L	Mn BL
Pb W	-0.081	-0.626	-0.237	-0.397
Cu W	0.690	-0.266	-0.475	-0.553
Mn W	0.744	-0.441	-0.167	-0.871
Cd W	-0.494	0.504	0.409	0.713
Cr W	0.185	0.263	-0.105	0.084
Fe W	0.386	-0.803	0.022	-0.992**

***Correlation is significant at the 0.01 level.*

Table 4.16d Correlation matrix between metals in water and Cd in crop samples in dry season

	Cd M	Cd S	Cd L	Cd BL
Pb W	-0.517	-0.050	0.002	0.478
Cu W	0.928*	0.619	0.395	0.733
Mn W	0.428	0.286	-0.144	0.313
Cd W	-0.024	0.311	0.660	0.460
Cr W	-0.493	-0.279	-0.425	-0.811
Fe W	0.249	-0.076	-0.425	0.279

**Correlation is significant at the 0.05 level.*

Table 4.16e Correlation matrix between metals in water and Cr in crop samples in dry season

	Cr M	Cr S	Cr L	Cr BL
Pb W	0.963**	-0.628	-0.363	-0.664
Cu W	0.615	0.861	0.063	0.147
Mn W	0.292	-0.317	0.775	0.306
Cd W	-0.176	0.116	-0.852	-0.072
Cr W	-0.689	0.464	0.619	0.454
Fe W	0.606	-0.212	0.617	-0.173

***Correlation is significant at the 0.01 level.*

Table 4.16f Correlation matrix between metals in water and Fe in crop samples in dry season

	Fe M	Fe S	Fe L	Fe BL
Pb W	-0.037	-0.362	0.466	0.754
Cu W	0.089	0.355	0.061	0.024
Mn W	-0.518	0.756	0.342	-0.186
Cd W	0.557	-0.752	-0.331	0.146
Cr W	-0.174	0.575	-0.248	-0.621
Fe W	-0.758	0.426	0.732	0.286

4. 4 Transfer Factor (TF)

Water – crop transfer is one of the key components of human exposure to metals through the food chain.Tranfer factor were determined for Pb, Cu, Mn, Cd, Cr and Fe to quantify the relative difference in bioavailability of metals to food crops through the water. From the results presented in Table 4.17a-f, value of transfer factors range from 31.28 (Site E) – 1651.58 (Site A) and 58.19 (Site D) – 6826.50 (Site E) for Pb, 65.50 (Site C) – 6950.50 (Site E) and 365.50 (Site D) – 10607.50 (Site B) for Cu, 47.00 (Site B) – 3249.88 (Site C) and 141.06 (Site B) – 2755.63 (Site B) for Mn, 98.50 (Site B) – 1228.50 (Site A) and 14.50 (Site B) – 956.50 (Site E) for Cd, 87.28 (Site E) – 1732.60 (Site B) and 91.86 (Site D) – 4227.25 (Site C) for Cr, and 3.35 (Site C) – 2151.37 (Site A) and 21.07 (Site A) – 1537.46 (Site E) for Fe in both wet and dry season respectively. High transfer factors were observed in dry season for all metals studied with exception of Cd. The TF for lettuce was generally higher than other crop in all seasons.

Table 4.17a The concentrations of Pb in crops relative to their concentrations in irrigation water (Transfer Factor, TF)

		Wet Season		
Site	**PbM**	**PbS**	**PbL**	**PbBL**
A	227.42	1628.42	1651.58	684.75
B	485.15	252.13	493.53	339.80
C	276.50	231.50	1081.50	630.10
D	277.94	221.85	463.79	144.25
E	39.64	31.28	186.76	62.26
		Dry Season		
	PbM	**PbS**	**PbL**	**PbBL**
A	1180.25	2137.25	2557.25	1118.25
B	72.31	598.00	328.31	301.13
C	238.36	136.36	580.50	319.21
D	58.19	151.06	131.38	235.50
E	2286.50	4528.50	6826.50	2936.50

Table 4.17b The concentrations of Cu in crops relative to their concentrations in irrigation water (Transfer Factor, TF)

	Wet Season			
Site	**CuM**	**CuS**	**CuL**	**CuBL**
A	420.33	1344.50	2688.17	1176.67
B	104.92	524.25	988.83	636.83
C	390.07	65.50	1670.86	350.29
D	162.50	652.75	514.67	460.67
E	1211.50	2186.50	6950.50	3025.50
	Dry Season			
	CuM	**CuS**	**CuL**	**CuBL**
A	905.00	3380.50	9020.00	4088.00
B	1003.50	4998.50	10607.50	2849.00
C	545.50	1344.83	2373.50	862.17
D	365.50	1319.17	2558.50	994.00
E	1519.50	2839.50	7836.50	3265.00

Table 4.17c. The concentrations of Mn in crops relative to their concentrations in irrigation water (Transfer Factor, TF)

		Wet Season		
Site	**MnM**	**MnS**	**MnL**	**MnBL**
A	48.20	279.50	1423.70	1666.40
B	47.00	974.92	1459.75	1670.83
C	333.13	864.63	3249.88	1026.50
D	266.60	544.50	1789.30	662.60
E	161.57	654.86	1519.71	404.07
		Dry Season		
Site	**MnM**	**MnS**	**MnL**	**MnBL**
A	154.04	382.54	1647.04	501.32
B	141.06	742.06	2755.63	2497.56
C	174.04	1041.46	1592.39	751.82
D	206.96	501.25	737.25	533.54
E	250.72	5214.39	1964.78	3381.94

Table 4.17d. The concentrations of Cd in crops relative to their concentrations in irrigation water (Transfer Factor, TF)

	Wet Season			
Site	**CdM**	**CdS**	**CdL**	**CdBL**
A	194.50	158.50	1228.50	255.50
B	98.50	274.50	389.50	125.00
C	NA	NA	NA	NA
D	NA	NA	NA	NA
E	104.33	161.83	371.17	37.33
	Dry Season			
Site	**CdM**	**CdS**	**CdL**	**CdBL**
A	NA	NA	NA	NA
B	89.50	14.50	368.50	115.00
C	191.50	495.50	957.50	329.50
D	NA	NA	NA	NA
E	127.50	403.50	956.50	104.00

Table 4.17e. The concentrations of Cr in crops relative to their concentrations in irrigation water (Transfer Factor, TF)

	Wet Season			
Site	**CrM**	**CrS**	**CrL**	**CrBL**
A	178.49	103.85	116.86	98.00
B	838.10	1200.50	1732.60	2535.60
C	98.45	10.81	104.99	197.30
D	163.46	201.16	199.16	264.33
E	87.28	106.73	371.38	258.51
	Dry Season			
Site	**CrM**	**CrS**	**CrL**	**CrBL**
A	150.92	385.17	1123.00	248.88
B	662.63	865.38	1467.13	43.13
C	1248.25	1090.00	4227.25	1628.25
D	401.07	91.86	1434.14	415.21
E	109.05	320.85	739.40	475.60

Table 4.17f The concentrations of Fe in crops relative to their concentrations in irrigation water (Transfer Factor, TF)

Site	FeM	FeS	FeL	FeBL
A	188.97	1330.76	2151.37	267.99
B	100.17	2045.12	1912.99	630.13
C	3.35	244.80	495.69	153.58
D	4.63	1229.33	1157.18	420.37
E	83.48	122.28	586.93	139.79
Site	**FeM**	**FeS**	**FeL**	**FeBL**
A	21.07	424.45	459.08	140.22
B	64.40	482.37	814.35	398.89
C	37.39	382.44	441.13	165.06
D	41.22	463.47	424.63	153.78
E	254.48	1937.10	1537.46	442.83

CHAPTER FIVE

DISCUSSION

The results of this study show that leafy vegetables grown at all farmland along river Kubbani and Galma have high levels heavy metals. This was due to the fact that the farmlands are irrigated with waste water contaminated with these heavy metals.

The following trend among crops were found from the mean (±SEM) and range of the heavy metal contents of maize, spinach, lettuce and bitter leaf samples in the wet and dry seasons:

Pb: Lettuce > Spinach > Bitter Leaf > Maize

Cu: Lettuce > Bitter Leaf > Spinach > Maize

Mn: Lettuce > Bitter Leaf > Spinach > Maize

Cd: Lettuce > Spinach > Maize > Bitter Leaf

Cr: Lettuce > Bitter Leaf > Maize > Spinnach

Fe: Lettuce > Spinach > Bitter Leaf > Maize for wet season.

While the dry season samples revealed the following pattern;

Pb: Lettuce > Spinach > Bitter Leaf > Maize

Cu: Lettuce > Spinach > Bitter Leaf > Maize

Mn: Lettuce > Spinach > Bitter Leaf > Maize

Cd: Lettuce > Spinach > Bitter Leaf > Maize

Cr: Lettuce > Spinach > Bitter Leaf > Maize

Fe: Lettuce > Spinach > Bitter Leaf > Maize

In general, lettuce accumulated more of the metals than any other crops, this is similar to study on metal contents of vegetables from Addis Ababa Market that lettuce contained high amount of Cd compared to other vegetables (Fisseha, 2002). Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments (Ejaz et al, 2007). Difference in metal concentration in vegetables seems to imply that different types of vegetables have different abilities to accumulate the metals. Different vegetable species accumulate different metals depending on environmental conditions (Lokeshwari and Chandropper,2006).

The concentration of Pb in maize was generally high in wet season compared to dry season, with few exceptions of Sites A and C. Analysis of variation between wet and dry season however revealed no significant ($p > 0.05$) for maize, spinach and lettuce across the sites with exception of bitter leaf. The values of Pb were much higher in wet season compared to dry season. Highest mean of 123.26mgkg^{-1} recorded in lettuce (wet season) Jeanne and Sidle (1991) reported the presence of Pb in vegetables grown near busy traffic highways. The results of this study generally showed high concentration of Pb in crops from all sites exceed the (0.3mgkg^{-1}) FAO/WHO (2001) recommended limit. This may be as a result of gas emissions from the traffic on the road along the sites as well as municipal and domestic activities in the neighbourhoods.

However, it is not uncommon to find farmland sited where ancillary vehicle workshops are also found, e.g site D. This is an indication of a high potential risk of Pb exposure at all irrigated farmlands in Zaria. Pb is non-essential element for plant and animals, and should not be available in plants even in low quantity (Alloway and Ayres, 1993).

The amount of Cu in maize ranged between 6.30 (Site B) – 27.31mgkg^{-1} (Site C) and 9.05 (Site A) – 16.37mgkg^{-1} (Site C) in wet and dry season respectively. The results for Cu showed high concentration in lettuce in wet season (116.96mg/kg SiteC) this value is higher than 1.15 and 0.851mgkg^{-1} reported for lettuce (Zhuang *et al*., 2009,). However, Cu levels especially for leafy vegetables are within the toxicity range 20 – 100 (Awofolu *et al*., 2005). Compare to standard limit, value obtained in this study with exception of lettuce (wet season) are within 73.3mg/kg limit recommended (FAO/WHO, 2001).

The negative correlation observed among the metals could indicate uncommon source of this metal among the crops while positive correlation indicates common sources, an indication of pollution due to a source of Cu which could be due to metal scraps deposited in the farms. The intake of Cu through the consumption of leafy vegetable is high and does pose potential health risk to consumers of vegetable, though alleviated by drying the plant. Adverse health effects are thus expected from Cu intake from the diet of leafy vegetables.

Mn is detected at higher concentration, second to Fe in all the crops. Similar trend of accumulation to Cu was found with Mn. Whereas the highest concentration (469.30mgkg^{-1}) occurred in spinach (dry season), the lowest (2.41mgkg^{-1}) was in maize. Heenan and Campbel (1980) reported that at a high Mn supply, the leaves accumulated higher concentrations with age. The highest Mn reported in this study is however within the 500mgkg^{-1} recommended limits (FAO/WHO, 2001). From the values obtained in this study, values of Mn from various sites could be due to high amount of Mn present in the natural form in savanna soils (Awode *et al*., 2008). Since this metal is one of the microelement required for plant growth and a macroelement required in human diet, toxicity could not be implied from the amount reported in this study.

From the results of Cd studied, it was found that the presence of Cd in all crops is beyond the recommended limit 0.2mgkg^{-1} (FAO/WHO, 2001). The reason for this accumulation is that Cd is relatively easily taken up by food crops and especially by leafy vegetables (Lokeshwari and Chandrappa, 2006). Also, it may be due to the foliar absorption of atmospheric deposits on plant leaves (Mido and Satake, 2003). The concentration of Cd in food crops has linear relationship with the degree of Cd contamination of the soil (although not in this study). Compare to other study, values of Cd obtained in this study was higher than the 0.117mg/kg (spinach) and 0.09mg/kg (maize) reported by Faruk et al (2006), a study that was carried in river Kubanni and Galma. This could be due to different activities carried out in different study areas. In Zaria there are two leather tanning industries, the effluents generated by the tanneries are drain into the river. Consequently, the waste generated by the tanning industries causes contamination of the water and food crops grown along the river bank. This could be responsible for high Cd levels in this study. It could also be attributed to soil contamination from heavy metals in compost like fertilizer and manure which are used extensively at the sites.

Cr concentrations in all crops were more than the maximum limit of 2.30mgkg^{-1} (FAO/WHO, 2001). The highest mean concentration of Cr in maize in this study is 123.16mg/kg in wet season; this observation is similar to that reported by Garba et al (2006). This is as a result of the use of sewage sludge as fertilizer at the sites and also some of the sites contain dumped refuse from mechanical workshops, commercial centre, tanning industries waste and domestic sewage sludge. The wet season might have favoured leaching of heavy metal (Cr) as a runoff into the water as well as absorption from soil and atmosphere by plant tissues (Zayed et al 1998).

Generally, the concentration of Fe was found to be higher magnitude compare to other metals in both seasons. Higher concentrations of Fe were found in leafy vegetable as compare to maize. This could imply high accumulation of this metal by the leafy vegetable. Significant variation ($p < 0.05$) was found between wet and dry season samples across the sites with exception of maize in wet season. This could be due to low rate input of these metals in the soil in both seasons. Fe concentration in all crops was below the maximum limit 425.50mg/kg (FAO/WHO, 2001) with the exception of lettuce and spinach which were very high. Elevated Fe content in plants could be due to iron in effluents from metal industries, which enters the irrigated water.

In the irrigation water, Pb levels of 0.24mg/l was higher than mean values of 0.19mg/l reported in a similar study in Zaria (Yakasai *et al*., 2004). The elevated levels of Pb in the present study could be due to high vehicular emission, disposal of discarded batteries and other lead containing materials, burning of solid waste and painted woods weathering of lead containing paints on buildings.

The high level of Cr obtained may not be certain, however, metal scrap waste could be responsible for the high concentration. Pb and Cr levels observed far exceeded the $0.01mgl^{-1}$ and 0.05mg/l respectively, WHO (1993) recommended limits for the metals especially in wet season. Pb may impair renal function, red blood cell production, the nervous system and causes blindness (Asonye *et al*., 2007). Cr, though an essential trace nutrient and a vital component for the glucose tolerance factor, damages the liver, lung and causes organ hemorrhages (Q'Flaherty, 1995).

All samples contained Mn, however, values obtained in the study indicate that Mn does not seem to be concentrated in the water, since the levels were below $0.5mgl^{-1}$ WHO (1993)

standard limits. The observed levels tend to agree with those reported elsewhere in Nigerian rivers (Kakulu and Osibanjo, 1992 and Fakayode, 2005). Therefore, results from the samples showed no threat from Mn poisoning. Toxicity from Mn manifests with profound increase in the incidence of respiratory diseases. In chronic causes, there may be a neuro-psychiatric disorder characterized by irritability, difficulty in walking, speech disturbance, compulsive behaviour that may involve running, fighting and singing (Asonye *et al*., 2007). If there is chronic Mn toxicity, it results to Parkinsonlike syndrome (Mena *et al*., 1967). This neural manifestation is due to the ease with which Mn crosses the blood brain barrier coupled with its relatively longer half life in brain than the rest of the body.

Cu was generally below the recommended limits of 2.0mgl^{-1} (WHO1993) and 1.5 mgl^{-1} (FEPA,1998). Cu is a useful metal and has been known to participate in the ecosystem from many sources like household tools, wood and metal manufacturing, pesticides applications, fertilizers and septic tanks waste (Markert, 1993). For all the samples, Cd was slightly above 0.01mgl^{-1} (at some sites) FEPA (1998) standard limits, and above the 0.003 mgl^{-1} WHO (1993) standard limits. Similar report that was done in this river showed a high level of 0.087mg/l (Faruk et al., 2006). Likewise, Cr was slightly above 0.05mg/l WHO (1993) in some sites. It was observed that the highest value for Cr in this study is 0.73mg/l, which is less than the 1.46mg/l reported by Garba et al (2006). Also Fe was generally above 0.3mg/l WHO (1993).The heavy metal content of the irrigation water was higher than the natural elemental levels in freshwater (Lokeshwari and Chandropper, 2006). This indicates that the heavy metal concentration in this water is due to the waste from industrial, municipal and domestic activities in neighbourhoods. There is no treatment that is applied to the industrial discharges to detoxify

the wastewater draining into the river. So, metals/metalloids emitted in such manner are easily transferred to all of the food chain, thereby affecting human and animal health.

The concentrations of heavy metal in food crops in this study suggests heavy metal contamination of the crops through irrigation water and hence accumulation in the plant cultivated in the soil.

However, the results observed in wet season for all samples were higher. This could be due to the fact that all the sampling site were surrounded by refuse dumping sites that collects domestic and industrial sewage from the neighbourhoods. Farmers uses sewage sludge as fertilizer at site C. Site D contains dumped refuse from mechanical workshops, commercial centre and domestic sewage sludge while Site E had effluents from industries.

A comparison of the results between the two seasons revealed that a general increase in the mean of these heavy metals concentration was observed in the wet season relative to the dry season. The relatively higher values observed during the wet season could be due to rain water washing the metals from the soil and municipal drainages into river Kubanni and Galma. In contrast, during the dry season most parts of rivers Kubanni and Galma were dried and there was little washing of municipal drainages into the major tributaries that serve these rivers. Another possible reason for the the variations observed could be the slightly acidic pH value (6.3 – 6.5) observed in the wet season and according to Awofolu et al, 2005, water acidity is known to influence metal solubility and thereby making them readily available to be absorbed by the plant.

Several researchers (Yakasai et al, 2004; Faruk et al, 2006; Garba et al, 2006; Faruk et al, 2007; Musa and Yakasai, 2008) have carried out studies on the heavy metal concentration in water and vegetable crops in Zaria metropolis, river Kubanni and Galma inclusive. These authors have documented high levels of these metals in their studies and so, agreeing with the findings of the

present study. This shows that the recommendations made by these researchers have not been fully effected. However, due to increase in Zaria population, leading to increase in vehicular traffic and usage of gasoline powered generators due to power outages. Also, there are a lot of dumping sites within Zaria metropolis which are neglected by the disposal agencies. These dumps sites contain discarded batteries and other sources of heavy metals and are equally used as part of the organic manure used by most of the farmers. In addition, some of the heavy metal can easily be washed into the rivers by rainwater during wet season. All these activities occurring in Zaria are the major source of contaminant leading to heavy metal pollution. It was necessary, therefore to carry out a further study on the river Kubanni and Galma to assess the levels these metal, whether there were decrease in the level. It was observed that the value is still high compared with the standard limit.See fig 4.5 and fig 4.7 that shows high level of Cr and comparing with a similar study reported by Garba et al.,(2006).

The transfer factors as suggested by Kloke et al, (1984) for Cd and Zn (1 – 10) were used as a generalized range for comparisons. However, the patterns of mean availability of the metals in the two seasons were:

Wet Season: Cu > Pb >Mn > Fe > Cr > Cd

Dry Season: Cu > Pb >Mn > Cr > Fe > Cd

The correlation between the uptake of the metals by the crops in comparison with the concentration in the water shows that crops accumulate more of Cu and Pb in both season especially the leafy vegetables (spinach, lettuce and bitter leaf).

The high transfer factor of metal is attributed to low concentration of metals in water compare to food crops, an indication that metal concentration in food crops could be from other source such as traffic emission, mechanic workshops, domestic waste and industrial waste

deposition along the sites. The TF of lettuce was generally higher than those of other crop in all season, an indication of high accumulation of metal in lettuce compare to other crops. The accumulation of metals by leafy vegetables with such high factors shows that it may act as scavengers while still maintaining health status. These observations are in agreement with those reported by Fayed and Abdel-Shafy (1985) and Abdel-Shafy *et al*. (1987).

From the transfer factor (TF), the accumulation of metals in leafy vegetable was much higher than other crop (maize). This could be due to the fact that leafy vegetables have higher translocation and transpiration rate as compared to other crops in which transfer of metals from root to stem and then to fruit takes longer time and hence results in lower accumulation than leafy vegetable (e.g lettuce). Metals levels in the plant are to a large extent governed by air-borne contamination which makes leaves and leafy vegetables most vulnerable to the air-borne deposition, but also cereal grains have been shown to absorb substantial amounts of lead via the air (CCFAC,1995).

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Based on the results of this study, the following conclusions can be made:

1. Leafy vegetables grown along river Kubbani and Galma contain high levels of these heavy metals (Pb, Cu, Mn, Cd, Cr and Fe) possibly through irrigation of the farmlands with waste water from the river. This is due to the fact that there are a lot of accumulation of solid waste around river kubanni and Galma, the untreated leather tannery waste that are discharged into the river. This causes a risk on our water used for irrigation and the food crops cultivated along with it and may pose a risk to the health of the consumers of these vegetables, especially lettuce.
2. The concentrations of Cu and Mn, were below the International permissible limits for water quality (WHO, 1993) while Pb, Cd, Cr and Fe were higher.
3. From the transfer factor (TF), the accumulation of metals in leafy vegetable was much higher than other crop (maize).
4. From this result, it is also observed that other than contamination of food crops by irrigation water, other sources of heavy metal like Indusrial waste,accumulation of solid waste from the community, vehicular emission from the traffic road etc could be responsible.
5. Although the practice of irrigation system is aimed at producing socio-economic benefits, it may not be safe in the long-term

6.2 Recommendations

It is recommended that agricultural and postural activities close to the river should be prohibited to prevent further pollution of the water and the food crops.

It is recommended that leafy vegetables should not be cultivated near roadsides farmland since it has been discovered that vehicular emission is a major source of heavy metal.

To avoid contamination of water and food crops, municipal waste should not be drained into rivers and farmlands without prior treatment. The community should be educated on the need for proper waste disposal.

It is also important to utilize alternative measures of cleaning up the already contaminated irrigation water.

Industrial effluents should also be controlled or appropriately treated before being discharged into the rivers.

There should be continuous assessment of heavy metal contents of soil, plant and water quality for prevention of metals contamination of the vegetables.

There should also be a routine monitoring of biological fluids of consumers of these food crops in order to prevent potential health hazard to human beings.

The Federal Government should develop regulations and recommendations to protect public health. The Environmental Protection Agency (EPA), the Occupational Safety and Health Administration (OSHA) and the Food and Drug Administration (FDA) are some Federal agencies that develops regulations for toxic substances, to help the public health in reducing the risk exposure of these heavy metals to human being and using various recommendations provided by Agency for Toxic Substances and Disease Registry (ATSDR) to protect public health.

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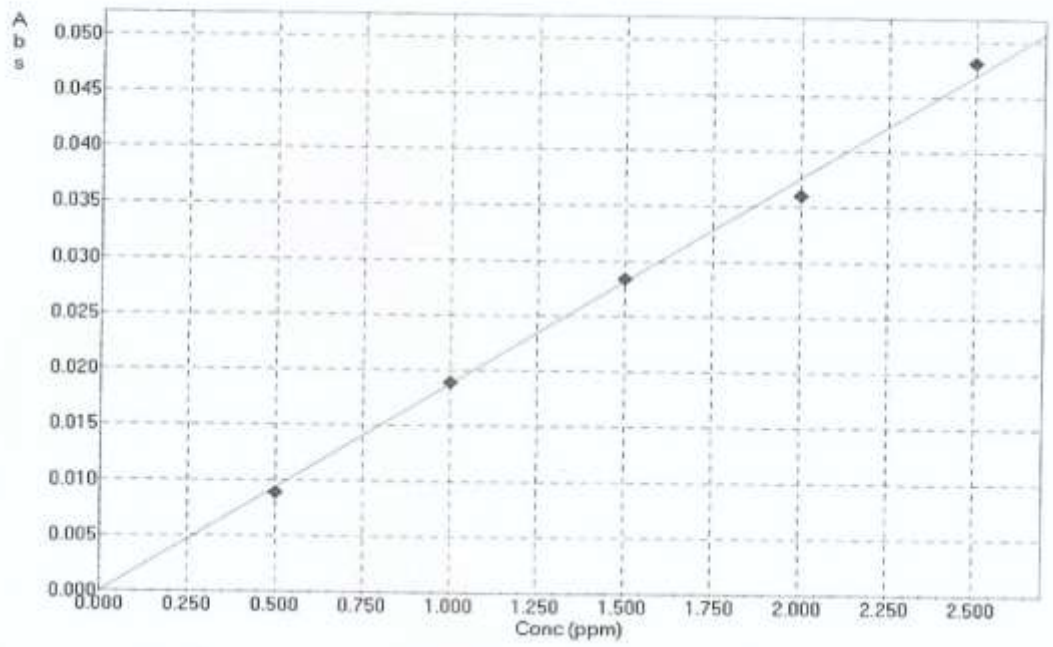
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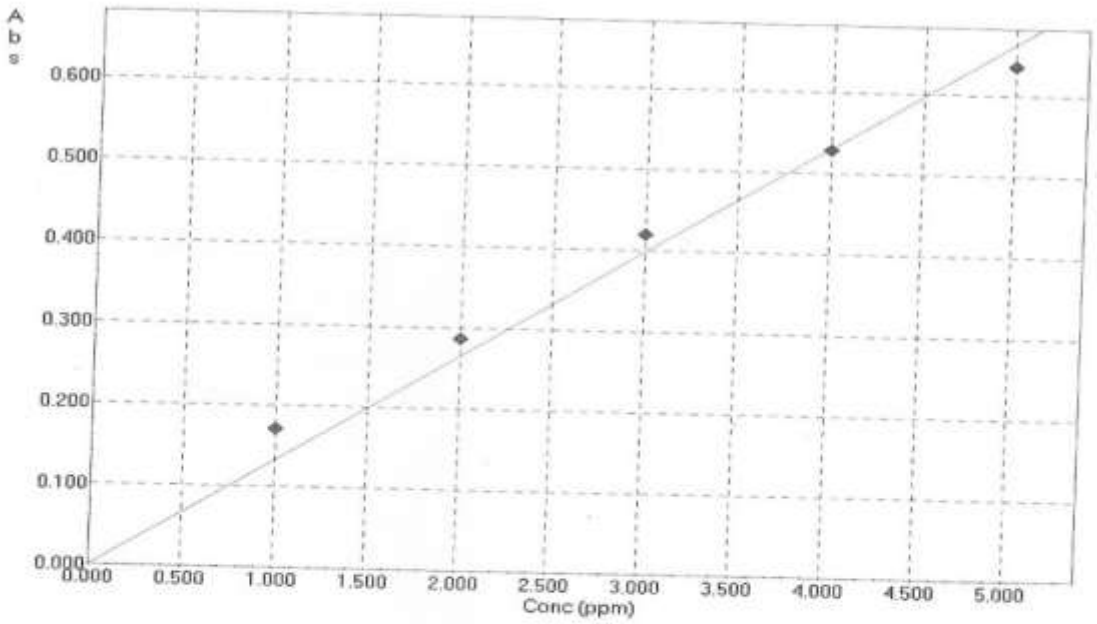
APPENDIX I



Abs=0.0187782Conc+ 0 r=0.9980

CONC	ABS
0.5000	0.0089
1.0000	0.0189
1.5000	0.0284
2.0000	0.0360
2.5000	0.0481

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

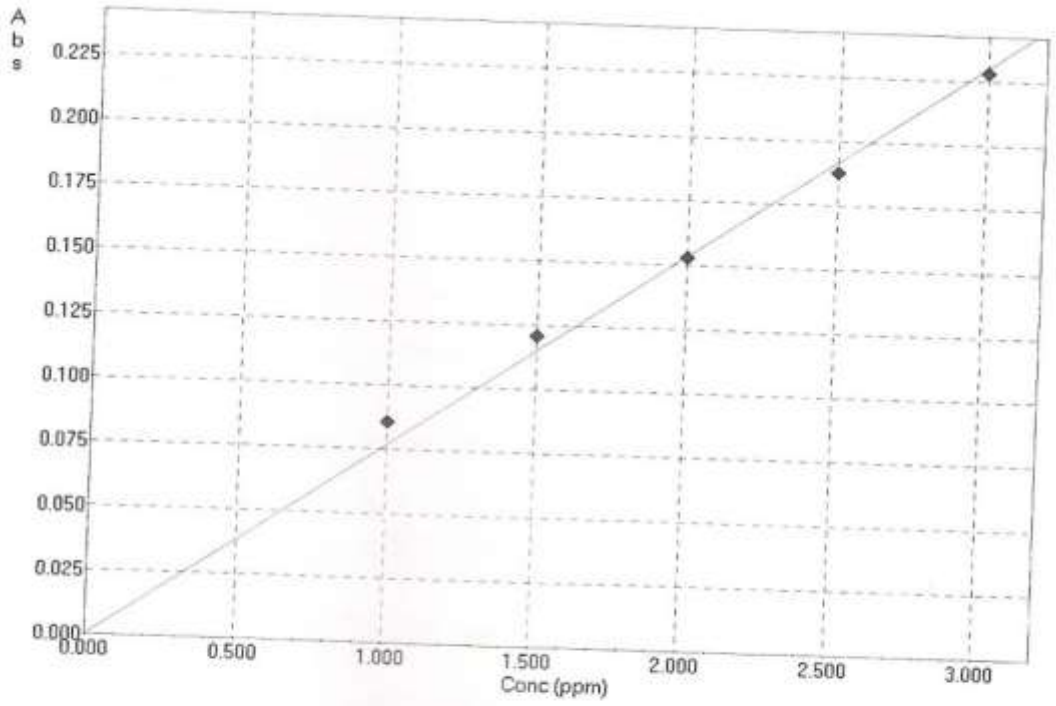


Abs=0.132684Conc+ 0 r=0.9993

CONC
1.0000
2.0000
3.0000
4.0000
5.0000

ABS
0.1714
0.2866
0.4194
0.5287
0.6360

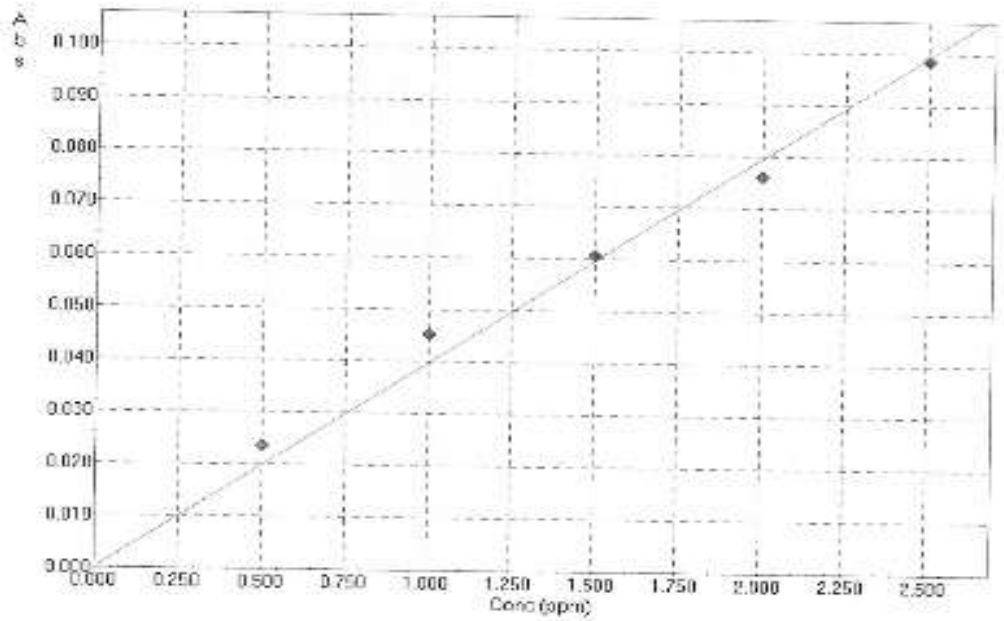
AAS Calibration Curve of Absorbance vs Concentration (mg/l) of Copper



Abs=0.0767267Conc+ 0 r=0.9992

CONC	ABS
1.0000	0.0855
1.5000	0.1208
2.0000	0.1529
2.5000	0.1877
3.0000	0.2282

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

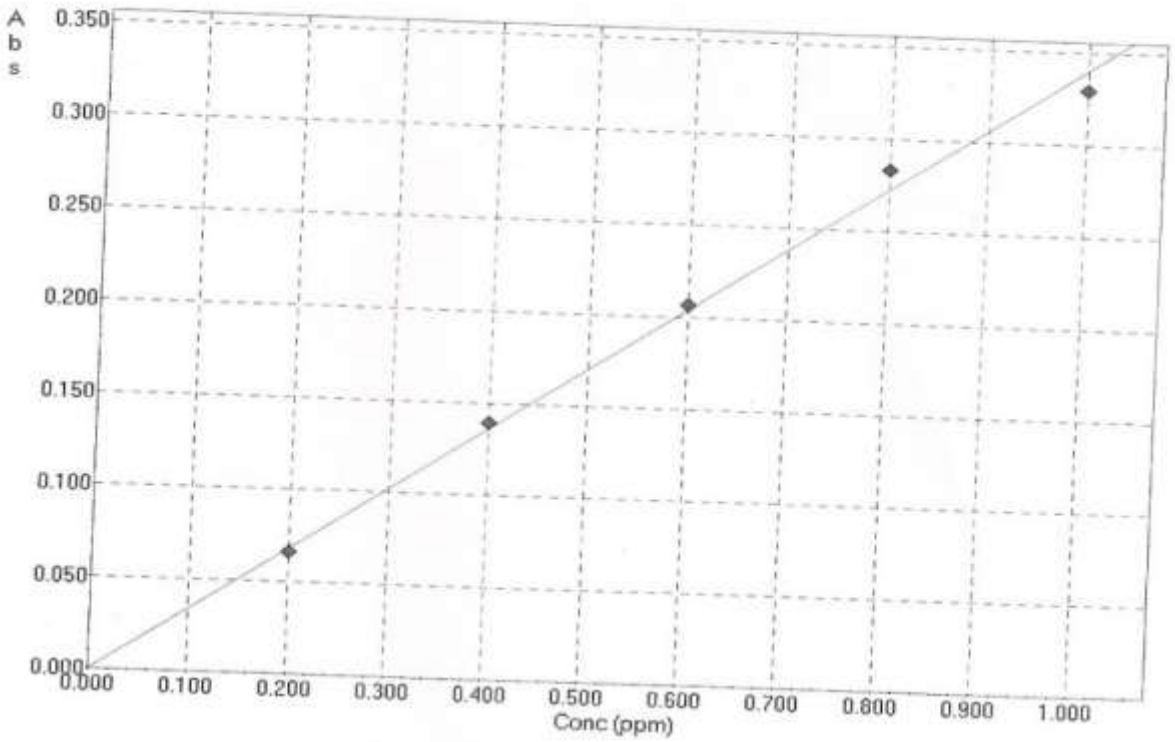


Abs=0.0397527Conc+ 0 r=0.9973

CONC
0.5000
1.0000
1.5000
2.0000
2.5000

ABS
0.0236
0.0452
0.0606
0.0761
0.0986

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

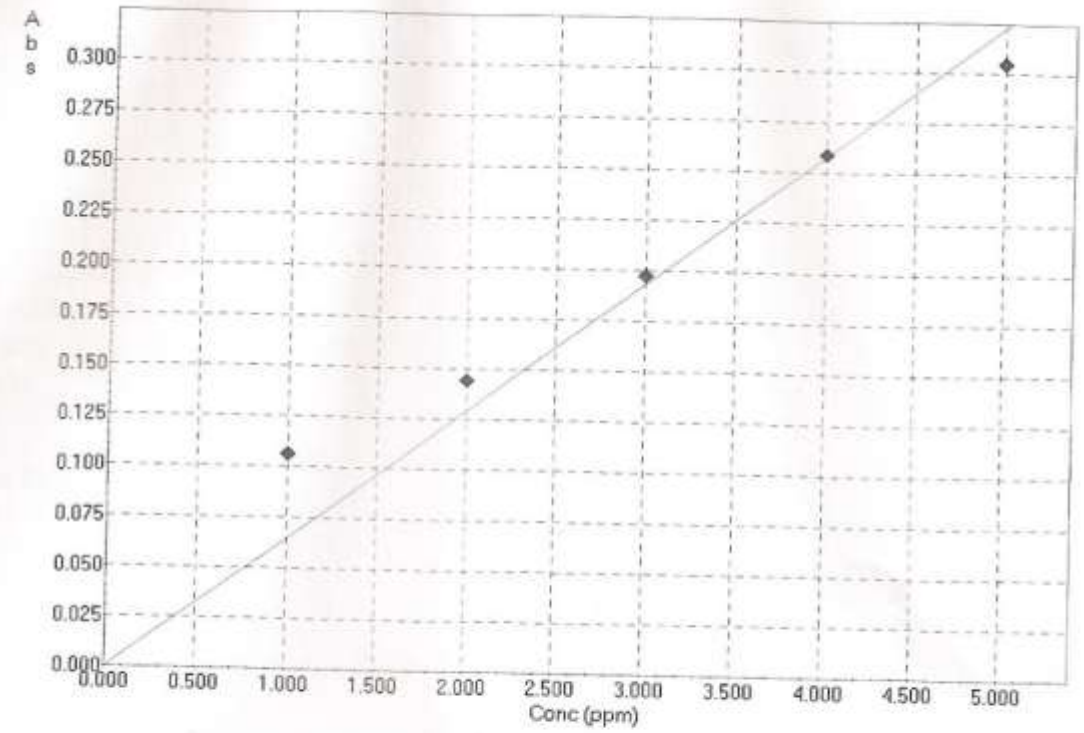


Abs=0.340291Conc+ 0 r=0.9973

CONC
0.2000
0.4000
0.6000
0.8000
1.0000

ABS
0.0660
0.1392
0.2066
0.2830
0.3294

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



Abs=0.0644709Conc+ 0 r=0.9974

CONC	ABS
1.0000	0.1061
2.0000	0.1443
3.0000	0.1975
4.0000	0.2588
5.0000	0.3047

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

APPENDIX 11a

Table I: Mean and Standard Deviation of Pb Concentration in Food Crops (mg/kg)

Site	Season	Maize		Spinach		Lettuce		Bitter leaf	
		DW	**WW**	**DW**	**WW**	**DW**	**WW**	**DW**	**WW**
A	Wet	4.45±0.07	13.65±0.01	31.51±0.01	97.71±0.01	19.42±0.02	99.10±0.01	11.74±0.01	41.09±0.09
	Dry	7.87±0.01	23.61±0.01	8.38±0.01	42.75±0.01	4.88±0.01	51.15±0.01	6.39±0.01	22.37±0.01
B	Wet	31.25±0.07	97.03±0.00	9.89±0.01	50.43±0.01	31.51±0.01	98.71±0.01	19.43±0.01	67.96±0.07
	Dry	1.87±0.01	5.79±0.01	9.38±0.01	47.84±0.00	2.55±0.07	26.27±0.02	6.89±0.01	24.09±0.01
C	Wet	4.46±0.01	13.83±0.01	2.27±0.01	11.58±0.01	5.16±0.01	54.08±0.01	8.87±0.01	31.51±0.70
	Dry	5.39±0.01	16.69±0.01	1.88±0.01	9.55±0.01	3.88±0.01	40.64±0.01	6.39±0.01	22.35±0.02
D	Wet	21.51±0.01	66.71±0.01	10.45±0.01	53.25±0.01	35.91±0.01	111.31±0.01	9.89±0.00	34.62±0.00
	Dry	1.45±0.07	4.66±0.01	2.38±0.01	12.09±0.01	1.00±0.01	10.51±0.01	5.39±0.01	18.84±0.01
E	Wet	8.42±0.03	26.17±0.01	4.05±0.01	20.65±0.01	11.75±0.01	123.26±0.01	11.74±0.00	41.09±0.00
	Dry	7.39±0.01	22.87±0.01	8.89±0..01	45.29±0.01	6.45±0.07	68.27±0.02	8.40±0.03	29.37±0.05

APPENDIX 11b

Table II: Mean and Standard Deviation of Cu Concentration in Food Crops (mg/kg)

Site	Season	Maize		Spinach		Lettuce		Bitter leaf	
		DW	**WW**	**DW**	**WW**	**DW**	**WW**	**DW**	**WW**
A	Wet	4.07±0.01	12.61±0.01	7.91±0.01	40.34±0.01	7.69±0.01	80.65±0.01	10.17±0.01	35.30±0.42
	Dry	3.01±0.01	9.05±0.07	6.64±0.01	33.81±0.01	8.60±0.01	90.20±0.00	11.69±0.01	40.88±0.42
B	Wet	2.03±0.01	6.30±0.01	6.17±0.01	31.46±0.01	5.66±0.01	59.33±0.01	10.91±0.01	38.21±0.01
	Dry	3.24±0.01	10.04±0.01	9.75±0.07	49.99±0.01	10.10±0.00	106.08±0.04	8.17±0.04	28.49±0.00
C	Wet	8.82±0.01	27.31±0.01	0.90±0.01	4.59±0.01	11.15±0.01	116.96±0.01	7.01±0.01	24.52±0.03
	Dry	5.28±0.01	16.37±0.01	7.91±0.01	40.35±0.01	6.79±0.01	71.21±0.02	7.44±0.07	25.87±0.01
D	Wet	3.16±0.01	9.75±0.07	7.68±0.01	39.17±0.01	2.95±0.01	30.88±0.01	7.91±0.01	27.64±0.06
	Dry	3.54±0.01	10.97±0.01	7.77±0.01	39.58±0.01	7.31±0.01	76.76±0.01	8.43±0.13	29.82±0.00
E	Wet	3.92±0.01	12.12±0.01	4.29±0.00	21.87±0.01	6.64±0.02	69.51±0.01	8.64±0.04	30.26±0.08
	Dry	4.85±0.07	15.20±0.01	5.58±0.01	28.40±0.01	7.47±0.01	78.37±0.05	9.23±0.04	32.65±0.34

APPENDIX 11c

Table III: Mean and Standard Deviation of Mn Concentration in Food Crops (mg/kg)

Site	Season	Maize		Spinach		Lettuce		Bitter leaf	
		DW	WW	DW	WW	DW	WW	DW	WW
A	Wet	0.78±0.00	2.41±0.01	2.75±0.01	13.98±0.01	6.79±0.01	71.19±0.01	23.81±0.01	83.32±0.03
	Dry	7.20±0.01	21.57±0.01	10.50±0.01	53.56±0.01	21.93±0.04	230.59±0.01	20.08±0.04	70.19±0.01
B	Wet	0.91±0.01	2.82±0.00	11.47±0.01	58.58±0.01	8.35±0.01	87.59±0.02	17.72±0.02	100.25±0.04
	Dry	3.64±0.01	11.29±0.01	11.64±0.01	59.37±0.01	20.99±0.02	220.45±0.07	57.08±0.03	199.8±0.13
C	Wet	4.35±0.07	13.33±0.01	6.79±0.01	34.59±0.01	12.39±0.01	130.00±0.01	11.73±0.00	41.06±0.00
	Dry	7.86±0.01	24.37±0.01	28.60±0.01	145.81±0.01	21.25±0.03	222.94±0.02	30.06±0.01	105.26±0.06
D	Wet	4.35±0.07	13.33±0.00	5.35±0.01	27.23±0.01	8.48±0.01	89.47±0.76	9.47±0.01	33.13±0.01
	Dry	9.36±0.01	28.98±0.01	13.77±0.01	70.18±0.01	9.84±0.01	103.22±0.01	21.35±0.01	74.70±0.01
E	Wet	3.66±0.01	11.31±0.01	8.99±0.00	45.84±0.01	10.13±0.01	106.38±0.03	8.04±0.06	28.29±0.01
	Dry	7.29±0.01	22.57±0.01	92.03±0.01	469.30±0.01	16.88±0.01	176.83±0.01	86.94±0.01	304.38±0.18

APPENDIX 11d

Table IV: Mean and Standard Deviation of Cd Concentration in Food Crops (mg/kg)

Site	Season	Maize		Spinach		Lettuce		Bitter leaf	
		DW	WW	DW	WW	DW	WW	DW	WW
A	Wet	0.63±0.01	1.95±0.01	0.31±0.00	1.59±0.01	1.14±0.05	12.29±0.01	0.73±0.01	2.56±0.05
	Dry	0.20±0.01	0.64±0.01	0.15±0.01	0.71±0.01	0.06±0.00	0.63±0.00	0.15±0.01	0.50±0.01
B	Wet	0.31±0.01	0.99±0.01	0.54±0.00	2.75±0.01	0.38±0.01	3.90±0.01	0.37±0.01	1.25±0.07
	Dry	0.30±0.01	0.90±0.01	0.03±0.01	0.15±0.01	0.36±0.01	3.69±0.01	0.32±0.00	1.15±0.04
C	Wet	0.76±0.01	2.32±0.00	0.53±0.01	2.72±0.01	0.91±0.01	9.58±0.03	0.43±0.00	1.51±0.00
	Dry	0.62±0.01	1.92±0.01	0.97±0.01	4.96±0.01	0.93±0.03	9.58±0.02	0.95±0.01	3.30±0.01
D	Wet	0.27±0.01	0.85±0.01	0.75±0.01	3.77±0.01	0.55±0.02	5.57±0.01	0.74±0.00	2.59±0.00
	Dry	0.68±0.01	2.15±0.07	0.59±0.01	3.02±0.01	0.49±0.02	5.26±0.01	0.39±0.01	1.36±0.04
E	Wet	1.02±0.01	3.13±0.00	0.97±0.02	4.86±0.01	1.05±0.02	11.14±0.01	0.32±0.00	1.12±0.00
	Dry	0.41±0.01	1.28±0.01	0.80±0.01	4.04±0.01	0.91±0.00	9.57±0.01	0.30±0.01	1.04±0.03

APPENDIX 11e

Table V: Mean and Standard Deviation of Cr Concentration in Food Crops (mg/kg)

Site	Season	Maize		Spinach		Lettuce		Bitter leaf	
		DW	**WW**	**DW**	**WW**	**DW**	**WW**	**DW**	**WW**
A	Wet	39.73±0.00	123.16±0.01	14.06±0.01	71.66±0.01	15.81±0.01	80.64±0.01	19.31±0.01	67.62±0.00
	Dry	6.04±0.01	18.11±0.01	9.07±0.01	46.22±0.01	12.86±0.02	134.76±0.06	8.56±0.01	29.87±0.09
B	Wet	13.51±0.01	41.91±0.01	11.77±0.01	60.03±0.01	8.25±0.01	86.63±0.01	36.21±0.01	126.78±0.01
	Dry	8.56±0.01	26.51±0.01	6.80±0.01	34.62±0.02	5.68±0.15	58.69±0.29	0.45±0.07	1.73±0.04
C	Wet	26.36±0.00	81.72±0.01	1.76±0.01	8.98±0.01	28.12±0.01	87.15±0.01	46.77±0.01	163.76±0.04
	Dry	8.05±0.01	24.97±0.01	4.29±0.01	21.80±0.03	8.06±0.01	84.55±0.04	9.30±0.00	32.57±0.02
D	Wet	32.17±0.00	99.71±0.01	24.57±0.72	122.71±0.01	39.20±0.01	121.49±0.01	46.08±0.00	161.24±0.06
	Dry	9.07±0.01	28.08±0.01	1.26±0.01	6.43±0.01	9.57±0.01	100.39±0.01	8.35±0.07	29.07±0.02
E	Wet	20.56±0.01	63.72±0.01	15.28±0.01	77.92±0.01	25.81±0.01	271.11±0.01	53.92±0.01	188.71±0.01
	Dry	3.53±0.01	10.91±0.01	6.37±0.11	32.09±0.01	7.07±0.04	73.94±0.03	13.59±0.01	47.56±0.04

APPENDIX11f

Table VI: Mean and Standard Deviation of Fe Concentration in Food Crops (mg/kg)

Site	Season	Maize		Spinach		Lettuce		Bitter leaf	
		DW	WW	DW	WW	DW	WW	DW	WW
A	Wet	28.07±0.01	86.93±0.08	120.03±0.01	612.15±0.07	94.26±0.01	989.63±0.01	35.11±0.16	123.28±0.01
	Dry	14.61±0.01	43.84±0.01	173.12±0.01	882.87±0.01	238.58±0.03	954.89±0.01	83.49±0.26	291.66±0.15
B	Wet	12.55±0.0.7	39.07±0.01	156.40±0.01	797.60±0.01	71.05±0.00	746.07±0.05	70.20±0.01	245.75±0.07
	Dry	23.90±0.01	74.06±0.01	108.75±0.01	554.73±0.23	89.21±0.02	936.50±0.00	131.47±0.57	458.72±0.03
C	Wet	1.95±0.07	6.20±0.00	88.82±0.01	452.88±0.01	277.82±0.01	917.02±0.01	80.72±0.05	284.12±2.10
	Dry	24.98±0.01	74.41±0.01	149.26±0.05	761.06±0.06	83.62±0.03	877.85±0.07	92.98±0.11	328.46±0.76
D	Wet	1.16±0.01	3.57±0.01	204.82±0.01	946.59±0.01	174.71±0.01	891.03±0.01	92.46±0.06	323.69±0.05
	Dry	26.06±0.01	80.79±0.01	197.74±0.01	908.41±0.01	79.28±0.03	832.27±0.05	86.10±0.01	301.41±0.13
E	Wet	44.43±0.01	137.75±0.07	39.57±0.01	201.76±0.01	256.07±0.04	968.44±0.03	65.80±0.14	230.66±0.01
	Dry	33.67±0.01	104.34±0.01	105.75±0.02	794.21±0.01	60.07±0.05	630.36±0.06	51.71±0.15	181.56±0.31

APPENDIX 11g

Table VII: Mean and Standard Deviation of Metals Concentration in Raw Water and Treated Water (mg/L)

Site	Season	Pb	Cu	Mn	Cd	Cr	Fe
A	Wet	0.06±0.01	0.03±0.00	0.05±0.01	0.01±0.01	0.69±0.02	0.46±0.01
	Dry	0.02±0.00	0.01±0.00	0.14±0.01	0.00±0.00	0.12±0.01	2.08±0.01
B	Wet	0.20±0.03	0.06±0.01	0.06±0.01	0.01±0.00	0.05±0.01	0.39±0.01
	Dry	0.08±0.01	0.01±0.00	0.08±0.01	0.01±0.00	0.04±0.01	1.15±0.07
C	Wet	0.05±0.01	0.07±0.00	0.04±0.02	0.00±0.00	0.83±0.04	1.85±0.00
	Dry	0.07±0.00	0.03±0.01	0.14±0.06	0.01±0.00	0.02±0.00	1.99±0.01
D	Wet	0.24±0.07	0.06±0.01	0.05±0.01	0.00±0.00	0.61±0.02	0.77±0.01
	Dry	0.08±0.00	0.03±0.01	0.14±0.06	0.00±0.00	0.07±0.00	1.96±0.01
E	Wet	0.66±0.01	0.01±0.00	0.07±0.01	0.03±0.01	0.73±0.04	1.65±0.06
	Dry	0.01±0.00	0.01±0.00	0.09±0.01	0.01±0.00	0.10±0.01	0.41±0.01
F(treated water)	Wet	0.03±0.00	0.08±0.01	0.04±0.01	0.02±0.01	0.03±0.00	0.01±0.00
	Dry	0.10±0.01	0.01±0.00	0.04±0.01	0.02±0.01	0.03±0.00	0.01±0.00