SEASONAL CONCENTRATION OF SOME HEAVY METALS IN VEGETABLE CROPS AND ASSOCIATED SOILS ALONG HUNKUYI ROAD, ZARIA, NIGERIA

BY

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ABSTRACT

This study was conducted to analyze the seasonal concentration of some heavy metals in selected vegetable crops and soils along Hunkuyi road. Metal concentrations were determined using Atomic Absorption Spectrophotometer (AAS) after wet digestion. From the result obtained, metal concentrations were of the range: Cu (0.9-22.4mg/kg), Pb (9.1-336mg/kg), Cd (0.4-3.1mg/kg), Zn (48.7-107 mg/kg), and Cr (1.0-172mg/kg). The values were found to be above the value recommended by FAO/WHO except for Cu and Zn which were below the maximum recommended limit for vegetable crops. There was a reduction generally in metal levels (except for Pb and Cr) in the samples collected during rainy season when compared to samples collected during dry season. There was an observed variation of metal levels in the various crops from one farmland to another which could be attributed to soil factors and root morphology of the vegetables crops. The difference in Cu, Cd and Cr levels in cabbage, onion bulbs, tomato fruits and farmland soils respectively between dry and wet seasons was not statistically significant($p>0.05$).The difference in Pb concentration of onion bulbs, cabbage and farmland soils between dry and wet seasons was statistically significant($p>0.05$) while the difference in Pb concentration of tomato fruits between dry and wet season was statistically significant ($P<0.05$) with the Pb levels of the wet season being significantly higher than that of the dry season. The difference in Zn concentration of farmland soil, onion bulb and tomato fruits between dry and wet seasons was not statistically significant ($P>0.05$). On the other hand, the difference in concentration of Zn in cabbage between dry and wet seasons was statistically significant ($P<0.05$) with the concentration in wet season significantly higher than the dry season.

CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health (Sprynskyy *et al*., 2007). The absorption by plant roots is one of the main routes of entrance of heavy metals in the food chain (Jorda, 2006). Absorption and accumulation of heavy metals in plant tissue depend upon many factors which include temperature, moisture, organic matter, pH and nutrient availability. Heavy metal accumulation in plants depends upon plant species and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil to plant transfer factors of the metals (Khan *et al*., 2008). For example, elevated Pb levels in soils may decrease soil productivity, and a very low Pb concentration may inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short roots (Bhattacharyya *et al*., 2008). Heavy metals are potentially toxic and phytotoxicity for plants result in chlorosis, weak plant growth, yield depression, and may even be accompanied by reduced nutrient uptake, disorders in plant metabolism and reduced ability to fixate molecular nitrogen in leguminous plants (Guala *et al*., 2010). Seed germination was found to be gradually delayed in the presence of increasing concentration of lead and have been due to prolonged incubation of the seeds that resulted from the neutralization of the toxic effects of lead by some mechanisms e.g. leaching, chelation, metal binding and/or accumulation by microorganism (Ashraf and Ali, 2008) .The plant uptake of heavy metals from soils at high concentrations may result in a great health risk taking into consideration food-chain implications.

Utilization of vegetable crops contaminated with heavy metals is a major food chain route for human exposure. The food plants whose system of monitoring is based on exhaustive and continuous cultivation, have great capacity of absorbing elements from soils. The cultivation of such plants in contaminated soil represents a potential risk since the vegetable tissues can accumulate heavy metals (Jordao et al., 2006).

Vegetables contain essential nutrients and trace elements (Abdullah and Chmielnicka, 1990). They constitute an important part of human diet since they contain carbohydrates, proteins, as well as vitamins, minerals, trace elements and fibers, and also have beneficial anti oxidant properties (Dastane, 1987). They did not constitute a major part of the diet not until recently. However, their consumption is increasing gradually, particularly among the urban community. This is due to increased awareness on food value of vegetables, as a result of exposure to other cultures and acquiring proper education (Fisseha , 2002). Wastewater irrigation results in significant mixing of heavy metal content of agricultural land (Mapanda *et al.,* 2005). The major cause is the waterways through which heavy metals are leached out of the soil and are taken by the vegetation. If plants decay, these toxic metals are redistributed and as a consequence their enrichment in the agricultural soil occurs. Bioaccumulation, geoaccumulation and biomagnifications may result because of entrance of these heavy metals into the ecosystem. Thus long term wastewater irrigation leads to build up of heavy metals in soils and food crops (Khan *et al.,* 2008). Rapid industrialization and urbanization with insufficient environmental monitoring planning often results in discharging of the industrial and sewage waste into rivers and lakes which lead to gradual pollution of our water resources. Many times such wastewater is drained to the agricultural land where the polluted water is used for irrigating crops including vegetables. Thus, polluted effluent water is found to be rich not only in organic matter and nutrients but also

in heavy metals like lead, chromium, cadmium, nickel, cobalt and others that finally get to the soil of agricultural farmlands. This leads to food chain contamination as crops and vegetables absorb them from the soil. Heavy metals are not easily biodegradable and as such lead to their accumulation in human vital organs causing varying degrees of illness on acute and chronic exposure (Ward *et al*., 1995). Heavy metal contamination of vegetables cannot be underestimated as these foodstuffs are important components of human diet. Long term weathering and soil mineralization may lead to the accumulation of heavy metals in agricultural soils and plants. Food safety issues and potential health risks make this as one of the most serious environmental concerns (Cui *et al*. 2004). Vegetables accumulate heavy metals in their edible and non edible parts. Some of these heavy metals such as As, Cd, Hg, Pb and Se are not essential for plants growth, since they do not perform any known physiological function in plants. Others such as Co, Cu, Fe, Mn, Mo, Ni and Zn are essential elements required for normal growth and metabolism of plants, but these elements can easily lead to poisoning when their concentrations are greater than optimal values (Garrido et al., 2002; Rascio and Izzo, 2011). With the increasing awareness of risk assessment of heavy metal in food crops, evaluation of concentration of these metals in vegetable is therefore critical as it gives information in nutritional planning and provides data for epidemiological studies (Bruce and Bergstrom, 1983). Hence, this present work deals with the quantification of heavy metal concentrations in soil and vegetables grown along Hunkuyi road, Zaria, Nigeria.

1.2 Justification

Irrigation in Hunkuyi involves the application of stream water that flows through residential areas to irrigate vegetable crops, which are mostly consumed by the city dwellers. The use of these water sources for irrigation in addition to the exposure of the land to exhaust discharge from vehicles

that are ever on the increase in the city, constitutes the risk of the soils of these irrigated lands to be contaminated with both organic and inorganic pollutants. A study of heavy metals by road side soils and associated crops is critical in assessing the potential environmental impacts of automobile emission on the soil and associated crops. Emission from heavy traffic on roads contains lead cadmium, zinc and nickel, which are present in fuel as anti-knock agents (Suzuki *et al*., 2008; Atayese *et al*., 2009). The deposition of vehicle derived metal and the relocation of metals deposited on road surface by air and runoff water have led to contamination of soil (Viard *et al*., 2004; Nabuloa *et al*., 2006; Ogbonna and Okezie, 2011). Contamination of soils by heavy metals is the most serious environmental problem and has significant implications for human health (Moore *et al*., 2009). Soil to plant transfer is one of the key processes of human exposure to heavy through the food chain. Heavy metals uptake via the roots from contaminated soils and direct deposition of contaminants from the atmosphere onto plant surfaces can lead to plant contamination by heavy metal (Zhuang *et al*., 2009).

Plants undoubtedly absorb heavy metals from the soil through their root. This absorption is influenced by among other factors the pH of the soil (Anderson and Nibon, 1974). The soil's heavy metals retaining capacity and availability could be attributed not only to differences in acidity, but also to the organic matter content (Jaakkola and Ylaranta, 1976). These researchers showed that a large amount of organic matter in the soil limited the availability of cadmium to plants. Organic matter in the soil forms the strongest metal complexes and hence retains the metal more firmly.

Some trace metals when present in high concentration in food materials can lead to the formation of stable bonds in some active sites of some enzymes (Giddings, 1973). This chemicals affinity is the basis of metal toxicity in man. The attachment to an enzyme of this metal impairs the normal metabolic roles of such enzyme (Giddings, 1973). The most important mechanism of toxic action is through the poisoning of enzyme. The metals, notably copper, mercury and silver, have great

affinity for amine and sulphdryl groups which are doubtless reactive sites of many enzymes, and readily chelated by organic molecules (Bowen, 1979).

Against the background information enumerated above, with lack of published data on the heavy metal contamination of vegetable crops in Hunkuyi, is this work initiated to x-ray the levels of contamination of vegetable crops grown along Hunkuyi road Zaria, Nigeria.

1.3 Aim and objectives

The aim of this research is to assess level of trace metals (Cu, Cr, Zn, Cd, and Pb) in the vegetables (tomato, onion, and cabbage) and associated soils along Hunkuyi road Zaria. This shall be achieved through the following objectives:

i. to investigate the extent of heavy metals contamination in vegetable crops.
ii. to investigate the extent of heavy metals contamination in soils.
iii. to compare the levels of heavy metals obtained in vegetables with those of the Internationally allowed limits.

iii to carry out the physicochemical parameter of soil.

CHAPTER TWO

LITERATURE REVIEW

2.1 Occurrence and emission of heavy metals

The term “heavy metal” refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). “Heavy metal” is a generic term, which applies to the group of metals and metalloids with atomic density greater than 4g/cm^3, or 5 times or more, greater than the density of water (Huton and Symon, 1986; Battarbee *et al.,* 1988; Nriagu and Pacyna 1988; Nriagu, 1989; Garbarino *et al*., 1995; Hawkes, 1997). Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr) copper (Cu) iron (Fe), and the platinum(Pt) group.

They occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or decomposed. To a small extent, they enter the body system through food, air, and water and bio-accumulate over a period of time. (Lenntech, 2004; UNEP/GPA, 2004). They can be released into the environment by both natural and anthropogenic sources. Anthropogenic sources of heavy metal contamination are widespread. Agricultural activities such as pesticide and herbicide application, contaminated irrigation water, use of municipal waste for fertilization (Alloway and Jackson, 1991) and even mineral fertilizer containing traces of heavy metals (Gray *et al*., 1999) and major sources of enrichment. Direct deposition of waste by man on land (Merian

et al., 2004), mining activities, use of lead as anti-nock in gasoline, traffic emission (Nriagu, 1990); building materials like paints, cigarette smoking, metallurgy and smelting, aerosol cans and sewage discharge, among others, are all anthropogenic sources of heavy metals. The atmosphere, in turn, may be loaded with heavy metals by the disintegration of applied waste materials which gradually release the heavy metals in them. Agbenin (2002) however, observed Pb accumulation in a Nigerian soil as a result of long-term cultivation. Anguelov and Anguelova (2009) reported a significant increase in the concentration of Zn in pasture fields as a result of manure application. Similarly, soils of the Nigerian savannah, Agbenin (2002) reported addition of some trace metals through farmyard and mineral fertilizer application. Some reseachers (Sorme and Lagerkvist, 2002; Iijima *et al*., 2007) identified heavy metal emissions from several sources such as wearing of automobile tyre and brake linings in the traffic , roofs and food remnants in the residential as well as other domestic by-products as refuse. Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to a typically high bio-availability.

2.2 Heavy metals in soil and vegetables

It has been reported that sewage, industrial effluents and municipal waste water discharged into rivers or stream contain appreciable amount of major essential plant nutrients and therefore the fertility levels of soil are improved considerably under sewage irrigation of farmlands (Rajesh *et al*., 2004). However, studies on the water of Vasai Creek, Maharashtra, revealed that the presences of toxic heavy metals like Fe, 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 of contaminating crops growing under such irrigation.

Also, in several studies, the concentration of Cd in soil has been reported to be high (Torabian and Baghuri, 1996). The highest concentration of Cd in plant has been reported in Taiwan in brown rice contaminated soil (Chen *et al*., 1994). In Taiwan more than 800acres of land have been contaminated with industrial effluent water.

Delibacak *et al*. (2002) reported the levels of trace metal in vegetables (tomato, pepper, purslane,), fruits (apple, plum, pomegranate, walnut, watermelon, peach, cherry, grape, orange) and leafy samples, collected from 12 different places being irrigated with Gediz River of the Aegean Region. The amount of trace elements (Fe, Mn, Zn, Cu, and B) and heavy metals (Co, Ni, Cr, Pb, Cd) were measured in samples and compared with permissible limits of the metals. Significant levels of trace metals were recorded in the vegetables, fruits and leafy samples. However, the vegetables and fruits contained more trace elements and metals than the non edible parts.

In order to evaluate the contribution of vegetables to daily intake of Cd and Pb in Spain six essential elements, Cd and Pb were determined in some horticultural species cultivated in greenhouse boarders by atomic absorption spectrophotometry (Zuera-Cosano *et al*., 2006). The study found that if the mean levels of Cd and Pb (0.029 mg kg^{-1} and 0.0221 mg kg^{-1} respectively) were taken into account, the daily intake contribution of these metals will be 1.4 g day^{-1} for Cd and 11 g day^{-1} for Pb.

Similarly, in a study of Cd and trace elements (Fe, Cu, Mn, Zn) in spices commonly consumed in Turkey (Faruk, *et al*., 2006), 15 samples of all spices (*Pimenta dioica* (L.) Merrill), blackpepper (*Piper nigrum* L.), cinnamon (*Cinnamomum zeylanicum* L.), nutmeg (*Myristica fragrans* Houtten),clove (*Szygium aromaticum* L. Merrill), galangal (*Alpina officinarum* Hance), cardamom (*Elettaria cardamomum* (L.) Maton), ginger (*Zingiber officinale* Roscoe) and turmeric (*Curcuma longa* L.) were analysed. The results showed that Cd in the samples ranged from 13 mg kg^{-1} in clove to 206 mg kg^{-1} in blackpepper; Fe varied

between 28 mg kg^{-1} in nutmeg to 374 mg kg^{-1} in blackpepper; Cu ranged from 3.0 – 11 mg kg^{-1}, Mn ranged from 10 mg kg^{-1} in turmeric to 355 mg kg^{-1} in clove samples and zinc of the samples ranged between 4 – 25 mg kg^{-1} with cardamom containing the highest. Their results showed that the value of all metals studied were below the FAO/WHO permissible limits.

Lokeshwari and Chandrappa (2006) also assessed the extent of Fe, Zn, Cu, Ni, Cr, Pb and Cd contamination in vegetation due to irrigation with sewage-fed Bellandur lake water in India on agricultural land. The results showed the presence of some of the heavy metals in rice and vegetables, beyond the limits of India permissible limits. Metals transfer factors from soil to vegetation were also reported to be significantly high for Zn, Cu, Pb and Cd. Comparing the results of heavy metals in water, soil and vegetation with their respective natural levels, it was observed that the impact of lake water on vegetation is more than the soil. Presently, there is a growing public concern in Zimbabwe over the cultivation of vegetables on soils amended with sewage sludge or irrigated with admixtures of sewage and sewage sludge. Excessive accumulation of heavy metals in agricultural soils may not only result in environmental contamination, but lead to elevated heavy metal uptake by crops, which may affect food quality and safety. Based on this finding, Muchuweti *et al*. (2006) investigated heavy metal concentrations in crops irrigated with sewage sludge and sewage/sewage sludge admixtures at Firle Municipal Farm in Harare. The results showed that Tsunga leaves contained 3.68 mg kg^{-1} Cd, over 18 times the permissible level by the European Union standards (0.2 mg kg^{-1}); Cu was 111 mg kg^{-1}, 5 times the European Union Standard (20 mg kg^{-1}); concentrations of Pb was 6.77 mg kg^{-1}, over 22 times the permissible levels allowed by both EU standards and UK guidelines (0.3 mg kg^{-1}); Zn concentration was 221 mg kg^{-1}, over 4 times the guideline value (50 mg kg^{-1}). The other plants (beans, maize, peppers and sugarcane) also contained concentrations of heavy metals above the permissible levels.

The impact of wastewater irrigation on heavy metal content of Beta vulgaris (Palak); a highly nutritious leaf that is widely cultivated and consumed in urban India was investigated by Rajesh *et al*. (2004). Samples of irrigated water, soil and the edible portion of Palak (Beta Vulgaris L. var All green HI) were collected and analysed for Cd, Cu, Zn, Pb, Cr, Mn and Ni. Heavy metals concentrations in water and soil were below the internationally (WHO) recommended maximum permissible limits set for agricultural use for all heavy metals except Cd at all sites. Furthermore, the edible portion of B. vulgaris, contained Cd levels that was higher than permissible limits during summer, whereas Pb and Ni concentrations were higher in both summer and winter seasons. The study concluded that the use of treated and untreated wastewater for irrigation had increased the contamination of Cd, Pb and Ni in edible portion of vegetables causing potential health risk in the long term for consumers.

Similarly, in a field experiment carried out by Jamali *et al*. (2007) to predict the uptake of Cd, Cu, Cr, Ni, Pb and Zn by different vegetables grown on agricultural soil irrigated with untreated domestic wastewater and sewage sludge found high levels of heavy metals. The study concluded that continuous irrigation of agricultural land with wastewater and solid sewage sludge increased consumer health risk in the long term.

2.3 Heavy metals in soil and vegetables in Nigeria

Vegetables constitute the lowest source of essential trace elements for the majority of people in developing nation such as Nigeria. Iyaka (2007) in his study of Cu and Zn contents in some selected samples of vegetables found in North-central zone of Nigeria showed that Cu concentration was 5mgkg^{-1} in pepper, 4mgkg^{-1} in onion and 5.5mgkg^{-1} in tomato, while the Zn levels were 13.5mgkg^{-1} in pepper, 16.75mgkg^{-1} in onion and 15.5mgkg^{-1} in tomato. He concluded that Cu and Zn contents obtained showed that vegetables from this part of the globe could serve as good dietary sources for essential trace metals, and the levels were within safety baseline content for human consumption.

Adeyeye (2005) assessed the levels of Zn, Mn, Co, Se, Cu, Mo, Cr, Fe, Al, Pb and Cd in plants organs (buds, flowers, fruits, seeds, leaves, stems, root, cobs, styles, shaft, grains and effloresences) and underlying soils of three Fadama farms located in Ifaki-Ekiti, Ado-Ekiti and Ikere-Ekiti of Ekiti State, Nigeria at 0-15cm topsoil. The findings revealed common trend in Zn concentration. Only Zn and Fe were mostly concentrated in the plant organs with Mn in very few plants. Also, the index of bioaccumulation (ratio in plant/soil) were recorded for only Zn and Fe with the degree of accumulation ranging from medium to intensive (0.87 – 1.34) in Fe but only intensive (1.41 – 4.42) for Zn.

Audu and Lawal (2005) also investigated the variation of metal contents of plants in irrigated vegetable garden sites in Kano metropolis. The relative abundance of metals in the vegetables analysed were found to follow the sequence Fe > Zn > Mn > Cu > Ni > Pb > Co > Cr. Reduction of metal levels ranging from 8.25% Fe in onions to 45.19% Ni in okra were recorded in rainy season samples over those of the dry season. Also the vegetables analysed generally show higher retention capacity for essential metals (Zn, Mn and Cu) than for the toxic ones (Ni, Pb, Co and Cr).

Similarly, Hart *et al*. (2005) studied the concentration of trace metals in crops harvested in some oil prospecting location in River state, Nigeria and found mean concentration of Pb to be $1.1 mgkg^{-1}$ in cocoyam, and $9.1 mgkg^{-1}$ in okro among other things. Their investigation concluded that the results reflect higher concentrations of metals in crops from the industrialized locations, with green vegetable, having the highest uptake than other crops. This finding gives cause for concern, particularly as trace metals are bio-accumulative in the system and pose a serious health risk to man and animals.

2.4 Toxicity of heavy metals

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues (Sobha *et al*., 2007). Chronic level ingestion of toxic metals has undesirable effects on humans and the associated harmful impacts become perceptible only after several years of exposure (Khan *et al*., 2008). The biotoxic effects of heavy metals refer to the harmful effects of heavy metals to the body when consumed above the bio-recommended limits. Although individual metals exhibit specific signs of their toxicity. the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminium poisoning: gastrointestinal (GI) disorders, diarrhoea, stomatitis, tremor, hemoglobinuria causing a rust–red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled. The nature of effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic.

2.4.1 Cadmium

Cadmium is a well known heavy metal toxicant with a specific gravity 8.65 times greater than water. The target organs for Cd toxicity have been identified as liver, placenta, kidneys, lungs, brain and bones (Sobha *et al*., 2007). Depending on the severity of exposure, the symptoms of effects include nausea, vomiting abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary odema and death. Pulmonary effects (emphysema, bronchiolitis and alveolitis) and renal effects may occur following subchronic inhalation exposure to cadmium and its compounds (Duruibe *et al*., 2007). The Itai-itai disease in Japan brought the dangers of environmental Cd to world attention. Cd has been associated to a lesser or greater extent with many clinical conditions including anosmia, cardiac failure cancers, cerebrovascular infarction, emphysema, osteoporosis, proteinuria cataract formation in the eyes. Yet, it has been difficult to tie down obvious links of environmental exposures with morbidity and mortality (Lalor, 2008).

2.4.2 Zinc

Zinc is considered to be relatively less-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and reproduction. The clinical signs of zinc toxicosis have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anemia (Duruibe *et al*., 2007).

2.4.3 Copper

Copper is an essential element in mammalian nutrition as a component of metalloenzymes in which it acts as an electron donor or acceptor. Conversely, exposure to high levels of Cu can result in a number of adverse health effects. Exposure of humans to excess Cu occurs primarily from the consumption of food and drinking water. Acute Cu toxicity is generally associated with accidental ingestion; however, some members of the population may be more susceptible to the adverse effects of high Cu intake due to genetic predisposition or disease (Stern *et al*., 2007). Excessive human intake of Cu may lead to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also occur.

2.4.4 Lead

Lead is physiologically and neurologically toxic to humans. Acute Pb poisoning may results in a

dysfunction in the kidney, reproduction system, liver and brain resulting in sickness and death (Odum, 2000). Pb poses a threat even at extremely low concentrations (Kazemipour et al., 2008). A notably

serious effect of lead toxicity is its teratogenic effect. Lead poisoning also causes inhibition of the synthesis of haemoglobin; cardiovascular system and acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS).

Other chronic effects include anemia, fatigue, gastrointestinal problems and anoxia. Lead can cause difficulties in pregnancy such as high blood pressure, muscle and joint pain (Odun, 2000). Other effects include damage to the gastrointestinal tract (GIT) and urinary tract resulting in bloody urine, neurological disorder and can cause severe and permanent brain damage. While inorganic forms of lead, typically affect the CNS, PNS, GIT and other biosystems, organic forms predominantly affect the CNS. Lead affects children particularly within the range of 2-3 years old by leading to the poor development of the grey matter of the brain, thereby resulting in poor intelligence quotient (IQ). Its absorption in the body is enhanced by Ca and Zn deficiencies (Duruibe *et al*., 2007).

2.4.5 Chromium

Chromium is present in human tissues in variable concentrations and its deficiency is characterised by disturbance in glucose, lipid and protein metabolism (Bae *et al*., 2000). It also plays an essential role in enhancing the activity of insulin in human body. However, its compounds are well known toxins particularly Cr (vi) which, due to its oxidising potentials, easily permeates biological membranes and can also cause renal damage and various forms of cancer (Bae *et al*., 2000).

2.5 Chemistry of toxicity

The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes. Heavy metals have a great affinity for amine and sulphryl (-SH) groups which are doubtless reactive sites of many enzymes, and readily chelated by organic molecules (Bowen, 1979). When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}) and combine with the body's

biomolecules such as proteins and enzymes to form strong and stable chemical bonds. According to Ogwuegbu and Ijioma, (2003), the most toxic forms of these metals in their ionic species are the most stable oxidation states. For example, Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+} in their most stable oxidation states, form very stable biotoxic compounds with the body's bio-molecules, which become difficult to be dissociated, due to their bio-stabilities, during extraction from the body by medical detoxification therapy

2.6 Principle of flame atomic absorption spectrometry

Flame atomic absorption spectrometry (FAAS) was proposed and developed by a team of Australian Chemist led by Alan Walsh during 1950s. 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 atoms become excited. The 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).

In practice, air is blown through a venturi, and the sample solution is drawn into the air stream as a spray of fine droplets. A large fraction (~ 90%) of the drops falls out of the air stream in the cloud chamber but the very small ones remain suspended (Goulden, 1978). In the flame the sample vaporizes and forms a cloud of atoms in the gaseous state. Radiation of a characteristic wavelength corresponding to the radiation (energy) required to raise the atoms of the particular element being analyzed from their ground state to an excited state from a hollow cathode discharge lamp is passed through the flame. The decrease in intensity is measured, using a monochromator and detector system. This decrease is related to the concentration of the element in the sample solution.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Treatment of Glass-wares, Sample Containers and Crucibles

Glassware, crucibles and plastic containers were washed with liquid soap, rinsed with distilled water and soaked in 10% HNO_3 for 24h; cleaned with distilled – deionized water.

3.1.2 The Study Area

The research was conducted on the irrigated vegetable crops and soils along Hunkuyi road in Zaria metropolis. The study area is located in Kudan Local Government Area of Kaduna State, covering an area extending between latititude $11^0$06′N and $11^0$22′N and longitude $7^0$25′E and $7^0$55′E. Figure 3.1.2 shows the location of Kudan Local Government Area in the map of Kaduna State, Nigeria.

3.1.3 Description of Sampling Sites

The sampling sites are farmlands that spread around a river bank along Hunkuyi road. The sites are located at both sides of the road. It is not a residential area but located before a village called Ungwan Mijinyawa. Figure 3.1.3 shows the location of the sampling sites.

3.1.4 Sample Collection and Pre-Treatment

Samples were collected twice in the year 2012 from three different farms: 1, 2 and 3. The first round of sampling was carried out in March towards the end of the dry season while the second round was in September at the peak of the rainy season. Three different vegetable samples namely: cabbage, onion bulb and tomato fruits were collected in each of the farms during dry and wet seasons. Also three different associated soil samples from the three different farms were collected during each season.

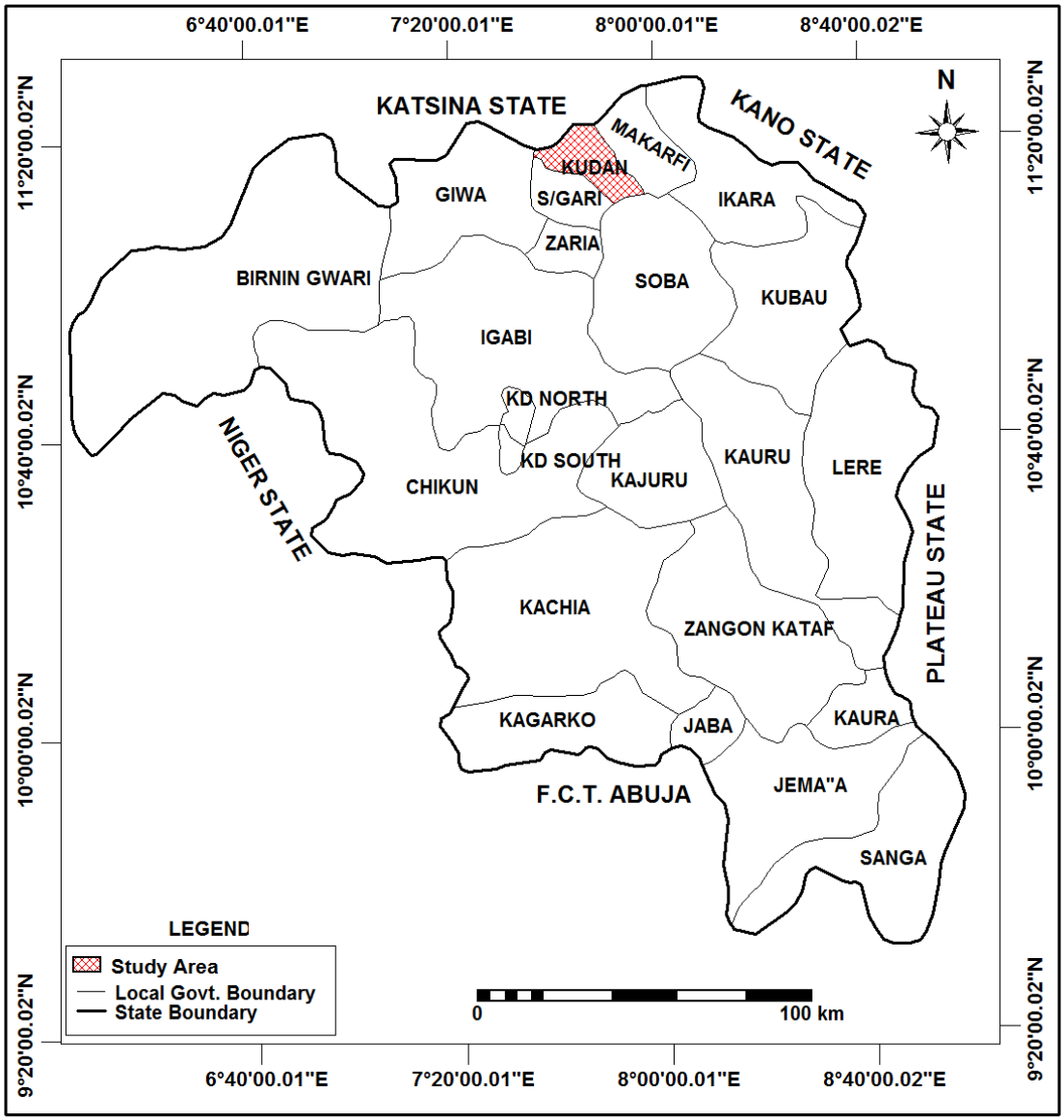

Figure 3.1: Map of Kaduna State showing Kudan Local Government Area: The study Area
Source:Adopted and modified from admnistrative map of Kaduna State.

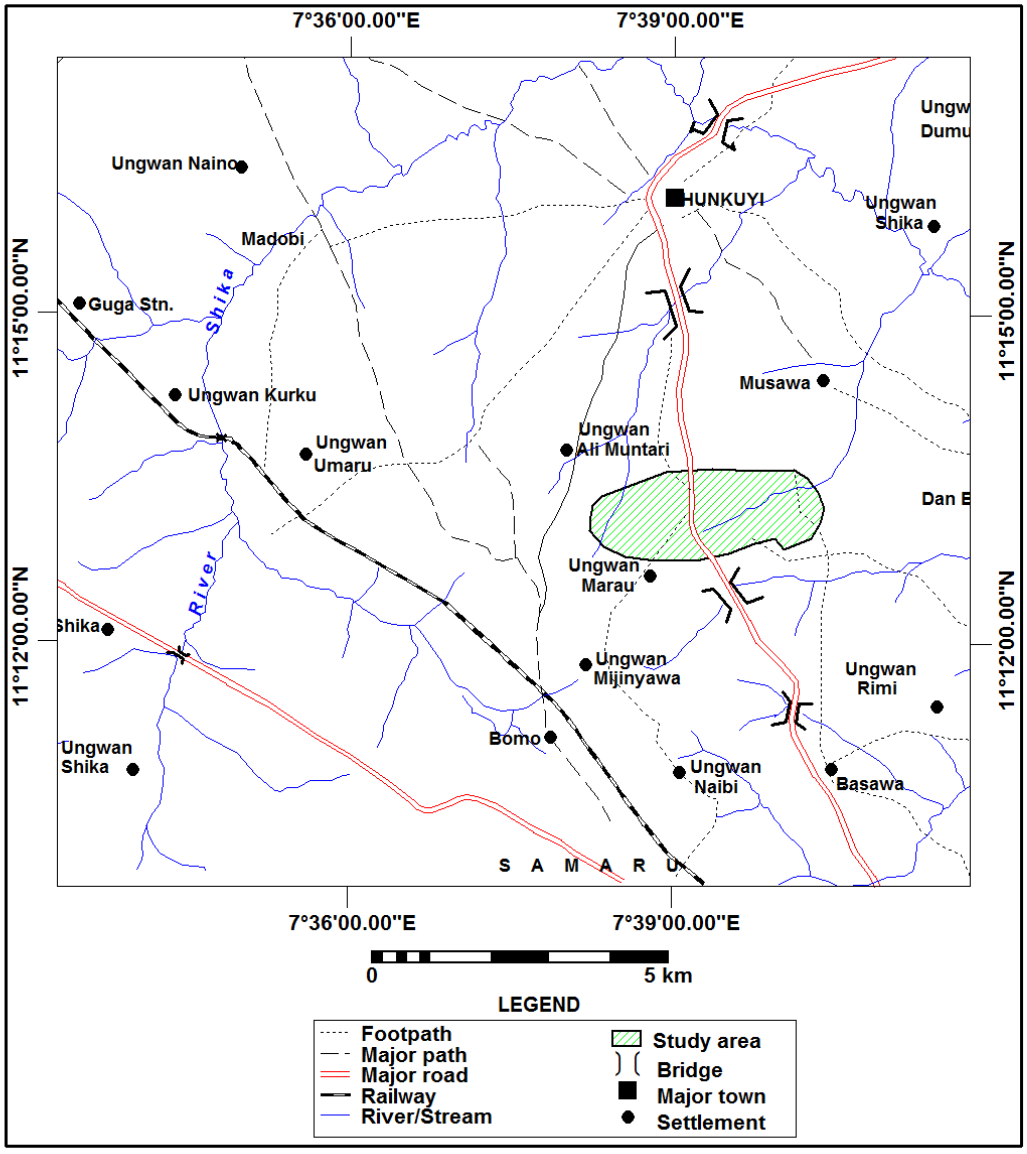

Figure 3.2 Location of sampling sites
Source: Adopted and modified from Topo Map of Zaria sheet 102 S.W.

3.1.4.1 **Soil Sample**

Soil samples were collected within the rooting depth (0 – 15cm) of the plants at a time when the crop was harvested. Six sub-samples of 20 g each were collected at a sampling site. The sub-samples for each sampling location were then placed in a cellophane bag (Bamgbose, *et al*., 2000), labeled and taken to the laboratory for processing/pre-treatment and analysis.

Soil samples were processed according to Awofolu (2005). Soil sub-samples from each site were mixed together to make a composite sample representative of a particular site. The composite samples were then homogenized by grinding using an acid washed mortar and pestle. Weights of homogenized samples to be dried were taken and dry weights taken thereafter. The samples were then dried in the oven at 30°C for 16h and passed through 2mm sieve. All metallic determination from soil samples was based on the fine particles obtained.

3.1.4.2 Vegetable **Samples**

Vegetables collected are tomatoes, cabbage and onion. Fresh matured vegetables were randomly handpicked from farms: 1, 2 and 3 each during dry and wet seasons. The samples were wrapped in a big brown envelope with adequate room for air movement within the bag and labeled (Mumba, *et al*., 2008). In the laboratory, each sample was washed with tap water and then with distilled water. All the washed samples were dried in an oven at 80°C (Larry and Morgan, 1986) at this stage, no micro organism can grow and care was taken to avoid any source of contamination.. At the end of the drying, the oven was turned off and left overnight to enable the sample cool to room temperature. Each sample was grounded into a fine powder, sieved and finally stored in a 250cm^{3} screw capped plastic bottle appropriately labeled.

3.2 Methods

3.2.1 Determination of Physico-Chemical Parameters of Soil

3.2.1.1 Determination of pH (Herdershot *et al*., 1993) The pH of soil samples were measured with a soil: water ratio of 1:2 (w/v) using Crison MicropH 2000, pH meter as follows: 10 g of 2mm sieved air-dried soil samples were weighed into plastic containers and 20cm^3 of distilled – deionized water was added. The mixture was stirred several times for 30min. Then the soil suspension was allowed to stand for 30mins more undisturbed. The electrode of the pH was then inserted into the settled suspension and the pH of the soil measured (Bamgbose *et al*.x, 2000). Before use, the pH meter was calibrated with standard buffers of pH solutions 4, 7 and 9 (Chimuka *et al*., 2005).

3.2.1.2 Determination of Electrical Conductivity (Herdershot *et al*., 1993) The electrical conductivities of soil samples were measured with a soil: water ratio 1:2 (w/v) using Digital Conductivity meter model No PT360 as follows: 10g of 2 mm sieved air-dried soil samples were weighed into plastic containers and 20cm^3 of distilled – deionized water added. The mixtures were stirred several times for 30min. Then the soil suspensions were allowed to stand for 30min more undisturbed. The electrodes of the conductivity meter were then inserted into the settled suspension and the electrical conductivity of the soil measured (Bamgbose *et al*., 2000). Before use, the electrical conductivity meter was calibrated using 0.1M KCl.

3.2.1.3 Organic Matter Determination. The organic matter of the soil samples was determined by the method of Walkley and Black (1934). Soil sample (1 g) was weighed in triplicates into 250cm^3 conical flask. Exactly

10 cm^3 of 0.02 mol dm^{-3} potassium dichromate was pipetted into each flask and was swirled gently to disperse the soil followed by addition of 20cm^3 concentrated H_2SO_4. The flask was swirled gently until soil and reagents were thoroughly mixed. The mixture was then allowed to stand for 30min on a glass plate after which 100 cm^3 of distilled water was added followed by the addition of 4 drops of ferroin indicator, after which it was titrated with 0.25moldm^{-3} ammonium ferrous sulphate. Blank titration was similarly carried out.

% Organic carbon is given by the equation = $\frac{\text{(Blank titre – Actual titre) x 0.3 x M x f}}{\text{Weight of air-dried soil taken}}$ --- (3.1)

where f = correction factor = 1.33, M = concentration of ferrous ammonium sulphate

Then % Organic matter in soil = $\% \, Organic \, carbon \times 1.729$

3.2.1.4 Particle Size Distribution

Particle size distribution was determined by the hydrometer method as described by Bauyocos (1951). Soil (50 g) was weighed into a 250cm^3 plastic beaker. About 100cm^3 of 50% calgon was added and then stirred with a glass rod. Then 100cm^3 of distilled water was added and stirred. The beaker was left to stand for about 30min with occasional stirring. The mixture was then transferred into a 250cm^3 plastic container and shaken on an end to end shaker for 10min. The shaken sample was next transferred into a 1000cm^3 measuring cylinder and made to the 1000cm^3 mark with distilled water. Before the hydrometer reading was taken, the suspension in the cylinder was mixed vigorously using a long handle plunger making sure that the sediment at the bottom was thoroughly disturbed. Hydrometer readings at 40s and 2h were taken. A blank cylinder was prepared by making 100cm^3 of the 50% calgon solution up to the 1000cm^3 mark

with distilled water. The blank hydrometer reading was taken at the respective time interval. The temperature of the suspension and blank was also taken.

The corrected hydrometer readings C (g/l) were obtained by subtracting the blank reading R_L (g/l) from the hydrometer *readings* in the soil suspensions R (g/l) and adding 0.36g/l for every degree above 20^0C.

$$C = R - R_L + (0.36T)$$

where T = Room temperature at 20^0C.

$$\% \text{ Clay} = \frac{\text{Corrected 2hrs reading} - \text{blank} \times 100}{\text{Weight of soil taken}} \quad \text{---------- (3.2)}$$

$$\%\text{Silt} = \frac{\text{Corrected 40s reading} - \text{blank} \times 100}{\text{Weight of soil taken}} \quad \text{---------- (3.3)}$$

$$\% \text{ Sand} = 100 - (\% \text{ Clay} + \%\text{Silt}) \quad \text{---------- (3.4)}$$

3.2.1.5 Exchangeable Cations

The exchangeable cations were determined by the method described by Hendershot *et al*. (1993). The cation exchange capacity (CEC) was determined by the sum of exchangeable cations (Banerjee *et al.*, 2004): Soil (2 g) was weighed into 30cm^3 centrifuge tube. 20 cm^3 of 0.1 mol dm^{-3} $BaCl_2.2H_2O$ was added and shaken for 2h. After the tube was removed from the shaker, it was then placed in a centrifuge and centrifuged at about 10,000rpm for 30 min and the supernatant decanted carefully. It was filtered into plastic bottle and taken for AAS and flame photometer determinations.

3.2.2 Digestion of Samples

3.2.2.1 Soil Samples

Soil samples were digested according to Sharidah (1999). Accurately 5 g of soil sample was weighed into 250cm^3 conical flask and moistened with few drops of water to prevent sputtering. 3 cm^3 of 30 % H_2O_2 was then added and was left to stand for 60 min until the vigorous reaction ceased. About 75cm^3 of 0.5$moldm^{-3}$ solution of HCl was added and the content heated gently at low heat on the hot plate for 2h. The digest was allowed to cool, and then filtered into 50cm^3 standard flask. The content was then diluted to 50cm^3 mark with the same acid solution. Triplicate digestions of each sample together with blank were carried out. This method has been widely applied and recognized as informative in environmental metallic investigations where metal fractions associated with carbonate, sulphides, soluble salts organic matter held, Fe-Mn oxides are removed (Awofolu, 2005).

3.2.2.2 Plant Sample

Exactly 2 g of each of the sample was weighed out into a Kjaedahl flask mixed with 20cm^3 of concentrated perchloric acid and concentrated nitric acid in the ratio 1: 4:by volume respectively and left to stand overnight. Thereafter, the flask was heated at 70°C for about 40 min; the temperature was increased to 120°C for about 20 min. The mixture turned black after a while (Erwin and lvo, 1992). The digestion was completed when the solution became clear and the appearance of white fumes. The digest was diluted with 20cm^3 of distilled water and boiled for 15 min. This was allowed to cool, transferred into 100 cm^3 volumetric flasks and diluted to the mark with distilled water. The sample solution was filtered through a filter paper into a screw capped polyethylene bottle.

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

Actual concentration in sample (mg/kg) = AAS reading of Digest (mg/l) × Dilution factor (l/kg);

where,

$$\text{Dilution factor} = \frac{Volume\ of\ digest\ used}{\text{Weight sample digested (for soil and vegetable samples)}} \quad \text{---------- (3.5)}$$

CHAPTER FOUR

RESULTS

4.1 Heavy Metal Content of the Vegetable sample

Average concentration of metals in the vegetable crops of both dry and wet seasons is presented in Figures 4.1- 4.10. The results in Figures 4.1 and 4.2 show the mean concentration of Cu in cabbage, onion, and tomato from farms 1 to 3 during dry and wet seasons. In Figure 4.1 the mean concentration of Cu in cabbage during dry season ranged from 0.9 mg/kg (farm 3) to 1.6 mg /kg (farm2); in onion, it ranged from 1.3 mg/kg (farm3) to 1.7 mg /kg (farm 3). In tomatoes, it ranged from 2.1 mg/kg (farm3) to 2.7 mg /kg (farm1). During wet season as shown in Figure 4.2, the mean concentration of Cu in cabbage ranged from 1.1 mg /kg(farm1) to 22.4 mg /kg; in onion 0.9 mg /kg(farm3) to 2.2 mg /kg(farm2); in tomatoes, 1.6 mg /kg(farms 1 and 2) to 2.5 mg /kg(farm3).

Figures 4.3 and 4.4 revealed the mean concentration Pb in cabbage, onion and tomatoes the three different farms. During dry season, the mean concentration of Pb in cabbage ranged

from 9.1 mg/kg(farm 1) to 99.5 mg/kg(farms 2 and 3); in onion, it ranged from 11.4 mg/kg(farm 1) to 130.8mg/kg(farm 3). In tomatoes, it ranged from 24.5 mg/kg(farm2) to 39.8 mg/kg(farm3). During wet season, for cabbage, it ranged from 59.7 mg/kg (farm1) to 336.6 mg/kg (farm3); for onion, it ranged from 105.2 mg/kg(farm1) to 147 mg/kg (farm 3); for tomtoes, it ranged from 59.7 mg/kg (farm 1) to 110.9 mg/kg (farm 3).

Figures 4.5 and 4.6 show the mean concentrations of Cd in cabbage, onion and tomatoes from the three different farms during dry and wet seasons. Cd concentration in cabbage ranged from 0.4 mg/kg (farm 3) to 1.2 mg/kg (farm1); onion ranged from 0.7 mg/kg (farm 3) to 3.1

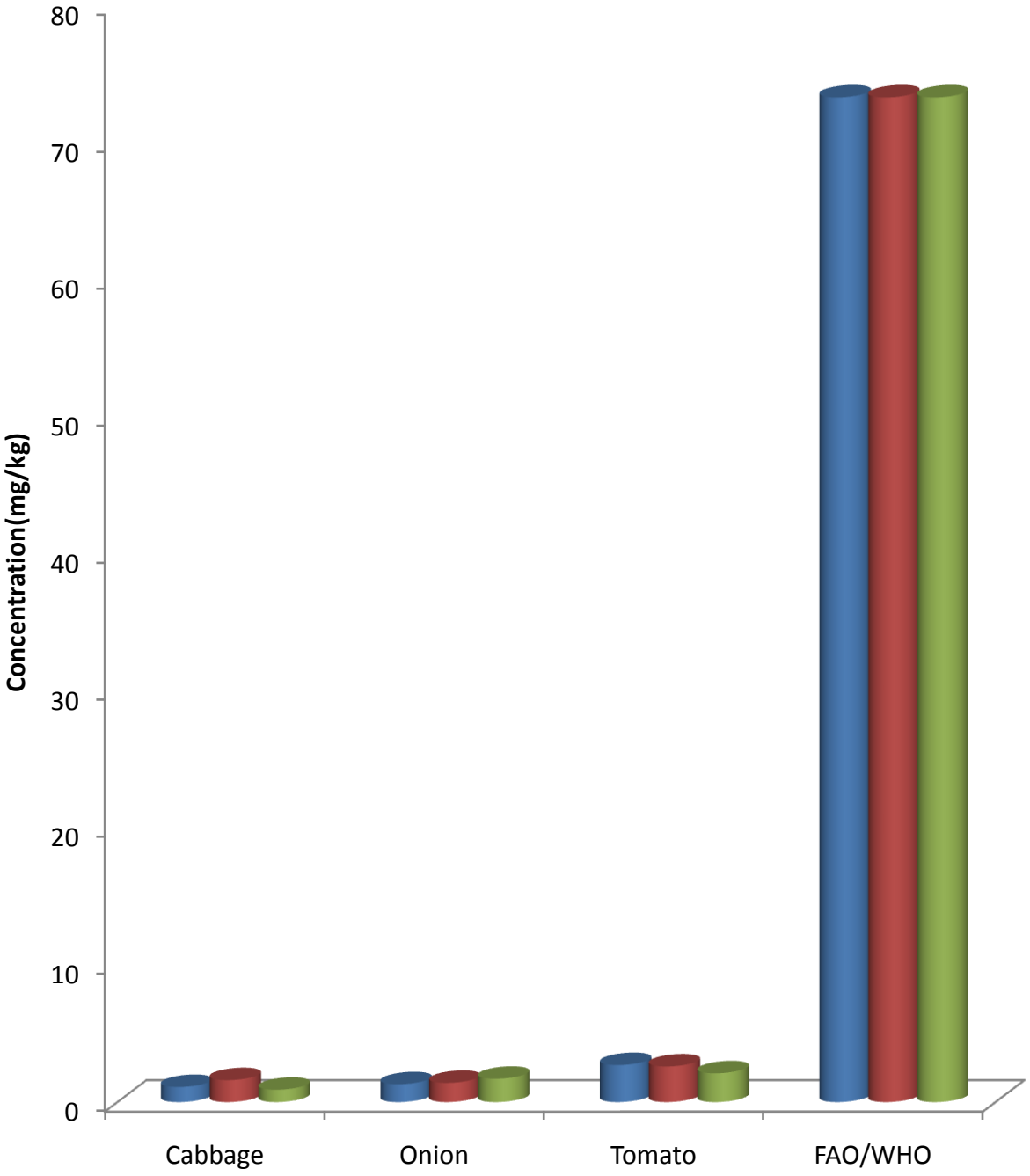

Figure 4.1: Cu concentration in the vegetable crops from the different farms during dry season

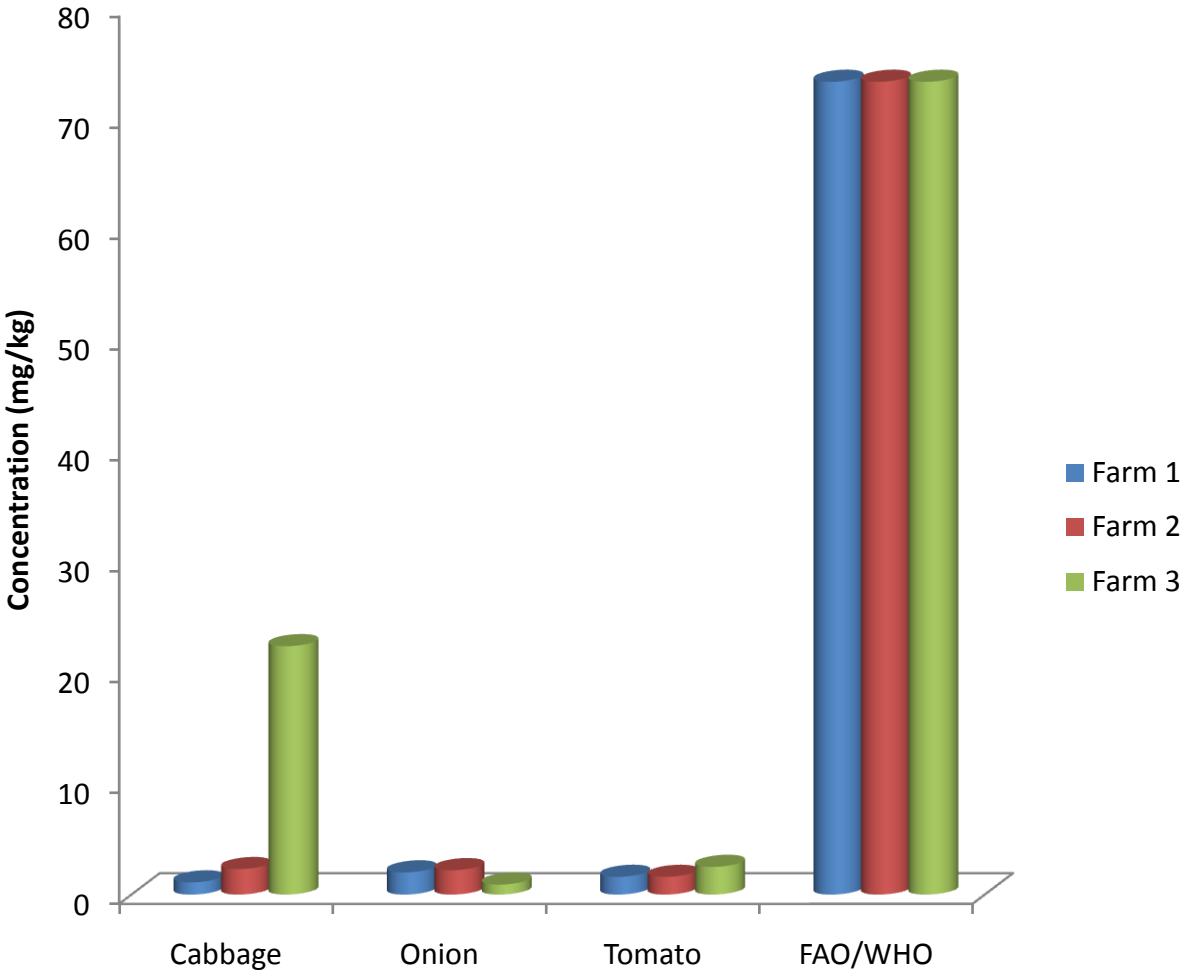

Figure 4.2: Cu concentration in the vegetable crops from the different farms during wet season

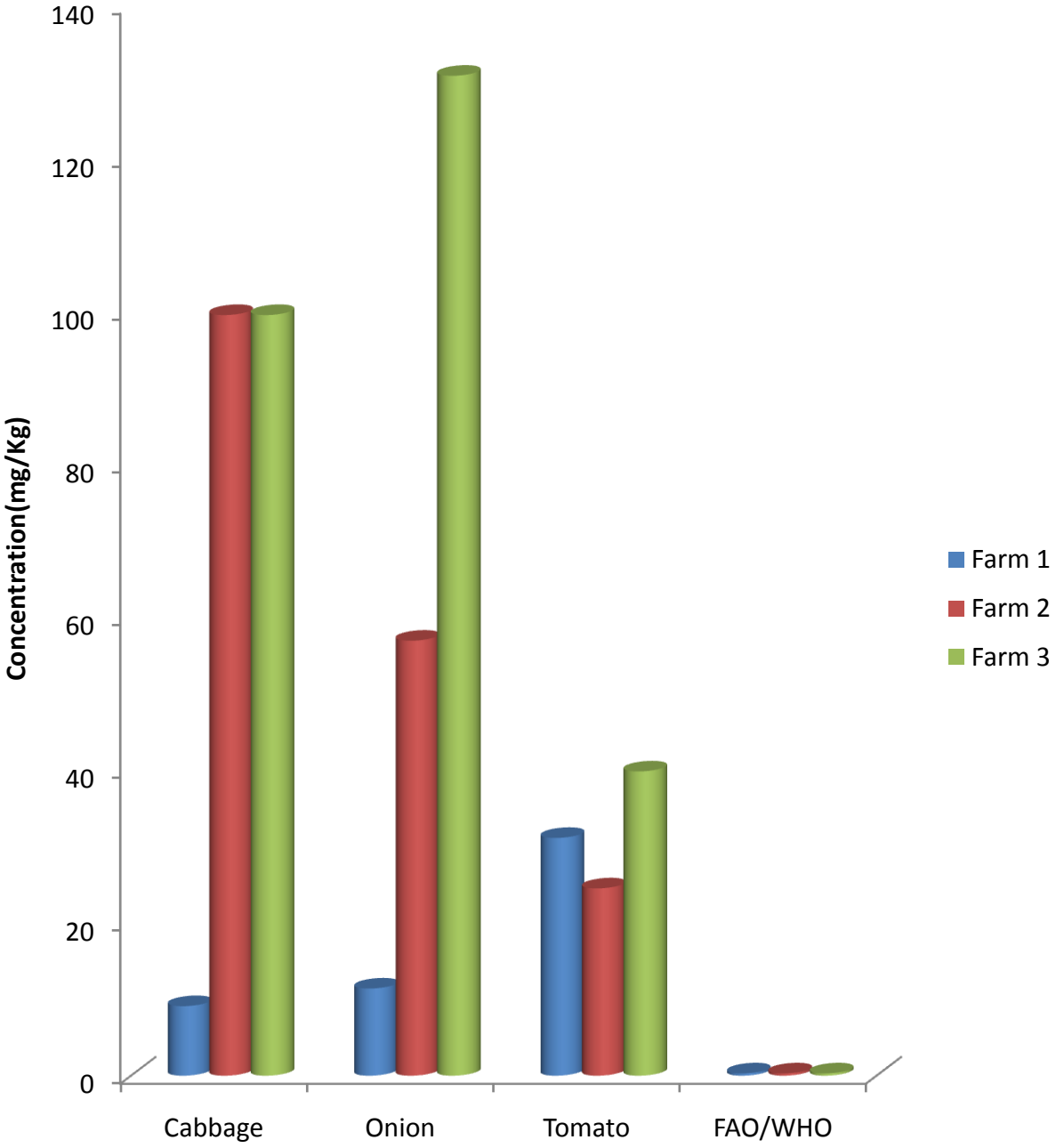

Figure 4.3: Pb concentration in the vegetable crops from the different farms during dry season

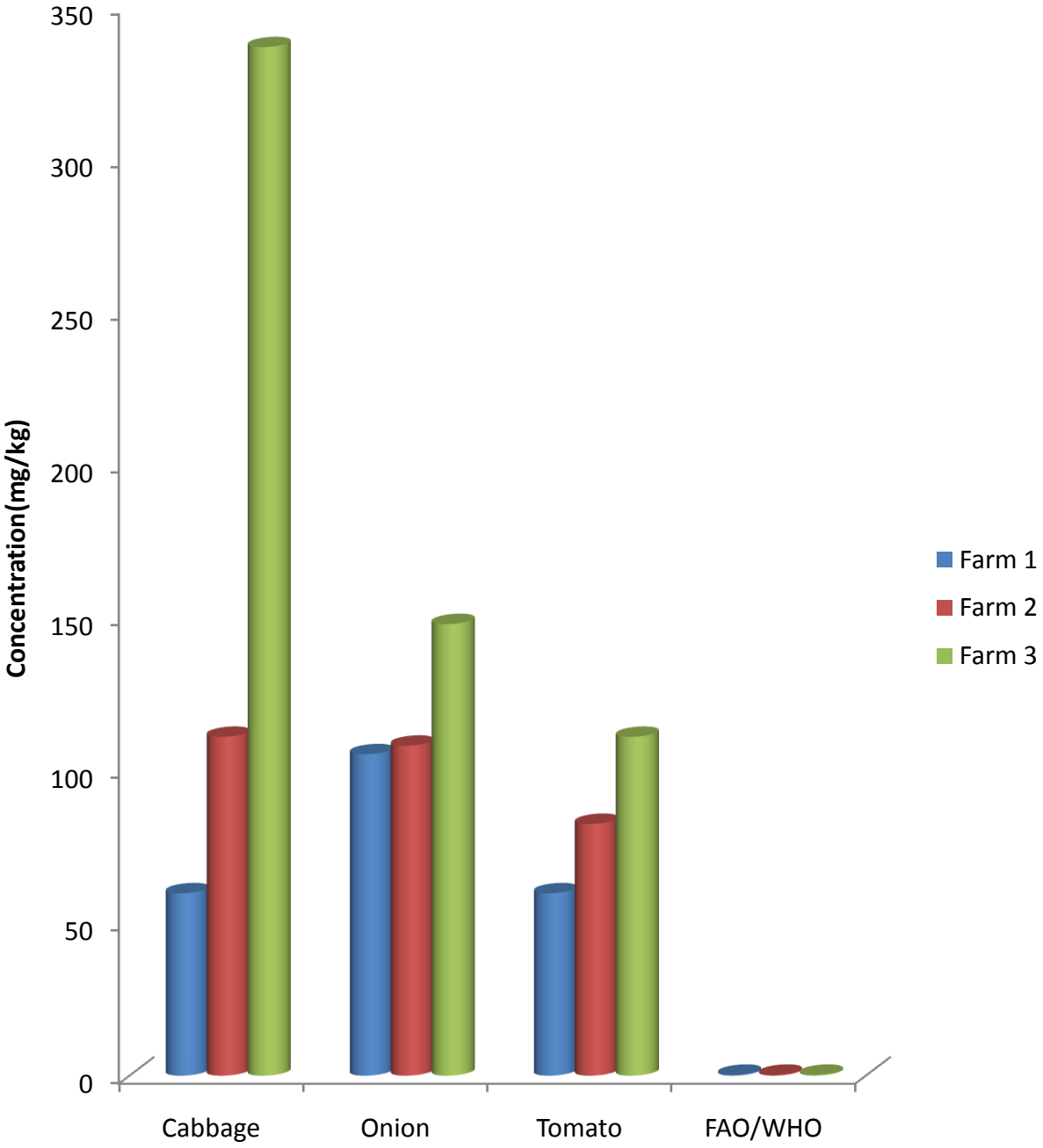

Figure 4.4: Pb concentration in the vegetable crops from the different farms during wet season

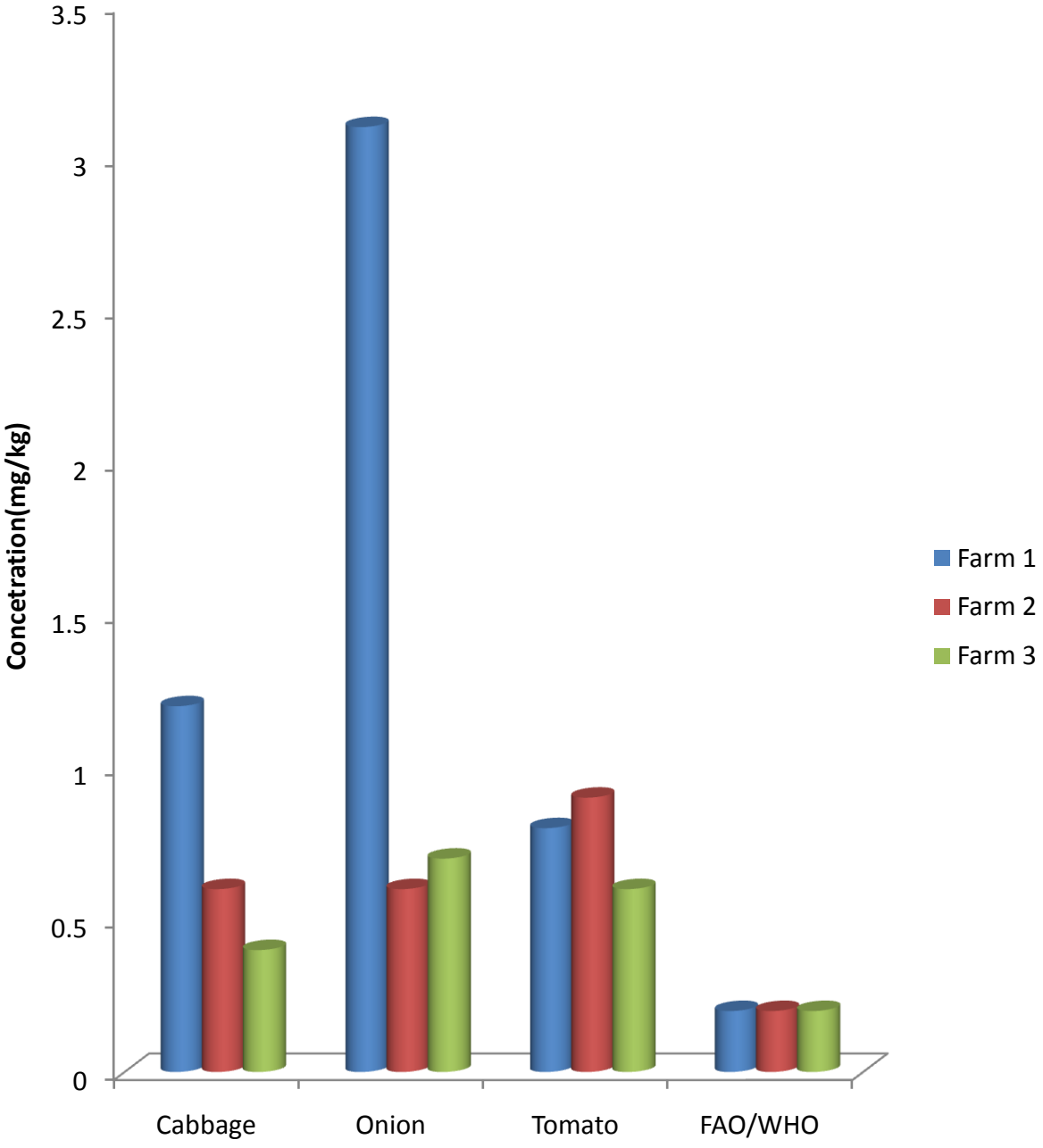

Figure 4.5: Cd concentration in the vegetable crops from the different farms during dry season

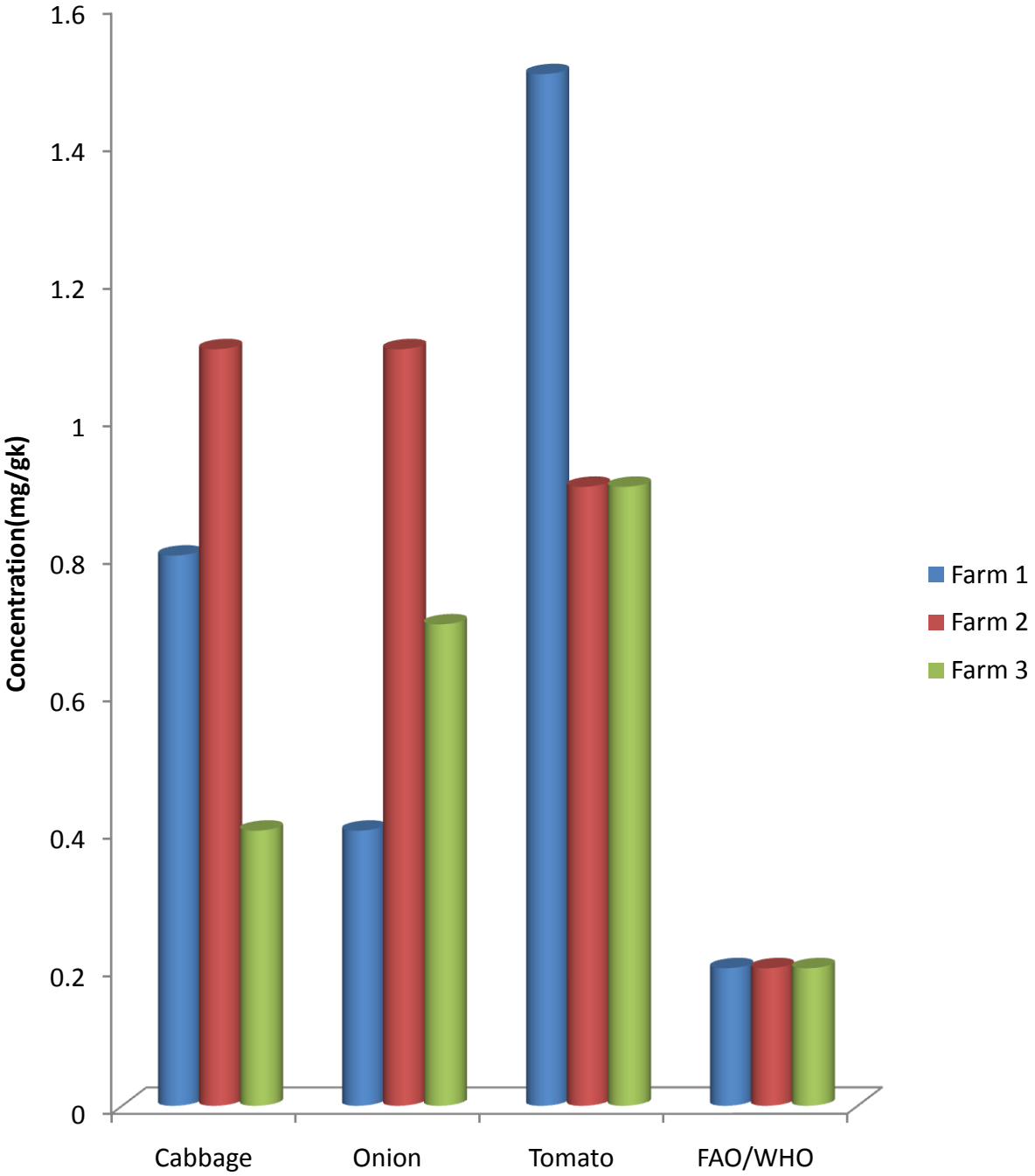

Figure 4.6: Cd concentration in the vegetable crops from the different farms during wet season

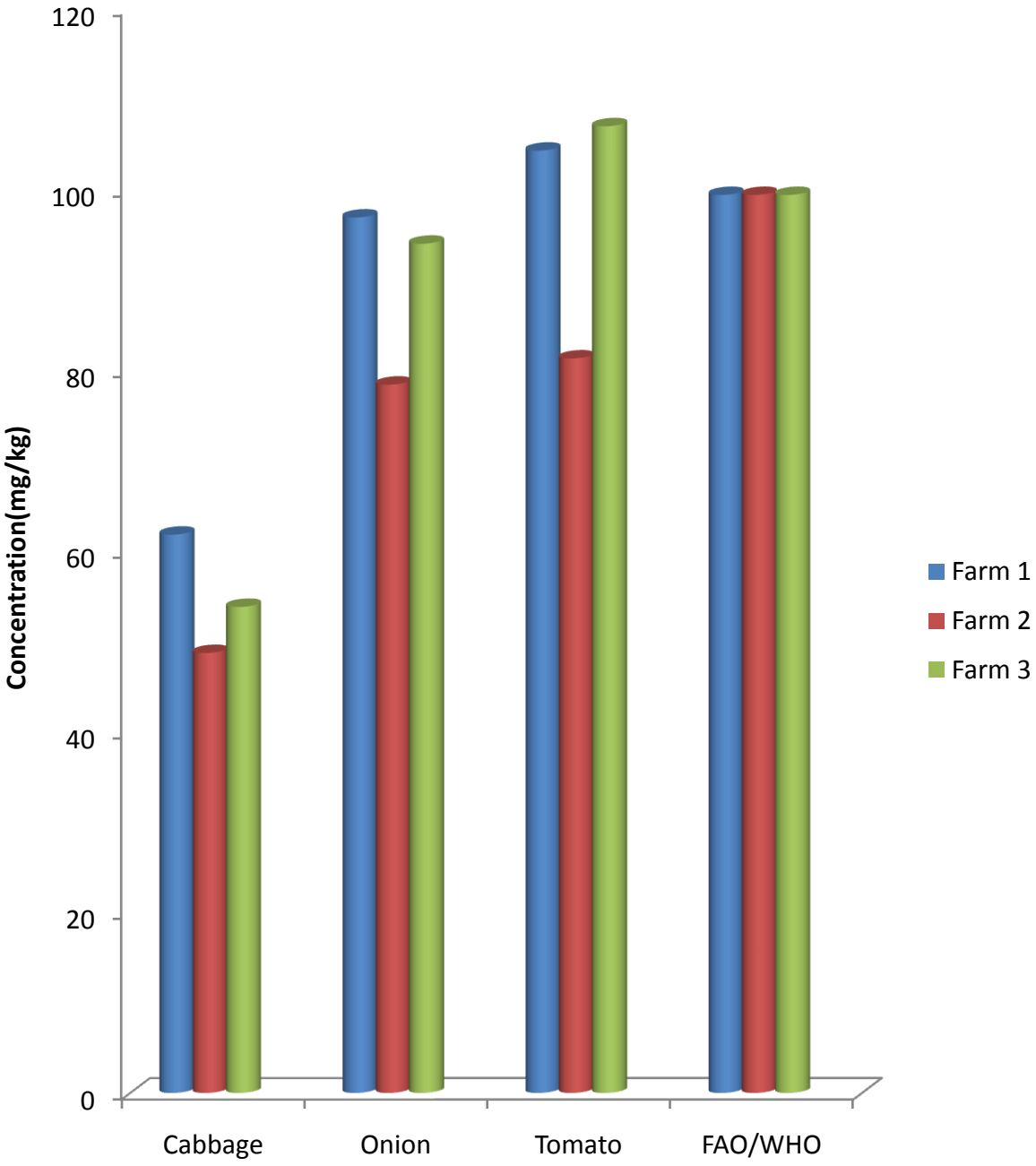

Figure 4.7: Zn concentration in the vegetable crops from the different farms during dry season

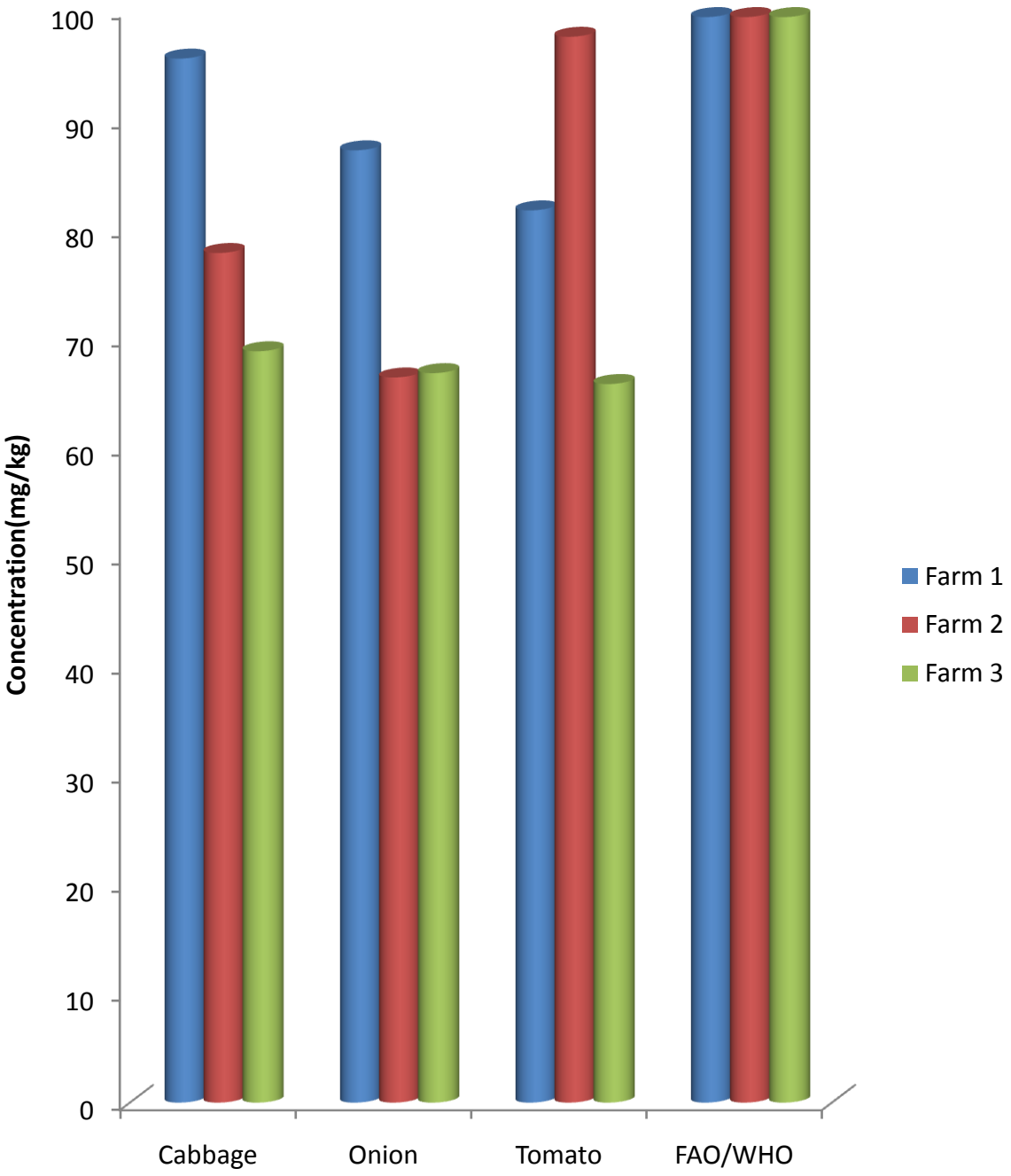

Figure 4.8: Zn concentration in the vegetable crops from the different farms during wet season

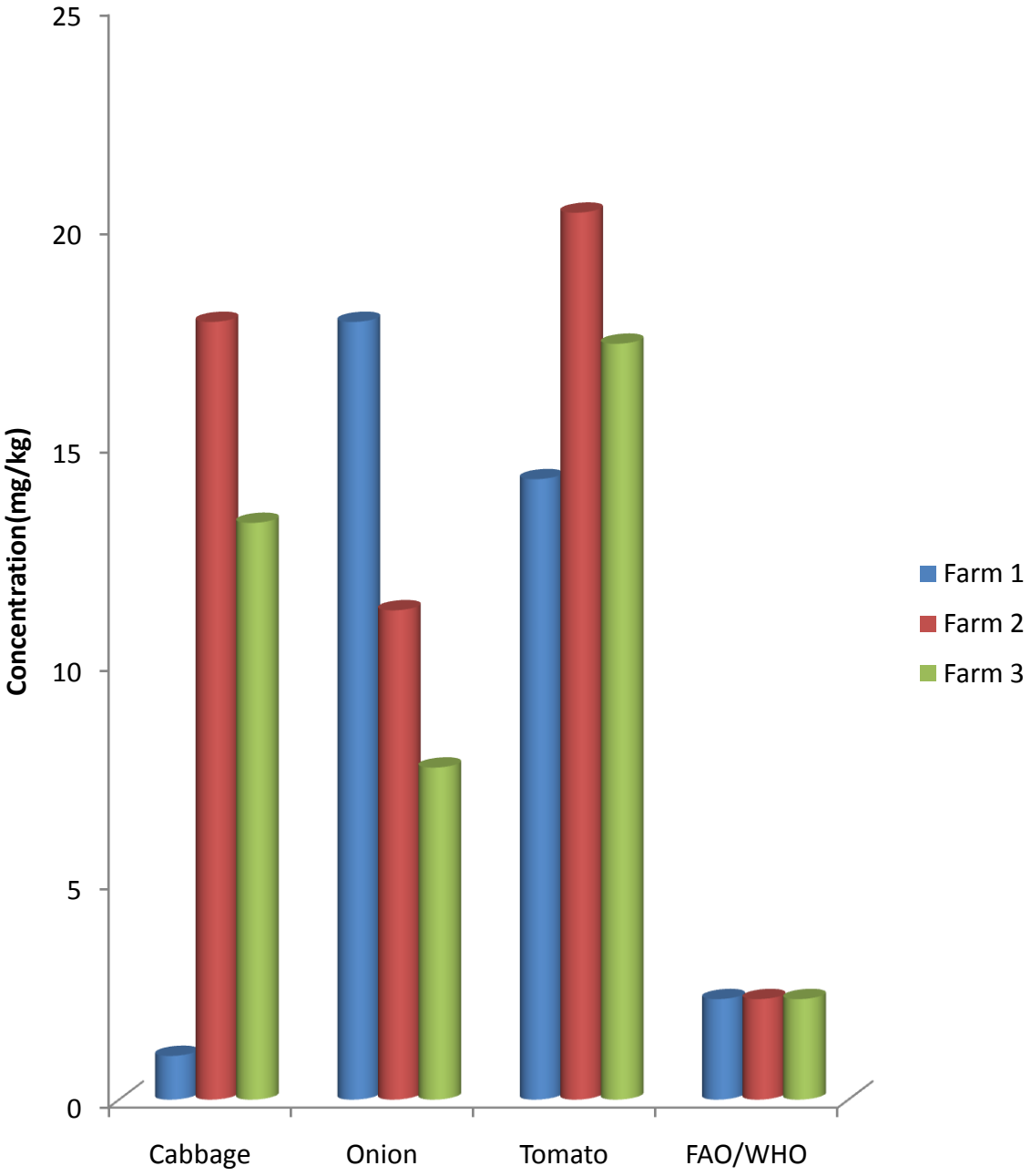

Figure 4.9: Cr concentration in the vegetable crops from the different farms during dry season

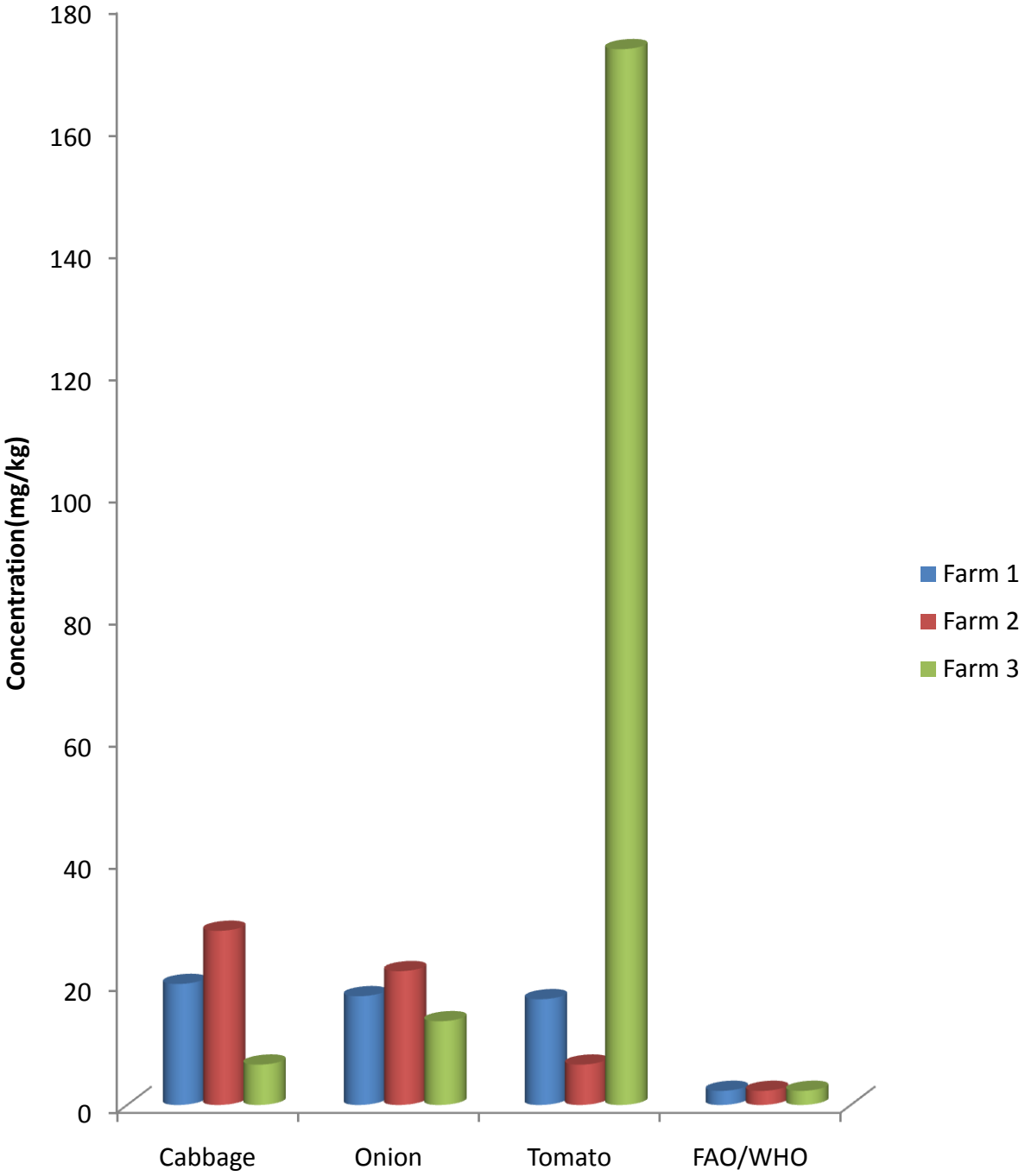

Figure 4.10: Cr concentration in the vegetable crops from the different farms during wet season

from 0.4 mg/kg (farm 3) to 1.2 mg/kg (farm1); onion ranged from 0.7 mg/kg (farm 3) to 3.1 mg/kg (farm 1); tomatoes ranged from 0.6 mg/kg (farm 3) to 0.9 mg/kg (farm 2). During wet season, for cabbage, it ranged from 0.4 mg/kg (farm 3) 1.1 mg/kg (farm 2); for onion, it ranged from 0.4 mg/kg (farm 1) to 1.1 mg/kg (farm 2); for tomatoes, it ranged from 0.9 mg/kg (farm 2 and 3) to 1.5 mg/kg (farm 1).

Figures 4.7 and 4.8 show the mean concentrations of Zn in cabbage, onion and tomatoes from the three different farms during dry and wet seasons respectively. During dry season, for cabbage, it ranged from 48.7 mg/kg (farm 2) to 61.8 mg/kg (farm 1); for onion, , it ranged from 78.9 mg/kg (farm 2) to 96.9 mg/kg (farm 1); for tomatoes, it ranged from 81.3 mg/kg (farm 2) to 1107.0 mg/kg (farm 3). During wet season, for cabbage, it ranged from 68.8 mg/kg (farm 3) to 95.6 mg/kg (farm 1); for onion, it ranged from 66.4 mg/kg (farm 2) to 87.2 mg/kg (farm 1); for tomatoes, it ranged from 65.8 mg/kg (farm 3) to 97.6 mg/kg (farm 2).

Figures 4.9 and 4.10 show the mean concentration of Cr of the vegetable crops during both seasons. During dry season, for cabbage, it ranged from 1.0 mg/kg (farm 1) to 17.8 mg/kg (farm 2); for onion, , it ranged from 7.6 mg/kg (farm 3) to 17.8 mg/kg (farm 1); for tomatoes, it ranged from 14.2 mg/kg (farm 1) to 20.3 mg/kg (farm 2). During wet season, for cabbage, it ranged from 6.6 mg/kg (farm 3) to 28.5 mg/kg (farm 2); for onion, , it ranged from 13.7 mg/kg (farm 3) to 12.9 mg/kg (farm 2); for tomatoes, it ranged from 6.6 mg/kg (farm 3) to 172.8 mg/kg (farm 3).

4.2 Heavy metal in the soil

The results of the level of trace metals in the soils of both the dry and wet season soils are presented in Figures 4.11 and 4.12. During dry season, the mean concentration of Zn

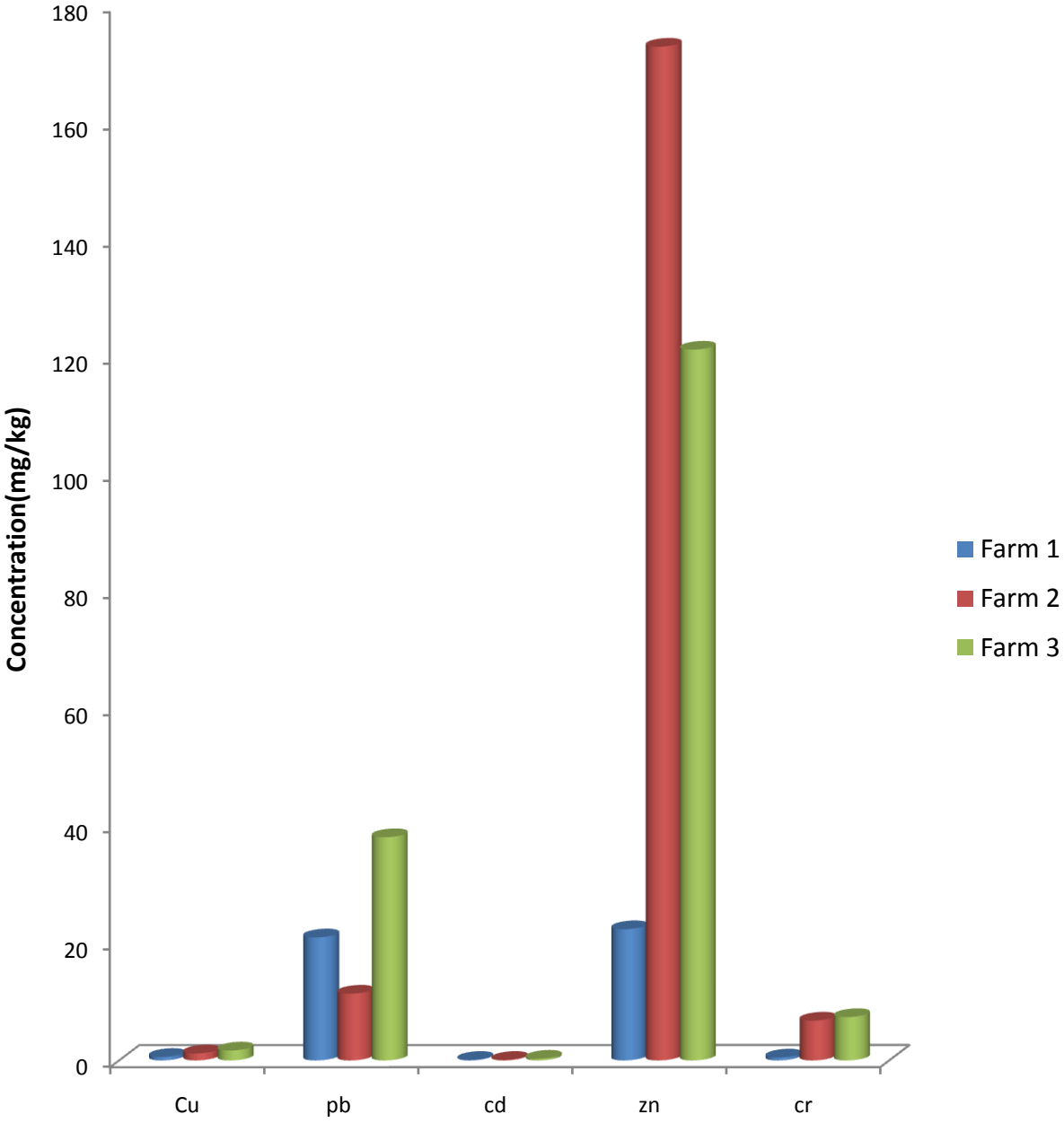

Figure 4.11: Metal concntration in the soil from the different farms during dry season

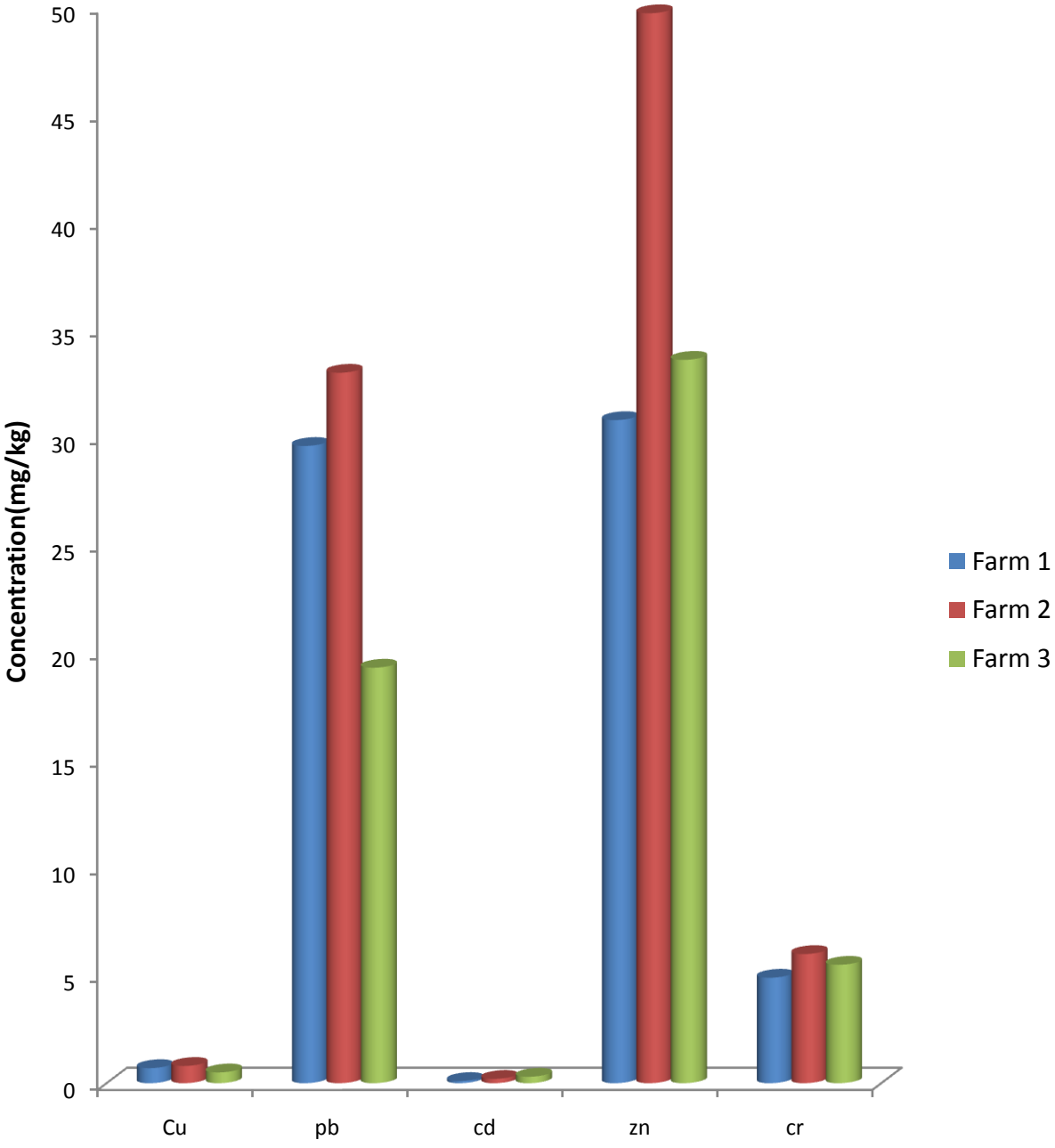

Figure 4.12: Metal concentration in the soil from the different farms during wet season

ranged from 22.4 mg/kg (farm 1) – 173.0 mg/kg (farm 2). Cr ranged from 0.5 mg/kg (farm 1) - 7.4 mg/kg (farm 3). Pb ranged from 11.4 mg/kg (farm 2) –38.1mg/kg (farm 3). Cd ranged from 0.1 mg/kg (farm 1 and 2) – 0.3 mg/kg (farm 3). Cu ranged from 0.6 mg/kg (farm 1) – 1.7 mg/kg (farm 3). During wet season, the mean concentration of Cu ranged from 0.5 mg/kg (farm 1) – 0.8 mg/kg (farm 2). Pb concentration ranged from 19.3 mg/kg (farm 3) – 33.0 mg/kg (farm 2). Cd ranged from 0.1 mg/kg (farm 1) – 0.3 mg/kg (farm 3). Zn ranged from 30.8 mg/kg (farm 1) – 49.7 mg/kg (farm 2). Cr concentration ranged from 5.5 mg/kg (farm 3) – 49.7 mg/kg (farm 2).

4.3 Soil physicochemical properties

The results of the soil physicochemical properties are displayed in Tables 4.1 and 4.2

4.4 Statistical analysis

Tables 4.3 – 4.20 showed the result of statistical analysis (correlation matrix and t-text) on the result of heavy metal concentration in the vegetable crops and soil, and soil physicochemical properties.

Table 4.1: Physicochemical properties of the dry season soils

Farms	Clay(%)	Silt (%)	Sand(%)	pH	EC(µs/cm)	OM(%)	CEC (cmol/kg)	Text class
1	16	28	56	5.90	380	2.103	8.50	Sandy loam
2	16	32	52	7.50	500	2.710	12.40	Sandy loam
3	16	28	56	6.20	250	2.974	11.40	Sandy loam

Table 4.2: Physicochemical properties of the wet season soils

Farms	Clay(%)	Silt(%)	Sand(%)	pH	EC(µs/cm)	OM(%)	CEC (cmol/kg)	Text class
1	14	36	50	6.30	70	0.903	4.50	Loam
2	14	30	56	7.60	150	1.107	4.50	Sandy loam
3	16	30	54	6.20	14	1.431	4.80	Sandy loam

Table 4.3: Correlation coefficient of Cu concentration among vegetable crops and soil during dry season

	Cabbage	Onion	Tomatoes	Soil
Cabbage	1.000			
Onion	0.790	1.000		
Tomatoes	0.079	0.674	1.000	
Soil	0.160	0.732	0.997	1.000

Table 4.4: Correlation coefficient of Cu concentration among vegetable crops and soil during wet season

	Cabbage	Onion	Tomatoes	Soil
Cabbage	1.000			
Onoion	-0.981	1.000		
Tomatoes	0.999*	-0.990	1.000	
Soil	-0.927	0.982	-0.945	1.000

Table 4.5: Correlation coefficient of Pb concentration among vegetable crops and soil during dry season

	Cabbage	Onoion	Tomatoes	Soil
Cabbage	1.000			
Onoion	0.790	1.000		
Tomatoes	0.079	0.674	1.000	

Soil	0.160	0.732	0.997	1.000

Table 4.6: **Correlation coefficient of Pb concentration among vegetable crops and soil during wet season**

	Cabbage	Onoion	Tomatoes	Soil
Cabbage	1.000			
Onoion	0.993	1.000		
Tomatoes	0.960	0.921	1.000	

Soil	-0.915	-0.956	-0.766	1.000

Table 4.7: Correlation coefficient of Cd concentration among vegetable crops and soil during dry season

	Cabbage	Onion	Tomatoes	Soil
Cabbage	1.000			
Onoion	0.962	1.000		

Tomatoes	0.419	0.154	1.000	
Soil	-0.693	-0.469	-0.945	1.000

Table 4.8: Correlation coefficient of Cd concentration among vegetable crops and soil during wet season

	Cabbage	Onion	Tomatoes	Soil
Cabbage	1.000			

Onoion	0.500	1.000		
Tomatoes	0.082	-0.822	1.000	
Soil	-0.569	0.427	-0.866	1.000

Table 4.9: Correlation coefficient of Zn concentration among vegetable crops and soil during dry season

	Cabbage	Onion	Tomatoes	Soil

Cabbage	1.000			
Onoion	0.875	1.000		
Tomatoes	0.734	0.971	1.000	
Soil	-0.109	0.385	0.595	1.000

Table 4.10: Correlation coefficient of Zn concentration among vegetable crops and soil during wet season

	Cabbage	Onoion	Tomatoes	Soil
Cabbage	1.000			
Onoion	0.938	1.000		
Tomatoes	0.330	-0.017	1.000	
Soil	-0.319	-0.627	0.789	1.000

Table 4.11: **Correlation coefficient of Cr concentration among vegetable crops and soil during dry season**

	Cabbage	Onion	Tomatoes	Soil
Cabbage	1.000			
Onoion	-0.812	1.000		
Tomatoes	0.970	-0.645	1.000	
Soil	0.941	-0.962	0.829	1.000

Table 4.12: **Correlation coefficient of Cr concentration among vegetable crops and soil during wet season**

	Cabbage	Onion	Tomatoes	Soil
Cabbage	1.000			
Onoion	0.993	1.000		
Tomatoes	-0.940	-0.893	1.000	
Soil	0.346	0.454	-0.005	1.000

Table 4.13: t-test for Cu levels in cabbage onion bulb, tomato fruits and farmland soils between dry and wet season

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	T	df	Sig. (2-tailed)
Cu in soil	Equal variances assumed	2.268	0.207	1.515	4	0.204
	Equal variances not assumed			1.515	2.306	0.253
Cu in onions	Equal variances assumed	6.084	0.069	-0.553	4	0.609
	Equal variances not assumed			-0.553	2.351	0.628
Cu in cabbage	Equal variances assumed	14.730	0.018	-1.071	4	0.345
	Equal variances not assumed			-1.071	2.004	0.396

Cu in tomato	Equal variances assumed	1.661	0.267	1.606	4	0.183
	Equal variances not assumed			1.606	3.335	0.197

Table 4.14: t-test for Pb levels in cabbage onion bulb, tomato fruits and farmland soils between dry and wet season

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	T	df	Sig. (2-tailed)
Pd in soil	Equal variances assumed	0.600	0.482	0.192	4	0.857

	Equal variances not assumed			0.192	3.724	0.858
Pd in onion	Equal variances assumed	1.963	0.234	-1.442	4	0.223
	Equal variances not assumed			-1.442	2.610	0.258
Pd in cabbage	Equal variances assumed	4.653	0.097	-1.105	4	0.331
	Equal variances not assumed			-1.105	2.494	0.364
Pd in tomato	Equal variances assumed	2.255	0.208	-3.398	4	0.027

Table 4.15: t-test for Cd levels in cabbage onion bulb, tomato fruits and farmland soils between dry and wet season

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	T	df	Sig. (2-tailed)
Cd in soil	Equal variances assumed	15.663	0.017	-0.997	4	0.375
	Equal variances not assumed			-0.997	2.000	0.424
Cd inonion	Equal variances assumed	8.275	0.045	0.871	4	0.433
	Equal variances not assumed			0.871	2.245	0.467
Cd in cabbage	Equal variances assumed	0.216	0.667	-0.106	4	0.921
	Equal variances not assumed			-0.106	3.890	0.921
Cd intomato	Equal variances assumed	4.000	0.116	-1.525	4	0.202
	Equal variances not assumed			-1.525	2.749	0.233

Table 4.16: t-test for Zn levels in cabbage onion bulb, tomato fruits and farmland soils between dry and wet season

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	T	df	Sig. (2-tailed)
Zn in soil	Equal variances assumed	5.419	0.080	1.515	4	0.204
	Equal variances not assumed			1.515	2.071	0.265
Zn in onion	Equal variances assumed	0.261	0.636	1.821	4	0.143
	Equal variances not assumed			1.821	3.879	0.145
Zn in cabbage	Equal variances assumed	1.660	0.267	-2.968	4	0.041
	Equal variances not assumed			-2.968	2.889	0.062
Zn in tomato	Equal variances assumed	6.490	0.063	1.208	4	0.294

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	T	df	Sig. (2-tailed)
Zn in soil	Equal variances assumed	5.419	0.080	1.515	4	0.204
	Equal variances not assumed			1.515	2.071	0.265
Zn in onion	Equal variances assumed	0.261	0.636	1.821	4	0.143
	Equal variances not assumed			1.821	3.879	0.145
Zn in cabbage	Equal variances assumed	1.660	0.267	-2.968	4	0.041
	Equal variances not assumed			-2.968	2.889	0.062
Zn in tomato	Equal variances assumed	6.490	0.063	1.208	4	0.294
	Equal variances not assumed			1.208	2.295	0.337

Table 4.17: t-test for Cr levels in cabbage onion bulb, tomato fruits and farmland soils between dry and wet season

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	T	df	Sig. (2-tailed)
Cr in soil	Equal variances assumed	10.930	0.030	-0.254	4	0.812
	Equal variances not assumed			-0.254	2.083	0.822
Cr in onion	Equal variances assumed	0.262	0.636	-1.469	4	0.216
	Equal variances not assumed			-1.469	3.802	0.219
Cr in cabbage	Equal variances assumed	0.127	0.740	-0.942	4	0.399
	Equal variances not assumed			-0.942	3.791	0.402
Cr in tomato	Equal variances assumed	14.615	0.019	-0.899	4	0.420
	Equal variances not assumed			-0.899	2.004	0.463

Table 4.18: Correlation coefficient of heavy metals in soil samples

	Cu	Pb	Cd	Zn	Cr
Cu	1.000				
Pb	0.362	1.000			
Cd	0.277	0.428	1.000		

	0.795	-0.224	0.002	1.000	
Zn					
Cr	0.629	0.240	0.486	0.645	1.000

Table 4.19: Correlations amongst soil physicochemical parameters

	pH	EC	OM	CLAY	SAND	SILT	CEC
pH	1.000						
EC	-0.859*	1.000					
OM	-0.910*	0.741	1.000				
CLAY	-0.695	0.487	0.781	1.000			

SAND	-0.242	0.119	0.307	0.306	1.000		
	0.442	-0.266	-0.526	-0.600	-0.945**	1.000	
CEC	-.0925**	0.847*	0.968**	0.682	0.131	-0.344	1.000

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

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

Table 4.20: Correlation coefficient of heavy metals and physico-chemical parameters of the soil samples

	pH	EC	OM	CLAY	SAND	SILT	CEC
Cu	-0.596	0.422	0.776	0.285	0.174	-0.244	0.763
Pb	0.200	-0.449	-0.140	-0.462	0.344	-0.130	-0.237
Cr	0.148	-0.135	0.211	-0.084	-0.173	0.174	0.212
Zn	-0.581	0.655	0.766	0.399	-0.106	-0.047	0.842*
Cd	0.212	-0.500	0.133	0.263	0.482	-0.495	-0.085

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

CHAPTER FIVE

DISCUSSION

5.1 Heavy metal in the vegetable crops

The concentration of metals in all the vegetable crops were significantly high above the value recommended by FAO/WHO (2001) except for Cu and Zn which were below the maximum recommended limit of 73.3 and 99.4 mg/kg respectively. In general, the extent of Pb,Cd and Cr contamination in the vegetable crops are of great concern as this may pose health risk to man. From the survey of literature, the main source of Pb is th\e akyl derivatives in petroleum. It also comes from other sources like metal manufacturing sewages, paints, fertilzer, pestcides and ashes. This could probabbly be the mechanism of anthropogenic Pb contributon into the soil and consequently into the vegetable crops. The elevated levels of Pb (9.1-336.0 mg/kg) far exceeded the recommended limit(of 0.3 mg/kg) in the vegetable crops especially during wet season could indicate other source such as vehicular emission than contaminants from irrigation water. Pb is most ubiquitos toxicant in the environment (Goyer, 1993). Pb may impair renal function, red blood cell production, nervours system, causes blindness (Asonye *et al*., 2007).

The concentration of Cd of all the samples under investigation were above the maximum permisible concentration (of 0.2mg/kg) of Cd (FAO/WHO 2001) This high level of Cd might be due to the use of cadmium-containig phosphate fertilizers. Cadmium has a long biological life of

20 – 30 years in the kidney (WHO, 1993). Chronic exposure may eventually accumulate to toxic levels as a result of high levels obtained in this study. This may lead to anaemia, damage proximal tubules, severe bone pain and mineral loss (Bae *et al*., 2000).

Cr though an essential trace nutrient and a vital component for the glucose tolerance factor, Cr toxicity damages the livers, lungs and causes organ hemorrhages (Bae *et al*., 2000). The high value of Cr might be attributed to the fugitive emissions from road dust (DEFRAEA, 2002).

High concentration of metals observed in the vegetable crops is related to the concentration of metals in the soil (Al- Jasir *et al*., 2005; Lawal and Audu, 2011). The high concentration could be as a result of high traffic density along that road. This is in agreement with the results of Abechi *et a*l (2010) and Ibrahim and Jaal (2013)

There was a reduction generally in the metal levels (except for Pb and Cr) in the samples collected during rainy season as compared to samples collected during dry season. This may consequently be the effect of the use of irrigation water or increase in water volume which reduces the concentrations of the metals available for uptake by plant. Also it could be as result of leaching away of some parts of the metals accumulated in the soil resulting in the reduction of the quantity of the metals available to plants in the soil (Lawal and Audu 2011). On the contrary negative values recorded for the percentage loss of metal in rainy season samples over the dry season samples could be attributed to the possibility of runoffs from the surrounding land containing metal salts being washed into the farmlands (Lawal and Audu, 2011).

There is an observed variation in the levels of these metals in the various crops from one farmland to another. These changes could be due to certain factors such as soil factors and root morphology of the vegetable crops (Awode, *et al*., 2008). These factors could be attributed to the difference in plant uptake and sensitivity of these metals. Common trend was observed in this study

generally and that is, the levels of the metals obtained were quite higher in the vegetable crops than the associated soils. This implies that these vegetable crops could be suitable for use in the environment as bioindicators(Kasanen and Venetvaara, 1991).

The correlation coefficient of each of the metal concentrations among vegetable crops and soil of the respective seasons were calculated in order to understand their distributions. As recorded in Tables 4.3 to 4.12. For Cu concentration during dry season, positive correlation was observed in cabbage and tomatoes, onion and soil while negative correlation was observed in cabbage and soil, onion and tomatoes, tomatoes and soil. During wet season, there was a significant correlation ($p<0.05$) between cabbage and tomatoes. Negative correlations were observed among the vegetable crops.

In the case of Pb concentration, correlation coefficients among these crops soil were positive during dry season as well as during wet season except for all the vegetable crops versus soil which were all negative.

Also for Cd, the correlation coefficients among the crops were all positive except with the soil during dry season. Cabbage and soil; onion and tomatoes; tomatoes and soil correlated negatively while the rest had positive relationships during wet season.

Negative correlation was observed between cabbage and soil for both seasons; also in (onion: tomatoes and soil) for wet season, with the rest correlating positively for Zn concentration.

Positive correlation occurs in Cr concentration thus: cabbage: (tomatoes and soil); tomatoes and soil for dry season. Cabbage; (onion and soil); onion and soil for wet season. Negative correlation was observed in cabbage and onion; onion: (tomatoes and soil) for dry season. Cabbage and tomatoes; onion and tomatoes; tomatoes and soil, for wet season.

Significance and positive correlations could indicate common source of these metals during the season while changes in the relation among these vegetable crops and soils could indicate different sources of these metals. Poor and negative correlation observed among the vegetable crops and soil could also be attributed to the soil physicochemical parameters and the nature of each of the vegetable crops. The positive relationships among the vegetable crops and soil content of the metals might be a cause of heavy metal toxicities to both plant and animal through their entry into the food chain (Awode *et al*., 2008).

In the analysis of independent t-test (Tables 4.13- 4.17) for all the various vegetable crops and farmland soils, the difference in Cu, Cd and Cr levels of cabbage, onion bulbs, tomato fruits and farmland soils respectively between dry and wet season was not statistically significant ($p>0.05$). The difference in Pb concentration of onion bulbs, cabbage and farmland soils between dry and wet season was not statistically significant ($p>0.05$) while the difference in Pb concentration of tomato fruits between dry and wet season was statistically significant ($P<0.05$) with the Pb levels of the wet season being significantly higher than that of dry season. The difference in Zn concentration of farmland soil, onion bulb and tomato fruits between dry and wet season was not statistically significant ($P>0.05$). On the other hand, the difference in concentration of Zn in cabbage between dry and wet season was statistically significant ($P<0.05$) with the concentration in wet season significantly higher than the dry season.

These significance differences in Pb and Zn could be attributed to the dissolved salts of Pb and Zn present in the environment that get to the root of the crop at the on-set of rain.

5.2 Heavy metals in the soil

The variation in the concentration of the metals in the soil could be attributed to the differences in the sources of the metals.

A correlation coefficient for heavy metals in the soil of the different farms of the respective seasons was calculated to see if some metals were interrelated with each other as shown in the Table 4.18. Positive correlation was observed among the metals except for Pb and Zn that showed negative correlation. The positive and negative correlations observed could indicate common and uncommon sources of these heavy metals respectively.

5.3 Soil physicochemical properties

All samples from both dry and wet seasons were generally dominated by high average percentage sand fraction followed by silt and then clay as shown in the Table 4.1 and 4.2 respectively. The general pH range for the soil was 5.90 (farm 1) – 7.50 (farm 2) and 6.20 (farm 3) – 7.60 (farm 2) for both dry and wet seasons respectively. These values depict that the environment is slightly acidic to neutral. Electrical conductivity values ranged from 250µs/cm (farm 3) - 500 µs/cm (farm 2) and 14µs/cm (farm 3) – 150µs/cm (farm 2) for both dry and wet seasons respectively. This is quite high, indicating significance presence of some soluble inorganic salts in the soils (Akpoveta, *et al*., 2010). The organic matter content (OM) of the soils for dry season ranged from 2.10% (farm 1) - 2.97% (farm 3). OM for wet season soils ranged from 0.90% (farm 1) 1.43% (farm 3). The cation exchange capacity (CEC) of the soil samples ranged from 8.50cmol/kg (farm 1) - 12.40cmol/kg (farm 2) and 4.50cmol/kg (farm 1 and2) – 4.80cmol/kg (farm 3) for dry and wet seasons respectively. The CEC is described as the amount of positively charged cation a soil can hold and is related to the ability of soil to hold onto plant nutrients. The CEC of soil is related to the nature and quality of clay and organic matter. Hence, the CEC is characteristically low, a typical of savanna soils dominated by sandy soils and low in organic matter (Agronomy Fact Sheet Series 22, 2007).

The analysis of the correlation amongst the soil physicochemical parameters of both dry and wet season soil samples as shown in Table4.19 revealed the presence of positive correlation thus: (pH and silt), (EC:OM, clay content, sand CEC), (OM: clay content, sand and CEC), (clay: sand and CEC). On the other hand, negative correlation was evident in pH and other parameters except silt; silt and other parameters except pH; (CEC: pH and silt. Significant positive or negative correlation could indicate the effect of one factor on another.

Table 4.20 reveals the correlation between the heavy metals in the soils and the soil physicochemical parameters. Negative correlation was observed between (Cu: pH and silt), Pb and soil physicochemical parameters except pH and sand. Also negative correlation was observe between (Cr: EC, clay and sand), (Zn: pH, sand and silt), (Cd: EC, silt and CEC). Others correlated positively. Positive correlation between metal concentrations and physicochemical parameters of the soils could be an implication of the significance effect of these of these parameters on the amount of these metals present in the soil. This is in line with the result reported by McEldowney *et al*., 1993 that the mobility and bioavailability of metals present in the soils depends on the physicochemical properties of the soil. On the other hand negative correlation could indicate that these parameters had mild or lesser effect on the metal mobility in the soil.

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CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The results obtained from this study have shown that there is increased danger of growing vegetable crops by Hunkuyi road Zaria. This could also be applicable to other major roads. This is in agreement with elevated levels of Pb, Cr and Cd in cabbage, onion and tomatoes obtained in this study which is above the recommended standard limits. The study showed that abundance concentration of heavy metals especially Pb, Cr and Cd could be directly related to the amount in the environment including the soil.

The variability of heavy metals concentrations in soil also showed that actual uptake by plants of these elements from soil depended on some physicochemical parameters such as pH, organic matter content and particle size.

Thus from the results of the present investigation, it could be concluded that in the vicinity of the farmlands by Hunkuyi road, Zaria, the uptake of these heavy metals by the vegetable crops may increase especially during dry season.

6.2 Recommendations

High levels of metals especially Pd, Cd and Cr were detected in the crop and vegetable, which could directly pose risk to human health. Therefore, a clean-up procedure should be embarked on to reduce the heavy metal concentration in the soil either by use of bioremediation, particularly phytoremediation which involves the use of plants in the detoxification of the soil or the land should be reclaimed by top soiling with uncontaminated soils from offsite to a depth that would minimize uptake

of heavy metals by vegetations. With respect to the information obtained from this study, a research should be carried out on the source of irrigation water to actually ascertain the major source of these pollutants. Also routine and periodic assessment of metal pollution in agricultural soils in relation to vegetable production and depending on waste water irrigation in dry season is important because of the potential risk posed to animals and human through food chain.

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Appendix I

Mean concentration (mg/kg) of metals in vegetable crops and soils from the different farms during dry season

Metal	Farms	Cabbage	Onion	Tomato	Soil
Cu	1	1.1	1.3	2.7	0.6
	2	1.6	1.4	2.6	1.2
	3	0.9	1.7	2.1	1.7
Pd	1	9.1	11.4	31.1	21
	2	99..5	56.9	24.5	11.4
	3	99.5	130.8	39.8	38.1
Cd	1	1.2	0.4	3.1	1.1
	2	0.6	1.1	0.6	0.1

	3	0.4	0.7	0.7	0.3	
Zn	1	61.8	96.9	104.3	22.4	**FAO/WHO**
	2	48.7	78.4	81.3	173.0	
	3	53.8	94.0	107.0	121.3	
Cr	1	1.0	17.8	14.2	0.5	**73.3**
	2	17.8	11.2	20.3	6.8	
	3	13.2	7.6	17.3	73.84	

0.3

0.2

99.4

2.3

Appendix II

Mean concentration (mg/kg) of metals in vegetable crops and soils from the different farms during wet season

Metal	Farms	Cabbage	Onion	Tomato	Soil
Cu	1	1.1	2.0	1.6	0.7
	2	2.3	2.2	1.6	0.8

	3	22.4	0.9	2.5	0.5	
Pd	1	59.7	105.2	59.7	29.6	**FAO/WHO**
	2	110.9	108.0	82.4	33.0	
	3	336.6	147.8	110.9	19.3	
Cd	1	0.8	0.4	1.5	0.1	**73.3**
	2	1.1	1.1	0.9	0.2	
	3	0.4	0.7	0.9	0.3	
Zn	1	95.6	87.2	81.7	30.8	
	2	77.8	66.4	97.6	49.7	**0.3**
	3	68.8	94.0	65.8	33.6	
Cr	1	19.8	17.8	17.3	4.9	
	2	28.5	21.9	6.6	6.0	
	3	6.6	13.7	172.8	5.5	**0.2**

99.4

2.3