HEAVY METAL BURDEN OF SOILS AND THEIR ACCUMULATION POTENTIALS IN SOME FOOD CROPS OF SELECTED FARMS IN KOGI STATE, NIGERIA

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DEDICATION

I dedicate this work to Almighty God for His mercy and abundant treasures. Also, to my darling wife Olubunmi Marvelous and my children Oghenetega and Emmanuella for their encouragement, understanding and endurance during the course of this research work.

ABSTRACT

Heavy metal contamination in soil may be reflected in food crops due to plant uptake and such crops when consumed may cause adverse health effects. The assessment of toxic metal burden of soils and the capacity of food crops to accumulate these metals are essential. Such studies have not been reported in literature for Kogi State, a state noted for intense agricultural activity. The aim of this study was to determine heavy metals in soils, food crops, irrigation waters and sediments of dam of selected farms in Kogi State and also metals uptake potentials and toxicity threshold limits in crops.

Soils and plants from nine major farms, three from each senatorial district, and a control site (another farm), were randomly sampled quarterly from May, 2007 to February, 2009. Thirty-two soil samples were obtained from 0-15 and 15-30 cm depths in each farm and control site, to make 320 composite samples. A total of 640 plants samples (leaves and edible parts each of pumpkin 64, passion fruit 96, maize grain 96, sugar cane stem 64 and tubers of cassava 320) were collected. Fifty-six samples of each of irrigation waters and sediments were collected. Soils, water and sediments were each digested with HNO_3 while 3:1 HNO_3:$HClO_4$ was used to digest the crops. Digests were analysed for Cd, Co, Cu, Ni, Pb and Zn by atomic absorption spectrophotometry. Speciation of metals in soil was done by Tessier sequential extraction procedure and soil-plant transfer factor was determined as the ratio of metal concentration in plants to soil. A soil-plant equilibrium model (STRATA) was used to analyse soil-plant metal data in order to obtain crop uptake characteristics and toxicity threshold limits. Data were analysed using ANOVA at $p = 0.05$.

The mean concentrations of Cd, Co, Cu, Ni, Pb and Zn in top soils were 0.6±0.7, 5.4±3.9, 4.3±2.3, 15.7±9.2, 11.8±6.1 and 26.0±17.0 mg/kg respectively, while subsoil values were 0.7±0.7, 5.0±3.3, 3.9±2.1, 14.6±8.3, 11.7±5.4 and 25.0±14.0 mg/kg respectively. These did not vary significantly among farms. Proportions in non-residual soil phases were 82.6% Cd, 48.6% Co, 72.5% Cu, 73.2% Ni, 41.9% Pb, and 84.3% Zn. Mean concentrations (mg/kg) in edible crop parts were: Cd 0.5±0.1, Co 4.4±3.0, Cu 4.4±0.2, Ni 25.5±9.2, Pb 0.2±0.1 and Zn 20.1±1.3. Nickel levels in cassava tubers and leaves

(34.5±19.0 and 29.0±16.0 mg/kg respectively) were significantly higher than in the control (3.1±0.5 mg/kg) and exceeded Chinese standard limit of 10 mg/kg. Metals levels in water and sediments were within standard limits of 0.001-3.0 and 6.0-25.0 (mg/kg) respectively. Soil-plant transfer factors indicated low accumulation into crops. Transfer factors for Cd, Co, Cu, Ni, Pb and Zn in maize grain were: 0.4, 0.01, 0.6, 1.9, 0.02, and 1.2 respectively, and in tubers were: 0.4, 0.01, 1.8, 2.5, 0.01 and 0.7 accordingly. Metal concentrations in crops parts were generally lower than model-derived threshold limits for toxicity in plants.

There was no heavy metal contamination in investigated food crops except nickel in cassava. Therefore, the soil may not require any form of remedial action.

Keywords: Heavy metals in food crops, Soil and sediment contamination, Metal uptake, Metal speciation, Toxicity in plant.

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CERTIFICATION

I certified that this research was carried out under my supervision by **EMUROTU, JUDE EHWEVWERHERE** in the Department of Chemistry, University of Ibadan, Ibadan.

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ADP	Agricultural Development Programme
ATP	Adenosine Triphosphate
AJA	Ajaokuta
ANY	Anyigba
ANK	Ankpa
COD	Chemical Oxygen Demand
CTR	Control
DO	Dissolved Oxygen
EDTA	Ethylenediaminetetraacetic acid
EJU	Ejule
FEPA	Federal Environmental Protection Agency
FAO	Food and Agriculture Organization
GPS	Global Positioning System
GW	Groundwater
IBA	Ibaji
IDA	Idah
KSU	Kogi State University
LKJ	Lokoja
MAC	Macks
NPK	Nitrogen (N), Phosphorus (P), Potassium (K)
ppm	Parts per million
QA	Quality Assurance
QC	Quality Control
SD	Sediment
SL	Soil
SON	Standards Organisation of Nigeria
SW	Surface water
TF	Transfer factor
TOC	Total Organic Carbon
TOM	Total Organic Matter
USEPA	United State Environmental Protection Agency
WHO	World Health Organisation

CHAPTER ONE

INTRODUCTION

1.1 ENVIRONMENTAL POLLUTION

Pollution can be defined as the introduction by man, directly or indirectly of substances or energy into the environment, liable to cause hazards to human health, harm to living resources, hindrance to marine activities including fishing, impairment of quality for use of seawater and reduction of amenities (GESAMP, 1993). Such a substance has to be present in the environment above a set of tolerance limits, before it is considered a pollutant. Environmental pollutants from many different sources contaminate air, land, and water, putting humans and ecosystems at risk (Gleick, 2001; Khan *et al*., 2010). Over the past decades, there has been increasing global concern over increased disease burdens resulting from environmental pollution. The World Health Organization (WHO) has estimated that about a quarter of the diseases facing mankind today are the results of prolonged exposure to environmental pollution (Khan *et al*., 2010).

Since the industrial revolution, man's activities have progressively altered the structures and functions of the environment. Human population growth has placed ever-increasing demands on both aquatic and terrestrial ecosystems, and the use of up to one-half of the land's surface has been transformed. Man has dramatically changed the globe by land clearing, agriculture, forestry, animal husbandry and urbanization, and by altering hydrological cycles (Vitousek *et al*., 1997). There has also been significant alteration of the composition of many natural biological communities through harvesting activities, and by the unintentional and deliberate introduction of non-native species (Chapin, *et al.*, 1993; Matson *et al.*, 1997; Bottsford *et al.*, 1997; Dobson *et al*, 1997; Noble and Dirzo, 1997). Human activities have also had profound impacts upon the global biogeochemical cycles of carbon, nitrogen, and phosphorus (Schlesinger, 1991; Vitousek and Howarth, 1991; Vitousek *et al*.,1997). Addition of agrochemicals to soils and crops is an important practice in agriculture, for nutrient supply in soil and crop protection and disease control. As a result, this may cause chemical degradation of the soil as the contaminants are accumulated (Garcia *et al*., 1995). The fertilizers and the pesticides usually contain significant amounts of heavy metals such as Cu, As, Co, Cr, Mo, Sr, Ti, V, Mn, Fe, Ni, Zn, Cd, Pb, Hg, Ba and Sc (Garcia *et al*., 1995; Abdel-Haleem *et al*., 2001; El-Bahi *et al*., 2004). Long term application of these agrochemicals may lead to pollution of soils and crops and subsequently affects man and other resources through the food chain. It is therefore important to closely monitor the agricultural environment where agrochemicals are applied.

1.2 TYPES OF POLLUTION

1.2.1 Air Pollution

Air pollution is the contamination of indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere. Household combustion devices, motor vehicles, industrial facilities and forest fires are common sources of air pollution. Pollutants of major public health concern include particulate matter, carbon monoxide, ozone, nitrogen dioxide and sulfur dioxide (WHO, 2013). Serious concerns have been raised about the health hazards of air pollution in a number of countries (Kandlikar and Ramachandran, 2000). World Health Organization (WHO, 2002) points out that outdoor air pollution contributes as much as 0.6 to 1.4% of the burden of disease in developing regions.

1.2.2 Water Pollution

Water pollution is the degradation of water quality as measured by biological, chemical, and physical criteria. The main sources of water pollution include inorganic and organic wastes, such as wastes from industries, municipal wastes, agricultural wastes, and acid mine drainage. Human diseases and casualty arising from water pollution attracted worldwide attention after the ‘‘Minamata disease’’ and ‘‘itai-itai-byo’’ episodes which occurred in Japan during the 1940s and 1950s. Minamata disease was caused by eating fish and shellfish laden with highly toxic methylmercury, while itai-itai-byo disease was mainly attributed to ingestion of rice contaminated with high levels of cadmium (Ming-Ho, 2004).

1.2.3 Land or Soil Polution

Soil pollution is a buildup of toxic chemical compounds, salts, pathogens (disease-causing organisms), or radioactive materials that can affect plant and animal life. Unhealthy soil management methods have degraded soil quality, causing soil pollution, and enhanced erosion. Treating the soil with chemical fertilizers, pesticides, and fungicides interferes with the natural processes occurring within the soil and destroys useful organisms such as bacteria, fungi, and other microorganisms. For instance, strawberry farmers in California (Pandey, 2006) fumigate the soil with methyl bromide to destroy organisms that may harm young strawberry plants. This process indiscriminately kills even beneficial microorganisms and leaves the soil sterile and dependent upon fertilizer to support plant growth. This results in heavy fertilizer use and increases polluted runoff into lakes and streams.

1.2.4 Noise Pollution

Unwanted sound, or noise, such as that produced by airplanes, traffic, or industrial machinery, is considered a form of pollution. Noise pollution is at its worst in densely populated areas. It can cause hearing loss, stress, high blood pressure, loss of sleep, distraction, and loss of productivity (Pandey, 2006). Sounds are produced by objects that vibrate at a rate that the ear can detect. Most humans can hear sounds between 20 and 20,000 hertz, while dogs can hear high-pitched sounds up to 50,000 hertz. While high-frequency sounds tend to be more hazardous and more annoying to hearing than low-frequency sounds, most noise pollution damage is related to the intensity of the sound, or the amount of energy it has. Measured in decibels, noise intensity can range from zero, the quietest sound the human ear can detect, to over 160 decibels. Conversation takes place at about 40 decibels, a subway train is about 80 decibels, and a rock concert is from 80 to 100 decibels. The intensity of a nearby jet taking off is about 110 decibels a (Pandey, 2006; Vimalha, 2012). The threshold for pain, tissue damage, and potential hearing loss in humans is 120 decibels. Long-lasting, high-intensity sounds are the most damaging to hearing and produce the most stress in humans (Pandey, 2006; Vimalha, 2012).

1.3 HEAVY METAL POLLUTION OF AGRICULTURAL SOIL

1.3.1 Natural Source

The initial sources of heavy metals in soils are the parent materials from which the soils were derived, but the influence of parent materials on the total concentrations and forms of metals in soils is modified to varying degrees by pedogenetic processes (Herawati *et al.*, 2000). In areas affected lightly by human activities, heavy metals in the soils derived mainly from pedogenetic parent materials, and metals accumulation status was affected by several factors such as soil moisture and management patterns (Herawati *et al.*, 2000). In Gansu province, China, Li *et al*. (2008) concluded that the main factor for heavy metals accumulation was lithological in three arid agricultural areas. Soil *aqua regia* soluble fraction of Co, Ni, Pb, and Zn were highly correlated with soil Al and Fe. These elements were associated with indigenous clay minerals in the soil high in Al and Fe.

1.3.2 Mining as Source of Heavy Metals

Mining is one of the important sources by which soils, plants, and surface waters are contaminated. Sources of metal contamination in mining areas, includes grinding, concentrating ores and disposal of tailings (Adriano, 1986; Wang *et al.*, 2004). Inappropriate treatment of these tailings and acid mine drainage could pollute the agricultural fields surrounding the mining areas (Williams and Lei, 2009). In Tongling copper mine of Anhui province in China, metal mining had been an important economic base from ancient time. The major mining areas have been concentrated in a narrow star-shaped basin called Fenghuang Mountain. Long-term mining activities in this area caused widespread metal pollution. The soil concentration of average total Cu was 618 mg/kg, with a wide range of 78-2830 mg/kg. Lead concentration in soil also showed a large variability with a mean of 161 mg/kg. The total Zn concentration varied from 78 to 1280 mg/kg, with an average of 354 mg/kg (Wang *et al.*, 2004). It was reported that the majority of agricultural soils were contaminated with As (Patel *et al.*, 2005). High As concentration in these soils may be attributed to arsenopyrite which is known to occur in many areas of Southeast Asia, especially in tin mining regions (Patel *et al.*, 2005).

1.3.3 Heavy Metals from Smelting and Fly Ash

In the smelting of metal ores, emissions from non-ferrous metal smelters produce a fly ash. Such particles usually contain heavy metals. Atmospheric deposition has been responsible for 43%-85% of the total As, Cr, Hg, Ni and Pb inputs to agricultural soils in China (Luo *et al.*, 2009). Most heavy metal pollutants in air derived from fly ash are caused by anthropogenic activities (Liu *et al.*, 2005) such as electric power generation, mining, metal smelting and chemical plants. The most common elements derived from such atmospheric deposition are Hg, Pb, As, Cd and Zn. Non-ferrous metal smelting and coal combustion are two of the most important sources of metal pollutants in the air. Streets *et al.* (2005) have pointed out that in China, approximately 38% of Hg comes from coal combustion, 45% from non-ferrous metal smelting, and 17% from miscellaneous activities, of which battery and fluorescent lamp production and cement production are of most importance. Zn was the metal deposited in agricultural soils in largest amount from the atmosphere in China, followed by Pb and Cu.

1.3.4 Heavy Metals from Fertilizers and Agrochemicals.

Heavy metals occur naturally in soils and in source materials used to manufacture fertilizers. In addition, heavy metals (and other hazardous constituents) occur in products as a result of blending fertilizers with recycled industrial wastes (e.g., steel mill flue dust, mine tailings). These heavy metals present as minerals, salts and other compounds can be absorbed by plants and incorporated into the food chain. Lu *et al.* (1992) reported that the phosphate fertilizers were generally the major source of trace metals among all inorganic fertilizers. Much attention has also been paid to the concentration of Cd in phosphate fertilizers (Lu *et al*., 1992).

Agricultural use of pesticides is another source of heavy metals in arable soils. Although pesticides containing Cd, Hg and Pb had been prohibited in China in 2002, there were still other trace elements-containing pesticides in existence, especially copper and zinc. It was estimated that a total input of 5000 tons of Cu and 1200 tons of Zn were applied as agrochemical products to agricultural land in China annually (Wu, 2005; Luo *et al.*, 2009). Coca, groundnut, mustard and rice had elevated concentrations of heavy metals (especially Cu and Zn) (Luo, *et al.*, 2009). This may have been contributed by the widespread use of Cu and Zn based pesticides on these crops. Another survey (Pandey and Pandey, 2009) showed that heavy metal concentration in surface horizon and in edible parts of vegetables increased over time. Pandey *et al.* (2000) reported that the metal concentration in soil increased from 8.00 to 12.0 mg/kg for Cd, and from 278 to 394 mg/kg for Zn. They also suggested that if the trend of atmospheric deposition continues, it would lead to a destabilizing effect on sustainable agricultural practice and increase the dietary intake of toxic metals. In India, Sinha *et al.* (2006) found that vegetables and crops growing in areas with persistent application of inorganic pesticides constituted risks due to accumulation of metals.

1.3.5 Heavy Metals from Wastewater Irrigation

Sewage irrigation can alleviate water shortage to some extent, but it can also bring some toxic materials, especially heavy metals, to agricultural soils, and cause serious environmental problems. This is particularly a problem in densely populated developing countries where pressure on irrigation water resources is extremely great. For example in northern dryland China, the amount of wastewater released was 5.25×1010 tons in 2005, of which industrial wastewater accounted for 2.43×1010 tons (Luo *et al.*, 2009; SEPA, 2006). In Chhattisgarh, central India (Patel *et al.*, 2005), soil was irrigated with arsenic polluted ground water. People in this region suffered from arsenic caused diseases. The arsenic concentration ranged from 15 to 825 μg/L in the polluted water, exceeding the permissible limit of 10 μg/L (Patel *et al.*, 2005). The contaminated soil had the median level of 9.5 mg/kg. Many industrial plants in this region operate without any, or minimal, wastewater treatment and routinely discharge their waster into drains, which either contaminate rivers and streams or add to the contaminant load of biosolids (sewage sludge). Biosolids are increasingly being used as soil ameliorants and streams and rivers are the primary source of water for irrigation.

1.4 BEHAVIOUR OF TOXIC ELEMENTS IN THE SOIL-PLANT SYSTEM

Toxic elements enter the soil-plant systems through a variety of sources. Sewage wastes and fertilizers are the major contributors. Once in the soil, these elements interact with organic and inorganic constituents. Transformations such as adsorption, chelation, dissolution-precipitation and methylation, control the availability of toxic elements to plants and consequently to humans and animals. The toxic effects of these elements are exhibited either through reduced plant growth or sick animal/humans. Among the various toxic elements, B and Ni are important in terms of their phytotoxicity. Cadmium, Pb and Hg, though potentially hazardous to animals, generally accumulate preferentially in leaves and roots rather than in fruits or grains (Singh and Sandana, 1987). Phytotoxicities of Zn, Cu, and Ni provide barriers to the toxic levels of Cd, Pb and Hg in the food chain.

1.5 BACKGROUND AND JUSTIFICATION OF THE STUDY

Prolonged farming activities involving the use of fertilizers, herbicides and insecticides tend to expose the environment to potential hazards of soil pollution. Once soil is polluted, the contaminants will be transferred to other environmental components, and to humans via the food chain (Cui *et al*., 2005; Zhang *et al*., 2007). Rapid industrialization during the 1960s brought about dangerous pollution of soil by heavy metals in Japan (Makino *et al*., 2010). The South and Southeast Asian countries, such as Peninsular Malaysia, Vietnam, India, Thailand, Philippines, Indonesia, Bangladesh, and Pakistan have paid much attention to contamination of agricultural soils and crops by heavy metals (Herawati *et al*., 2000).

In a number of studies worldwide, high levels of heavy metals have been reported in soils and food crops (Lalor, 2008). This suggests that some kinds of food crops can accumulate heavy metals from the soil and this can endanger human health. The concentration of cadmium in soils of certain regions of Jamaica has been reported to be remarkably high (Lalor *et al*., 1998). Mean soil concentrations of naturally occurring lead and cadmium are much higher than worldwide average values (Waldron, 1980). It has been reported that Cd concentrations in non-mineralized Jamaican soils varied from less than 0.3 mg/kg to over 400 mg/kg (Lalor *et al*., 1998). The average level of Cd in Jamaican soils was 20 mg/kg compared with a world average of less than 1 mg/kg; and concentrations as high as 409 mg/kg had been observed by Lalor *et al*. (1998). Levels of some other metals (As - 373, Cr - 1063, Cu - 657, Pb - 897, Hg - 830, and Zn - 936 mg/kg) were also exceptionally high in these Jamaican soils (Lalor, 1995). Heavy metal pollution of soils is also of concern in China (Luo and Teng, 2006; Brus *et al.*, 2009). Wei and Chen (2001) estimated that nearly 20 million hectares of arable soils (approximately one fifth of the total areas of farmland) were contaminated by heavy metals, and this has resulted in a reduction of more than 10 million tons of food supplies in China annually. In Dabaoshan mined area of Guangdong Province, China, surrounding farmlands have been seriously contaminated with Cd and other toxic metals as a result of long-term mining (of mainly iron and copper) as well as discharge of untreated wastewater. The paddy soil at Fandong village was heavily contaminated with Cu (703 mg/kg), Zn (1100 mg/kg), Pb (386 mg/kg) and Cd (5.5 mg/kg) (Zhuang *et al.*, 2009). The proportion of exchangeable fractions of Cd in soil of Zhangshi irrigation area in Shenyang, Liaoning province of China with the history of sewage irrigation over 45 years was much higher than that of Cu and Pb. It was suggested that Cd would be the most mobile element in the soil (Xiong *et al.*, 2003) and more available to crop, with great risk of moving into the food chain. As a consequence, Cd contamination in the arable soils became the most serious problem in this region (Xiong *et al.*, 2003).

Accumulation of heavy metals in crops grown in metal-polluted soils may cause damage to human health through the food chain. Fu *et al.*, (2008) conducted an investigation on heavy metal contents in rice sampled from Taizhou city in Zhejiang province in China, and found that the geometric mean of Pb in polished rice 0.69 mg/kg was 3.5-folds higher than the maximum allowable concentration (MAC) (0.20 mg/kg) (Fu *et al.*, 2008) of the safety criteria for milled rice. In Japan, the average levels of Cd, Cu, and Zn in rice-fields were 446 mg/kg, 19.5 mg/kg, and 96.4 mg/kg, respectively (Herawati *et al.*, 2000). The estimated average levels of Cd, Cu and Zn in rice were 75.9 mg/kg, 3.71 mg/kg and 22.9 mg/kg^{-} respectively (Herawati *et al.*, 2000). In Dabaoshan Mined area of Guangdong Province, China, the average concentration of cadmium in rice exceeded 150 times of the State Food and Health Standards (Lin *et al.*, 2005). Norra *et al*. (2005) reported the concentration of As in the winter wheat grain as 0.7 mg/kg in cultivated agricultural area of west Bengal Delta Plain. Where agricultural activities are intensive and food production is high, it is very critically important to monitor contaminant levels in soils and food crops to determine the degrees of soil contamination and migration into food crops. Concerns about the effects of heavy metals such as cadmium on human health have led to numerous guidelines and regulations limiting their concentrations in soils and food and allowable human intakes (Lalor, 2008). These have socio-economical consequences in terms of land use and the marketing of food (Lalor, 2008). Jamaican agricultural soils are known to contain orders of magnitude higher than world normal concentrations of cadmium (Lalor, 2008) resulting in elevated Cd concentrations in several foodstuffs and significant transfers to humans, which represent a risk factor for increased mortality and/or morbidity in the local populations (Lalor, 2008). Exposures to heavy metals have caused a variety of clinical conditions and fatalities (Hallenbeck, 1984; Lalor, 2008).

1.5.1 Metals Pollution in Zamfara State

The incidence of abnormally high levels of metals has been reported in Zamfara State northwestern Nigeria (Lar, 2013). The concentration of Pb in Anka town in Zamfara was found to range from 6.19 mg/kg to 4152 mg/kg, with a mean of 1171.4 mg/kg (Lar, 2013). Other metals Cd, As and Hg had concentrations of 10 mg/kg, 173.2 mg/kg and 12.9 mg/kg respectively in Anka while in Kwalli, maximum Zn concentration of 1657 mg/kg was recorded. The concentration of Hg ranged from 2.15 mg/kg in Bagega to 12.9 mg/kg in Anka mine processing sites (Lar, 2013). The high concentration of Pb in these areas was attributed to the release from the mine dumps around Kuba, Kwalli and Zuzzurfa State mines as well as the gold sulphide vein which contains some heavy metals. In many areas in all villages sampled in Zamfara State, Nigeria, including family homes and compounds, the soil lead concentration exceeded 100,000 mg/kg, far above the recommended maximum of 400 mg/kg considered acceptable for residential areas (Galadima and Garba, 2012). Surface water in ponds, rivers and lakes in Zamfara State were not spared. High concentrations of lead (1,000 μg/L) were often found in ponds, rivers and lakes sampled (Galadima and Garba, 2012). This is not surprising since surface water sources are often used for processing ore. Lead poisoning in Zamfara State have claimed the lives of over 500 children, and left thousands in severe health situations in 2010 (Galadima and Garba, 2012). This shows that even in Nigeria, heavy metals pollution has not spared our environment. How can we be sure that such cases of heavy metals pollution will not occur in other parts of Nigeria? Some years ago there were no issues of lead poisoning in any part of Nigeria but has now been reported in Zamfara State. The major concern therefore is that, heavy metals in crops grown in these areas may eventually be transferred from soil to crops and eventually find their way to the food chain.

1.5.2 Heavy Metals Study in the Kogi State Farmland Environment

Farming is a very important and major activity in Kogi State. The state is considered as one of the food basket regions of Nigeria. The farms are owned by government parastatals, corporate private organization, and individuals. The National Food Reserve Agency (2008) reported that cassava production in Kogi State increased from 2.8million metric tons to 3.6 million metric tons in 2003, which is the highest in Nigeria. The state's per hectare yield is currently 14.88 tons, which is among the highest in Nigeria (Tables 1.1). Table 1.2 shows a similar pattern for maize. Most farmers grow cassava as a source of cheap energy food, and it could be grown on marginal soils with the least input requirements. However, because of increasing demand for food production, fertilizers and other agrochemicals inputs are always applied. Given the issues highlighted in the foregoing section, the long term application of agrochemicals may lead to pollution of soils and crops. It is therefore imperative to monitor agricultural soils and examine food crops grown thereon. In the Kogi State farmland environment, there is paucity of data on the level of metals in soil and food crops as similar works recently carried out by Lar (2013) on Kogi State environment was sketchy and mainly focused on iron ore mining company site at Itakpe. Also the study carried out by Matthews-Amune and Kakulu (2013) focused on a farm at Adogo town and this may not give a general reflection of the Kogi State farmland soils.

Table 1.1: Cassava production (‘000mt) in North Central Zone of Nigeria

State	1999 AC*	1999 AP*	2000 AC*	2000 AP*	2001 AC*	2001 AP*	2002 AC*	2002 AP*	2003 AC*	2003 AP*
FCT	0.83	7.01	0.71	6.37	0.85	8.19	1.03	10.21	1.02	10.21
Niger	86.53	666.28	80	569.75	67	500	45.00	350.00	57.3	422.07
Benue	286.09	3,531.67	252.2	3,516.15	269.39	3,585.22	269.45	3,578.09	269.88	3,577.92
Kogi	**200**	**2,793.30**	**186**	**2,506**	**182**	**2704**	**177.90**	**2,785.12**	**173.199**	**2854.83**
Kwara	33.91	455.76	30	438.40	29	411	35.00	500	36	510.00
Nassarawa	36.92	338.19	25	250.00	25	245.5	23.00	240.00	19.17	204.76
Pleteau	39.75	500.06	30.156	400.00	23.525	290.06	24.00	292.23	24.60	282.23

Table 1.1 contd:

	2004 AC*	2004 AP*	2005 AC*	2005 AP*	2006 AC*	2006 AP*	2007 AC*	2007 AP*
FCT	1.12	12.00	3.58	39.1	4.10	45.71	3.99	44.80
Niger	57	450.00	50.94	448.24	56.07	456.00	71.04	584.20
Benue	262.73	3,579.20	270.12	3,584.82	270.56	3,595.10	271.17	3,571.48
Kogi	**175.24**	**2,969.63**	**180.75**	**2,666.41**	**214.18**	**3,394.71**	**243.96**	**3,631.94**
Kwara	37	480	59.4	740.30	77.50	1,004.49	85.42	1.111.27
Nassarawa	22.04	242.42	89.71	1,115.94	97.34	1,276.62	61.08	871.12
Pleteau	26	294.83	27.5	323.94	28.54	350.15	29.45	334.79

Source: National Food Reserve Agency, NFRA (2008)
*AC: Area cultivated (‘000ha); *AP: Amount produced.

Table 1.2: Maize production (‘000mt) in North Central Zone of Nigeria

	1999 AC*	1999 AP*	2000 AC*	2000 AP*	2001 AC*	2001 AP*	2002 AC*	2002 AP*	2003 AC*	2003 AP*
FCT	7.277	18.54	6.868	15.77	8.024	17.92	9.70	22.04	10.098	22.34
Niger	328.82	493.36	276.51	384.71	290.116	369.79	282.14	323.46	311.89	377.08
Benue	108.05	148.89	110.29	146.37	109.45	148.31	109.48	148.32	109.58	146.42
Kogi	**149.50**	**252.15**	**141.007**	**245.80**	**137.181**	**234.62**	**130.45**	**240.85**	**129.00**	**250.00**
Kwara	60.12	73.83	62.889	72.37	52.48	62.15	57.89	71.35	57.3	75.45
Nassarawa	75.19	114.13	59.381	93.71	60.372	101.50	56.73	88.84	52.27	85.61
Pleteau	236.93	473.90	217.85	458.93	185.687	353.68	180.13	382.44	172.16	352.45

Table1.2 contd:

	2004 AC*	2004 AP*	2005 AC*	2005 AP*	2006 AC*	2006 AP*	2007 AC*	2007 AP*
FCT	12.6	27.27	16.45	34.26	19.87	508.31	20.43	446.42
Niger	298.44	329.00	365.73	432.39	405.15	508.31	356.34	446.42
Benue	109.51	148.41	109.55	149.48	109.57	152.78	109.74	151.05
Kogi	**132.14**	**256.00**	**120.48**	**213.95**	**150.64**	**264.52**	**180.81**	**289.29**
Kwara	64.4	87.22	82.9	112.40	110.42	150.35	109.22	149.89
Nassarawa	57.34	91.92	70.12	124.46	72.35	125.90	69.73	128.00
Pleteau	136.35	298.45	160.35	369.30	149.77	376.74	121.17	304.57

Source: National Food Reserve Agency, NFRA, 2008
*AC: Area cultivated (‘000ha).
*AP: Amount produced

1.6 AIMS AND SCOPE OF THE STUDY

This study was designed with the overall aim of assessing the exposure risk of heavy metal contamination in man that may arise from the consumption of food crops grown in Kogi State farmland soils. The specific work objectives in achieving this include the following:

- to determine selected physicochemical parameters of soils of selected farms in Kogi State;
- to determine heavy metals (Cu, Co, Cd, Pb, Zn and Ni) levels in these soils and the speciation of metals in the soils;
- to determine some physicochemical parameters in surface water and groundwater use for irrigation in some of the farms;
- to determine heavy metals (Cu, Co, Cd, Pb, Zn and Ni) levels in the irrigation waters;
- to determine heavy metals (Cu, Co, Cd, Pb, Zn and Ni) levels in sediments of the surface water bodies;
- to determine the levels of the heavy metals in parts of food crops (leaves and edible plant parts) grown in the farms;
- to estimate the transfer factors of heavy metals from soil into parts of the crops; and,
- to assess the prevailing soil-plant heavy metal relationships, and fit these into an existing equilibrium model for determining the toxic metals threshold limits to the plants/crops. .

CHAPTER TWO

LITERATURE REVIEW

2.1 BIOACCUMULATION OF HEAVY METALS IN PLANTS

The uptake and bioaccumulation of heavy metals in vegetables are influenced by a number of factors such as climate, atmospheric depositions, the concentrations of heavy metals in soil, the nature of soil on which the vegetables are grown and the degree of maturity of the plants at the time of harvest (Lake *et al*, 1984; Scott *et al*., 1996; Voutsa *et al.*, 1996). Air pollution may pose a threat to post-harvest vegetables during transportation and marketing, causing elevated levels of heavy metals in vegetables (Agrawal, 2003). Elevated levels of heavy metals in vegetables are reported from the areas having long-term uses of treated or untreated wastewater (Singh *et al*., 2004; Sinha *et al.*, 2005; Sharma *et al*., 2006; Sharma *et al.*, 2007). Other anthropogenic sources of heavy metals include the addition of manures, sewage sludge, fertilizers and pesticides, which may affect the uptake of heavy metals by modifying the physico-chemical properties of the soil such as pH, organic matter and bioavailability of heavy metals in the soil. Whatmuff (2002) and McBride (2003) found that increasing concentrations of heavy metals in soil increased the crop uptake.

Cultivation areas near highways are also exposed to atmospheric pollution in the form of metal containing aerosols. These aerosols can be deposited on soil and are absorbed by vegetables, or alternatively deposited on leaves and fruits and then adsorbed. Voutsa *et al*. (1996) have reported high accumulation of Pb, Cr and Cd in leafy vegetables due to atmospheric depositions. Field studies have found positive relationships between atmospheric metal deposition and elevated concentrations of heavy metals in plants and top soil (Larsen *et al*., 1992; Sanchez-Camazano *et al.*, 1994). The magnitude of heavy metal deposition on vegetable surfaces varied with morpho-physiological nature of the vegetables (Singh and Kumar, 2006). Jassir *et al*. (2005) have shown that unwashed leafy vegetables sold on roadside of Riyadh city, Saudi Arabia had higher levels of heavy metals compared to washed leafy vegetables. Demirezen and Aksoy (2006) have reported higher concentrations of Pb, Cd and Cu in *Abelmoschus esculentus* collected from urban areas of Kayseri, Turkey compared to those from rural areas. The partitioning of heavy metals is well known, with accumulation of greater concentrations in the edible portions of leafy or root crops than the storage organs or fruits (Jinadasa *et al*., 1997; Lehoczky *et al*., 1998; Sharma and Agrawal, 2006).

2.2 FACTORS AFFECTING METAL AVAILABILITY IN SOIL

Plants usually cannot access the total pool of a metal present in a growth substrate. The fraction of metal which plants can absorb is known as the available or bioavailable fraction. Metals present in a soil can be classified into a number of fractions including, the soluble metal in the soil solution, metal-precipitates, metal sorbed to clays, hydrous oxides and organic matter, and metals within the matrix of soil minerals. These different fractions are all in dynamic equilibrium with each other (Norvell, 1991). However, while the soluble metal in the soil solution is directly available for plant uptake, other soil metal pools are less available (Davis and Leckie, 1978; del Castilho *et al*., 1993). For example, change in the concentration of metal in soil minerals matrix is slow relative to exchange and desorption reactions between clays, hydrous oxides, organic matter and the soil solution (Shuman, 1991; Whitehead, 2000). Metals in soil solution are the only soil fraction directly available for plant uptake (Fageria *et al*., 1991; Marschner, 1995; Whitehead, 2000). Hence, factors which affect the concentration and speciation of metals in the soil solution will affect the bioavailability of metals to plants. Soil factors which have an effect on metal bioavailability include the total metal present in the soil, pH, clay and hydrous oxide content, organic matter and redox conditions.

2.2.1 Total Metal Concentration in Soil

The total metal concentration of a soil includes all fractions of a metal, from the readily available to the highly unavailable. Other soil factors, such as pH, organic matter, clay and redox conditions, determine the proportion of total metal which is in the soil solution. Hence, while total metal provides the maximum pool of metal in the soil, other factors have a greater importance in determining how much of this soil pool will be available to plants (Wolt, 1994). In addition, researchers have found that while total metal correlates with bioavailable soil pools of metal, it is inadequate by itself to reflect bioavailability (Lexmond, 1980; Sauve *et al*., 1996; McBride *et al*., 1997; Sauve *et al*., 1997a; Peijnenburg *et al*., 2000).

2.2.2 Soil pH

The equilibrium between metal speciation, solubility, adsorption and exchange on solid phase sites is intimately connected to solution pH (Olomu *et al*., 1973; Kalbasi *et al*., 1978; Cavallaro and McBride, 1984; Sauve *et al*., 1997b). Hence, numerous studies have found soil pH to have a large effect on metal bioavailability (Turner, 1994; McBride *et al*., 1997). Metals bioavailability is strongly affected by soil pH (McGrath *et al*., 1988; Turner, 1994). As soil pH decreases, Mn and Zn compete with the extra H and Al for positions on the exchange sites, solubility of Mn and Zn increases in the soil solution and a greater proportion is present as highly available free metal ions in the soil solution (Kalbasi *et al*., 1978; McBride, 1982; Bar-Tal *et al*., 1988; Msaky and Calvet, 1990; Sauve *et al*., 1997b). This increases the concentrations of Mn and Zn in the directly bioavailable fraction, i.e., the soil solution (Jeffery and Uren, 1983). In accordance with the changes in metal bioavailability associated with a change in pH, many studies (Parker *et al*., 1990; Davis-Carter and Shuman, 1993) have found that plant uptake of Mn and Zn increases as soil pH decreases. Hence, in Zn contaminated soils, as pH decreased Zn concentration increased in shoots of *Arachis hypogaea* (peanut) (Parker *et al*., 1990; Davis-Carter and Shuman, 1993) and the potential for Mn toxicity in *Vigna unguiculata* (cowpea) (Vega *et al*., 1992) increased in acid soils.

While solution pH affects Cu speciation, solubility, complexation and adsorption (Payne and Pickering, 1975; Msaky and Calvet, 1990; Reddy *et al*., 1995) some soil studies have found little relationship between soil pH and Cu concentration in the soil solution (Jeffery and Uren, 1983; McGrath *et al*., 1988; Sauve *et al*., 1997b). The reason for this is the strong affinity of Cu for organic matter (Norvell, 1991). Therefore, the amount of organic matter dissolved in soil solution, especially in soils high in organic matter, can be a more important determining factor on Cu solubility than pH.

2.2.3 Organic Matter in Soil

Metal ions can be complexed by organic matter, altering their availability to plants. The COO^- groups in both solid and dissolved organic matter form stable complexes with metals (Stevenson, 1976; Baker and Senft, 1995). Hence, as the amount of organic matter present in soil increases, the opportunity for forming stable metal-organic matter complexes increases. In general, plants are unable to absorb the large metal-complexes and so the bioavailability of metals decreases. Copper ions form strong coordination complexes with organic matter (Stevenson, 1976, 1991). Hence, Cu is often predominantly found bound to the organic matter fraction in the soil and soil organic matter can be the most important soil factor in determining Cu bioavailability (del Castilho *et al*., 1993). In a Chernozem, between 37 and 91% of the total soil Cu was present in the organic fraction depending on level of Cu contamination (Pampura *et al*., 1993). In a range of Cu contaminated soils, greater than 98% of the Cu in the soil solution was bound to organic complexes, irrespective of pH (Sauve *et al*., 1997b). Also, in a different range of soils, approximately 95% of soil solution Cu was complexed, irrespective of pH (Fotovat *et al*., 1997). Reddy et al. (1995) found that the proportion of Cu bound to organic matter in the soil solution increased from 37 to 95% as the pH decreased. In addition, Cu applied as sewage sludge was retained in the soil solution in greater quantities than Cu applied as a sulphate because it was bound to dissolved organics from the sludge (Miller *et al*., 1987) and the activity of the highly available Cu^{2+} has been inversely correlated with soil organic matter (McBride *et al*., 1997).

The amount of organic matter found in soils also affects the bioavailability of Zn (Shuman, 1975; Bar-Tal *et al*., 1988; del Castilho *et al*., 1993). However, while Zn readily forms complexes with organic matter, it does not compete for these sites as well as Cu (Cavallaro and McBride, 1984) and other more prevalent cations such as Ca^{2+} (Fotovat *et al*., 1997). In the same Chernozem experiment as described in the paragraph above, between 2 and 6% of the total soil Zn was found in the organic fraction (c.f. 37 to 91 % of Cu) (Pampura *et al*., 1993). In soil solution, the activity of the highly bioavailable Zn^{2+} in the soil solution decreased as organic matter increased across a range of contaminated soils (McBride *et al*., 1997). Across a range of soils greater than 50% of the soil solution Zn was present as the free ion (Lorenz *et al*., 1997). Also, soil solution Zn was found to be between 23 and 93% organically complexed dependent on soil pH (Reddy *et al*., 1995). Hence, organic matter, while important, does not tend to be as big a factor as pH in determining Zn bioavailability (Elrashidi and O'Connor, 1982).

Manganese tends to form weak coordination complexes with organic matter (Olomu *et al*., 1973; McBride, 1982). This means that Mn^{2+} is unable to compete effectively with Cu^{2+}, Zn^{2+} and other more prevalent cations, such as Ca^{2+} and Mg^{2+} for sites on organic matter, and hence, less Mn is generally found bound to organic matter than for Cu and Zn (McGrath *et al*., 1988). For example, across a range of soils approximately 30% of the soil solution Mn was present as organic complexes (Olomu *et al*., 1973). Complexed Mn in the soil solution of a sandy loam increased from 10 to 55% as the amount of organic matter in the soil increased (McGrath *et al.*, 1988). In contrast, only one study has ever found Mn-organic matter complexation to approach that of Cu. Geering *et al*. (1969) found between 84 and 99% of the Mn present in the soil solution to be bound to organic matter in soils from a variety of areas. In majority of cases, organic matter has less importance in the bioavailability of Mn than for Zn and especially, Cu.

2.2.4 Clays and Hydrous Oxides

Clays and hydrous oxides, of Al, Fe and Mn, play an important role in the availability of metals. Clays and hydrous oxides determine metal availability mainly by specific adsorption to surface hydroxyl groups (Miller *et al*., 1987; Pampura *et al*., 1993). Nonspecific adsorption (exchange) (Kalbasi *et al*., 1978; Basta and Tabatabai, 1992), coprecipitation and precipitation occur as discrete metal oxide or hydroxide (Martinez and McBride, 1998). Hence, increasing clay and hydrous oxide contents in soils provides more sites for adsorption of metals, thus reducing the bioavailable metal directly (Shuman, 1975; Ghanem and Mikkelsen, 1988; Barrow, 1993; Qiao and Ho, 1996).

2.2.5 Oxidation and Reduction Conditions of a Soil

The oxidation/reduction (redox) conditions of a soil can play a role in the availability of metals. The redox status of soils can be affected by many factors including waterlogging and compaction. Redox conditions can affect the availability of metals by affecting the proportion of particular metal species (e.g. Mn(II) vs. Mn(IV) in soil solution and by affecting solubility of metals in soil solution (Patrick and Jugsujinda, 1992; Evangelou, 1998). Under waterlogged conditions, increases in Mn uptake and symptoms of Mn toxicity have been noted in Malus sp. (apple) and Pyrus sp. (pear) trees (Grasmanis and Leeper, 1966). Hence, reducing soil conditions, such as flooding and soil compaction, tend to increase the availability of soil Mn and enhance toxicity (Cheng and Ouellette, 1971).

Most Cu and Zn are present as the divalent forms in soils with the monovalent forms being highly unstable (Knezek and Ellis, 1980; Whitehead, 2000). Hence, neither Cu nor Zn tends to be significantly reduced under low redox conditions (Moraghan and Macagni Jnr, 1991; Whitehead, 2000). However, Zn deficiency has been noted in flooded soils and it was suggested that this was due to the precipitation of Zn as compounds such as $ZnFe_2O_4$ under reducing conditions (Sajwan and Lindsay, 1986; Moraghan and Macagni Jnr, 1991). As such, redox conditions play a smaller role in the availability of Cu and Zn when compared with Mn

2.3 NUTRIENT AND METAL IONS FROM SOIL SOLUTION

The immediate source of nutrient and metal ions to a plant is from the soil solution (Fageria *et al*., 1991; Marschner, 1995; Whitehead, 2000). The percentage of any metal occurring in the soil solution is usually small compared to the total metal pool in the soil (McGrath *et al*., 1988; Pampura *et al*., 1993; Sauve *et al*., 1997a). Metals in soil solution are in dynamic equilibrium with the larger soil solid fraction, and so, as metals are removed from the soil solution by plant uptake, or by other processes such as leaching, replenishment of the soil solution will occur. This replenishment can come from exchangeable ions, adsorbed salts, precipitated compounds, mineralisation of organic matter and weathering of soil minerals (Pearson, 1971; Whitehead, 2000).

To adequately assess the toxicity of a metal to plants, analytical approaches must quantify that portion of the total pool of metal in the soil which the plant can access, (the bioavailable fraction). The immediately bioavailable soil fraction is within the soil solution. However, because the soil is in dynamic equilibrium, measures of the ability of the soil to buffer and/or to replenish the concentration of metals in the soil solution could be important in determining bioavailability over a longer time frame. The criterion to assess whether metals present in soils are at toxic levels is not standardised world-wide and varies from one country and land use to another (Ross and Kaye, 1994).

2.3.1 Measures of Total Metal

Metals are frequently measured and regulatory decisions made, for toxicity, on the basis of the total metal concentration in a growth substrate (Gupta *et al*., 1996). Different extractants, generally strong acids such as HNO_3, HF, $HClO_4$ and aqua regia, have been utilised to determine the total or .pseudo-total metal in a soil (Becket, 1989). However, many factors control the availability of metals to plants, making total metal a poor measure of bioavailable metal. It is incorrect to assume that total metal concentration is just an indirect measure of available metal (Miles and Parker, 1979; Pampura *et al*., 1993). Some studies have found good relationships between total metal and plant responses (Aery and Jagetiya, 1997). However these results have tended to be soil specific and, therefore, do not demonstrate the effectiveness of total metal as a tool for measuring the effects of excess metal on plants.

2.3.2 Soil Solution and Pseudo-measures of Soil Solution

The concentration of a metal in a soil solution is a measure of immediate bioavailable metal (Pearson, 1971). Soil solution is technically defined as the aqueous liquid phase of soil at field conditions. Thus, true measures of soil solution occur at moisture levels of field capacity or less (Wolt, 1994). Studies have regularly found good correlations between soil solution metal concentrations and factors affecting metal availability (Wolt, 1994). For example, soil solution Cu, Zn and Cd have been found to correlate well with pH, organic matter, and total metal concentration in the soil (McBride *et al*., 1997).

2.3.3 Speciation and Toxic Forms

The speciation of an element is the chemical form(s) that it takes in solution. Some researches suggest that the free metal ion is the most toxic form of metals (Reddy *et al*., 1995; Sauve *et al*., 1997b). Free metal activity in a wide variety of soils and with a variety of metals correlates well with factors such as organic matter and pH, suggesting that it is a good measure of plant available metal (Reddy *et al*., 1995; Sauve *et al*., 1997b). Research with plants, especially in solution culture, has supported the free metal ion hypothesis (Sparks, 1984; Bell *et al*., 1991; Ibekwe *et al*., 1998). Original suggestions that not all metal in solution was available to plants began with the findings of DeKock and Mitchell (1957) on the effect of chelators on uptake of metals. Subsequent work with Al has further supported this theory (Alva *et al*., 1986; Menzies *et al*., 1994).

The "free ion as the bioavailable species" theory has often been assumed in the literature with very little rigorous research to ground the hypothesis (Parker and Pedler, 1997). Work with chelates and organic acids has shown that metals complexed with organic compounds are more available than the free-ion activity would suggest (Bell *et al*., 1991; Laurie *et al*., 1991a; Laurie *et al*., 1991b; Srivastava and Appenroth, 1995; Parker *et al*., 2001). At a given activity in solution, plant uptake of Zn and Cd has been found to be greater in the presence of a ligand compared to the absence of a ligand (McLaughlin *et al*., 1997a) and that this difference was amplified as the metal-ligand binding constant increased (McLaughlin *et al*., 1997a). Work with Cd in both soil and solution culture has shown that Cl complexed Cd is also available to plants (Smolders and McLaughlin, 1996; Smolders *et al*., 1998). In contrast, research with *Kandelia candel* (mangrove) has suggested that NaCl reduces Zn and Cu toxicity (Chiu *et al*., 1995) but from the experimental design this could just as easily indicate competition between Na^{+} and Zn^{2+} or Cu^{2+} for uptake, or a positive effect of NaCl on growth in this halophytic species. Research with Cu toxicity has shown that plant responses cannot be explained by the Cu^{2+} ion alone (Lexmond and van der Vorm, 1981). Parker and Pedler (1997) conducted computer simulations of various nutrient systems and found that while the free ion activity is generally a good measure of plant available metal, there are certain situations outside the bounds of the model. For instance, use of the free ion activity as the measure of plant available metal assumes that the solution is not replenished from solid phases, while this holds in most solution cultures it does not in soil studies. They also found that larger deviations from the model were likely to occur at high root to solution ratios, as in soil.

Research between metals and the free metal ion in soil solution is inconclusive on whether the free metal ion is the best predictor of metal availability (Reichman, 2002). In *R. sativus*, *L. sativa* and *Lolium perenne* (perennial rye grass) free ion activities were better measures of plant Cu uptake than total Cu or $CaCl_2$ extracted Cu in eight contaminated urban soils (Sauve *et al*., 1996). Research with *T. subterraneum* and *Panicum virgatum* (switch grass) found plant uptake of Mn to be equally well correlated with Mn^{2+} activity and the soil solution Mn concentration across 11 soils (Wright *et al*., 1988). The activity in soil solution has been found not to predict *P. vulgaris* Cu uptake (Minnich *et al*., 1987). Concentration of Cd in *Solanum tuberosum* (potato) tubers from 50 soils was not related to the Cd^{2+} activity in the soil solution but rather to the degree of Cd-Cl complexation in the solution, suggesting a role for more than the free ion in Cd toxicity (McLaughlin *et al*., 1997b). While the debate continues, evidence suggests (McLaughlin *et al*., 1997b) that the immediately bioavailable fraction of a metal is somewhere between the total amount in the soil solution and the free ion activity. Until the answer is found for each metal either the free ion activity or total soluble metal in solution appear to be the best estimates.

2.3.4 Plant Factors

While soil factors have a large impact on the bioavailablity of metals to plants, different species or varieties grown on the same soil have different metal uptakes (Miles and Parker, 1979). Therefore, there are species specific factors affecting plant uptake. Jarvis and Whitehead (1981) suggested that a true measure of plant available metals will not be attained unless the extent of soil exploitation by the roots is accounted for. However, it should be noted that while two plant species may take up different amounts of metal within a given time frame, it does not necessarily mean they are extracting from different soil pools of metal.

2.3.5 Nature of Vegetation

Vegetation or plant physiological uptake of elements from the subsurface and their release to the surface via litter is a potential mechanism of rapid metal transfer. However, the ability of plants to tap water sources for their nutrient content is critical to the transfer mechanism; otherwise higher metal content plants merely indicate recycling of a soil anomaly. The potential of plant-assisted metal transfer from deeper groundwater comes from deuterium isotopic studies on facultative pheratophytes plants having dimorphic roots systems with laterals and sinker or tap roots (vertical), the latter roots acquiring water and nutrients from deeper groundwater source, especially during summer (Pate *et al*. 1999). Previous work on plant-metal relationships in the Northern Yilgarn suggests plants take up ore-related metals from groundwater at depth (Pate *et al*. 1999). Additionally, hydraulic lift and redistribution of deeper water acquired by sinker roots to near surface soil horizons to be used by laterals (Caldwell *et al.* 1998) is capable of rapid transfer of water and possibly metals within the overburden. Diurnal uptake and transfer of groundwater to surface soil has been confirmed (Caldwell *et al.* 1998) but no data exist on ore metal transfer.

The depth of rooting is critical to the ability of vegetation in transferring water and possibly ore metals upwards. A global survey indicates that deep roots, especially sinkers, are ubiquitous with > 10 m depths regularly reached and confirmed in several climatic settings (Canadell *et al*. 1996). Plants are known to take up mineral elements that are essential micronutrients (Zn, Mo, Se) plus other ore metals (Au, Ni, Cu, Pb) and even potentially toxic metals such as As in significant concentrations (Meharg and Hartley-Whitaker 2002). Plant physiological processes biotransform specific metals within their tissues, thereby influencing the effectiveness of selective leaches and element mobility once the metals are released on the surface via litter.

2.4 HEAVY METALS SOLUBILITY IN SOILS

Trace metal mobility is closely related to metal solubility, which is further regulated by adsorption, precipitation and ion exchange reactions in soils. Although much effort has been spent on modelling trace metal solubility (Sposito, 1984; Cederberg *et al*., 1985; Martin *et al*., 2003), such predictions under field conditions suffer from much uncertainty. This is partially due to the difficulty in assessing the effects of dynamic soil solution chemistry on trace metal speciation (Jensen *et al*., 1999). However, changes in soil solution chemistry, such as pH, redox potential and ionic strength, may also significantly shift the retention processes of trace metals by soils (Gerringa *et al*., 2001). These effects may be further complicated by ligand competition from other cations (Amrhein *et al*., 1994; Norrstrom and Jacks, 1998).

Trace metals are highly persistent and widespread contaminants. They enter the food webs through pathways such as air, water, soil and living organisms, by agricultural runoff, industrial effluent, mining and mineral processing, storm-water runoff, volcanism, natural bedrock erosion atmospheric transport, and biogeochemical cycles (Burger and Gochfeeld, 1995). Once soil is polluted, the contaminants will be transferred to other environmental components, and indirectly threaten human health through water supply or food chain (Cui *et al*., 2005; Zhang *et al*., 2007).

2.5 MOBILITY OF HEAVY METALS IN SOIL

Pollution induced by trace elements in soils is a major environmental problem because, compared to atmospheric and water pollution; the soil environment is much less resilient. The total content of a trace element in the soil is a poor indicator of environmental risk. Mobility and bioavailability must be assessed to elucidate trace elements' behaviour in soils and prevent potential toxic hazards (Sauvé *et al*., 2000; Yin *et al*., 2002; Banat *et al*., 2005; Wu *et al*., 2006; Navarro *et al*., 2006; Margui *et al*., 2007). The mobility and bioavailability of these elements depend on soil characteristics such as pH, organic matter, cation-exchange capacity, and soil redox potential (Adriano, 1986) and also on physical, chemical, and biological processes, including microbial activities (Deneux-

Mustin *et al*., 2003). Organic matter plays a significant role in the availability and mobility of heavy metals in soils. The humified organic matter is involved in the formation of soluble complexes especially with Cu and Zn (Vega *et al*., 2004). The soil solution speciation of trace elements is critical for assessing their bioavailability and potential threat to the environment (Sauvé *et al*., 1997a). The effect of microorganisms on the fate of contaminants in soils can be direct or indirect. Microbial activity changes the physical and chemical characteristics of the environment and may, therefore, indirectly affect contaminant speciation and mobility. Microbial activity in soils is, in turn, strongly affected by physical and chemical soil characteristics (acidity, redox potential, nutrient availability, pore space, etc.). Biogeochemical processes in soils influence the fate of trace elements, that is, their speciation, mobility, and, therefore, their bioavailability and toxicity (Deneux-Mustin *et al*., 2003).

2.6 MECHANISM OF UPTAKE OF SOIL HEAVY METALS BY PLANTS

Uptake of metals into plant roots is a complex process involving transfer of metals from the soil solution to the root surface and inside the root cells. Understanding of uptake processes is hampered by the complex nature of rhizosphere which is in continual dynamic change interacted upon by plant roots, the soil solution composing it and microorganisms living within the rhizosphere (Laurie and Manthey, 1994).

Plants have a natural ability to take up inorganic chemicals (including metals) from soil and sediment. Some of these mineral elements are essential nutrients to the plant, while others have no known physiological function in plants (Ernst, 1996). The most common route of chemical uptake into plants is through the root via an aqueous phase. Ions and organic molecules move to roots from soil and sediment through plant transpiration (ion transport from the soil water into the root occurs simultaneously with water transport), diffusive transport, and microbial facilitated transport (Committee on Bioavailability of Contaminants in Soils and Sediments, 2003). The plasma membrane serves as a barrier to uptake; chemicals need to cross the plasma membrane into the cytoplasm of the root cells. Different mechanisms have been identified which control chemical uptake by plants (Marschner, 1995). Some chemicals can enter root tissue by altering pH through efflux of hydrogen (H^+) ions, resulting in an electrochemical gradient that facilitates transport of cations and anions. This mechanism is termed a proton pump and requires cellular energy in the form of adenosine triphosphate (ATP). Most divalent cations are absorbed through ion channels. Ion channels can also mediate uptake and release potassium ions (K^+). There is also evidence for carrier-mediated active transport of K^+, SO_4^{2-}, NO^{3-}, and Mg^{2+} that uses ATP as an energy source (Marschner, 1995). For metals, another possible mechanism of uptake is transport of metal-chelate complexes. Whenever there is a metal deficiency, plants produce and release chelating agents into the rhizosphere. The complexed metal form is then transported into the plant through a transport protein specific for that metal (Kochian, 1993; Von Wiren, *et. al*., 1996). The selectivity of many of these mechanisms is limited; ions that have the same charge or same size can share the same carrier or channel with nutrients, resulting in an increased uptake of metal contaminants (Oliver *et al*., 1994; Fan *et al*., 2001). Plant-availability of nutrients as well as potentially risk elements is predominantly driven by soil conditions in rhizosphere (Schoettelndreier and Falkengren-Grerup 1999; Dakora and Phillips 2002). Organic acids, such as malate, citrate and oxalate, have been proposed to be involved in many rhizosphere processes, including nutrient acquisition and metal detoxification, alleviation of anaerobic stress in the roots, mineral weathering and pathogen attraction.

Water temperature may influence water chemistry, metal solubility, and metal uptake by plants, and plant growth. According to Zumdahl (1992), seasonal variation in water temperature has no direct effect on the solubility of metals in water. However, cool water contains more dissolved oxygen than does warm water. Thus, metal concentration in the interstitial water of the sediment may decrease with decreasing temperature, as more metals are bound to sediment colloids at high rather than low redox potentials (Förstner, 1979). In addition, temperature has a profound effect on plant growth rates and higher temperatures will thus result in greater biomass production and distribution of submersed macrophyte communities (Marschner, 1995; Rooney and Kalff, 2000). A plant of relatively high biomass may have a greater metal uptake capacity; this results from lower metal concentration in its tissue because of a growth rate that exceeds its uptake rate (Ekvall and Greger, 2003). Changes in temperature further change the composition of the plasma membrane lipids (Lynch and Steponkus, 1987). This alters the plant membrane fluidity, resulting in lower membrane permeability at low temperatures and lower metal uptake (Marschner, 1995). In the aquatic environment, Cu adsorption to the alga *Dunaliella tertilecta* increases with increasing temperature (Gonzalez-Davila *et al*., 1995). Further, in the lichen *Peltigera horizontalis* (Beckett and Brown, 1984) and the liverwort *Dumortiera hirsute* (Mautsoe and Beckett, 1996), both intracellular and extracellular uptake of Cd was stimulated by an increase in temperature. Similarly, several studies of terrestrial plants grown at high root temperatures found higher uptakes of Zn, Pb, Ag, Cr, Sb, and Cd than was the case with plants grown at low root temperatures (Hooda and Alloway, 1993; Macek *et al*., 1994; Baghour *et al*., 2001; Albrecht *et al*., 2002). Therefore, a general increase of metal uptake with increasing temperature seems likely.

In order that measurement of the metal content of different cellular fractions is useful in biomonitoring studies, it is essential to understand the kinetics of metal uptake and discharge in each of these compartments; the kinetics data can then be fitted to suitable models, and the values of maximum uptake, time of uptake, etc. can be calculated. To date, most modelling studies of the kinetics of uptake and discharge of heavy metals in aquatic bryophytes have referred to total metal (Mouvet *et al*., 1988; Rasmussen and Andersen, 1999 ; Samecka-Cymerman *et al*., 2002), and to a lesser extent, extracellular and intracellular metal contents (Vazquez *et al*., 1999; Vazquez *et al*., 2000).

There are, furthermore, diverse factors that influence the bioavailability of a metal to a bryophyte. One of these is the acidity of the environment, which determines the chemical speciation of the metal and therefore its affinity for extracellular binding sites and for membrane transporters. In conditions of high acidity, the protons compete with metal cations, and this may inhibit their uptake even though they are present in the environment (Vazquez *et al*., 2000).

2.6.1 Plant Uptake of Cadmium

Cadmium background concentrations in soil depend predominantly on parent material and degree of weathering. After weathering of parent material, or dissolution of solid phase Cd in fertilizers or sludges, Cd exists in solution mostly as the divalent cation, Cd^{2+}. In some solutions, Cd may also be present as a complex ion in solution in association with inorganic ligands , the most important in soil solutions being complexes with Cl^-, SO_4^{2-} or HCO_3^- (McLaughlin *et al*., 1996). In contrast to other trace metals, such as Cu or Zn, it seems that organic ligands do not have great significance in the overall speciation of Cd in soil solutions (Tills and Alloway, 1983; Holm *et al*., 1995). Cadmium tends to be very mobile in soil systems and therefore very available to plants. Cd^{2+} is the main species in soil solution. Accumulation of cadmium in food crops at soil concentrations that are not phytotoxic is a significant concern (Curtis and Smith, 2002; Fritioff *et al*. 2007).

Anthropogenic additions of cadmium to soils occur via short- or long-range atmospheric deposition, additions in fertilizers/ manures and in municipal sewage wastes (effluents and biosolids), urban compost and industrial sludges. In fertilizers, Cd is found predominantly in phosphatic fertilizers due to the presence of Cd as impurity in all phosphate rocks. The contribution of the atmosphere, fertilizer, sludges, manure or compost to the total annual Cd addition to soils varies widely between countries and between regions within countries (Jensen and Bro-Rasmussen, 1992; McLaughlin *et al*., 1996). Plant uptake of Cd is governed by a number of factors such as pH, total Cd concentration in soil, metal sorption capacity of soil (organic matter, cation exchange capacity, clay, Fe and Mn oxides), temperature, moisture content, compaction, aeration and flooding (Chaney and Hornick, 1978). John *et al*. (1972), and others have shown the effect of soil acidity on the uptake of Cd. Plant availability of Cd appears to be affected by soil acidity in a manner similar to that of other metals such as Ni, Zn, Fe, and Cu (Lindsay, 1972). Cd availability increases with increasing soil acidity, probably due to increased solubility of Cd compounds such as hydroxides, phosphates, and carbonates.

2.6.2. Plant Uptake of Lead

Lead is strongly retained by most soils such that in soil solution Pb concentrations are very low especially in relation to other metals such as Cd, Zn, and Cu (Brummer and Herms, 1983). Several factors affect Pb content in urban-grown vegetables, including soil pH, level of Pb in the soil, organic matter content, cation exchange capacity, presence of other elements (especially P and S), plant age and species (Chaney, *et al*. 1984; Kneip, 1978). Lead is especially accumulated in surface horizon of soil because its low water solubility within an environmentally relevant pH range results in very low mobility (Curtis *et al*. , 2002; Barkirdere *et al*., 2008). On account of the strong sorption by soils, surface applications of Pb, whether from atmospheric sources or inadvertent additions in fertilizers, manures or sludges or deliberate use of Pb-containing agricultural chemicals, are retained in the upper or plough layer of soil profiles (Cartwright et. al., 1977; Gulson et. al 1981; Merry *et. al*., 1983). Mechanism of Pb acquisition by plants are little understood, largely due to the difficulty of working at realistically low solution Pb concentrations and adequately accounting for surface contamination of plant surfaces (Peterson, 1978).

2.7 IMPACT OF SOIL METAL POLLUTION ON PLANTS

Soil serves many vital functions in our society, particularly for food production. It is thus of extreme importance to protect this resource and ensure its sustainability. Deteriorating environmental conditions and increasing reliance on agrochemicals have led to a growing public concern over the potential accumulation of heavy metals and other contaminants in agricultural soils (Nriagu and Pacyna, 1988; Alloway, 1990; Kabata-Pendias, 1995).

Toxicity of heavy metals to plants depends on the bioavailability of the elements in the soil, length of exposure period and physiological activity of the plant roots and their associated microorganisms. The total concentration of metals in the soil is not representative of the metal available to plants (Ernst, 1974). Based on the experiences of determining deficiency or just efficiency of those heavy metals which are minor nutrients in agriculture (Cox and Kamprath, 1972) various types of extractants have been used to simulate bioavailability of metals in metal-enriched soils (Ernst *et al.,* 1992; Prueess, 1992; Carter, 1993; Holm, 1995), but without any good correlation to plant responses.

At high concentrations, some metals have strong toxic effects and are regarded as environmental pollutants (Nedelkoska and Doran, 2000; Chehregani *et al*., 2005). Heavy metals are potentially toxic for plants. Phytotoxicity results in chlorosis, weak plant growth and yield depression, and may even be accompanied by reduced nutrient uptake, and disorders in plant metabolism (Dan *et al*., 2008).

In soils polluted by metals, plant growth can be inhibited by metal absorption. However, some plant species are able to accumulate fairly large amounts of metals without showing stress, which represents a potential risk for animals and humans (Oliver, 1997). Metal uptake by crops growing in contaminated soil is a potential hazard to human health due to transmission in the food chain (Brun *et al*., 2001; Gincchio *et al*., 2002; Friesl *et al*., 2006). There is also concern with regard to metal transmission through natural ecosystems (MacFarlane and Burchett, 2002; Walker *et al.,* 2003). Parameters connected with metal uptake have been used as sensitive indicators of metal toxicity (Wilke, 1991; Nannipieri *et al*., 1997). The toxicity of metals in soil varies significantly according to the characteristics of the soil and the time elapsed after contamination by metals (Doelman and Haanstra, 1984; Speir *et al*., 1995).

2.8 SOIL-PLANT TRANSFER FACTORS FOR HEAVY METALS

Transfer factor is one of the key components of human exposure to metals through the food chain. The soil-to-plant transfer factor (also termed uptake factor, accumulation factor, and concentration factor) is an index for evaluating the transfer potential of a metal from soil to plant. The transfer factor is generally defined as the ratio of metal concentration in plant to the total metal concentration in soil (Chumbley and Unwin, 1982; Cui *et al*., 2004; Harrison and Chirgawi, 1989). Sajjad *et.al.* (2009) defined transfer factor as the relative tendency of a metal to be accumulated by a particular species of plant. Generally, transfer factor expresses the bioavailability of a metal at a particular position on plant species. This is however, dependant on different factors such as the soil pH and the nature of the plant itself. Different authors have reported different transfer factors for the same species of plant and across different parts of the plants, such as roots and leafy parts (Ma *et al*., 2006). Transfer factor can also be calculated based on the total metal content of the whole plant without taking into consideration the various parts of the plant. Vegetables cultivated in contaminated soils may take up heavy metals in large enough quantities to cause potential health risks to the consumers. In order to assess the health risks, it is necessary to identify the potential of a source to introduce risk agents into the environment, estimate the amount of risk agents that come into contact with the human-environment boundaries, and quantify the health consequence of the exposure (Ma *et al*., 2006). The higher the value of transfer factor, the more mobile/available the metal is. Hence, the high transfer factor values may exert potential risk to human health. Transfer factor values are always used to describe the accumulation of chemicals in organisms, especially, those that live in contaminated environments (Wang *et al*., 2004. According to USEPA (1992), transfer factor values are major parameters, determining the risk of human exposure to metals in soils.

2.9 ENVIRONMENTAL ASSESSMENT INDICES

2.9.1 Geoaccumulation Index ($\mathbf{I_{geo}}$). Geoaccumulation index (I_{geo}) can be used to assess the extent of pollution of topsoil of a study area. Geoaccumulation index (I_{geo}) first used by Muller (1969), is a tool that indicates the extent of pollution of soil with regards to the background concentrations of the pollutants. The geo-accumulation index (I_{geo}) was distinguished into seven classes by Müller (Buccolieri *et al.*, 2006): $I_{geo} \leq 0$, class 0, unpolluted; $0 < I_{geo} \leq 1$, class 1, from unpolluted to moderately polluted; $1 < I_{geo} \leq 2$, class 2, moderately polluted; $2 < I_{geo} \leq 3$, class 3, from moderately to strongly polluted; $3 < I_{geo} \leq 4$, class 4, strongly polluted; $4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted; and $I_{geo} > 5$, class 6, extremely polluted. I_{geo} is estimated as indicated in the following equation:

$$Geoaccumulation\ index = \log_2 \left[\frac{C_n}{1.5 \times B_n} \right] \qquad (1)$$

where C_n is the measured concentration of the examined metal *n* in the soil, and B_n is the background concentration or reference value of the metal *n*. Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

2.9.2 Contamination Factor and Degree of Contamination. The assessment of soil contamination can also be carried out using the contamination factor (C^i_f) and degree of contamination (C_d). The C^i_f is the single element index, the sum of contamination factors for all elements examined represents the C_d of the environment and four classes are recognized (Hakanson, 1980). Contamination factor is estimated as indicated in the following equation:.

$$C^i_f = \frac{C^i_0}{C^i_n} \qquad (2)$$

Where C^i_0 is the mean of metals from at least five sampling sites and C^i_n is the pre-industrial concentration of the individual metal.

Table 2.1 shows the different contamination factor classes and levels.

2.9.3. Pollution Load Index (PLI)

The pollution load index (PLI) was proposed by Tomlinson *et al*. (1980) for detecting pollution which permits a comparison of pollution levels between sites and at different times. The PLI is normally obtained as a concentration factor of each heavy metal with respect to the background value in the soil. According to Angula (1996), the PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. A PLI value of ≥100 indicates an immediate intervention to ameliorate pollution; a PLI value of ≥50 indicates a more detailed study is needed to monitor the site, whilst a value of <50 indicates that drastic rectification measures are not needed. PLI is estimated as follows:

$$PLI = n\sqrt{Cf_1 \times Cf_2 \quad \ldots \ldots \ldots \times Cf_n} \qquad (3)$$

Where n is the number of determination, Cf is the concentration factor of each heavy metal with respect to the background value in the soil.

Table 2.1: Classification of contamination factor levels (C_f^i) for soil

C_f^i Value	Contamination factor level
$C_f^i < 1$	Low contamination factor indicating low contamination
$1 \leq C_f^i < 3$	Moderate contamination factor
$3 \leq C_f^i < 0$	Considerable contamination factor
$6 \leq C_f^i$	Very high contamination fact

2.10 SOIL-PLANT EQUILIBRIUM MODELING

Scientific modeling is the process of generating abstract, conceptual, graphical and/or mathematical concepts and language. Modeling is an essential and inseparable part of all scientific activity, and many scientific disciplines have their own ideas about specific types of modeling. A scientific model seeks to represent empirical objects, phenomena, and physical processes in a logical and objective way. All models are simplified reflection of reality, but, despite their inherent falsity, they are nevertheless useful (George and Draper, 1987). Chemicals in soil enter plants primarily through the root system and the degree of uptake from soil into root tissues appears to be proportional to the octanol/water partition coefficient, K_{ow} (Rippen, 2000). Thus, studies on the bioconcentration of nonionic organic chemicals have focused on correlations between partition factors and chemical properties that express relative solubility, such as K_{ow} (Rippen, 2000). But the pool of data available for making soil-plant uptake models is limited. As a result, only relatively simple models are available to express plant uptake in terms of chemical properties such as K_{ow}. Metal solubility in soils may be modeled using an equation based upon a pH-dependent Freundlich relation (Jopony and Young 1994). This can be used to predict free metal ion activity in the soil pore water [M^{2+}] from total soil metal content [Msoil] and soil pH. As humus is often considered to be the primary adsorber of metal ions in the soil (Sauve *et al*., 2000), a further refinement is to assume that metals are exclusively adsorbed on humus to increase comparability between soils. Total metal concentrations in the soil [Msoil] were therefore re-expressed as if adsorbed on organic carbon [MC]

De Leo *et al*. (1993) modeled the interaction between soil acidity and forest dynamics when aluminum is mobilized with acid deposition. Guala *et al*. (2009) simplified this model, in order to allow it to be validated experimentally. In their study, they consider the model applicable to other metals in soil, modifying it in order to make it independent of acid deposition, assuming the mobility of other metals in natural pH levels in soil. In order to model the dynamic interaction, general mathematical expression of the model that describes the dynamics of soil acidity with respect to aluminum mobility and the characteristics of trees, according to the model proposed by De Leo *et al*. (1993), and modified by Guala *et al*. (2009) was adopted.

The concentration of metals in plants, and in parts of plants, can be predicted by a simple kinetic model based on the concentration of metals in the soil. This fact can be linked to physiological absorption mechanisms in plants. Hamon *et al*. (1999) found out a plateau in the accumulation of metals by plants attributed to physiological reasons. The pattern of accumulation by plants is quite similar to saturable uptake of metals described for root membrane transporters of Cd, Zn or Hg (Esteban *et al*., 2008; Lombi *et al*., 2009).

The model makes it possible to characterize the nonlinear behavior of the soil-plant interaction with metal pollution, in order to contribute towards establishing threshold values for the toxic effects of metals on plants and eventual plant mortality. The model can be applied to different plants or crops in order to understand how the different concentrations of metals that can be found in the soil can influence their growth. Also knowing the threshold values for toxic effects on plants and knowing the concentrations of metals that are in the soil will help to choose the most suitable crop for each field in order to remediate the soil contamination by means of biouptake. The effects of metals on plant development vary according to the different soil characteristics, the type of plant and the type of metal. As a result, the model makes it possible to directly compare the relative fragility of different environments to the same pollutant. However, many studies do not compare the metal uptake to the available metal concentration in soil denoted by A, but instead to the total metal content of soil, T (Poulik, 1997; Athar and Ahmad, 2002; Moreno *et al*., 2006; Ryser and Sauder, 2006). In this case, T was defined as a proportional sum of the places where the metal is located: the metal uptake S, the available metal content in soil A and the metal adsorbed in the soil matrix (assuming a Freundlich linear relationship for the purpose of simplicity). In equilibrium this is $T = k_1S + A + k_2A$, where k_1, k_2 are the corresponding proportional coefficients for uptake and Freundlich adsorption, respectively.

A soil-plant equilibrium model is a mathematical interaction model, validated by experimental result and can be employed to model the metal uptake by plants and used to determine threshold limits of heavy metal in plant, by knowing metals in soils (Guala *et* *al*, 2010). The model relates the dynamics of the uptake of metals from soil to plants. In order to model the dynamic interaction, they adapted the general mathematical expression of the model that describes the dynamics of soil acidity with respect to aluminum mobility and the characteristics of trees (De Leo *et al*., 1993), and modified by Guala *et al*. (2009). According to their definition, the concentration of available metal in soil, A, is a function of the concentration of metals in plants, S, was explicitly written as:

$$A = \frac{1}{\alpha}\left(\frac{-C + f\,S}{-e + S}\right)S = \alpha\left(\frac{-C/\alpha + (f/\alpha)S}{-e + S}\right)S \qquad (4)$$

Where A is the concentration of available metal in soil, S is the concentration of metals in plants, c/α, *f*/α, and e are the coefficients of absorption

The process of determining coefficients is difficult, and the known empirical methods yield widely varying results (De Leo *et al*., 1993; Guala *et al*., 2009). Therefore, the model needs to be written in a way whereby the relationship A-S may be inferred from fitting Equation (4). However, the coefficients c/α, *f*/α, and e can be fitted by experimental results in order to establish the relationship between A and S. It should be noted that the relationship between A and S is independent of the growth function of plants, which makes it possible to generalize the model to a wide range of plants. We can now test the model in order to verify whether it provides us with reliable results when we introduce realistic values, in this case testing the model when referring particularly to different parts of plants. This is possible by writing in a general mathematical form, where the constant terms are put together in aggregate coefficients to be fitted, giving us:

$$A = \frac{-C_2 S + C_2 S^2}{-C_2 + S} \qquad (5)$$

C_1, C_2, $C_3 > 0$.

However, many studies do not compare the metal uptake to the available metal concentration in soil A, but instead to the total metal content of soil, T (Poulik, 1997; Athar and Ahmad, 2002; Moreno *et al*., 2006; Ryser and Sauder, 2006).

CHAPTER THREE

MATERIALS AND METHODS

3.1 STUDY DESIGN

The design and execution of the study included the following major components:

(i) Selection of farms for study: Eight farms in various parts of Kogi State were selected for study. These are located at:

- Ofoke (ADP farm),
- Ankpa,
- Ajaokuta,
- Adavi (Macks Farm)
- Ibaji,
- Idah,
- Ejule,
- KSU,

A control farm site was selected at Anyigba. A non-farm, forest location at Lokoja was also studied as part of the control system. The locations of the farms in Kogi State are given in Fig. 3.1.

(ii) Study of the Topsoil and Subsoil Characteristics:

Types of soils: Topsoil samples (0-15 cm) and subsoils (15-30 cm) were studied.

Nature of soil collected: The soils were mainly ultisol and predominantly loamy sand.

Location of soil sampling points within farms: Soil samples were obtained from the cropping areas.

Periodicity of sampling: Samples were collected quarterly.

Number of samples collected: At each farm, during each sampling visit, two composite topsoil samples were collected. Two sub-subsoils at these locations were also obtained. Numbers of soil samples collected are provided in Table 3.1.

Parameters determined in soil samples: Soil samples were analyzed for heavy metals and some physicochemical parameters.

(a) heavy metals determined were cadmium, cobalt, copper, lead, nickel and zinc.

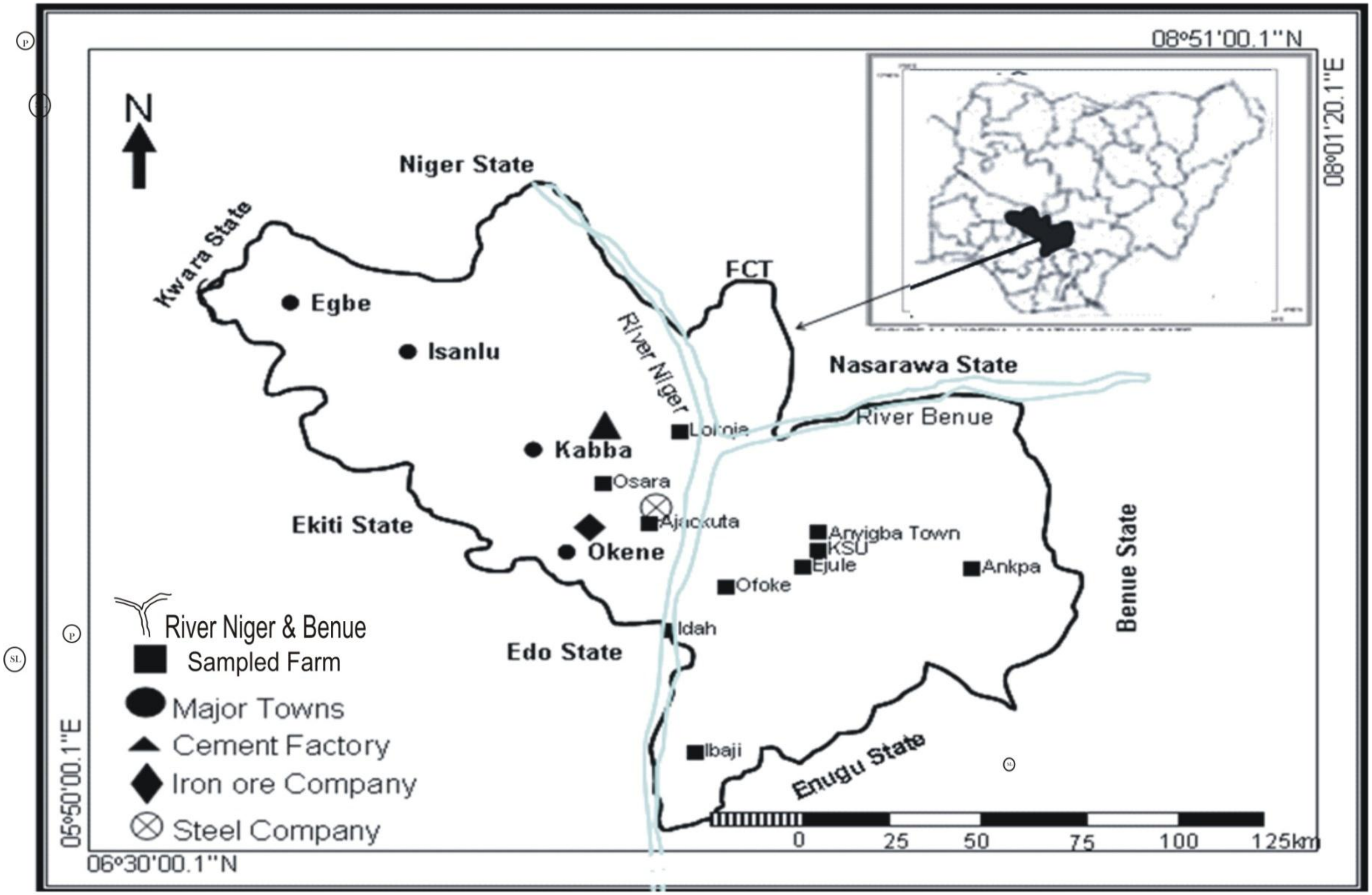

Figure: 3.1. Location of Sampled farms in Kogi State, Nigeria

Table 3.1: Number of soil and plant samples collected per farm

Farms	Soil*	Food crops	
		Leaves	Edible parts
Ofoke	32	40	40
Macks	32	40	40
KSU	32	40	40
Ibaji	32	40	40
Ankpa	32	35	35
Ajaokuta	32	35	35
Ejule	32	35	35
Idah	32	35	35
Anyigba (control)	32	20	20

*Consist of topsoil and subsoil.

(b) Physicochemical parameters were pH, total organic carbon, total organic matter and mechanical properties (% sand, % silt and % clay).

(iii) *Study of irrigation water*

In farms where crops were irrigated using water from groundwater or surface water, such irrigation water samples were also analysed to determine possible contribution to the crop characteristics.

(a) Surface water: This was available at three of the farms – Ofoke, Ibaji and Macks.

Location of Sampling Point: Large pool of dam water from which channels are used for irrigation.

Number of samples collected per trip: Two water samples each at Ofoke and Ibaji; and three at Macks farm.

Periodicity of sampling: Water samples were collected quarterly.

Parameters determined in irrigation water samples: Samples were analyzed for:

- *Physicochemical parameters* - pH, temperature, alkalinity, total hardness, calcium, magnesium, sulphate, phosphate, nitrate, Dissolved Oxygen (DO) and Chemical Oxygen Demand (COD).
- *Heavy metals*– cadmium, cobalt, copper, lead, nickel and zinc.

(b) Groundwater (borehole):

Number of samples collected per trip: Two water samples were collected.

Periodicity of sampling: Samples were collected quarterly.

Parameters determined in irrigation water samples: As determined in surface water.

(iv) Study of bottom sediment irrigation streams:

Number/Location of samples per sampling trip: Samples were obtained at same locations and time where/when surface water samples were collected.

Periodicity of sampling: Samples were collected quarterly

Parameters determined in sediment samples: cadmium, cobalt, copper, lead, nickel and zinc.

(v) Study of metals levels in food crops.

*Types of food crop*s: The following crops were studied:

- pumpkin,
- maize,
- passion fruit,
- sugar cane, and
- cassava.

In each farm, crops were sampled as available.

Parts of crop sampled: The leaves, tuber, fruits, grains or stem as appropriate to a particular crop were sampled.

Location of crop sampling points: Samples were collected in the general vicinities of the soil sampling point

Number of sample collected per farm: For each crop collected during a sampling trip, four composite sample of each of a given crop parts were obtained. Details of number of samples collected and types of crop are provided in Table 3.1 and Table 3.2 respectively..

Periodicity of sampling: Sampling was carried out quarterly.

Parameters determined in plant samples: Samples were analysed for heavy metals cadmium, cobalt, copper, lead, nickel and zinc.

(vi) Modeling of metal concentration in soils and crops.

Data of metal concentrations in soil and crops parts were fitted into an existing soil-plant equilibrium model.

3.2 DESCRIPTION OF SAMPLING SITES

The soil and food crop samples were collected from sampling locations quarterly from May, 2007 to February, 2009 across the three senatorial district of Kogi State, North Central, Nigeria. A schematic diagram of each of the sampled farm area is given in Figs 3.2 to Fig 3.10. Code names for sampled farms, soil, water, sediment and other acryonym used are given in Table 3.3.The GPS and size of farm is given in Table 3.4 while the geological features and vegetation are on Table 3.5.

Table 3.2: Plant species sampled

Sampling site	English name	Scientific name	Part sampled
Ofoke (ADP)	Maize,	*Zea mays* Linn	Leaves and grain
Macks	Passion fruit	*Passiflora edulis* Linn	Leaves and fruit
KSU	Pumpkin	*Cucurbita pepo* Linn	Leaves and fruit
Ibaji	Sugar cane	*Saccharum officinarium* Linn	Leaves and stem
Ankpa	Cassava	*Manihot esculenta* Crantz	Leaves and tuber
Ajaokuta	Cassava	*Manihot esculenta* Crantz	Leaves and tuber
Ejule	Cassava	*Manihot esculenta* Crantz	Leaves and tuber
Idah	Cassava	*Manihot esculenta* Crantz	Leaves and tuber
Anyigba	Cassava	*Manihot esculenta* Crantz	Leaves and tuber

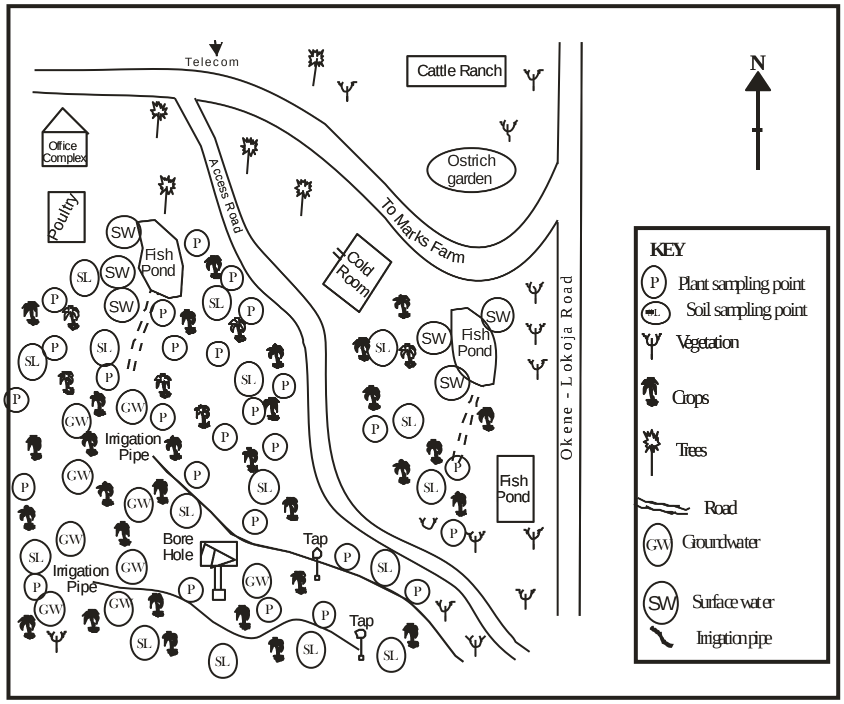

Fig 3.2: Sketch of Macks farm showing the sampling points.

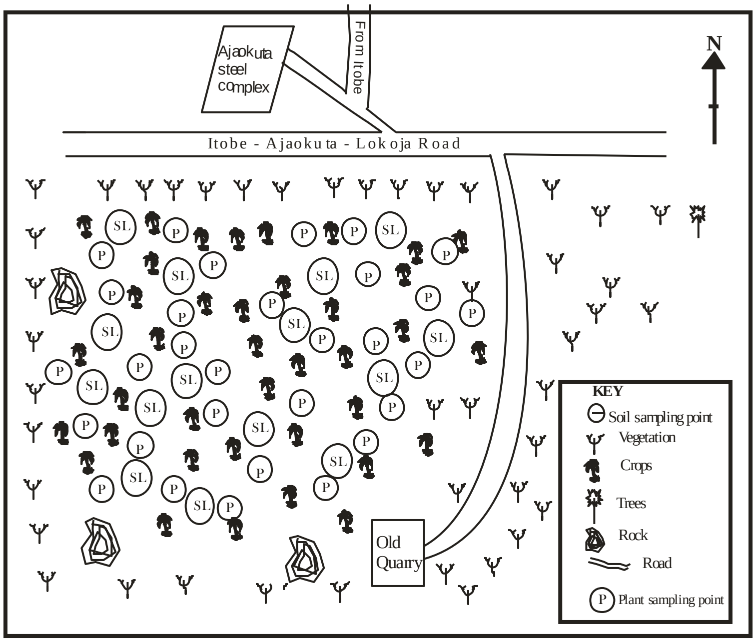

Fig 3.3: Sketch of Ajaokuta farm showing sampling points

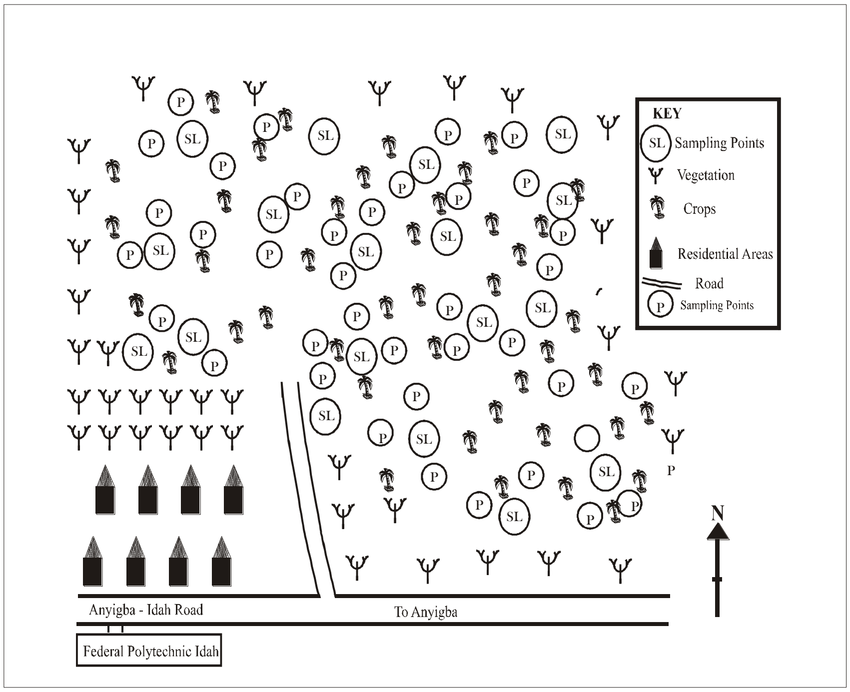

Fig3.4: Sketch of Idah Farm Showing Sampling Points

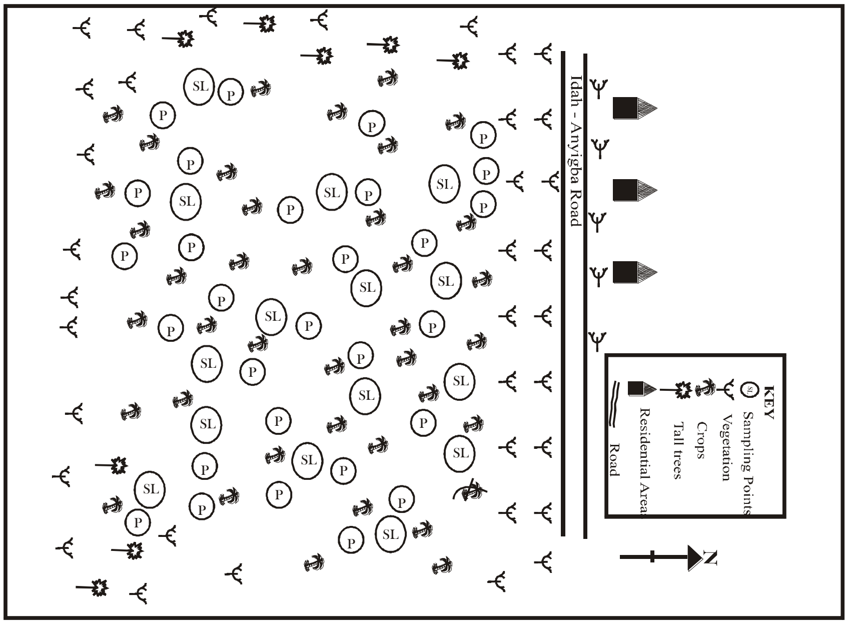

Fig3.5: Sketch of Ejule farm showing sampling points

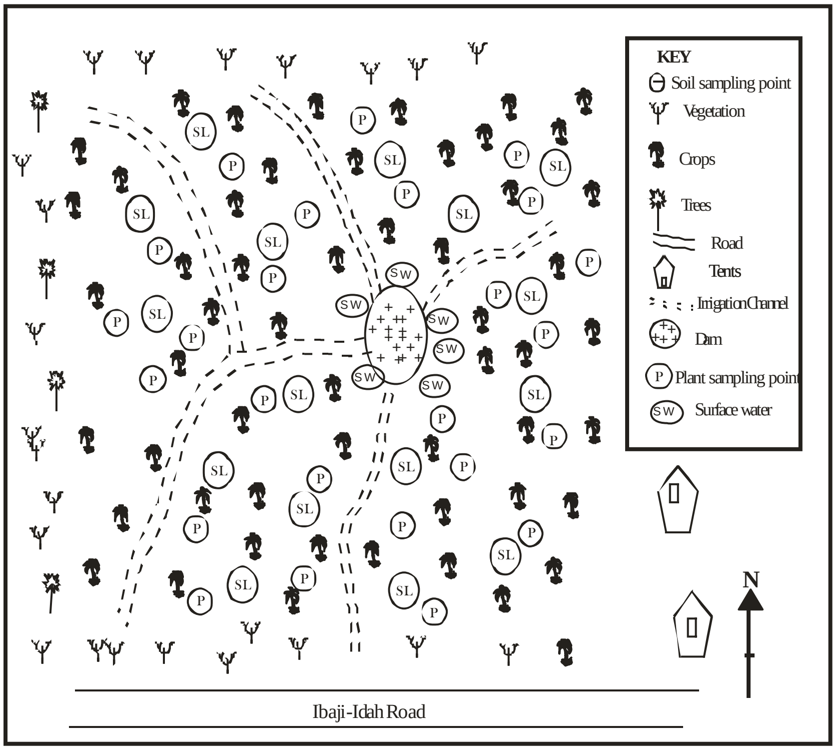

Fig3.6: Sketch of Ibaji farm showinng sampling points

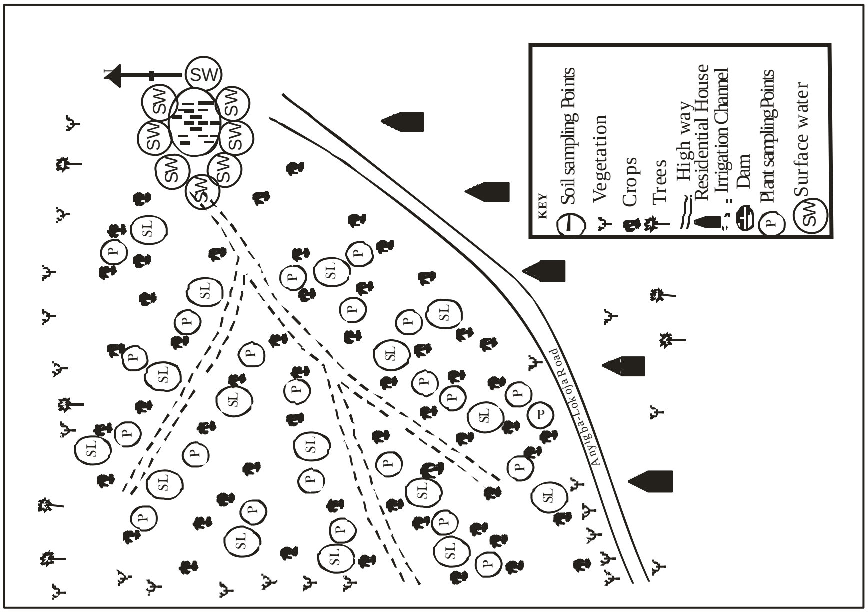

Fig3.7: Sketch of Ofoke farm showing sampling points

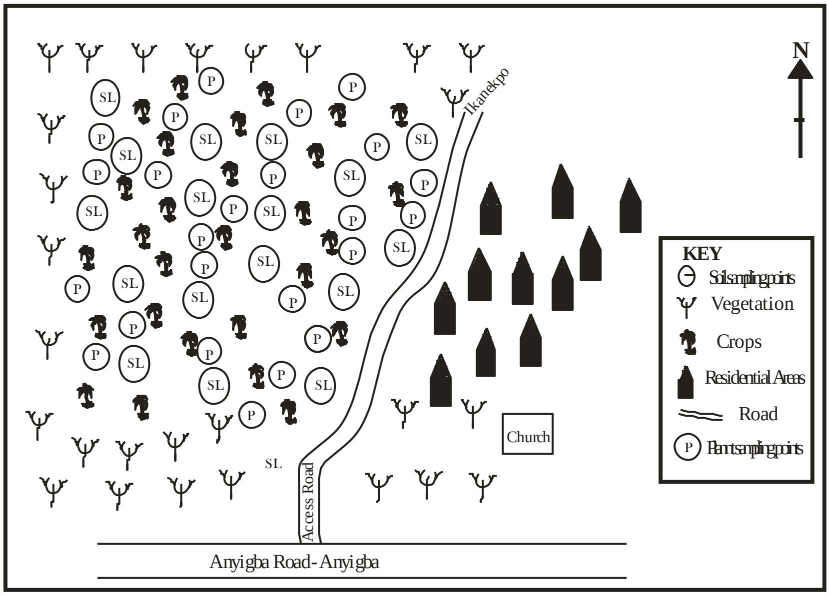

Fig3.8: Sketch of Ankpa farm showing sampling points

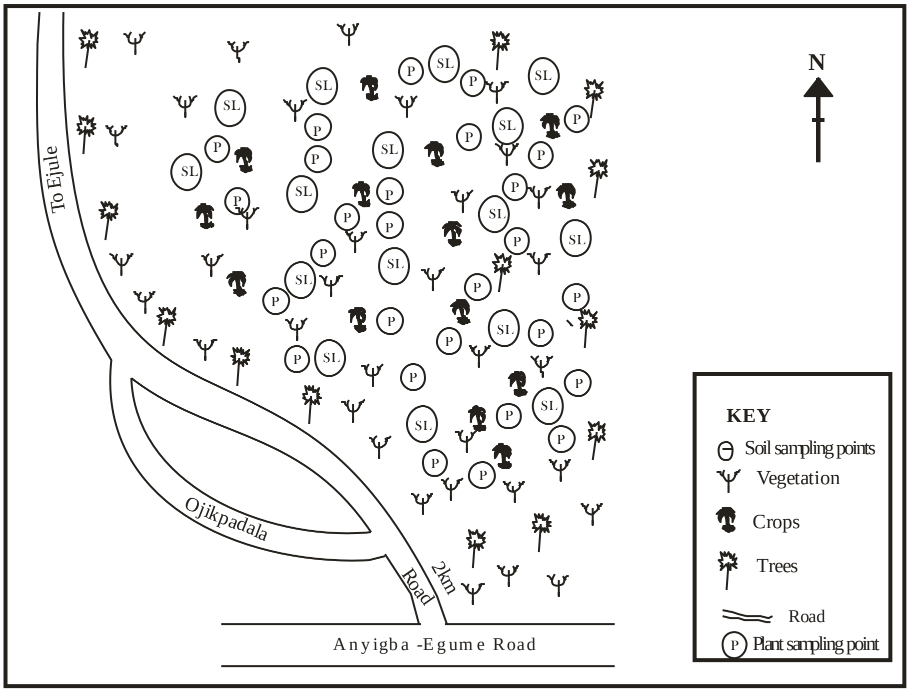

Fig3.9: Sketch of Anyigba (Control Site sampling points

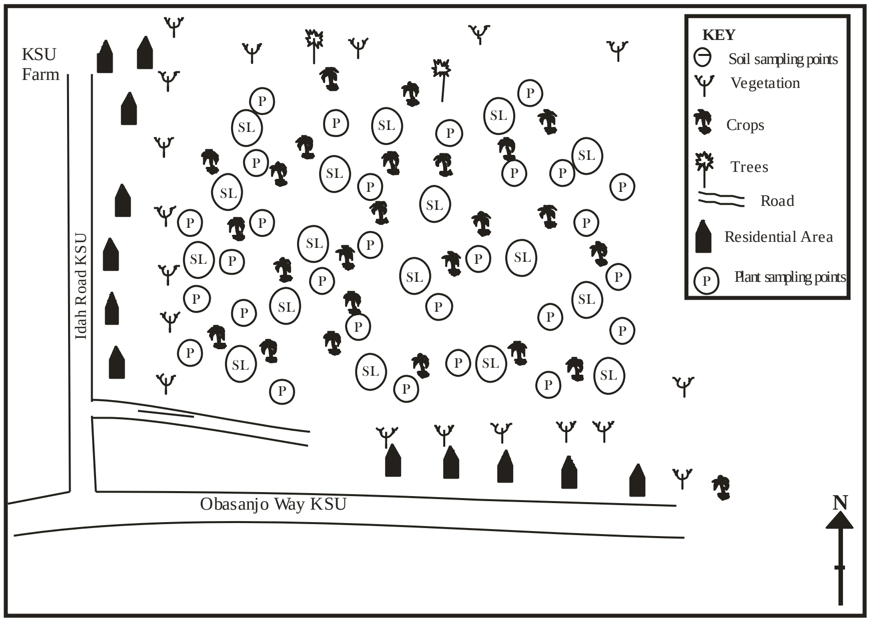

Fig3.10: Sketch of KSU farm showing sampling points

Table 3.3: Some features of the study sites

Station	Descriptive key	GPS position		Sea level	Size of farm	Crop sampled
		Latitude	Longitude			
Ofoke	OFK	07^0 24′ 9.5″ N	06^0 46′ 34.2″ E	58m	20 hectares	Maize
Ajaokuta	AJA	07^0 31′ 40.6″ N	06^0 40′ 24.8″ E	83m	20 hectares	Cassava
Macks	MAC	07^0 42′ 07.4″ N	06^0 27′ 39.2″ E	157m	45 hectares	passion fruits
Idah	IDA	07^0 08′ 46.0″ N	06^0 46′ 09.7″ E	80m	20 hectares	Cassava
Ibaji	IBA	07^0 03′ 47.8″ N	06^0 44′ 10.9″ E	66m	25 hectares	sugar cane
Ejule	EJU	07^0 22′ 04.7″ N	07^0 06 46.4″ E	365m	25 hectares	Cassava
Ankpa	ANK	07^0 22′ 46.4″ N	07^0 37′ 54.2″ E	352m	20 hectares	Cassava
KSU	KSU	070 28′ 41.9″ N	07^0 10′ 50.1″ E	402m	20 hectares	pumpkin
Lokoja	LKJ	07^0 48′ 07.4″ N	06^0 41′ 05.1″ E	110m	25 hectares	uncultivated
Anyigba (CTR)	ANY	07^0 29′ 01.4″ N	070 10′ 43.2″ E	371m	25 hectares	Cassava

Table 3.4: Geological features and vegetation of sampled sites

Sampling site	GPS		Topography	Vegetation
	Latitude	Longitutde		
Ofoke	07^{0} 24′ 9.5″ N	06^{0} 46′ 34.2″ E	Undulating landscape to a flat and minimum rugged land form surface	Typical of rainforest and Guinea savannah
Ajaokuta	07^{0} 31′ 40.6″ N	06^{0} 40′ 24.8″ E	Underlain by igneous and metamorphic rocks belonging to the basement complex composed of granite, miccshists, gneisses and metasediment which are igneous and metamorphic	It lies within the savannah belt,
Macks	07^{0} 42′ 07.4″ N	06^{0} 27′ 39.2″ E	It is generally hilly and rocky underlain by igneous and metamorphic rocks belonging to the basement complex	It lies within the savannah belt, an area characterized by tall trees and grasses
Idah	07^{0} 08′ 46.0″ N	06^{0} 46′ 09.7″ E	Underlain by sedimentary rock of upper cretaceous age which is of false embedded shales, sand clays, sandstone and mindstone.	Wooded savannah, rain and mangrove forest
Ibaji	07^{0} 03′ 47.8″ N	06^{0} 44′ 10.9″ E	Underlain by sedimentary rock of upper cretaceous age which is of false embedded shales, sand clays, sandstone and mindstone.	Wooded savannah, and rain and mangrove forest
Ejule	07^{0} 22′ 04.7″ N	07^{0} 06 46.4″ E	Underlain by sedimentary rock of upper cretaceous age which is of false embedded shales, sand clays, sandstone and mindstone.	Typical of rainforest and Guinea savannah
Ankpa	07^{0} 22′ 46.4″ N	07^{0} 37′ 54.2″ E	Made of vast flat land towards the west and vast undulating plain coupled with hills to the east and the area is covered by sedimentary rock. The soil is predominantly deep sandy, derived from alluvium deposits	Guinea savannah

Table 3.4: (contd):

Sampling site	GPS		Topography	Vegetation
	Latitude	Longitutde		
KSU	07^0 28′ 41.9″ N	07^0 10′ 50.1″ E	It is situated in part of the east-west of the Udi Pleateau with an undulating landscape to a flat and minimum rugged land form surface with a general elevation. Anyigba is underlain by sedimentary rock of upper cretaceous age which is of false embedded shales, sand clays, sandstone and mindstone.	Typical of rainforest and Guinea savannah
Anyigba	07^0 29′ 01.4″ N	07^0 10′ 43.2″ E	Anyigba is underlain by sedimentary rock of upper cretaceous age which is of false embedded shales, sand clays, sandstone and mindstone.	Typical of rainforest and Guinea savannah
Lokoja	07^0 48′ 07.4″ N	06^0 41′ 05.1″ E	Lokoja and its surrounding area are underlain by igneous and metamorphic rocks belonging to the basement complex composed of granite, miccshists, gneisses and metasediment which are igneous and metamorphic	It lies within the savannah belt, an area characterized by tall trees and grasses.

3.2.1 Ajaokuta Farm

Soil characteristics and types: The soil is ultisol and sandy loam

Industrial activity: The site is about 500m from an abandoned old Quarry site and about 3 km from Ajoakuta Steel Company.

Automobile traffic characteristics: Traffic density along a nearby road (100 m) is high.

Crop selected for study: Cassava

Application of agrochemical: NPK

3.2.2 Macks Farm

Soil characteristics and types: Soil is ultisol and loamy sand

Industrial activity: No industrial activities near this farm.

Automobile traffic characteristics: Traffic density in the area is low.

Crop selected for study: Passion fruit

Application of agrochemical: NPK fertilizer, alachlor, and butachlor. Cow dung was used as organic manure

3.2.3 Idah Farm

Soil characteristics and types: The soil is ultisol and sandy loam

Industrial activity: There are no industrial activities.

Automobile traffic characteristics: It is an urban–rural transitional area, situated in the eastern part of Kogi State with low traffic density.

Crop selected for study: Cassava

Application of agrochemical: Application of fertilizers and herbicide (atrazine and butachlor).

3.2.4 Ibaji Farm

Soil characteristics and types: The soil is ultisol and sandy loam

Industrial activity: There are no noticeable industrial activities as the area is remote.

Automobile traffic characteristics: Traffic is low.

Crop selected for study: Sugar cane

Application of agrochemical: NPK fertilizers and herbicides.

3.2.5 Ofoke Farm

Soil characteristics and types: Ultisol and sandy loam

Industrial activity: Remote area and no industrial activities

Automobile traffic characteristics: There is high traffic density at a nearby major route (50 m away).

Crop selected for study: Maize

Application of agrochemical: NPK fertilizer and herbicides

3.2.6 Ejule Farm

Soil characteristics and types: The soil is ultisol and sandy loam

Industrial activity: No industrial activities

Automobile traffic characteristics: Traffic is low.

Crop selected for study: Cassava

Application of agrochemical: NPK fertilizer and herbices (altrazine and butachlor).

3.2.7 Ankpa Farm

Soil characteristics and types: The soil is ultisol and loamy sand.

Industrial activity: There is no industrial activity.

Automobile traffic characteristics: Traffic is low.

Crop selected for study: Cassava

Application of agrochemical: No application of agrochemicals

3.2.8 KSU Farm

Soil characteristics and types: Ultisol and loamy sand

Industrial activity: No industrial activity.

Automobile traffic characteristics: Traffic density is low

Crop selected for study: Pumpkin

Application of agrochemical: NPK and herbicides.

3.2.9 Lokoja Farm

Soil characteristics and types: The soil is ultisol.and sandy loam

Industrial activity: No industrial activities.

Automobile traffic characteristics: Traffic density along a nearby route (100m away) is high.

3.2.10 Anyigba (control) Farm.

Soil characteristics and types: Ultisol and loamy sand

Industrial activity: No industrial activities

Automobile traffic characteristics: No traffic

Crop selected for study: Cassava

Application of agrochemical: No agrochemical inputs and fertilizer application.

3.3 SAMPLING

3.3.1 Collection of Soil Samples

Soil samples were obtained from 0-15 and 15-30 cm depths in each farm and control site, to make 320 composite samples. Composite sample each of topsoil (0-15cm) was collected. Subsamples were collected within an area of 10m by 10m with auger sampler to make a composite. Similarly, subsoil (15-30 cm) was collected. Summary of number of soil samples collected is shown in Table 3.1. The air dried soil samples were ground and sieved through a plastic sieve of 2 mm mesh size, stored at ambient temperature in polyethylene bags till analysis time.

3.3.2 Collection of Plant (food crops) Samples

A total of 640 plants samples (leaves and edible parts) were collected,

(i) *Leaves:* Leaves sample was collected by hand into new polyethylene bags composite. Subsamples of leaves of crops were collected within an area of 10m by 10m to make a composite. Samples where collected in the vicinities were soil samples were collected.

(ii) *Fruits*. Fruits sample was collected by hand into new polyethylene bags composite. Subsamples of fruit of crops were collected within an area of 10m by 10m to make a composite,

(iii) *Grain*. Sample of grains was collected by hand into new polyethylene bags composite. Subsamples of grain of crops were collected within an area of 10m by 10m to make a composite,

(iv) *Stem*. Stem sample was collected by hand into new polyethylene bags composite. Subsamples of stem of crops were collected within an area of 10m by 10m to make a composite,

(v) *Tuber*. Tuber sample was collected by hand into new polyethylene bags composite. Subsamples of tuber of crops were collected within an area of 10m by 10m to make a composite,

In the laboratory, the leaf samples were washed with distilled water. The samples were then cut into small pieces, with stainless steel knife, air dry for 7 days. This was done to facilitate drying. The leaf samples were placed in clean acid-washed porcelain crucible labeled and oven-dried at 60^oC for 3 hours until they were brittle and crisp. The dried plant samples were ground using acid washed mortar and pestle and sieved to obtain fine powder. These were finally stored in screw capped plastic containers and labeled appropriately for analysis. Tubers of cassava were peeled prior to washing, stem and grains of samples were also washed with distilled water, cut into small pieces and dried at ambient temperature. Prior to grinding they were oven dried at 60°C. The samples were subjected to chemical analysis.

3.3.3 Collection of Water Samples

56 samples irrigation waters (surface water) and16 underground waters were also collected.

(a) Samples for physicochemical analysis: Water sample was collected from large pool of water in a dam with cleaned plastic bottles and kept in ice chest. Water for dissolved oxygen (DO) was collected in DO bottles and fixed on site.

(b) Samples for heavy metals analysis: Water sample was collected from a pool of water in dam with cleaned plastic bottles. Concentrated nitric acid (2ml) was added to each water sample and stored in ice chest.

3.3.4 Collection of Sediment Samples

Sediments (56 samples) were collected from the top 10 cm layer of bottom sediment. A stainless steel trowel was used to scoop sediment samples into new polyethylene bags as composites. In the laboratory, sediment samples were air-dried, ground using mortar and pestle, sieved through a plastic sieve of 2 mm mesh size, and stored at room temperature in polyethylene bags.

3.4 ANALYSES OF WATER SAMPLES

Water samples were analysed by standard methods (APHA-AWWA-WPCF, 1998).

3.4.1 Determination of pH

The pH of water samples was determined using a portable pH meter (Mettler Toledo 420 model). The pH meter was calibrated with buffer solutions 7 and 4. All measurements were done at the sampling sites.

Reagents:

Buffer 7: A mass of 3.375g of KH_2PO_4 and 3.525g of Na_2HPO_4 were weighed and dissolved in little distilled water in a 1L volumetric flask and diluted to the mark.

(*Buffer* 4: A mass of 10.21g of potassium hydrogen phthalate (KHP) was weighed and dissolved in little distilled water in a 1L volumetric flask, and diluted to the mark.

3.4.2 Temperature Measurement

Temperature of water samples was read with a thermometer at the point of collection.

3.4.3 Determination of Alkalinity

Alkalinity was determined by titration with standard hydrochloric acid to a methyl orange indicator endpoint.

3.4.4 Determination of Total Hardness

Ethylenediaminetetra acetic acid (EDTA) titrimetric method was used in the determination of total hardness.

3.4.5 Determination of Calcium

Calcium was determined in the presence of magnesium by titration with disodium ethylenediaminetetraacetate dihydrate (EDTA). This method involved addition of dilute NaOH solution to raise the pH of sample to about 12, so that the magnesium is precipitated as hydroxide. The solution at pH of 12 to 13 was then titrated with standard EDTA solution, using calcon as indicator.

3.4.6 Determination of Magnesium

The difference in titre values between the total hardness and calcium was used as titre value for magnesium.

3.4.7 Determination of Sulphate

The turbidimetric method was used. The principle involves precipitation of sulphate ions in acid medium with barium chloride to form barium sulphate crystals uniformly dispersed in a conditioning reagent. The absorbance of the turbid solution of standards and samples is then measured with a spectrophotometer at a wavelength of 420nm. The absorbance of blank solution was measured as well at the same wavelength.

3.4.8 Determination of Phosphate

Phosphate was determined by the molybdenum blue colorimetric method, which involves the reaction of phosphate ions with ammonium molybdate and potassium antimonyl tartrate in acid medium to form phosphomolybdic acid. This is then reduced to intensely coloured molybdenum blue by ascorbic acid and the absorbance was measured at a wavelength of 880nm.

3.4.9 Determination of Nitrate

Nitrate was determined using the phenoldisulphonic acid colorimetric method (Marczenko, 1986). The nitration of 2, 4-phenoldisulphonic acid forms 6-nitrophenol-2, 4-disulphonic acid, which on subsequent addition of ammonium hydroxide solution produces a yellow coloured compound whose absorbance is measured at a wavelength of 410nm.

Reagents:

Phenoldisulphonic acid reagent: Phenol (25g) was weighed and dissolved in 150ml conc. H_2SO_4. 75mL of 15% fuming sulphuric acid was added, and the mixture heated for 2 hours on a hot water bath.

Nitrate stock solution: 0.7216g of KNO_3 was weighed and dissolved in little distilled water and diluted to 1 litre in a volumetric flask, (1.0mL x 100µg NO_3-).

Silver sulphate solution: 4.397g of silver sulphate crystal was weighed and dissolved in a little distilled water, and diluted to 1 litre.

Ammonium hydroxide solution (conc.)

Nitrate Working Solution (10.0µg/mL): A 50mL of nitrate stock solution was transferred quantitatively into a 500ml volumetric flask and diluted with distilled water to mark.

Instrument Calibration: Appropriate volumes (1.0, 2.0, 3.0, 4.0 and 5.0mL) of nitrate working solution were measured into a series of crucibles to cover the range 10 to 50µg NO^{3-}. These were evaporated to dryness on a water bath. The residue in the crucibles was then rubbed with 2mL of phenoldisulphonic acid reagent, and heated mildly to dissolve the residue. A 5mL of ammonium hydroxide solution and 10mL of distilled water were added and mixed together. This solution was then transferred to 50mL volumetric flask and made up to mark with distilled water. Absorbance of this solution was measured at a wavelength of 410nm (Fig 3.6). Blank determination was done following the same procedure. Distilled water was used in place of nitrate working solution.

Procedure for samples: A volume of silver sulphate solution equivalent to chloride contents of the water sample was added to 50mL clear water sample, mixed together and allowed to stand for 15 minutes to allow the precipitation of interfering chloride. The precipitate was then filtered off. This sample solution was evaporated to dryness on a hot water bath. The residue was then rubbed with 1mL of phenoldisulphonic acid reagent, heated mildly to dissolve all solids. Distilled water (10mL) was added followed by 3mL of ammonium hydroxide solution. This solution was then transferred to a 50mL volumetric flask and made up to mark with distilled water. Absorbance of this solution was measured at a wavelength of 410nm. Blank determination was done using distilled water, and the same procedure was followed. Number of µg of nitrate in the sample was estimated from calibration curve, and the concentration calculated as:

$$NO_3\text{-}\ (\mu g/mL) = \frac{No.\ of\ \mu g\ NO_3^-\ from\ calibration\ extrapolation}{Volume\ of\ Sample\ (mL)}$$

3.4.10 Determination of Dissolved Oxygen (DO)

Dissolved oxygen contents were determined using the Winkler's titration method. This method is based on the addition of manganous sulphate solution and alkali-iodide-azide solution to the water sample. This results in the formation of manganous hydroxide precipitate. Any dissolved oxygen present in sample solution then rapidly oxidizes an equivalent amount of the dispersed manganous hydroxide precipitate to form higher hydroxide. Subsequent acidification of this solution liberates iodine in an amount chemically equivalent to the original dissolved oxygen content of the sample. The iodine is then determined by titration with a standard solution of sodium thiosulphate.

3.4.11 Determination of Chemical Oxygen Demand

Chemical Oxygen Demand was determined by using the method of oxidation with a measured amount of excess standard potassium dichromate, followed by titrimetric determination of the unreacted dichromate with standard iron (II).

3.4.12 Deternination of Heavy Metals in Water Samples

The method used involved digestion of water sample with concentrated nitric acid. The metal concentration in the digest was then determined using atomic absorption spectrophotometer (AAS).

Sample Digestion for Heavy Metal Analysis: 200mL of a well-mixed water sample was measured into a clean beaker and 3mL of conc HNO_3 was added. The beaker was heated on a boiling water bath to concentrate the solution to about 15mL. The solution was allowed to cool and filtered into a 25mL volumetric flask. The beaker and filter paper were rinsed with a little amount of distilled water. The solution was made up to the mark with distilled water and transferred into a plastic bottle for instrumental analysis. Blank digestion was done following the same procedure with distilled water being used in place of sample.

Instrument Calibration and sample reading: The equipment was calibrated with commercial stock standards of the metals to be run. Working standard solutions were prepared by diluting a volume of a stock standard solution of 1000ppm concentration of each of the metals to required concentrations in standard volumetric flasks. These were used to calibrate the AAS. The absorbance values of blank and working standard solutions were measured using a Buck Scientific (model 200A) flame atomic absorption spectrophotometer. The spectrophotometer of 0.2nm slit width was operated in the air-acetylene flame mode. The lamps for heavy metals (Cd, Co, Cu, Ni, Pb, Zn) were operated at wavelengths specified by the manufacturer's manual. The operating condition of the spectrophotometer is shown on Table 3.6. A blank reading was subtracted from those of analyte samples and the corrected absorbance values obtained. Metal concentrations in the sample solutions were calculated using the expression below:

$$\text{Metal concentration, mg/L} = \frac{A \times B}{C}$$

Where A = concentration of metal (instrument reading) in digested solution (mg/L)

B = final volume of digested solution after make up to the mark (mL)

C = initial sample volume taken (mL)

3.5 ANALYSES OF SOIL SAMPLES

3.5.1 pH Determination

Soil and sediment pH were measured in H_20 (1:1 soil to water) electrometrically (Page, 1982).

Table 3.5: Operating conditions for the atomic absorption spectrophotometer

Element	Wavelength (nm)	Slit Width (nm)	Lamps current (mA)	Flame type	Range of Working Standards (mg/L)
Cd	228.8	3	2	Air-C_2H_2	0-10
Co	240.7	1	6	Air-C_2H_2	0-15
Cu	324.7	2	4	Air-C_2H_2	0-10
Ni	232.0	1	8	Air-C_2H_2	0-10
Pb	217.0	3	4	Air-C_2H_2	0-10
Zn	312.9	2	4	Air-C_2H_2	0-10

3.5.2 Determination of Particle Size Distribution

Particle size distribution was determined by Bouyoucos hydrometer method (Gee and Bauder, 1979).

3.5.3 Determination of Organic Carbon and Organic Matter

Organic carbon of dry sediment and soil samples were determined using Walkley-Black method. The method measures the amount of degradable organic matter in sediment and soil. Sediment and soil organic carbon is almost completely oxidized with potassium dichromate ($K_2Cr_2O_7$) in the presence of H_2SO_4, leaving the fraction present in inorganic form. The excess dichromate is determined by titration with ferrous sulphate (Nelson and Sommers, 1996).

3.5.4 Analyses of Soil Samples for Heavy Metals

Metals in dry samples were extracted with *aqua regia*. Determination of Cd, Co, Cu, Ni, Pb, and Zn, was carried out on the extracts using atomic absorption spectroscopy.

Procedure for Digestion of Soil: *Aqua regia* was prepared by adding 150 mL of 36% hydrochloric acid to 50 mL of 70% nitric acid in a 500-mL conical flask. A mass of 1.0g of the sieved air-dried soil or sediment sample was weighed out into a clean 250mL beaker. *Aqua regia* (5ml) solution was measured and added to the contents in a beaker and covered with a watch glass. The beaker was placed in a boiling water bath to digest the sample. At intervals of 15 minutes, the beaker was withdrawn, the contents swirled and the beaker then replaced. The digestion was carried out for 2 hours and the contents were allowed to cool. The extract was then filtered into a 25mL volumetric flask. A sample blank digestion was also carried out. The digested soil and sediment samples were analyzed for Cd, Co, Cu, Ni, Pb, and Zn, using the atomic absorption spectrometer.

3.6 ANALYSES OF SEDIMENTS FOR HEAVY METALS

The procedure is as describe for soil samples (section 3.5.4).

3.7 ANALYSES OF PLANT SAMPLES FOR HEAVY METALS

Procedure for Digestion: Metals in dry samples were extracted with a mixture of 3:1 HNO_3:$HClO_4$. A 0.5g powdered food crop sample was weighed into a 100 ml beaker. A 10mL mixture 3:1 HNO_3:$HClO_4$ was added to the sample in the beaker, and this was allowed to stand for few minutes. The mixture was heated at 70^oC until a transparent solution was obtained (digestion complete). In some cases additional volume was added to complete the digestion. The sample was then cooled, diluted and filtered into a 25mL standard flask and two 5 ml portions of distilled water were used to rinse the beaker and the contents filtered into the 25 mL flask. The filtrate was allowed to cool to room temperature before dilution was made to the mark and the content mixed thoroughly by shaking. A sample blank digestion was also carried out. The digested plant samples were analyzed for Cd, Co, Cu, Ni, Pb, and Zn.

3.8 METAL SPECIATION STUDY

The sequential extraction procedure of Tessier *et al*. (1979) was used. The chemical partitioning of heavy metals allows distinguishing five fractions representing the following chemical phases: exchangeable metals, bound to carbonates, bound to Fe–Mn oxides, bound to sulphides and organic matter, and residual fraction.

Procedure: The procedure was carried out with an initial weight of 1 g of sieved dry soil sample.

Step 1: **The exchangeable phase.** The samples were extracted at room temperature for 1 h with 8 ml of 1 M $MgCl_2$ (pH 7) with continuous stirring. The extracts were centrifuged for 30 min to achieve good separation. The supernatant was removed with a pipette and used for metal measurement and the solid residues were subjected to subsequent extractions.

Step 2: **The carbonate phase.** The washed residue from step 1 was leached at room temperature with 8 mL of 1M NaOAc (adjusted to pH 5 with HOAc) for 6 h with continuous stirring. The pH was controlled after 3 h and adjusted to pH 5 with HOAc at room temperature, centrifuged. The supernatant was collected and the solid residue was for the following extraction.

Step 3: **The oxide phase:** The residue from step 2 was extracted with 20 mL of 0.04 M $NH_2OH.HCl$ in 25% HOAc (v/v) for 6 h at 96 °C in a water bath with occasional stirring. The supernatant was subjected to metal analysis and the solid residues were used in step four

Step 4: **The organic phase.** To the solid residue from step 3 was added 3 mL of 0.02 M HNO_3 and 5 mL of H_2O_2 30% (adjusted to pH 2 with HNO_3). The mixture was heated to 85 °C and occasionally stirred. After 2 h, 3 mL of 30% H_2O_2 was added once more (adjusted to pH 2 with HNO_3). The temperature and the occasional stirring were maintained for another 3 hours. After cooling, 5 mL of 3.2 M NH_4OAc (in 20% HNO_3 (v/v)) and 4 mL of deionized water was added and the mixture was agitated continuously for 30 min. The supernatant was subjected to metal analysis and the solid residues were used in step five

Step 5: **Residual:** The residue from step 4 was digested with 7 mL of HNO_3 (65%) and 7 mL of HF (40%). The liquid was evaporated and after that, it was dissolved again with 2 mL of HNO_3, 2 mL of HCl and 10 mL deionized with low temperatures. The samples were diluted to 50 mL with deionized water. The supernatant was subjected to metal analysis.

After each step, the extracts were centrifuged for 30 min to achieve good separation. The supernatant was removed with a pipette. The residue was washed with 8 mL of deionized water. After another 30 min of centrifugation, the wash solution was discarded. The mixtures were diluted to 20 ml with deionized water because of liquid losses due to evaporation.

3.9 APPLICATION OF A PLANT-SOIL MODEL TO DETERMINATION OF THRESHOLD LEVELS OF HEAVY METALS IN PLANTS

Metals concentrations in soil and crops parts were fitted into an existing soil-plant equilibrium model. This was achieved with the aid of STRATA statistical software.

3.10 STATISTICAL ANALYSIS OF DATA

Data obtained were subjected to analysis of variance using the General Linear Models. Two way analysis of variance (ANOVA) (<0.05) were used to assess whether metal concentrations in soil varied significantly between rainy season and dry season. All statistical calculations were performed with SPSS 17.0 for Windows.

3.11 EVALUATION OF TRANSFER FACTORS FOR HEAVY METALS

The transfer factors (TF) of Cd, Co, Cu, Ni, Pb, and Zn, from soils to crops were calculated as follows:

$$\text{TF} = \frac{\textit{metal concentration in crop tissue}}{\textit{metal concentration in soil from where the plant was grown}}$$

3.12 ASSESSMENT OF METAL POLLUTION IN SOILS

3.12.1 Index of geoaccumulation

The Index of geo-accumulation of metals in soil was calculated using the equation

$$\textit{Geoaccumulation index}\left(I_{geo}\right)=\log_2\left[\frac{C_n}{1.5\times B_n}\right]$$

where C_n is the measured concentration of the examined metal n in the soil, and B_n is the background concentration or reference value of the metal n. Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

Table 3.6 shows the index of geoaccumulation (I_{geo}) for contamination levels in soil.

3.13 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Quality Assurance (QA) is a set of operating principles that if strictly followed during sample collection and analysis will produce data of known and defensible quality, that is, the accuracy of the analytical result can be stated with high level of confidence. Some quality assurance measures were incorporated into various steps of the sampling and analyses. The essence was to

Table 3.6: Index of geoaccumulation (I_{geo}) for contamination levels in soil

I_{geo} Class	I_{geo} Value	Contamination level
0	$I_{geo} \leq 0$	unpolluted
1	$0 < I_{geo} \leq 1$	unpolluted to moderately polluted
2	$1 < I_{geo} \leq 2$	moderately polluted
3	$2 < I_{geo} \leq 3$	Moderately to strongly polluted
4	$3 < I_{geo} \leq 4$	Strongly polluted
5	$4 < I_{geo} \leq 5$	Strongly to extremely polluted
6	$I_{geo} > 5$	Extremely polluted

detect and correct problems in the measurements and ensure that the analytical procedures were operating within acceptable control limits.

3.13.1 QA/QC in Sampling

- Plastic containers for the determination of general physicochemical parameters were thoroughly washed with teepol detergent and rinsed with distilled water. Plastic sample containers that were used for metal analysis were first soaked in HNO_3 for two days, and thoroughly rinsed with distilled water.
- Hand trowel used for collecting sediment from the dam was made of stainless steel. The polyethylene bags used for collecting sediment samples were new and clean.
- Reagents used were of Analar-grade.

3.13.2 QA/QC in Preparation and Preservation of Sample

- The water samples collected for metals analyses were fixed on the field with concentrated nitric acid.
- The samples collected for other general physicochemical parameters were stored in an ice chest right on site. On arrival in the laboratory, the samples were subsequently preserved in the fridge until the commencement of the analysis.
- It was ensured that the mortar and pestle for grinding were washed with teepol detergent, rinsed with distilled water and dried before use.

3.13.3 QA/QC in Calibration of the Instruments

- The pH meter was frequently calibrated with buffer 4 and 7 solutions prepared from analar grade salts.
- Appropriate standard solutions prepared from analar grade salts, were used to calibrate the atomic absorption spectrophotometer for metal analysis.
- The instruments were generally operated according to manufacturer specifications and kept in good working conditions.

3.13.4 QA/QC in Sample Analysis

- Sample blanks were measured for determination of anions and metals and appropriate corrections made.
- Samples were generally analysed in duplicates.

3.13.5 Recovery study of Heavy-Metal Determination in Samples

Recovery study for heavy metal was carried out to check whether there could have been losses or contamination of samples in the process of sample preparation and analysis. This could have resulted from the digestion procedure and systematic errors in the instrument analysis with the atomic absorption spectrophotometer (Roshan, 2004).

Procedure for Spiking and Re-determination of Metal Concentration in Soil Sample: 10.0g of previously analysed sample was weighed into a crucible. An appropriate volume of standard was carefully spiked into a cone shape made in the soil. The volume of the standard spiked was such as not to over-wet the soil sample in the crucible. The spiked soil sample was dried in an oven for another 30 minutes and allowed to cool in a desiccator. The spiked sample was then homogenised thoroughly with a glass rod. 5.0g of soil was then weighed out of the spiked homogenised sample into another clean crucible. The sample was re-dried in an oven for another 30 minutes, cooled in a dessicator and re-weighed until constant weight was obtained. The sample was quantitatively transferred into a beaker and digested with aqua regia as previously described (section 3.5.4). The results of the recovery study for metal determinations are shown in Tables 3.7 to Table 3.24

The level of increase achieved by spiking = $\dfrac{number\ of\ \mu\mathrm{g}\ \mathrm{of}\ metal\ added}{Weight\ of\ sample\ taken}$

Percent recovery = $\dfrac{(Metal\ conc.\ from\ re\text{-}analysis - Original\ metal\ conc)}{Increase\ in\ conc.\ achieved\ by\ spiking} \times 100$

Table 3.7: Results of recovery study for copper determination in soil samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked (g)	Conc. of standard for spiking (µg/mL)	Volume of standard spiked (mL)	Increased conc. achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Cu	IBA-SL	7.82	5.0	50	0.8	8.0	15.8	16.0	103.0
	MAC-SL	6.60	5.0	50	0.7	7.0	13.6	13.0	91.3
	EJU-SL	4.13	5.0	50	0.4	4.0	8.1	7.8	92.4
	LOK-SL	3.12	5.0	50	0.3	3.0	6.1	5.8	90.1
	AJA-SL	2.13	5.0	50	0.2	2-0	4.1	3.9	89.0

Table 3.8: Results of recovery study for zinc determination in soil samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked (g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Zn	LOK-SL	63.2	5.0	250	1.3	65.0	128.2	129	102.3
	IDA-SL	26.1	5.0	100	1.3	26.0	52.8	51.5	93.0
	AJA-SL	15.8	5.0	100	0.7	14.0	29.8	28.5	91.0
	ANK-SL	6.32	5.0	50	0.6	6.0	12.3	11.8	91.3
	AYB-SL	6.12	5.0	50	0.6	6.0	12.1	12.0	98.2

Table 3.9: Results of recovery study for lead determination in soil samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Pb	MAC-SL	17.6	5.0	100	0.9	18.0	35.6	36.2	103.3
	IBA-SL	15.9	5.0	100	0.8	16.0	31.9	30.5	91.4
	OFK-SL	7.21	5.0	50	0.7	7.0	14.2	13.5	90.3
	AJA-SL	7.16	5.0	50	0.7	7.0	14.2	13.8	88.0
	IDA-SL	5.36	5.0	50	0.6	6.0	11.4	11.8	106.0

Table 3.10: Results of recovery study for cadmium determination in soil samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Cd	ANK-SL	0.40	5.0	10	0.20	0. 4	0.80	0.73	82.5
	IDA-SL	0.21	5.0	10	0.13	0.2	0.41	0.38	85.0
	EJU-SL	0.26	5.0	10	0.13	0.26	0.52	0.50	84.6
	OFK-SL	0.28	5.0	10	0.14	0.28	0.56	0.53	89.3
	KSU-SL	0.07	5.0	10	0.05	0.1	0.17	0.19	120.0

Table 3.11: Results of recovery study for nickel determination in soil samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Ni	LOK-SL	21.7	5.0	100	1.1	22.0	43.7	45.1	106.3
	AJA-SL	12.6	5.0	100	0.6	12.0	24.6	23.8	93.3
	KSU-SL	10.2	5.0	50	1.0	10.0	20.2	19.5	93.0
	OFK-SL	7.32	5.0	50	0.7	7.0	14.3	15.2	12.9
	IDA-SL	5.89	5.0	50	0.6	6.0	11.9	11.6	95.0

Table 3.12: Results of recovery study for cobalt determination in soil samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Co	IBA-SL	7.86	5.0	50	0.8	8.0	15.9	16.1	102.5
	MAC-SL	5.26	5.0	50	0.5	5.0	10.3	9.8	90.1
	EJU-SL	4.78	5.0	50	0.5	5.0	9.8	10.2	107.9
	AJA-SL	2.89	5.0	50	0.3	3.0	5.9	6.5	119.9
	OFK-SL	2.24	5.0	50	0.2	2.0	4.2	4.0	89.8

Table 3.13: Results of recovery study for copper determination in leaf samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Cu	IDA	13.4	5.0	100	0.7	14.0	27.9	27.2	95.0
	AJA	9.93	5.0	50	1.0	10.0	19.9	18.8	89.0
	MAC	7.14	5.0	50	0.7	7.0	14.1	13.8	95.7
	KSU	2.60	5.0	50	0.3	3.0	5.60	5.20	86.6

Table 3.14: Results of recovery study for zinc determination in leaf samples

Metal	Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Zn	AJA	56.2	5.0	250	1.3	65.0	121	120	99.0
	KSU	29..7	5.0	150	1.0	30.0	59.7	59.2	98.3
	OFK	20.2	5.0	100	1.0	20.0	40.2	39.0	94.0
	EJU	1.67	5.0	10	0.9	1.8	3.47	3.42	97.2

Table 3.15: Results of recovery study for lead determination in leaf samples

Metal	Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Pb	MAC	0.52	5.0	10	0.3	0.6	1.12	1.07	91.6
	IBA	0.33	5.0	10	0.2	0.4	0…73	0.75	105
	EJU	0.21	5.0	10	0.1	0.2	0.4	0.38	89.0
	KSU	0.13	5.0	10	0.7	13	0.26	0.24	84.6

Table 3.16: Results of recovery study for cadmium determination in leaf samples

Metal	Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Cd	IBA	0.90	5.0	10	0.5	1.0	1.9	1.7	80.0
	IDA	1.67	5.0	10	0.8	1.7	3.4	3.3	97.6
	KSU	0.23	5.0	10	0.2	0.4	0.63	0.58	87.5
	ANK	0.06	5.0	10	0.03	0.06	0.12	0.1	66.7

Table 3.17: Results of recovery study for nickel determination in leaf samples

Metal	Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Ni	AJA	50.7	5.0	250	1.0	50.0	101	103	104.3
	IDA	39.6	5.0	250	0.8	50.0	90	94	108.0
	KSU	39.6	5.0	100	1.3	21.0	41.0	40.0	87.6
	MAC	12.4	5.0	100	0.6	13.0	25.0	23.5	88.0

Table 3.18: Results of recovery study for cobalt determination in leaf samples

Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
ANK	30.1	5.0	250	0.6	30	60.1	59.0	96.7
AJA	8.69	5.0	50	0.9	9.0	17.7	16.2	83.4
EJU	3.59	5.0	50	0.4	4.0	7.6	7.2	90.0
KSU	0.16	5.0	50	0.8	8.0	8.2	7.8	95.0

Table 3.19: Results of recovery study for copper determination in edible**s**

Metal	Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. Of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Cu	MAC	9.80	5.0	50	1.0	10	19.8	19.2	94.0
	ANK	4.38	5.0	50	0.4	4.0	8.4	7.9	87.6
	IDA	3.16	5.0	25	0.6	3.0	6.2	6.0	92.0
	IBA	2.63	5.0	25	0.6	3.0	5.6	5.1	83.2

Table 3.20: Results of recovery study for zinc determination in edible plant parts

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. Of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Zn	OFK	36.7	5.0	250	0.7	35	72.0	69.3	93.1
	MAC	18.3	5.0	100	1.0	20	28.3	28.0	97.0
	KSU	10.9	5.0	100	0.5	10	20.9	19.3	84.0
	EJU	5.93	5.0	50	0.1	1.0	7.0	6.83	84.1

Table 3.21: Results of recovery study for lead determination in edible plant parts

Metal	Sample	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. Of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Pb	OFK	0.75	5.0	10	0.4	0.8	1.55	1.38	78.8
	IBA	0.17	5.0	10	0.1	0.2	0.37	0.40	115.0
	KSU	0.09	5.0	10	0.1	0.2	0.30	0.32	109.0
	EJU	0.06	5.0	10	0.1	0.2	0.26	0.30	120.0

Table 3.22: Results of recovery study for cadmium determination in edible plant parts

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Cd	OFK	0.22	5.0	10	0.1	0.2	0.42	0.43	105
	IDA	0.14	5.0	10	0.1	0.2	0.34	0.30	80.0
	EJU	0.09	5.0	10	0.1	0.2	0.29	0.31	110.0
	KSU	0.03	5.0	10	0.1	0.2	0.23	0.20	85.0

Table 3.23: Results of recovery study for nickel determination in edible samples

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Ni	OFK	59.4	5.0	250	1.2	60	119	114	91.9
	IBA	26.3	5.0	250	0.5	25	51.3	49.7	93.6
	MAC	8.04	5.0	50	0.8	8.0	16.4	15.2	89.5
	ANK	6.48	5.0	50	0.6	6.0	12.5	12.1	93.4

Table 3.24: Results of recovery study for cobalt determination in edible plant parts

Metal	Sample site	Original sample conc. (µg/g)	Weight of sample spiked(g)	Conc. of standard spiked (µg/mL)	Volume of standard spiked (mL)	Increased conc. Achieved (µg/g)	Total expected by analysis (µg/g)	Results of re-analysis (µg/g)	% Recovery
Co	IBA	0.90	5.0	10	0.5	1.0	1.9	1.7	80.0
	IDA	1.67	5.0	10	0.8	1.7	3.4	3.3	97.6
	KSU	0.23	5.0	10	0.2	0.4	0.63	0.58	87.5
	1BA	0.11	5.0	10	0.1	0.2	0.21	0.17	60.0

3.13.6 Summary result of recovery studies

The summary result of the spike recovery test is presented in Table 3.25. The results show that the average heavy metals recoveries for soil and food crops (leaves and edibles) were in most cases within acceptable range of 90 – 100%. In soil, recovery ranged from 80±38% in Ni to 102±13% in Co. Corresponding range in leaves was 83±13% in Cd to 97.1±2.2% in Ni while in edibles the range of recovery was 81±16% in Co to 105±18% in Pb. The percentage recoveries for the metals were within 100±10%, a limit that demonstrates that uncertainties in the methods of analyses used were within acceptable limits. It therefore means that a good recovery was obtained for the metals with the methods employed and the results obtained were of good accuracies.

Table 3.25: Average recoveries (%)

Metal	Soil	Leaves	Edible
Cd	92±16	83±13	95±15
Co	102±13	91.2±6.0	81±16
Cu	93.0±5.7	91.6±4.5	89.2±4.8
Ni	80±38	97±11	92.1±1.9
Pb	95.6±8.3	92.6±8.8	105±18
Zn	95.0±4.8	97.1±2.2	89.6±6.5

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PHYSICOCHEMICAL CHARACTERISTICS OF THE SOILS

The soil physicochemical parameters are very important in understanding the characteristics and behaviour of heavy metals and contaminants present in the soil and the ability of soil to retain these metals, and subsequent release to crops.

4.1.1 Mechanical Properties

Average levels of topsoil particle size were 72±15 %, 15.6±6.9 % and 12.6±7.3 % for sand, clay and silt respectively (Table 4.1). The differences between topsoil and subsoil values were statistically not significant. Average seasonal values of sand during rainy and dry seasons were 73±13% and 70±14% respectively. Corresponding values for clay and silt were 15.3±6.3%, 17.2±6.7% and 11.7±8.5%, 12.8±9.8% respectively. Soil high in sand retains fewer metals within it (Wenzel, 2005). The value obtained for topsoils at different sites compared with the control value is also not significant (Table 4.2). The clay contents of the studied soils were less than 20% therefore these soils can be classified as coarse textured soils in terms of Czech regulations (Komarek *et al.*, 2008). Generally, the soil textural characteristics ranged from loamy sand to sandy loam.

4.1.2 Percentage Organic Carbon and Organic Matter in Soil

Average level of total organic carbon (TOC) in topsoil (0-15cm) was 4.87±0.47%, and in subsoil (15-30 cm) it was 4.55±0.24 % (Table 4.3). Values in topsoil ranged from 3.82% to 10.1% while corresponding subsoil values ranged from 3.43% to 6.74% (Table 4.4). Average values of total organic matter (TOM) in topsoil and subsoil were 8.42±0.78% and 7.87±0.39% respectively. The difference between rainy season average value (4.86±0.51 %) and dry season (4.89±0.49 %) in topsoil is not statistically significant. Values of TOM obtained in topsoil ranged from 6.60 to 17.5% and subsoil ranged from 5.86% to 11.7% (Table 4.5). The TOC values are adequate for

Table 4.1: Average soil particle size (%)

Depth (cm)	Rainy season			Dry season			Mean (all seasons)		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
0-15	73±15	11.9±8.4	15.1±6.3	71±16	12.7±9.6	16.3±7.3	72±15	12.4±8.5	15.6±6.9
15-30	73±13	11.4±8.9	15.6±6.3	69±14	13.0±8.7	18.0±5.9	71±13	12.2±9.6	16.8±6.3
0-15 (CTR)*	78.9±3.7	7.3±1.5	13.8±2.9	79.9±4.2	5.3±1.1	14.8±3.5	79.4±4.6	6.3±1.8	14.3±3.6
15-30 (CTR)*	76.5±6.2	10.4±5.8	13.1±7.4	73.9±5.3	6.0±1.9	20.1±3.6	75.2±5.9	8.2±4.8	16.6±6.1

* CTR: control

Table 4.2: Physicochemical characteristics of soil at different depths

Site code	Depth (cm)	pH	%TOC	%TOM	% Sand	%Silt	% Clay	Soil Type
OFK-SL	0-15	5.59±0.78^{a}	5.3±1.1^{a}	9.1±1.9^{a}	59±18	23±12	18.0±8.8	Sandy loam
	15-30	5.2±1.0	4.8±0.4	8.4±0.8	62±12	19.4±9.4	18.6±6.0	
ANK-SL	0-15	5.99±0.39^{abc}	4.33±0.3 6^{a}	7.38±0.35^{a}	84.4±4.1	4.7±2.8	11.9±4.3	Loamy sand
	15-30	5.55±0.66	4.53±0.04	7.28±0.25	82.4±5.3	4.6±1.7	13.0±5.4	
LKJ-SL	0-15	6.27±0.85^{bcd}	5.2±1.4^{a}	8.9±2.4^{a}	68±14	11.0±2.9	21±11	Sandy loam
	15-30	5.83±0.41	4.8±0.3	8.25±0.49	72±11	9.5±5.0	18.5±7.8	
AJA-SL	0-15	6.9±0.7^{d}	4.29±0.37^{a}	7.42±0.63^{a}	78.9±5.5	9.3±4.8	10.8±2.1	Loamy sand
	15-30	6.13±0.55	4.29±0.19	6.4±0.3	78.5±3.5	10.9±3.9	10.6±1.8	
MAC-SL	0-15	6.6±0.4^{cd}	5.1±1.2^{a}	8.8±1.9^{a}	78.9±5.7	8.5±4.0	12.6±3.4	Loamy sand
	15-30	6.49±0.54	4.7±0.7	8.2±1.1	75.9±6.9	8.6±3.8	15.5±4.8	
IBJ-SL	0-15	6.41±0.6 4^{bcd}	5.25±0.5 8^{a}	9.1±1.0^{a}	47±15	36±11	17.0±5.7	Sandy loam
	15-30	6.14±0.72	4.82±0.18	8.3±0.14	44.5±7.1	34.1±7.0	21.4±3.4	
IDA-SL	0-15	6.73±0.64^{d}	4.31±0.25^{a}	7.27±0.64^{a}	84.4±5.3	4.6±2.3	11.0±3.0	Loamy sand
	15-30	6.33±0.56	4.17±0.09	6.86±0.64	80.8±7.5	5.8±3.9	13.4±4.2	
EJU-SL	0-15	5.79±0.25^{ab}	4.67±0.19^{a}	8.08±0.33^{a}	67.2±7.9	11.3±2.5	21.5±6.6	Sandy loam
	15-30	5.41±0.23	4.41±0.08	7.63±0.17	63±11	14.6±5.3	22.4±5.7	

Table 4.2: contd.

Site code	Depth (cm)	pH	%TOC	%TOM	% Sand	%Silt	% Clay	Soil Type
KSU-SL	0-15	6.81±0.35 ^{d}	5.5±2.1 ^{a}	9.1±4.1 ^{a}	78.3±7.9	5.9±1.6	15.8±6.8	Loamy sand
	15-30	6.42±0.14	4.49±0.29	7.5±1.1	75.7±5.8	7.0±2.1	17.3±6.4	
Mean	0-15	6.29±0.27 ^{bcd}	4.87±0.47 ^{a}	8.42±0.78 ^{a}	72±15	12.4±8.5	15.6±6.9	Loamy sand
	15-30	5.88±0.37	4.55±0.24	7.87±0.39	71±13	12.2±9.6	16.8±6.3	
CTR	0-15	6.87±0.76 ^{d}	5.6±2.3 ^{a}	9.3±4.6 ^{a}	76.7±4.6	7.0±1.9	14.3±3.9	Loamy sand
	15-30	6.18±0.66	4.44±0.08	7.33±0.33	75.0±5.9	8.5±4.8	17.5±6.1	

Values with different superscript (a,b,c,d) within the same column are significantly different at P=0.05

Table 4.3: Average TOC and TOM levels in the soil

	TOC			TOM		
Depth (cm)	Rainy	Dry	Overall mean	Rainy	Dry	Overall mean
0-15	4.86±0.51	4.89±0.49	4.87±0.47	8.40±0.88	8.45±0.77	8.42±0.78
15-30	4.46±0.19	4.65±0.32	4.55±0.24	7.71±0.33	8.04±0.55	7.87±0.39
0-15 (CTR)	6.2±3.3	4.94±0.36	5.6±2.3	10.7±5.9	8.54±0.61	9.6±4.0
15-30 (CTR)	4.5±1.0	4.38±0.42	4.45±0.33	7.8±1.8	7.58±0.73	7.7±1.3

Table 4.4: Total organic carbon (TOC) in soil (%)

Site code	Depth (cm)	Rainy season					Dry season				
		May-07	Aug-07	May-08	Aug-08	Mean	Nov-07	Feb-08	Nov-08	Feb-09	Mean
OFK-SL	0-15	3.82	6.56	4.68	4.90	5.0±1.1	6.67	6.44	4.51	4.44	5.5±1.2
	15-30	3.43	6.19	4.17	4.38	4.5±1.2	6.28	5.70	4.37	4.31	5.17±0.98
ANK-SL	0-15	4.06	4.69	3.93	4.77	4.36±0.33	4.78	4.16	4.14	4.08	4.29±0.32
	15-30	3.51	5.83	3.77	4.94	4.5±1.1	5.88	4.56	3.92	3.86	4.56±0.94
LOK-SL	0-15	3.82	7.18	4.12	5.14	5.1±1.6	7.58	4.56	4.46	4.41	5.3±1.6
	15-30	3.39	6.64	3.69	4.53	4.6±1.5	6.74	4.58	4.40	4.23	5.0±1.2
AJA-SL	0-15	4.1	4.07	3.98	5.13	4.32±0.54	4.24	4.45	4.17	4.20	4.26±0.13
	15-30	4.3	4.06	4.09	5.26	4.43±0.57	4.44	4.23	3.97	3.99	4.15±0.22
MAC-SL	0-15	3.98	6.68	4.36	5.24	5.1±1.2	7.00	4.74	4.32	4.26	5.1±1.3
	15-30	3.51	6.03	4.03	4.93	4.6±1.1	6.17	4.36	4.11	3.96	4.7±1.0
IBA-SL	0-15	5.23	4.84	4.55	6.16	5.20±0.70	4.91	5.94	5.52	4.83	5.30±0.52
	15-30	4.23	4.75	4.14	5.96	4.77±0.84	4.79	5.95	4.35	4.42	4.88±0.74
IDA-SL	0-15	4.11	4.34	4.12	4.40	4.24±0.14	4.40	4.78	3.97	4.40	4.39±0.33
	15-30	3.82	4.18	4.06	4.34	4.10±0.21	4.22	4.53	3.82	4.34	4.23±0.30
EJU-SL	0-15	4.35	4.79	4.43	4.71	4.57±0.21	4.84	4.87	4.66	4.71	4.77±0.10
	15-30	3.95	4.63	4.26	4.54	4.35±0.31	4.375	4.90	4.08	4.54	4.47±0.34
KSU-SL	0-15	10.1	4.77	4.54	4.23	5.9±2.8	7.3	5.08	4.11	4.08	5.1±1.5
	15-30	4.49	4.33	4.15	4.13	4.28±0.17	6.08	4.90	3.98	3.97	4.7±1.0
CTR-SL	0-15	11.3	4.68	4.32	4.53	6.2±3.3	4.71	5.46	4.82	4.77	4.94±0.35
	15-30	6.01	3.73	4.06	4.26	4.5±1.0	3.76	4.5	4.64	4.63	4.38±0.42

Table 4.5: Total organic matter (TOM) in soil (%)

Site code	Depth (cm)	Rainy season					Dry season				
		May-07	Aug-07	May-08	Aug-08	Mean	Nov-07	Feb-08	Nov-08	Feb-09	Mean
OFK-SL	0-15	6.60	11.3	8.09	8.47	8.6±1.9	11.5	11.1	7.80	7.68	9.5±2.1
	15-30	5.93	10.7	7.20	7.57	7.9±2.0	10.9	9.86	7.56	7.45	8.9±1.7
ANK-SL	0-15	7.01	8.11	6.79	8 .24	7.30±0.71	8.26	7.19	7.16	7.05	7.41±0.57
	15-30	6.06	10.1	6.52	8.54	7.8±1.8	10.2	7.88	6.78	6.67	7.9±1.6
LOK-SL	0-15	6.60	12.4	7.12	8.88	8.8±2.6	13.1	7.88	7.71	7.62	9.1±2.6
	15-30	5.86	11.5	6.38	7.83	7.9±2.5	11.7	7.92	7.61	7.31	8.6±2.1
AJA-SL	0-15	7.09	7.04	6.88	8.87	7.47±0.94	7.33	7.69	7.21	7.26	7.37±0.22
	15-30	7.43	7.02	7.07	9.09	7.65±0.98	7.68	7.31	6.86	6.90	7.18±0.38
MAC-SL	0-15	6.88	11.5	7.53	9.05	8.7±2.1	12.1	8.20	7.46	7.37	8.8±2.2
	15-30	6.07	10.4	6.96	8.52	7.9±1.9	10.7	7.80	7.10	6.85	8.1±1.8
IBA-SL	0-15	9.04	8.36	7.86	10.7	8.9±1.2	8.49	10.3	9.54	8.35	9.17±0.92
	15-30	7.31	8.21	7.15	10.3	8.2±1.4	8.28	10.3	7.52	7.64	8.4±1.3
IDA-SL	0-15	7.11	7.50	7.12	7.60	7.33±0.25	7.61	8.26	6.86	7.60	7.58±0.57
	15-30	6.60	7.22	7.02	7.50	7.09±0.38	7.29	7.83	6.60	7.50	7.31±0.52
EJU-SL	0-15	7.52	8.28	7.66	8.14	7.90±0.37	8.36	8.42	8.06	8.14	8.25±0.17
	15-30	6.82	8.01	7.36	7.84	7.51±0.53	7.50	8.47	7.05	7.85	7.71±0.59
KSU-SL	0-15	17.5	8.24	7.85	7.31	10.2±4.9	12.6	8.78	7.11	7.05	8.8±2.6
	15-30	7.76	7.48	7.17	7.14	7.38±0.29	10.5	8.47	6.88	6.86	8.2±1.7
CTR-SL	0-15	19.5	8.09	7.46	7.83	10.7±5.9	8.14	9.44	8.33	8.24	8.53±-0.61
	15-30	10.4	6.45	7.02	7.36	7.8±1.8	6.50	7.78	8.02	8.00	7.58±0.72

agricultural farmland. Organic matter increases buffering and exchange capacity of soils and make nutrient available to crops. It also form chelates with metals such as Cu and Zn which increases their solubility and make them available to crops. However, an increase in organic carbon or organic matter leads to a stronger adsorption of heavy metals to soil particles and decreases their availability to crops. Organic carbon content of 2.5% is considered adequate for arable land crop production in Southwestern Nigeria. Eludoyin and Wokocha (2011) had reported a mean of 0.96% organic carbon in plots under repeated maize cropping and 2.02% organic carbon in forest soils around Ibadan. There is no significant difference between samples values and control value. This shows that there is no local difference in soil texture and general characteristics of these soils.

4.1.3 pH of the Soil

Table 4.6 shows the average pH (6.29±0.18) in topsoil and subsoil (5.89±0.15).There is no significant difference between rainy season value (6.33±0.16) and dry season (6.26±0.38) values in topsoil. Corresponding average seasonal pH in subsoil is 5.92±0.45 in rainy season while dry season value was 5.89±0.31. Soil pH were weakly acidic in the farmlands as shown in Table 4.2. The differences observed at various farms compared with control is not significant except at Ofoke, Ankpa and Ejule sampled sites (P=0.05). Average pH value of 6.29 in this study is higher than the average pH value of 5.2 reported for some Nigerian soils by Onofiok and Ojobo (1993).

4.2 HEAVY METAL LEVELS IN THE SOILS

4.2.1 Lead Levels in Soil

Lead concentration varied from one farmland to another. The average lead concentration in topsoil was 12.8±8.2 mg/kg (Table 4.7). The values ranged from 6.1±2.3 mg/kg in Ankpa to 27±11 mg/kg in Macks (Table 4.8). Corresponding subsoil values were not significantly different from topsoil values. The highest average value (27±11 mg/kg) recorded at Macks farm compared to other farms in this study could be as a result of the use of cow dung as manure. Davies (1990) had reported the presence of Pb and other heavy metals in animal manure including cow dung. The overall average concentration of lead for all farms is twice that of the control value (6.1±3.2 mg/kg) in topsoil. The differences observed between the concentrations of lead in soil samples at

Table 4.6: Average pH of the soils

Depth (cm)	Rainy season	Dry season	Mean
0-15	6.33±0.16	6.22±0.38	6.29±0.18
15-30	5.92±015	5.85±0.31	5.89±0.15
0-15 (CTR)	6.98±0.17	6.8±1.1	6.87±0.57
15-30 (CTR)	6.10±0.56	6.27±0.81	6.18±0.66

Table 4.7: Cumulated average concentrations (mg/kg) of heavy metals in soils (all farms).

Heavy metals	Depth (cm)	All Rainy Seasons	All Dry Seasons	Overall Mean
Cd	1-15	0.7±1.0	1.0±1.6	0.6±1.2
	15-30	0.37±0.29	0.42±0.38	0.37±0.07
Co	1-15	9.0±8.9	3.76±0.96	6.0±7.1
	15-30	7.2±7.8	2.71±0.76	4.9±3.2
Cu	1-15	6.1±4.8	3.89±0.28	4.8±3.9
	15-30	5.0±3.7	2.81±0.25	1.5±2.4
Ni	1-15	22±14	18±10	17±14
	15-30	13.8±0.7	11.7±1.4	12.8±1.5
Pb	1-15	15.0±5.5	12.0±2.4	12.8±8.2
	15-30	13.2±3.9	10.1±2.1	11.7±2.2
Zn	1-15	35±18	24.6±2.5	28±23
	15-30	31±20	19.0±2.7	25.0±8.5

Table 4.8: Concentration of heavy metals (mg/kg) in soil at the sampled farmlands

Site code	Depth (cm)	Pb	Cd	Cu	Co	Ni	Zn
OFK-SL	0-15	9.1±3.2	0.40±0.11	7.4±2.1	3.0±2.2	9.2±1.6	20±17
	15-30	5.7±1.0	0.32±0.15	6.9±1.6	2.6±2.2	8.8±4.9	24±17
ANK-SL	0-15	6.1±2.3	0.35±0.11	2.7±5.7	5.0±8.0	16.8±7.8	16±25
	15-30	7.3±5.0	0.47±0.41	2.1±4.4	4.5±8.4	15±11	12±18
AJA-SL	0-15	8.4±1.9	0.28±0.16	3.0±3.6	4.1±2.7	14.5±5.7	20±14
	15-30	10.2±4.7	0.27±0.20	2.7±2.9	3.1±1.3	12.8±3.3	22±25
MAC-SL	0-15	27±11	1.4±3.4	7.1±4.0	9.2±5.6	19.8±1.8	21±23
	15-30	20.8±5.8	0.8±1.9	5.5±2.9	5.2±4.9	14.4±2.8	18±26
IBA-SL	0-15	18.4±3.9	0.24±0.17	7.9±2.5	12±11	20.3±8.5	25±12
	15-30	16.3±3.6	0.7±1.7	5.4±2.3	8.1±4.5	16.7±5.8	23±14
IDA-SL	0-15	6.2±1.2	1.0±1.5	2.3±2.4	2.7±3.4	6.8±2.5	27.0±1.5
	15-30	5.2±0.8	1.6±1.9	2.1±2.2	2.1±3.2	4.9±2.6	24.3±4.1
EJU-SL	0-15	17.4±6.4	0.50±0.37	5.5±4.6	8.1±9.0	24±27	54±13
	15-30	14.8±3.5	1.4±3.2	3.4±2.9	7.8±11	17±13	40±15
KSU-SL	0-15	16.7±5.2	0.51±0.82	3.7±3.1	8.4±9.1	14±13	17±10
	15-30	14.0±2.8	0.40±0.61	2.9±2.9	6.0±7.0	11±11	13.5±9.8
LOK-SL	0-15	12.2±5.3	0.22±0.29	5.4±2.4	5.2±7.9	36±19	69±12
	15-30	10.7±4.0	0.44±0.94	4.2±2.6	5.4±8.6	31±16	48.4±5.2
MEAN	0-15	13.5±6.9	0.54±0.39	5.0±2.1	6.4±3.2	17.9±8.7	30.±18
	15-30	11.6±5.2	0.71±0.48	3.9±1.6	4.97±2.1	14.6±7.2	25±12
CTR	0-15	6.1±3.2	0.64±0.79	2.7±2.4	2.6±1.1	9.6±5.2	11.6±6.9
	15-30	5.7±5.5	0.72±0.87	2.5±2.4	2.5±1.8	8.3±3.9	9.8±4.6

various farms and in the control were statistically significant except at Ofoke, Ankpa, Ajaokuta and Idah (P=0.05). Results obtained showed that average rainy season values were only slightly higher than those of dry season (Table 4.7) and the differences observed were not significant. However, among the various farms the differences were significant (Table 4.8). Cumulative average concentration of lead in rainy season (15.0±5.5 mg/kg) and dry season value (12.0±2.4 mg/kg) were significantly higher than 3.32±1.99 mg/kg, 2.98±0.86 mg/kg, 3.22±1.34 mg/kg and 1.3±1.0 mg/kg for Osun, Kwara, Oyo and Ogun respectively (Olatunji *et al*., 2013) in Southwestern Nigeria. The difference between the mean lead levels (12.8±8.2 mg/kg) from this study and the 18.0±7.5 mg/kg reported by Iyaka and Kakulu (2012), for agricultural soils in Minna, Niger State is not significant but it is significant with 23.4±0.2 mg/kg for agricultural soils of Enyigba, Ebonyi State (Nweke *et al*., 2008), Nigeria. Average Pb concentration of 29.7 mg/kg reported for agricultural soils in Yargalma area, Zamfara State, Nigeria (Tsafe *et al*., 2012), is also significantly higher compared to this study. The range of Pb concentration 6.1±2.3 mg/kg to 27±11 mg/kg of this study is not significantly different from 7.7 mg/kg to 22 mg/kg reported by Iyaka and Kakulu (2012) for agricultural topsoils in Niger State, Nigeria. However, the range is significantly different from 0.87 to 5.68 µg/g reported by Olatunji *et al* (2013) for agricultural soils in Southwestern Nigeria, 32.5mg/kg to 67.4mg/kg in peri-urban Han of agricultural soils in Vietnam (Marcusson *et al*., 2008), 8.9 mg/kg to 34.5 mg/kg (Mico *et al*., 2006) for agricultural soils in Alicante, Spain. The mean (12.8±8.2 mg/kg) of this study is significantly lower than mean (47 mg/kg) value for Jamaica soils and Pb concentrations as high as 897 mg/kg has been reported (Lalor, 1995). Values obtained in this study fall within the Canadian Soil Quality Guidelines (70mg/kg) and within regulatory guidelines for agricultural soils (Table 4.9). There are no known Nigerian regulatory limits of levels of metals in agricultural soils. Table 4.10 provides comparison with studies from other countries.

4.2.2 Cadmium Levels in Soils

Average Cd concentration was 0.6±1.2 mg/kg in topsoil while subsoil value was 0.37± 0.07 mg/kg (Table 4.7). The concentration of Cd at the various farms ranged from 0.22±0.29 mg/kg in Lokoja to 1.6 ±1.9 mg/kg in Idah (Table 4.8). Average concentration of cadmium in dry season (1.0 ±1.6 mg/kg) is not significantly different from rainy season value of 0.7±1.0 mg/kg (Table 4.7). The cadmium concentration of 9.80 mg/kg at Macks farm and 9.43 mg/kg at Ejule farm in

Table 4.9: Regulated limits of metal (mg/kg) in agricultural soils of selected countries

	Cu	Zn	Pb	Cd	Ni	Co	Reference
Canada	63	200	70	1.4	50	40	CCME,1999
European Union Standard	140	300	300	3.0	75	-	EU, 2002
Nigeria(this study) mean	4.77	28.1	12.8	0.55	17.0	6.01	

Table 4.10: Comparison of metal concentrations (mg/kg) in agricultural soils of this study with values from other countries

	Cu	Zn	Pb	Cd	Ni	Co	Reference
Nigeria (this study) mean	4.77	28.1	12.8	0.6	17.0	6.01	
England / Wales Mean	23.1	97.1	74	0.80	-	-	Alloway,1995; MaGrath and Loveland, 1992
USA Mean	29.6	56.5	12.3	0.27			Alloway,1995; Holmgren, *et al.*,1993
China Mean	33.0	84.7	40	-	-	-	Wong *et al.*,2002
Italy Mean	30.0	94.0	215	-	-	-	Abollino,*et al.*, 2002
Canada	-	-	-	0.56	-	-	Frank, *et al.*, 1976
Netherlands	-	-	-	0.40	-	--	Ros and Slooff, 1988
New Zealand	-	-	-	0.44	-	-	Roberts *et al.*, 1994
Germany (Berlin)	15	50	30	-	5	-	Birke and Rauch, 2000

rainy season showed a high potential ecological risk and this may be attributed to the application of superphosphate fertilizers in these farms (Bohn *et al*., 1979). Increased Cd levels can also be attributed to widespread intensive use of organic and especially mineral fertilizers (Adriano, 2001). There was no significant difference between the average values and control value 0.64±0.79 mg/kg. Unlike other metals the concentration of Cd is higher in subsoil in most of the farms. However, the differences between topsoil and subsoil levels were not significant. The higher concentration of cadmium at the subsoil is supported by values obtained for the soil texture. At some of the farms were the concentration of Cd is highest at subsoil, % silt is highest at the subsoil and also the % sand is lowest at the subsoil. These factors will support higher capacity to retain pollutants. The variation of Cd levels among farms and control site was not significant. Average concentration of cadmium in dry season (1.0 ±1.6 mg/kg) was not significantly different from rainy season value of 0.7±1.0 mg/kg (Table 4.7). The average concentration of cadmium recorded in this study was lower than 2.55 mg/kg, 3.47 mg/kg, 2.29 mg/kg, and 3.92 mg/kg reported by Olatunji *et al*. (2013) for agricultural soils in Kwara, Ogun, Oyo and Osun State respectively, 6.78±0.33 mg/kg in Zira and 10.6±1.1 mg/kg in Mirnga (Akan *et al*., 2013) both in Borno State, Nigeria. The difference between mean value (0.6±1.2 mg/kg) of this study and the mean of 10.3 mg/kg and 5.30 mg/kg of studies by Mashi and Alhassan (2007) and Awode *et al*. (2008) respectively in soils in vegetable garden irrigated with wastewater in Kano is significant. The range of cadmium concentration in this study is significantly different from range of values (2.3 mg/kg to 4.8 mg/kg) obtained from similar study in Kano (Abdu *et al*., 2011), and 0.26 mg/kg to 5.75 mg/kg (Olatunji *et al*., 2013) in southwest Nigeria. The differences in range of Cd levels in Kogi State, Nigeria compared with range of 0.35 mg/kg to 0.46 mg/kg and 0.46 mg/kg to 0.59 mg/kg (Abdu *et al*., 2011) in Bobo-Dioulasso (BurkinaFaso) and Sikasso (Mali) respectively are not significant but significant with levels reported in Jamaica. Lalor *et al*. (1998) reported that range of Cd concentration in non-mineralized Jamaican soils varies from 0.3 mg/kg to over 400 mg/kg. Residual soils developed from shales have been reported (Lund *et al.,* 1981) to have Cd mean concentrations of 7.5 mg/kg, whereas soils derived from sandstones and basalts have concentrations with a mean of 0.84 mg/kg. Alluvial soils with parent materials from mixed sources have intermediate Cd levels of 1.5 mg/kg (Adriano 1986). The average value of 20 mg/kg of Cd in soils in Jamaican has also been reported (Lalor *et al*., 1998). The overall average value 0.6±1.2 mg/kg of this study compared with other values for agricultural soil from other countries of the world is given (Table 4.10). Chen *et al*. (1999) reported that total mean concentrations of cadmium in rural soils of several countries (mg/kg) were 0.4 for Sweden; 0.8 for Denmark; 1.0 for Norway; 1.5 for Italy; 2.0 for France, Australia, and S. Africa; 3.0 for U.K and Canada; 4.0 for Taiwan; 5.0 for Germany; 12.0 for Belgium; 20.0 for China; 20.0 and 39.0 for USA before and after using sewage sludge. The average concentration in this study soils contain lower concentrations of Cd than rural soils of all the above mentioned countries except Sweden. Cadmium overall average concentration 0.6±1.2 mg/kg for all farms in this study is within the regulated level of 1.4 mg/kg set by Canadian Soil Quality Guidelines for the protection of Environmental and Human Health and European Union (3.0 mg/kg) regulated limit (Table 4.9). Thefore the soils of farmlands studied do not need any clean up as present concentrations do not pose threat to humans.

4.2.3 Copper Levels in Soil

Table 4.7 shows average concentration of copper (4.8±3.9 mg/kg) in topsoil of farmland soils in Kogi State. Subsoil average value was 1.5±2.4 mg/kg. Average copper level ranged from 2.3±2.4 mg/kg in Idah to 7.9±2.5 mg/kg in Ibaji (Table 4.8). The variation of Cu concentration among farms is statistically significant. The concentration of copper in soil decreases from topsoil to subsoil. The control value is not significantly different (P=0.05) from values obtained among the sites except at Ofoke, Macks and Ibaji. This is expected as there were no activities in the farms that will account for differences among sampled farms and control site. The area is mainly rural and there are no noticeable industrial activities that would influence high concentrations of metals in the soils. There is significant difference in range of value of copper (2.3±2.4 mg/kg to 7.9±2.5 mg/kg) of this study and 12 mg/kg to 89 mg/kg reported by Iyaka and Kakulu (2009) for urban agricultural soils of Niger State, Nigeria, and 6.17 mg/kg to 20.87 mg/kg for agricultural soils in South Western Nigeria (Olatunji *et al.*, 2013). The mean Cu concentration of 4.8±3.9 mg/kg obtained for farmland soil samples was lower than the mean concentration for world soils of about 20.0ppm for Cu (Alloway, 1995) and also lower than 21.4mg/kg reported by Zauyah *et al.* (2004) for some cultivated soils of Malaysia Peninsula. Average concentration of copper for all farms (Table 4.7) in topsoil was within regulated limit of 63 mg/kg of the Canadian Soil Quality Guidelines, Vietnamese limit of 50 mg/kg, European Union limit of 140 mg/kg and the 50.0mg/kg established as the limit in Germany (Kabata-Pendias, 1995). Copper concentrations in this study were compared with those of other countries in Table 4.10. The concentrations can be considered to be at natural background levels and present little or no environmental effects.

4.2.4 Nickel Levels in Soil

The average concentration of nickel in topsoil for all farms is 17±14 mg/kg (Table 4.7) and the values ranged from 6.8±2.5 mg/kg in Idah to 36±19 mg/kg in Lokoja (Table 4.8). The average nickel concentration decreases from topsoil to subsoil but inter and intra farm differences were not significant except at Ejule and Lokoja. The highest average concentration of Ni (36±19 mg/kg) at Lokoja is four times higher than the control (Table 4.8). Nickel like copper and zinc have high mobility under acidic conditions due to formation of sparingly soluble sulphides. Metal sulphide has very low mobility under reducing conditions. These metals in soils can either be enriched or depleted relative to parent material and depending on the dominant factors that exist in the weathering environment (Mattigod and Page, 1983). The soil pH of this study is weakly acidic and can enhance the mobility of these metals. Average nickel concentration 17±14 mg/kg in this study is significantly different from 1.9±1.0 mg/kg reported by Iyaka and Kakulu (2012). The average Ni concentration in this study in both seasons were well within Dutch limit of 35 mg/kg, Canadian Regulated limits (50 mg/kg) and European Union regulated limits (75 mg/kg) for agricultural soils as given in Table 4.9. Values within standard limits suggest no enrichment of soil with nickel as average concentration lies within the threshold value and therefore the soils do not require clean up. There are no industrial activities around the sampled farms. The concentration of nickel is thus still within background levels.

4.2.5 Zinc Levels in Soil

Average zinc concentrations for all farms for the period of study (Table 4.7) is 28±23 mg/kg in topsoil, and this ranged from 16±25 mg/kg in Ankpa to 69±12 mg/kg in Lokoja (Table 4.8). Average value for subsoil was 25.0±8.5 mg/kg. As is the case with other metals determined, the concentration of zinc during rainy season (35±18 mg/kg) is higher than dry season value of 24.6±2.5 mg/kg; and the difference is significant. The relative increase in concentration of metals during rainy season would be attributed to enhanced dissolution of residual minerals (Sondag *et al.*, 1997). However, the differences observed in zinc concentrations among farms are not significant. Cumulated average level (28±13 mg/kg) was more than twice the control value

(11.6±6.9 mg/kg), but this difference was not significant. The highest value 69±12 mg/kg was observed at Lokoja sample site which is an uncultivated farm. The level of Zn in these farms is largely governed by the amount of Zn in the parent material. The range of values is not significantly different from 12.9 mg/kg to 38.9 mg/kg reported by Olatunji *et al*. (2013) for agricultural soils in southwest, Nigeria, but differs from the 0.42mg/kg to 0.83 mg/kg obtained by Francis (2005) in his study of livestock farmlands in southern Nigeria. Iyaka and Kakulu (2009) also reported similar range of Zn concentration (2.8 mg/kg to 41 mg/kg in Minna and 0.57 mg/kg to 36 mg/kg in Bida) in Niger State, Nigeria. The 13 mg/kg to 285 mg/kg obtained by Nafiu, *et al*., 2011, also differs significantly from this study. In other parts of the world, a range of 1.0 mg/kg to 170 mg/kg was reported for surface soil samples of South Carolina (Canova,1999), and 2.8 mg/kg to 12.0 mg/kg was reported by Gough *et al*. (1994) as baseline elemental contents of the Bull Island soils in South Carolina, U.S.A. The average Zn concentration (28±23 mg/kg) obtained from this study is higher than the mean content of 20 mg/kg found in Florida agricultural surface soils (Holmgren *et al*., 1993), but lower that the average 45 ppm value reported in the literature for world sandy soils by Kabata-Pendias and Pendias (1992). Average concentration of zinc for both seasons was within Canadian regulated limits (200 mg/kg) for agricultural soils and European Union limits of 300 mg/kg (Table 4.9). Table 4.10 provides further comparisons.The average values in this study are lower than those reported for different countries land use and did not exceed the regulated limits of metals in agricultural soils of selected countries.

4.2.6 Cobalt Levels in Soil

Table 4.7 shows average cobalt concentration for all farms as 6.0±7.1 mg/kg in topsoil. Among farms, cobalt levels ranged from 2.7±3.4 mg/kg in Idah to 12±11 mg/kg in Ibaji in topsoil (Table 4.8). Corresponding subsoil average value was 4.9±3.3 mg/kg. Subsoil values ranged from 2.1±3.2 mg/kg to 8.1±4.5 mg/kg. The difference in concentration of cobalt among farmland soils is not significant. All values obtain were higher than the control value 2.6±1.1 mg/kg. The highest value obtained at Ibaji is six times higher than the control and the difference compared to the control is statistically significant. The level of Co decreases from topsoil to subsoil at all sites. Result also shows that average rainy season concentration (9.0±8.9 mg/kg) is about three times higher than dry season value (3.76±0.96 mg/kg) in topsoil as given in Table 4.7. Regulated limit (40 mg/kg) of cobalt concentrations in agriculture soil in Canada are given in Table 4.9.

4.3 INTER-ELEMENT RELATIONSHIPS OF METALS AND SOIL PROPERTIES

The correlation coefficient (Pearson) matrixes between the metal concentrations and soil properties in the farmland soils are presented in Table 4.11. The pairs whose correlation coefficients are slightly significant at 0.05 are % organic carbon and nickel (0.142), zinc and lead (0.168), nickel and lead (0.193), but highly significant in cadmium and nickel (0.95). Some pairs have correlation coefficients that are significant at 0.01 confidence limit (99%), these pairs are indicated by double asterisks in Table 4.11. All the metal pairs that have high correlation coefficients (whose correlation coefficient are significant at α =0.05 or α =0.01) indicate identical sources for the metal pairs. There are no industrial activities that will introduce heavy metals into the farmlands. The significant correlation coefficients between the metals except zinc and % organic carbon show that the concentration of the metal depends on the retention ability of the soil. The greater the value of percentage organic carbon or organic matter the greater the retention ability of that soil.

4.4 POLLUTION INDEX OF METAL IN FARMLAND SOIL

4.4.1 Geoaccumulation index: Geoaccumulation index (I_{geo}) rating is presented in Table 4.12. The content accepted as background is multiplied in each case by a factor (1.5) in order to account for natural fluctuations of a given metal in the environment and as well as small anthropogenic influences (Loska and Wiechula, 2003). Geoaccumulation index (I_{geo}) rating indicated that all topsoil (0-15cm) analysed belong to unpolluted class (<0) except lead and Zn with Igeo value of 0.48 and 0.63 that fall within the category of class 1 of slightly polluted. Cadmium showed I_{geo} of <0 for all samples indicating that all soil samples were practically uncontaminated by Cd.

This suggests that Cd input in the soil is associated with the parent material that formed the soil or other natural or small anthropogenic non-point sources. Geoaccumulation index of heavy metals in agricultural soil was compared with other countries (Table 4.13). This study results

Table 4.11: Correlation coefficient among metals and soil properties

	pH	TOC	TOM	Cu	Zn	Pb	Cd	Ni	Co
pH	1								
TOC	-0.096	1							
TOM	-0.095	1.000.**	1						
Cu	-0.113	0.043	0.043	1					
Zn	-0.107	0.029	0.030	0.519**	1				
Pb	0.164	-0.171	-0.171	0.300**	0.168	1			
Cd	-0.053	0.069	0.070	0.409**	0.238*	0.061	1		
Ni	-0.107	0.142	0.143	0.514**	0.486**	0.193	0.95	1	
Co	0.167	-0.029	-0.028	0.752**	0.390**	0.346**	0.364**	0.644**	1

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

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

Table 4.12: Geoaccumulation index (I_{geo}) of heavy metals in top soil samples of farmland

Sample site	Cd	Co	Cu	Ni	Pb	Zn
OFK-SL	-0.41	-0.03	0.28	-0.17	0.01	0.08
ANK-SL	-0.46	0.12	-0.86	0.10	-0.15	-0.02
AJA-SL	-0.57	0.03	0.19	0.03	0.48	0.11
MAC-SL	-0.62	0.38	0.26	0.16	0.36	0.11
IBA-SL	-0.63	0.49	0.30	0.17	0.26	0.19
IDA-SL	-0.03	-0.15	-0.22	-0.30	-0.16	0.22
EJU-SL	-0.31	0.34	0.15	0.25	0.29	0.55
KSU-SL	-0.29	0.35	-0.02	0.003	0.28	0.02
LOK-SL	-0.68	0.13	0.14	0.42	0.14	0.63

I_{geo} classification: $I_{geo} \leq 0$, class 0, unpolluted,

$0 \leq I_{geo} \leq 1$, class 1, from unpolluted to slightly polluted,

$1 < I_{geo} \leq 2$, class 2, moderately polluted,

$2 < I_{geo} \leq 3$, class 3, from moderately polluted to strongly polluted,

$3 < I_{geo} \leq 4$, strongly polluted,

$4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted,

$I_{geo} > 5$, class 6, extremely polluted.

compared well with values obtained in China and Banglandish but significantly different from results obtained in Greece.

4.5 SPECIATION OF METAL IN SOIL

Table 4.14 shows speciation of metals in soil. A speciation study of metals is a useful tool that is normally used to determine the concentrations of pollutants in fractions of soil samples. It gives an estimate of the amount of metals available to ecological materials. The results showed that the proportion in non-residual soil phases was 41.9% Pb, 48.7% Co, 72.5% Cu, 73.2% Ni, 82.6% Cd and 84.3% Zn. Cadmium, zinc and nickel are mostly abundant in exchangeable fraction. This means that these metals are more mobile in this environment than other metals that are mostly abundant in the remaining four geochemical phases. The presence of these metals in the highly mobile exchangeable phase and pH-sensitive carbonate-bound fractions than in residual or organic-bound fraction makes the metal even more bioavailable in the soil. The high exchangeability of Cd could be explained by the low adsorptive constant of the complex formed with organic matter (Ramos *et al.,* 1994; Zerbe *et al*., 1999). The result also shows that Cu is mostly abundant (41.8±3.9%) in the fraction bound to organics. Copper can easily complex with organic matter because of high degree of formation of organic-Cu compounds (Haung *et al*., 2007). The abundance of copper in the residual fraction was 27.5±8.1%. The bio-available (non-residual) fraction of lead is 41.9% while the residual fraction has the largest percentage of lead - 58.1%. This result is different from those of other workers (Levy *et al*., 1992; Ip *et al*., 2007) that have reported that lead has the highest concentration in the ferrous-manganese oxide bound fraction. Onianwa (2001) has also reported high Pb abundance in this phase. The low concentration of lead in the non-residual fraction (41.9 %) and the highly mobile exchangeable phase and pH sensitive carbonate phase shows no increase in anthropogenic input of Pb into the environment. Therefore, Pb cannot be easily released to other environmental component such as crops. The low percentage abundances exhibited by the metals in the oxidizable phase (organic-bound phase) (except Cu) could be attributed to the level of organic matter load in the soil. Many of the metals determined show low abundances in the carbonate bound phase, except Ni (21.2%)

Table 4 13: Geoaccumulation index of heavy metals in agricultural soil compared with other countries.

	Cd	Pb	Cu	Co	Ni	Zn
This study (mean)	-0.20	-0.82	0.04	0.14	0.06	0.20
China[a]	1.08	-0.04	-0.07	-	-0.38	0.06
Greece[b]	5.1	2.6	1.33	-	-	2.27
Bangladesh[c]	0.28	0.13	0.28	-	0.12	0.13

a.Binggan and Linsheng, 2010
b. Nikorlaidis *et al*., 2010
c .Rahman *et al*., 2012

Table 4.14: Average speciation (% in geochemical phases) of the metals in soil

Phases	Cu	Zn	Pb	Cd	Ni	Co
Exchangeable	3.5±1.2	37±12	3.1±1.5	41.5±3.2	35.3±2.6	6.9±1.3
Carbonate- bound	4.6±2.4	9.8±2.3	8.6±3.1	15.9±1.5	21.2±4.7	10.1±2.5
Fe-Mn Oxide bound	24.6±4.5	24.5±7.1	10.7±1.9	14.6±1.5	8.1±1.6	12.4±5.2
Organic bound	41.8±3.9	13.0±7.1	19.5±2.7	11.0±1.6	8.6±1.6	19.2±2.2
Residual	27.5±8.1	15.7±3.8	58.1±3.3	17.4±3.4	26.8±5.1	51.4±3.6

and Cd (15.59%) which show relatively high percentage abundances. Lead and cobalt showed the highest phase (58.1±3.3% and 51.4±3.6% respectively) in the residual phase. This result agrees with that of Ramirez *et al*. (2005), who reported that Pb is mostly associated with the residual phase. The higher the metals present in this fraction the lower the degree of pollution (Howari and Benat, 2001). Sum of concentrations of metals in different geochemical phases can be used to express the potential mobility of metals. The potential mobility of a metal can be assessed by adding up the results of the exchangeable phase, carbonate phase, oxide and organic phase of that metal (Haung *et al*., 2007). The exchangeable phase represents the mobile and bioavailable heavy metal fraction. In this phase, the heavy metals can easily be released into the environment. The presence of heavy metals in this phase where they can be taken up by plants from the soils is hazardous to the ecosystem. In this study, Cd, Ni, and Zn had high fractions in the exchangeable phase and therefore could be highly mobile and available to plants. Despite this high concentration, the observed levels do not pose a serious risk since the overall concentrations of metals determined in the soil are within regulated limits

4.6 IRRIGATION WATER QUALITY

Irrigation, the addition of water to lands via artificial means is essential and profitable to crop production. Irrigation water maintains moisture in the soil and moisture is necessary for the germination of seeds. Seeds do not grow in dry soil. Irrigation is essential for the growth of the roots of crop plants. Thus irrigation is necessary for the absorption of mineral nutrients by the plant from the soil. It is essential for the general growth of plant.

4.6.1. Variation of Physicohemical Parameters

The parameters discussed here are pH, temperature, alkalinity, hardness, nitrate, sulphate, phosphate, dissolved oxygen and chemical oxygen demand. The overall average level of the physiochemical parameters in irrigation water at three locations is given in Table 4.15. Average pH of irrigation water was 6.86±0.62 and the values ranged from 6.36 to 7.23. Alkalinity and total hardness averaged 87±69 mg/L and 40±17 mg/L respectively.

Table 4.15: Average quality of physicochemical parameters of irrigation water at each sampling station

Sampling Site	pH	Temp. (^oC)	Alkalinity (mg/L)	Total Hardness (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Nitrate (mg/L)	Sulphate (mg/L)	Phosphate (mg/L)	DO (mg/L)	COD (mg/L)
OFK-SW	7.02±0.83	28.3±2.2	40±21	35±21	2.99±0.86	7.9±5.2	5.74±3.3	19.9±8.5	0.34±0.16	3.93±2.6	86.0±8.4
IBA-SW	6.39±0.29	29.0±1.3	64±20	42±18	3.4±1.2	9.0±4.2	6.4±3.9	24.7±7.8	0.51±0.63	1.5±1.5	115±19
MAC-SW	7.15±0.35	30.0±1.6	154±78	43±13	3.85±0.91	9.1±3.2	8.4±6.8	37.9±8.3	8.9±10.1	3.9±2.4	140±41
Overall mean	6.86±0.62	29.5±1.7	87±69	40±17	3.4±1.0	8.7±4.1	6.8±4.9	27±11	3.3±6.9	3.1±2.4	114±40

The surface water at Macks farm had the highest value of alkalinity (154±78 mg/L). The differences observed in the level of a given physiochemical parameters among the three sampled stations were found not to be statistically significant. The quarterly variation of the parameters is illustrated in Appendix 4.1 to 410. The trend in monthly concentration of the parameters determined did not vary significantly. The parameters determined are within the various guidelines for irrigation water as given by Canadian Council of Ministers of the Environment (CCME, 1999) (Table 4.16). Therefore, there contamination of farmland and food crops is not likely to be derived from the application of irrigation water.

4.6.2. Heavy Metals in Surface Water: Table 4.17 shows the average concentrations of heavy metals in the three sampling stations for surface water. A comparison of the mean values shows that there are no significant differences in any one metal among the stations, except for Cu. The concentration of copper was highest at Ofoke with a value of 0.16±0.17 mg/L. Figures 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6 illustrate the quarterly variation of cadmium, lead, copper, cobalt, nickel and zinc respectively at the different sampling locations. Copper and lead showed similar trends that differ from those of cobalt, nickel and zinc. The average concentrations of metals obtained in this study were within regulated limits for irrigation water for agricultural soils (Table 4.18) as given by the Canadian Council of Ministers of the Environment (CCME, 1999).

4.6.3 Physicochemical Properties of Groundwater: Table 4.19 shows overall average of physicochemical properties of ground water. Result showed that all average values were within WHO limits (Table 4.20) for drinking water. Results were also within regulatory limits for some African countries (UNBS, 2008; MBS, 2005).

4.6.4 Heavy metals in ground water: Average values of metal concentrations in ground water are given in Table 4.21. Zinc had the highest concentration (0.36±0.32 mg/L) followed by lead (0.04±0.09 mg/L). Copper and cadmium had similar concentration of 0.01±0.01 mg/L. The concentrations of metals determined were within WHO (2006) drinking water limit (Table 4.22) except Pb (0.04±0.09 mg/l). There is no guideline for zinc concentration for drinking water

Table 4.16: Some water quality standards

Parameters	This study	Irrigation water[a]	WHO (2006)	Nigeria (FEPA, 1991)	FAO (1984)	Nigeria (SON, 2007)	Uganda (UNBS, 2008)	Malawi (MBS, 2005)
pH	6.86	5.0-9.0	6.5-9.5	6-9	6.5-8.4	6.5-8.5	6.5-8.5	-
Temp. (^{o}C)	29.5	35^{o}C	30-32	-	-	-	-	
Alkalinity (mg/L)	87	120-200	200	-	-	-	-	-
Total Hardness (mg/L)	40	-	500	-	-	150	500	100
Calcium (mg/L)	3.4	-	-	-	-	-	-	-
Magnesium (mg/L)	8.7	-	-	-	-	-	-	-
NO_3^-N (mg/L)	6.8	15	3	20	10	50-100	45	45
Sulphate (mg/L)	27	250	250	500		100	200	200
Phosphate (mg/L)	3.3	-	0.5	5	8.6	-	-	-
DO (mg/L)	3.1	-	5-8	-	-	-	-	-
COD (mg/L)	114	90	-	80	-	-	-	-

a: Ayers and Westcot (1985)

Table 4.17: Average metal concentrations (mg/L) in surface water at sampling locations

Metals	OFK	IBA	MAC
Cu	0.16±0.17	0.02	0.02±0.01
Zn	0.13±0.18	0.19±0.16	0.13±0.12
Pb	0.01±0.01	0.02±0.01	0.07±0.05
Cd	0.01±0.01	0.004±0.01	0.002
Ni	0.03±0.01	0.045±0.02	0.03±0.02
Co	0.01±0.01	0.03±0.02	0.01±0.01

Table 4.18: Comparison of mean of metals concentration (mg/L) with guidelines for irrigation water

	Cd	Pb	Cu	Co	Ni	Zn
This study (mean)	0.01	0.03	0.06	0.02	0.03	0.15
Guidelines[a]	0.01	2.0	0.2	0.05	0.2	2.0
Guidelines[b]	10	65	17	50	1400	200

a: CCME, 1999

b: Ayers and Westcott, 1985

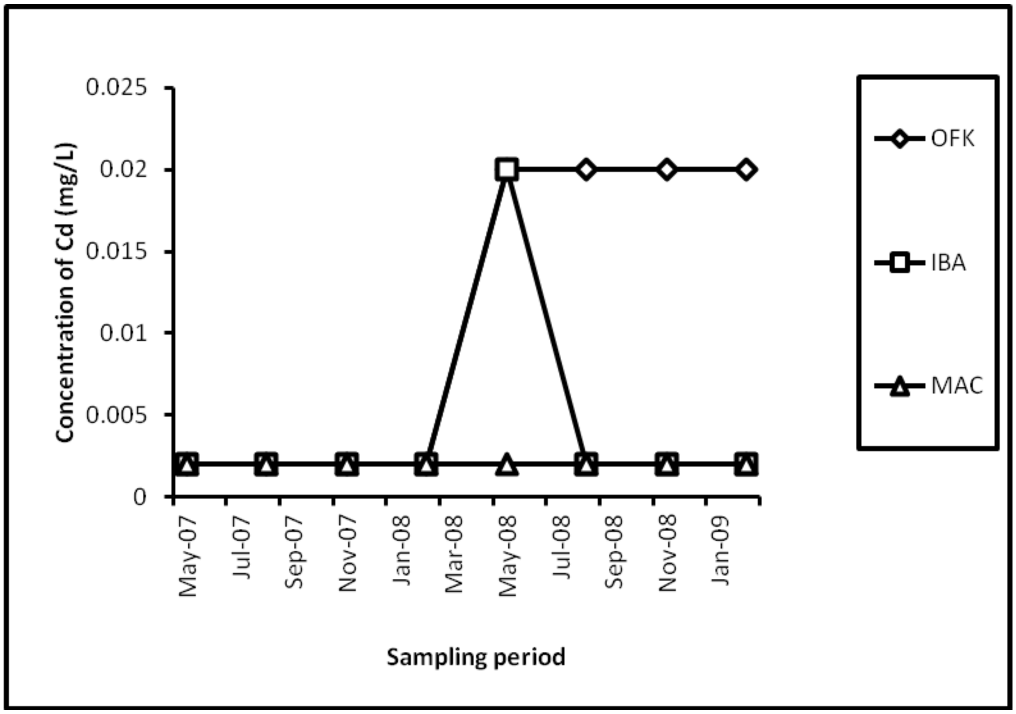

Fig 4.1: Variation of water Cd levels with sampling period

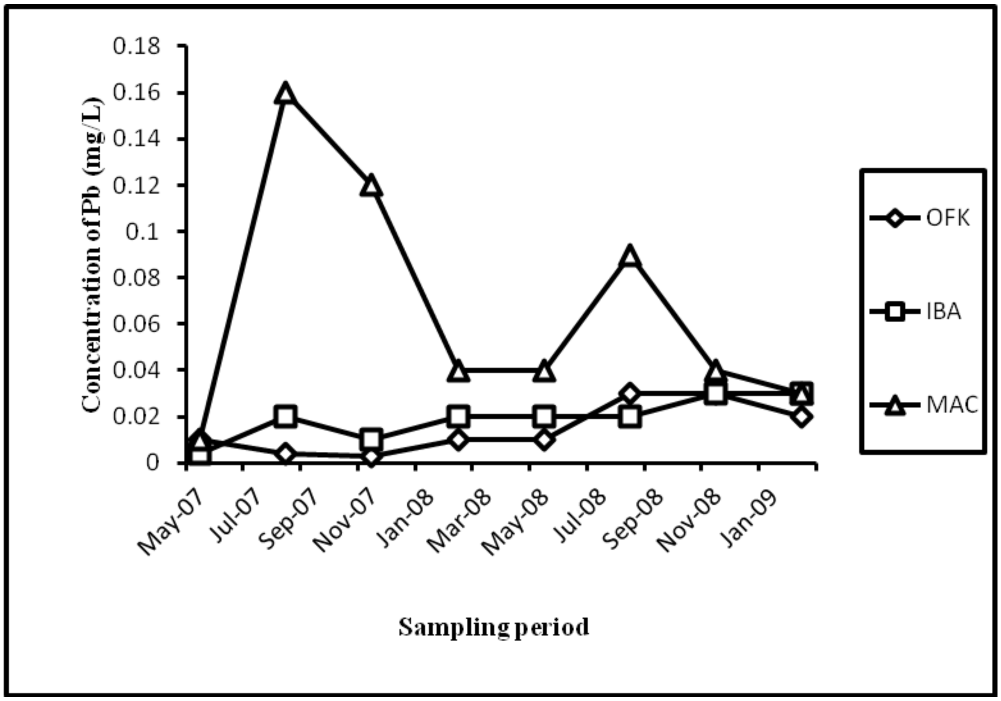

Fig 4.2: Variation of water Pb levels with sampling period

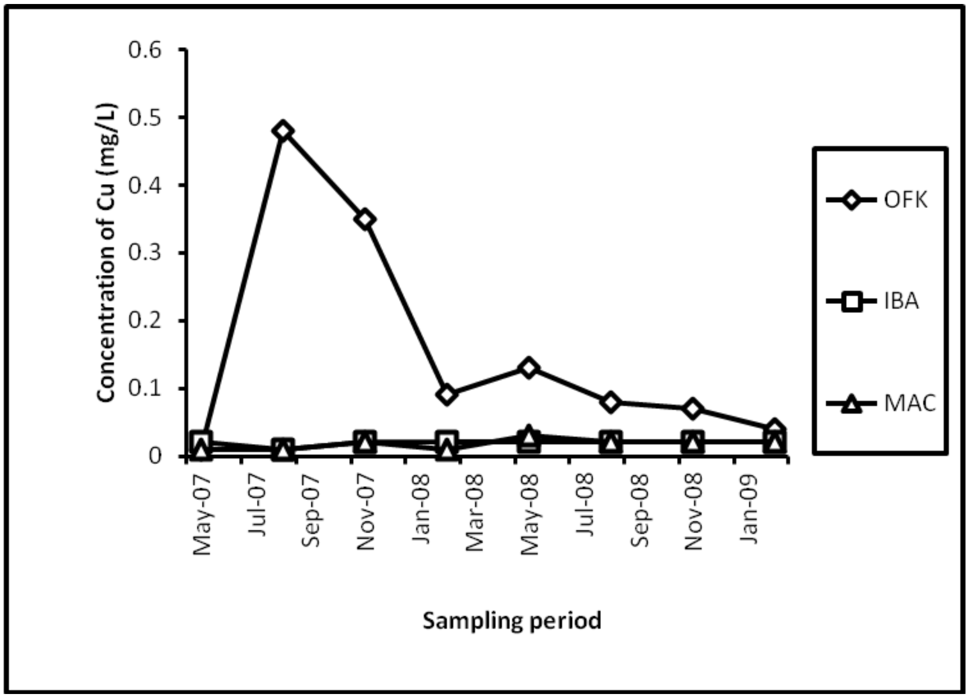

Fig 4.3: Variation of water Cu levels with sampling period

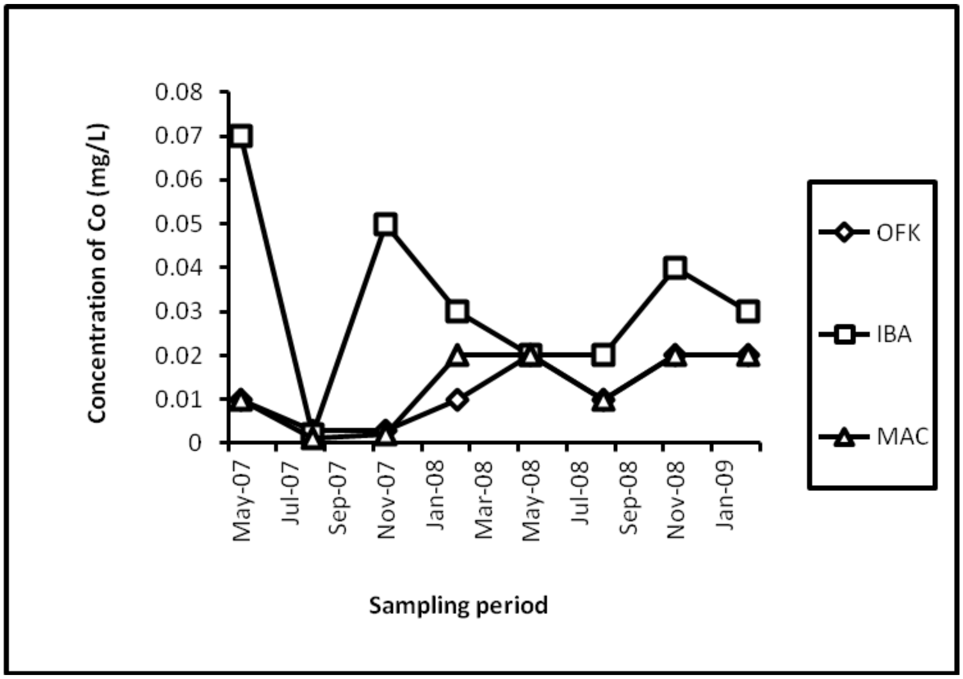

Fig 4.4: Variation of water Co levels with sampling period

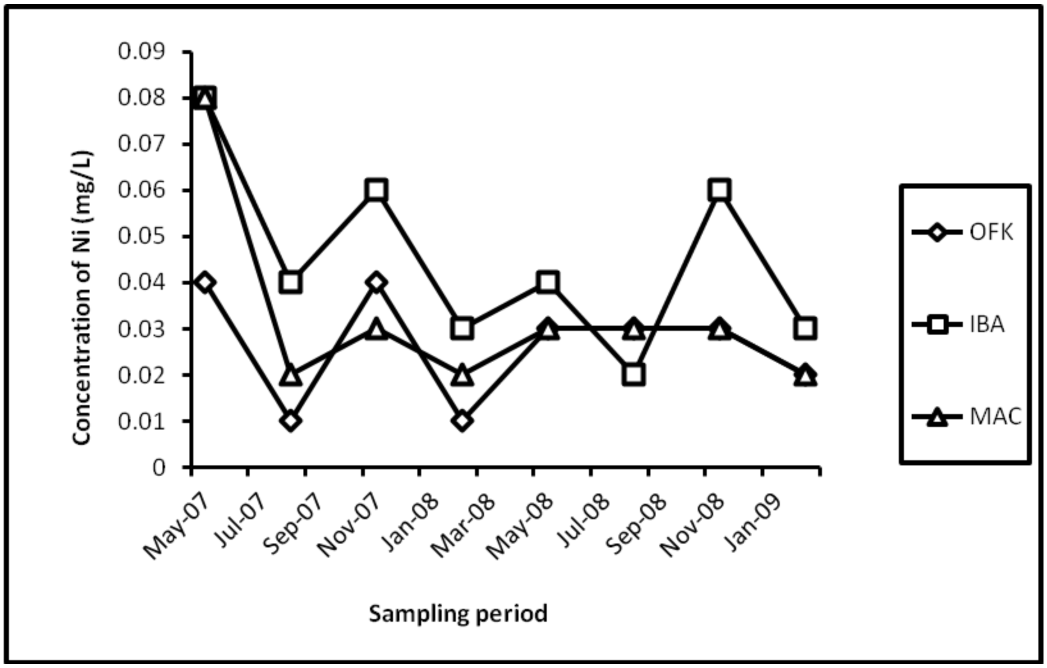

Fig 4.5: Variation of water Ni levels with sampling period

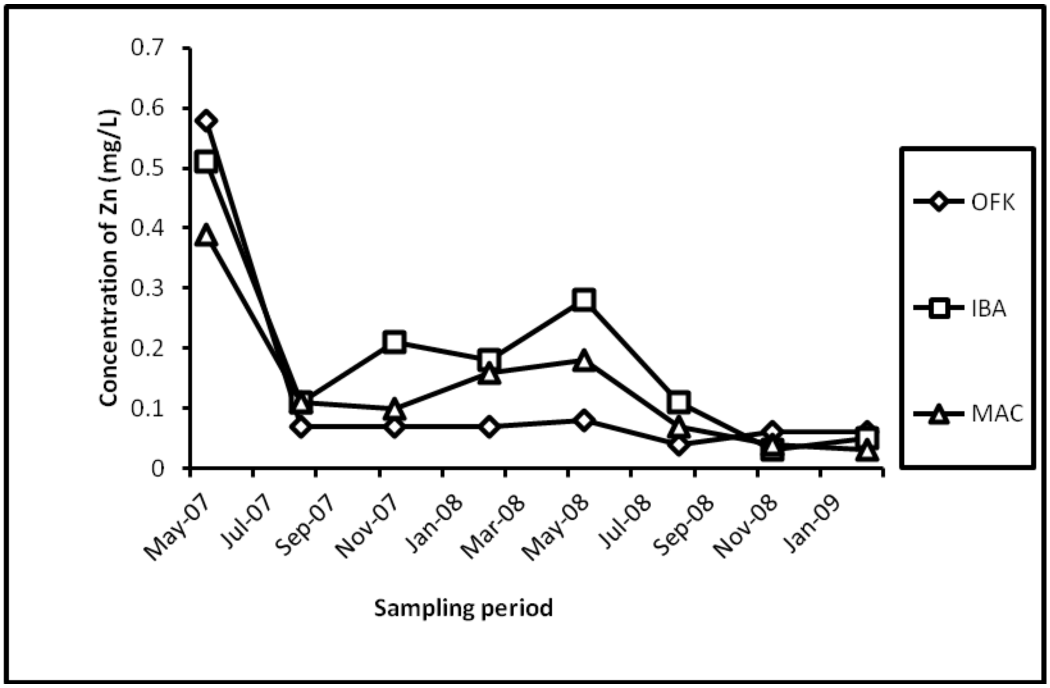

Fig 4.6: Variation of water Zn levels with sampling period

Table 4.19: Overall physicochemical properties of ground water

Sampling sites	Season	pH	Tempt (^{o}C)	Alkalinity (mg/L)	Total Hardness (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	No$_3^-$N (mg/L)	Sulphate (mg/L)	Phosphate (mg/L)	DO (mg/L)	COD (mg/L)
MAC-UD	Rainy	6.66±0.29	30.4±2.9	33.3±2.3	32.5±7.1	1.37±0.38	7.5±1.8	1.89±0.50	25±14	0.02±0.02	7.55±0.46	24.8±3.4
	Dry	6.81±0.50	26.5±4.8	51±14	36.0±3.7	2.1±0.9	8.1±1.0	1.12±0.12	27±11	0.07±0.08	5.0±3.3	25.4±1.0
Overall mean		6.74±0.39	28.4±4.2	42±13	34.2±5.6	1.71±0.74	7.8±1.4	1.45±0.51	26±11	0.05±0.06	6.3±2.6	25.1±2.3

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Table 4.20: Ground water quality compared with some water quality standards

Parameters	This study	WHO (2006)	Nigeria (FEPA, 1991)	FAO (1984)	Nigeria (SON, 2007)	Uganda (UNBS, 2008)	Malawi (MBS, 2005)
pH	6.74	6.5-9.5	6-9	6.5-8.4	6.5-8.5	6.5-8.5	-
Temp. (^{o}C)	28.4	30-32	-	-	-	-	-
Alkalinity (mg/L)	34.2	200	-	-	-	-	-
Total Hardness (mg/L)	34.2	500	-	-	-	500	100
Calcium (mg/L)	1.71	-	-	-	-	-	-
Magnesium (mg/L)	7.8	-	-	-	-	-	-
No_3^-N (mg/L)	1.45	3	20	10	50-100	45	45
Sulphate (mg/L)	26	250	500	-	150	200	200
Phosphate (mg/L)	0.05	0.5	5	8.6	-	-	-
DO (mg/L)	6.3	5-8	-	-	-	-	-
COD(mg/L)	25.1	-	-	-	-	100	-

Table 4.21: Overall concentration of metals (mg/L) in groundwater

	Cu	Zn	Pb	Cd	Ni	Co
Rainy season	0.01±0.01	0.46±0.43	0.07±0.12	0.01±0.01	0.04±0.02	0.02±0.01
Dry season	0.02±0.01	0.26±0.13	0.01±0.01	0.01±0.01	0.03±0.01	0.01±0.01
Overall mean	0.01±0.01	0.36±0.32	0.04±0.09	0.01±0.01	0.03±0.02	0.02±0.01

Table 4.22: WHO's drinking water standard, 2006

Metals	Levels normally found infresh water/surface water/groundwater	Guidelines by the WHO
Cd	<1µg/L	0.003mg/L
Pb	-	0.01mg/L
Co	-	-
Cu	-	2.0mg/L
Ni	<0.02mg/L	0.07mg/L
Zn	-	no guideline

4.7. SEDIMENT QUALITY

4.7.1 Concentration of Heavy Metals in Sediment:

Overall mean metal concentrations in sediments is given in Table 4.23. Average copper concentration was 9.3±5.2 mg/kg. Average values for all season ranged from 4.15±0.33 mg/kg in Ibaji to 19±20 mg/kg in Macks (Table 4.24). The intra-farm and inter-farms variation of copper levels were statistically significant. The average concentrations of copper were within WHO (2004) regulatory limit of 25 mg/kg (Table 4.25). There are no industrial activities at the various dams sampled and no cases of discharge of effluent from industries. Therefore, high concentration of copper was not expected, as concentrations depended mainly on runoff from agricultural soils. Copper concentrations within regulatory limits had also been reported for soil samples and water samples in previous sections. Range of copper levels obtained in this study is lower compared to range of 26.3±0.02 mg/kg to 51.3±0.01 mg/kg obtained by Akan *et al.*, (2010) from River Ngada in Maiduguri Nigeria sediment is significant. Abdo and El-Nasharty, (2010) have reported a range of 2 mg/kg to 36.4 mg/kg for Ismailia Canal sediment in Egypy.These values were significantly higher than the result of this study.

Table 4.23 shows average concentration of lead as 19.8±7.4 mg/k, with values ranging from 9.4±2.4 mg/kg in Macks to 29±14 mg/kg in Ofoke (Table 4.24). The differences observed in the concentrations of sediment Pb in the different sampled sites were statistically significant. However, the values were within regulatory limits (WHO, 2004) (Table 4.25). The highest mean concentration 29±14 mg/kg was observed during rainy season at Ofoke while the lowest value (9.4±2.4 mg/kg) was observed at Macks during dry season. The range of values from this study is within the range of 10 mg/kg to 43.2 mg/kg reported for Ismailia Canal sediment in Egypt. The same range has been reported for the Nile sediment in Egypt (Abdel-Satar, 2005).

Average level of cadmium was 0.34±0.62 mg/kg (Table 4.23). Seasonal average values ranged from 0.01±0.01 mg/kg in Macks to 1.6±3.1mg/kg in Ibaji (Table 4.24). Cadmium concentration was the lowest of all the metals determined. The differences observed in cadmium concentrations among the farms during the period is not statistically significant (P=0.05). The average value of

Table 4.23: Overall concentrations (mg/kg) of heavy metals in sediment

Heavy metals	Sampled sites			Overall mean
	OFK	IBA	MAC	
Cu	8.8±5.3 ^{a}	5.9±3.6 ^{a}	13±15 ^{a}	9.3±5.2
Zn	55±30 ^{a}	60±31 ^{a}	44±37 ^{a}	54±26
Pb	27±11 ^{b}	16.2±5.9 ^{a}	15.5±8.7 ^{a}	19.8±7.4
Cd	0.16±0.23 ^{a}	0.8±2.2 ^{a}	0.05±0.14 ^{a}	0.34±0.62
Ni	10.5±5.5 ^{a}	21.2±7.5 ^{a}	18±15 ^{a}	16.7±6.5
Co	6.8±5.9 ^{a}	7.5±4.2 ^{a}	8.7±10.2 ^{a}	7.6±3.0

Values within column with different superscript (a, b) are significantly different at P=0.05

Table 4.24: Seasonal concentrations of heavy metals (mg/kg) in sediment

Heavy metals	OFK		IBA		MAC	
	Rainy season	Dry season	Rainy season	Dry season	Rainy season	Dry season
Cu	10.7±6.1	6.9±4.2	7.6±4.8	4.15±0.33	19±20	7.5±3.2
Zn	67±37	45±21	68±36	53±28	62±43	27±24
Pb	29±14	26.0±8.8	18.8±5.6	13.6±5.9	22±8.5	9.4±2.4
Cd	0.20±0.34	0.12±0.04	1.6±3.1	0.01±0.01	0.10±0.20	0.01±0.01
Ni	12.7±7.1	8.3±3.1	21.7±7.5	20.7±8.5	23±19	13.5±8.9
Co	9.1±7.8	4.5±2.8	9.4±2.5	5.5±2.3	12±14	5.0±1.6

Table 4.25: Comparison of average metal concentrations (mg/kg) in sediments with regulatory standard

Metals	This study			WHO (2004)	USEPA (1999)
	OFK-SD	IBA-SD	MAC-SD		
Cu	8.8	5.88	13.3	25	-
Zn	56	60	44	123	-
Pb	27.4	16	15.5	-	40
Cd	0.16	0.8	0.05	6	-
Ni	15.0	21.2	18.3	20	-
Co	6.8	7.5	16.8	-	-

)

Table 4.26: Average concentration of the present work compared with levels elsewhere

Metals	This study			Egypt (Omer, 2003)	Egypt (Abdel Satar, 2005)	Egypt (Moalla *et al.*, 2006)	New York (Mason and Moor, 1982)	Netherlands (McLennan and Taylor, 1999)
	OFK-SD	IBA-SD	MAC-SD					
Cu	8.8	5.88	13.3	116	27	36	50	25
Zn	58	61	45	227	162	170	90	70
Pb	27.5	16	15.7	51	23	16	20	20
Cd	0.16	0.8	0.06	1	3	3	0.3	0.5
Ni	15.0	21.2	18.3	74	44	-	80	20
Co	7.0	7.5	16.8	43	49	14	20	10

0.8 mg/kg obtained at Ibaji is not different from 0.99 mg/kg recorded by MacDonald *et al*. (1996) for Florida coastal sediment. The range of Cd concentration in this study is significantly lower than the range of 1.6 mg/kg to 9.00 mg/kg reported for Ismailia Canal sediment, Egypt (Abdo and El-Nasharty, 2010). All cadmium concentrations observed in this study were within regulatory sediment guidelines (Table 4.25).

Average nickel concentration in sediment was 16.7±5.9mg/kg. Seasonal concentrations ranged from 8.3±3.1mg/kg in Ofoke to 23±19 mg/kg in Macks. The differences in concentration of nickel were found not to be statistically significant. The highest nickel concentration of 23±19 mg/kg observed at Macks slightly exceeded the Effect Range Low value of 20.9 mg/kg and WHO (2004) value (20 mg/kg)(Table 4.25) but did not exceed Effect Range Median of 51.6 mg/kg. Average values of Ni concentration also did not exceed probable-effects-level (PEL) guidelines (42.8 mg/kg) for toxic biological effects established by USEPA (1999).

Average concentration of cobalt in sediment was 7.6±3.0 mg/kg. Average values ranged from 4.5±2.8 mg/kg in Ofoke to 12±14 mg/kg in Macks. The differences in concentration of cobalt in the three sampled stations were found not to be statistically different. There was no available standard guideline for cobalt for comparison with the present study. Range of cobalt concentration of 2.0 mg/kg to 36.4 mg/kg has been reported for Ismailia Canal sediment in Egypt (Abdol and El-Nasharty, 2010).

Overall average Zn concentration in sediment was 54±16 mg/kg and seasonal average ranged from 27±24 mg/kg to 68±36 mg/kg. This study range of value is within the range of 28 mg/kg to 193.2 mg/kg for Ismailia Canal sediment in Egypt (Abdo and El-Nasharty, 2010). There was no significant difference in Zn concentration among sampled sites. All values obtained for Zn during the period of study were within WHO standard limit of 0.12 mg/kg for the survival of aquatic system and PEL guidelines (271 mg/kg). All zinc concentrations are also within the sediment quality guideline as given in Table 4.25. Table 4.26 compared this study sediment heavy metals concentrations results with others studies elsewhere. Figs 4.7 to 4.12 illustrate quarterly variations of metal concentrations in sediment.

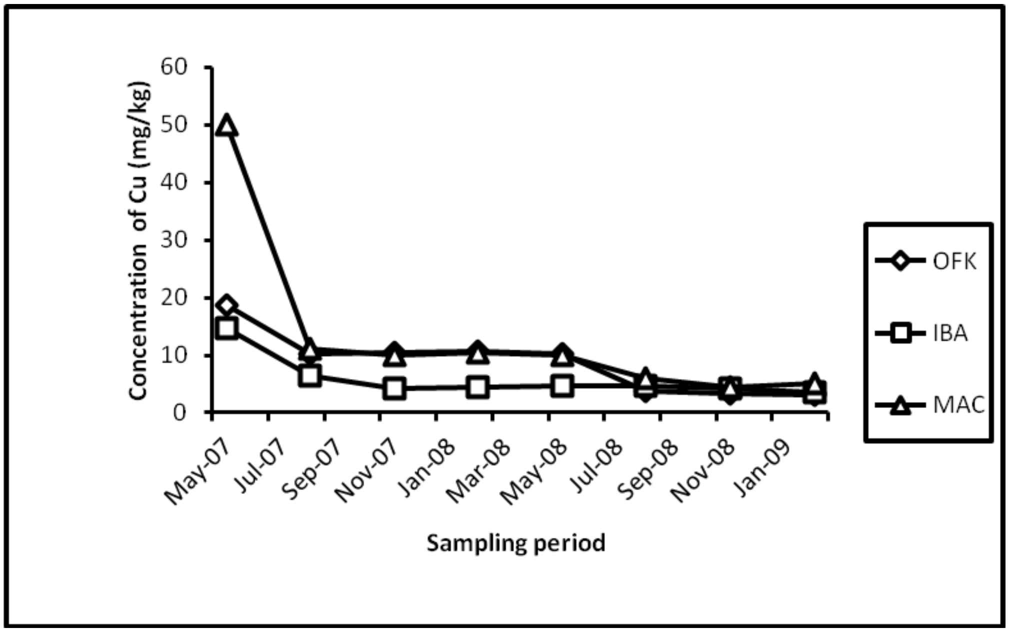

Fig 4.7: Variation of sediment Cu concentration with location

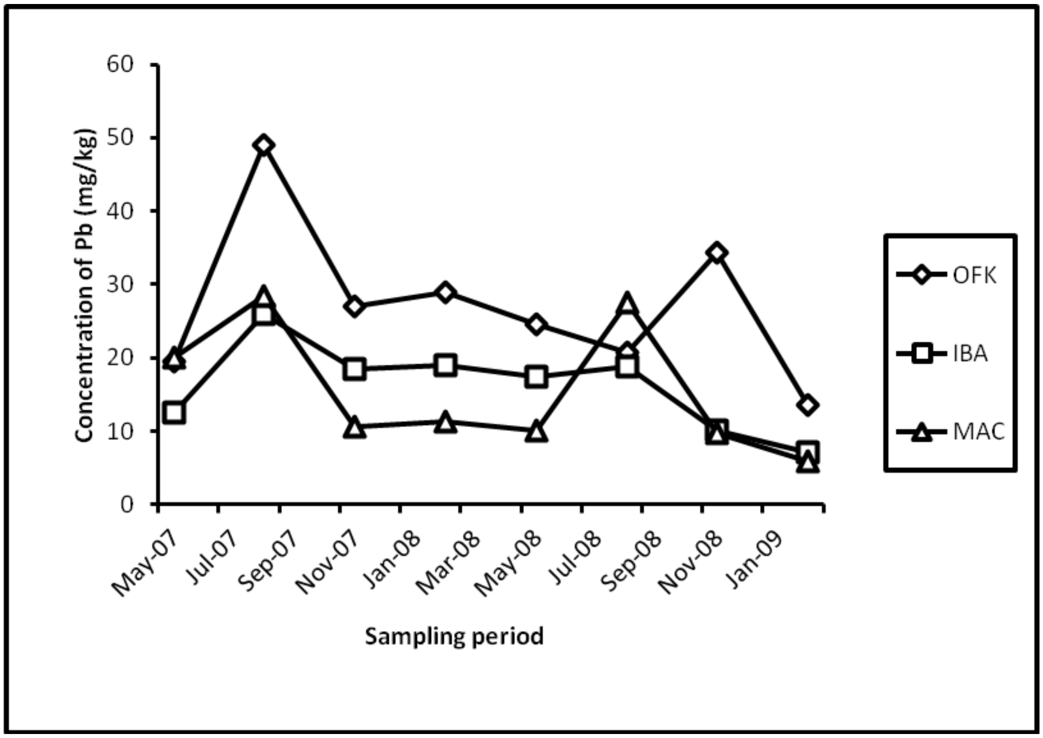

Fig 4.8: Variation of sediment Pb concentration with location

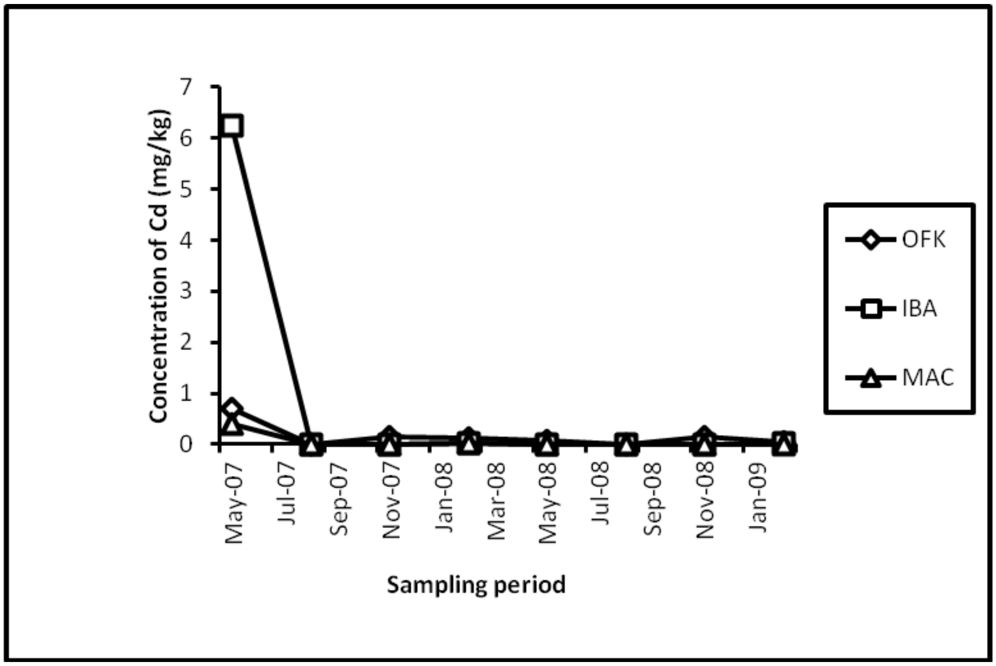

Fig 4.9: Variation of sediment Cd concentration with location

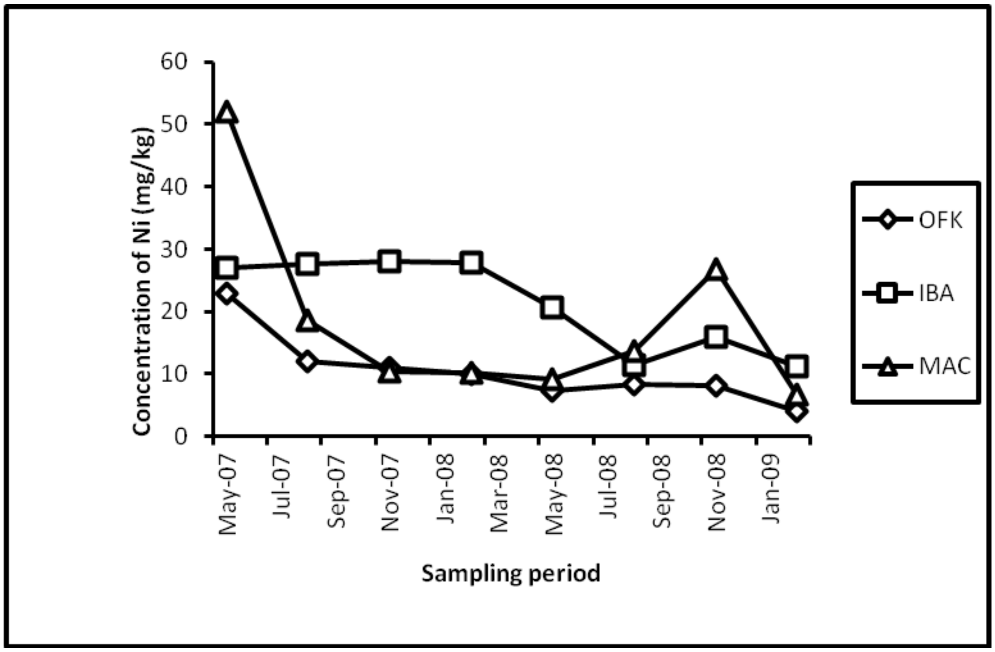

Fig 4.10: Variation of sediment Ni concentration with location

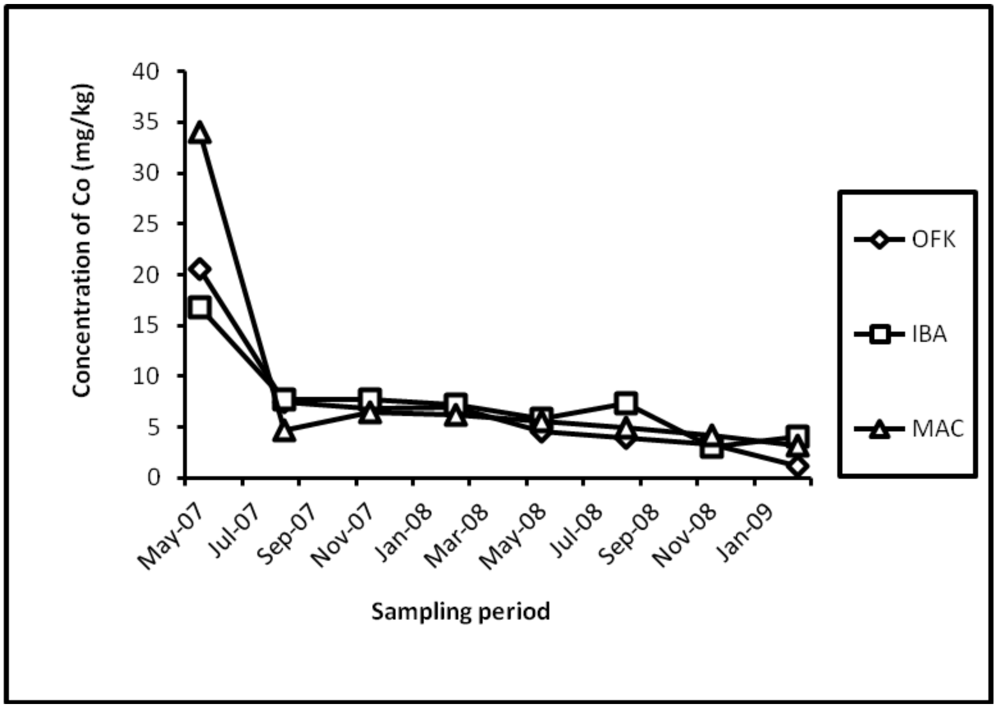

Fig 4.11: Variation of sediment Co concentration with location

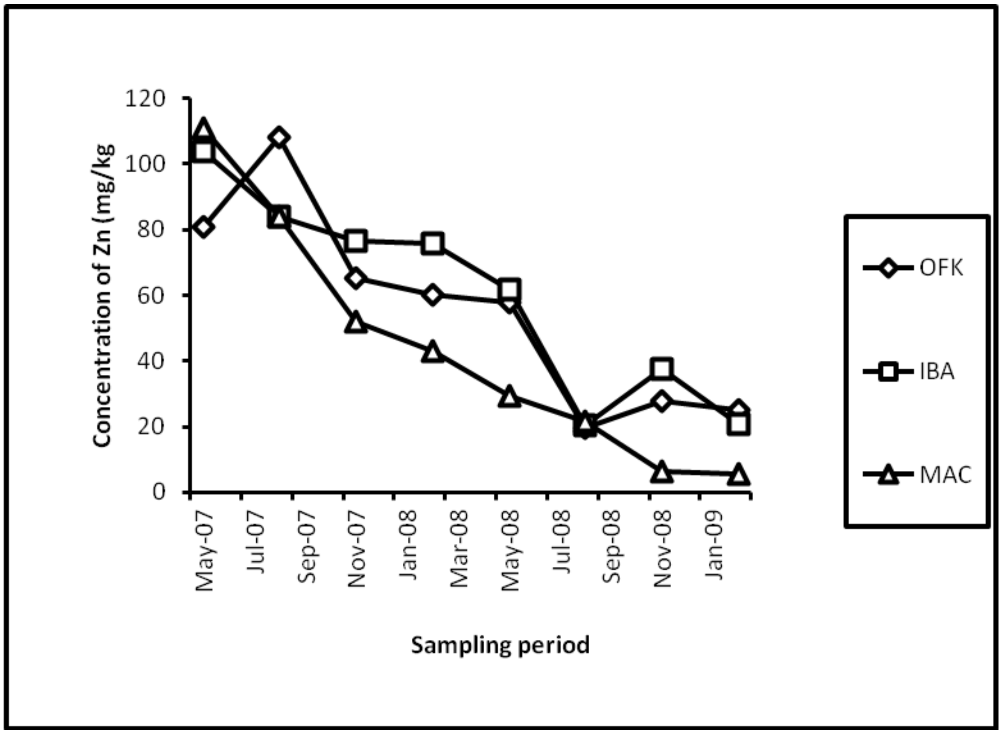

Fig 4.12: Variation of sediment Zn concentration with location

4.8 CONCENTRATION OF HEAVY METALS IN PLANT SAMPLES

4.8.1 Concentration of Heavy Metals in leaves and fruits of Pumpkin (*Cucurbita pepo* Linn)

The average concentrations of cadmium in pumpkin leaves and edible part (fruits) were 0.41±0.42 mg/kg and 0.05±0.01mg/kg respectively (Table 4.27). Seasonal concentration ranged from 0.19±0.03 mg/kg (dry season) to 0.7±1.0 mg/kg (rainy season) in leaves while in fruit levels ranged from 0.04±0.03 mg/kg to 0.05±0.02 mg/kg (Table 4.28). The average concentration of cadmium was higher in leaves and the difference is statistically significant. The leaves of pumpkin are edible and the presence of high level of Cd in leaves may expose consumers of such leaves to health hazards, if the concentration exceeds regulatory limits. Cadmium is a very toxic heavy metal that has no beneficial functions in the human body. Cadmium, unlike most heavy metals, can be taken up by several plants. It is capable of accumulating in food chains and the accumulation depends on factors such as pH and temperature (Voogt *et al*., 1981). Levels of cadmium in pumpkin were higher than control site values of 0.04±0.03 mg/kg and 0.03±0.01 mg/kg in leaves and fruits respectively and the differences were significant.

The average lead concentration was 0.15±0.05 mg/kg in leaves and 0.08±0.05mg/kg in edible part (Table 4.27). Dry season average value was 0.11±0.03 mg/kg while rainy season was 0.19±0.08 mg/kg (Table 4.27) and the difference is not significant. Corresponding levels of Pb in fruits were 0.12±0.06 mg/kg and 0.28±0.11 mg/kg in rainy and dry season respectively. The variation of Pb concentrations in different parts of pumpkin is statistically significant. Concentration of Pb in samples is higher than in control (0.03±0.04 mg/kg). The differences between control value and average concentration was significant.

Average concentration of copper in pumpkin was higher in edible parts, unlike the case with cadmium and lead that had higher concentrations in the leaves compared to the edible parts. The differences between average Cu level in leaves (1.76±0.19 mg/kg) and fruits (4.50±0.67 mg/kg) is significant.

Average concentrations of cobalt were 0.47±0.82 mg/kg and 0.02±0.01mg/kg (Table 4.29) in leaves and fruits respectively. Seasonal average values in leaves were 0.09±0.08 mg/kg and 0.8±1.5 mg/kg (Table 4.30) in dry and rainy season respectively. Corresponding values in fruits

Table 4.27: Average concentrations (mg/kg) of Cd, Pb and Cu in parts of crops

Crop specie	Cd		Pb		Cu	
	Leaves	Edibles	Leaves	Edibles	Leaves	Edibles
Pumpkin	0.41±0.42	0.05±0.01	0.15±0.05	0.08±0.05	1.76±0.19	4.50±0.67
Passion Fruit	0.32±0.41	0.15±0.05	0.30±0.13	0.29±0.17	6.34±0.27	8.13±0.29
Maize	0.53±0.50	0.19±0.03	0.22±0.08	0.42±0.22	7.2±2.4	2.43±0.29
Sugar cane	0.47±0.35	0.14±0.04	0.16±0.04	0.20±0.12	2.95±0.77	2.88±0.23
Cassava	0.58±0.52	0.13±0.01	0.18±0.06	0.10±0.05	3.95±0.54	2.44±0.17
Control samples	0.04±0.08	0.03±0.01	0.13±0.05	0.16±0.02	1.30±0.28	0.76±0.35

Table 4.28: Concentrations (mg/kg) of Cd, Pb and Cu in parts of crops

Crop species	Parts of crop	Cd		Pb		Cu	
		Rainy season	Dry season	Rainy Season	Dry Season	Rainy Season	Dry Season
Maize	Leaves	0.69±0.79	0.38±0.23	0.25±0.08	0.19±0.16	5.5±2.6	9.0±1.3
	Grain	0.22±0.06	0.17±0.01	0.49±0.22	0.36±0.20	2.44±0.57	2.42±0.12
Passion fruit	Leaves	0.56±0.80	0.10±0.04	0.39±0.11	0.21±0.01	6.3±4.5	6.40±0.91
	Fruits	0.19±0.07	0.11±0.02	0.13±0.01	0.04±0.02	8.4±1.2	7.90±0.27
Pumpkin	Leaves	0.7±1.0	0.19±0.03	0.19±0.08	0.11±0.03	1.93±0.68	1.60±0.14
	Fruits	0.05±0.02	0.04±0.03	0.12±0.06	0.28±0.11	4.9±1.5	4.14±0.15
Cassava	Leaves	0.61±0.59	0.57±0.54	0.23±0.09	0.15±0.54	4.5±3.4	3.79±0.97
	Tubers	0.14±0.06	0.13±0.02	0.15±0.04	0.06±0.02	2.60±0.36	2.36±0.40
Sugar cane	Leaves	0.46±0.51	0.49±0.37	0.19±0.10	0.14±0.02	2.3±1.9	3.60±0.23
	Stem	0.18±0.06	0.11±0.02	0.12±0.06	0.28±0.11	2.73±0.23	3.02±0.44

Table 4.29: Average concentrations (mg/kg) of Co, Ni and Zn in parts of crops

Crop specie	Co		Ni		Zn	
	Leaves	Edible	Leaves	Edible	Leaves	Edible
Pumpkin	0.47±0.82	0.02±0.01	1.1±1.2	14.2±2.4	12.8±6.1	15.0±5.4
Passion Fruit	4.8±8.1	0.02±0.01	18±20	14.7±6.2	16.7±1.3	12.2±3.1
Maize	7.4±5.6	0.12±0.13	26.0±5.2	25±10	36±15	33.1±2.4
Sugar cane	2.1±2.5	0.02	21.6.1±4.2	14.2±2.3	21.8±9.5	16.5±0.8
Cassava	4.9±5.7	0.20±0.05	29±16	34±19	19.7±7.0	14.7±1.7
Control samples	0.78±0.52	0.01	4.3±2.3	3.3±1.1	5.1±0.9	1.93±0.65

Table 4.30: Concentrations (mg/kg) of Ni, Co and Zn in parts of crops

Crop species	Parts of crop	Ni		Co		Zn	
		Rainy Season	Dry Season	Rainy Season	Dry Season	Rainy Season	Dry Season
Maize	Leaves	28±53	23.8±1.1	11.7±9.2	3.2±1.3	51±56	21.6±1.0
	Grain	24±26	25±11	0.19±0.24	0.03±0.01	35.0±4.5	31.3±0.5
Passion fruit	Leaves	24±12	12.1±0.30	9±15	1.0±1.1	16.5±8.7	17.0±2.0
	Fruits	21±21	8.32±0.29	0.02±0.01	0.02±0.01	32±49	13.9±6.7
Pumpkin	Leaves	1.9±2.6	0.31±0.05	0.8±1.5	0.09±0.08	12±12	13.7±7.2
	Fruits	15.8±4.4	12.6±0.8	0.02±0.01	0.01±0.01	18±14	12.4±1.2
Cassava	Leaves	36±21	23.2±4.3	7±10	2.8±2.7	16±14	19.2±8.3
	Tubers	39±15	29.0±2.6	0.03±0.01	0.02±0.01	16.0±6.0	12.8±2.5
Sugar cane	Leaves	20.5±9.8	22.7±2.6	1.8±3.5	2.5±4.2	20±21	24±11
	Stem	17±18	21.5±5.4	0.02±0.01	0.02±0.01	16.7±0.9	16.3±3.2

were 0.01±0.01 mg/kg and 0.02±mg/kg. The level of cobalt in leaves is significantly different from the fruits.

Average nickel concentration is given in Table 4.29. The average concentration in leaves was 1.1±1.2 mg/kg while in fruits. it was 14.2±2.4 mg/kg. Copper concentration in leaves of pumpkin was significantly different from the levels at the control site.

Table 4.29 shows that average nickel concentration in leaves was 1.9±2.6 mg/kg (rainy season) and 0.31±0.05 mg/kg (dry season), while in fruits it was 15.8±4.4 mg/kg and 12.6±0.8 mg/kg respectively. Nickel levels were higher in edible part of pumpkin than in the leaves. The accumulation in the edible parts is about fourteen times higher than in the leaves, and the difference is statistically significant.

Average concentrations of Zn were 12.8±6.1 mg/kg in leaves and 15.0±5.4 mg/kg in fruits. In both seasons, average levels of Zn in leaves were 12±12 mg/kg and 13.7±7.2 mg/kg and in fruits were 18±14 mg/kg respectively (Table 4.30).

4.8.2 Concentration of Heavy Metals in Leaves and Fruits of Passion Fruit (*Passiflora edulis* Sims)

Average cadmium concentration in passion fruit leaves (0.32±0.41 mg/kg) was twice the level in the fruit (0.15±0.05 mg/kg) (Table 4.27). The observed differences is significant (P=0.05). Cadmium concentrations in the sample of passion fruit crop were higher than control site levels in leaves (0.04±0.08 mg/kg) and fruits (0.03±0.01 mg/kg). The differences were statistically significant.

Average Pb concentration in leaves was 0.30±0.13 mg/kg while in the fruit, it was 0.29±0.17 mg/kg. Seasonal average Pb concentrations in leaves were 0.39±0.11 mg/kg and 0.21±0.01 mg/kg in rainy and dry seasons respectively, while in fruits was 0.13±0.01mg/kg and 0.04±0.02 mg/kg (Table 4.28). The differences in concentration between leaves and fruits were not significant.

Average Cu levels in leaves and fruits were 6.34±0.27 mg/kg and 8.13±0.29 mg/kg respectively and seasonal concentrations were 6.3±4.5 mg/kg and 6.40±0.91 mg/kg in leaves and 8.4±1.2

mg/kg and 7.90±0.27 mg/kg in fruits. Difference in concentrations between fruits and leaves were was significant.

Table 4.29 shows average concentration of Co, Ni and Zn in passion fruits. Average cobalt concentration in leaves was 4.8±8.1 mg/kg and in fruit was 0.02±0.01 mg/kg. Rainy seasonal Co concentrations in leaves and fruits were 9±15 mg/kg and 0.02±0.01 mg/kg respectively, while in dry season there was no difference (0.02±0.01mg/kg) (Table 4.30). Differences between the concentration in leaves (4.8±8.1 mg/kg) and fruits (0.02±0.01 mg/kg) is statistically significant. The variation in seasonal concentrations in leaves was also statistically significant while in fruits variation was not significant.

Average Ni concentrations in leaves and fruits were 18±20 mg/kg and 14.7±6.2 mg/kg respectively. Average concentration in leaves in rainy season was 24±12 mg/kg and in dry season was 12.1±0.30 mg/kg. Corresponding levels in fruits were 21±21 mg/kg and 8.32±0.29 mg/kg in rainy and dry seasons respectively. The difference between Ni level in leaves (18±20 mg/kg) and in fruits (14.7±6.2 mg/kg) was significant.

Average Zn concentration in leaves was 16.7±1.3 mg/kg and in fruits was 12.2±3.1 mg/kg. The average concentration of Zn in leaves in rainy season is not significantly higher than dry season value. However, average concentration in fruit in rainy season (32±49 mg/kg) was significantly different from dry season value (13.9±6.7 mg/kg).

4.8.3 Concentration of Heavy Metals in Leaves and Fruits of Maize (*Zea mays* Linn)

Average cadmium concentration in maize grain was 0.19±0.03 mg/kg, and in leaves was 0.53±0.50 mg/kg (Table 4.27). Seasonal average levels of Cd ranged from 0.17±0.01 mg/kg in grain to 0.69 mg/kg in leaves (Table 4.28). Average level of Cd in leaves is higher than in the grain and the difference is significant. The control value result was lower than the samples concentrations.

Average concentrations of Pb were 0.22±0.08 mg/kg and 0.42±0.22 mg/kg in leaves and grains respectively. Average seasonal levels in leaves were 0.25±0.08 mg/kg (rainy) and 0.19±0.16 mg/kg (dry), and in fruits were 0.49±0.22 mg/kg and 0.36±0.20 mg/kg respectively (Table 4.28). The average concentration of Pb in leaves (0.42±0.22 mg/kg) was twice the level (0.22±0.08

mg/kg) in the grains. The observed differences were significant. High Pb concentration in maize is a potential threat to human health. However, the level of Pb in maize is within regulatory standards and therefore do no pose threat to human.

Copper average concentration in leaves was 7.2±2.4 mg/kg, while in grains this was 2.43±0.29 mg/kg. Average concentration in leaves in rainy season (5.5±2.6 mg/kg) was lower than dry season (9.0±1.3 mg/kg). The difference between average concentration in leaves and grains was significant.

Table 4.29 shows the average concentrations of Co, Ni and Zn in maize leaves and grains. Average Co concentration in leaves was 7.4±5.6 mg/kg, and in grains was 0.12±0.13 mg/kg. Average levels ranged from 0.03±0.01 mg/kg in grains to 11.7±9.2 mg/kg in leaves. The average level of Co in grains is lower than in the leaves. The average Co concentrations in the control in both seasons are higher than the sample concentrations

Average Ni concentration in leaves was 26.0±5.2 mg/kg, and in grains was 25±10 mg/kg. The difference between average Ni concentration in leaves and grains is not significant. Average Ni concentration in leaves 26.0±5.2 mg/kg is significantly higher than the control value 4.3±2.3 mg/kg. Also the observed difference between the grains (25±10 mg/kg) and control value (3.3±1.1 mg/kg) is significant.

Average Zn concentration was 36±15 mg/kg in leaves, while in grains was 33.1±2.4 mg/kg. Table 4.31 shows that average Zn concentrations in leaves in rainy season (51±56 mg/kg) was twice the dry season value (21.6±1.0 mg/kg). In grains, observed average levels in both seasons were not significantly difference. Average Zn levels in leaves (36±15 mg/kg) and grains (33.1±2.4 mg/kg) were higher than corresponding control values of 5.1±0.9 mg/kg and 1.93±0.65 mg/kg.

4.8.4 Concentration of Heavy Metals in Leaves and Stem of Sugar cane (*Saccharum officinarium* Linn)

Table 4.27 shows average concentrations of Cd, Pb and Cu in sugar cane. Cadmium concentrations were 0.45±0.35 mg/kg in leaves and 0.14±0.04 mg/kg in stem. Average level of

Cd in leaves (0.46±0.51 mg/kg) in dry season was not significantly different from rainy season value (0.49±0.37 mg/kg). The observed values in samples are significantly higher than control values.

Average Pb concentration in leaves and stem were 0.16±0.04 mg/kg and 0.20±0.12 mg/kg respectively. Average Pb concentration in sugar cane ranged from 0.12±0.06 mg/kg in rainy season to 0.28±0.12 mg/kg in dry season (Table 4.28). The difference between average Pb concentration in leaves (0.16±0.04 mg/kg) and stem (0.20±0.12 mg/kg) was not significant. The observed concentrations in the samples were comparable to the control values.

Average Cu level in leaves was 3.95±0.54 mg/kg while stem was 2.44±0.17 mg/kg. Season apparently had no influence on the concentration of Cu in sugar cane leaves and stem as observed Cu levels in both seasons in leaves and stem were not significantly different (Table 4.28). Average Cu concentration in leaves and stem were higher than in control. The differences in stems were significant.

Average concentrations of Co, Ni and Zn in sugar cane were given in Table 4.29. Average concentration of Co was 2.1±2.5 mg/kg in leaves. In the stem the level was 0.02±0.01 mg/kg. Cobalt average concentrations ranged from 0.02 mg/kg in leaves to 2.5±4.2 mg/kg in stem. The difference between leaves and stem was statistically significant.

Average Ni concentration in leaves was 21.6±4.2 mg/kg and stem was 14.2±2.3 mg/kg. The difference between the concentration in leaves and stem is statistically significant. Tables 4.30 provide further information on seasonal average concentrations in leaves and stem of sugar cane in both seasons.

Average Zn concentrations in leaves and stem were 21.8±9.5 mg/kg and 16.5±0.8 mg/kg respectively. Seasonal average levels in leaves ranged from 20±21 mg/kg to 24±11 mg/kg in both seasons. These values were significantly higher than corresponding average levels in stem 16.3±3.2 mg/kg and 16.7±0.9 mg/kg. Average control values (5.1±0.9 mg/kg) in leaves and (1.93±0.65 mg/kg) in stem were lower than average concentrations in the samples and the differences were significant.

4.8.5 Concentration of Heavy Metals in Leaves and Tuber of Cassava (*Manihot esclenta* Crantz)

Table 4.27 shows average concentrations of Cd, Pb and Cu in cassava leaves and tuber. Cadmium average concentration in leaves (0.58±0.52mg/kg) is significantly higher than the tuber (0.13±0.01 mg/kg) value. The major consumed part of cassava is the tuber. The significantly lower Cd concentration in the tuber means cassava tuber in this study will not pose threat to consumers. Average values in tubers are within regulatory limits. This result is comparable with other findings (Sanita di Toppi and Gabbrielli, 1999) that the amount of cadmium accumulated in the aerial parts of a plant is higher than in the parts below the ground (tuber). Average seasonal concentration in leaves and stem is further provided in Table 4.28. Average concentrations of Cd in samples were higher than control values and the differences were statistically significant.

Average Pb concentration in leaves (0.18±0.06 mg/kg) is about twice the average concentration (0.10±0.05 mg/kg) in tuber. In some parts of the world some people also eat the leaves. Therefore, if Pb concentration is above critical limits it will be of great concern both in the tubers and leaves. Generally in this study, average Pb concentrations observed in leaves and in tubers are within regulatory limits. Control sample average concentration (0.16±0.02 mg/kg) in tuber was higher than sample average (0.10±0.05 mg/kg) value. Average concentrations of metals were higher in samples of the study area than in control samples with the exception of Pb in cassava tuber.

Average concentration of Cu in leaves was 3.95±0.54 mg/kg and stem was 2.44±0.17 mg/kg. Copper average concentration ranged from 2.36±0.40 mg/kg in tubers to 4.5±3.4 mg/kg in leaves. The concentration of Cu in food crop within regulatory limits is essentials because of its functions in human. Apart from its function as a biocatalyst, Cu is necessary for body pigmentation, maintenance of a healthy central nervous system and prevention of anaemia (Akinyele and Osibanjo, 1982). Generally, plants contain the amount of Cu, which is inadequate for normal growth of plants. Application of micronutrient fertilizers and copper based fungicides may sometimes increase it to alarming levels

Table 4.29 shows average concentration of Co, Ni and Zn in leaves and tubers of cassava. Average Co concentration in leaves was 4.9±5.7 mg/kg and in tuber was 0.20±0.05 mg/kg. The differences between average levels in leaves and tuber is significant. Table 4.31 provides further information on average Co concentrations in leaves and tubers in both seasons.

Average Ni concentrations were 29±16 mg/kg and 34±19 mg/kg in leaves and tuber respectively. Seasonal average Ni concentrations ranged from 23.2±4.3 mg/kg in tubers to 39±15 mg/kg in leaves (Table 4.30). The concentration of nickel in leaves is significantly different from the tubers. Average Ni concentrations in leaves and tubers were higher than regulatory standards. Weigert (1991) had indicated that Ni concentrations up to 68 mg/kg may still be safe for consumption since more than 90 % of Ni taken in is held in the organic form that can be safely excreted. Thus the risk of exposure to Ni from cassava products of this study is low since concentrations are significantly lower than 68 mg/kg threshold limit reported by Weigert (1991).

Average Zn concentration in leaves was 19.7±7.0 mg/kg and in tubers was 14.7±1.7 mg/kg. Seasonal concentrations ranged from 12.8±2.5 mg/kg to 19.2±8.3 mg/kg. The level of Zn in leaves is significantly different from the tubers. Like Cu, Zn is an essential element for plants and animals, but slight increase in its levels may interfere with physiological processes.

4.9 COMPARISON OF CONCENTRATION OF HEAVY METALS IN PARTS OF CROPS OF THE STUDY WITH OTHER STUDIES

Table 4.31 shows the levels of heavy metals in crops from similar studies elsewhere. This study average concentrations of cadmium in pumpkin 0.41±0.42 mg/kg (leaves) and 0.05±0.01 mg/kg (fruits) are higher than average concentrations obtained by Oti Wilberforce and Nwabue (2012) for pumpkin 0.003±0.01 mg/kg in Enyigba and 0.002±0.01 mg/kg in Abakaliki both in Ebonyi State, Nigeria. Similarly average Cd concentrations in cassava were 0.58±0.52 mg/kg (leaves) and 0.13±0.0 1 mg/kg (tubers) in this study. Average concentration of cadmium in this study are generally lower than the average obtained by Gideon-Ogero (2008) for cassava 4.88 mg/kg, 4.63mg/kg, and 4.52 mg/kg at Afiesere, Ekugbo and Ofoma respectively in Nigeria. They are also lower than 4.8±1.2 mg/kg for cassava in Wassa Amenfi in Ghana (Musah *et al.*, 2013), and 7.05 mg/kg for fresh fruits in Bangalorie City, Indian (Mahdavian and Somashekar, 2008). In this study, average Cd concentrations in maize 0.53±0.50 mg/kg (leaves) and 0.19±0.03 mg/kg (grians) are higher than 0.01 mg/kg (grains) and 0.01 mg/kg (leaves) in maize in Dunhua, China

(Liang *et al*., 2011). Average concentration of Cd in sugar cane leaves was 0.47±0.35 mg/kg and stem was 0.14±0.04 mg/kg. These values are lower than the values obtained by Wang *et al*. (2012) for the bagasse of various sugar cane varieties 0.99±0.29 mg/kg (*Guitang*21), 0.84±0.41 mg/kg (*Guiyin*5), 0.60±0.11 mg/kg (*Xintaitang*92-2817) and 0.56± 0.25 mg/kg (*Guitang00*-122) in southern China.

Average concentration of lead for pumpkin 0.15±0.05 mg/kg (leaves) and 0.08±0.05 (fruits) are comparable to average Pb concentrations reported by Oti Wilberforce and Nwabue (2012) for pumpkin 0.21±0.21 mg/kg and 0.20±0.21 mg/kg in Enyigba and Abakaliki respectively. Average Pb concentration of 19.1±3.2 mg/kg in shoot of maize obtained by Osiele *et al*. (2012) in Guadalupe, Zacatecas in Mexico is higher than the values for leaves of maize 0.22±0.08 and 0.42±0.22 mg/kg in grains obtained in this study. Average lead concentrations 0.16±0.04 mg/kg (leaves) and 0.20±0.12 mg/kg (stem) of sugar cane in this study are lower than the 12.1±1.3 mg/kg (sugar cane) reported by Evaristo (2013) in Mufulira in Zambia. Similarly, concentrations of 0.15±0.05 in leaves and 0.08±0.05 mg/kg in fruits of pumpkin are lower than 24.5 mg/kg in pumpkin obtained by Evaristo (2013) in Kafue in Zambia. Also average Pb concentration in cassava 0.18±0.06 mg/kg (leaves) and 0.10±0.05 mg/kg (tubers) are lower than 65.0±2.8 mg/kg for cassava in Ghana (Musah *et al*., 2013).

Average copper concentrations in the studied species were: pumpkin - 1.76±0.19 mg/kg (leaves) and 4.50±0.67 mg/kg (fruits), passion fruit - 6.34±0.27 mg/kg (leaves) and 8.13±0.29 mg/kg (fruits), maize - 7.2±2.4 mg/kg (leaves) and 2.43±0.29 mg/kg (grains), sugarcane - 2.95±0.77 mg/kg (leaves) and 2.88±0.23 mg/kg (stem), and cassava - 3.95±0.54 mg/kg (leaves) and 2.44±0.17 mg/kg (tubers). They are comparable to the 2.86 mg/kg and 2.06 mg/kg obtained by Gideon-Ogero (2008) for cassava in Orogun and Ofoma respectively. This study results are lower than 789 mg/kg and 11.1±4.2 mg/kg obtained by Evaristo (2013) in Zambia for pumpkin leaves in hot wet season and hot dry season respectively. Similarly the results are also lower than 29.5±2.0 mg/kg and 22.5±1.3 mg/kg for sugar cane stem in Zambia (Evaristo, 2013). The 99±23 mg/kg in shoot of maize obtained by Osiel *et al*. (2012) in Guadalupe, Zacatecas in Mexico is higher than 7.2±2.4 mg/kg (leaves) of maize in this study.

Table 4.31: Comparison of concentrations of heavy metals in food crops of this study with other studies elsewhere`

Country location		Plant species	Concentration (mg/kg)						References
			Cd	Pb	Cu	Co	Ni	Zn	
Nigeria	Afiesere	Cassava	4.88	<0.002	1.21	-	-	111.6	Gideon-Ogero (2008)
Nigeria	Ekugbo	Cassava	4.63	<0.002	1.93	-	-	16.3	Gideon-Ogero (2008)
Nigeria	Orogun	Cassava	4.28	<0.002	2.86	-	-	23.9	Gideon-Ogero (2008)
Nigeria	Ofoma	Cassava	4.52	<0.002	2.06	-	-	14.3	Gideon-Ogero (2008)
Nigeria	Enyigba	Cassava	-	0.21±0.21	-	-	-		Oti Wilberforce and Nwabue (2012)
Nigeria	Abakaliki	Manihot esculenta	-	0.20±0.21	-	-	-	-	Oti Wilberforce and Nwabue (2012)
Nigeria	Okirika	Cassava	BDL	BDL	3.33±0.25	-	3.08±0.14	16.4	Akininwor *et al*. (2005)
Ghana	Wassa-Amenfi	Manihot esculenta	4.81±1.2	65.0±2.8	41.2±1.1	-	42.1±1.2	163.5	Musah *et al*. (2013)
Ghana		Musa paradisiacal	5.58±0.18	54.0±5.9	88.6±5.1	-	37.3±2.7	297±6.3	Musah *et al*. (2013)
Zambia	Mufulira and Kafue	Sugarcane	-	12.1±1.3	29.5±2.0	1.91±0.51	6.19±1.4	-	Evaristo (2013)
Zambia		Pumpkin	-	24.5 0.31±0.31	789 11.1±4.2	20.0 ND	31.6 0.06±0.06	-	Evaristo (2013)
India	Bangalorie City	Fresh fruits	7.05	53.9	10.9	40.9	53.9	30.0	Mahdavian and Somashekar (2008)
China		Guitang21	0.99±0.29	-	-	-	-	-	Wang *et al*. (2012)
China		Guiyin5	0.84±0.41	-	-	-	-	-	Wang *et al*. (2012)
China		*Xintaitang* 92-2817	0.60±0.11	-	-	-	-	-	Wang *et al*. (2012)

Table 4.31: contd.

Country	Location	Plant species	Concentration (mg/kg)						References
			Cd	Pb	Cu	Co	Ni	Zn	
China	Dunhua	Maize	0.01	-	-	-	-	-	Liang *et al*. (2011)
Mexico	Guadalupe	Maize	-	19.1±3.2	99±23	-	-	297±260	Osiel *et al*. (2012)
Nigeria	Kogi	Pumpkin	0.41±0.42 (0.05±0.01)	0.15±0.05 (0.08±0.05)	1.76±0.19 (4.50±0.67)	0.47±0.82 (0.02±0.01)	1.1±1.2 (14.2±2.4)	12.8±6.1 (15.0±5.4)	This study
Nigeria	Kogi	Passion fruit.	0.32±0.41 (0.15±0.05)	0.30±0.13 (0.29±0.17)	6.34±0.27 (8.13±0.29)	4.8±8.1 (0.02±0.01)	18±20 (14.7±6.2)	16.7±1.3 (12.2±3.1)	This study
Nigeria	Kogi	Maize	0.53±0.50 (0.19±0.03)	0.22±0.08 (0.42±0.22)	7.2±2.4 (2.43±0.29)	7.4±5.6 (0.12±0.13)	26.0±5.2 (25±10)	36±15 (33.1±2.4)	This study
Nigeria	Kogi	Sugar cane	0.47±0.35 (0.14±0.04)	0.16±0.04 (0.20±0.12)	2.95±0.77 (2.88±0.23)	2.1±2.5 (0.02)	21.6.1±4.2 (14.2±2.3)	21.8±9.5 (16.5±0.8)	This study
Nigeria	Kogi	Cassava	0.58±0.52 (0.13±0.01)	0.18±0.06 (0.10±0.05)	3.95±0.54 (2.44±0.17)	4.9±5.7 (0.20±0.05)	29±16 (34±19)	19.7±7.0 (14.7±1.7)	This study

This study's average cobalt concentrations were: pumpkin - 0.47±0.82 mg/kg (leaves) and 0.02±0.01 mg/kg (fruits), passion fruits - 4.8±8.1 mg/kg (leaves) and 0.02±0.01 mg/kg (fruits), and maize - 7.4±5.6 mg/kg (leaves) and 0.12±0.13 mg/kg (grains). Values for sugar cane were 2.1±2.5 mg/kg (leaves) and 0.02±0.01 mg/kg (stem), and for cassava - 4.9±5.7 mg/kg (leaves) and 0.20±0.05 mg/kg (tubers). The sugar cane results are comparable to the result (1.91±0.51 mg/kg) obtained by Evaristo (2013) for in sugar cane stem in Zambia. The average Co concentrations in this study are lower than 20.0 mg/kg (Evaristo, 2013) for pumpkin in Mufulira and Kafue in Zambia, and also lower than 40.9 mg/kg for fresh fruits, obtained by Mahdavian and Somashekar (2008) in Bangalotie, India.

This study average nickel concentrations in pumpkin - 1.1±1.2 mg/kg (leaves) and 14.2±2.4 mg/kg (fruits), passion fruit - 18±20 mg/kg (leaves) and 14.7±6.2 mg/kg (fruits), maize - 26.0±5.2 mg/kg (leaves) and 25±10 mg/kg (grains), sugarcane - 21.6±4.2 mg/kg (leaves) and 14.2±2.3 mg/kg (stem) and cassava - 29±16 mg/kg (leaves) and 34±19 mg/kg (tubers) were higher than 3.08±0.14mg/kg for cassava by Akininwor *et al*. (2005) in Okirika in River State, Nigeria. Similarly they are also higher than 6.19±1.4 mg/kg for cassava in Zambia (Evaristo, 2013). However, this study results were lower than 37.3±2.7mg/kg for cassava obtained by Musah *et al*. (2013) in Ghana. Also the pumpkin leaves result (1.1±1.2 mg/kg) is lower than 31.6 mg/kg obtained by Evaristo (2013) for pumpkin leaves in Zambia. Sugar cane stem values of 1.91±0.51 mg/kg and 1.67±0.42 mg/kg obtained by Evaristo (2013) are lower than this study (14.2±2.3 mg/kg) and the difference was significant.

Average zinc concentrations from this study are compared to those of other studies listed in Table 4.32. The results for this study are lower than values of 163.5mg/kg for cassava (Musah *et al*., 2013) from Ghana and 297±260 mg/kg for shoot of maize in Mexico by Osiel *et al*. (2012).

4.10 COMPARISON OF CONCENTRATION OF HEAVY METALS IN CROP PLANTS WITH REGULATORY STANDARDS

Lead: The average Pb concentration was highest in passion fruit leaves (0.30±0.13 mg/kg) and lowest in pumpkin 0.15±0.05 mg/kg. In the edible part of food crops, concentration of Pb ranged from 0.08±0.05 mg/kg in pumpkin to 0.42±0.22 mg/kg in maize. Fig 4.13 shows that the levels of Pb in this study are mostly within permissible limit of 0.3μg/g set by the Commission of the

European Communities (EC) (EEC, 1977.) and the World Health Organization (FAO/WHO, 2011), and the 9.0 mg/kg of the State Environmental Protection Administration of China (SEPA, 2005). There are no Nigerian regulatory standard for comparison.

Cadmium: The average concentration of Cd in leaves of crops was highest in cassava (0.58±0.52 mg/kg) and the lowest was in passion fruit (0.32±0.41 mg/kg). Average Cd concentration observed in this study were slightly higher when compared with the 0.2 mg/kg FAO/WHO standard for Cd in vegetable (Codex Alimentarius Commission, 2011) and also exceeded the limit of 0.1 to 0.2 mg/kg set by SEPA (2005) (Fig 4.14), however, the average concentration for edible parts of crops were all within the standard limit of 0.2 mg/kg (Fig 4.14) given by the EC and FAO/WHO (2011) and also within the limits of 0.1µg/g for stem and root vegetables (Jamali *et al.,* 2007). The level of Cd found in this study compares well with background concentration of fruit type vegetable (0.11mg/kg) in rural Taiwan (Lin, 1991). In China, the tolerance limit of cadmium in food is 0.03mg/kg (MHPRC, 2005).

Copper: The average concentration of copper in leaves of crops was highest in maize (7.2±2.4 mg/kg) and lowest in pumpkin (1.76±0.19 mg/kg). In edible part of crops, passion fruit had the highest average copper concentration with a value of 8.13±0.29 mg/kg. The average concentrations of copper in all species of crops (leaves and edible) were within FAO/WHO (2002) and Chinese SEPA regulatory limit of 20 mg/kg (Fig 4.15). Therefore concentrations were below levels of concern to human health.

Cobalt: The average cobalt concentration in species sampled for the study period is given in Table 4.29. Leaves of maize had the highest concentration of 7.4±5.6 mg/kg. The lowest concentration was observed in pumpkin (0.47±0.82 mg/kg). Values in edible parts had 0.20±0.01 mg/kg in cassava tuber as the highest. The other species recorded similar value of 0.02±0.01 mg/kg except maize (0.12±0.12 mg/kg. Concentrations of Co were slightly higher in the leaves of sampled crops than in the edible part. Cobalt concentrations in edible parts are within WHO (1996) permissible limit of 0.01 mg/kg (Fig 4.16). Although the values were higher in the leaves than WHO permissible limit, they are within safety limit for human consumption of 0.05 mg/kg to 1mg/kg in humans (ATSDR, 1994).

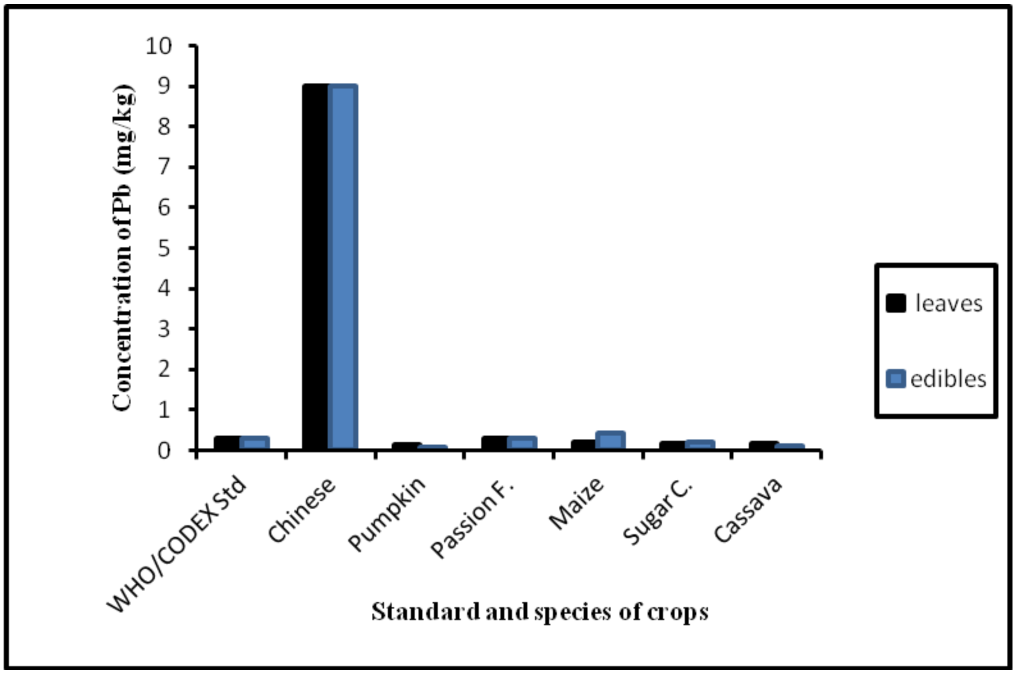

Fig 4.13: Concentration of Pb in crops compared with regulatory standards

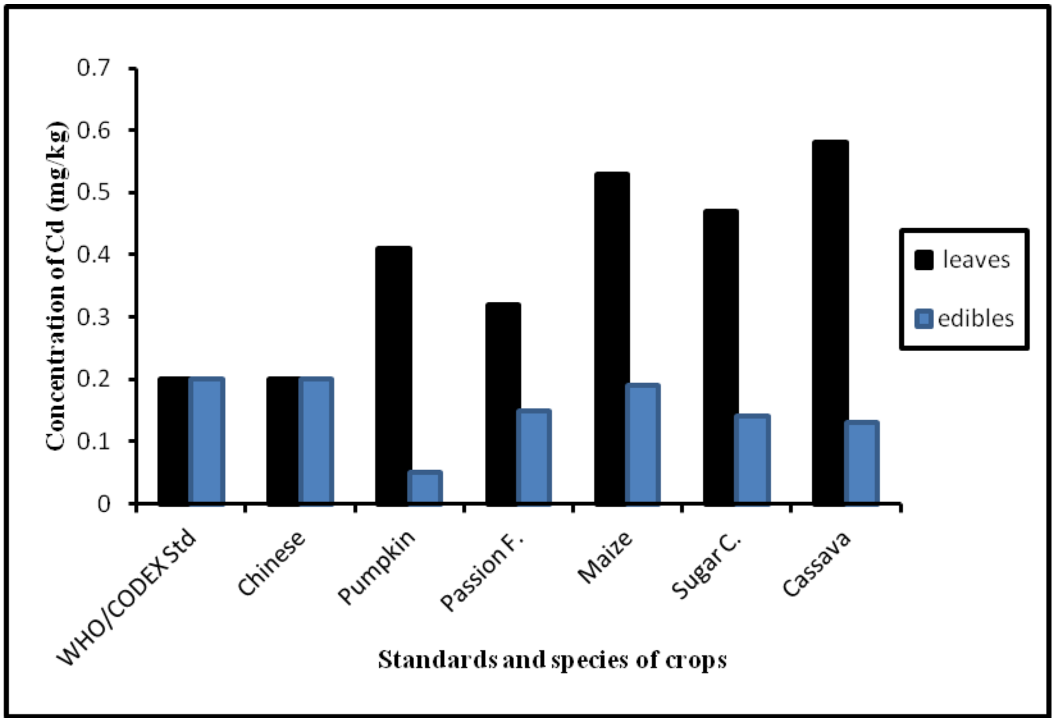

Fig 4.14: Concentration of Cd in crops compared with regulatory standards

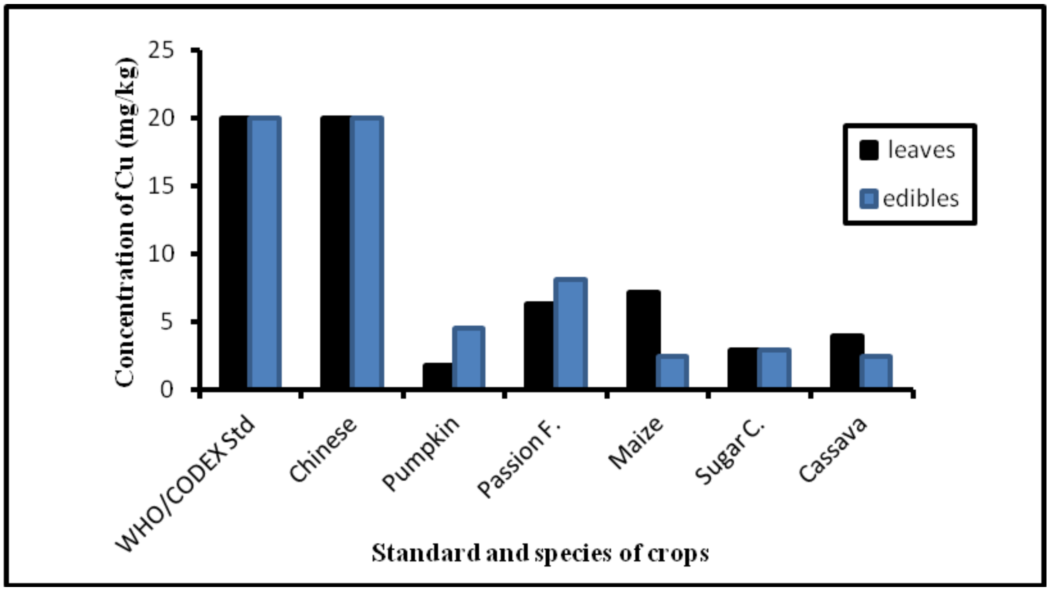

Fig 4.15: Concentration of Cu in crops compared with regulatory standards

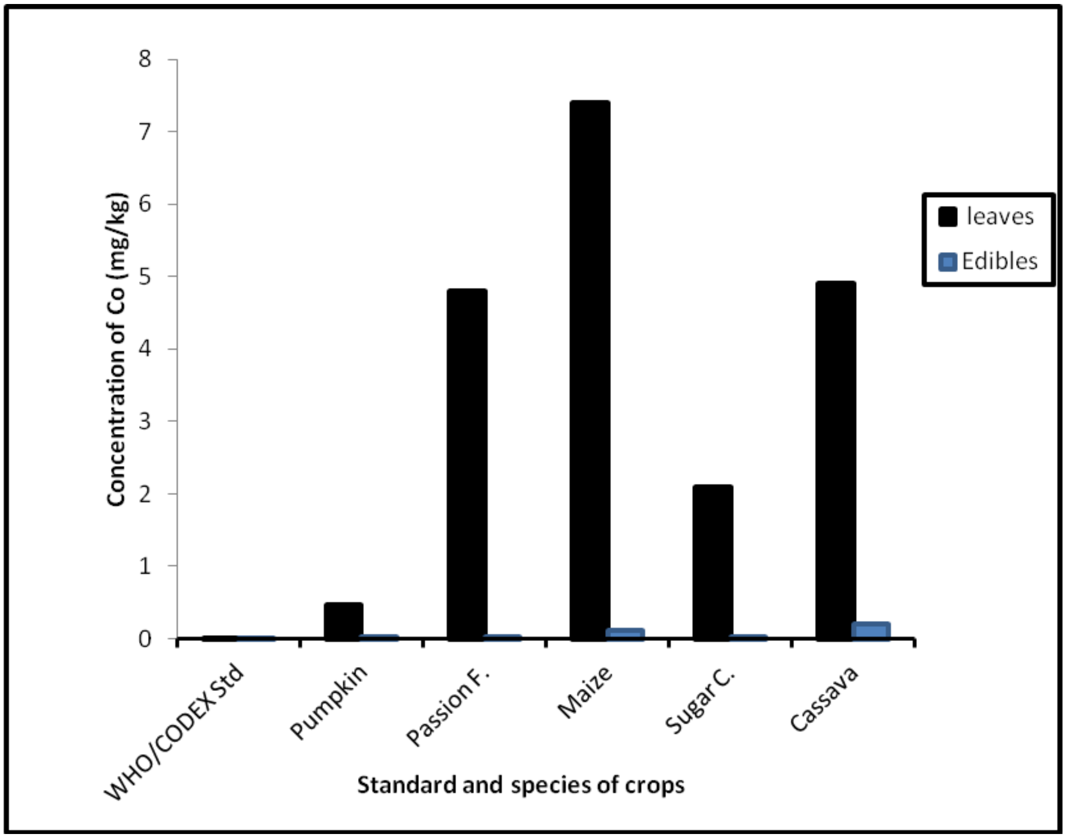

Fig 4.16: Concentration of Co in crops compared with regulatory standards

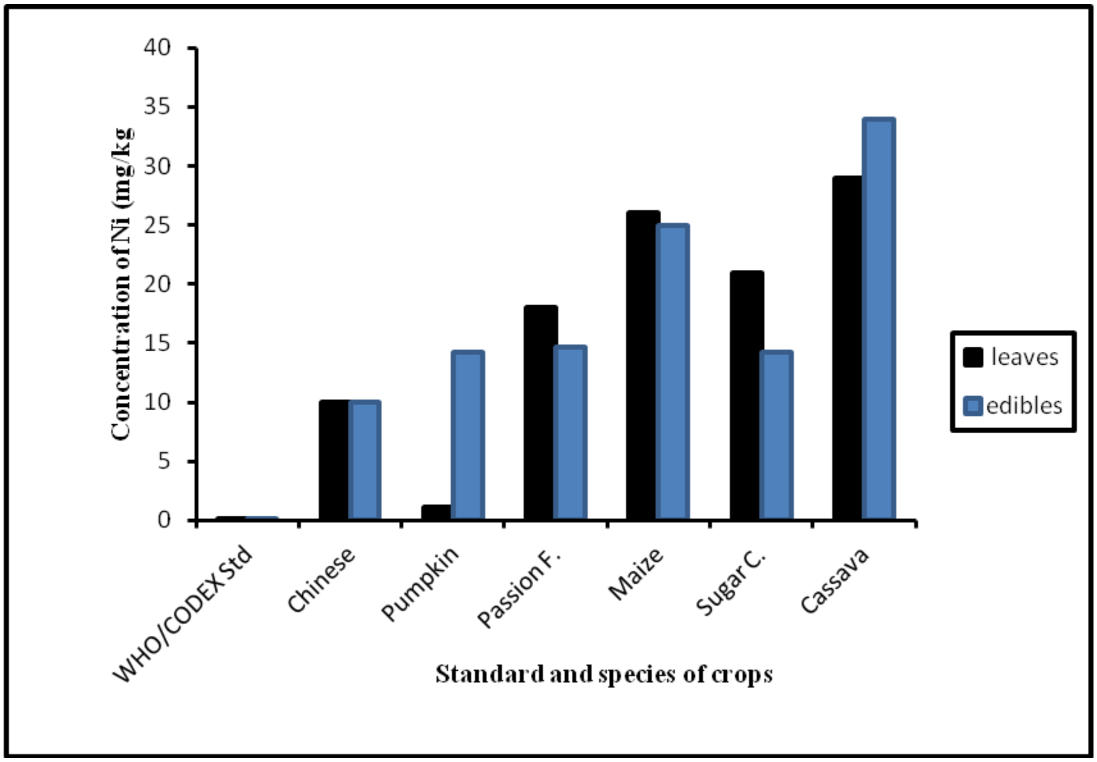

Fig 4.17: Concentration of Ni in crops compared with regulatory standards

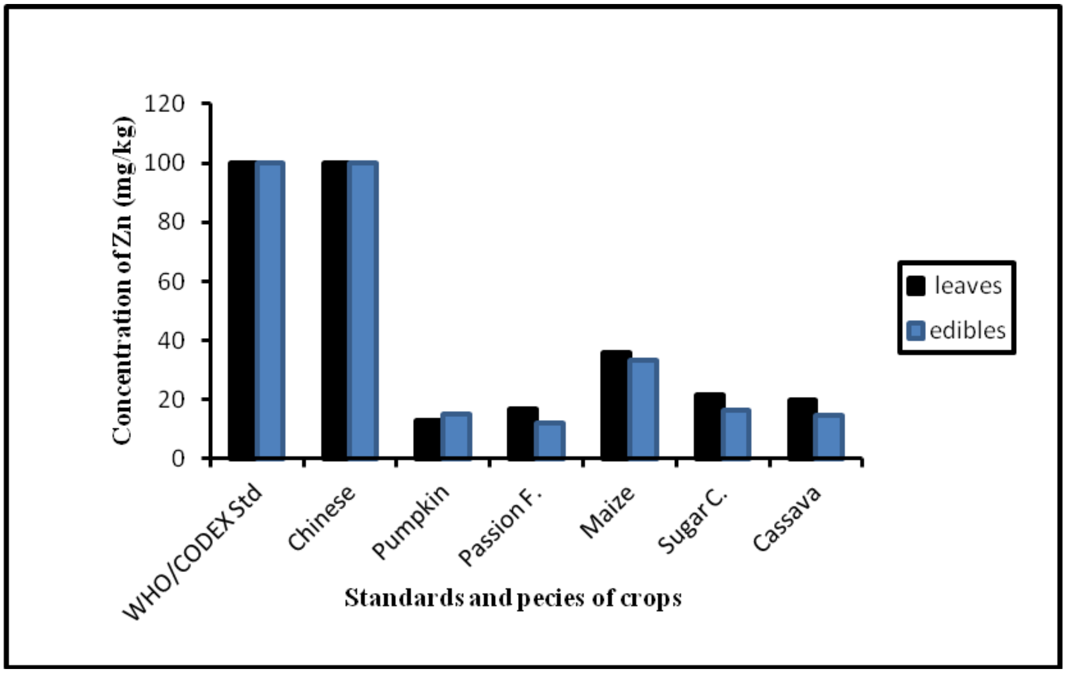

Fig 4.18: Concentration of Zn in crops compared with regulatory standards

Nickel: The highest average value of 29±16mg/kg was observed in cassava leaves and the lowest concentration was observed in pumpkin (1.1±1.12mg/kg). Corresponding values in edible parts showed that cassava tuber has the highest concentration (34±19 mg/kg) and lowest in pumpkin (14.2±2.4 mg/kg). All values obtained were higher than the Chinese regulatory limit of 10 mg/kg (SEPA, 2005), with the exception of the value for pumpkin leaves.

Zinc: The overall concentration of zinc in parts of food crops are given in Table 4.27 and average seasonal variation are shown in Table 4.26. Results showed that zinc concentration in leaves was slightly higher than in edible parts except for pumpkin. The highest zinc concentration was 36±15 mg/kg in maize and in pumpkin which had the lowest Zn concentration was 12.8±6.1 mg/kg. The corresponding value in edible parts was 33.1±2.4 mg/kg in maize and 12.2±3.1 mg/kg in passion fruits as highest and lowest observed concentrations respectively. Zn is an essential element in human diet. Too little Zn can cause problems. However, too much Zn is also harmful to human health (Agency for Toxic Substances and Diseases Registry, 2004). Generally the average Zn concentration shows that values obtained were all within the permissible limit of 100mg/kg (FAO/WHO, 2011) and the Chinese SEPA guidelines. Among all metals examined Zn is least toxic and an essential element in the human diet as it is required to maintain the proper functions of the immune system. It is also important for normal brain activity and is fundamental in the growth and development of the foetus. Although the average daily intake of Zn is 7 – 10.3 mg/day, the recommended dietary allowance for it is 15 mg/day for men and 12 mg/day for women (ATSDR, 1994). On the contrary, high concentration of Zn in vegetables may cause vomiting, renal damage, cramps, etc.

4.11 COMPARISON OF THE CONCENTRATION OF METALS IN SOIL, LEAVES AND EDIBLE CROP PLANT PARTS

Results generally showed that Zn and Ni contents were dominant in soil, leaves and edible parts. At Ofoke, the orders of Zn and Ni concenttations were: leaves > edible > soil. At Ankpa the trend was: edible > leaves > soil. At Macks farm Zn and Cu showed similar trend of - edible > soil > leaves, while Ni showed leaves > soil > edible.

Pb was present mostly only in soil, cobalt was higher in soil followed by leaves, while the level in edible parts were very low. Similar trend was observed at KSU farm. Pb and Co were dominant in soil and very low in leaves and edible parts. At Idah the observed trend was for Zn in soil > leaves > edible and Ni in leaves > edible > soil. The other metals were similar but with very low concentrations. The trends in levels of metals in soil compared with levels in parts of crops are given in Figs 4.19 to 4.26.

4.12 TRANSFER FACTORS

Table 4.32 shows transfer factors for the various metals. The transfer factors (TF) of Cd, Pb, Cu, Ni, Co and Zn from soils to edible parts of crops were calculated. Soil-to-plant transfer is one of the key components of human exposure to metals through the food chain. According to Sutherland and Tack (2000), five contamination categories are generally recognized on the basis of the enrichment factor: TF<2, depletion to mineral enrichment; 2≤TF<5, moderate enrichment; 5≤TF<20, significant enrichment; 20≤TF<40, very high enrichment; and TF>40, extremely high enrichment. The TF values for Cd, Pb, Cu, Co, Ni and Zn for the crops varied between crop species sampled (Table 4. 33). The TF values for Cd ranged from 0.21 in passion fruit to 2.63 in cassava. The correlation of Cd TF with pH and TOC gives a regression of -0.707 and -0.089 respectively (Table 4. 34.). Organic carbon content and pH are soil parameters having influence on respectively (Table 4. 34.). Organic carbon content and pH are soil parameters having influence on TF. There is significant correlation between Cd TF and clay content. Transfer factor values for Pb ranged from 0.01in passion fruit to 0.03 in cassava. Values for Pb are lower than those for Cd. Significantly negative correlation was established between Pb TF and pH while with organic carbon was positive. The TF values for Zn were generally higher than Pb values but lower than those of Cd. For Zn, significant negative correlations were observed between TF and soil properties (pH, TOC and clay content). This indicates higher Zn TF on soils with low clay content and low organic carbon content. The TF values for Cu are of similar range of variation as was observed in Zn. As was observed in Zn, significant negative correlation was estimated between Cu TF and organic carbon. This indicates that more Cu is transferred at low organic carbon content. The TF values for Co ranged from 0.05 (sugar cane) to 1.70 (cassava). Regression analysis showed significant negative correlation between Co TF and pH and no correlation with organic carbon. However, correlation with clay content was significant as it gives a regression of 0.549. Transfer factor for Ni was the highest for all metals determined.

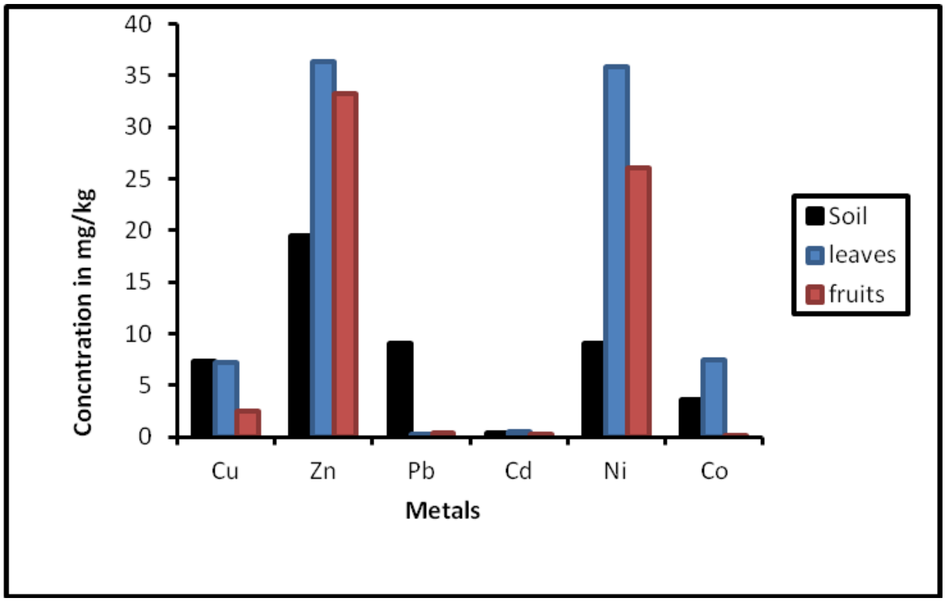

Fig 4.19: Levels of metals in soil compared with levels in crops parts at Ofoke

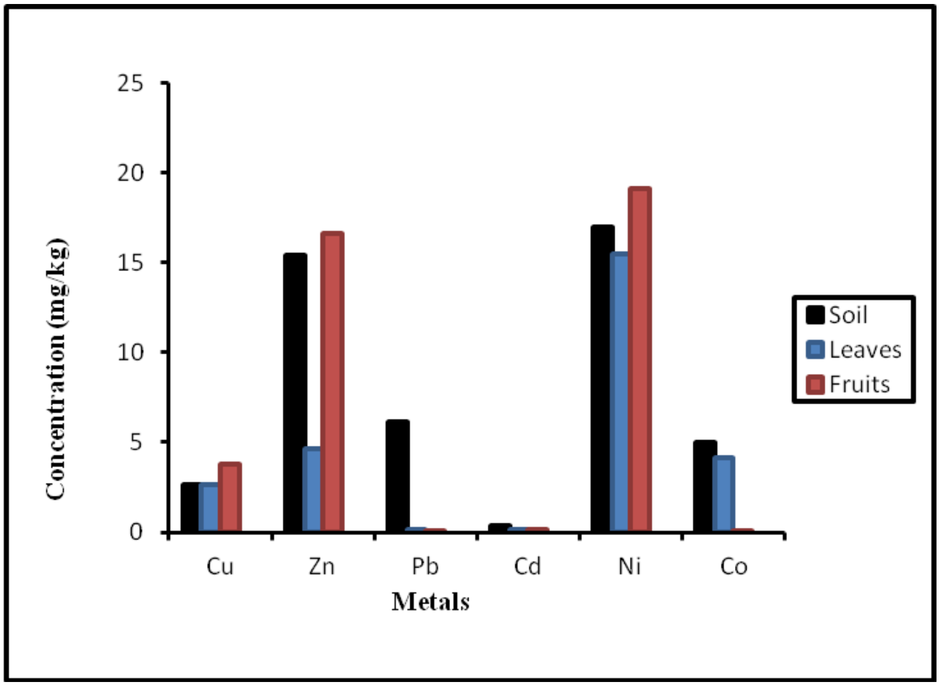

Fig 4.20: Levels of metals in soil compared with levels in crops parts at Ankpa

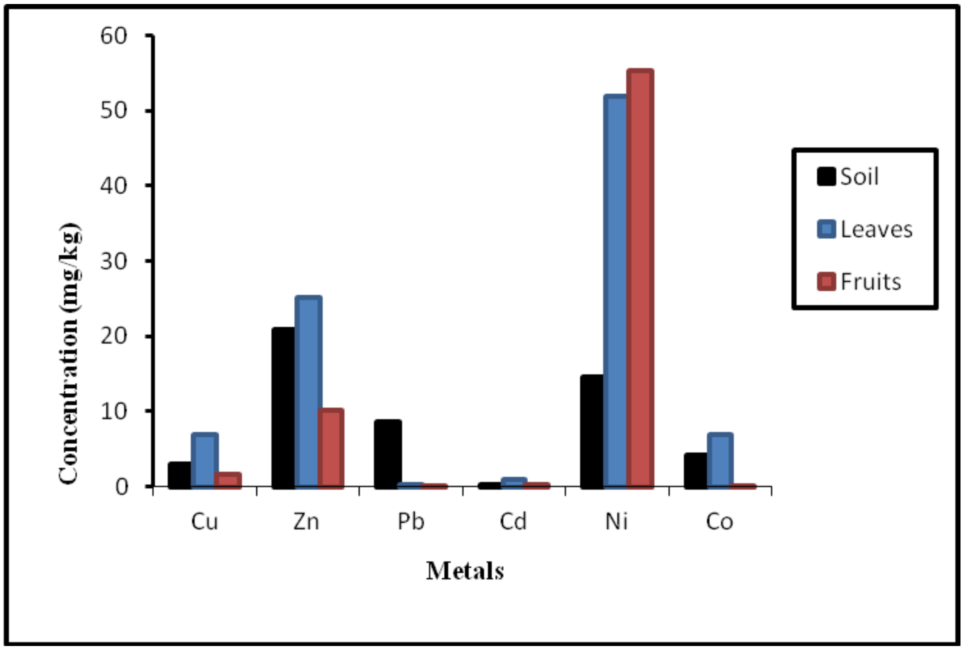

Fig 4.21: Levels of metals in soil compared with levels in crops parts at Ajaokuta

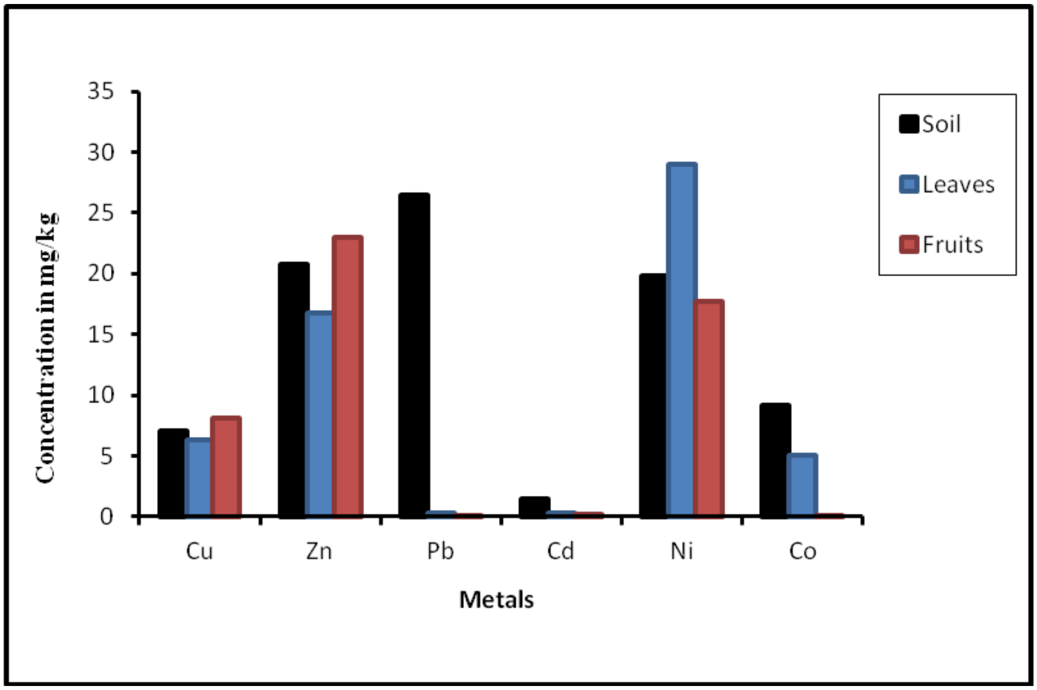

Fig 4.22: Levels of metals in soil compared with levels in crops parts at Macks

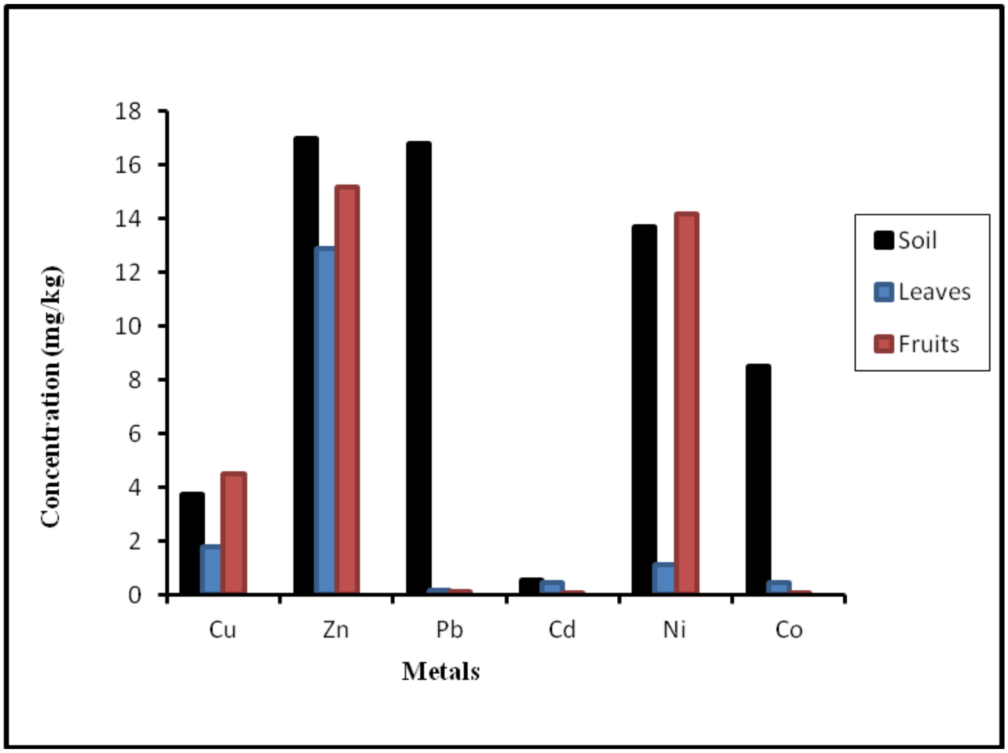

Fig 4.23: Levels of metals in soil compared with levels in crops parts at KSU

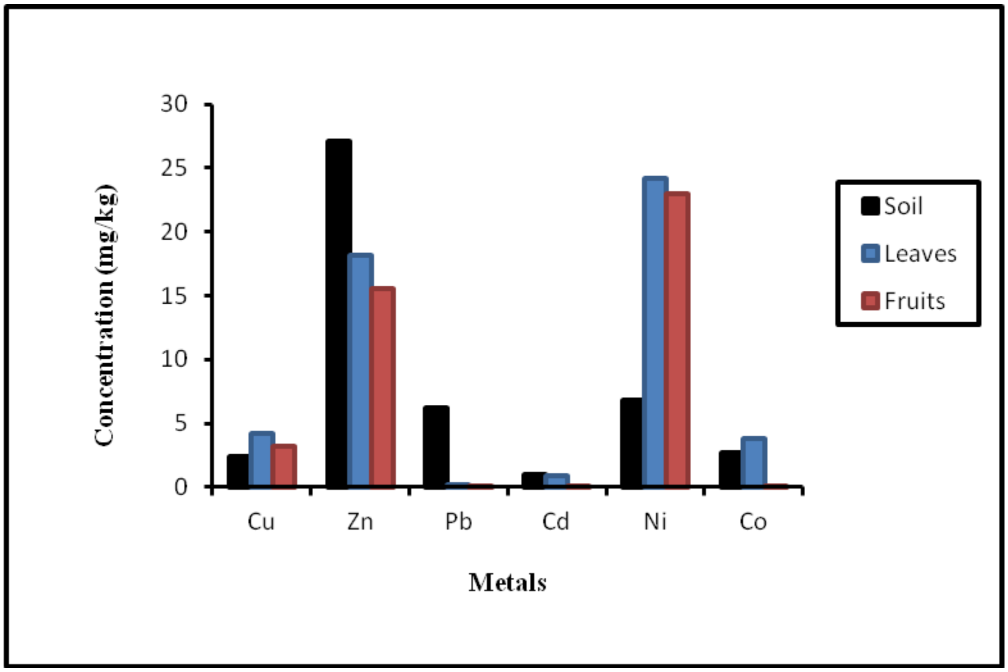

Fig 4.24: Levels of metals in soil compared with levels in crops parts at Id

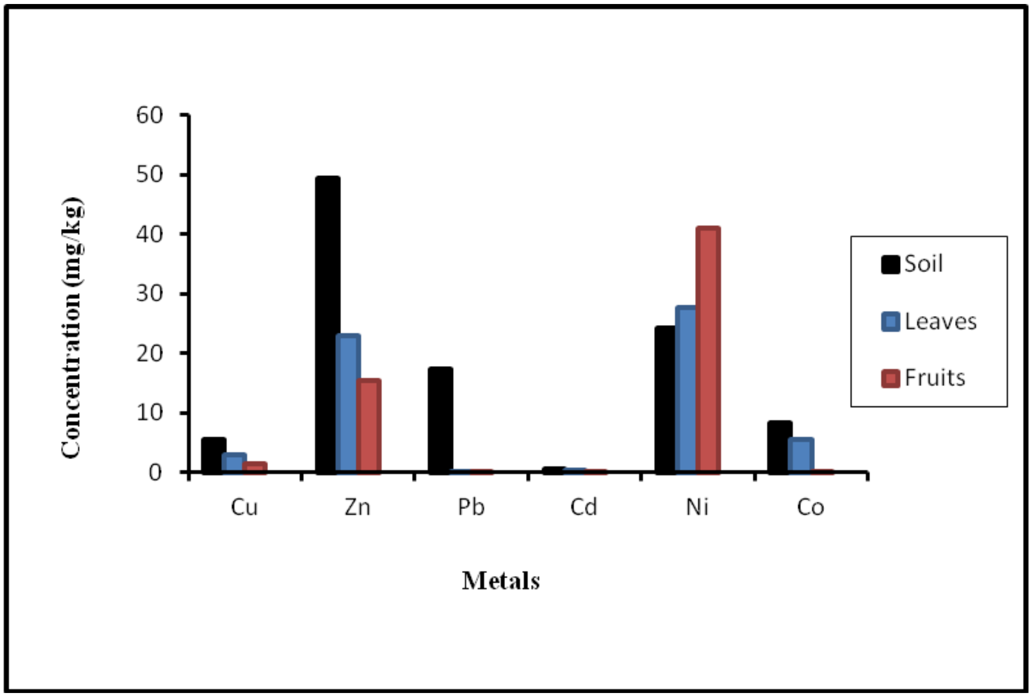

Fig 4.25: Levels of metals in soil compared with levels in crops parts at Ejule

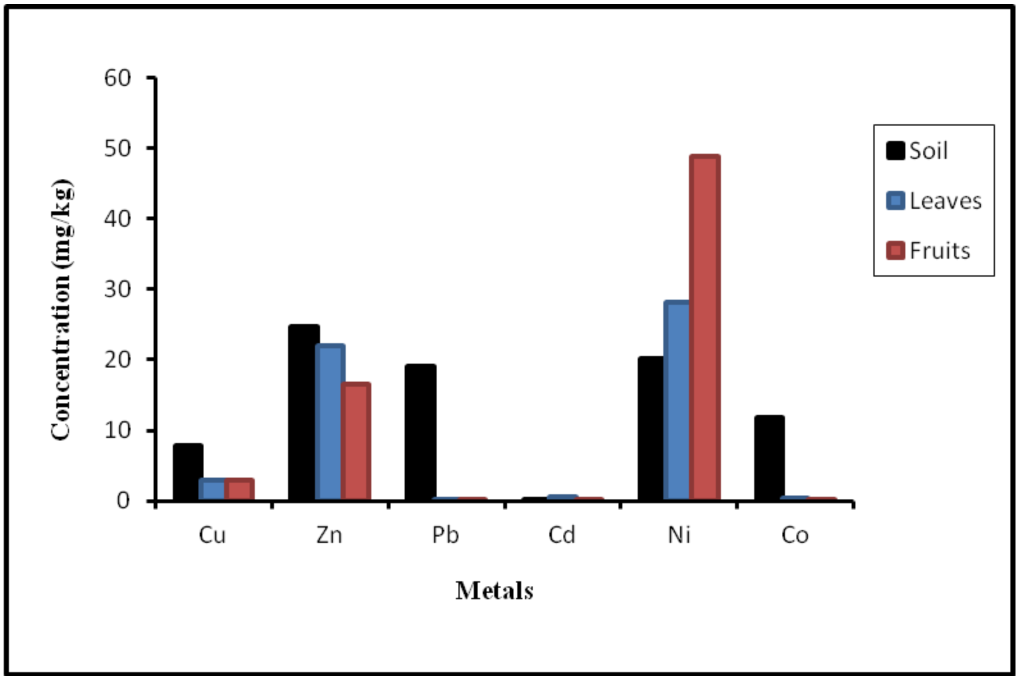

Fig 4.26: Levels of metals in soil compared with levels in crops parts at Ibaji

Table 4.32: Comparison of transfer factors of this study with other studies

Sample point	Crops	Cu	Zn	Pb	Cd	Ni	Co	Reference
OFK	Maize	0.71	1.96	0.03	1.68	0.77	2.48	This study
MAC	Passion fruit	0.77	0.51	0.01	0.21	1.44	0.69	This study
KSU	Pumpkin	0.38	0.57	0.01	0.88	0.11	0.07	This study
ANK	Cassava	0.71	0.21	0.03	0.87	1.33	1.01	This study
AJA	Cassava	1.62	0.92	0.03	1.63	3.8	1.70	This study
IDA	Cassava	1.35	0.79	0.03	0.97	2.75	0.78	This study
EJU	Cassava	0.37	0.22	0.01	0.94	0.98	0.75	This study
IBA	Sugar cane	0.38	0.77	0.01	1.44	0.94	0.05	This study
From other studies		0.4	1.5	0.05	0.55	0.06	-	Baes *et al*. (1984)
		0.123	0.358	0.038	0.514	0.034	-	BJC (1998)
		0.12	0.37	0.039	0.59	0.018	-	Efroymson *et al*. (2001)
		0.26	0.44	0.012	0.17	0.024	-	Lopes *et al*. (2012)

Table 4.33: Correlation coefficient among metals and soil properties as it influence metal uptake

	pH	TOC	Clay	Cu	Zn	Pb	Cd	Ni	Co
pH	1								
TOC	0.0581	1							
Clay	-0.581	0.542	1						
Cu	0.309	-0.814	-0.590	1					
Zn	-0.102	-0.723	-0.465	0.839	1				
Pb	-0.947	0.246	0.691	-0.493	-0.031	1			
Cd	-0.707	-0.089	0.555	-0.428	-0.370	0.567	1		
Ni	-0.850	-0.279	0.630	-0.044	0.121	0.705	0.795	1	
Co	-0.952	0.028	0.549	-0.240	0.246	0.961**	0.462	0.734	1

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

Values ranged from 0.11 (cassava) to 4.77 (maize). Correlation of Ni TF with pH and organic carbon estimated regression value of -0.850 and -0.229 respectively.

In this study the transfer factors for edible parts of sampled crops species shows that the crops were not contaminated. In this study, results showed that there was moderate enrichment of Ni in maize grain (4.77), and cassava at Ajaokuta and Idah with TF values of 3.8 and 2.75 respectively. Cobalt showed moderate enrichment in maize grain at Ofoke, and cadmium in cassava tuber at Ajaokuta. Generally the transfer factors in edible parts of crops determined were class 1 which is the category of depletion to mineral enrichment. From the result, the conclusion can be drawn that the edible parts of the crops determined are relatively safe and do not pose any health risk. This is also evident as the various metals determined in parts of crops are within regulatory standards recommended by various regulating bodies.

4.13 MODELING THE SOIL PLANT METAL INTERACTIONS

The model can be applied to different plants or crops in order to understand how the different concentrations of metals that can be found in the soil can influence their growth. Also knowing the threshold values for toxic effects on plants and knowing the concentrations of metals that are in the soil will help to choose the most suitable crop for each field in order to remediate the soil contaminated by means of biouptake. The model makes possible to characterize the nonlinear behavior of the soil- plant interaction with metal pollution, in order to contribute towards establishing or predicting threshold toxicity limit (referential values) values for the toxic effects of metals on plants and eventual plant mortality. Experimental data obtained from soil and plant (leaves and edible parts) in the study were used. The model measured the dynamic interaction between metal levels in soil and plants parts. Experimental data used for the modeling and the corresponding coefficients of equation 3 in Section 2.11 are presented. Threshold limits were obtained and compared with current concentrations in food crops. The R^2 values obtained were all very satisfactory. The results obtained are predictive metal concentration dose (referential values) on plants as a result of experimental fitting for the model. Figures obtained showed the threshold limit of metals concentration in parts of plants (leaves and edible parts). Above these threshold limits the metals become toxic to the plants. These threshold limits are represented by the coefficient C_2 of equation 2 (Section 2.11). Table 4.34 shows the experimental results for metals in soils, and corresponding levels in leaves and edible parts of crops. From these the threshold limits of the respective metals were derived (Tables 4.35).

Experimental results obtained for Zn metal concentration in passion fruit was 19.4 mg/kg in leaves and 20.7 mg/kg in edible for the corresponding value of 10.7 mg/kg of Zn in soil. The model predicts threshold toxicity limit (referential values) for Zn to be 17.6 mg/kg to 72.1 mg/kg in fruits and 13.5 mg/kg to 31.7 mg/kg in leaves. Among the species of crops the threshold limits in leaves ranged from 31.726 mg/kg in passion fruit to 78.321 mg/kg in maize. Corresponding limits in edible ranged from 33.407 mg/kg in sugar cane stem to 78.643 mg/kg in maize grain. The threshold limit in passion fruit (72.101 mg/kg) is twice the limit in the leaves (31.726 mg/kg) as given in Table 4.35. The R^2 values ranged from 0.8762 mg/kg in cassava to 0.9981 mg/kg in passion fruit. This showed that threshold limits generated from the model are significant.

Observed levels of Pb in maize leaves and grains were 0.16 mg/kg and 0.42 mg/kg respectively corresponding to a dose of 10.5 mg/kg of Pb in soil. For Pb the model predicts a threshold toxicity limit (referential values) of 11.0 mg/kg and 11.2 mg/kg in maize grain and leaves respectively. The threshold limits for Pb for all species are given in Table 4.35. Generated threshold limits for leaves ranged from 11.201 mg/kg in maize to 16.32 mg/kg 1 in sugar cane. Corresponding value in edibles ranged from 11.044 mg/kg in maize to 26.438 mg/kg in cassava with satisfactory R^2 values.

From the experimental result the concentration of Cd in leaves of crops ranged from 0.06 mg/kg in passion fruit to 1.64 mg/kg in pumpkin. In edibles concentrations ranged from 0.01 mg/kg to 0.20 mg/kg in passion fruit (Table 4.33). For Cd the model predicted threshold limit values that ranged from 10.135 mg/kg in pumpkin to 19.437 mg/kg in sugar cane in leaves and in edibles 10.159 mg/kg in pumpkin to 23.305 in cassava (Table 4.34). The highest threshold limit in edible was 23.305 in cassava tuber while in leaves was 19.437 in sugarcane.

Experimental results obtained for Co concentration in leaves of crops species ranged from 0.01 mg/kg in passion fruit to 7.98 mg/kg in cassava. Corresponding levels in edible parts ranged

Table 4.34: Experimental heavy metals concentrations in soil and crop parts (mg/kg)

	Pb			Cd			Zn		
	Soil	Leaves	Edible	Soil	Leaves	Edible	Soil	Leaves	Edible
Passion fruit	17.6	0.22	0.06	0.09	0.09	0.01	8.65	17.8	6.35
	18.7	0.21	0.03	0.09	0.08	0.09	8.86	15.5	10.2
	24.2	0.21	0.03	0.34	0.15	0.12	10.1	15.4	18.2
	40.8	0.20	0.02	0.34	0.06	0.2	10.5	19.4	20.7
Maize	5.62	0.08	0.24	0.28	0.13	0.16	8.68	21.9	31.4
	7.21	0.18	0.16	0.32	0.24	0.15	8.79	21.5	31.8
	10.4	0.42	0.62	0.47	0.54	0.17	17.2	20.2	30.7
	10.5	0.16	0.42	0.49	0.62	0.18	17.3	22.7	31.3
Cassava	14.3	0.15	0.04	0.26	0.12	0.12	42.2	`14.2	18.2
	14.6	0.14	0.06	0.31	0.09	0.12	42.3	13.7	9.48
	15.4	0.14	0.06	0.77	0.59	0.16	40.4	45.1	14.7
	16.1	0.21	0.05	0.80	0.72	0.12	43.3	50.0	5.93
Pumpkin	7.43	0.13	0.09	0.10	0.32	0.12	12.5	8.72	12.4
	7.63	0.11	0.10	0.13	0.14	0.14	12.6	6.43	13.8
	12.5	0.07	0.12	0.18	1.64	0.15	12.9	18.9	10.9
	13.3	0.13	0.26	3.23	1.35	0.12	14.0	20.9	12.4
Sugar cane	15.7	0.14	0.21	0.10	0.14	0.11	20.3	15.0	18.2
	15.9	0.12	0.18	0.12	0.20	0.11	20.9	13.4	16.1
	15.8	0.16	0.32	0.17	0.70	0.11	26.4	34.8	19.0
	15.8	0.13	042	0.23	0.90	0.11	26.9	32.2	11.9

Table 4.34: contd:

	Co			Cu			Ni		
	Soil	Leaves	Edible	Soil	Leaves	Edible	Soil	Leaves	Edible
Passion fruit	4.62	1.82	0.02	5.21	5.84	8.03	8.65	8.73	8.46
	5.26	0.01	0.01	5.62	5.42	8.21	8.86	8.43	8.67
	5.67	1.96	0.02	6.60	7.14	7.75	10.3	8.89	8.13
	5.88	0.09	0.03	6.94	7.21	7.62	10.5	8.21	8.04
Maize	2.08	4.59	0.04	6.76	7.83	2.37	6.41	18.7	22.6
	2.24	2.04	0.02	6.97	9.21	2.29	7.32	19.4	21.2
	2.36	2.16	0.04	7.12	8.24	2.46	7.35	21.4	28.5
	3.21	4.04	0.05	7.23	10.7	2.56	8.21	19.7	46.2
Cassava	6.78	0.70	0.02	3.15	4.27	1.71	14.0	0.22	36.5
	7.48	0.20	0.02	3.17	3.18	1.68	14.3	0.09	20.2
	7.86	0.14	0.02	4.36	2.13	1.56	15.5	35.2	43.9
	7.98	0.90	0.02	16.9	0.14	1.23	63.1	32.7	51.8
Pumpkin	4.36	0.14	0.02	2.75	1.32	3.11	8.76	0.27	11.7
	4.73	0.03	0.01	2.90	1.36	4.16	9.26	0.37	12.2
	5.36	0.01	0.01	3.28	2.43	4.32	9.58	0.27	13.2
	5.52	0.16	0.01	11.2	2.60	4.95	10.2	0.32	13.4
Sugar cane	6.78	1.19	0.02	7.78	5.84	2.63	16.2	24.6	20.4
	7.48	0.01	0.02	7.78	5.42	2.78	16.8	30.5	30.5
	7.86	0.03	0.02	7.80	7.14	3.03	17.3	26.3	21.3
	7.98	8.71	0.02	7.82	7.21	3.65	18.3	25.3	29.7

Table 4.35: Aggregate coefficients corresponding to the threshold limits (mg/kg) of metals in crops parts

Crops	Coefficient	Pb		Cd		Zn	
		Leaves	Edible	Leaves	Edible	Leaves	Edible
Passion fruit	C_1	9.214	6.321	2.4740	2.748	13.54	17.595
	C_2	12.431	11.431	18.346	19.327	31.726	72.101
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.9964	0.9736	0.8956	0.8763	0.9981	0.9961
Maize	C_1	2.079	2.972	1.0924	2.7310	12.374	11.239
	C_2	11.201	11.044	15.063	15.186	78.321	78.643
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.8268	0.9422	0.8477	0.9327	0.9248	0.8932
Cassava	C_1	3.4062	5.0473	2.6431	6.587	4.217	3.2180
	C_2	21.4731	26.438	19.436	23.305	56.742	54.363
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.9763	0.8965	0.7866	0.8943	0.8762	0.9418
Pumpkin	C_1	2.1475	1.4830	0.0090	7.0880	10.432	9.5350
	C_2	11.486	11.175	10.135	10.159	45.024	47.066
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.8762	0.9267	0.7128	0.9778	0.9364	0.9228
Sugar cane	C_1	4.4371	3.8732	3.3047	0.9674	6.0430	10.271
	C_2	16.321	14.885	19.437	19.786	31.731	33.407
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.8946	0.9372	0.9463	0.9674	0.8766	0.8942

Table 4.35: Contd:

Crops	Coefficient	Co		Cu		Ni	
		Leaves	Edible	Leaves	Edible	Leaves	Edible
Passion fruit	C_1	3.2104	3.9357	5.3520	2.748	10.217	9.2470
	C_2	32.007	32.162	45.372	46.741	37.437	38.403
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.9705	0.9483	0.9326	0.8715	0.9476	0.8764
Maize	C_1	10.214	10.037	6.3965	5.4731	2.0681	2.3571
	C_2	20.374	20.782	26.312	25.467	18.056	18.173
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.9277	0.8753	0.9375	0.9781	0.8637	0.8946
Cassava	C_1	17.516	2.0160	3.4386	3.9031	19.037	10.403
	C_2	21.475	9.9480	26.437	28.326	69.430	71.353
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.6926	1.0000	0.9372	0.8768	0.7074	0.8944
Pumpkin	C_1	5.0143	4.9641	1.1860	8.8930	5.0472	5.8901
	C_2	16.135	16.763	5.5540	9.0830	17.321	16.846
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.9741	0.9213	0.9408	0.9289	0.8367	0.8725
Sugar cane	C_1	13.794	12.649	9.2409	8.9776	4.730	4.8649
	C_2	62.173	60.477	17.635	18.104	56.072	58.480
	C_3	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	R^2	0.9776	0.9320	0.8993	0.9321	0.9641	0.8967

from 0.01 mg/kg in pumpkin to 0.04 mg/kg in maize. For Co, the model predicts crops threshold toxicity limit in leaves that ranged from 16.135 in pumpkin to 62.173 in sugar cane. Corresponding limits in edible ranged from 9.9480 in cassava tuber to 60.477 in sugar cane stem.

Experimental results obtained for Cu concentration in leaves of crops ranged from 0.14 mg/kg in cassava to 9.21 mg/kg in maize. The edibles levels ranged from 1.23 mg/kg in cassava tuber to 8.21 mg/kg in passion fruit. Aggregate coefficient results correspond to the threshold limits (mg/kg) of Cu concentration ranged from 5.5540 in pumpkin to 45.372 in passion fruit (leaves) and 9.0830 in pumpkin fruit to 46.741 in passion fruit (edible).

Experimental Ni levels in sols and corresponding levels in crops parts are given in Table 4.33. The model predicts threshold toxicity limit of 17.321 in leaves of pumpkin to 69.430 in cassava leaves. Corresponding limits in edible ranged from 16.846 in pumpkin fruit to38.403 in passion fruit. The results showed that metal concentrations in crops parts were generally lower than model-derived threshold limits for toxicity to the plants

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5. 1 SUMMARY AND CONCLUSIONS

5.1.1 Heavy Metals in Kogi State Farmland Soils

Average levels of all the metals determined were generally low and fell within the regulatory standards requirements for metals in agricultural soils. Current levels therefore do not appear to constitute hazards to the food chain. The levels of metals in the soils were not influenced by seasons, and did not vary significantly among the farms.

5.1.2 Heavy Metals in the Farm Crops

The levels of metals in leaves were mostly higher than in edible parts of all crops species examined. However, these levels were generally within regulatory standards, except for nickel levels that were marginally higher than some regulatory standards.

5.1.3 Soil–Plant Uptake Factors (Transfer Factor)

Soil metal levels were generally higher than the levels in plant parts. Soil–plant uptake factors revealed that accumulation of heavy metals into the crops investigated was low, except for nickel in cassava. Among species of food crops examined, cassava tuber had the highest overall mean uptake.

5.1.4 Overall Risk Assessment

The observed metal concentrations in crops parts were generally lower than the soil-plant equilibrium model derived threshold limits for toxicity to the crops. This implies that levels of metals in the crops investigated do not pose threat to human.

5.2 RECOMMENDATIONS

The levels of heavy metals in this study were generally low in soils and food crops. That the current levels are low does not mean that it will continually be so. Therefore, there should be no complacency in the efforts at monitoring what happens in agricultural farmlands where food crops are produced. Recent incidents of metals poisoning in some part of Nigeria, which arose from soil contamination clearly underscore the need for vigilance with respect to soil and crop contaminant levels. Therefore, I recommend:

(i) regular and more elaborate monitoring of agricultural soils and food crops and irrigation water of the Kogi State farmlands for various contaminants.

(ii) in view of the relatively higher average levels of nickel in cassava crop in this study, further investigation should be carried out to examine the critical factors which contribute to the transfer of nickel from soil to the cassava crop.

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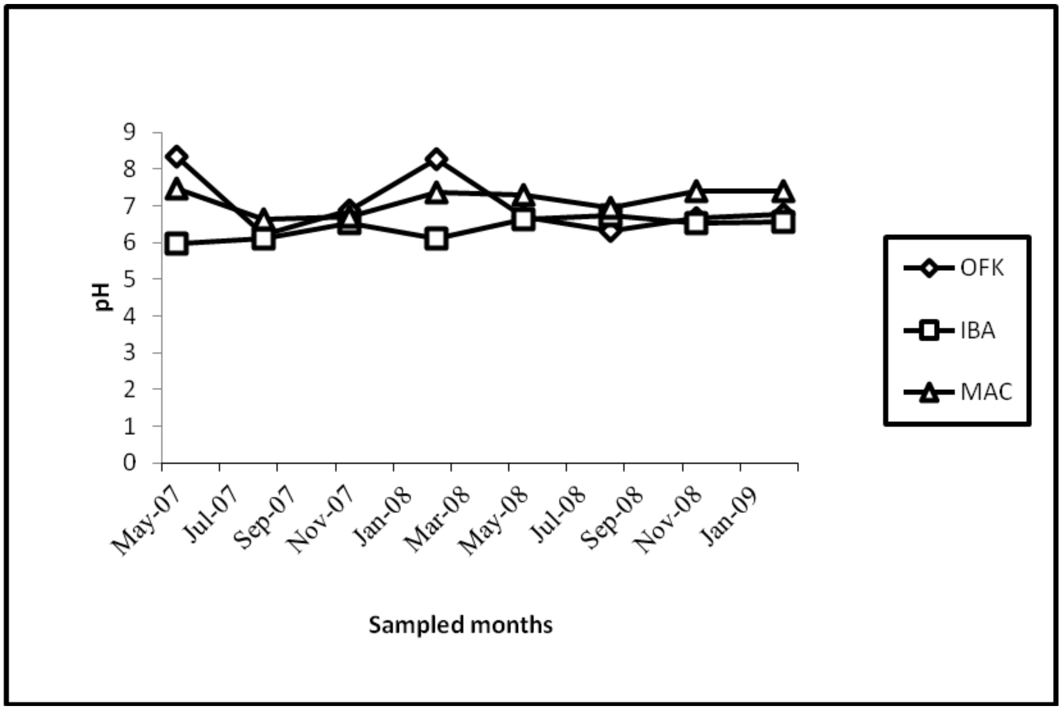
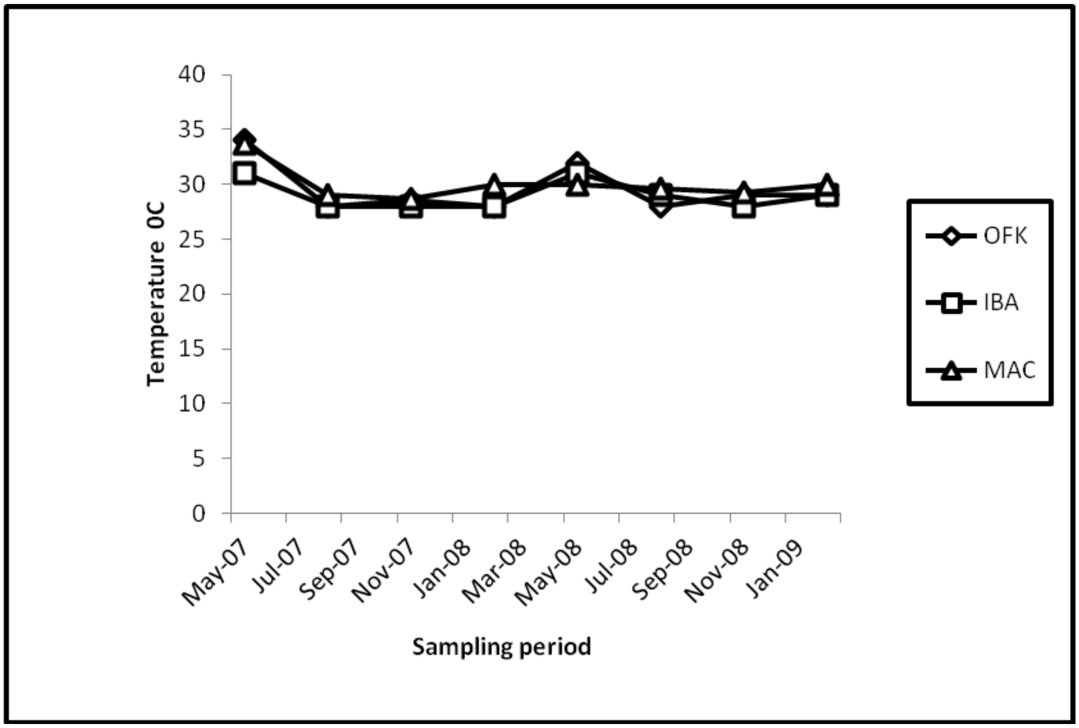
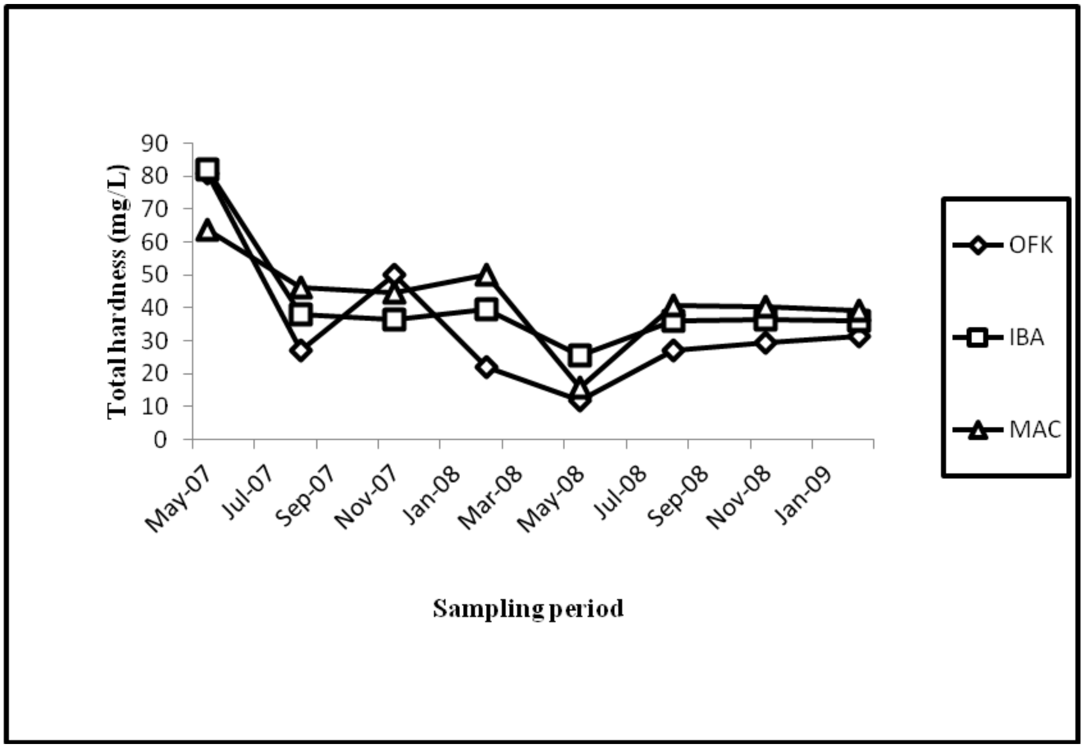
APPENDIX



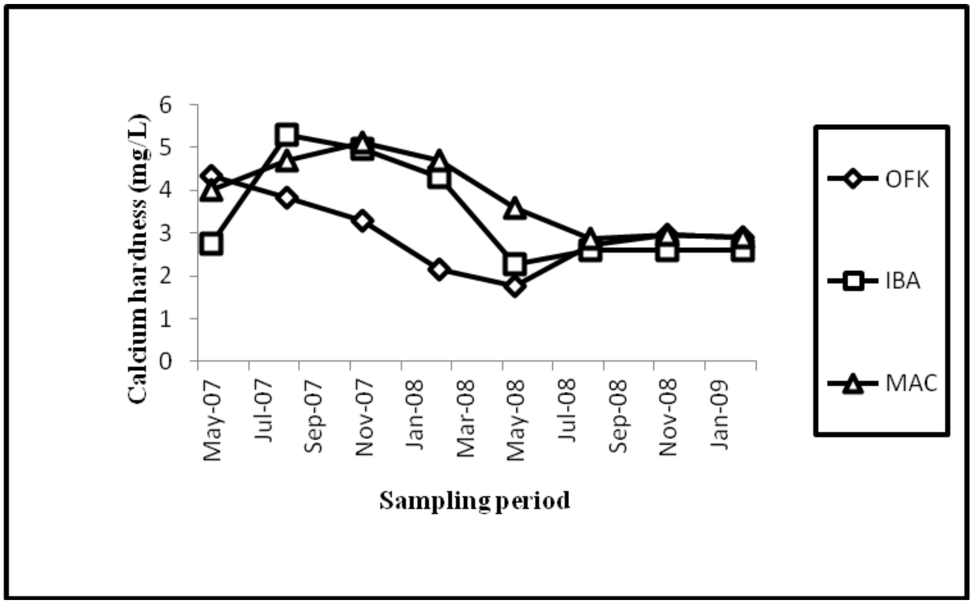
Appendix 1: Monthly variation of pH with locations



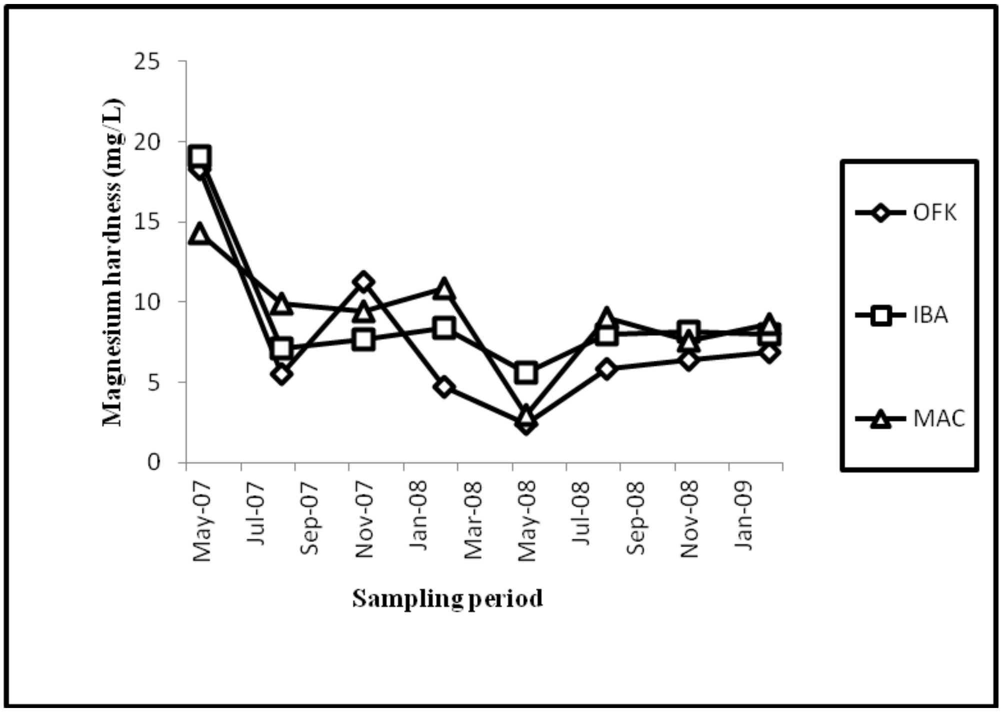
Appendix 2: Monthly variation of temperature with locations



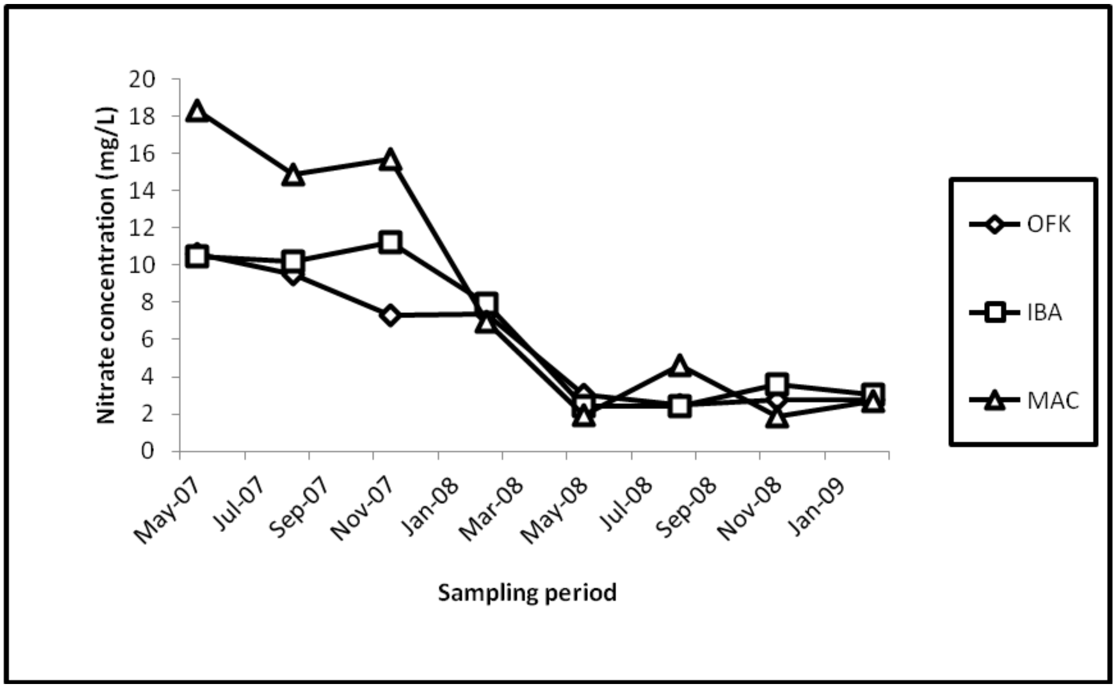
Appendix 3: Monthly variation of total hardness with locations



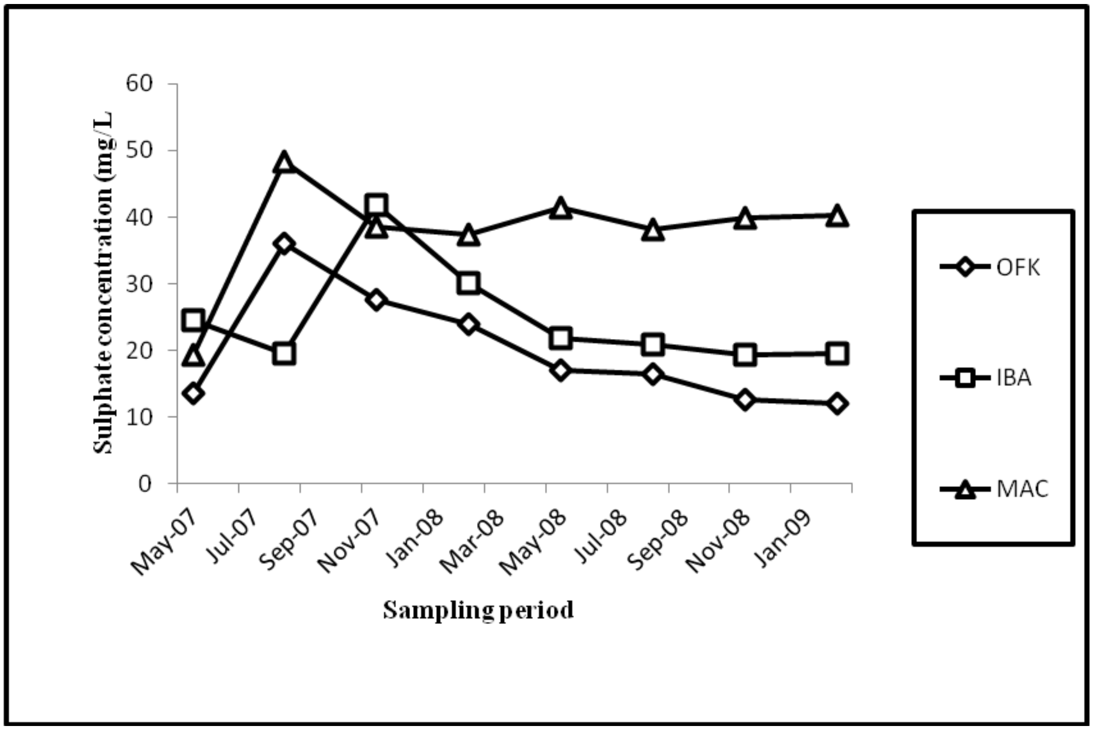
Appendix 4: Monthly variation of calcium hardness with locations



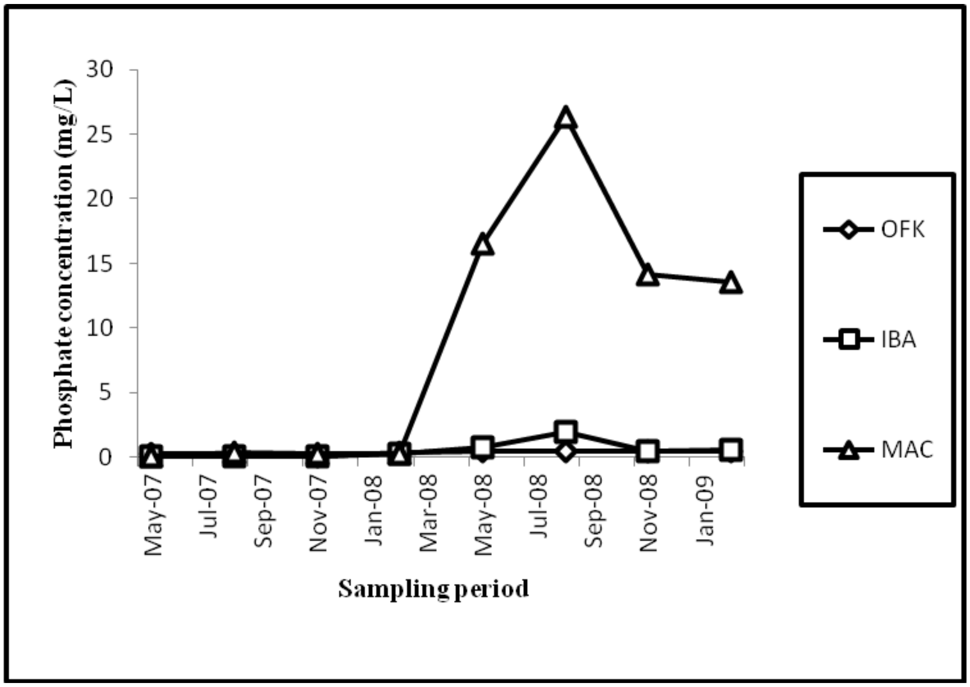
Appendix 5: Monthly variation of magnesium hardness with locations



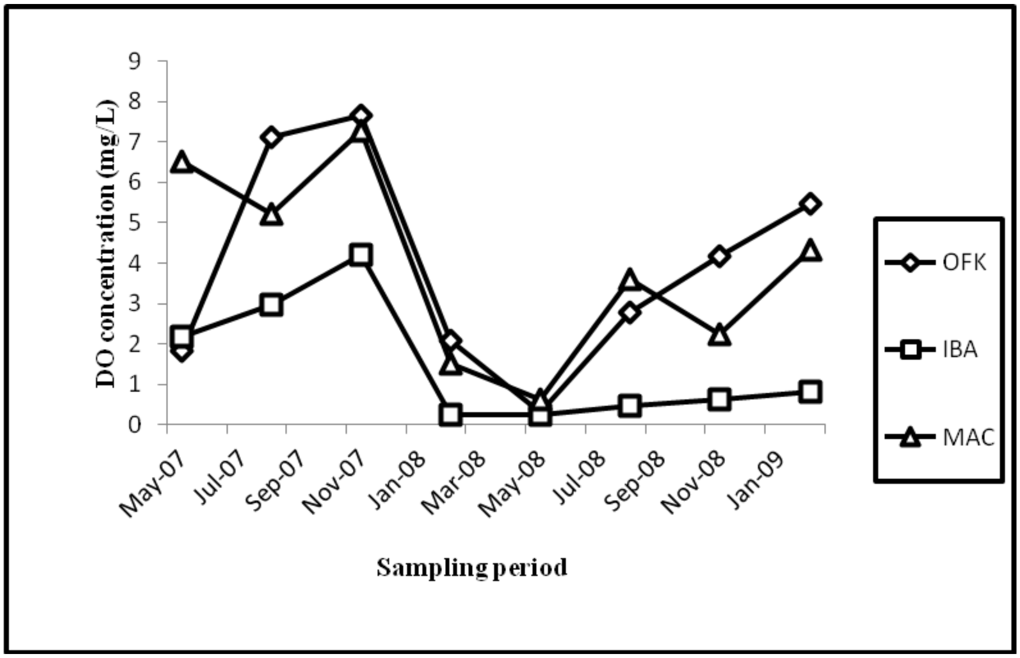
Appendix 6: Monthly variation of nitrate with locations



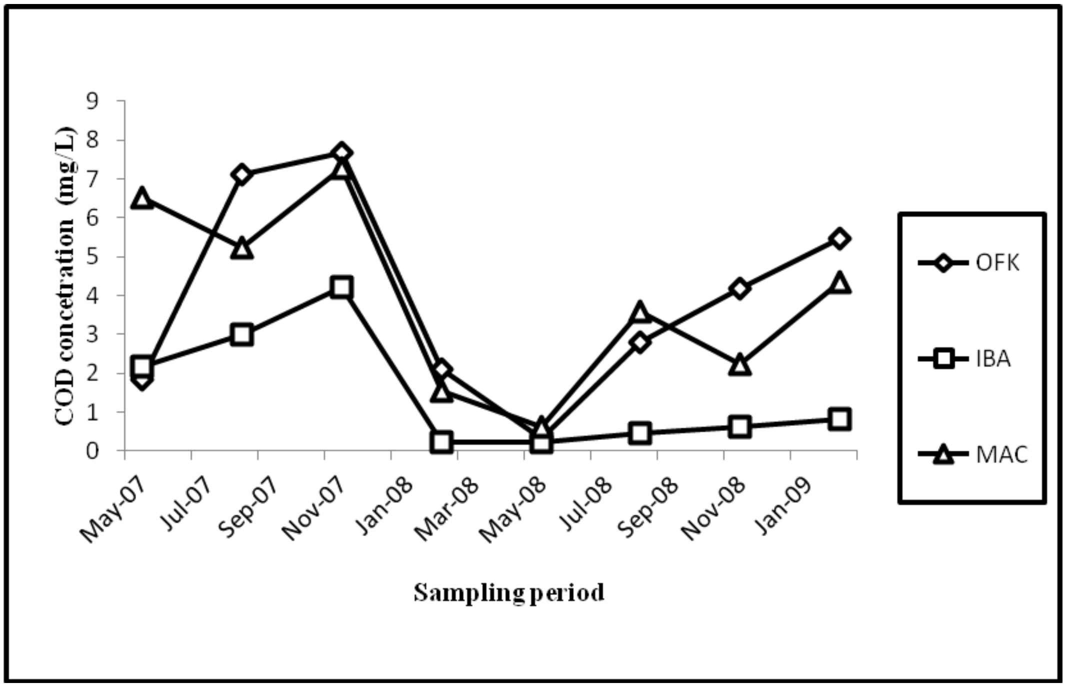
Appendix 7: Monthly variation of sulphate with locations



Appendix 8: Monthly variation of phosphate with locations



Appendix 9: Monthly variation of DO with locations



Appendix 10: Monthly variation of COD with locations