TRACE METAL CONTENTS AT SELECTED GROWTH STAGES OF WHEAT AND MAIZE GROWN ON ROADSIDE SOIL AT KADAWA KANO STATE, NIGERIA

By

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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN BIOLOGY

DEPARTMENT OF BIOLOGICAL SCIENCES, FACULTY OF SCIENCE,
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JUNE, 2015

DECLARATION

I declare that this dissertation entitled 'Trace Metal Contents at Selected Growth Stages of Wheat and Maize grown on Roadside Soils at Kadawa Kano State, Nigeria' has been carried out by me in the Department of Biological Sciences. The information derived from the literature has been duly acknowledged in the text and the list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other Institution.

M'ember Catherine ANONGO ----------------------------------- ------------------

Signature Date

CERTIFICATION

This dissertation entitled "**TRACE METAL CONTENTS AT SELECTED GROWTH STAGES OF WHEAT AND MAIZE GROWN ON ROADSIDE SOIL AT KADAWA, KANO STATE, NIGERIA** " By M'ember Catherine ANONGO, meets the regulations governing the award of the degree of Doctor of Philosophy (Ph.D.) in Biology of the Ahmadu Bello University, Zaria, and is approved for its contribution to scientific knowledge and literary presentation.

Prof. S.P. Bako Chairman, Supervisory Committee Department of Biological Sciences Ahmadu Bello University, Zaria.	--------------------------------- Signature	---------------- Date
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DEDICATION

This dissertation is dedicated to the following; God Almighty (Ominiscience) who saw me through my studies. My parents especially my Daddy, Mr. T.S. Anongo whose persuasion encouraged me to enroll for Ph. D degree and for their endless love, understanding, tolerance, patience and the financial and moral support they rendered. May God grant you and give you long life to reap the fruits of your labour. God bless you all.

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ABSTRACT

Risk assessment of selected trace metals Cr, Cd, Pb, Zn and Cu at selected growth stages (15 days – germination or seedling stage, 30 days – tillering stage, 45 days – booting/shooting stage, 60 days – heading/earing stage, 75 days – flowering stage and 90 days – ripening stage) of two varieties each of wheat - *Triticum aestivum* L. (Pavon-76 and Siettecerros) and yellow maize-*Zea mays* L. (TZEE-Y) *and* Popcorn (*Zea mays everta* L.) were investigated in Kano State, a cereal growing Sudan savanna zone of Nigeria. Doruwa Salau at a distance of 345.79metres perpendicular to the Kano-Zaria Highway with average daily traffic density of 19,288 is the experimental site. The control site was the Irrigation Research Station (IRS), Kadawa at a distance of 1934.61metres from the roadside with an average daily traffic density of 3. A preliminary analysis of the trace metals and physico-chemical parameters of the soils was determined. Samples of leaf, stem and root at the selected growth stages were collected in triplicates from the two cultivars of wheat and maize grown at the experimental and control sites. Corresponding soil samples were collected in duplicates. Pb, Cd and Cu, Cr, Zn of the plant and soil samples were assessed using atomic absorption spectrophotometer and energy dispersive X-ray fluorescent respectively. Selected risk assessment techniques like soil-plant transfer coefficient (TC), plant uptake factor (PUF) and translocation factor (TF) were worked out. Trace metal levels were highest in the crops than in the soils at both sites indicating atmospheric origin. Plant parts trace metals levels were higher at Doruwa Salau than at the IRS, Kadawa, indicating proximity to the source of pollution. The total trace metal concentration was generally higher at the 15-days and 30-days growth stages reflecting the growth dilution of chemicals as the plant biomass increases. ANOVA for individual trace metals was highly significant ($P = 0.01$) for Zn (Pavon-76), Cr, Cu and Zn (yellow maize) and Cr (popcorn) indicate a strong selective ability of the crops to accumulate certain metals. ANOVA for leaf trace metal level was highly significant in Pavon-76 indicating influence of the plant parts to metals in crops. ANOVA for soil trace metals among the four sampling units was non-significant suggesting that the crop trace metal levels were of atmospheric origin and not from the soil. Correlation analysis identified a weak and non-significant relationship between soil and cereal crops indicating atmospheric deposition. Cu (15.70 – 107.17mg/kg), Zn(29.75 – 903.36mg/kg), Cr (3.25 – 20.65mg/kg), Pb (200 – 2520mg/kg) and Cd (115 – 370mg/kg) exceeded the permissible limits of the Joint FAO/WHO Food Standards (2006) (Pb = 0.1mg/kg; Cd = 0.01mg/kg; Cr = 1.30mg/kg; Cu = 10.00mg/kg; Zn = 5.00mg/kg). Health risk assessment of metals in roadside grown crops consumed by humans is a very good technique for predicting threats to life. Pavon-76 and Popcorn were identified with high phyto-remediation potentials and can be classified as hyper-accumulators. They can be employed in bioremediation approach for clean-up of polluted lands. It could be concluded that metals in the cereal crops originated from polluted atmosphere by motor vehicles and not from the soils.

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CHAPTER ONE

1.0 INTRODUCTION

The increase of metals in the biosphere from anthropogenic and natural sources requires constant global monitoring (Reuben *et al*., 2008). Human activities have led to high levels of heavy metals accumulation from the metal related industries, the premises of old mines, rural areas where the soils along highways and/or roads are p olluted by automotive exhausts and fields contaminated with fertilizers containing heavy metals (Antosiewicz, 1992, Giordani, *et al*.,2005; Hatamzadeh *et al.*, 2012).A substantial amount of pollutants is released into highway ecosystems as a result of automobile traffic. Major components of these pollutants are hydrocarbon combustion products as well as the heavy metals like Pb, Cd, Ni and Zn. These are released as a result of combustion of leaded gasoline, combustion of lubricating oils (nickel) and wears of automobiles (cadmium and zinc) (Scanlon, 1980).These metals are released during different operations of the road transport such as combustion, component wear, fluid leakage and corrosion of metals. Lead, cadmium, copper, and zinc are the major metal pollutants of roadside environments and are released from burning of fuel, wear out of tyres, leakage of oils, and corrosion of batteries and metallic parts such as radiators (Dolan *et al*., 2006).

The contribution of cars and road transports to the global emission of atmospheric pollutants is regularly increasing. These pollutants have an impact on the environment: road transports contaminate the atmosphere, water and soil near the highway via atmospheric fallout. Traffic pollutants include potentially toxic metals to health like lead, cadmium and zinc (ATSDR, 1994, 1999a,b; Caussy *et al*., 2003). Many studies have shown contamination by these elements, at the vicinity of highways (Zhang *et al*., 1999; Turer and Maynard, 2003). In 1994, 28 390 tons of lead were emitted to the atmosphere, with a road transport contribution of 70%

(Gromov and Emelina, 1994). In 2010, it was estimated that the total emissions will decrease to 12,600 tons, with a road transport contribution of 60%(Viard *et al*., 2004).The dispersion of contaminants and concentrations of metals in roadside soils is influenced bymeteorological conditions, like wind (Piron-Frenet *et al*.,1994), rainfall profiles (Bennouma, 1988) or traffic intensity (Garcia and Millan, 1998) and by soil parameters (Viard *et al*., 2004).

Heavy metals could get into our human bodies by different ways such as respiration, eating food and drinking water (Moosavi *et al.,* 2012). Heavy metals are a menace because of their roles as environmental pollutants and toxins. They could significantly increase ecological, evolutionary, nutritional and environmental pollutions (Fathi *et al*., 2011). Metal accumulation by plants is affected by many factors aside those of anthropogenic sources which directly influence heavy metal concentration on and within plants (Muchuweti *et al*., 2006) such as climate, atmospheric deposition, nature of soil upon which the crop is grown and the degree of maturity of the plant at harvesting (Lake *et al*., 1984; Scott *et al*., 1996; Voutsa *et al*., 1996; Margaret, 1998; Omoloye *et al*., 2009). In general, metal accumulation in plants is influenced by variations in plant species, the growth stage of the plants and element characteristics such as control absorption, accumulation and translocation of metals. Furthermore, physiological adaptations also control toxic metal accumulations by sequestering metals in the roots (Guilizzoni 1991; Nouri *et al*., 2009). It is known that metal sensitivity and toxicity to plants are influenced by not only the concentration and the toxicant types, but are also dependent to several developmental stages of the plants (Liu *et al*., 2005; Hatamzadeh *et al*., 2012). Also, according to the Becerril *et al*., (1989), heavy metals caused lower water uptake and transport in plants. Bewley and Black (1983) supported this opinion and expressed that it may pertain to the failure in water absorption at high metallic salt levels (Hatamzadeh *et al*., 2012).

Concentrations of heavy metals in plant tissues are associated with toxicity symptoms and are usually in the several hundred ppm range (Akinci and Akinci, 2010). These heavy metals accumulate in plant tissue and may be transmitted in the food chain and, because of their high toxicity, present a threat to crop production and animal and human health (Korentejar, 1991; Ergün and Öncel, 2012). Among these heavy metals, Cd is a potential pollutant which can pollute the soil resulting in its accumulation in different parts of plants because it is a very mobile element and can easily be taken up by plants. Owing to the high solubility and toxicity of Cd, it has deleterious effects on plant growth (Pinto *et al.*, 2004; Ahmad *et al.*, 2012). When Zn is accumulated in excess in plant tissues, it causes alterations in vital growth processes such as photosynthesis and chlorophyll biosynthesis (Doncheva *et al*., 2001) and membrane integrity (De Vos *et al*., 1991). An excess of Zn has been reported to have a negative effect on mineral nutrition (Chaoui *et al.*, 1997; Fathi *et al.*, 2012). Jadia and Fulekar (2008) reported that cadmium and lead are very toxic heavy metals at 50 ppm concentration (Moosavi *et al.*, 2012). Chromium interferes with several metabolic processes, causing toxicity to plants as exhibited by reduced seed germination or early seedling development (Sharma *et al*., 1995), root growth and biomass, chlorosis, impairment of photosynthetic activity and finally, plant death (Scoccianti *et al*., 2006). Copper causes injury at cellular level by the formation of free radicals. Cellular injury by this type of mechanism is well documented for copper as well as other metals (Shi *et al*., 1993; Gupta and Kalra, 2006). Copper being one of the common heavy metals in industrial discharge of aeronautic, metal and metallurgy, and refinery industries shows toxic effects on plants and animals (Houshmandfar and Moraghebi, 2011).

Wheat (*Triticum aestivum* L.) is one of the most important cereals which areused as a main food material in many parts of the world. Corn ranks third in the global cereal production and is utilized as food, feed and fodder. Large quantities of corn are used in extracting oil, manufacturing cellulose products, and mild abrasives (Mahmood *et al.*, 2005). Maize (*Zea* *mays L.)* is the most important cereal after sorghum and millet with the widest geographical spread in terms of production and utilization among the cereals in Nigeria (Adu, 1982; Agboola *et al*., 1993; CIMMYT/FAO, 1999; Omoloye, 2009). Production and utilization have increased tremendously in recent times probably due to encouragement from government through different initiatives such as the National Poverty Eradication Programme (NAPEP) and the National Directorate of Employment (NDE) (Omoloye, 2009).

Different plant species and varieties show a wide range of plasticity in Cd tolerance, varying from the high degrees of sensitivity to the hyper accumulating phenotype of some tolerant higher plants (Yang *et al.,* 2000; Liu *et al.*, 2003; Asgharipour *et al.,* 2012).

It also brings the possibility to develop crop varieties with low accumulation and high tolerance of heavy metals, which could be planted in slightly to moderately contaminated soils. Two popular wheat varieties, Pavon-76 and Siettecerros, and commonly grown maize varieties TYZEE-Y and popcorn are widely cultivated in the northern states of Nigeria especially Kano State. Therefore they were chosen for examining the toxicological effects of Cd, Cr, Cu, Pb and Zn at selected growth stages.

1.1 Statement Of Research Problem

Contamination and subsequent pollution of the environment by toxic heavy metals have become an issue of global concern due to their sources, widespread distribution and multiple effects on the ecosystem (Nriagu, 1990), as well as their cumulative behavior, toxicity and potential hazardous effects not only on crop plants but also on human health (Das *et al.*, 1997).The situation is even more worrisome in the developing countries where research efforts towards monitoring the environment have not been given the desired attention by the stake holders (Oluyemi *et al*., 2008). Several researches in Nigeria have focused largely on the agronomy of agricultural crops, agricultural land use management practices, soil fertility and assessments with less emphasis on ecotoxicological studies.

Excessive accumulation of heavy metal in agricultural land through traffic emissions may results in soil contamination and elevated heavy metal uptake by crops, and thus affects food quality and safety (Garcia and Millan, 1998) and human health (Miclean *et al*., 2007; Bako *et al*., 2009a and b). The Nigerian situation is further exacerbated by the reality of increasing large-scale importation of old/fairly used vehicles for use on the Nigerian highways (Alo, 2008).

Atmospheric emissions from automobiles is a major contributing factor to the abundance of heavy metals in the Nigerian Environment (Onianwa and Egunyomi,1983; Onianwa and Ajayi,1987; Adekunle *et al.*,2004), and this is much higher than permissible level in some pollution conscious countries (Sridhar,2001; Rim-Rukeh and Okokoyo, 2003). These metals are used in the manufacture of vehicle lubricating oils and some components of vehicle engines (Abubakar *et al.*,2004).

Heavy metals are of significant ecological and environmental concern because of their non-biodegradability or persist in the environment for a longer period oftime, as they are not easily degraded by soil microorganismsand therefore, can easily be absorbed by plants (Raghunath *et al.*, 1999; Gallego *et al.*, 2002; Shao *et al.*, 2011)and their long half-lives in the biological systems(Adeniyi, 1996).The chemical substances (heavy metals) are known to exert harmful effects (inhibitory) on the physiology and biochemistry of crop plants lowering yield, and more alarmingly may cause health hazards through accumulation in the food chain (De, 1994; Prasad, 1997; Mishra and Choudhuri, 1999, Abubakar *et al*., 2004).On sites with low or medium contamination levels, metal concentration in crops is mostly not as high to cause acute toxicity, but in the long run it may provoke chronic damage to health (Adriano, 2001). Due to the heavy metal burden in human nutrition, there is need for measures to reduce the metal transfer into agricultural plants.

Higher plants are usually the first indicators of changes in the chemical and biological composition of natural ecosystem, where other indicators are absent; they have appeal in air and soil pollution monitoring in highly polluted areas (Mulgrew and Williams, 2005).

Pollution of plants is of concern for two major reasons. Firstly, pollutants may have direct phytotoxic impacts which constitutes injury resulting directly from exposure to the pollutant (e.g. gaseous uptake of the pollutant by vegetation resulting in internal cellular damage or changes to biochemical or physiological processes), or indirect phytotoxic impacts on the plants themselves, leading to a decline in crop yields and threatening our food supplies. Secondly, the plants may act as a vehicle for transferring pollutants into the food chain. For example, Cd is readily accumulated by plants and may get to levels which are adverse to the plants themselves, consequently posing a significant threat to animals and humans that consume plants (Radojevic and Bashkin, 1999). Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air.

Heavy metals concentrations in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal methods (Eja *et al.,* 2003; Zauyah *et al.*,2004). The main sources of heavy metals to vegetables and/or crops are their growth media (soil, air, nutrient solutions) from which these heavy metals are taken up by the roots or foliage (Lokeshwari and Chandrappa, 2006). Studies reveal that the presence of toxic heavy metals like Fe, Pb and Hg reduce soil fertility and agricultural output (Lokhande and Kelkar, 1999) which have the potential to contaminate crops growing under such irrigation.

The rate of release of heavy metals from vehicular emissions into the atmosphere and subsequent uptake by plant could also result in phytotoxicity and/or bioaccumulation. Plant and animal cells have mechanisms for bioaccumulation (the selective and storage of great variety of molecules). This allows them to accumulate nutrients and essential minerals, but at the same time, they also absorb and store harmful substances such as heavy metals. Accordingly, toxins are rather dilute in the environment and can reach dangerous levels inside cells and tissues through this process of bioaccumulation.

The overall effects of heavy metals are shown to prohibit the growth of seed germination of different plant species (An *et al.*,2009). Plants make up the most vital trophic level of the biomass pyramids known as the primary producers. Because they are at the bottom of the pyramid, every other organism in an ecosystem relies on the health and abundance of the primary producers in order to survive. If plants are battling with the problems of diseases relating to exposure to chemicals (heavy metals), other organisms will either die because of starvation or obtain the diseases by eating the plants or animals already infected. So ecotoxicity is an ongoing battle that stems from many sources and can affect everything and everyone in the ecosystem (An *et al*., 2009). There is limited information on heavy metal absorption, translocation and accumulation by edible crop plants especially wheat and maize grown on roadside soils in the Sudan Savanna ecological zone.

1.2. Justification

Most concepts of ecology have been largely focused on wild flora and fauna in their natural habitats with less emphasis on agricultural crops who have effectively adapted to their ecological zones. The climatic factors of the semi-arid ecological zone in this study with a characteristically low rainfall and high evapotranspiration are extremely significant in understanding the distribution of elements/heavy metals in the soil, as well as distribution among the selected growth stages. Global climate changes studies have reported that vegetation, especially forests are becoming the major sources and sinks of carbondioxide which are exchanged within the biosphere (Brown, 1997; Clark *et* al., 2001; Chave *et al*., 2005; Xie *et al.,* 2008). In a similar dimension, plants in this zone could play a significant role as a sink for atmospheric pollutants, particularly particulate heavy metals. The idea of atmospheric capture by plants is based on the role of the aboveground biomass in plants as carbondioxide sinks. There is the tendency of these cereal crops also becoming sinks for these pollutants. Many ecotoxicological studies have reported that heavy metals in plants are largely from the soil. The use of cereal crops in this study is to view ecotoxicity beyond the soil with respect to atmospheric pollution.

Moreso, there have been more emphases on the conservation of endangered, threatened and critical species of flora and fauna, while not much have been done on the preservation of agricultural and/or domesticated crops. The integration of conservation practices with ecotoxicity should also be done on agricultural crops which are the primary producers that have already adapted to their ecological zones. Therefore agricultural crops should also be conserved especially wheat and maize which are among the 'the big three' and should not be tempered with since they could easily be endangered because of the toxicity in the environment. Although several eco-toxicity studies of both agricultural crops and medicinal plants and trees have been carried out in other parts of the world, there is no empirical data on ecotoxicity in Nigeria particularly on the widely cultivated and consumed varieties of wheat and maize. In ecotoxicity studies, plant parameters such as plant growth, biomass production, metal uptake and plant metabolism have been used to evaluate the level of toxic metals in plants (Farrag *et al*., 2012).

The implications associated with metal (embracing metalloids) contamination are of great concern, particularly in agricultural production systems. These areas are of particular value since they contribute to local and national economic growth. Metals most often found as contaminants in vegetables include As, Cd and Pb. These metals can pose a significant health risk to humans, particularly in elevated concentrations above the very low body requirements (Gupta and Gupta, 1998). Unfortunately, much of the land not currently utilised is often far from centres of population where infrastructure is poor. In addition, nearly 40% of this land is found in only three countries (the Democratic Republicof the Congo, Nigeria and the Sudan) (Velissariou, 1992), so the potential for agricultural extensification and associated benefits are likely to be unevenly distributed across the region.

Although the presence of heavy metals like Cd, Cu and Zn in the soil has been considered to be one of the environmental constraints to growth of several crops including maize and wheat (Mishra and Choudhuri, 1999; Hall,2002; Kalisova-Spirochova *et al*.,2003;Keller *et al*.,2003; Mantovi *et al*.,2003; Chan and Hale,2004), not much information is available on the actual uptake in the plant parts, translocation and accumulation patterns of these metals in the plants particularly in the sudan savanna of Nigeria. There is also limited information on the incorporation of ecotoxicity studies with agricultural land use management in crop productivity.

Due to the foregoing, it becomes significant to emphasize the role of eco-toxicological researches in crop productivity and land use management practices which is still at its infancy in northern Nigeria. It is also important to highlight the role of toxic metals in food chain contamination and their attendant health risks.A large proportion of maize and wheat cultivation in Nigeria is at a subsistence level in farms that are commonly located near major highways and industries due to availability and accessibility of land and accessibility to markets.

Given the relatively short period of elevated emissions in many regions, it is crucial to ascertain the immediate effects of air pollutants before considering these longer-term impacts (Emberson, 2012). There is also little evidence that productive crop systems are sensitive to atmospheric metallic components deposition, since the impact of air pollutants on crop production as well as the economic significance is likely of greatest concern in most developing countries.

At present, there is no scientific documentation on the ecotoxicity of these metal levels on roadside grown wheat and maize in the Sudan savanna ecological zone of Nigeria. However, reports on the potential of cereal crops to grow in metal-contaminated soils in field conditions are scarce. Most of the work done on maize prior to 1950 and wheat prior to 1959 can be described as agronomic. Given the poor nutrition and sanitation in these areas of Nigeria, an appreciable increase in heavy metal concentrations in the environment could cause adverse health effects particularly in the able-bodied farmers, women and children who are the main maize and wheat producers and processers respectively. Maize and wheat are the most widely used articles of human diet worldwide, and most widely cultivated cereals in Nigeria especially in northern Nigeria. Wheat is the major raw material for the production of bread, biscuits and pastas (like macaroni, spaghetti and noodles), cakes, pastry, crackers etc. Among all irrigated crops, Wheat tends to be the most profitable enterprise in the wheat growing zones of Nigeria (Orakwue *et al*.,1990). Maize being the largest of all cereals is the only cereal that is used in so many ways. Maize is one of the major foods crop as well as a source of raw materials for livestock feeds, manure, fuel and industries, utilized by millions of Nigerians. Maize production in the northern Guinea savanna offers greater yield potential than the forest agroecology (Ishaya, 2002).

In this study, the ecotoxicological effects of Cd, Cr, Cu, Pb and Zn in a small field-scale study using developmental stages of wheat (*Triticum aestivum* L.), yellow maize (*Zea mays* L.) and popcorn (*Zea mays everta* L.*)* were used as model crops. Not only is wheat one of the most important food crops, it is also easier to culture, to maintain in laboratory conditions, and even to use in toxicity tests for examining the effects of heavy metals especially cadmium (Henning *et al*., 2001). This research therefore is aimed at investigating the heavy metal levels in the roadside soil and plant parts obtained from cultivated farmlands along highways.

It is worth considering briefly how agriculture in these regions has changed in recent years and the impact this may have, both now and in the future, on sustainable food production for the needs of the human population. It is especially important to consider air pollution impacts in the context of other environmental constraints on agriculture, since the added stress of air pollution may well compound and exacerbate environmental problems that are perhaps currently more widely acknowledged.

Developing countries currently comprise about 52% of the world arable land and 75% of the world population. In the future, the area covered by arable land is expected to stay the same or decline, in contrast the population of developing countries is expected to increase to 90% of the world total by 2050. Furthermore, at least three billion (about 30% of the population) will live in arid and semi-arid regions with severe water shortage problems and desertification (Lal, 2000). A study by UNEP (2000) reveals that the area of arable land available per head of population is decreasing in all regions, and that the global availability of cropland has now fallen by 25% over the past two decades (Emberson, 2012). As a result of declining food security, the number of undernourished people in Africa nearly doubled from 100 million in the late 1960s to nearly 200 million in 1995 (UNEP, 2000). However, the agricultural potential of the country has not yet been fully realised; of an estimated 632 million hectares of arable land in Africa, only 179 million hectares are currently cultivated (FAO, 1997). Unfortunately, much of the land not currently utilised is often far from centres of population where infrastructure is poor.

Several studies have been conducted in Nigeria on atmospheric heavy metal contamination in vegetables (Sridhar, 1988; Adeniyi 1996; Fatoki, 1996; Uwah *et al.*,2009), but not much research has been carried out with regard to atmospheric metal pollution in the plant parts of cereal crops, whose fodders are also used as forage crops for livestock. This study is the first of it kind in the Sudan savanna.

The research therefore aimed at evaluating the accumulation patterns of the Cu, Cr, Cd, Pb, Zn in plant tissues (leaves, stems and roots) of two varieties of wheat, popcorn and yellow maize in cultivated farmlands near roadside with high traffic volume.

1.3 Aim

The main aim of the present study was an assessment of the status of metal contamination of the cereal crops cultivated on soils of the Kano-Zaria Highway, Kadawa, Kano State, Nigeria.

1.4 Objectives

This study will therefore focus on six main objectives,

1. To assesses the status of heavy metal concentrations in the soils at the Kano-Zaria Highway and at the Irrigation Research Station, Kadawa in the Sudan Savanna area of Nigeria.

2. to determine the heavy metal concentration (Cr, Cd, Pb, Zn, Cu) in the plant parts (leaves, stems and roots) of the two varieties of wheat, popcorn and yellow maize at the different growth stages.
3. to determine whether differences between the two varieties of wheat, popcorn and maize accumulation patterns for Cr, Cd, Pb, Zn, Cu remained consistent throughout the life cycle.
4. to identify the routes of metal accumulation in the two varieties of wheat, popcorn and yellow maize
5. to measure the soil-plant transfer coefficient (TC), Plant uptake Factor (PUF) and the translocation factor (TF) in the crops and their relationships and to indicate the toxicity order of heavy metals in the crops.
6. to identify which of the two varieties of wheat, popcorn and maize has a high accumulation potential.

1.5. Hypotheses

1. There is no significant difference in the soil heavy metal concentration at the Kano-Zaria Highway and Irrigation Research Station, Kadawa, Kano State.
2. There is no significant difference in the metal concentrations of the roots, stems and leaves of maize and wheat at the six different growth stages.
3. There is no significant difference in the sources of trace metal accumulation in the two varieties of maize and wheat.
4. There is no significant difference in the accumulation potential of the two varieties of wheat, popcorn and maize**.**
5. There is no significant difference in the soil-plant Transfer Coefficient (TC), Plant uptake Factor (PUF) and translocation (TF) and the toxicity level of trace metals in the crops.

6. There is no significant difference in the accumulation potentials of each of the varieties of wheat, popcorn and maize

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Cereals

2.1.1 Historical background.

Cereals have existed throughout history and are unquestionably the most important sources of food for humans and livestock. All of the original ancestors of cereals have been lost over the millennia that they have been cultivated. The development of all the major cereals occurred long before recorded history for all the oldest civilizations were already familiar with several kinds of barley, wheat and other grains. Also the actual origin of these cereals had been so long forgotten that they were given supernatural powers and played a part in the religious ceremonies of the various nations of Antiquity (Economic Plants Index, 2005).

In ancient Rome they held festivals at seedling time and harvest in honour of the goddess of Ceres, whom they worshipped as the giver of grain. They brought offerings of wheat and barley to these festivals, the "cerealia munera" or gift of Ceres, from which the name 'cereals" was derived. In ancient Greece, similar religious ceremonies were observed. In America, the natives of Mexico worshipped an agricultural deity to whom they brought the first fruits of their harvest (Economic Plants Index, 2005).

All cereals are members of the grass family, Gramineae, and are similar in possessing the characteristic fruit of that family, the Karyopsis. The term 'grain" is given either to this type of fruit or to the plant that produces it. There are six true cereals in the world today, which are wheat, rye, oats, barley, rice and maize. Among these wheat, maize and rice are the most important, and each has played roles in the development of civilizations. The millets, sorghums and even buckwheat are often referred to as cereals, but they belong to a different classification.

2.1.2 Importance of cereals.

There are many reasons why cereals are such important crops. One or more of these grasses is available in each of the different world climates. The northern regions have barley and rye, the temperate regions wheat and the tropics and warmer temperate areas, rice and maize.

Cereals also have wide ranges of soil and moisture requirements. They can be cultivated with a small amount of effort and give a high yield. The grains are relatively easy to handle and store because of their low water content, and they are very high in food value. Cereals contain a higher percentage of carbohydrates than any other food plants as well as a considerable amount of protein and some fats. There are even vitamins. In modern times, the quest for greater yields has sometimes sacrificed flavour, and low yielding varieties that may possess characteristics of quality are gradually being ignored or even lost. This is especially noticeable in the cold cereal industry that produces an array of products few of which match up in flavour or texture to those of the earlier 20th century. Some high latitude areas of South America have managed to continue production of superior cold cereal products for local consumption.

2.2 Wheat

2.2.1 Historical background.

This is the most widely grown cereal of temperate regions. Its native home is not definitely known because it is so ancient. There are some indications that highlands in Syria and Palestine might be the place of origin, but the central Asian plateau and the Tigris and Euphrates valleys might be included. Of course Vavilov considered wheat to have had multiple origins, the soft wheat originating in the mountains of Afghanistan and the southwestern Himalayas, while the durum or hard wheat may be from Abyssinia, Algeria and Greece and the einkorn variety from Asia Minor. Archeological evidence indicates that wheat had already been cultivated by earlier than 4,000 B.C. Wheat was at the core of Babylonian civilization and it was cultivated by all the other Old World Nations of antiquity. Aristotle, Pling and Theophrastus all mentioned numerous varieties of wheat. In China it was grown by 2,700 B.C and was used by the lake Dwellers of Switzerland and Hungary, civilizations that go back to the Stone Age. Wheat was first introduced into America at Mexico in 1529. Wheat was sown in New England in 1602 and it reached Virginia by 1611, California by 1769 and Minnesota by 1845 (Hill, 1952).

2.2.2 Characteristics of wheat

Wheat is an annual grass in the genus *Triticum* that comprises a large number of wild as well as cultivated species. The wild species are often weeds. Cultivated Wheat, *Triticum aestivum*, reaches a height of 2-4 ft. The flower is a terminal spike or head consisting of 15-20 spikelets that are borne on a zigzag axis. Individual spikelets are sessile and solitary, consisting of 1-5 flowers each. The mature grain consists of the embryo (6%), a starchy endosperm (82-86%), the nitrogenous aleurone layer (3-4%) and the husk or bran (8-9%). The husk is made up of the remains of the nucellus, the integuments of the seed coat and the ovary walls or pericarp.

2.2.3 Kinds of wheat

Innumerable species and varieties of wheat have arisen over its long period of cultivation. This was the result of intentional or unintentional selection on the part of humans of forms that had some particularly desirable qualities. Eight principal kinds of wheat were differentiated as species by Hackel:

- Einkorn Wheat. *Triticum monococcum* is the most primitive and is called the “one-grained wheat” because it has only one fruit in each spikelet. It is one of the oldest species dating back to the Stone Age. It is usually grown in very poor soil and will therefore be useful in regions where other types cannot survive. It is a small plant about 2 feet in height with a very low yield. It is still cultivated to some extent in mountainous regions of southern Europe, especially in Spain. It is used primarily for animal feed and grown for experimental purposes.

- Emmer Wheat. *Triticum dicoccum* is also known as “starch wheat”, “Rice wheat” or “Two-grained spelt”. It has flattened head with bristles or awns. It is another very old type that was grown in Babylonia and by all the early Mediterranean civilizations and the lake Dwellers of Europe. It is still cultivated in the mountainous areas of Italy, Spain, Germany, Switzerland, Russia and United States. It thrives in dry soil and is used for livestock and breakfast foods and in experimental breeding efforts.
- Spelt Wheat: *Triticum spelta* is another primitive wheat of antiquity. Spelt is hardy and can be grown in the poorest soils. It had been cultivated in the Mediterranean region for centuries and is still grown in Spain. In North America is has been used a livestock feed.
- Polish Wheat: *Triticum polonicum* is also known as the giant rye”, has a very characteristic appearance due to the long papery bracts surrounding each spikelets. The stems are solid and the bluish-green ears are flattened. The species is of comparatively recent origin. Despite its name it did not originate in Poland. It has been grown chiefly in Spain and Italy, Turkestan and Abyssinia. It is a large plant with small yield of little value.
- Poulard Wheat: also known as “English wheat” or River wheat: *Triticum turgidum,* is an old species that probably originated in dry portions of the southern Mediterranean region. The heads are large but the yield is small and is only of important in England. Elsewhere, it is grown only in small quantity.
- Club Wheat: *Triticum compactum (tenax),* also called “Dwarf wheat” or “Hedgehog wheat” is different from all others species in having short compact heads and small kernels. The plants are small and have a very stiff and strong straw. Club wheat is well

adapted to poor soil and is grown chiefly in the mountainous areas of central Europe, Abyssinia and Turkestan. It has been grown in Chile and in the Western United States. The grains are soft and have low protein content, so the flour is not used for bread but rather for pastry flour.

- Durum Wheat: *Triticum durum* has a thick head with long stiff beards and large, hard, amber or red grains that are rich in gluten. This species has been cultivated for a long time in the arid regions of the Old World. It is the main wheat in Spain and is also gown in Algeria, India and Russia. It was introduced into North America from Russia and has been extremely valuable. The low rainfall and high temperatures typical of the Great Plains renders the region unsuitable for most other crops without irrigation. They are very hardy and drought tolerant. Their high gluten content makes them especially suitable for macaroni, semolina and other types of pastas. They are mixed with other flour in bread making. Red durum wheat is used for livestock.
- Common Wheat: *Triticum vulgare* is the principal source of bread flour. This wheat occurs in innumerable varieties differing in both external morphological and physiological characteristics. There are bearded and beardless varieties, red and white varieties and hard and soft varieties. The hard wheats are richer in proteins and usually have small grains; the soft wheats produce large grains that are richer in starch. The physiological characteristics include such things as yield per acre, late or early maturing, resistance to drought, cold or disease, behaviour in milling and baking, and the season that they are sown (spring winter). Spring wheat is sown in the spring and harvested in late summer while winter wheat is planted in the autumn. Winter wheat has a higher yield, is more resistant to disease and matures earlier.
- Timopheevi Wheat: *Triticum timopheevi* is from Russia and is especially resistant to disease and thus has been used in breeding programs with standard varieties.

2.2.4 Wheat production and consumption.

The world production of wheat increases steadily with the United States producing over one quarter the amount. Kansas and North Dakota are the leading states. Other large wheat producing countries are Russia, China, Canada, India, France, Italy, Germany, Argentina, Turkey and Australia.

France has led in the per capita consumption of wheat, followed by New Zealand, Australia, the United States, Great Britain, Germany and Canada. The United States per capita consumption of wheat was once estimated at 4.5 bushels (Kochhar, 1986).

Wheat is best adapted to moderately dry temperate climate and is not grown in warm humid regions. Climates with a growing season of at least 90 days and annual rainfall of not less than 9 inches are essential; over 30 inches of rain is detrimental. Generally regions with a cool moist spring merging into warm, bright, dry harvest periods are best, but the various kinds of wheat differ in their requirements. Good climatic conditions for wheat are found in nine different areas in the world and these are the principal wheat-producing regions. They include the plains of southern Russia and the Danube, the Mediterranean countries Northwestern Europe, the central plains of the United States and Canada, the Columbia River Basin in the Pacific Northwest, Northwest India, north central China, Argentina and Southeast Australia (Kochhar, 1986)

2.2.5 Historical background and wheat production in Nigeria.

Wheat was introduced to West Africa by the Arabs in the 12th Century. The cultivation of the crop in Nigeria dated many centuries and was grown mainly in the Sahel and Sudan savanna zones, usually in the low lying poorly drained soils of the Fadama along river banks and irrigated by Shaduf system (Olugbemi *et al.*, 1989). Today wheat is grown commercially in some areas lying between latitudes 10-14^{o}N, mainly the Sudan sand Sahel zones, where the cool "Harmattan" period lasting from about November to February provides the required climatic conditions for the growth and development of the crops. Since this period falls within the dry season, commercial cultivation of the crop in the country is presently by irrigation.

In Old Kano state, wheat cultivation started long before the colonial time particularly in Mai Alkama area of Hadeijia Local Government (Olugbemi *et al.*, 1989). Its cultivation in this area started declining after the construction of the Tiga Dam when the amount of flood in the Hadeijia valley area declined.

Three of the 11 River Basin schemes established in the country in 1976, namely, the ChadBasin (Borno state), the Sokoto-RimaRiver Basin (SokotoState) and Hadeijia-Jama'are River Basin (Kano State) schemes which are located in the Sudan Savanna and Sahelian zones were to grow wheat primarily (Olugbemi *et al*, 1989). The three irrigation schemes according to projections were to irrigate a total of 345,000 hectares of land by 1990. About 50% of the land area was to go into wheat and the rest into the production of vegetables, rice, cotton and sugarcane. The crop is usually grown in November/December and harvested in March/April (Olugbemi *et al.*, 1989)

The 1987 ban onWheat importation into Nigeria led to increased production of Wheat particularly in Kano State. In 1988/89 season, a total of 213,881 hectares of land was said to have been put into wheat in Nigeria, from which 81.78 percent was in Kano State since then local wheat production in Kano State and Nigeria as a whole made a remarkable and commendable progress in recent years (Olugbemi *et al*., 1989).

Currently, feasibility trials of rainfed wheat have been conducted in some northern states such as Adamawa and Taraba.

2.2.6 Wheat products

Wheat products are almost certainly the most widely used articles of the human diet. The flour is used mainly for making wheat bread. Where other cereals are used, the produce is called corn bread or rye bread, etc. The hard wheat provides bread flour while the flour from soft wheat is used for cakes, biscuits, pastry, crackers, etc. Other edible by-products are breakfast foods and the various farinas; and the pastas such as macaroni, spaghetti and noodles. Semolina and Durum wheat are used for macaroni.

Wheat is also used in the manufacture of beer and other alcoholic beverages and industrial alcohol. It is an excellent livestock feed and a special kind is grown for the preparation of starch for use in the sizing of textile fibers. Wheat straw excels all other kinds because of its very great strength. It has been used for seats of chairs, mattress stuffing and the manufacture of such diverse articles as straw carpets, string, baskets, beehives and wickerwork. Leghorn hats are straw hats made from the beaded wheat of Tuscany. Wheat straw is also used for packing and thatching and as fodder and manure. The entire wheat plant is also a valuable source of fodder (Kochhar, 1986).

2.3 Maize

2.3.1 Historical background.

Indian corn or maize, *Zea mays*, is America’s main contribution to the important group of cereals. Maize had been thought to have originated in a wild state in the lowlands of Southern Mexico and Central America from which it spread to the Andes where its cultivation goes back to prehistoric time. The ancestor was probably teosinte a primitive ancestor that bore a single row of kernels in a husk. Selection in Southern Mexico resulted in a cob with several rows of kernels. Later development produced the longer cob or ear familiar as the commercial maize of modern times. Grains of this later variety of maize found in the tombs of the Incas in Peru represent several different varieties, so that the plant must have been grown for many centuries prior even to the period of the Inca civilization. From Peru it has been thought to have moved northward again and played a prominent role in the civilization of the Mayas and Aztecs. The Amerindians in New Mexico grew it as early as 2,000 B.C. By the time of Columbus, maize was growing all the way from the Great lakes and the lower St. Lawrence valley to Chile and Argentina (Kochhar, 1986).

Maize was introduced into Europe by Columbus, or possibly earlier, and into Asia by earlier Portuguese explorers. It is now grown worldwide. Large yields are possible from maize even under primitive conditions of agriculture (Kochhar, 1986).

2.3.1.1 Historical background, maize productionand consumption in Nigeria.

In Nigeria, maize (*Zea mays* L.) is used both for human consumption and for livestock feed. It is eaten either at the green stage, as boiled or roasted ears, or dried and prepared into a jelly-like “pap” or “eko” (Alika *et al*., 1990). Palady *et al*., (1986) observed that in Africa, a temporary but critical period of food shortage exists at the beginning of the rainy season and that this period is commonly known as “hunger season". During this period, which may be prolonged due to unfavorable weather conditions, the first food crop to be harvested is usually maize. It is commonly picked at the green stage when the silks have turned brown and is eaten off the cob as boiled or roasted ears (Alika *et al*., 1988). Maize has been in the diet of Nigerians for centuries. It started as a subsistence crop and has gradually become more important crop. Maize has now risen to a commercial crop on which many agro-based industries depend on as raw materials (Iken and Amusa, 2004). Although maize is increasingly being utilized for livestock feed, it is still a very important staple food for millions of Nigerians (Iken and Amusa, 2004). Yellow maize varieties are increasingly being requested for producing livestock feed in order to impart yellow color on the egg yolk (Iken and Amusa, 2004).

Popcorn (*Zea mays everta*) grown solely for human consumption in the developed countries has now become a popular and cherished snack for several decades in Nigeria (Iken and Amusa, 2010). The production and utilization of popcorn enhances the availability of the field corn for livestock and for other industrial uses. Popcorn has approximately the same chemical composition and feeding value as feed corn. The use of popcorn confections, the rapid increase in the use of popcorn as snacks at amusement parks, motion- picture theatres, or around family televisions and while traveling, has greatly increased the demand for popcorn, thus making it a profitable outlet for commercial production. Popcorn is a delight of millions to eat and enjoy (Iken, 1991). The Nupe popcorn women hawkers have been most popular in the south-westerns parts of the country for many years. Demand for popcorn increased very sharply from the mid-seventies resulting in large scale roadside vending in big town and cities. This was possible due to the introduction of popping technology (Iken and Amusa, 2004). The ready-to-eat popcorn segment led the popcorn market in Nigeria in 2009, with a share of 76.7% (Research and Market Brochure, 2013).

Until recent years, the bulk of grain produced in Nigeria was from the southwest zone. Ogunbodede and Olakojo (2001) reported that western Nigeria generally produced about 50% of Nigerian green maize, the remaining 50% being split between the north and the east. Although, large proportion of the green maize is still produce of the south-western part, there has been a dramatic shift of dry grain production to the savanna especially the northern Guinea savanna. This can now be regarded as the maize belt of Nigeria (Iken and Amusa, 2004). The Federal Government imposed ban on the importation of rice, maize and wheat had geared up local production to meet the demands for direct human consumption, breweries, pharmaceutical companies, baby cereals, livestock feeds and other industries (Iken and Amusa, 2004). Maize is most productive in the middle and northern belts of Nigeria, where sunshine is adequate and rainfall is moderate (Obi, 1991).

2.3.2 Characteristics of maize

The largest of all cereals, maize is a tall annual grass that can attain a height of 3-15ft. The jointed stem is solid and contains a considerable amount of sugar when not mature. The leaves are large and narrow with wavy margins and an extensive fibrous root system with aerial prop roots at the base of the stem. There are two kinds of flowers, the tassel at the top of stem which bears the staminate flowers and the cob or ear with pistillate flowers. The ear is produced lower down on the stalk and protected by the leaves. The ovary has a long silky style or corn silk later becomes the mature grains, and is produced in rows on the cob. The grains have a hull (6%), protein or aleurone layer (8-14%), endosperm (70%) and embryo (11%). There are two kinds of endosperm present: a hard, yellow endosperm and a soft white starchy endosperm (Kochhar, 1986).

2.3.3 Kinds of maize

There are no known wild species of the genus *Zea,* but the original ancestor was most likely a pod corn that gave rise to maize through hybridization between some species of *Tripsacum* and Teosinte, *Euchlaena mexicana,* a wild relative in Mexico. It is comparatively easy to perform breeding trials with maize; even the Amerindians had learnt how to select, produce and preserve the best varieties that gave rise to easily cultivated and rapidly maturing varieties.

No other cereal has so many different varieties that fall into seven quite distinct classes, all of which breed true to type. Although they readily hybridize, there are very little intermediate types produced. The classes differ mainly in the nature of the endosperm and the shape of the grain and have been considered by some authorities to be species and others to be varieties. Hill (1952) believed that they should be considered as agronomic groups. These are

a. Pod Maize**:** called pod Maize because each grain is covered with a husk in pod maize. The plant is very leafy and the tassels are heavy. The grains may resemble those of any of the succeeding types, which suggest that pod maize might be very close to the primitive form from which the others had been derived. Pod maize has little if any commercial value.

b. Flint Maize**:** The embryo and white endosperm are entirely surrounded by the hard endosperm in flint maize leaving an undented grain. Plants attain a height of 5-9ft; and tend to have two ears. The ears are long and cylindrical with hard smooth grains in 8-16rows that tend toward different colours. Flint maize matures early and so is grown in New England and other colder areas of North America.

c. Dent Maize**:** derives it name by the extension of the endosperm to the top of the grain with the hard endosperm being present only on the side. This causes an indentation of the mature grain at the top due to the shrinking of the softer material. This is the largest maize with the stems sometimes attaining a height of 15ft producing only one ear. They are very large, up to 10 inches long, weighing three-quarter pounds and sometimes having as many rows as 48 rows. The deep wedge-shaped grains are generally yellow or white. Dent maize is the main type grown in the Corn Belt of the United States as it gives an enormous yield. It is the source of most of the commercial grain and also of livestock fodder and ensilage. Over 330 varieties have been developed.

d. Soft or flour Maize**:** This is a very old type that was extensively cultivated by the Amerindians because of the ease with which it could be crushed. Soft maize completely lacks an endosperm. The grains resemble flint maize in shape and appearance, but the size varies from small forms to the large Cuzco variety of Peru that are ¾ inches or more in diameter. Over 30 different varieties are known. Maturity is very late in the season and it is not grown in any quantity in North America.

e. Sweet Maize: The entire endosperm is translucent, and the starch has been partially changed to sugar. The grains are broad and wedge-shaped with a typical wrinkled surface. The plant is adapted to the cooler areas and is the main type grown in northern areas of North America for canning purposes. The grain is used in the unripe state. Over 65 varieties have been developed.

f. Waxy Maize**:** The endosperm is waxy and the carbohydrates material occurs in a different form from that in other varieties. It is used as a substitute for tapioca. The starch is entirely amylopectin, whereas ordinary cornstarch is a mixture of amylopectin and amylose.

g. Pop Maize**:** The grains are usually elongated and oval. Although small in size, they are exceptionally hard and flinty with a tough hull. The endosperm is mostly of the hard glossy variety. It is also called popcorn, because the grains explode forming a snow-white, fluffy, palatable mass, on exposure to high temperatures. This results as the sudden expansion of the soft endosperm that turns the grain inside out. It is probably due to the expansion of the moisture content of each individual starch grain after partial hydrolysis during the heating phase. There are two kinds of popcorn; rice popcorn, in which the grains are pointed and tend to be imbricated, and pearl popcorn, in which the grains are rounded and very compact. The plants produce a large number of small ears. This type of maize was undoubtedly grown in prehistoric time. There are over 25 different varieties grown for human consumption.

2.3.4 Maize production

Usually the United States produces nearly one-half the world's supply of maize. Iowa and Illinois are the leading states, but through irrigation other states have begun to produce it also and various amounts are grown in every other state as well. The utilization of hybrid maize has greatly increased the production. The yield from hybrid seed has increased from 5-15 bushels per acre. The raising of hybrid corn and the production of the seeds has become an important enterprise. In order of amount produced, the United States leads the world followed by China, Argentina, Brazil, India, Mexico, South Africa, Italy and Russia (Kochhar, 1986).

Maize requires very definite environmental conditions for proper development. The plant does best in a fertile, friable, well-drained alluvium, such as the deep, warm, black loams along river bottoms and in drained swamps. These soils must have high organic and nitrogen contents and must not bake out. Additionally, temperature, sunlight and moisture are limiting factors. The temperature of both the air and soil is important, especially during the growing season from May to September in the Northern Hemisphere (November to March in the Southern Hemisphere). A mean average summer temperature of 75 degree Fahrenheit is optimum, but temperatures below 66 degree Fahrenheit are detrimental. Cloudy days hinder development. Adequate moisture is essential, with the optimum being a 20-inch annual rainfall occurring mostly in summer. There is a great difference in growth habit under different climatic conditions and there are varieties adapted to each type. A continental climate is most favourable. The growing season varies from 90-160 days, depending on the locality.

There are relatively few regions that have the right combination of the necessary environmental conditions and where maize can be raised as a commercial crop on a large scale. The principal maize growing regions of the world include the east, central and middle western United States; the Mexican plateau; the Argentine pampas; the highlands of Brazil; the basins of the Danube, Dnieper and Po River in Europe, northern India; China and Manchuria; Vietnam; Java; the Nile valley and South Africa. The most prolific area for maize is the great Corn Belt of the United States, located in the Mississippi valley in the states of Illinois, Indiana, Missouri, Iowa, Kansas and Nebraska (Kochhar, 1986).

2.3.5 Uses of maize

No cereal is used in so many ways as maize. About one-half of the crop is used as a food for livestock. The grain is very nutritious with a high percentage of easily digested carbohydrates, fats and proteins and very few deleterious substances. The pork industry is dependent almost entirely on maize in the United States and has used about 40 percent of the total amount raised. Cattle, horses and other domestic animals are also fed maize. It has been estimated that 10-12lbs. of maize is converted into 1-lb. of beef, while 5-6lbs. yields 1-lb of pork. Not only is the grain valuable as a livestock feed but the entire plant is an important fodder. It can be used green, dried or as silage. Stover, the residue after the ears have been removed, is also fed to cattle or used for silage.

2.4. The Effects of Air Pollutants on Vegetation

Currently, the air pollutants considered to be the most important in causing direct damage to vegetation are SO_2, NOx, O_3, F and SPM. Direct effects of air pollution can be further classified into visible and invisible injury. Visible injury normally takes the form of discolourations of the leaf surface caused by internal cellular damage. Such injury can reduce the market value of agricultural crops for which visual appearance is important (e.g tobacco and spinach). It can also lead to yield reductions, while the damaged parts of the leaf surface can provide points of entry for plant pathogens. Invisible injury results from pollutant impacts on plant physiological or biochemical processes and can lead to significant loss of growth or yield and changes in nutritional quality (e.g. protein content) (Ashmore and Marshall, 1999).

Visible injury tends to be associated with short-term exposures to high pollutant levels whilst invisible injury is generally a consequence of longer-term exposures to moderately elevated pollution concentrations. While visible injury can be identified in the field, loss of yield can only be identified with suitable control plants, and so can go undetected especially if there is little awareness of air pollution issues.

2.4.1 What is suspended particulate matter?

Suspended particulate matter (SPM) includes finely divided solids or liquids that range in size from 0.1 to approximately 25μm in diameter. However, the most common measure of particles used to quantify pollutant concentrations in developed countries is now PM_{10}, the abbreviation for particulate matter having an aerodynamic diameter less than 10 mm. This is the size range that includes the majority of the total suspended particles in the atmosphere by mass (Beckett *et al.*,1998). SPMs can be categorised into two groups viz, primary particles are emitted directly from source (e.g. from vehicle exhausts), and secondary particles are formed by interactions with other compounds, e.g. nitrate formation from the photo-oxidation of NOx. SPM tends to be an urban pollutant; however this does depend on the size of the particles under consideration. This is the reason for higher rates of deposition closer to particle emission sources and the classification of SPM as a local pollutant. Emission sources of SPM in developing regions may well differ from those in developed regions; for example forest fires, local industry and less developed infrastructure may contribute significantly to atmospheric SPM load.

The term "heavy metals" has received widespread usage for metals that are potentiallytoxic in high doses. The elements having a specific gravity > 4.5 g/cm3 (sometimes defined as 5.0 or 6.0) are called heavy metals (Streit and Stumm, 1993). Except for theirspecific gravity, heavy metals have no common chemical property or behaviour in biological or ecological systems (Salemaa, 2004).

2.4.2 Phytotoxicity of suspended particulate matter (SPM) on vegetation.

SPM can produce a wide variety of effects on the physiology of vegetation that in many cases depend on the chemical composition of the particles. Heavy metals and other toxic particles have been shown to cause damage and death of some species as a result of both the phytotoxicity and the abrasive action during turbulent deposition. Heavy loads of particles can also result in reduced light transmission to the chloroplasts and the occlusion of stomata, decreasing the efficiency of gaseous exchange (and hence water loss). They may also disrupt other physiological processes such as bud-break, pollination and light absorption/reflectance. Indirect effects of particulate deposition such as predisposition of plants to infection by pathogens and the long-term alteration of genetic structure have also been reported. In contrast, a few instances of particle deposition producing positive growth responses have also been observed and related to the capture and utilisation of nutrient particles from the atmosphere (Beckett *et al.*,1998).

Heavy metals can cause severe phytotoxicity and may act as powerful force for the evolution of tolerant plant populations. Therefore, it is possible to identify metal-tolerant plant species from natural vegetation in the field sites that are contaminated with various heavy metals (Nazir *et al.*,2011). Hyperaccumulation of metals have been found in temperate as well as tropical regions throughout the plant kingdom, but is generally restricted to endemic plant species growing on mineralized soil and related rock types (Baker *et al.*,1989).

The atmospheric deposition of heavy metals on ecosystems occurs mainly inparticulate and aerosol forms (Ross, 1994a; Luttermann and Freedman 2000). The area affected by the deposition of heavy metal containing particles is usually much morelocal than that of gaseous pollutants. The rates of deposition, either dry or wet, tend to be greatest near the pollution source. However, small particles are transported over longer distances, and have longer atmospheric residence times than larger ones (Hutchinson and Whitby, 1977). The factors that may affect the fate of atmospheric metal depositionin the receiving plant - soil systems include particle size, solubility, distance of thereceiving system from the metal source, and acidity of rainfall (Ross, 1994a). The phytotoxicity of heavy metals depends on their bioavailability, which is related to their occurrence in different chemical forms (Alva *et al.*,2000). Becausemany heavy metals are bound on plant surfaces and tissues (Rautio and Huttunen, 2003) and form stable complexes with organic matter in the soil (Alloway, 1995b), they may still have a long-lasting effect on forest ecosystems after the emissions have ceased (Ross, 1994a).

2.5. Food Chain Contamination by Heavy Metal and its Toxicity

Heavy metals are chemical elements mostly with density greater than 4g/cm3 found in all kinds of soils, rocks and water in terrestrial and freshwater ecosystems. The very low general level of their content in soils and plants as well as the definite biological roles of most of them makes them microelements (Lacatusu, 1998). They occur in typical background concentrations in these ecosystems. However anthropogenic releases can result in higher concentrations of these metals relative to their normal background values. When these occur, heavy metals are considered serious pollutants because of toxicity, persistence and nondegradable conditions in the environment, thereby constituting threat to human beings and other forms of biological life (Tam and Wong, 2000; Yuan *et al.*,2004; Nwuche and Ugoji, 2008; Aina *et al.*,2009; Mohiuddin *et al.*,2010).

Heavy metal pollution refers to cases where the quantities of these elements in soils are higher than the maximum allowable concentrations, and this is potentially harmful to biological life at such locations. As noted by Gazso (2001), heavy metals come from a variety of sources but human economic activities are principally responsible. Some of the heavy metals such as Cu, Ni and Zn are essential to plants and animals in very low concentrations by serving as components of enzymes, structural proteins, pigments and also helping to maintain the ionic balance of cells (Kosolapov *et al.*,2004). These and other heavy elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders.

Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air. Quarles *et al*., (1974) and Goldsmith and Scanlon (1977) reported that species high on the food chains are particularly vulnerable to heavy metal contamination. Goldsmith and Scanlon (1977) found low concentrations of Pb in insects and speculated that high Pb concentrationsin shrews were results of ingestion of other food probably earthworms. Among mammals, Scanlon (1980) found a considerably higher concentration of contaminants in shrew species than in such plant consuming species like *Peromyscus* and *Microtus.*Scanlon (1980) also reported a higher concentrations of heavy metals in shrews at the control areas, remarked that extremely high concentrations of heavy metals in earthworms may have been a source of contamination of the shrew species. As observed by Begum *et al*., (2009), large quantities of pollutants have continuously been introduced into ecosystems as a consequence of urbanization and industrial processes. Metals are persistent pollutants that can be biomagnified in the food chains, becoming increasingly dangerous to human beings and wildlife. A risk for contamination of the food chain may arise when heavy metals accumulate in plant tissues to concentrations above the admitted threshold level which is considered to represent a threat to humans or animals feeding on the same crops. Several works have attributed the major cause of livestock loss in farming to poisonous plants (Duffus, 1980). Improvement of crops for their efficiency in utilizing mineral nutrients, together with increasing concentrations of metals in soil, could increase the risk for an eventual ecosystem contamination. Besides interfering with micronutrient flow in plants and crops, heavy metals can affect soil quality and health also by influencing microbial enzymatic activities and microbial biomass (Kuperman and Carreiro, 1997; Anongo *et al*., 2005). Plant accumulation of metals depends on the bioavailability of the metal and physiological processes in the soil, and on the atmospheric deposition, either directly entering the plants through stomata or taken up by plant roots after its deposition on the soil surface (Alloway,1995;Haiyan and Stuanes,2003). Therefore, assessing the concentrations of pollutants in different components of the ecosystem has become an important task in preventing risk to natural life and public health.

Some of these heavy metals can be detrimental to human, plant and animal life if they are present above certain limits. Thuy *et al*., 2007 indicated that heavy metals are one of the pollutants of most concern around the world. Elevated concentrations of heavy metals in harvested plant tissue could expose consumers to excessive levels of potentially hazardous chemicals (Antonious *et al*., 2011). Cadmium and lead are the heavy metals of greatest concern to human health since plant can take them up and introduce them into the human food chain. Cadmium may accumulate in the human body and induce kidney dysfunction, skeletal damage and reproductive deficiency (European Commission Regulation, 2002). The primary Cd risk posed by the agricultural use of roadside soils is the increased dietary intake of people consuming crops grown on these soils (Antonious *et al*., 2011).

Furthermore, biochemical processes can mobilize them to pollute water supplies and impact food chains. Heavy metals such as Cu, Cr, Cd, Ni, and Pb are potential soil and water pollutants. Globally, the problem of environmental pollution due to heavy metals has begun to cause concern in most large cities since this may lead to geoaccumulation, bioaccumulation and biomagnifications in ecosystems.

Heavy metal contaminants in the environment are eventually deposited in soils in some form of a low solubility compound, such as pyrite (Huerta-Diaz and Morse, 1992) or sorbed on surface-reactive phases, such as Fe and Mn oxides (Cooper *et al.*,2005; Hamilton- Taylor *et al.*,2005). Generally, toxic metals cause enzyme inactivation, damage cells by acting as antimetabolites or form precipitates or chelates with essential metabolites. Lead (Pb) is the most common environmental contaminant found in soils. Unlike other metals, Pb has no biological role, and is potentially toxic to microorganisms (Sobolev and Begonia, 2008). Its excessive accumulation in living organisms is always detrimental. Furthermore, Pb exposure can cause seizures, mental retardation, and behavioral disorders in human beings. Heavy metal exposure to human beings occurs through three primary routes namely inhalation, ingestion and skin absorption. Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson, 2001). Human diseases have resulted from consumption of cadmium contaminated foods.

According to USDA (2000), acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but it is possible. Chronic problems associated with long-term heavy metal exposures are mental lapse (lead); toxicological effects on kidney, liver and gastrointestinal tract (cadmium); skin poisoning and harmful effects on kidneys and the central nervous system (arsenic). There is a link between long term exposure to copper and decline of intelligence in young adolescents (Lenntech, 2009).

The threat that heavy metals pose to human and animal health is aggravated by their low environmental mobility, even under high precipitations, and their long term persistence in the environment (Mench *et al.*,1994; Chirenje *et al.*,2004). For instance, Pb, one of the more persistent metals, was estimated to have a soil retention time of 150 to 5000 years (Sobolev and Begonia, 2008). Also, the average biological half-life of Cd, another accumulation poison similar to lead, has been estimated to be about 18 years (Forstner, 1995; Cheng, 2003).

Studies have shown that short-term exposure and long-term heavy metal contamination of soils has harmful effects on soil microbial activity, especially microbial respiration and enzyme activity (Brookes, 1995; Szili-Kovács *et al.*,1999; Holtan-Hartwig *et al.*,2002; Begonia *et al.*,2004) which manifests in numerous ways (Hemida *et al.*,1997). Moreover, habitats that have high levels of metal contamination show lower numbers of microbes than uncontaminated habitats (Kandeler *et al.*,2000; Anongo *et al.,* 2005). All these have deleterious effects on agriculture, and ultimately human beings. Short-term and long-term effects of pollution differ depending on metal and soil characteristics (Kádár, 1995; Németh and Kádár, 2005). In the after-effect of heavy metal pollutions, the role of pollutant bounding or leaching increases, which determine their bioavailability and toxicity.

The soil-plant barrier limits transmission of many heavy metals through the soil-crop-animal food chain, with the exception of Cd, Zn, Mo, and Se. Cadmium, which has lower affinity for metal-sorbing phases (for example, oxides) has the greatest potential for transmission through the food chain in levels that present risk to consumers (Chaney and Ryan, 1994; Chaney *et al.*,1999). Heavy metal pollution of soil entails plant uptake causing accumulation in plant tissues and eventual phytotoxicity and change of plant community (Ernst 1996; Zayed *et al.*,1998; Gimmler *et al.*,2002).

2.6 Heavy Metal Contamination of Roadside Soils and Vegetation

A large number of studies undertaken on the evaluation of environmental pollution during the last two decades have revealed that motor vehicles are the main source of heavy metal pollution in the environment (Onianwa, 1985; Osibanjo and Ajayi, 1989; Uwagboe and Hymore, 2001; Anongo *et al.*, 2005; Bako *et al.,* 2009a and b).

Roadside soils have long been known to contain high levels of heavy metals (EPA, 1999).There is general agreement that concentrations of metals decrease with depth and distance from the roadway (EPA, 1999; Turer and Maynard, 2003).There is also a general agreement that the extent of contamination of the topsoil and vegetation around roadsides are related to the traffic volume and proximity to the highway (Ho and Tai, 1988). Several studies have also revealed that the levels of heavy metal accumulation in the soil, vegetation, water, sediments and animals are affected by the season, the distance from the roadside, the density of traffic, the wind direction and the proximity to producing industry.

Mclean and Shields (1977), reported that, the lead content of all three crops *(Hordeum, Avena and Solanum)* grown near a motorway was greatest in plants located in a narrow zone by the side of the road, with a significant drop in contents of plant situated between 20-50m from the road, *Hordeum* had the highest lead content. They also observed that, there was reduction in the lead content of *Hordeum* and *Avena* as the leaves withered and fell off, whilst the lead content of *Solanum* crop became greater as leaf surface area increased to a maximum. They concluded that it would be preferable to use crops with low leaf surface area and ground cover, and to avoid crops whose leaves were used for human consumption in sites near heavily commuted roadways, especially if planting occurred within 20m from the edge of the road.

Gratani *et al.,*1992 studied the accumulation of Pb in agricultural soil and vegetation along the Fiano-San Cesareo highway in Italy. They documented an increase of Pb values in the soil within the few years that had passed since the highway was opened. Agricultural soils were found to accumulate more Pb, because the organic matter caused it to be bound to organic exchange sites, reducing its availability for root uptake. They also looked at oak leaves, which showed similar increases in Pb concentration with time.

Similar results have also been reported from Onyari *et al.,*(1992), who worked on roadside soils in Kenya where Pb is still used as a gasoline additive. They found that Pb concentrations within Nairobi City varied from 137 to 2196ppm with a mean of 659ppm. The highest value was measured in the Nairobi hill region, which may be explained by acceleration of motor vehicles because of the steep nature of the hill. The amount of Pb emitted as a percentage of Pb consumed increased as speed increased.

The mean number of plant species was significantly higher on the control site than on the other three sites, while the soil heavy metal contents Pb, Br, Nb, V, Co were generally higher on all the polluted sites than on the control site (Bako *et al*., 2008).

The release of metals into the environment would not pose problems if they were evenly distributed throughout the biosphere. Unfortunately, this is not the case. Anthropogenic activity frequently results in elevated local metal concentrations, even when dispersal is rapid and efficient localized contamination is normally evident. While dispersal helps to ameliorate metal concentrations in the immediate vicinity of the source, the contaminant spreads over a wider area (McEldowney *et al.,*1993). Exhaust emissions and combustion of fossil fuels have been identified as primary sources of atmospheric metallic burden, which finally settle on the soil and water (Ademoroti, 1996; Uwagboe and Hymore, 2001; Anongo *et al.,* 2005; Bako *et al.,* 2009a and b).

The contamination of agricultural soils is often a direct or indirect consequence of anthropogenic activities (McLaughlin *et al.,*1999). Sources of anthropogenic metal contamination in soils include - urban and industrial wastes; mining and smelting of non ferrous metals and metallurgical industries (Singh, 2001). Commercial and residential vegetable growing areas are often located in urban areas, and are subject to anthropogenic contamination.

The concentrations of heavy metals (Cd, Cu, Fe, Pb, Mn and Zn) in the soil and vegetable (*Talinum triangulare*) samples collected from the dumpsites were higher than those from the control sites as reported by Adeniyi (1996). He established that the trend has been observed before by other researchers and may be taken as an indication of pollution of dumpsites. Nevertheless, some of the heavy metals in the control and dumpsites may have been derived from aerial roots through foliar retention and absorption with vehicular traffic as probable pollutant source. He therefore, advised that land use for vegetable production or livestock foraging be restricted to a strip distance of more than 30m away from dumpsites. Similarly, soil heavy metal (Cd, Pb, Zn, Cu) concentrations of four regions in New South Wales, Australia, which were a mix of commercial and residential vegetable growing areas decreases with depth suggesting anthropogenic activities(Kachenko and Singh, 2006).

A predictive model of metal concentrations in forage maize and winter wheat was developed to optimize soil liming and sludge application strategies at a dedicated sewage sludge disposal site operated by a major water company in the UK during the 1999/2000 growing season (Hough *et al.*,2003). The model gave satisfactory predictions for uptake of Cd and Zn but less useful simulations for Pb, Cu and Ni. The results for Cd uptake also showed a greater dependence on soil pH in the case of wheat in comparison to maize. However the Cd content of maize may still exceed these guidelines, with a relatively minor contribution from contamination with soil dust. Similarly, Antoniuos *et al.*, 2011 investigated the concentration of seven heavy metals (Cd, Cr, Mo, Cu, Zn, Pb, and Ni) in sweet potato plant parts (edible roots, leaves, stem, and feeder roots), its yield and quality in soil amended with municipal sewage sludge (MSS) and observed that the overall plant available metals were greater in the soils amended with MSS compared to control plots (native soil). Concentration of Pb was greater in yard wastes (YW) than MSS amendments. Pb was also greatest in the leaves and feeder roots while Ni, Cr, Cu, Mo and Zn were higher in the edible roots. Total concentrations of Zn and Cu were greater in all the plant parts than the other metals. MSS+YW treatments increased sweet potato yield compared to plants grown in native soil. Concentration of heavy metals in MSS amended soil and in sweet potato roots were below their respective permissible limits.

Uwah *et al.,* 2009, recorded higher levels of metals in soils and leaves of *Talinum triangulare* from the sample areas than the one in the control samples in Maiduguri suggesting anthropogenic sources. However results were below the permissible levels recommended by the United States Environmental Protection Agency and World Health Organization.

Elevated concentration of heavy metals especially in vegetables were seriously contaminated by soil Cd, Pb, and Zn to levels higher than the edible standard and background value to some degree and their uptake was somewhat influenced by co-existing elements. Similarly it was also observed that elevated concentrations in all the surface waters of the Xiang River and accumulation of heavy metals mainly in the topsoil with little downward movement in Zhuzhou city indicated that their occurrence were of anthropogenic origin (Haiyan and Stuanes, 2003).

Metals may also enter the aquatic environment from both natural and anthropogenic sources. Entry may be as a result of direct discharges into both freshwater and marine ecosystems or through indirect routes such as dry and wet deposition and land runoff (Biney *et al.,* 1994). A study by Bako and Daudu,2007, reported higher levels of metals (As, Zn Cu, Pb, Ni, Mn and Ti) in the sediments of two lakes- Makwaye and Kubanni as well as shoots of two aquatic macrophytes (*Polygonum spp* and *Ludwigia spp)* in the Nigerian northern guinea savannah. These values were higher than levels internationally regarded as normal.

Contaminated roadside soils may constitute health hazards if the metals are transferred to other reservoirs. Sansalone and Buchberger (1997) sampled lateral pavement sheet flow from a study area along 1-75 in Cincinnati, during five rainfall events in 1995. They found that Zn, Cu, Pb and Cd often exceeded surface quality discharge standards during rainfall events. They also found that Cd, Cu and Zn were mostly in dissolved form, whereas Al, Fe and Pb were particulate-bound in storm water. Studies of roadside soils in the ManoaBasin on Oahu, Hawaii (Sutherland, 2000; Sutherland *et al.,* 2000; Sutherland and Tolosa, 2001) have shown that Cu, Pb and Zn have significant anthropogenic enrichments and that these contaminated soil particles can be washed into nearby water bodies where they form a potential source for bio-accumulation of Pb. These studies suggested that metals coming from highways could be a significant, unsuspected source of metal contamination in streams.

There are also reviews on the metallic-heavy elements levels of medicinal plants and trees obtained from sites in close proximity to highways. In a study carried out by Ademoroti (1996) on levels of heavy metals on bark and fruits of trees in Benin City, Nigeria, levels of Pb deposits in all cases were found to vary according to traffic volume; high levels (58.3-143.5(g/g) were recorded for areas of very high traffic volume and low levels (15.2-15.8(g/g) for areas of low traffic volume.

In order to study the health risks of *Croton zambesicus*, fresh plant parts (leaves, stem, root and fruit) of *Croton zambesicus* of Euphorbiaceae, a medicinal plant on the Ba'anwa Mountain of Adamawa State, were analysed for magnesium (Mg),Iron (Fe), Lead (Pb), Zinc (Zn), Nickel (Ni), Cadmium (Cd), Manganese (Mn) and Copper (Cu)(Reuben *et al*., 2008). They remarked that the leaves contained much higher elemental and metal concentrations than stem, roots and fruit, and their concentrations were higher than the FAO, WHO/EU and FAO/WHO allowed limit. Thus, the high values of these elements in the plant sample could put the use of this plant at health risk.

In another study on the estimation of heavy metals (Ni, Zn, Mn, Cu, Cr and Pb) in the leaves of Neem trees along the Katsina-Dutsinma-Funtua highway, samples from Katsina and Funtua indicated higher levels of Pb, Zn and Ni and Cu and Cr respectively (Lawal *etal*., 2011). However, the levels of all the metals were below the WHO/FDA permissible levels in herbal plants.

2.7. Plants as Pollution Indicators

Plants that cannot move away from adverse conditions, with the vegetative stages as indicators have a great advantage over animals as biological pollution indicators. It is certain that the sensitivities of plants to toxic substances will vary both qualitatively and quantitatively (Duffus, 1980). Vegetation may become contaminated by the direct uptake of metals from the soil and their subsequent translocation within the plant as soluble ionic and organic complexes or by particulate contamination of leaf surfaces (Merian, 1991).

Plants use a variety of methods to reduce their susceptibility to metal toxicity. In some species, uptake of the poisonous metals is greatly reduced. In other species, the elements are taken into the plants but mainly remain in the roots (Salisbury and Ross, 1985; Bako *et al.*, 2005). In some plants the metals reach other parts of the plants but then accumulate in the cell walls, where the metal is bound as a stable complex with either a pectin-like or proteinaceous substance (Bradshaw and McNeilly, 1981). Plants have also been found, which actively transport a large proportion of their absorbed zinc across the tonoplast into the cell vacuole. This prevents the zinc from interfering with the activity of cytoplasmic enzymes (Bradshaw and McNeilly, 1981). There seems to be a biochemical cost to being tolerant to heavy metal pollution. Such plants are often poor competitors and are seldom found growing away from the area where the heavy metals are concentrated.

Both commercial and residential growing areas are also subject to atmospheric pollution, in the form of metal containing aerosols. These aerosols can enter the soil and be absorbed by vegetables, or alternatively be deposited on leaves and adsorbed (Kachenko and Singh, 2006). Studies of vegetables grown in locations close to industry have reported elevated levels of heavy metals. Vousta *et al*., (1996) studied the impact of atmospheric pollution from industry on heavy metal contamination in vegetables grown in Greece. The results of the study indicated significantly higher levels of metal accumulation in leafy vegetables as compared with root vegetables. This partitioning of Cd is well known, with accumulation of greater concentrations in the edible leafy portions of crops, than the storage organs or fruit (Jinadasa *et al.*,1997; Lehoczky *et al.*,1998). Several studies indicated that plants have the ability to concentrate Pb (Sridhar, 1988). Leaf and root contain more Pb than stem and the contents of Pb in different plant organs were positively correlated to the Pb content in soils. Commonly the Pb does not concentrate in the edible-fruited part of the plant. Urban trees also concentrate Pb.
A laboratory study of two rice cultivars (Ratna and IR36) treated separately with 10^{-5} and 10^{-4} M $PBCl_2$ and $HgCl_2$ decreased their overall germination processes, and the phytotoxic effect of mercury was greater than lead at identical concentrations (Mishra and Choudhuri, 1999).It was also observed that IR36 appeared to be more tolerant than Ratna to these metals. Similarly Kalisova-Spirochova *et al.*, 2003, in a comparative study of heavy metal accumulation by selected plants (corn, sunflower and aspen) in both laboratory and field conditions, observed that corn exhibited better accumulation capacity than sunflower and Pb and Zn accumulated mainly in the roots and leaves and their accumulation level was relatively high, even under insufficient conditions for plant growth in polluted areas.

In a study of the appraisal of heavy metal contents in different vegetables grown in the vicinity of an industrial area in Pakistan, Farooq *et al.,(*2008) observed that the leaves of spinach, cabbage, cauliflower, radish and coriander had a higher concentration of Cr, Cd, Cu, Zn and Pb than the other parts of each vegetables. However the contents of Cr, Cd, Cu, Zn and Pb were below the recommended maximum acceptable levels proposed by the Joint FAO/WHO Expert Committee on Food Additives.

To assess the pollution status of the farm and hence the safety levels of the crops produced, the seasonal variations in concentrations of the heavy metals - As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn - in soil and crops from a farm near the refuse dump site of Obafemi Awolowo University, Ile-Ife, Nigeria, were investigated during the two major seasons of Nigeria (Oluyemi *et al*., 2008). The levels of heavy metals in soil and crops were higher in the dry season than in the wet season and the levels of As, Cd, Cr, Ni, and Pb were above the critical toxic level in plant leaves in both dry and wet seasons while Zn and Cu occurred at toxic levels only in the dry season. They concluded that the high TF value recorded for Cd, Co, Cr, Ni, Pb and Zn could be hazardous especially, that the accumulated metals in edible plants may end up in human food chain with the adverse attendant effects on human health.

2.8 Soil -Plant Transfer Coefficient

The soil-plant transfer factor, expressed as the ratio of plant concentration divided by the total concentration in soil, may be an indicator of the plant accumulation behaviour (Kabata-Pendias and Pendias, 1992). Lübben (1993) showed large differences in the transfer of Cd, Zn, Ni, Cu, Pb and Cr from soil to different plant parts. The lowest transfer factors of Cd were found for grains of maize, peas, oats and wheat, whereas the highest values were reported for leaves of spinach and lettuce and the roots of various plants. Low transfer factors of Zn were reported for carrot and grains of maize and pea, whereas the highest were found for leaves of spinach and roots of radish and other plants. The transfer factors in the investigated plants were reported to be similar also for Cu, Cr and Pb. The mechanism of uptake of heavy elements by plants is based on root uptake of metals and foliar absorption, including deposition of particulate matter on the plant leaves. Kloke *et al*. (1984) reported that Cd, Ti and Zn have the highest soil to plant transfer coefficient, in part because of their relatively poor sorption in the soil, while elements such as Cu, Co, Cr and Pb have low transfer coefficient, and are stably board to the soil structure. The intensity of extent of the uptake therefore influences the actual content of an element in the plant (Reuben *et al*., 2008).

Chao *et al*. (2007) investigated the different accumulation of Pb, Cu, Zn and Ni in the various parts of spinach, garlic, celery and cole and observed that Pb exhibitedthe highest TC value among the four metals, indicating that Pb was more likely to be transferred from roots to leaves than Cu, Zn, and Ni. Chao *et al*., 2007 revealed that this conformed to the fact that *garlic*, with the minimum surface areas of leaves of than the four vegetables, exhibited the lowest TC values of all vegetables. They remarked that higher accumulation in leaves might be related to atmosphericdeposition, which might be due to the rather bigger surface areas of leaves of spinach than that of other vegetables.Sinha *et al.*,(2006) also found that the accumulation of metals in edible parts was higher in the leafy vegetables (chloroplast rich) than that in non-leafy vegetables/crops. Khan *et al*. , (2009), argued that as the vegetables are the source of human consumption so the soil-to-plant transfer quotient is the main source of human exposure. A convenient way for quantifying the relative differences of bioavailability of metals to plants is the transfer quotient (Cui *et al*., 2004). The transfer quotient for Cd and Cu were higher than other metals i.e. Pb and Fe (Khan *et al*., 2008). The higher transfer quotient of heavy metal indicates the stronger accumulation of the respective metal by that vegetable. Transfer quotient of 0.1 indicates that plant is excluding the element from its tissues (Thornton and Farrag, 1997). Khan *et al*., (2009), also argued that the greater the transfer coefficient value than 0.50, the greater the chances of vegetables for metal contamination by anthropogenic activities will be and so the need for environmental monitoring of the area will be required (Sponza and Karaoglu, 2002). From the recent studies conducted by researchers it is concluded that the transfer coefficient of 0.2 indicates the anthropogenic contamination for leafy plants more than proposed by 0.50 by Kloke *et al.,* 1984 (Sridhara *et al*., 2008). They further argued that Kloke *et al.* gave a generalized transfer coefficient for soils and plants based on the root uptake of metals.

Leafy vegetables accumulate much higher contents of heavy metals as compared to other vegetables. This is because leafy vegetables have higher translocation and transpiration rate as compared to other vegetables in which transfer of metals from root to stem and then to fruits is longer which results in lower accumulation than leafy vegetables (Itanna, 2002). The trend of transfer of these metals was in the order Cd > Cu > Pb > Fe (Khan *et al*., 2008).

2.9 Accumulation of Metals in Plants and Plant UptakeFactor

In various literature plant uptake factoris also called enrichment ratio,enrichment coefficient,translocation coefficient, transfer factor, soil-plant transfer coefficient, accumulation factor,phytoaccumulation factor, biological adsorption coefficient, plant uptake factor (Miclean *et al*., 2006), bioconcentration factor anduptake coefficient (Zgorelec, 2009; Kisic *et al*., 2011). Currently, there are nine plant uptake factors (PUF). However, majority of the plant uptake literature focuses on the uptake of chemicals from sludge or biosolids and only little literature has focused on the uptake from atmospheric deposition.The relationship between contaminant concentrations in soil and edible plant material is highly specific to the plant species. The relationship between contaminant concentration in edible produce and the concentration in soil is described using the plant uptake factor (PUF), which is defined as follows

$$PUF = \frac{\text{Concentrations in edible portion of plant(mg/kg)}}{\text{Concentration in soil (mg/kg)}}$$

High accumulator plants EC between 1 - 10

Moderately accumulator plants EC between 0.1 – 1.0

Low accumulator plants EC between 0.01 – 0.1

Non accumulator plants EC < 0.01

Plants differ widely in their ability to accumulate heavy metals (Nouri *et al*., 2009). Heavy metal contents of the soils and six desert plants distributed in the six Kuwait Governorate areas representing the residential, industrial and recreational sites were assessed and showed higher levels in the sequence of leaves>soil> shoot>root irrespective of the species and areas (Bu-Olayan and Thomas, 2009). Translocation Factor (TF) and Plant uptake Factor (PUF) in all the plants were >1, thus labeling the plants, especially *Chrozophora tinctoria,* as the main heavy metals accumulator and pollution indicator than all the other species.

In another study of the pollution of soils with Pb, Cd, and Hg, and the transfer of these elements into the above-ground organs of four dominant herb species by Kuklova *et al.,* 2010, the concentrations of Pb (1.54-8.05 mg_kg-1 d.m) and Cd (0.15-1.92 mg_kg-1 d.m), found in *Vaccininium myrtillus*, *Dryopteris dilatata*, *Luzula luzuloides*, and *Rubus idaeus* species were within the toxicity range only. The transfer coefficients of Cd was substantially higher than 1 in the case of *D. dilatata*, *R. idaeus* and L. *luzuloides* species.

Nazir *et al.*, 2011 reported higher levels of all the metals studied (Cu, Pb, Zn) in the shoots than in the roots in more than 50% (24 plant species) of the 43 plant species investigated. These plant species which include *Amaranthus viridis* L., *Alternanthera pungens* Kunth., *Achyranthes aspera* L., *Brachiaria reptans* (L.) Gardner and Hubb.,*Cenchrus pennisetiformis* Hochst. and Steud.ex Steud., *Cannabis sativa* L., *Cynodon dactylon* (L.) Pers., *Chenopodium* *album* L., *Cyperus rotundus* L., *Dactyloctenium aegypticum* L., *Eclipta alba* (L.) Hassk., *Eleusine indica* (L.) Gaertn., *Erigeron conyzanthus* L., *Ipomoea hederacea* Jacq., *Malvastrum coromandelianum(*L.*)* Garcke, *Parthenium hysterophorus* L., *Portulaca oleracea* L., *Persicaria barbata* (L.) Hara, *Rumex nepalensis* Sprenge., *Ricinus communis* L., *Sorghum halepense* (L.) Pers., *Solanum nigrum* L. and *Xanthium strumarium* L. may be useful for phytostabilization since they could tolerate and accumulate heavy metals.

The trend in the bioaccumulation for metals in *E. indica* was in the following sequence: Zn>Cu>Pb>Mn>Cd>Cr (Abdallah *et al.,* 2012). However, the results indicated low bioaccumulation of metals by *E. indica*. Abdallah *et al.*, 2012, therefore, remarks that further dumping of toxic waste could lead to toxicity to man through the food chain.

2.10 Translocation of Metals in Plants and Translocation Factor

The translocation factor (TF), the ratio of shoot to root metals indicates internal metal transportation (Das and Maiti, 2007). The plant's ability to accumulate metals from soils and translocate metals from roots to shoots is estimated using the translocation factor (TF) (Das and Maiti, 2007) and to evaluate the extent of metal translocation from roots to shoots (Stoltz and Greger, 2002; Deng *et al.*, 2004). The concentrations of copper, zinc, iron, and magnesium accumulatedby native plant species were determined in field conditions of Hame Kasi iron and copper mine in the central part of Iran in Hamadan province. The results showed that metal accumulation by plants differed among species and tissue bodies. Metals accumulated by plants were mostly distributed in root tissues, suggesting that an exclusion strategy for metal tolerance exists widely amongst them. With high translocation factor, metal concentration ratio of plant shoots to roots indicates internal detoxification and metal tolerance mechanism.

Chakroun *et al*.,2010 conducted a study on the analysis of the contents of metallic-heavy elements (MTE) in the soil and two cultivated plant species broad beans (*Vicia faba* L.) and barley (*Hordeum vulgare* L.) of the Jebel Hallouf-Sidi Bouaouane mining-district. The results show that the concentration of metals in the soil are up to 39 mg kg^{-1}, 6.3 mg kg^{-1}, 56 mg kg^{-1} and 131 mg kg^{-1}, for lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu), respectively. The chemical analysis of the broad beans (*Vicia faba* L.) and barley (*Hordeum vulgare* L.), sampled inside the mining district, showed that the roots and the upper part (leaves and stem) are enriched for Pb (up to 508 and 220 mg kg^{-1}, respectively), Cd (up to 8 and 5 mg kg^{-1}, respectively), and Zn (up to 491 and 468 mg kg^{-1}, respectively) when compared with similar species collected far from the contaminated site (up to 9.6 and 0.8 mg $kg^{-1}$for Pb, up to 0.04 and 0.04 mg kg^{-1} for Cd, up to 44 and 15 mg kg^{-1} for Zn, respectively). Chakroun *et al*., 2010, remarked that at a preliminary stage, one should note that the TFs of all the elements are lower than one (0.085, 0.116, 0.346 and0.355, respectively for Pb, Cd, Zn and Cu), which meansthat the physiological need of the plant for theseelements is rather limited. Therefore, actions have to be taken in order to remedy this problem.

2.11 Principal Pathways of Chemical Uptake and Accumulation in Plants

There are four principal uptake pathways of chemicals in plants. These pathways include passive and active uptake through the root system, gaseous and particulate deposition to aboveground shoots, and direct contact between soil and plant tissues.

2.11.1 Soil-root interactions.

In general, plant roots are the most important site for uptake of chemicals from soil (Bell, 1992). Root systems take up organic chemicals from both water and air, which involve passive and diffusive transport, with chemicals carried into the plant during the natural transpiration cycle. Although chemical properties are important predictors of uptake potential, the physiology and composition of the plant root itself is also a significant influence (Collins *et al*., 2006).

Chemical transfers from the soil into the root are primarily mediated by the uptake ofsoil porewater during plant transpiration. Therefore, the factors that influence the chemical concentration in porewater also exert control over the passive uptake process. In principle, as the organic matter content of a soil increases (typically measured using the weight fraction of organic carbon present), so the proportion of the chemical in the porewater decreases. As the weight fraction of soil organic carbon increases, so the total amount of chemical taken up by the root decreases. Several models use the fraction of organic carbon as a key variable in the prediction of the uptake of contaminants by plants.

2.11.2 Transfer from roots to other plant parts.

Although the root is the most important site for chemical entry from soil, the edible fractions for many plants are the stems, leaves, tubers and fruits, and only if a chemical accumulates in these parts is there a potential risk to human health.The transport of water within the plant, which is also the major mechanism for movement of nutrients and energy-rich photosynthate, is known as translocation (Bell, 1992). It is also the principal route by which contaminants move from the root system to stems, leaves, and storage organs (McFarlane, 1995). The plant vascular system includes the xylem and the phloem. Water and solutes are transported upward from the root into other plant parts through the xylem by mass flow resulting from a pressure gradient. This driving force is created during transpiration, where water is drawn in through the root system to replace evaporative losses from stomata within the leaves, and is supplemented by capillary action (McFarlane, 1995).

While the direction of flow within the xylem is generally from the root to the shoot, movement within the phloem can be up or down. The primary role of the phloem is to carry sucrose formed by photosynthesis in the leaves to storage areas including fruits and tubers, where it is converted to starches and complex sugars. Although there are several theories on what drives this flow, McFarlane (1995) suggests it is a result of osmotic potential along the phloem between the sugar sources and sink regions. In mature plants, the phloem flows away from the leaves where photosynthesis results in a build-up of sugars. However, when the plant is under stress the direction may be reversed and materials stored in fruits, tubers and other plant tissues may be needed, changing the direction of phloem flow. Therefore, the lipid composition of above-ground plant tissues is likely to be an important factor determining chemical retention and accumulation.

2.11.3 Leaf uptake by vapour or gaseous uptake from ambient air.

In addition to the root system, another potential pathway for plant uptake is the absorption of chemical vapour from ambient air by shoots during respiration (Bell,1992). This pathway differs from root uptake because it is mediated via gaseous exchange rather than through aqueous solution. As a result, this pathway is likely to be important not just for highly volatile pollutants but those with a strong preference to partition to air rather than water (Bell, 1992). This has been shown to be the main uptake pathway into above ground plant parts for a variety of organic chemicals, including PAHs (Simonich and Hites, 1994), PCBs (Bohme *et al*., 1999) and tetra- and hexa-chlorinated PCDD/Fs (Meneses *et al*., 2002).

Chemicals enter the leaf by either crossing the cuticle (a waxy coating that covers the outer leaf) or by entering directly through the stomata, which regulate the exchange of carbon dioxide and oxygen (McCrady, 1994; Bacci *et al*., 1992). It is also the principal route by which water vapour from the transpiration stream is lost by the plant.

2.11.4 Particulate deposition on plant surfaces.

Organic chemicals bound to soil particles may be deposited on above-ground leaves and shoots as a result of wind resuspension or rain splash, and is a well-recognised phenomenon for metals and radionuclides (Smith and Jones, 2000; Thorne *et al*., 2004). Dry deposition of suspended particles with subsequent permeation into the cuticle represents the major pathway of contamination. Wet deposition is the process of gravitational coagulation of solid particles with water droplets.

Relatively little information is available on the wet deposition of particle bound and gaseous phase organic chemicals to plant surfaces, and this pathway is seldom considered when looking at the contamination of vegetation (Smith and Jones, 2000). Dry deposition of particles to plant surfaces involves diffusion, interception, impaction and sedimentation processes (Chamberlain, 1991). Once particles have been deposited on plant foliage they are subject to removal and degradation. Above-ground plant parts may become contaminated with organic chemicals via pathways involving direct contact between soil particles and plant surfaces, and chemicals retained on plant surfaces may subsequently be taken up into or through the plant cuticle (Riederer, 1995). Small particle-bound compounds may be taken up via the stomata, but the stomatal entry route will generally only be significant for chemicals present in air in the gaseous phase (Smith and Jones, 2000).

The most likely transfer pathway is through physical contact between the particle and the waxy leaf surface, where chemical transfer occurs via diffusion. Organic chemicals entering the plant cuticle become adsorbed to lipophilic tissues or permeate into the leaf interior (Riederer, 1995).There is currently insufficient understanding of this process and in particular, of how the physicochemical properties of organic compounds influence transfer from particles into the leaf.

2.12 Influence of Plant Species on Uptake of Chemicals

Plant uptake varies considerably between types of plant and individual species (Bell, 1992) and are influenced by certain factors like root growth and depth,transpiration rate, active uptake mechanisms, growth period, location of fruits and tubers, and the size and shape of leafy foliage (Buckley, 1982).

2.12.1 Foliage

Several researchers have also found that the exposed surface area of the plant foliage influence the foliar uptake rate for a variety of species (McCrady and Maggard, 1993; Schreiber and Schönherr, 1992). Plant characteristics that affect the rate of particle deposition and retention include theexposed surface area of the foliage and the presence or absence of leaf hairs. Little and Wiffen (1977) observed that rough or hairy leaf surfaces were more efficient at collecting aerosols than smooth surfaces, explained by the increased surface area and projection of roughness elements through the leaf-air boundary layer. Leaf loss and senescence can lead to the transfer of chemicals from plant foliage to the surrounding soil, thus reducing the chemical concentration in foliage. However, edible plant parts are likely to be harvested before leaf loss and senescence become significant chemical transport pathways.

For deposition during the growth stage of agricultural plants, the parameters associated with contamination by foliar absorption are relatively influential in long-term contamination as well as short-term contamination (Reeds, 2003). However, in most cases with active deposition occurring, the foliar interception pathway is usually dominant over the root uptake pathway (Reeds, 2003).

2.12.2 Growth dilution

Plant growth has been recognised as an important variable in the plant uptake ofradionuclides by root uptake and aerial deposition (Thorne *et al*., 2004). Over the growing season the biomass of plant increases, diluting the chemical concentration within plant tissues relative to the flux of chemical uptake, and increasing the aboveground canopy for interception of aerial deposition. The importance of growth dilution has been recognised in several dynamic plant uptake models (Samsøe-Petersen *et al*., 2003; Trapp and Matthies, 1995; Hung and Mackay, 1997). Collins and Finnegan (*in preparation*) noted the importance of growth dilution inpredicting foliar uptake of organic chemicals. Using growth dilution, the Trapp and Matthies (1995) model predicted a plateau region in uptake above octanol-air partition coefficients of greater than seven, in the region predicted by McLachlan (1999) to be kinetically limited.

CHAPTER THREE

3. 0 MATERIALS AND METHODS

3.1. Study Area

3.1.1 Site description**.**

Historically, Kano State has been a commercial and agricultural state, which is known for the production of groundnuts as well as for its solid mineral deposits. The state has more than 18,684 square kilometres (7,214 sq mi) of cultivable land and is the most extensively irrigated state in the country. Kano has a tradition of irrigated agriculture and is reckoned as the leading hydroagricultural state in Nigeria. Smallscale irrigation on fadamas has supported crops that require all year round water used for gardening crops for centuries. The distribution network operates under gravity receiving water from the Tiga dam through a 15km long main canal split into east and west branches. Major irrigated crops are wheat, maize, tomatoes and rice. The natural vegetation consists of the Sudan and the Guinea Savannah both having been replaced by secondary vegetation. Kano consists of wooded savannah in the south and scrub vegetation in the north and is drained by Kano-Chalawa-Hadejia river system. Kano State has the suitable climatic conditions for maize and wheat cultivation.

Kano State lies between latitude $10^o35^,$ and 13^oN, longitude $7^o40^,$ and 10^o $35^,$ E, and at altitude 240m -306m. The state has an area of 43,070 km^2 which is about 5 percent of the total land area of Nigeria. According to the 2006 census figures for Nigeria, Kano state has a population totaling 9,383,682. It is estimated that about 85 percent of the rural population is involved in agriculture, and the number of farm families is about 614,000. The average population density is 210 persons/km^2 which makes it the second largest and most densely populated state in Northern Nigeria with an estimated motor vehicle population of about 19,288. Infact both are competing in population density. The mean annual rainfall is 635mm starting from late June to September. The peak of rainfall period is from mid-August to early September. The period of

November to March is marked by dry northeasternly winds, the harmattan. Minimum mean temperature ranges from $12^{o}C$ to $20^{o}C$ while the maximum from $28^{o}C$ to $38^{o}C$. The bulk of the state is classified as the Sudan Savannah and a small portion of Sahel Savannah in the extreme north-eastern tip of the State.

3.2 Estimation of Vehicular Traffic Density

The average daily traffic density at both the experimental site in close proximity to the Kano-Zaria Highway and the Irrigation Research Station were estimated by counting the number of vehicles between 7am to 8am in the morning, at 12 noon to 1pm and at 4pm to 5pm in the afternoon and in the evening respectively. The average of the three estimates was obtained representing the average daily traffic density during preliminary survey. The same measurement was repeated before the collection of soil and plant samples and at the end of the sampling. The total average daily traffic density was then estimated.

3.2.1 Sampling

In ecotoxicity study, the selection of sampling sites and sampling units were by principle to represent the level of pollution in regions and towns with highest level of pollution, and also determined by possible pollutants at specific regions of interest (Misurovic, 1998). This study being an ecotoxicological research, all sampling points were selected by principle to represent the level of pollution near major traffic routes and are reference sampling points (Misurovic, 1998).

The research was conducted at Kadawa across the southern Sudan savannah zone of Kano State. The global positioning system (GPS) was used in recording the coordinates of the sampling units and geographical information system (GIS) was used to locate the map of the investigated sites (Fig. 1 and Fig. 2).

Two sampling units at the Doruwa Salau location perpendicular to the Kano-Zaria Highway, within the experimental site designated as S1 were selected. The Doruwa Salau location at close proximity to the highway has minimal residential and commercial activities. S1 is located outside the Kadawa irrigation research station at a distance of about 2438.28metres from the control sites and about 345.79metres from the roadside. Yellow maize farm designated as SU 3 is at a distance of about 100metres from the roadside and about 50metres from the Pavon-76 farm designated as SU 1. There had been extensive cultivation of rice, maize, millet, guinea corn, cowpea, garden egg, water melon and wheat along the roadside. The site had an average daily traffic density of 19,288, being the main exit from Kano State to various major towns of the country, particularly from upper northern States through the middle belt States to southern States and to the country's capital Abuja. Two sampling units were also selected within the control site, designated as S2 (at a distance of 1934. 61metres from the Kano – Zaria Highway) located inside the Irrigation Research Station (IRS), Institute of Agricultural Research (IAR), Kadawa, Kano State, which began operation in 1975. The distance between SU 4, the popcorn farm and SU 2, the Siettecerros farm being the two sampling units is about 250metres. The control site has been extensively used by private institutions, government researchers and both corporate and international research institutes and had an average daily traffic density of 3. The control and experimental sites are located in the village of Kadawa, on the outskirt of Kano City, and are a mix of research, minimal residential activities and largescale commercial maize, wheat and vegetable farms at the time of the research.

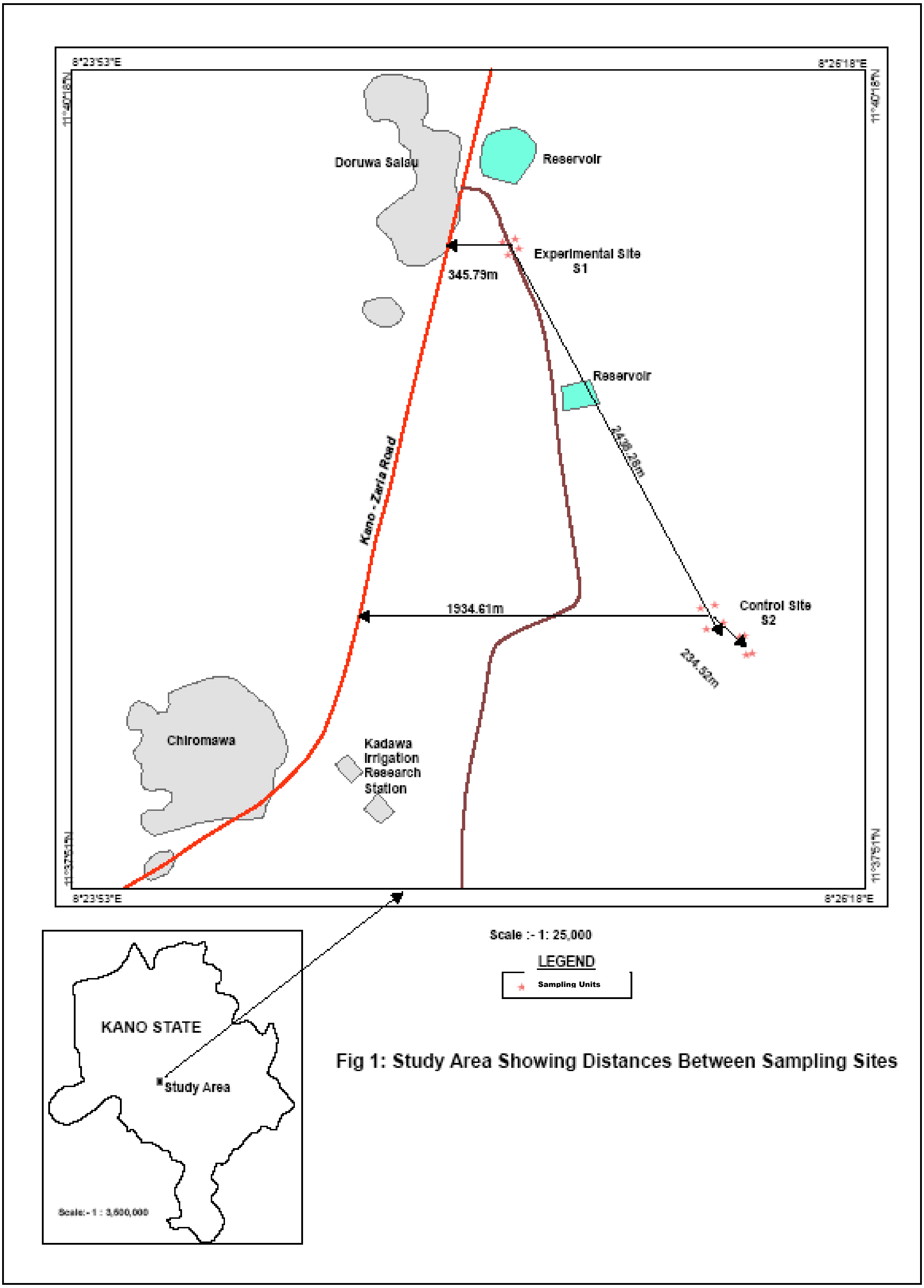

Fig 1: Study Area Showing Distances Between Sampling Sites

Fig 2: Satellite Image of the Study Sites Showing the Sampling Units

Both sites are significant for dry season (irrigation) farming, which is the main activity on both locations. There is presence of scanty residential housings and a major sub-channel of the Tiga Dam at S1 and absence of residential housing with a single one-room building used as a store for farm tools.

Both sites have irrigation channels connected to the Hadejia – Jama'are River Basin Dam which provides water for dry season irrigation of farmlands within and outside the Irrigation Research Station, Kadawa. The local farmers that have farmlands along the major highway from the Hadejia – Jama'are River Basin Dam down to the outside environs of the research station and the research station itself depend on this Dam whose water is obtained from Tiga Dam. There are sub-channels that network the Tiga Dam onto the farmlands of the local farmers and the irrigation research station.

According to the farmers interviewed, the cultivation of food crops on the experimental sites began since 1975 when Kano State Government regulated the use of roadside lands and allocated portions to poor local farmers for crop cultivation or farming at that time.

A main irrigation channel passed through the experimental site from the Tiga Dam, with sub-channels for the irrigation of the farmlands. There is an un-tarred road between the Tiga Dam and the irrigation sub-channels. The main human activities were the nomadic fulanis with their cattle and small round huts settlements, and farmlands belonging to the local farmers.

3. 3 Preliminary Soil Survey

A field study was conducted between the months of January 2007 – October 2008. Soil samples were collected in two replicates at a vertical depth of 0 – 25cm using the soil auger, for preliminary heavy metal and physico-chemical analyses, before cultivation of the two varieties each of the maize and wheat crops; *Triticum aestivum* – wheat (Pavon- 76 or

Samwhit-6) and *Zea mays* - yellow maize (2:95 TZEE- Y) at the experimental sites and *Triticum aestivum* – wheat (Siettecerros or Samwhit-5) and *Zea mays everta* – popcorn at the control sites. The four varieties are the most widely cultivated and consumed crops in Kano State, because they are very high yielding crops and are resistant to crop diseases. Not only is wheat one of the most important food crops, it is also easier to culture, to maintain in the laboratory conditions, and even to use in toxicity tests for examining the effects of heavy metals especially cadmium (Henning *et al*., 2001). Maize is generally preferred for cultivation and research for five (5) major reasons: (i) its tolerance to specific heavy metals; (ii) adaptation to soil and climatic conditions; (iii) fast growth of the plant; (iv) heavy metal uptake capability, and (v) spatial fittings of roots of pollution distribution (Keller *et al.,* 2003; Kalisova-Spirochova *et al.,* 2003). A portion of the preliminary samples were properly labeled and taken to the Department of Soil Sciences, University of Agriculture, Makurdi, BenueState, for physico-chemical analysis.The remainder of the preliminary samples were properly labeled, transferred to the laboratory, air–dried for 3 days, ground gently with mortar and pestle and sieved through 2 mm and 0.5 mm brass sieves. For heavy metal analysis, the samples were further ground to powdery form with agate mortar and pestle and filtered through a 100 mesh sieve.

3.3.1 Physicochemical analysis.

3.3.1.1 Analysis of soil particle-size distribution

The dry samples were dispersed in water and 10% calgon solution in a volume dispersing cup and filled up to mark with distilled water. The suspension was vigorously stirred, quantitatively transferred to the sedimentation cylinder and filled up to mark with distilled water. Three drops of amyl alcohol was added to the suspension to remove froth, a hydrometer was gently placed into the column and hydrometer readings were taken at 40 seconds to measure silt and clay, and after 2 hrs for clay in the suspension (Bouyoucos, 1962).

3.3.1.2 Determination of organic matter and organic carbon content

One gram of the ground soil (0.5 mm) sample was weighed in triplicate into 500 ml Erlenmeyer flasks and digested with 20 ml concentrated tetraoxosulphate (VI) acid and 10 ml aqueous potassium dichromate for 30 minutes. The residual potassium dichromate was back titrated with 0.25 M ferrous sulphate solution to a dark green endpoint using ferroin as indicator. The difference between added and residual potassium dichromate gave a measure of organic carbon content of the soil sample. A blank titration was made in the same manner. The organic matter = organic carbon x 1.729 (Walkley and Black, 1965; Nelson and Sommers, 1975; Amoo *et al*., 2004).

3.3.1.3 Determination of soil pH

Buffer solution (KCl solution and distilled water) was used to standardize the electrode. The electrode was then dipped into the analyte (soil solution) and the pH of the solution was displayed on the pH section of the pH meter. The pH was determined in a ratio of 1:2 W/V ratio with distilled water using standardized pH meter (pH =7.02). 20 g of air–dry soil samples were weighed into 40ml of distilled water in a 50 ml beaker. It was occasional stirred with a glass rod and left to stand for 30 minutes. The electrode was then immersed in the solution and the readings were displayed on the pH meter (Bates, 1954; Amoo *et al*., 2004).

3.3.1.4 Determination of exchangeable bases

Five grams of air-dry soil (<2 mm) was weighed into a clean plastic bottle with a stopper. 100 ml of 1 M ammonium acetate (NH4OAc) solution (pH 7) was added to the soil sample, shaken for 30 minutes and filtered through No 42 Whatman filter paper. The soil extract was analysed for Na and K by flame photometry and for Ca and Mg by atomic absorption spectrophotometry (Black, 1965; Amoo *et al*., 2004).

3.3.1.5 Determination of trace metals

One gram of finely powdered soil was accurately weighed into an evaporating dish and 30 ml of the acid mixture (4 parts H_2SO_4, 2 parts of HCI and 1 part of HNO_3) was added. The mixture was heated gently at first and then more strongly until white fumes ceased to evolved. The viscous mass was taken up with hot dilute hydrochloric acid, filtered and washed with hot acid and distilled water. The elements of interest (Zn, Cu, Cr) and (Pb, Cd) were determined in the filtrate using the energy dispersive X-ray fluorescent (EDXRF) and atomic absorption spectrophotometer respectively.

3.4 Experimental Set-up

The experimental set-up was the randomized block design (RBD) which comprised of three groups of treatments that included six growth stages, three plant parts of each variety and two varieties of the two crops.The six growth stages treatments were the germination/seedling stage (A = 15-days growth stage), tillering stage (B = 30-days growth stage), shooting/booting stage (C = 45-days growth stage), heading/earing stage (D = 60-days growth stage) and flowering stage (E = 75-days growth stage) and ripening stage (F = 90-days growth stage). The leaves, stems and roots of the two varieties each of *Triticum aestivum* L. and *Zea mays* L. were the plant parts collected at each of the growth stages. The seeds of the varieties of the two crops were Pavon-76 and Siettecerros for *Triticum aestivum* L.and TZEE-Yellow maize and popcorn for *Zea mays* L. and were obtained from IAR, Kadawa Station. Each of the groups was replicated three times.

3.5 Soil Sampling and Analysis

After sowing of the two varieties each of wheat and maize, a total of 72 soil samples were collected fortnightly in triplicates throughout the growing seasons of the two varieties each of wheat and maize during the growing season from December 2008 to early April 2009. 18 soil samples each were obtained from the yellow maize and Pavon-76 farms at the experimental site. 18 soil samples each were also obtained from the popcorn and siettecerros farms at the control sites. The corresponding soil samples were collected immediately after uprooting of the whole plant samples. Corresponding soil samples were collected at a vertical depth of 0 – 25cm using a soil auger at the six selected growth or developmental stages as follows : at 15 days (germination or seedling), 30 days (tillering), 45 days (shooting and booting), 60 days (earring or heading), 75 days (flowering and grain formation) and 90 days (maturity). Due to financial constraints, a total of 48 soil samples were selected in duplicates, air-dried and ground into smooth powder using a porcelain mortar and pestle.The soil samples were then packaged in well labeled envelopes and polyethene bag for heavy metal analyses. The soil samples were taken to Centre for Energy Research and Training, Ahmadu Bello University, Zaria in 2011 for the trace metal (Cd, Cr, Cu, Pb, Zn) analysis using the multi-elemental technique- Energy Dispersive X-ray Fluorescent (EDXRF).

3. 6 Plant Sampling and Tissue Analysis

The seeds of the varieties each of the widely cultivated and consumed wheat and maize were obtained from Institute of Agricultural Research, Irrigation Research Station Kadawa sub-station, Kano State. Due to the unavailability of farmlands both the local farmers and HJRBA for rentage of this study, four farmers volunteered to allow collection of specimens from their farmlands. The standard cultural practices of land preparation prior, to cultivation of the four farmlands were monitored by the researcher to ensure uniformity in the collection of data. Leaves, stems and roots of the two varieties of wheat; Siettecerros and Pavon- 76 and two varieties of maize; (popcorn) and yellow maize(2:95 TZEE-Y) were collected in four replicates throughout the growing season of the two varieties each of maize and wheat from the month of December 2008 to early April 2009. A total of 288 plant samples of the two varieties of maize and wheat were collected from the four sampling units on both the experimental and control sites. 72 plant samples each were obtained from the yellow maize and Pavon-76 farms at the experimental site. 72 plant samples each were also obtained from the popcorn and siettecerros farms at the control sites. The plant tissues or parts of the two varieties each of maize and wheat were collected at six growth or developmental stages. Both soil and plant samples were collected at the same time after the whole plant samples were uprooted from the soils.The wheat plants were harvested according to developmental stages rather than by calendar days because the growth rates of the two cultivars were slightly dissimilar. The experimental units were randomly chosen from within the cultivars populations. The time of sampling was fortnightly and based on visual inspection of the plant developmental stages and calendar days, though the cultivars matured at different rates. Prior to the analysis of the plant materials; the leaves, stems and roots each of the two crops were placed under running tapwater to washed off soil particles, separated and placed in large paper bags to air-dry at room temperature and later ground using a grinding mill model Foss Cyclotec ™ 1093 based on Tecator™ Technology at the Institute of Agricultural Research, Food and Science Technology Research Programme, Faculty of Agriculture, Ahmadu Bello University, Zaria, Nigeria. The ground plant samples were well packaged and taken to Centre for Energy Research and Training, Ahmadu Bello University, Zaria in 2011 for the determination of the concentrations of Cu, Cr and Zn using the multi-elemental technique- Energy Dispersive X-ray Fluorescent (EDXRF), while the concentrations of Cd and Pb were determined using the double beam spectrophotometer at National Animal Production Research Institute (NAPRI), Ahmadu Bello University, Zaria. A total of 216 samples (leaves, stems and roots) each of pavon-76, siettecerros, yellow maize and popcorn were assayed and analyzed individually in triplicates.

3.7 Trace Metal Analysis

3.7.1 Analysis of plant tissue

3.7.1.1 Analytical technique energy- dispersive x-ray flourescence (edxrf) for chromium, copper and zinc

Plant samples were ground into fine powder in a micro-blender. Subsequently, about 40 grams sub-sample from each sample was weighed out on a Mettler balance and placed in a Pyrex glass beaker. These were covered in put in a Muffle furnace at 550^oC for ashing. Ashed materials were then pelleted using 19mm diameter of plant samples each, which were prepared from 0.3-0.5g powder mixed with three drops of organic liquid binder and pressed afterwards at 10 tons pressure and subjected to elemental analyses. The system consisted of a 925 MBq^{109}Cd annular isotopic source whichemits Ag-K X-rays (22.1kev). The X-ray spectra were acquired with a computer based MCA card. Sensitivity calibration of the system was performed using thick pure metal foils (Ti, Fe, Co, Ni, Cu, Zn, Nb, Mo, Sn, Ta and Pb,) and stable chemical compounds (K_2CO_3, Ca Co_3, Ce_2O_3, WO_3, ThO_2, U_3O_8). The measurement time of 5000s was used for each sample and spectral analysis was performed with AXIL program (Van Espen and Janssens, 1993) from a QXAS software package (Bernasconi, 1996). The International Atomic Enery Agency distributed this package. Other details of the measurements are as described by Funtua, 1999a and Funtua, 1999b. Quantitative analysis of the samples was carried out using a modified version of E-T method (Kump, 1996, Angeyo *et al.*,1998; and it involves the use of pure target material (Mo) to measure the absorption factors in the sample.

The accuracy and precision of the measurements were confirmed through an analysis of IAEA – V10 (hay powder) and IAEA-359 (cabbage) certified reference material, distributed by International Atomic Energy Agency (IAEA). There was a general good agreement between measured and certified values (Appendix I). Uncertainties in the measurement included errors from counting statistics, calibration error and uncertainty of the absorption correction factor.

3.7.1.2 Double beam atomic absorption spectrophotometer for analysis of cadmium and lead

3.7.1.3 Sample preparation and wet digestion

Approximately 1 g of ground dried plant sample was weighed into a digestion vessel. 10 ml of concentrated HNO_3 was added into it and allowed to stand overnight. The mixture was carefully placed on a hot plate and heated for 4 hours at 125^{0}C until the production of red NO_2 fumes has ceased and the entire solids has disappeared and a transparent solution is obtained. Next, HCl and distilled water in a ratio of 1:1 was added to the digested sample and the mixture transferred to the digester again for 30 mins. The beaker was then removed from the hot plate and allowed to cool. A small amount (2-4 ml) of 70% $HClO_4$ was added, heated slowly at a low temperature and allowed to evaporate to a small volume. The cooled sample was then transferred into a 50-ml flask and diluted to the appropriate volume with distilled or deionised water and filtered through filter paper No 1. Determination of trace metals was done using the double beam atomic absorption spectrophotometer (model Shimadzu AA 650) after calibrating the equipment with stock standard solution of 1000 mg/L for Cd, 1.000 g of cadmium metal was dissolved in a minimum volume of (1+1) HCl and diluted to 1 liter with 1% (v/v) HCl while, the stock standard solution of 1000 mg/L for Pb was prepared by dissolving 1.598 g of lead nitrate -$Pb(NO_3)_2$- in 1% (v/v) HNO_3 and diluted to 1 liter with 1% (v/v) HNO_3. The acid digestion produces a clear solution without loss of any of the elements to be determined. A combination of nitric acid and perchloric acid is especially useful for the complete destruction of fats and proteins in biological samples (Amoo *et al.,* 2004).

3.8 Data and Statistical Analyses

Heavy metal concentrations were compared with the permissible limits of the Codex Alimentarius Commission of the Joint WHO/FAO food standards (2006) and with the European Commission Director- General for Environment (2010) and other world allowable limits for soils (Appendix III).

3.8.1. Soil-plant transfer coefficient

The transfer coefficient quantifies the relative differences in bioavailability of metals to plants and is a function of both soil and plant properties. The coefficient was calculated by dividing the concentration of a metal in the cereal crop (DW) by the total metal concentration in the soil.

$$TC = \frac{\text{Content of heavy metal in plant (mg/kg)}}{\text{Content of heavy metal in soil (mg/kg)}}$$

TC signifies the amount of metals that ended up in the test crop (Odai *et al*., 2008; Kumi *et al*., 2013). Higher transfer coefficients reflect relatively poor retention in soils or greater efficiency of plants to absorb metals. Low coefficients reflect the strong sorption of metals to the soil colloids (Alloway and Ayres, 1997; Hough *et al.*, 2003; Kachenko and Singh, 2006; Bu-Olayan and Thomas, 2009; Kuklova *et al.*, 2010; Nazir *et al.*, 2011). Kloke’s transfer coefficients are based on the root uptake of metals, with no consideration given to aerial deposition and foliar adsorption of elements. The TC > 1 means that the exposed cereal crops are assumed to be unsafe for consumption.

3.8.2. Plant uptake factor (Puf)

Plant uptake factor (PUF) is used to evaluate the ability of plants to accumulate heavy metals (Lou *et al*., 2012; Kumi *et al*., 2013) in these plants was determined by calculating the ratio of metal concentration in the aerial parts to that of the soil as given below:

$$PUF = C_p/C_{so}$$

where, C_p and C_{so} are metal concentrations in aerial parts of the plant (μg g^{-1}) and in soil (μg g^{-1}), respectively.

PUF signifies the ability of the test crop in accumulating metals within their plant parts (Odai *et al*., 2008; Kumi *et al*., 2013).The PUF> 1 means that the exposed cereal crops are assumed to be unsafe for consumption. PUF was categorized further as hyper-accumulators, accumulator and excluder to those samples which accumulated metals >10 μg g^{-1}, >1 and <1, respectively (Ma *et al*., 2001; Bu-Olayan and Thomas, 2009; Nazir *et al.*, 2011; Abdallah *et al.*, 2012).

3.8. 3. Translocation factor (Tf)

Translocation factor (TF) is also called the mobilisation ratio (Barman *et al.*, 2000; Gupta *et al*., 2008).TF signifies the fraction of total deposition on plant surfaces that is incorporated into edible parts of the plant (Reeds 2003). Heavy metals translocation in these plants from shoot to root was measured using TF which is given below:

$$TF = C_s/C_r$$

where, C_s and C_r are metal concentrations (μg g^{-1}) in the shoot and root, respectively.

Wherein, TF>1 indicates that the plant translocate metals effectively from root to the shoot (Baker and Brooks, 1989; Bu-Olayan and Thomas, 2009).The TF> 1 means that the exposed cereal crops are assumed to be unsafe for consumption.This one also gives indicators about the capacity of the plant to accumulate or to transfer the toxic elements from one organ to another and explain the adjustment capacity of a plant absorbing a solution enriched with metals from the rhizosphere.

In this study, the three models were integrated in a holistic way to explain heavy metals transferability and translocation from soil to plant parts, atmosphere to plants and accumulation potentials of the cereal crops investigated.

Data were reported as ranges and mean. Data were statistically analysed at $P < 0.01$(99%) using the statistical package SPSS 17.5 to determine the differences in the levels of each trace metals (Cd, Cr, Cu, Pb and Zn) between the sampling sites, sampling units; differences in the levels of trace metals among the growth stages of the two culivars each of wheat and maize; differences in the trace metals (Cd, Cr, Cu, Pb and Zn) levels among the plant parts of the two varieties each of *Triticum aestivum* L. and *Zea mays* L; to determine the differences of the effects of growth stages on the trace metal concentrations in the leaves, stems and roots of the two varieties each of wheat and maize, and to measure the effects of growth stages on the soil trace metal concentrations. Statistical significance between the means was computed using pair-samples student t-test (Microsoft Excel for Windows Xp 2007) to assess significant variation in the concentration levels of the trace metals in the cereal crops as well as in soils. Correlation coefficient was used to determine the association between the trace metals in the cereal crops at $p \leq 0.05$.In addition, graphical illustrations were used to measure the degree of relationship between plant metal concentrations and soil metal concentrations.

3.9 Approaches and Limitations of the Study

1) Acquisition of Experimental Sites

The intended experimental site with close proximity to the Kano-Zaria Highway at about 40 metres and its frequent use for crop cultivation proposed for this study was limited to two challenges;

a). Several difficulties were encountered during the period of obtaining a suitable site for the study because of the adamant nature of the local farmers who refused to rent out their farmlands for this research. The experimental site was obtained from a local farmerafter fourteen (14) months from where samples were collected for this research.

b) Irrigation channels had been constructed on both the left-hand and right-hand wings of the Kano-Zaria Highway around the Irrigation Research Station (IRS), Kadawa. The left wing of the channel was the most suitable but had been nonfunctional for a prolonged period of time. This resulted to the diversion of the water channels from the Tiga dam to the right wing of the irrigation channels along the Kano-Zaria Highway, situated between the Irrigation Research Station and the Hadejia-Jama're River Basin (HJRB). However, the experimental site later obtained was about 1km (1000metres) away from the highway. This was in line with the works of Tiller *et al.*, 1987 that experimental sites for atmospheric soil pollution should be several hundred metres away from the source of pollution.

2) Some morphological traits of the four cereal crops investigated could not be properly observed due to the inaccessibility of the farmlands under study, which belongs to the local farmers.

3) There is no established quantitative method for determining directly the exact or fractional amount of heavy metals that are bioavailable to plants. This is because of many factors such as variations in pH, temperature, chemical composition and redox conditions

4) Prolonged research

The research which initially involved the cultivation of the selected crops was marred by the closure of the Tiga Dam by Hadejia Jama'are River Basin (HJRB) authority in the month of December, 2007. The HJRB provides water for dry season irrigation of farmlands within and outside the irrigation research centre for local, international, private and corporate researches. This resulted to the closure of the dam and non-availability of water for irrigation due to some administrative/ bureaucratic bottlenecks. This action affected the field work, since the experimental sites were situated there, until December 2008.

5) Rainy Season Trial: High Water Table

The rainy season trial could not be conducted because of the high water table of the soils at the irrigation research station during the rainy season which would not favour the maximum growth and yield of maize and wheat. During that period, rice is the only feasible crop in the area. Also one-on-one interactions with the officers that have been working there for years revealed that rainy season trials ofwheat have not been conducted at the Irrigation Research Station, Kadawa.

CHAPTER FOUR

4.0 RESULTS

4.1 Preliminary Trace Metal Levels in Soils

The concentrations of trace metals in the soils during the development of the four varieties of cereal crops, from germination or seedling to ripening stages were higher than the trace metal concentrations of the soils before sowing (Table 4.1). Copper was not detected on the control site before sowing (Table 4.1). Soil Zn and soil Cu were the highest and lowest trace metals respectively at the SU 3 (344.2mg/kg and 3.24mg/kg) among the five trace metals investigated. Similarly, soil Pb was highest at SU 3 (160mg/kg), a sampling unit on the experimental site and lowest at SU 1 (40mg/kg) and SU 4 (40mg/kg). The levels of Cd were highest and lowest at SU 4 and SU 2. Chromium concentration was highest at SU 2 and SU 3. There was general decreasing trend of the soil trace metals as follows; Zn>Pb>Cr>Cd>Cu.

4.2 Physico-Chemical Parameters of the two Locations

The results obtained for physico-chemical parameters are presented in Table 4.2. The soil pH values ranged from 4.66 (SU 2) to 6.41 (SU 1). The soil pH at all the sampling units was basically moderately or slightly acidic. The organic content (% OC), organic matter (% OM) and cation exchange capacity (CEC) ranged from 0.65 to 1.82, 1.05 to 1.50 and 5.9 to 8.01 respectively. The soils of Kano-Zaria Highway (SU 3) and IRS (SU 4) had a higher Zn levels at pH of 5.75 and 6.21 respectively (Table 4.2). SU 1(1.50) and SU 3(1.05) recorded the highest and lowest organic matter respectively while the highest and lowest organic content was at SU 3 (1.82) and SU 2 (0.65) respectively. SU 1 and SU 4 had the same textural class of sandy clay loamy, the highest organic matter and slightly acidic pH, while SU 3 and SU 2 have a sandy loam texture, a higher organic matter and high pH. SU 3 has the highest organic carbon followed by SU 1, SU 4 and SU 2. The CEC ranges from 5.9 (SU 2) to 8.01(SU 4).

Table 4.1 Preliminary Trace Metal Concentrations (mg/kg) in soils from the two Locations: Doruwa Salau at close proximity to the Kano – Zaria Highway and the Irrigation Research Station (2008).

Sampling Units	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
SU 1	55	58.16	11.82	40	216.5
SU 2	45	62	ND	80	166
SU 3	65	62	3.24	160	344.2
SU 4	70	59	18.24	40	273

KEY
SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental Site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS), Kadawa
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa (Control Site)
ND = Not detected

Table 4. 2 Physicochemical Analysis of Soils from Doruwa Salau at close proximity to the Kano- Zaria Highway and the Irrigation Research Station before sowing (2008)

Site	% Sand	% Silt	% Clay	Textural Class	pH H_20 1:1	pH HCL 1:1	% OC	% OM	CEC
SU 1	62. 9	15. 2	21. 9	Sandy Clay loam	6. 41	5. 77	0. 88	1. 50	7. 25
SU 2	75. 5	12. 4	12. 1	Sandy loam	5. 48	4. 66	0. 65	1. 12	5. 9
SU 3	71.6	13.5	14. 9	Sandy loam	5.75	4. 86	1. 82	1. 05	6. 3
SU 4	60. 5	17. 2	22. 3	Sandy clay loam	6. 21	5. 40	0. 78	1. 36	8. 01

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria road
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS), Kadawa
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria road
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa

4.3. Trace Metal Concentrations in the Two Varieties of Wheat and Maize at Doruwa Salau (Close Proximity to the Kano-Zaria Highway(S1) and Irrigation Research Station (S2))

The total concentrations of Cd, Cr, Cu, Pband Zn in the two varieties of wheat and maize at both the experimental and control sites and their comparison of means are given in Table 4.3.

The Pavon-76 on SU 1 at Doruwa Salau at close proximity to the Kano – Zaria Highway exhibited higher levels of Pb at the 30-days growth stage than the other cereals (Table 4.3). Wheat variety Pavon-76 has the highest levels of Cd (370 mg/kg) and Cu (107.17 mg/kg) at the 90-days and 75-days growth stages respectively (table 4.3). Siettecerros on SU 2 at the IRS exhibited higher levels of Pb at the 30-days growth stage than the other cereals (Table 4.3). In contrast, popcorn on SU 4 at the 15-days growth stage contained the highest levels of Zn (903.36 mg/kg).Furthermore the concentration of Cr (20.65 mg/kg) was higher at the 90-days growth stage at IRS (Table 4.3).

The comparison of means was non-significant for Cr, Cu and Zn between the varieties of *Triticum aestivum* L. and significant for Pb andCd (Table 4.3). Between the two varieties of *Zea mays* L., it was significant for Cd, Cu and Pb and non-significant for Cr and Zn (Table 4.3).

Table 4.3 Cadmium, Chromium, Copper, Lead and Zinc (mg/kg) Levels in Pavon-76 and Yellow Maize at Doruwa Salau at close proximity to the Kano-Zaria Highway and Comparison of means between the varieties.

Sample site/ Growth Stages	**Cadmium (Cd)**		**Chromium (Cr)**		**Copper (Cu)**		**Lead (Pb)**		**Zinc (Zn)**	
Doruwa Salau/IRS *Triticum aestivum* L.	Sampling Units									
	SU 1	SU 2	SU1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2
15 days	215	115	12 .93	11.44	47. 77	105.26	1040	1280	639.32	453.45
30 days	170	280	12.16	12.77	65. 05	68.73	2520	1960	54.69	29.75
45 days	140	190	11. 73	10.58	69. 17	79.93	360	1080	285. 83	233.41
60 days	130	220	11. 84	12	65. 86	60.27	1080	740	56. 25	79.87
75 days	290	320	11. 53	11.55	107. 17	89.14	1220	800	383.12	297.81
90 days	370	150	13. 25	16.2	74. 12	67	620	1040	55. 28	52.09
T – test	**3.6951a**		**1. 6851b**		**2.0577b**		**6.5217a**		**2.2962b**	
Doruwa Salau/ IRS *Zea mays* L.	Sampling Units									
	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4
15 days	180	215	12. 02	9.88	39. 51	15.7	980	1700	330. 34	903.36
30 days	110	270	3. 25	13.74	42. 99	80.15	1920	1100	241. 83	60.29
45 days	160	280	11. 4	10.82	78. 15	53.75	200	700	433. 88	430.13
60 days	280	220	14. 91	11.89	37. 3	102.51	920	560	51. 08	76.53
75 days	240	320	11. 33	11.74	103. 53	30.45	880	220	277. 68	529.56
90 days	250	180	13. 66	20.65	66. 84	50.83	1200	960	32. 93	62.88
T – test	**4.7491a**		**1.2385b**		**4. 1335a**		**6.0445a**		**1. 9989b**	

Trace Metals (mg/kg)

FAO/WHO Safe Limits(Cd=0.01mg/kg; Cr=1.30mg/kg; Cu=10.00mg/kg; Pb=2.00mg/kg; Zn = 5.00mg/kg)

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)

SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)

SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)

SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)

a = significant at 0.05% level

b = non-significant

The one-way ANOVA for the individual metals in Pavon-76 was non-significant for Cd, Cr, Cu and Pb and highly significant (P=0.01) for Zn at all the growth stages (Apendix IVa - e). There was highly significant variations (P=0.01) for Cr, Cu and Zn, and non-significant variation for Pb levels in yellow maize (Appendix IVf – j).

There was no significant variation in the one-way ANOVA for Cd, Cr, Cu and Zn. Pb levels in Siettecerros at the control site washighly significant (Appendix IVk - o). There was significant variations in the levels of Cr in popcorn and non-significant in Cd, Cu, Pb and Zn (Appendix IVp – t).

The magnitude of trace metals detected in the different kinds of cereals was Cr<Cu<Cd<Zn<Pb.The most abundant trace metal among the cereal crops was Pb (2520 mg/kg) in Pavon-76 at close proximity to the Kano – Zaria Highway at the 30-days growth stage. Among the wheat varieties at both Doruwa Salau and IRS, the highest Pb level was also at the 30-days growth stage in Pavon-76. The lowest value of trace metals was observed for Cr (10.58mg/kg) in sietteccerros at the 45-days growth stage. Similarly, among the maize varieties, the highest and lowest value of trace metals was recorded for Pb (1920mg/kg) and Cr (3.25mg/kg) in yellow maize at the 30-days growth stage. Cd concentration was generally higher at both sites in the same ratio. Cd concentrations were also greatest in the wheat varieties than in the yellow maize and popcorn.

The magnitude of the accumulation level of trace metals in the cereal crops was pavon-76> siettecerros >yellow maize> popcorn. Pb was reportedly the highest in concentration followed by Zn, Cd and Cu at SU 1 than on the SU 3 both at the site close to the Kano-Zaria Highway. In contrast, the concentration of Cr was highest on SU 3 than on SU 1 (Table 4.3). At the control site (IRS), the levels of Pb and Cu were highest on SU 2, while Cd, Cr and Zn were highest at SU 4 (Table 4.3).

The contamination status of the investigated trace metals in the cereal crops were determined by comparing with the recommended maximum acceptable levels proposed by the Codex Alimentarius of the Joint FAO/WHO food standards (2006) and this exceeded the Joint FAO/WHO limits (Table 4.3).

4.4 Trace Metal Concentrations in the Soils

The total concentrations of Cd, Cr, Cu, Pb and Zinc in the representative soil samples at the six growth stages of the two varieties of wheat and maize obtained for this study are shown in Table 4.4.

Soil Pb, Cd, Cr, Cu and Zn were highest on SU 2 than on SU 4 both at the control site. Soil Zn was reportedly the highest followed by soil Cd> soil Cr> soil Pb> soil Cu. However, Pb levels were not detected in the representative soil samples. Soil Pb, Cu and Cr were below the allowable limits (Appendix IIIb). Soil Zn was generally above the allowable limits (Appendix IIIb).

Generally, total soil trace metal concentrations were highest at Doruwa Salau at close proximity to the Kano-Zaria Highway than at the control site- Irrigation Research Station, Kadawa.

The highest and lowest soil Cd concentrations (100 mg/kg - 40 mg/kg) were evident at the experimental site in yellow maize at the 90 days (ripening) and 60 days (heading) growth stages respectively (Table 4.4). Soil Cr levels was highest (75.8 mg/kg) SU 2 (IRS) in Siettecerros at the 90 days growth stage and lower (33.5 mg/kg) at SU 3 (Kano – Zaria Highway) in yellow maize also at the 90 days growth stage. Soil Cu levels was highest (60.16 mg/kg) at the 30 days growth stage on SU 2 (IRS) in Siettecerros and lower (1.2

mg/kg) at the 75 days (flowering) growth stage on SU 3 (Kano – Zaria Highway) in yellow maize (Table 4.4).

Soil Pb levels was highest (160 mg/kg) at the experimental site in both the Pavon-76 (SU 1) and yellow maize (SU 3) at the 75-days and 60-days growth stages respectively. Also soil Pb levels was not detected on both sites throughout the growth stages except at the 45-days (shooting) and 75-days (flowering) at the control site (Table 4.4). Soil Zn was highest (420. 45 mg/kg) in yellow maize (SU 3) at the experimental site and lowest (45. 7 mg/kg) in Siettecerros (SU 2) at the control site at the 60-days growth stage respectively (Table 4.4).

The comparison of means was non-significant (P = 0.05) for soil Cd, Cr and Pb and significant for Cu and Zn (P = 0.05) at both the experimental and control sites where *Triticum aestivum* L. was planted.At the sites where *Zea mays* L. was obtained, soil Cd, Cr, Cu and Zn levels were significant and non-significant for Pb (Table 4.4). Also comparison of the mean values with the ECDGE (2010) was below the limits for Cr, Cu, Zn and Pb and exceeded for Cd.

For SU 1, SU 2, SU 3 and SU 4, there were no significant differences for the individual ANOVA of the soil trace metals at the six growth stages (Table 4.4.1).

Table 4.4 Cadmium, Chromium, Copper, Lead and Zinc (mg/kg) Levels in Soil samples at the four sampling units and Comparison of mean between the varieties.

Growth Stage	Cadmium (Cd)		Chromium (Cr)		Copper (Cu)		Lead (Pb)		Zinc (Zn)	
	Trace Metals (mg/kg)									
Doruwa Salau/IRS *Triticum aestivum* L.	Sampling Units									
	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2
15 days	70	65	56	60.3	57. 39	30.71	ND	ND	186. 08	676
30 days	55	65	74. 7	62	10. 24	60.16	40	ND	218. 65	305.5
45 days	65	60	9. 53	67.2	19	9.19	40	40	171. 74	296.95
60 days	65	70	55. 5	59.9	36. 8	21.9	40	ND	235. 7	45.7
75 days	55	55	55. 25	54.9	10. 85	9.56	160	40	315. 5	221.79
90 days	85	95	49. 7	75.8	57. 65	13.23	80	ND	213. 34	298.16
T-test	**1.7017b**		**2.4640b**		**3.0265a**		**2.4433b**		**2.7724a**	
Doruwa Salau/IRS *Zea mays* L.	Sampling Units									
	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4
15 days	65	50	61. 6	61.14	9. 87	2.56	80	ND	343. 65	153
30 days	90	65	61. 6	57.46	12. 37	5.12	ND	ND	363. 29	98.5
45 days	80	70	64. 6	59.85	5. 15	8.5	40	ND	193. 68	118.5
60 days	40	70	55. 15	39.49	13. 67	47.19	160	ND	420. 45	184.89
75 days	70	80	53. 93	57.8	1. 2	18	80	ND	139. 65	236
90 days	100	70	33. 5	44.25	20. 4	24.99	ND	ND	148. 52	45.5
T-test	**5.1627a**		**2.9200a**		**2.5718a**		**2.4230b**		**4.8366a**	

See Appendix IIIb for Soil Allowable Limits (ECDGE, 2010)

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental Site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS), Kadawa (Control Site)
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental Site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)
a= significant at 0.05%
b = non-significant
ND = Not detected

TABLE 4.4.1 ANOVA for Soil Trace Metals at the four sampling units where the two Varieties each of Wheat and Maize were obtained.

Source of Variation	DF	SU	Variety	SS	MS	F-RATIO
Growth Stage(G -1)	5	SU 1	Pavon-76	2385190.85	477038.17	1.1207[b]
	5	SU 2	Siettecerros	427044.35	85408.87	1.3081[b]
	5	SU 3	Yellow Maize	136004.34	27200.86	1.3192[b]
	5	SU 4	Popcorn	99422.57	19884.51	2.8913[b]

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)
a = significant at 0.05 level
b = non-significant
ND = Not detected

There was also no significant differences in the combined ANOVA for soil trace metals at the six growth stages, but the combined ANOVA was significant (p=0.05) at the growth stages only (appendix VIf).

4.5. Trace Metal Concentrations in the Leaves of the Two Varieties each of Wheat and Maize.

The total concentrations of Cd, Cr, Cu, Pb and Zn in the leaves of the two varieties each of wheat and maize are given in Table 4.5.

The highest and lowest leaf trace metal levels in Pavon-76 were Pb at the 15-days and 30-days growth stages respectively (4.5). Also among the varieties of *Triticum aestivum* L., Pavon-76 recorded the highest trace metal levels particularly for Pb (Table 4.5). Cr had the lowest levels as compared to Cd, Cu, Pb and Zn. Pb was not detected in Pavon-76 at the 30-days growth stage.

In the case of *Zea mays* L. varieties, yellow maize had the highest leaf metal levels for Pb at the 30-days growth stage. While the lowest leaf metal levels was found in Cu (1.9mg/kg) at the 15-days growth stage in popcorn (Table 4.5).

The concentrations of the leaf Cr, Pb and Zn was invariably higher on SU 1 at the experimental site, while leaf Cu was highest on SU 3 with leaf Cd having the same concentration at both sampling units also at the experimental site. At the control site,
leaf Zn and Pb levels was highest on SU 2 while the concentrations of Cr, Cd and Cu was highest on SU 4.

Table 4. 5 Leaf Trace Metal concentrations (mg/kg) inWheat and Maize and the Comparison of means between the two varieties.

Growth stage	Cadmium (Cd)		Chromium (Cr)		Copper (Cu)		Lead (Pb)		Zinc (Zn)	
	Sampling Units									
	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2
15 days	75	35	5.47	4.03	21.32	22.5	0	300	234.22	283.88
30 days	80	40	3.75	3.53	30.6	20.21	960	820	18.08	12.4
45 days	40	80	4.03	3.93	20	6.9	60	560	73.63	111.7
60 days	60	110	3.75	4.08	18.1	14.4	360	260	25.33	26.88
75 days	50	80	3.85	3.7	31.78	30.72	800	320	242.6	124.13
90 days	120	40	4.28	6.5	22.51	22.41	40	480	18.18	23.95
T-test	**6.5336a**		**2.1818b**		**2.2162b**		**2.5586b**		**2.0016b**	
	Sampling Units									
	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4
15 days	120	75	3. 95	4.04	10. 06	1.9	260	140	130. 67	261.52
30 days	40	120	1.08	3.54	15. 06	36.3	820	320	64. 72	6.35
45 days	70	120	3. 93	3.99	4. 13	2.15	60	320	128. 21	184.93
60 days	100	80	4. 8	3.99	7. 5	17.26	240	160	24. 07	26.64
75 days	70	30	3. 83	3.98	37. 78	3.23	480	160	128. 13	212.46
90 days	100	40	3. 54	7.52	26. 3	19.8	160	320	7. 5	15.85
T-test	**4.5668a**		**1.9523b**		**2.8098b**		**3.7820b**		**2.9019b**	

KEY
SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental Site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental Site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)
a = significant at 0.05 level
b = non-significant
ND = Not detected

The comparison of means was significant for Cd only between the varieties of *Triticum aestivum* L. and *Zea mays* L. and non-significant in both varieties of *Triticum aestivum* L. and *Zea mays* L. for Cu, Pb and Zn (Table 4.5).

The individual ANOVA for leaf trace metals concentrations for all the cereal crops was highly significant (P=0.01) for growth stage in Pavon -76 only (Table 4.5.1, Appendix Va, Ve, Vi, Vm).

4.6. Trace Metal Concentrations in the Stems of the Two Varieties each of Wheat and Maize.

The total concentrations of Cd, Cr, Cu, Pb and Zn in the stems of the two varieties each of wheat and maize studied are given in Table 4.6.

The levels of stem trace metals were highest and lowest for Pb (960mg/kg) and Zn (1.1mg/kg) both in Siettecerros respectively (Table 4.6), among the varieties of *Triticum aestivum* L. Also between the varieties of *Zea mays* L., popcorn recorded the highest stem trace metal levels (760mg/kg) for Pb at the 15-days growth stage. The 30-days growth stage recorded the lowest stem trace metal levels for Cr in yellow maize (Table 4.6).

There was significant differences in the comparison of means for Pb, Cd (P=0.05) and Cu (P=0.05) between the varieties of *Triticum aestivum* L. Cd and Pb was significant for the varieties of *Zea mays* L. (Table 4.6).

Table 4.5.1 ANOVA for Leaf Trace Metal Levels at the sampling units where the two Varieties of each of Wheatand Maizewere obtained

Source of Variation	DF	SU	Variety	SS	MS	F-RATIO
Growth Stage						
(G – 1)	5	SU 1	Pavon-76	285604.94	57120.99	7.8322[a]
	5	SU 2	Siettecerros	47412.45	9482.49	0.6506[b]
	5	SU 3	Yellow Maize	114833.89	22966.78	3.5660[b]
	5	SU 4	Popcorn	21710.74	4342.15	0.5703[b]

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)

SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)

SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)

SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)

a = significant at 0.05 level

b = non-significant

Table 4.6 Stem Trace Metal concentrations (mg/kg) in Wheat and Maize and the Comparison of means between the two varieties.

Growth Stage	Cadmium (Cd)		Chromium (Cr)		Copper (Cu)		Lead (Pb)		Zinc (Zn)	
	Sampling Units									
	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2
15 days	90	50	6. 47	3.62	23. 75	35.49	400	580	202. 6	70.73
30 days	60	70	3. 1	1.14	17. 95	18.52	840	960	9. 9	1.1
45 days	50	40	3. 95	3.42	22. 42	29.7	80	460	131. 91	93.22
60 days	40	50	3. 92	3.74	22. 05	9.67	560	400	17. 17	38.42
75 days	150	120	3. 85	3.81	41. 19	42	180	320	76. 15	64.29
90 days	140	80	4. 05	5.12	91	9.8	320	400	19. 57	20.38
T-test	**3.1601a**		**2.3846b**		**3.3285a**		**4.1059a**		**1.7819b**	
	Sampling Units									
	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4
15 days	40	80	3. 92	4.16	16. 15	4.72	160	760	115. 48	465
30 days	20	90	1. 86	5.66	16. 1	10.25	480	300	81. 25	27.53
45 days	40	40	3. 8	3.31	34	31.5	60	240	127. 54	117.1
60 days	120	60	3. 65	3.65	18. 3	21.39	620	240	14. 28	15.4
75 days	50	80	3. 92	3.92	28. 8	2.82	240	60	107. 27	250
90 days	80	100	6. 73	6.73	20. 14	17.83	560	400	10. 2	30.17
T-test	**3.4814a**		**1.1635b**		**2.2720b**		**3.8742a**		**1.7549b**	

KEY
SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)
a = significant at 0.05 level
b = non-significant

Table 4.6.1 ANOVA for Stem Trace Metal Levels in the two Varieties of Wheat and Maize

Source of Variation	DF	SU	Variety	SS	MS	F-RATIO
Growth Stages (G – 1)	5	SU 1	Pavon-76	84329.75	16865.95	1.3598[b]
	5	SU 2	Siettecerros	571455.22	14291.04	2.5669[b]
	5	SU 3	Yellow Maize	114833.89	22966.78	0.7939[b]
	5	SU 4	Popcorn	224529.69	44905.94	2.7921[b]

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)

SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)

SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)

SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)

a = significant at 0.05 level

b = non-significant

The individual ANOVA for stem trace metals concentrations for the four cereal crops were generally non-significant at the growth stages (Table 4.6.1, Appendix Vb,Vf, Vj, Vn).

4.7. Trace Metal Concentrations in the Roots of the Two Varieties each of Wheat and Maize.

The total concentrations of Cd, Cr, Cu, Pb and Zn in the roots of the two varieties each of wheat and maize studied are given in Table 4.7. Among the varieties of *Triticum aestivum* L., Pavon-76 had the highest root Pb levels (720mg/kg) at the 30-days growth stage than for all the other trace metals. Similarly, the lowest value was found in Pavon-76 for Cr (0.99mg/kg) at the 15-days growth stage. The highest and lowest root metal levels among the varieties of *Zea mays* L. were found in popcorn for Pb (800mg/kg) at the 15-days growth stage and in yellow maize for Cr (0.31mg/kg) at the 30-days growth stage respectively. Pb was not detected in popcorn at the 75-days growth stage.

The decreasing trend in the accumulation pattern of trace metals was in the order of Pb>Zn>Cd>Cu>Cr respectively (Table 4.7) at both the experimental and control sites. The trace metal levels were generally higher at the experimental site than at the control site.

The root trace metal levels were non-significant for Cd, Cr, Cu, Pb and Zn for the wheat varieties and significant for Cd, Cu, Pb and Zn and non-significant for Cr in the Maize varieties (Table 4.7).

Table 4.7 Root Trace Metal concentrations (mg/kg) in Wheat and Maize and Comparison of means between the two varieties.

Growth Stage	Cadmium (Cd)		Chromium (Cr)		Copper (Cu)		Lead (Pb)		Zinc (Zn)	
	Sampling Units									
	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2	SU 1	SU 2
15 days	50	30	0. 99	3.79	2. 70	47.27	640	400	204. 5	98.84
30 days	30	170	5. 31	5.1	16. 5	30	720	180	26. 71	16.25
45 days	50	70	3. 75	3.23	26. 75	43.33	220	60	80. 29	28.49
60 days	30	60	4. 2	4.18	25. 5	26.2	160	80	13. 75	14.57
75 days	90	120	3. 83	4.04	34. 2	16.42	240	160	64. 37	109.39
90 days	110	30	4. 92	4.6	22. 61	24.8	160	160	17. 53	7.76
T-test	**2.7212b**		**1.7692b**		**2.4604b**		**2.3297b**		**2.3214b**	
	Sampling Units									
	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4	SU 3	SU 4
15 days	20	60	4.15	1.68	13. 3	9.08	560	800	84.19	178.84
30 days	50	60	0. 31	4.54	11. 83	33.6	620	480	95. 86	26.41
45 days	50	120	3. 67	3.52	40. 02	20.1	80	140	178. 13	128.1
60 days	60	80	6. 71	4.25	11. 5	63.5	60	160	12. 73	34.49
75 days	120	40	3. 66	3.84	36. 95	24.4	160	ND	42. 28	64.1
90 days	70	40	6. 3	6.4	20.4	13.24	80	240	15. 23	16.86
T-test	**3.6640a**		**2.2608b**		**2.7787a**		**5.2535a**		**3.0508a**	

KEY
SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)
a = significant at 0.05 level
b = non-significant

Generally, the result of the present analysis showed that the concentration of Cd was highest in the roots than in the stems and leaves occurring in the same ratio. The concentration of Cr and Pb were highest in the leaves followed by the stems, then the roots, while the roots accumulated higher levels of Cu and Zn than in the leaves and stems. There was also a general fluctuation and variations in the levels of trace metals among the six growth stages.

The individual ANOVA for the root trace metal concentrations for the cereal crops were also generally non-significant but significant (P=0.05) in popcorn (Appendix Vc, Vg, Vk, Vo, Table 4.7.1) at the growth stages.

The combined ANOVA for trace metals between plant parts was highly significant (P=0.01) for popcorn and Pavon-76 at the growth stages only and for Siettecerros at the replication within plant only, while there was no significant difference in yellow Maize.(Appendix VIa, VIb, VIc, VId)

The combined ANOVA for trace metals between the four crops was highly significant (P=0.01) at the two sites (experimental and control sites) at the replications within crops or varieties, growth stages and the interactions between plant parts, growth stages and crops or varieties. (Appendix VIe)

Table 4.7.1 ANOVA for Root Trace Metal Levels in the two varieties of Wheat and Maize

Source of Variation	DF	SU	Variety	SS	MS	F-RATIO
Growth Stages (G – 1)	5	SU 1	Pavon-76	123711.11	24742.22	1.7277[C]
	5	SU 2	Siettecerros	40337.27	8067.45	0.1160[C]
	5	SU 3	Yellow Maize	66462.03	13292.41	0.8570[C]
	5	SU 4	Popcorn	168925.65	33785.13	5.2786*

KEY

SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)

SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)

SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)

SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)

a = significant at 0.01 level

b = significant at 0.05 level

c = non-significant

ND = Not detected

4.8. Trace Metal Concentrations In the Soil-Plant Systems

Comparison of the soil trace metal levels in this study with the ECDGE (2010) exceeded the permissible or acceptable limits for Cd and Zn in all the member countries and according to literature by Bowen, (1976; 1979) and Greenwood (1984). (Appendix IIIa). Values for Cr, Cu and Pb were within the limits for all the countries too (Appendix IIIb).

Trace metal levels (Cd, Cr, Cu, Pb and Zn) were highest in all the plant parts of the cereal crops (siettecerros, pavon-76, yellow maize and popcorn) determined than in the soil, despite that the soil and plant samples were collected at the same spot and same time at the various growth stages. In contrast chromium levels were highest in the soils than in all the crops as earlier observed in Tables 4.3 and 4.4.

Plant Cd levels (110mg/kg), Cr levels (9. 88mg/kg) and Cu levels (15. 7mg/kg) were lowest at Doruwa, the site close to the Kano-Zaria Highway in yellow maize (SU 3) at 30 days growth stage and at IRS (SU 4) in popcorn at the 15-day growth stage respectively. Also plant Pb (200 mg/kg) was lower at the site cose to the Kano-Zaria Highway in yellow maize, while wheat (Pavon-76) at the 30-days growth stage contained lower Zn levels (29. 75 mg/kg).

The individual ANOVA for each of the trace metals was highly significant for Pb and Cu at SU 2 and SU 3 only respectively; highly significant for Cr in the two varieties of *Zea mays* L. at SU 3 and SU 4 only; and highly significant for Zn at SU 1 and SU 3 only (Appendix IVa - IVt).

The paired-student t-test between the soil trace metals and plant; siettecerros and yellow maize at the experimental site and popcorn at the control site were significant (P=0.05) and non-significant in pavon-76.

The concentration levels of trace metals in the leaves, stems and roots of the cereal crops at the two sites ranged from low to high as shown in Table 4.8. Trace metal levels ranged from 3.83mg/kg to 426.66mg/kg. Stem Pb had the highest averages at IRS (426.66mg/kg) and at Doruwa Salau (375mg/kg), while the lowest averages was stem Cr (3.83mg/kg) at Doruwa Salau and root Cr (4.09) at IRS (Table 4.8).

The mean levels of trace metals vary greatly among the plant parts (Table 4.9), among the selected growth stages and the four sampling units.Among the sampling units, the mean and SD values for mean leaf trace metal levels ranged from 65.88±25.90 to 376.07±86.01 at SU 1 respectively. Also the values ranged from 88.44±25.78 at SU 3 to 437.96±279.88 at SU 4 for mean stem trace metal levels while the mean root trace metal levels ranged from 45.11±11.43 to 349.20±91.00 at SU 4 respectively. In addition, among the sampling units, the mean soil trace metal levels ranged from 197.51±4.9 at SU 2 to 600.12± 13.88 at SU 3 (Table 4.9).

Among the growth stages withing the sampling units, the mean trace metal levels was highest (75-days) and lowest (45-days) both at SU 1 respectively. Mean stem trace

Table 4. 8. Ranges and averages (in parenthesis) of trace metal concentrations (mg/kg) in the leaves, stems and roots of the cereal crops at Doruwa Salau and the Irrigation Research Station, Kadawa.

SITE	Cd	Cr	Cu	Pb	Zn
Kano – Zaria Highway					
Leaf	40 – 120 (77. 08)	1. 08 - 5. 47 (3. 86)	4. 13 – 37. 78 (19. 69)	0 - 960 (361. 66)	7.5 - 242 (91.27)
Stem	20 – 150 (73. 33)	1. 86 – 4. 05 (3. 83)	16. 1 – 41. 19 (24. 15)	60 – 840) (375)	9. 9 – 202. 5 (76. 11)
Root	20 – 120 (60. 83)	0. 31 – 6. 71 (3. 98)	2. 70 - 40. 02 (21. 86)	60 - 720 (341. 66)	12. 73 –204. 5 (69. 63)
Irrigation Research Station					
Leaf	30 – 120 (70. 83)	3. 53-7. 52 (4. 40)	1. 9 - 36. 3 (16. 5)	140 – 820 (346. 66)	6. 35 - 283. 88 (107. 55)
Stem	40 – 120 (71. 66)	3. 31 – 6. 73 (4. 27)	2. 82 – 42 (21. 14)	60 – 960 (426. 66)	1.1- 465 (99. 44)
Root	30 – 170 (73. 33)	1. 68 – 6.4 (4. 09)	9. 08 – 63. 5 (29. 32)	0 – 800 (238. 33)	7. 76 – 178. 84 (60. 59)

Table 4.9 Overall Mean Trace Metals (Cd, Cr, Cu, Pb,Zn)(+ S.D) at the six growth stages of *Triticum aestivum* L.(var. siettecerros and pavon-76), *Zea mays* L. and *Zea mays everta* L. at the four sampling units.

SAMPLING UNITS	GROWTH STAGES	PLANT PARTS LEAF	STEM	ROOT	SOIL
SU 1	15 days	112.00 + 11.23	240.94 + 63.36	299.39+132.60	320.26+175.56
	30 days	364. 14 +164. 99	310.31+116.92	266.17+217.73	398.60 + 84.41
	45 days	65.88 + 25.90	96.09 + 54.77	126.93+103.08	259.89 + 5.86
	60 days	155.79 + 16.31	214.38+196.80	77.81 + 50.17	399.60+128.69
	75 days	376.07 + 86.01	150.39+ 83.24	144.13+188.33	591.17+227.93
	90 days	101.65 + 62.61	170.87+184.72	105.02 + 80.59	445.68+ 98.76
SU 2	15 days	215.13+ 67.84	246.61+ 42.00	193.30+114.80	447.56+ 64.85
	30 days	298.71+ 110.36	351.25+ 90.03	133.78+106.83	457.66+320.54
	45 days	254.17+ 224.11	208.78+ 90.03	74.35+ 16.13	473.33+29.05
	60 days	138.45+ 83.39	170.61+120.23	61.65 + 47.30	197.51 + 4.9
	75 days	186.19+ 130.53	183.37+ 47.86	136.61 + 23.54	381.24+125.78
	90 days	190.95 + 168.56	175.09+62.29	75.72 + 39.08	482.18+139.23
SU 3	15 days	174.89 +72.26	111.85 + 57.68	227.21+199.47	600.12 +13.88
	30 days	313.64 + 70.19	199.73+ 82.19	259.33 + 20.39	527.26 + 42.82
	45 days	88.75 + 12.33	88.44 + 25.78	117.27 + 54.26	508.67+214.69
	60 days	125.45 +21.78	258.66+237.71	50.31 +30.78	596.76+137.27
	75 days	239.91 + 93.17	143.30+78.31	120.96 +56.90	344.17+ 33.30
	90 days	99.11 +31.14	224.72+127.13	196.46+167.57	303.90+12.36
SU 4	15 days	160.82 + 116.57	437.96+279.88	349.20+ 91.00	342.16 + 42.76
	30 days	162.06 + 76.48	144.48 + 44.88	201.51+102.49	226.07 + 4.11
	45 days	210.35 + 128.53	140.63 + 90.82	137.24+13.57	256.85 + 42.83
	60 days	96.08 + 42.12	113.48 + 75.75	114.08+103.37	341.57+ 95.96
	75 days	136.55 + 44.80	132.24 + 28.35	45.11 + 11.43	382.80+181.58
	90 days	134.39 + 95.10	184.91+ 58.30	104.48 + 86.80	384.74+224.79

KEY
SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS), Kadawa
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa

metal levels was highest at the 15-days growth stage and lowest at the 45-days growth stages, while the mean root trace metal levels was highest and lowest at the 15-days and 75-days growth stages respectively.

The levels of trace metals in the soils on both sites were compared with the allowable limits of trace metal concentrations in soils (mg/kg) of other countries (Appendix IIIb). Soil Zn and Cd levels were higher (Table 4.4) than the allowable limits in all the countries, while soil Cr and Cu allowable limits tends to be higher than soils in this study. Generally soil Pb levels was not detected in about 54% of the 24 soil samples obtained from the study sites.

4.9. Mean Trace Metal Concentrations in Plant Parts and Soils

Figures 3 to 10 show the comparison in the concentrations of mean trace metal levels between Doruwa Salau at close proximity to the Kano-Zaria Highway (S1) and the IRS (S2) at the six stages of growth in the leaf, stem and root. In comparison between the wheat and maize varieties, the mean leaf trace metal level was highest in *Triticum aestivum* L. varieties than in the *Zea mays* L. varieties (Fig. 3 and Fig. 4). The mean leaf trace metal levels in Pavon-76 was highest at Doruwa Salau than in Siettecerros at the IRS which is the control site and at the 30-days, 60-days and 75-days growth stages as shown on Fig. 3. At the control site, mean leaf trace metal level was highest at 15-days, 45-days and 90-days growth stages. The highest mean leaf trace metal levels among the selected growth stages was at the 30-days and 45-days growth stages on IRS and at the 30-days and 75-days growth atsges on Doruwa Salau respectively. Also the mean leaf heavy metal levels in yellow maize was highest at Doruwa Salau than in popcorn at the IRS and at the 15-days,30-days, 60-days and 75-days growth stages (Fig. 4).

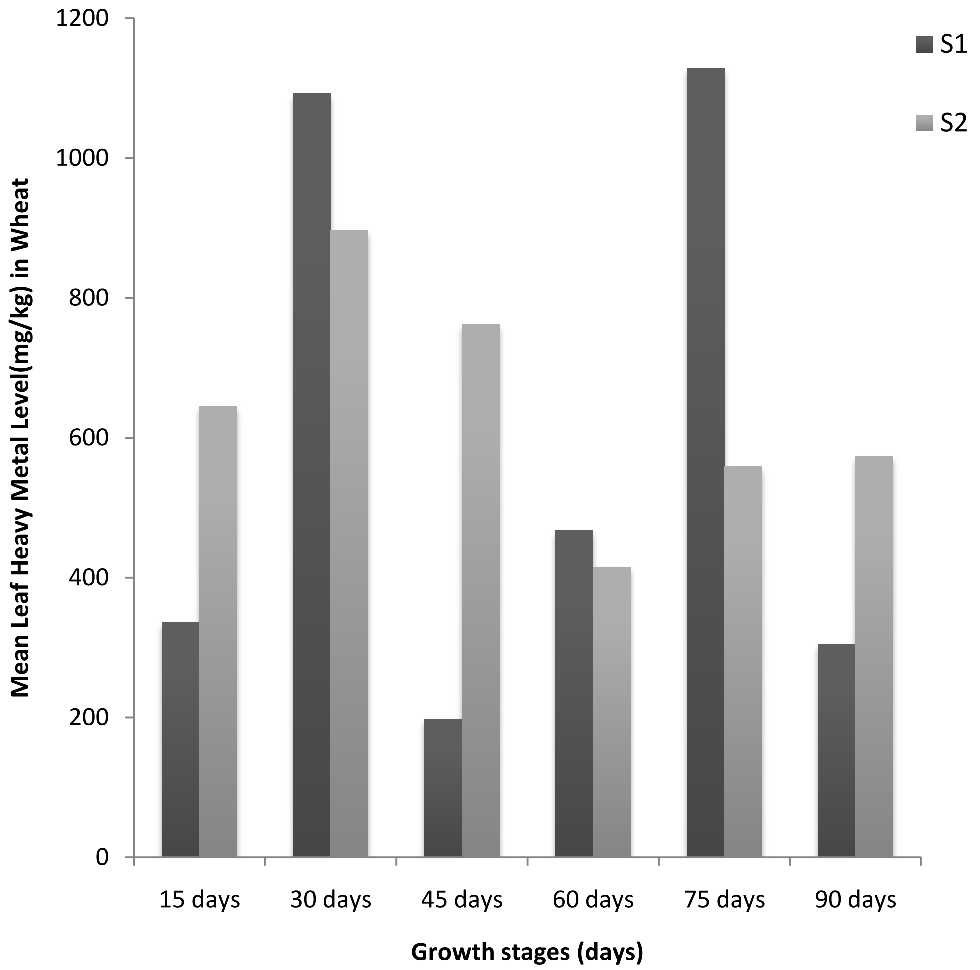

Fig 3: Mean Leaf Heavy Metal Levels between the two varieties of Wheat at Doruwa Salau (S1) and the IRS (S2)

KEY
SU 1 = Pavon-76 at Doruwa Salau
SU 2 = Siettecerros at Irrigation Research Station (IRS)

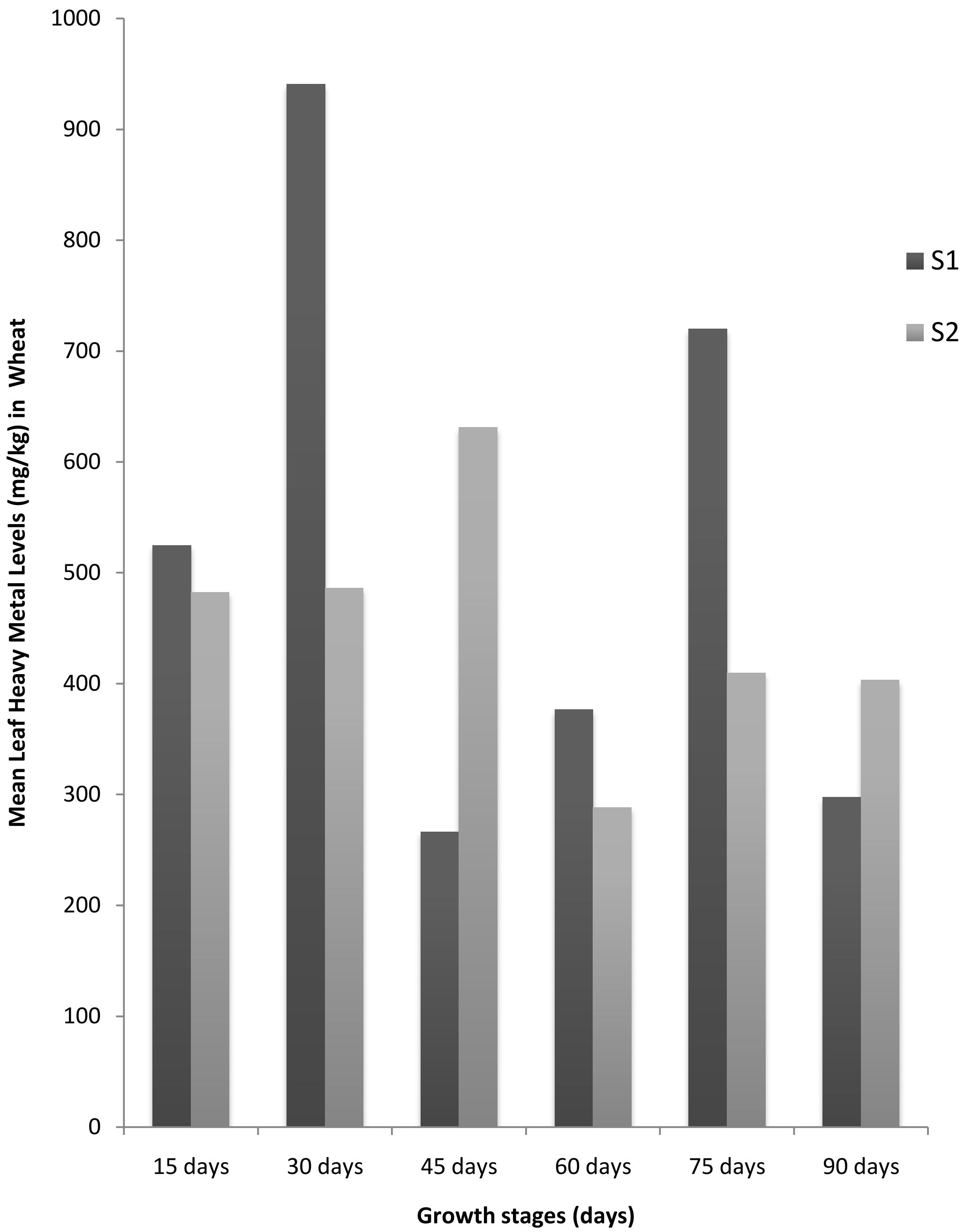

Fig 4: Mean Leaf Heavy Metal Levels between the two varieties of Maize at Doruwa Salau (S1) and the IRS (S2)

KEY
SU 1 = Yellow Maize at Doruwa Salau
SU 2 = Popcorn at Irrigation Research Station (IRS)

Among the selected growth stages, the mean trace metal levels was highest at the 30-days on Doruwa Salau and 45-days at IRS respectively.

Generally, the mean leaf metal concentration was highest at the 75-days growth stage at Doruwa Salau. In addition, mean trace metal concentration was generally highest at the 15-days and 30-days growth stages than at all the other growth stages on all the sampling units.

Also the mean stem trace metal level was highest in the wheat varieties than in the maize varieties (Fig. 5 and Fig.6). The mean stem trace metal level in Pavon-76 was highest in all the six growth stages at Doruwa Salau than in Siettecerros at the IRS. The 15-days and 30-days growth stages recorded the highest levels of mean stem trace metal levels at both Doruwa Salau and IRS (Fig. 5). Similarly, the next highest among the growth stages was at the 75-days also both on Doruwa Salau and IRS.

Doruwa Salau closest to the Kano-Zaria Highway recorded the highest stem trace metal levels in yellow maize at the 30-days, 60-days, 75-days and 90-days growth stages than in the popcorn at the IRS. Among the growth stages, the 15-days growth stage recorded the highest mean stem trace metal levels in *Zea mays everta* L. at IRS, while the 60-days growth stage recorded the highest stem trace metal levels at Doruwa Salau (Fig. 6).

In contrast, the mean root trace metal level was highest in maize varieties than in the wheat vatrieties (Fig. 7 and Fig. 8). The mean root trace metal levels between the two varieties of wheat, Pavon-76 and Siettecerros at Doruwa Salau and IRS respectively are

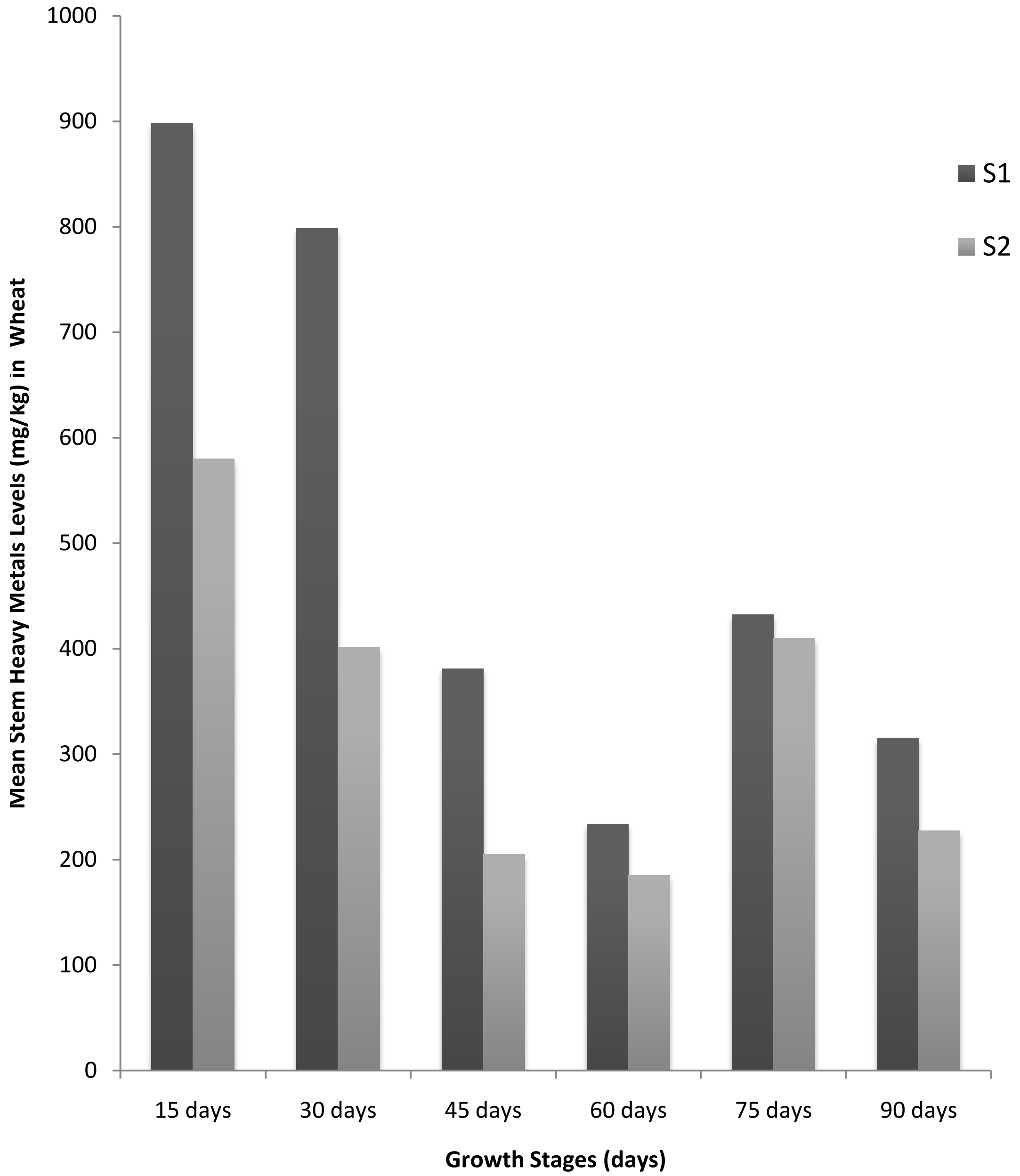

Fig 5: Mean Stem Heavy Metal Levels between the two varieties of Wheat at Doruwa Salau (S1) and the IRS (S2)

KEY
SU 1 = Pavon-76 at Doruwa Salau
SU 2 = Siettecerros at Irrigation Research Station (IRS)

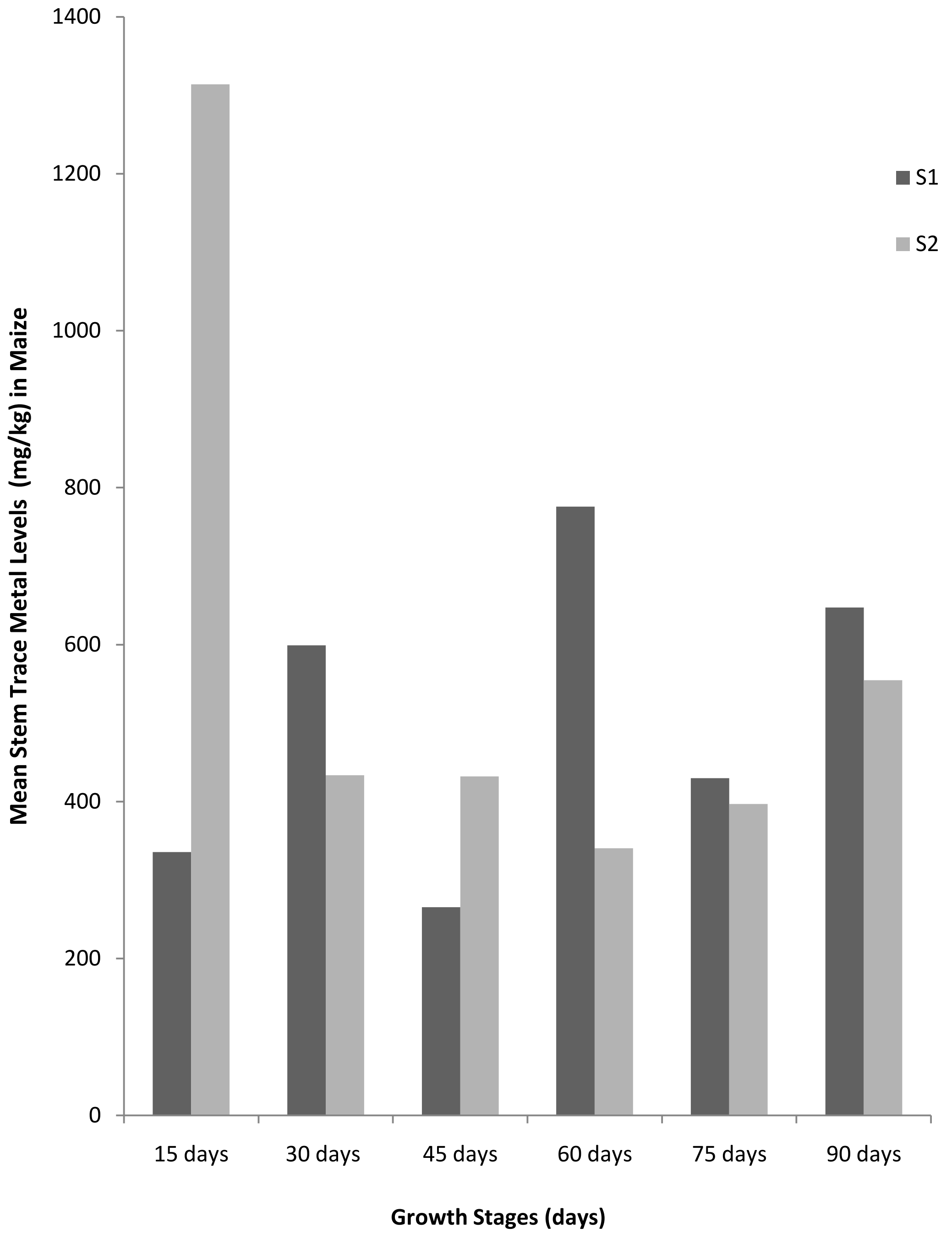

Fig 6: Mean Stem Trace Metal Levels between the two varieties of Maize at Doruwa Salau (S1) and IRS (S2)

KEY
SU 1 = Yellow Maize at Doruwa Salau
SU 2 = Popcorn at Irrigation Research Station (IRS)

shown in Fig. 7. The mean root trace metal level was observed to be highest in Pavon-76 for all the six growth stages at Doruwa Salau than in Siettecerros at the IRS. Both
Doruwa Salau (experimental site) and IRS (control site) had the highest mean root trace metal levels at the 15-days and 30-days growth stages respectively (Fig. 7).

Among the growth stages, the 15-days and 30-days growth stages recorded the highest mean root trace metal levels at both Doruwa Salau and IRS. However, the mean root trace metal level was highest on IRS at the 15-days growth stage and on Doruwa Salau at the 30-days growth stage (Fig. 8). At the 30-days, 75-days and 90-days growth stages, the trace metal levels were highest in the yellow maize closest to the Kano-Zaria Highway than in popcorn at the IRS (Fig. 8).

Fig. 9 and Fig. 10 represent the mean soil trace metal levels in the two varieties of wheat and maize at the selected growth stages at both Doruwa Salau and IRS. At the experimental site where Pavon-76 was planted, soil Pb was not detected at the 15-days growth stage while at the control where siettecerros was planted, soil Pb was also notdetected at the 15-, 30-, 60- and 90-days growth stages (Fig. 9). Soil Pb was not detected at the experimental site where yellow maize whole plant samples were obtained at the 30-days and 90-days growth stages. At the control site where popcorn was planted, soil Pbwas not detected throughout the growth stages (Fig. 10).

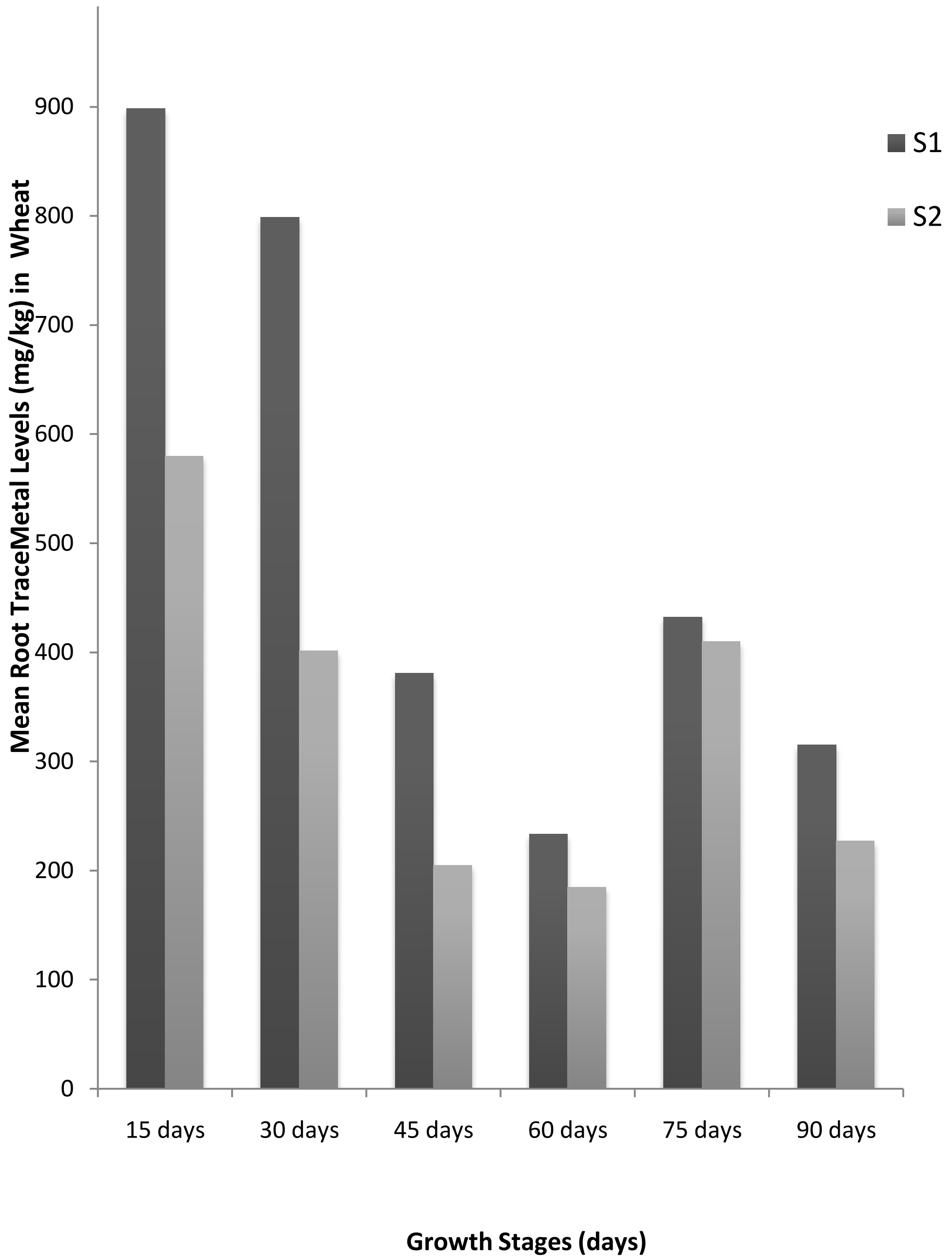

Fig 7: Mean Root Trace Metal Levels between the two varieties of Wheat at Doruwa Salau(S1) and the IRS (S2)

KEY
SU 1 = Pavon-76 at Doruwa Salau
SU 2 = Siettecerros at Irrigation Research Station (IRS)

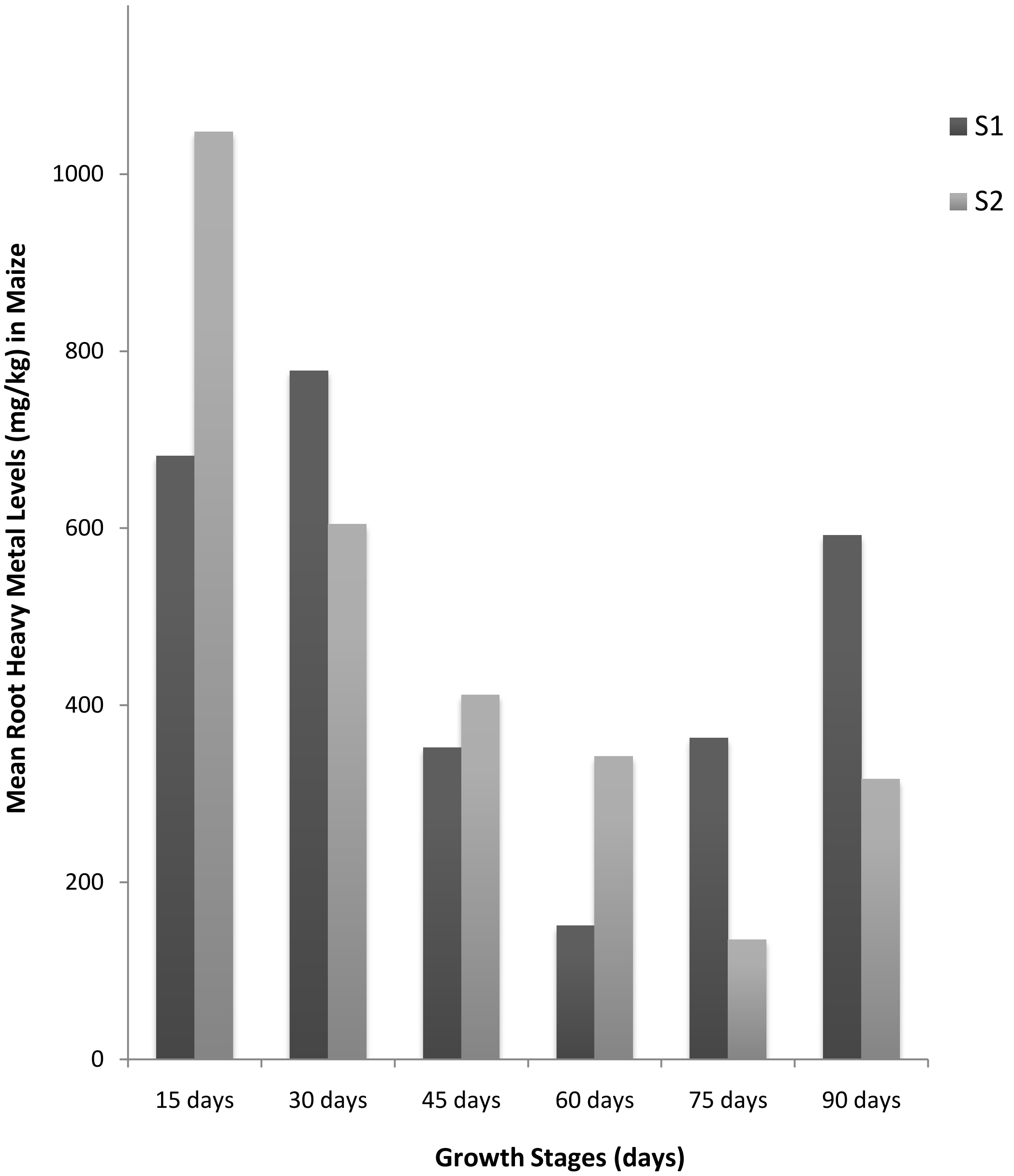

Fig 8: Mean Root Heavy Metal Levels between the two varieties of Maize at Doruwa Salau (S1) and the IRS (S2)

KEY
SU 1 = Yellow Maize at Doruwa Salau
SU 2 = Popcorn at Irrigation Research Station (IRS)

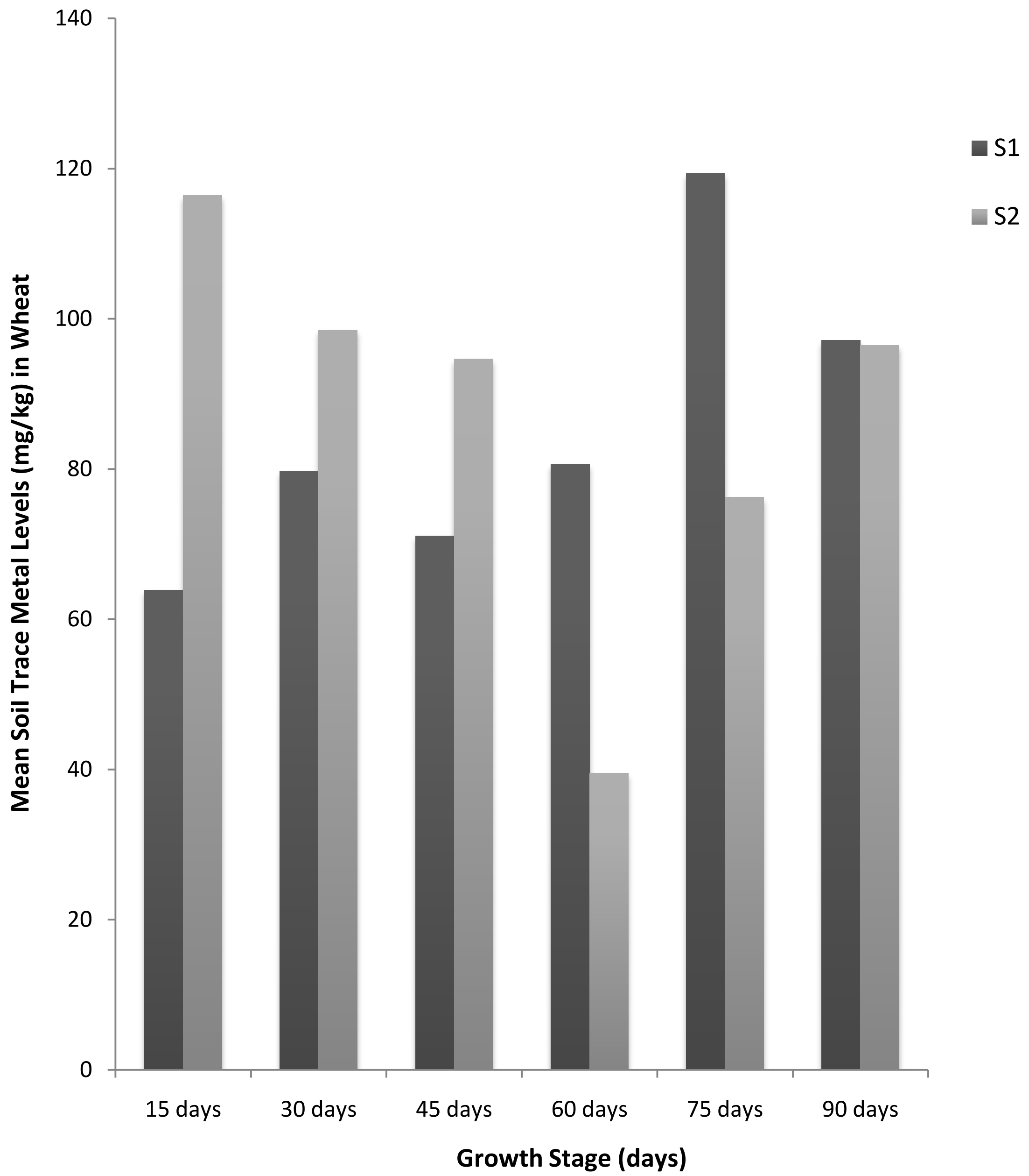

Fig 9: Mean Soil Trace Metal Levels during growth at the selected growth stages of the two varieties of Wheat at Doruwa Salau(S1) and the IRS (S2)

KEY
SU 1 = Pavon-76 at Doruwa Salau
SU 2 = Siettecerros at Irrigation Research Station (IRS)

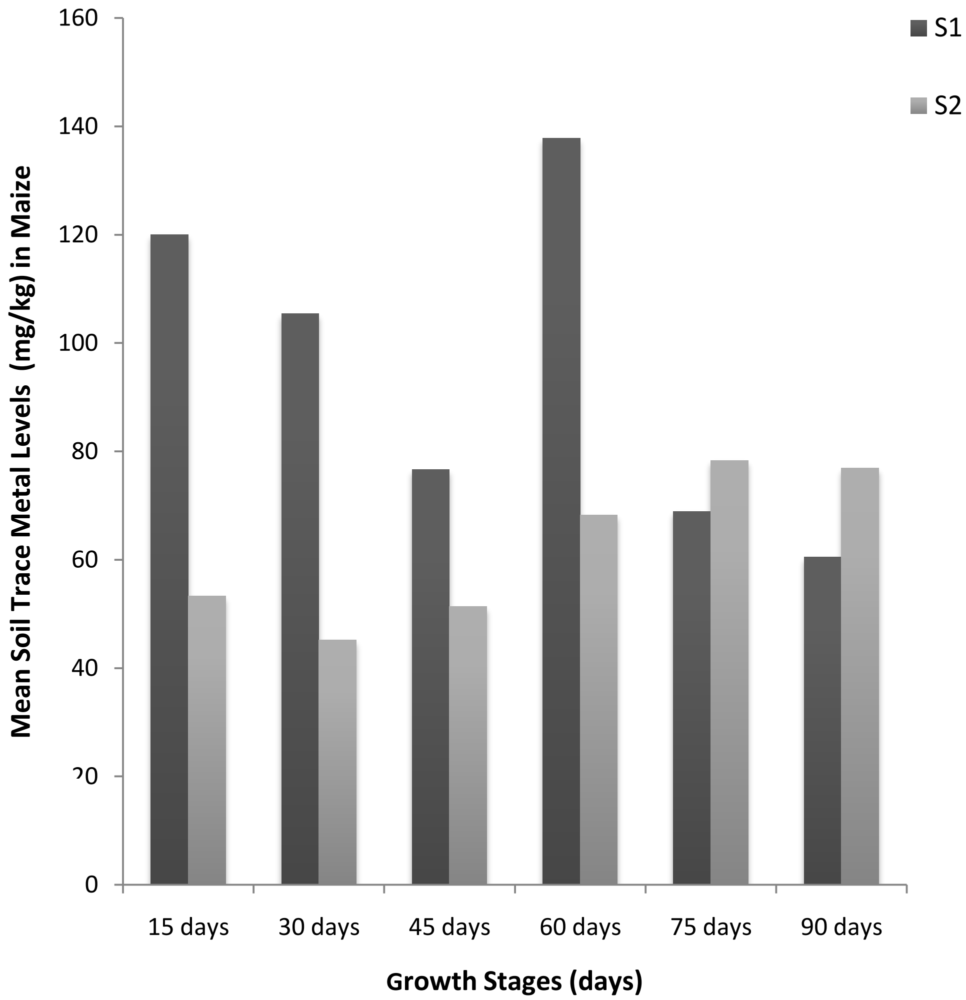

Fig 10: Mean Soil Trace Metal Levels during growth at the selected growth stages of the two varieties of Maize at Doruwa Salau (S1) and the IRS (S2)

KEY
SU 1 = Yellow Maize at Doruwa Salau
SU 2 = Popcorn at Irrigation Research Station (IRS)

4.10. Comparison of Plant and Soil Trace Metal Concentrations among the Growth Stages

The comparison of the individual trace metals levels in soil with plant trace metals of the two varieties of wheat and maize using correlation analysis are presented in Table 4.10 There were no significant variations or differences between the plants trace metal levels and the soil trace metal level (Table 4.10). Metal concentrations in plant parts were not correlated with metal concentration in soil, while there was no correlation in metal concentrations in soils. However, metal concentrations between stem and root were poorly and positively correlated (P=0.05) (Table 4.10).

Graphical illustrations were also used to further investigate the existence of any relationships as shown Fig. 11 to Fig. 30. The Figs 11 to 30 shows the comparison of the concentrations of individual trace metals between the soil and each of the two varieties of the cereal crops in relation to their growth stages.

Generally, the line graphs shows that there is no relationship between the plant part trace metals (Cd, Cr, Cu, Pb and Zn) and soil trace metals on the four sampling units at both the experimental site and control site. Individual plant trace metals were generally higher than the soil trace metals. This indicates that the concentrations of trace metals in the plant parts were not influenced by the soil trace metals. However, there were slight relationships between the plant Cu level and soil Cu level for Siettecerros at the Irrigation Research Station at the 30 days growth stage and for popcorn at the 15- and 75-days growth stages respectively; plant Pb level and soil Pb level in yellow maize at 45 days growth stage; and plant Zn level and soil Zn level at 30- and 60-days growth stages. There was also a close and direct relationship between plant Zn level and soil Zn level for Pavon-76 at the 75 days growth stage and plant Zn levels and soil Zn levels in Siettecerros at the 45-, 60- and 75-days growth stages respectively.

Table 4.10 Correlation Analysis between the levels of Individual Soil Trace Metals and Crop Trace Metals.

		Crop Trace Metals					
Soil Property	**Sampling Units**	**Cd**	**Cr**	**Cu**	**Pb**	**Zn**	**N**
Soil trace metal	Pavon-76-SU 1	0.5292[b]	-0.2992[b]	0.1100[b]	0.0826[b]	-0.0598[b]	6
	Siettecerros-SU2	-0.5147[b]	0.7109[b]	-0.1145[b]	ND	0.6847[b]	6
	Yellow Maize-SU 3	-0.4565[b]	-0.4207[b]	-0.6093[b]	0.6484[b]	-0.1689[b]	6
	Popcorn-SU 4	0.4979[b]	-0.5353[b]	0.6226[b]	ND	-0.0639[b]	6

KEY
SU 1 = Wheat (Pavon-76) on Doruwa Salau at close proximity to the Kano-Zaria Highway (Experimental site)
SU 2 = Wheat (Siettecerros) at the Control Site (Irrigation Research Station-IRS),Kadawa (Control Site)
SU 3 = Yellow Maize on Doruwa Salau at close proximity to the Kano –Zaria Highway (Experimental site)
SU 4 = Popcorn at the Control Site (Irrigation Research Station-IRS), Kadawa(Control Site)
a = significant at 0.05 level
b = non-significant
N = sample size

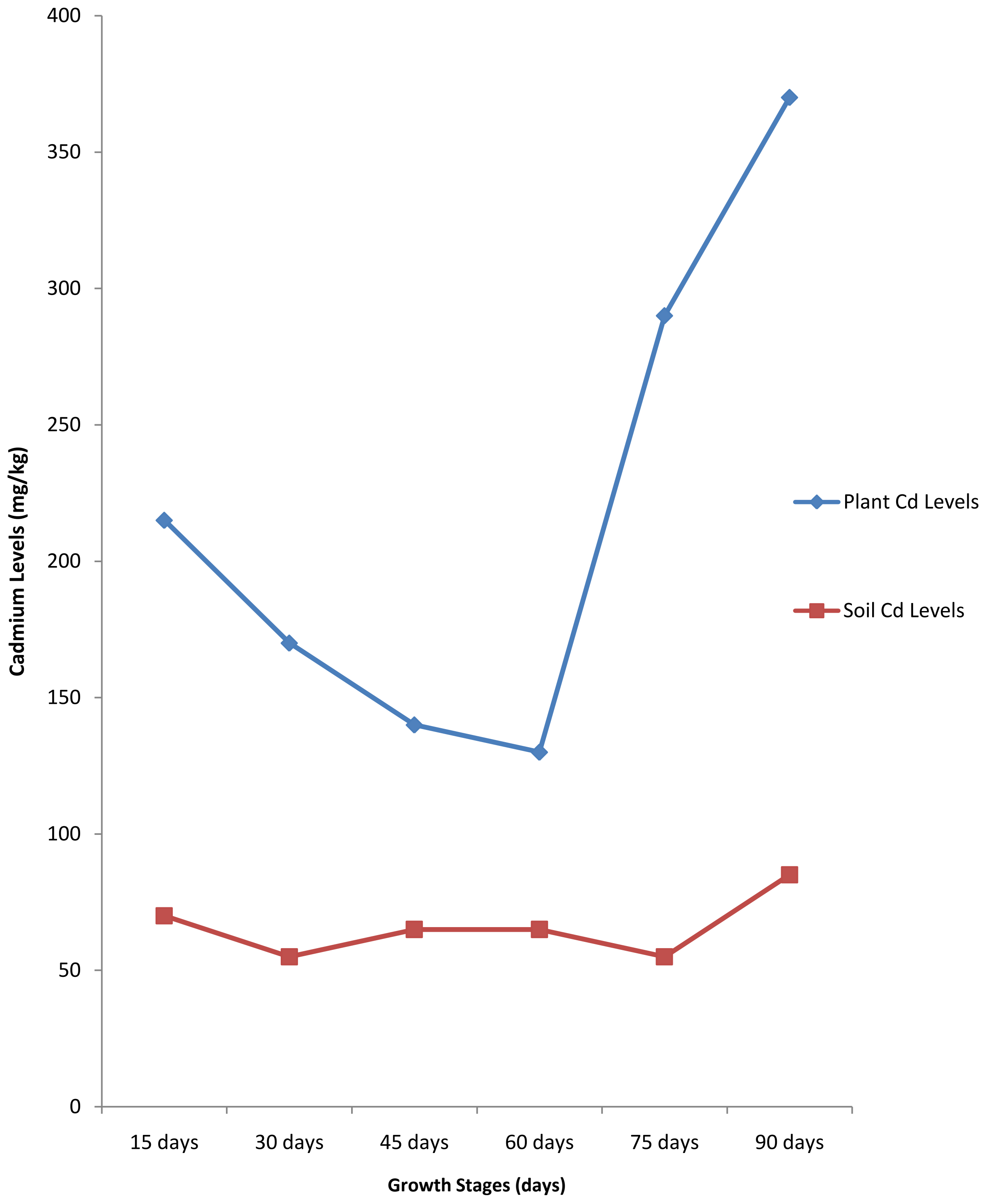

Fig 11: Cadmium Levels in Soil and Pavon-76 at Doruwa Salau

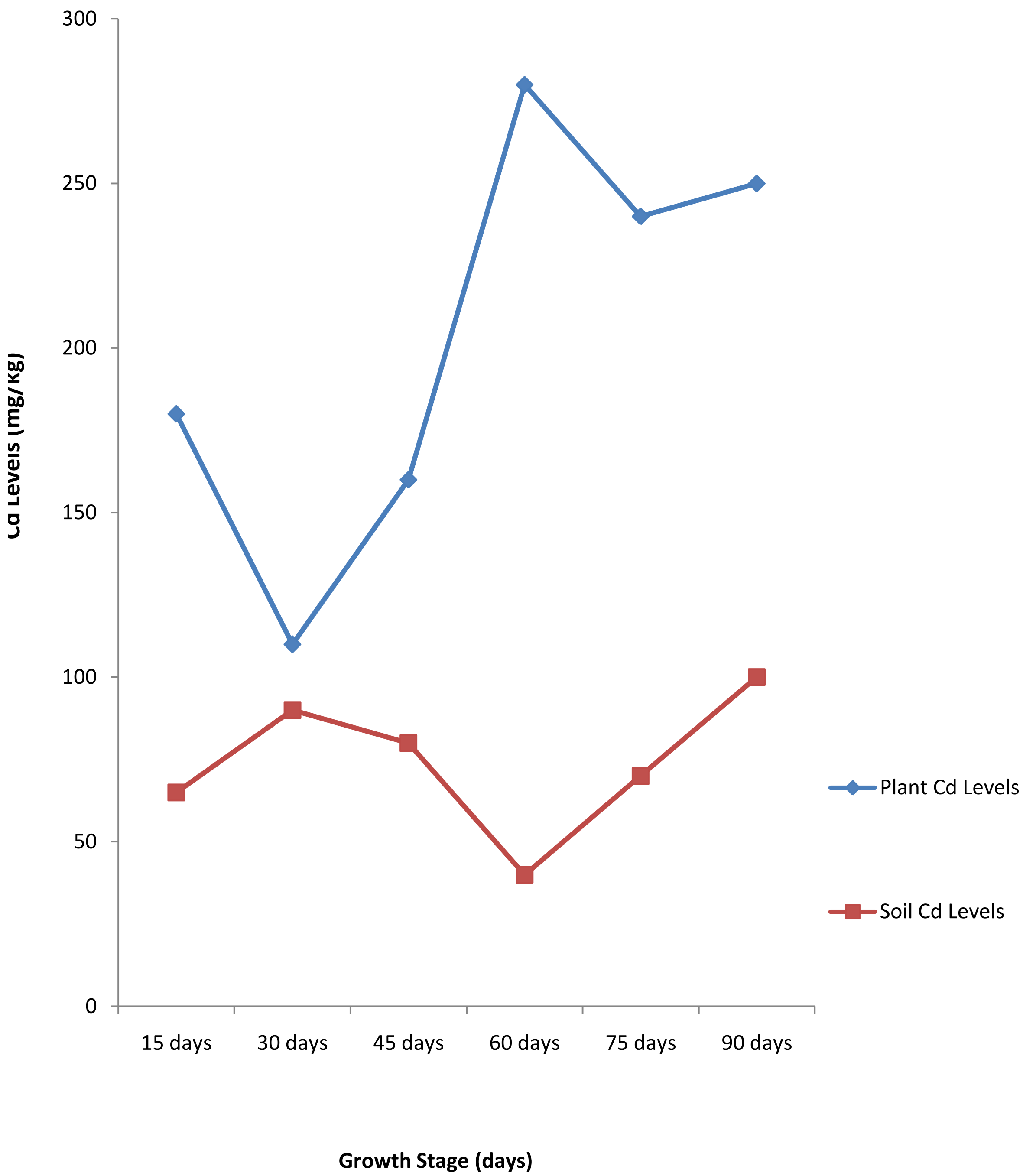

Fig 12: Cadmium Levels in Soil and Yellow Maize at Doruwa Salau

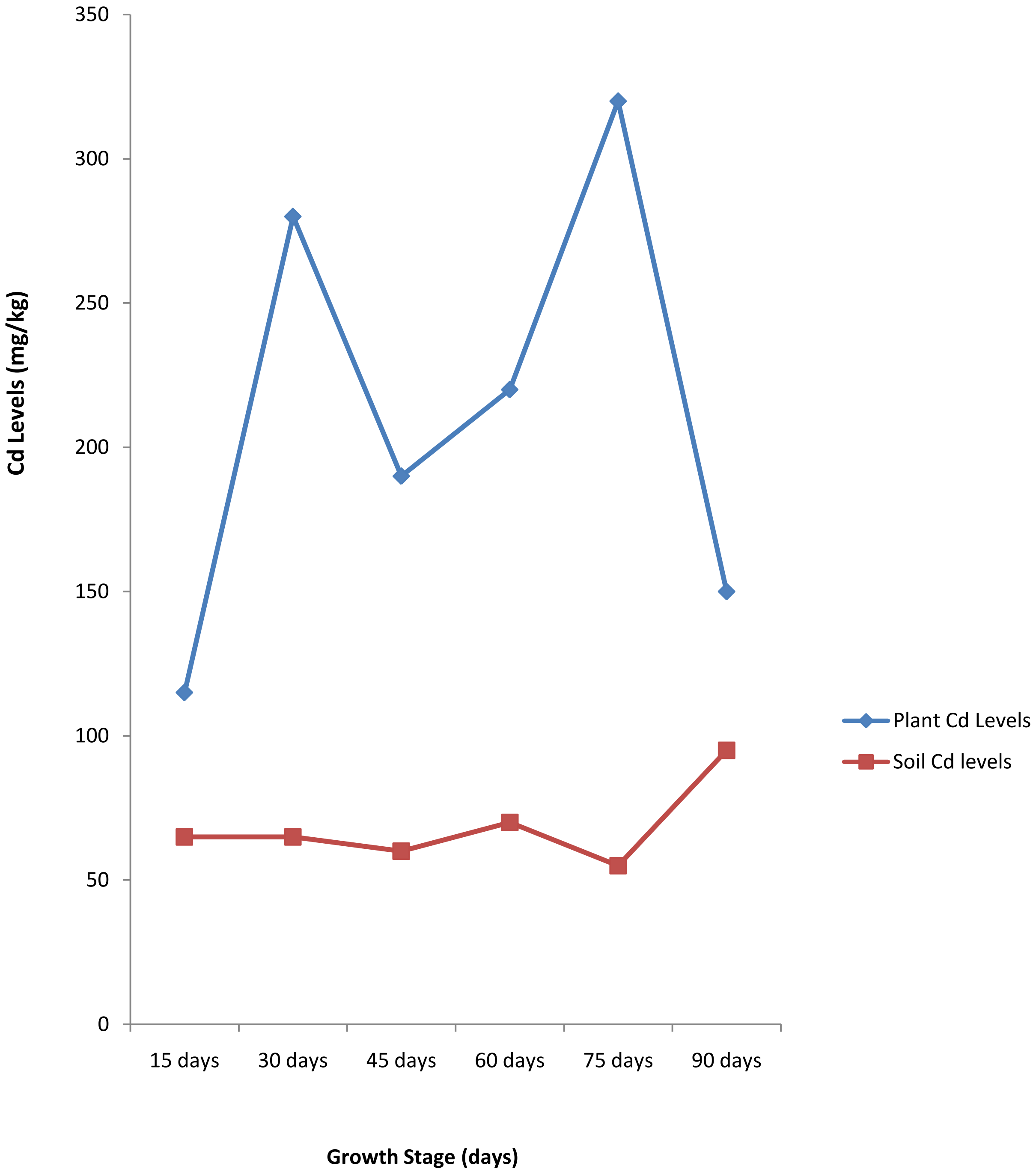

Fig 13: Cadmium Levels in Soil and Siettecerros at the Irrigation Research Station (IRS)

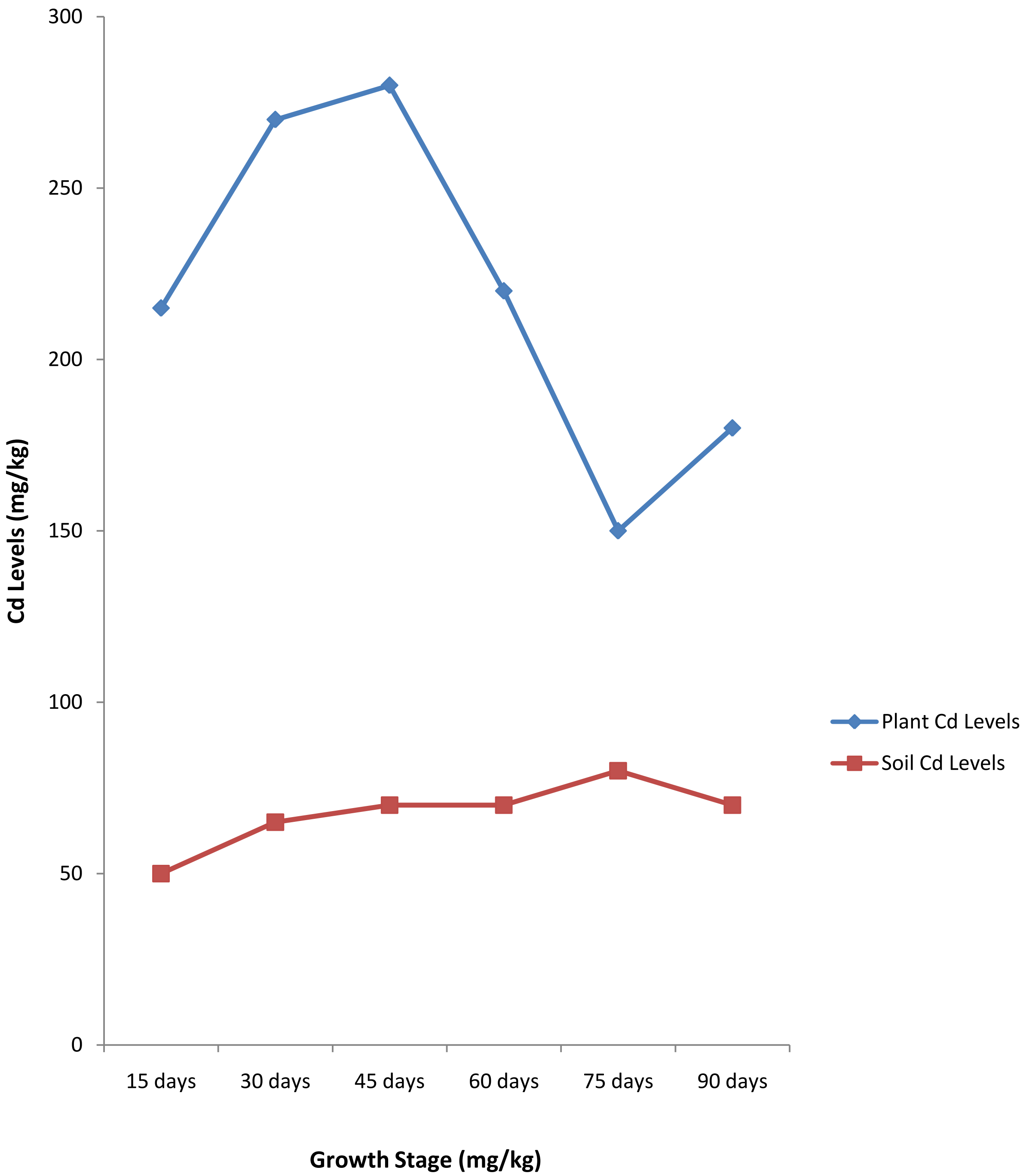

Fig 14: Cadmium Levels in Soil and Popcorn at the Irrigation Research Station (IRS)

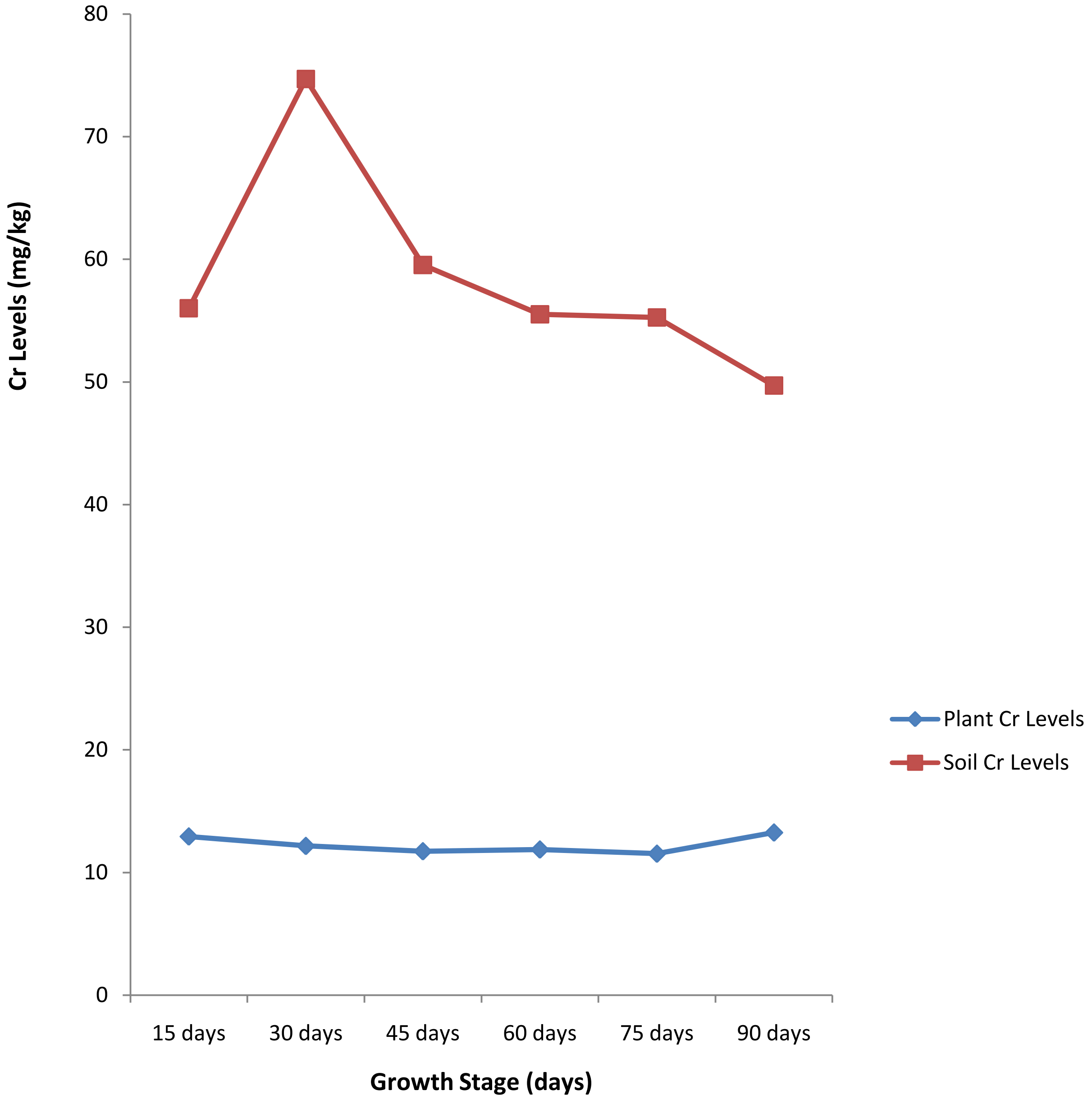

Fig 15: Chromium Levels in Soil and Pavon-76 at Doruwa Salau

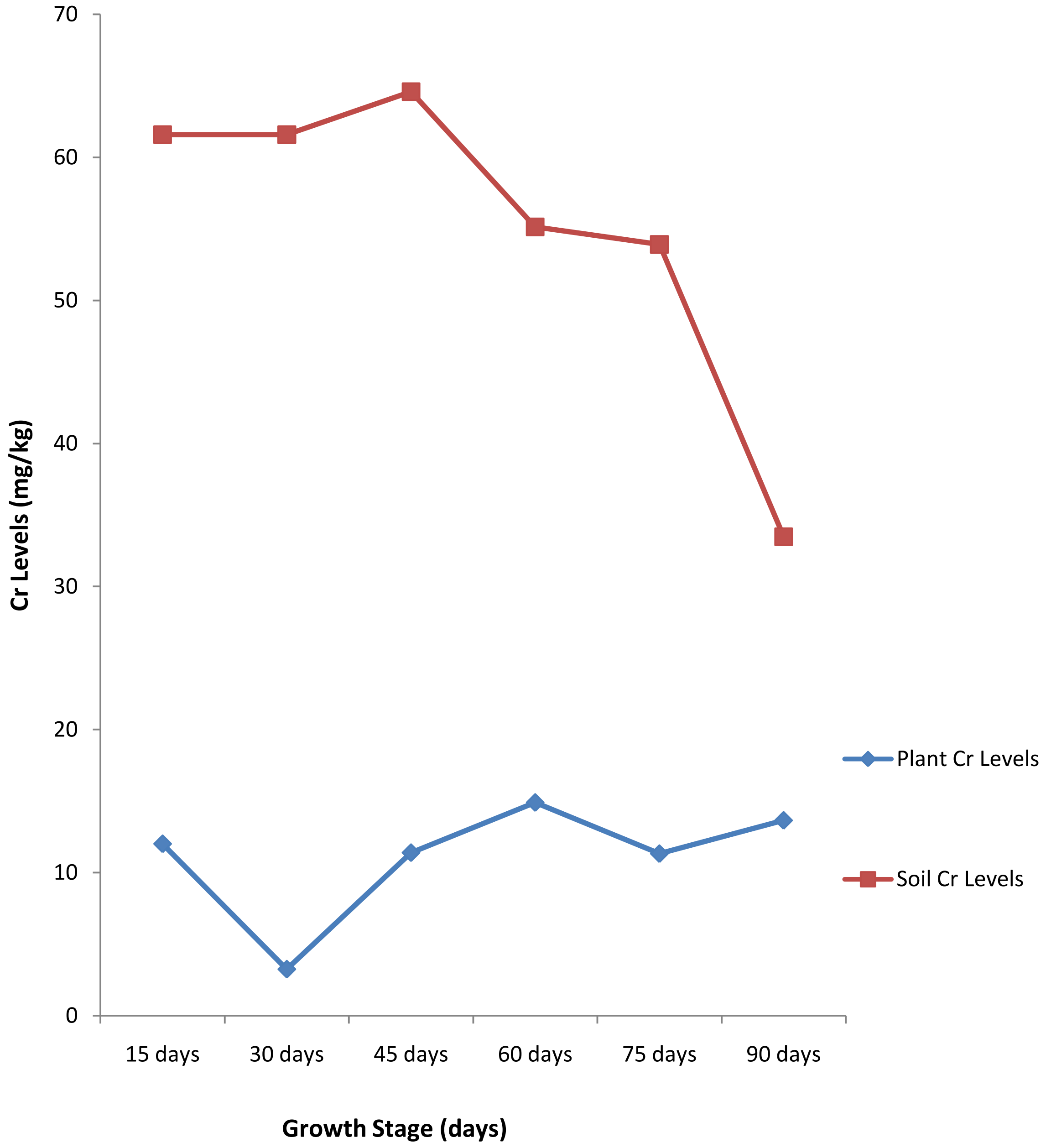

Fig 16: Chromium Levels in Soil and Yellow Maize at Doruwa Salau

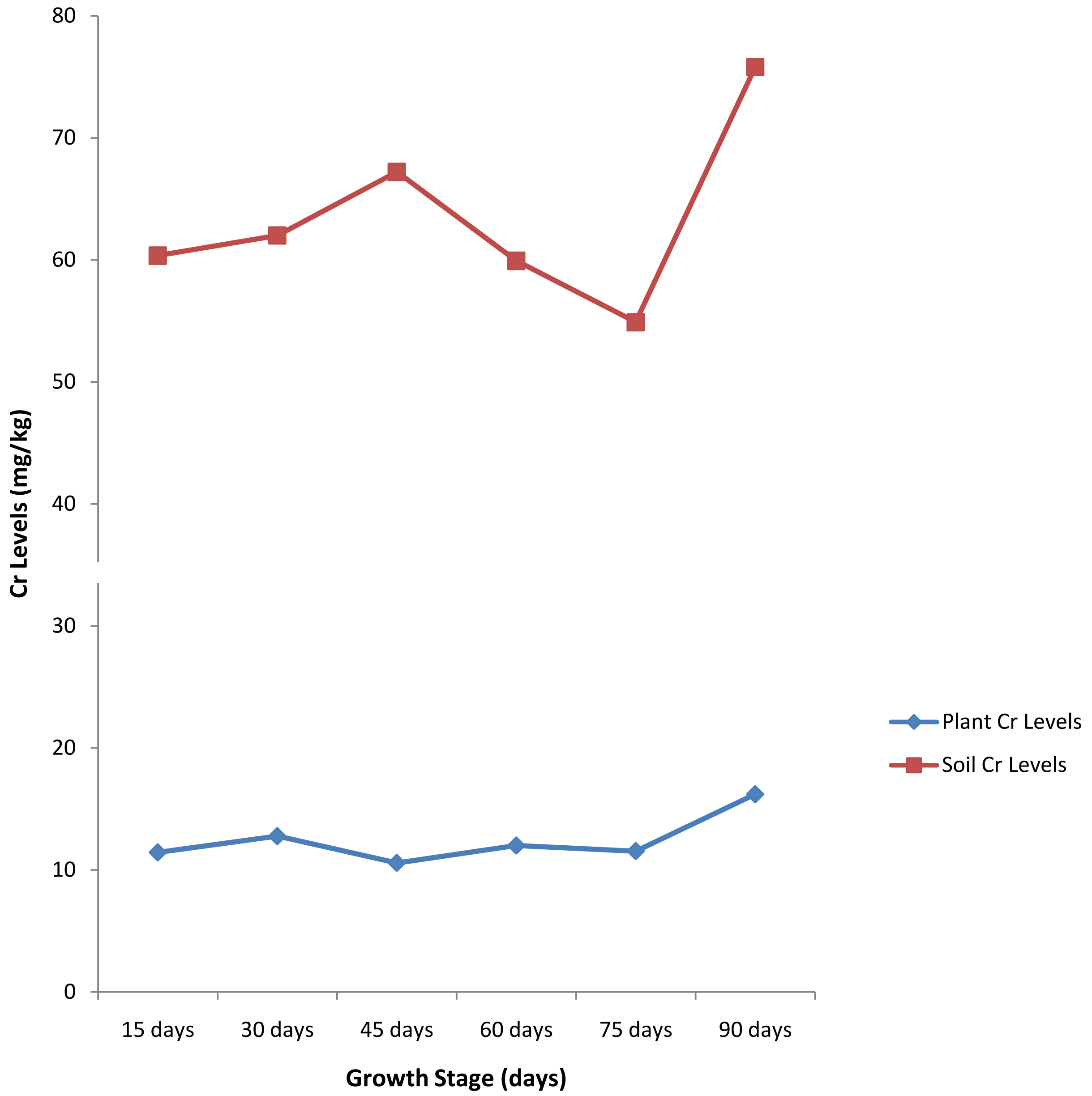

Fig 17: Chromium Levels in Soil and Siettecerros at the Irrigation Research Station (IRS)

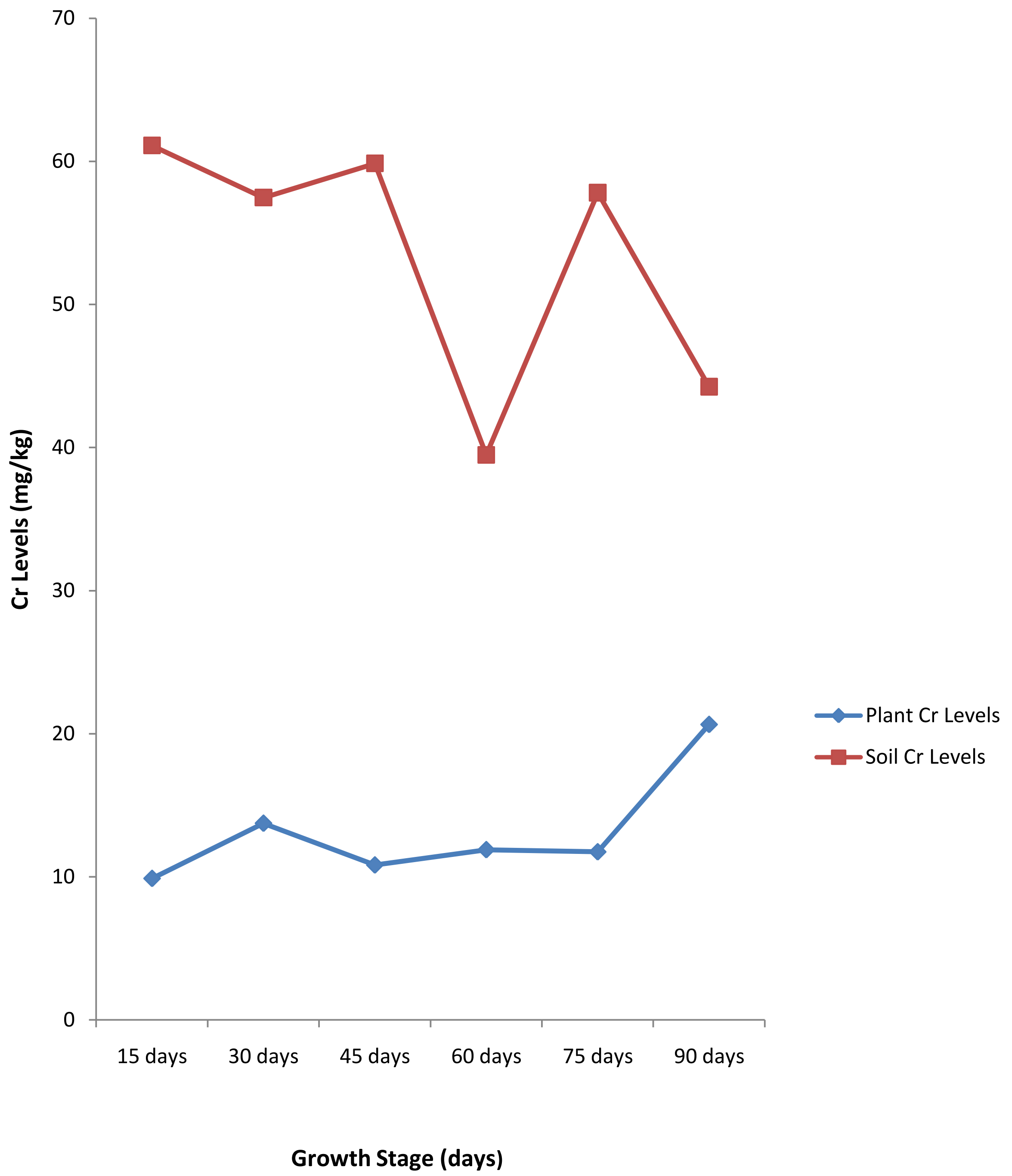

Fig 18: Chromium Levels in Soil and Popcorn at the Irrigation Research Station (IRS)

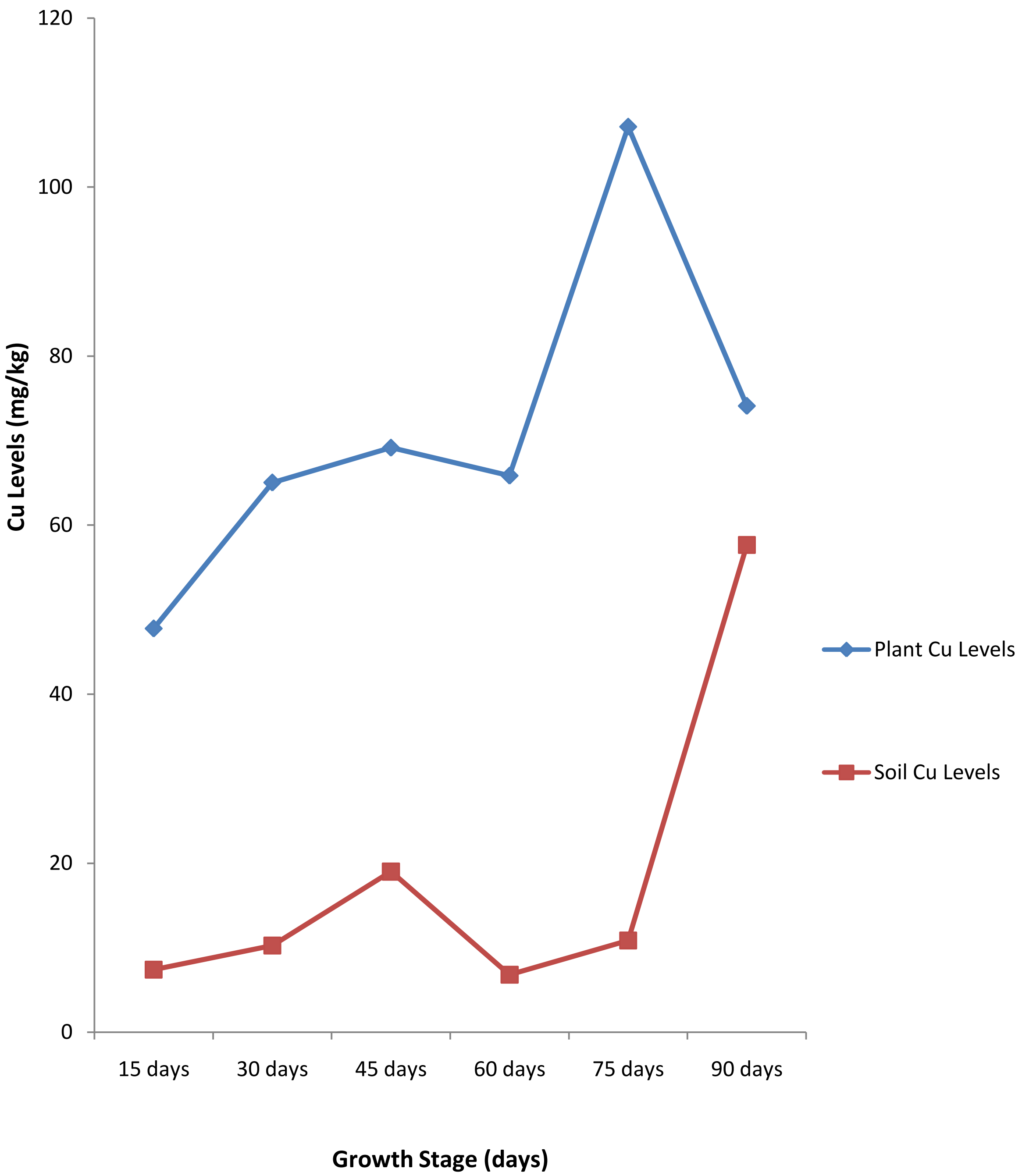

Fig 19: Copper Levels in Soil and Pavon 76 at Doruwa Salau

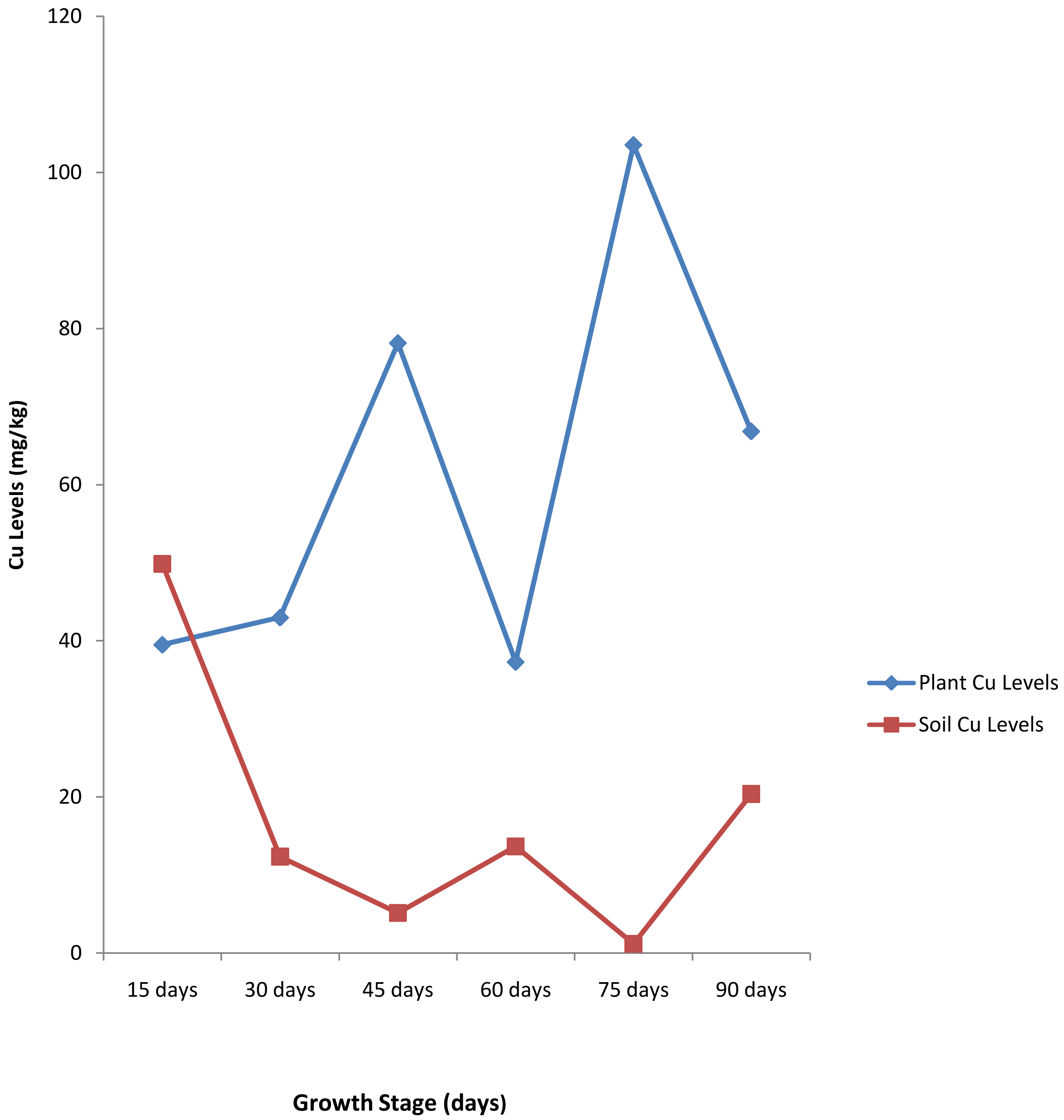

Fig 20: Copper Levels in Soil and Yellow Maize at Doruwa Salau

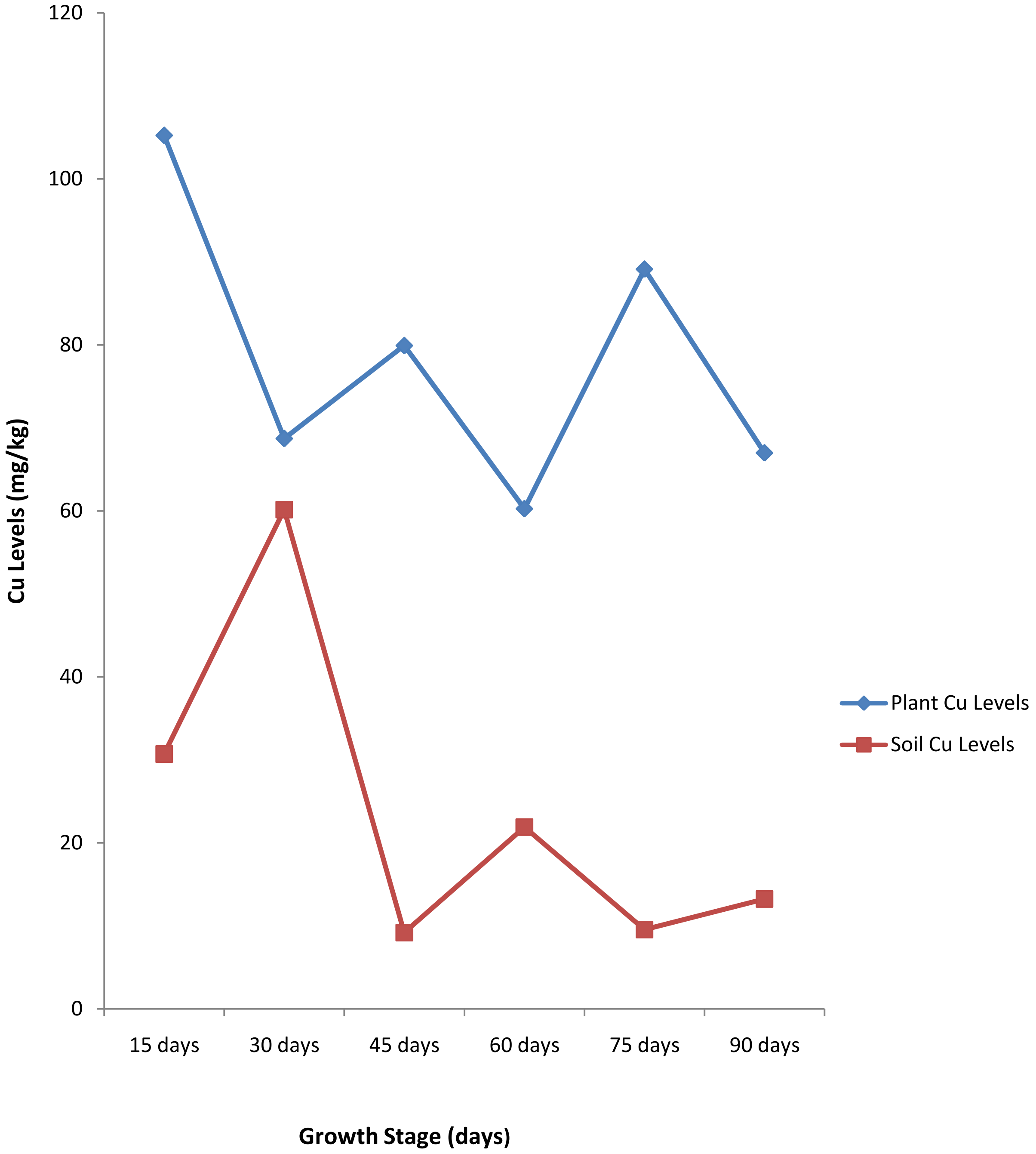

Fig 21: Copper Levels in Soil and Siettecerros at the Irrigation Research Station (IRS)

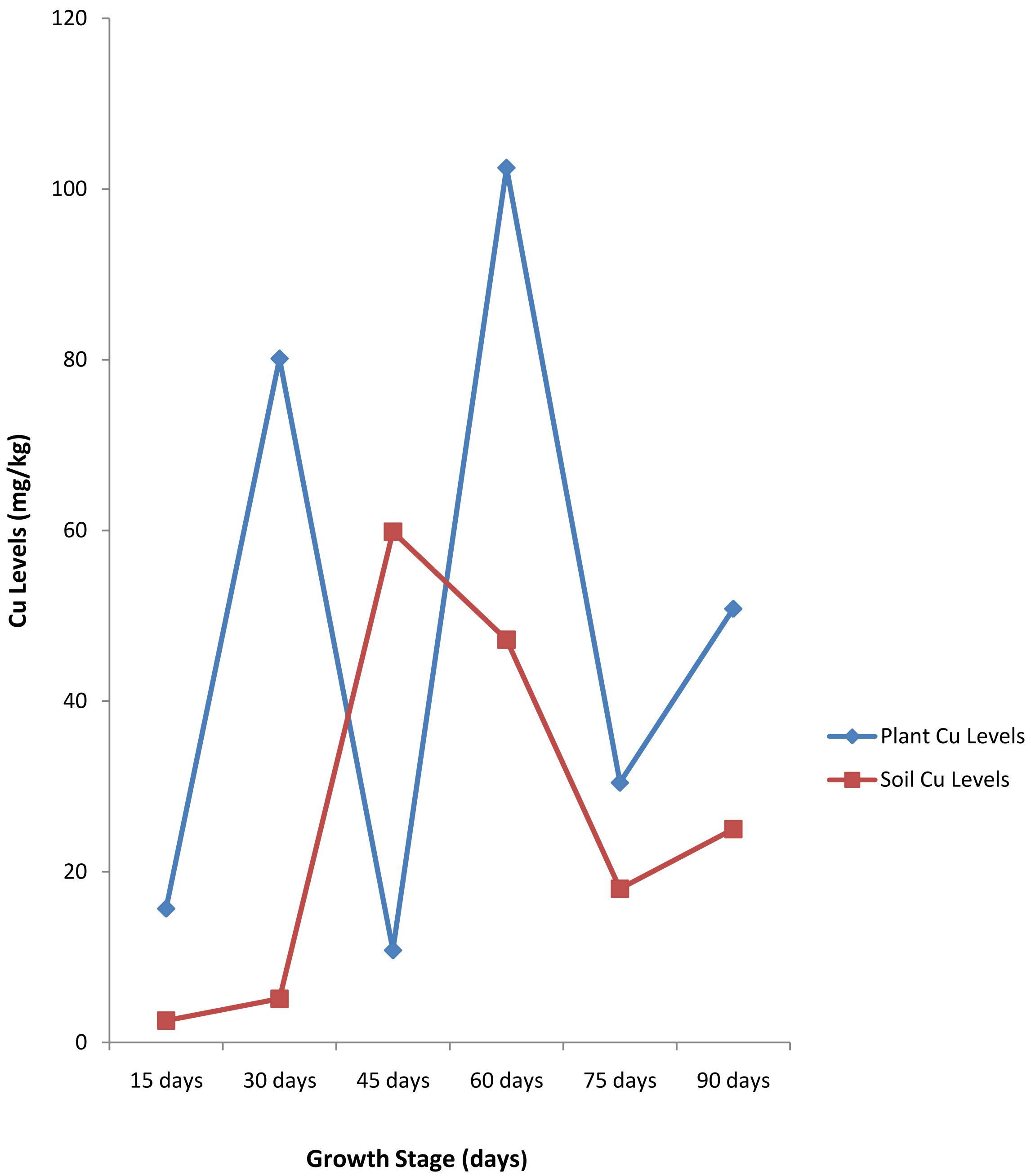

Fig 22: Copper Levels in Soil and Popcorn at the Irrigation Research Station(IRS)

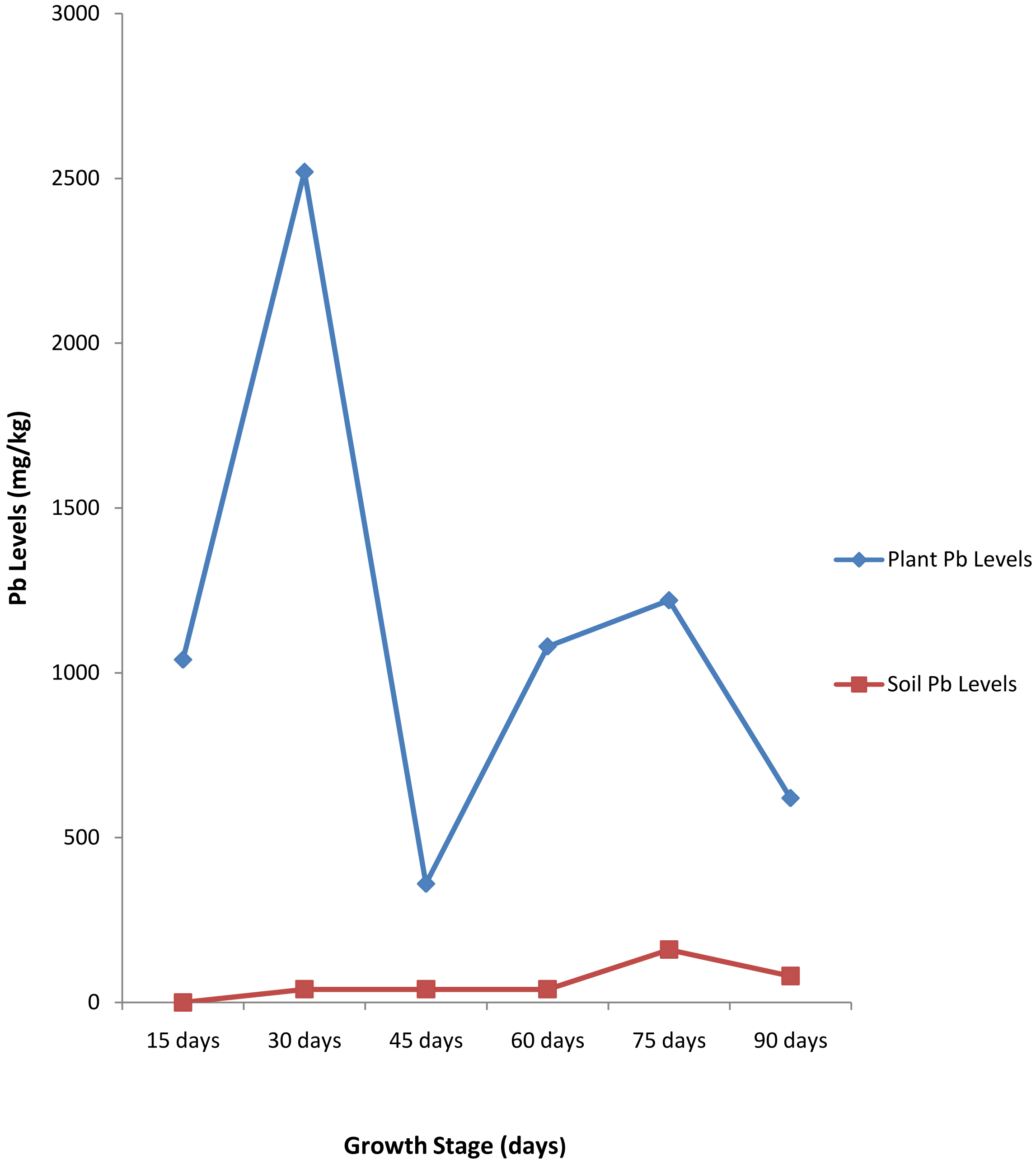

Fig 23: Lead Levels in Soil and Pavon 76 at Doruwa Salau

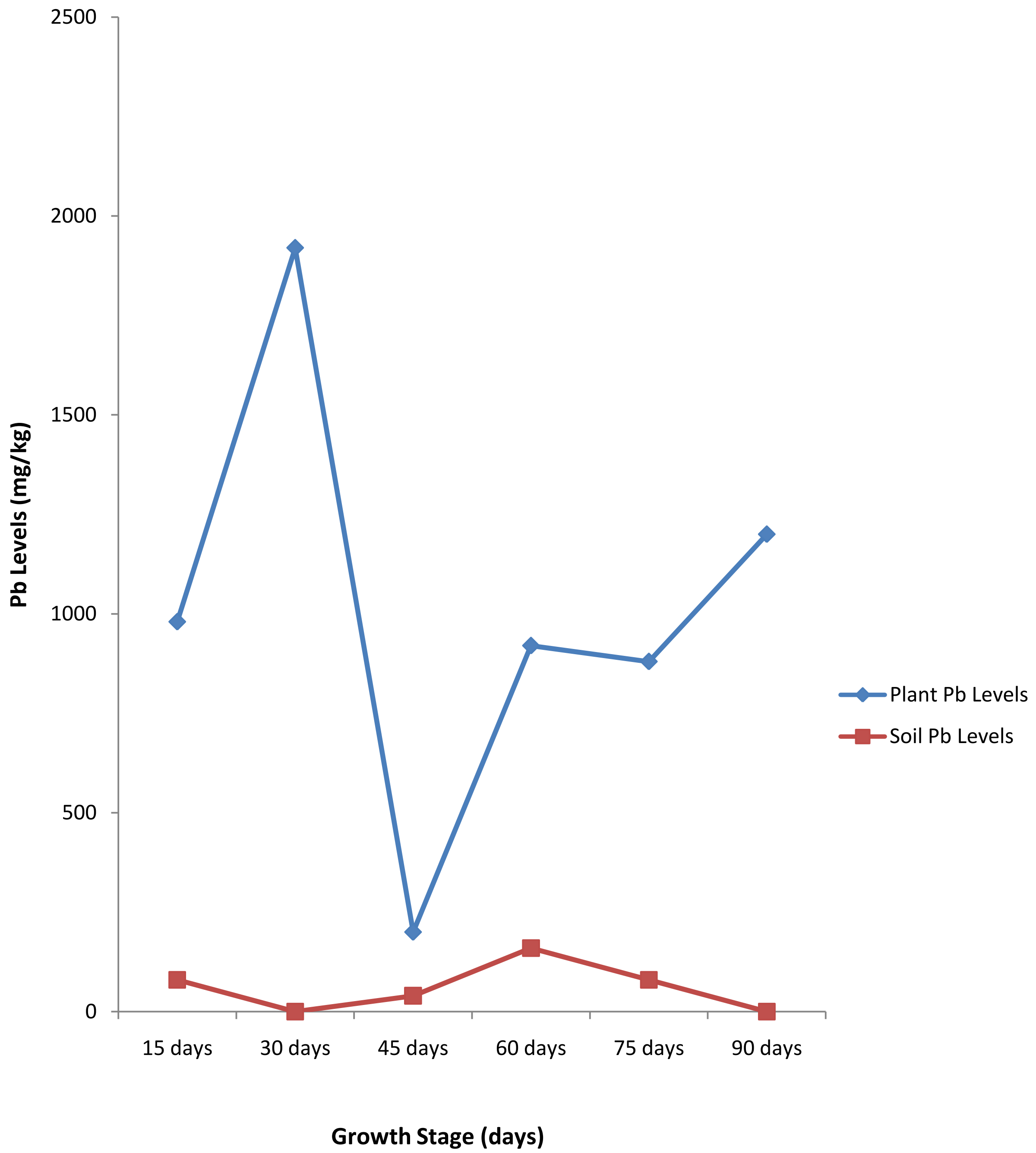

Fig 24: Lead Levels in Soil and Yellow Maize at Doruwa Salau

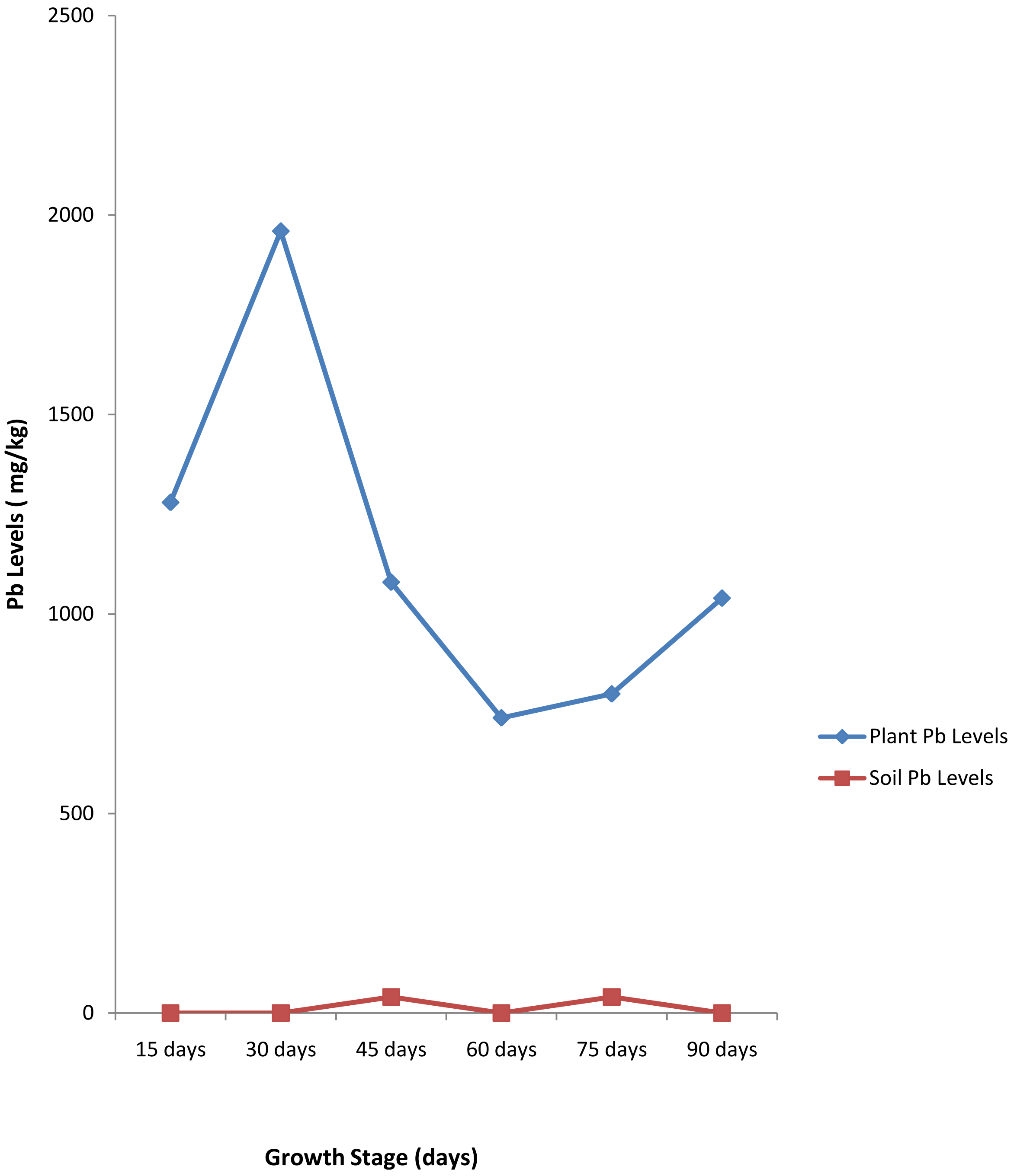

Fig 25: Lead Levels in Soil and Siettecerros at the Irrigation Research Station (IRS)

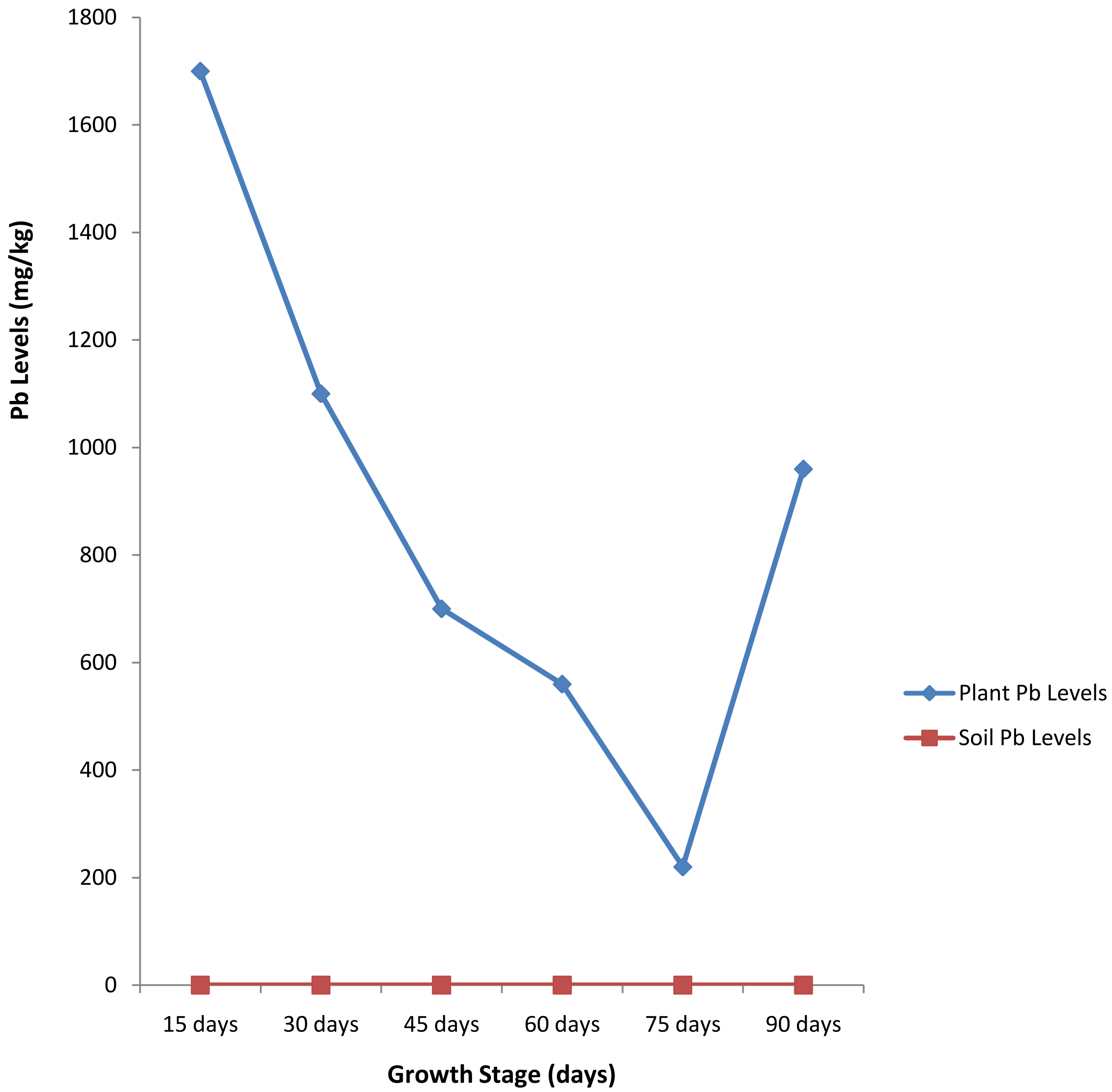

Fig 26: Lead Levels in Soil and Popcorn at the Irrigation Research Station (IRS)

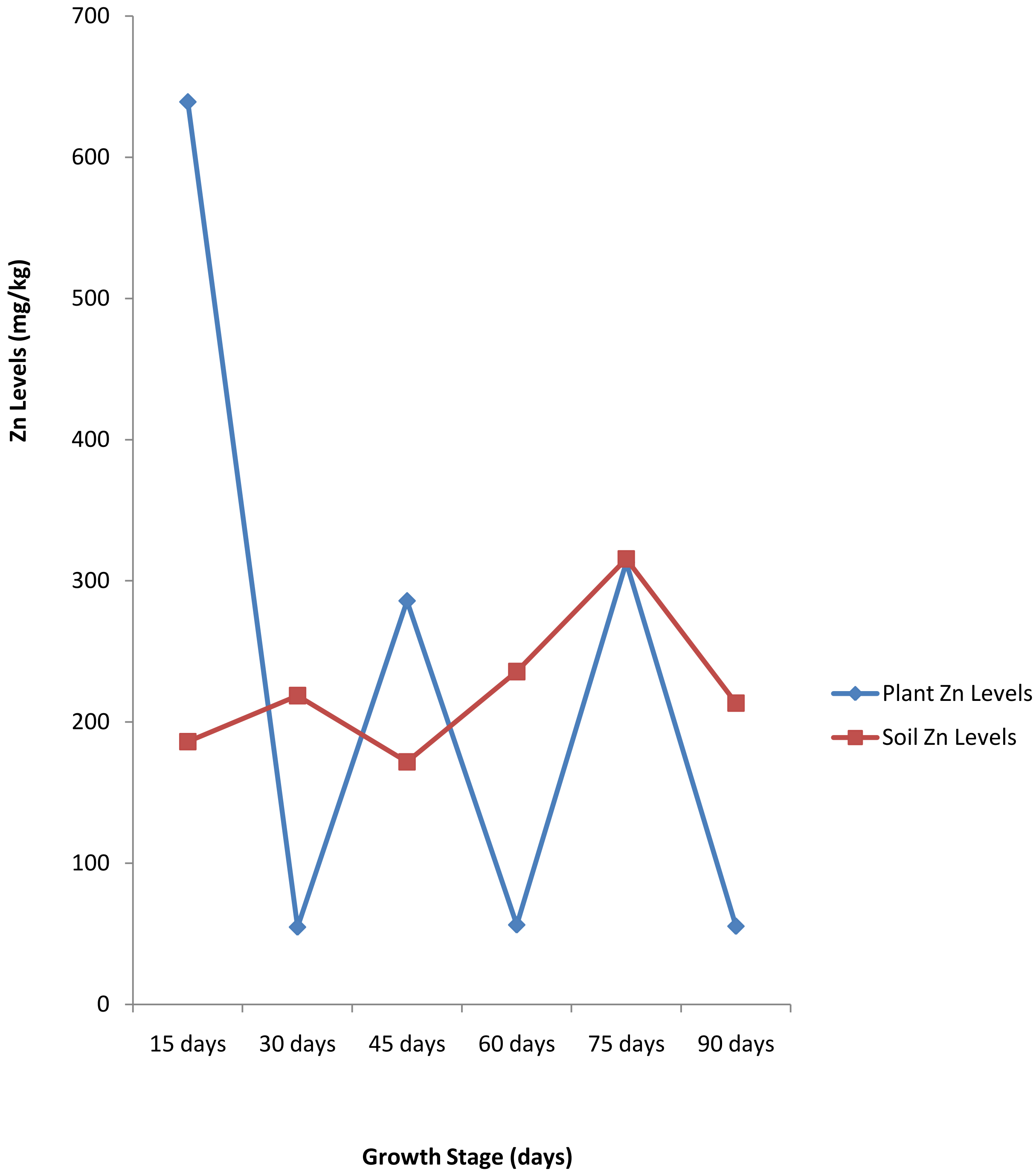

Fig 27: Zinc Levels in Soil and Pavon 76 at Doruwa Salau

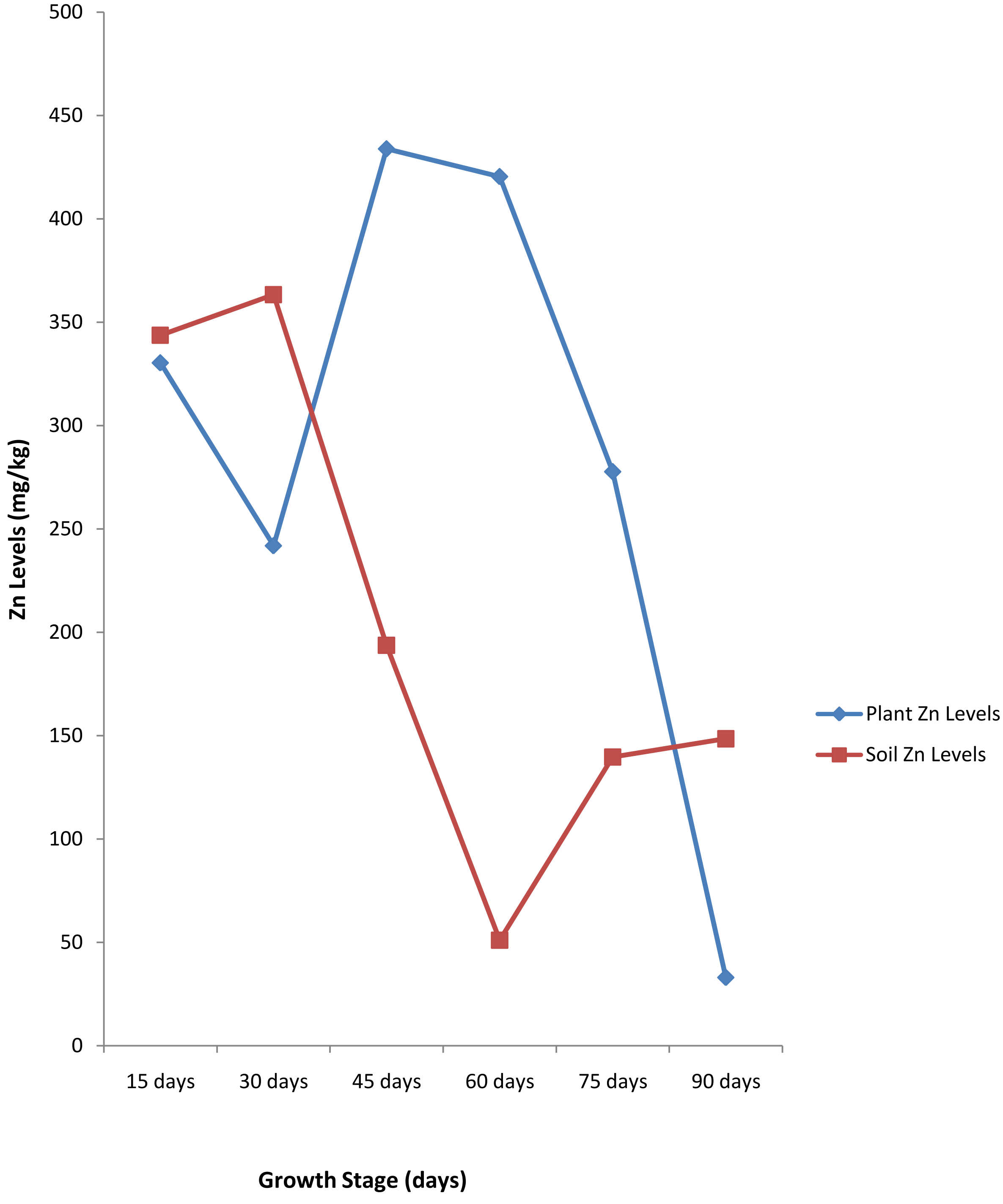

Fig 28: Zinc Levels in Soil and Yellow Maize at Doruwa Salau

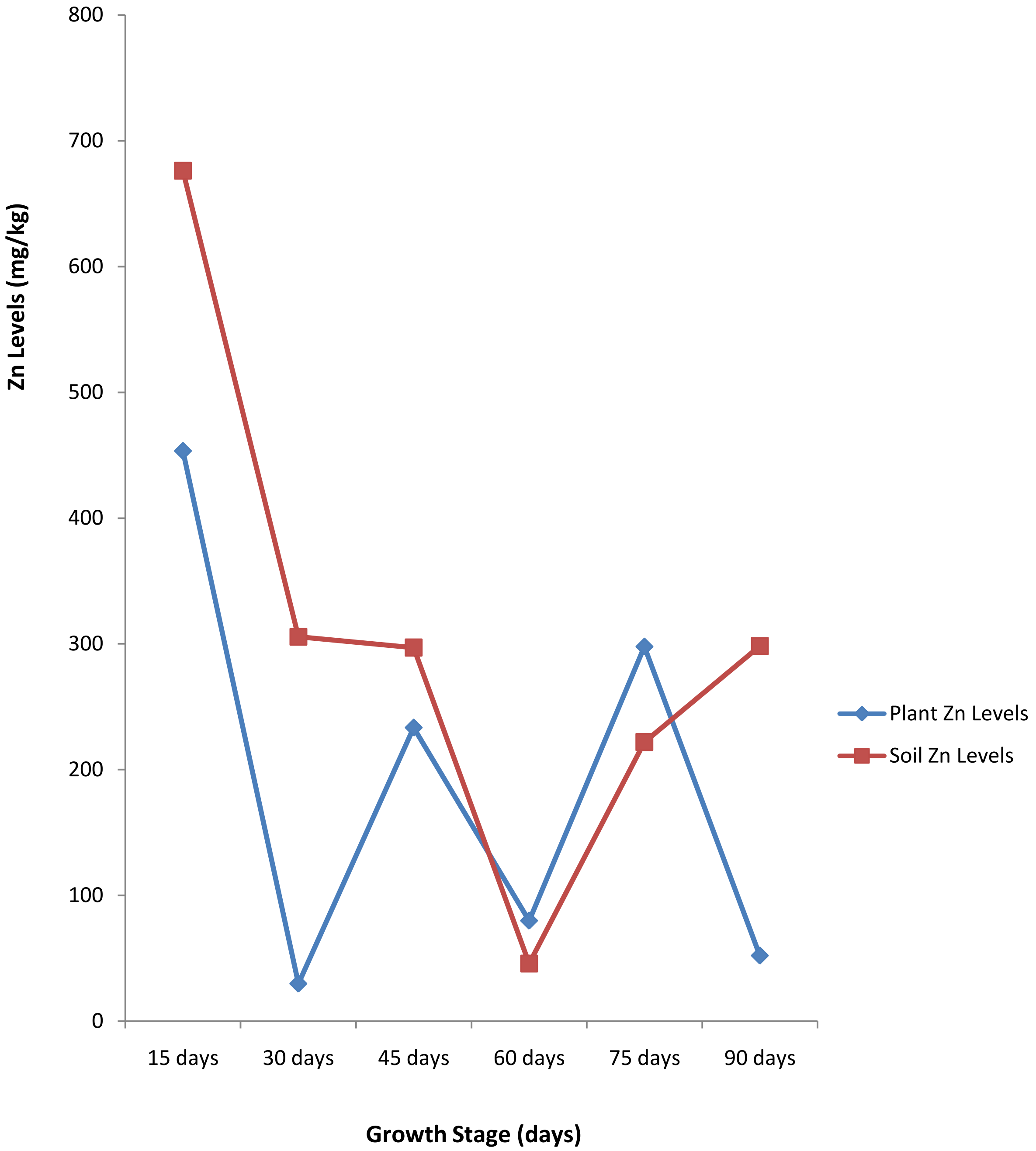

Fig 29: Zinc Levels in Soil and Siettecerros at the Irrigation Research Station(IRS)

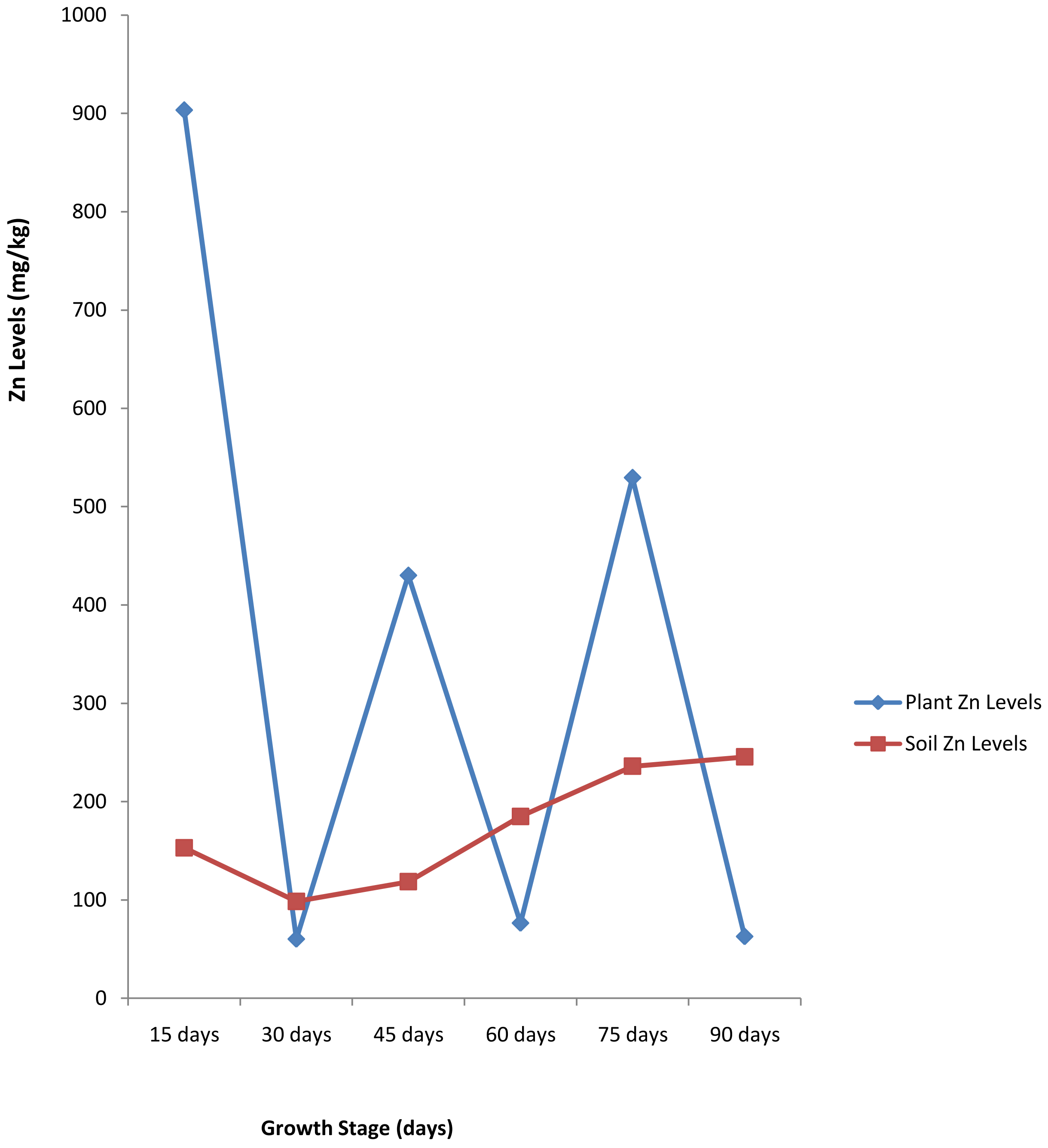

Fig 30: Zinc Levels in Soil and Popcorn at the Irrigation Research Station (IRS)

Generally, the total metal concentrations (mg/kg) of the leaves, stems and roots were higher in the Pavon-76 at Doruwa Salau than in Siettecerros at the Irrigation Research Station.

There was a general variation and fluctuation in the mean leaf, stem, root and soil metal concentrations between the two varieties each of wheat and maize at both the Irrigation Research Station and Doruwa Salau respectively as shown on Fig. 31, Fig. 32, Fig. 33 and Fig. 34. Also the mean metal concentration was highest in the stems, followed by the leaves and lastly in the roots and soils of all the four sampling units investigated at both sites (Fig 31, Fig 32, Fig 33 and Fig 34).

4.11. Soil-Plant Transfer Coefficient (TC)

A range of generalized transfer coefficients (Cd, Cu, Pb and Zn) calculated for each region as suggested by Kloke *et al*. (1984) is shown in Appendix B. Kloke's transfer coefficients are based on the root uptake of metals, with no consideration given to aerial deposition and foliar absorption of elements.

The standard soil-transfer coefficient used in this study is according to Kloke *et al.*,1984 and Korentejar *et al.*,2001). Most of the soil-plant transfer coefficients in this study were generally below the suggested range at both sites (Appendix B). Among the four sampling units and the five trace metals determined in this study, it was noted that SU 4 has the highest TC value for Pb and continued in the following magnitude Pb (6.32) at SU 1 > Pb (3.97) at SU 2 >Pb (3.96) at SU 3. It is also interesting to note that the transfer coefficient for Pb in the sandy clay loam soil were much higher than the sandy

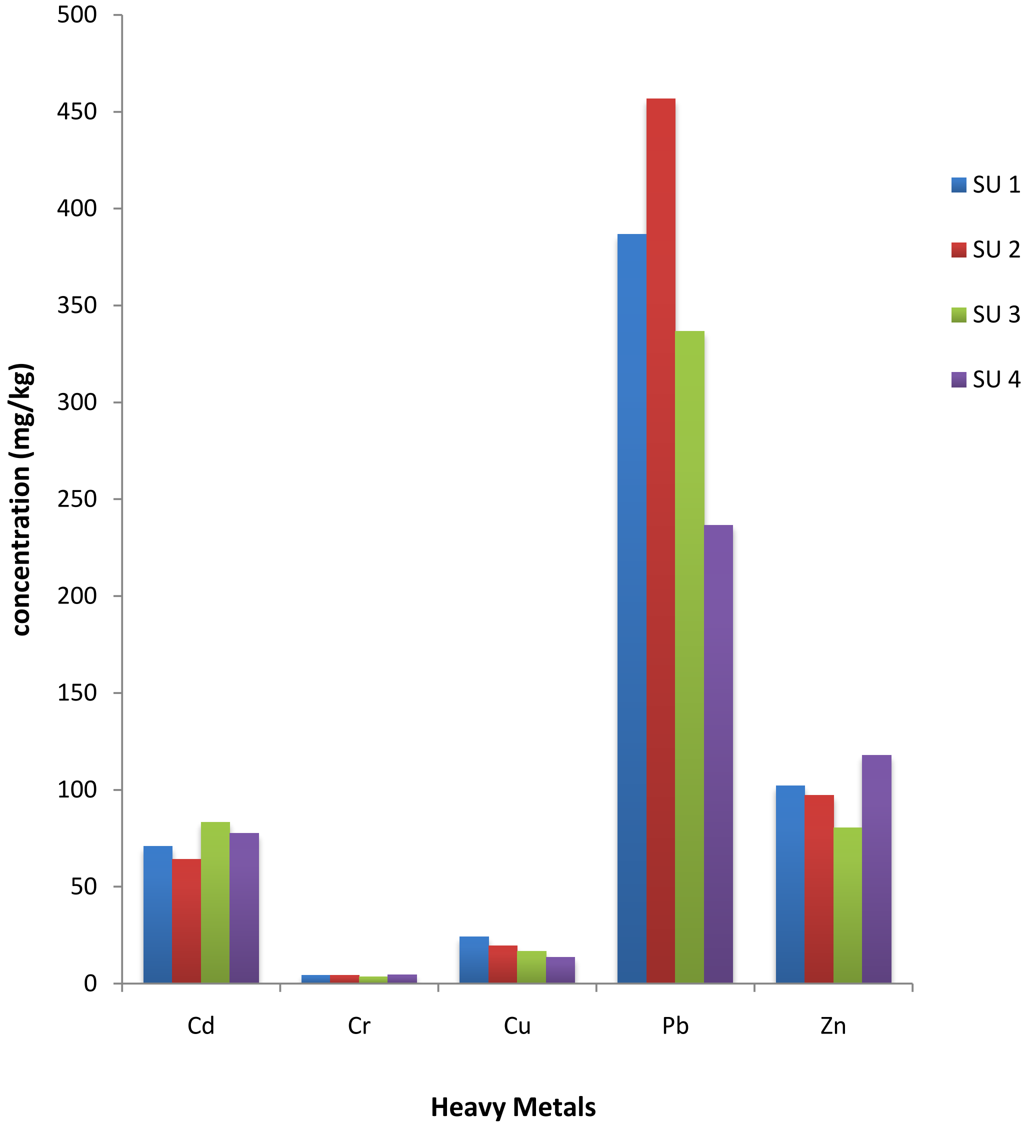

Fig 31:Mean Leaf Metal concentrations (mg/kg) at the four Sampling Units

KEY
SU 1 = Doruwa Salau
SU 2 = Irrigation Research Station, Kadawa
SU 3 = Doruwa Salau
SU 4 = Irrigation Research Station, Kadawa

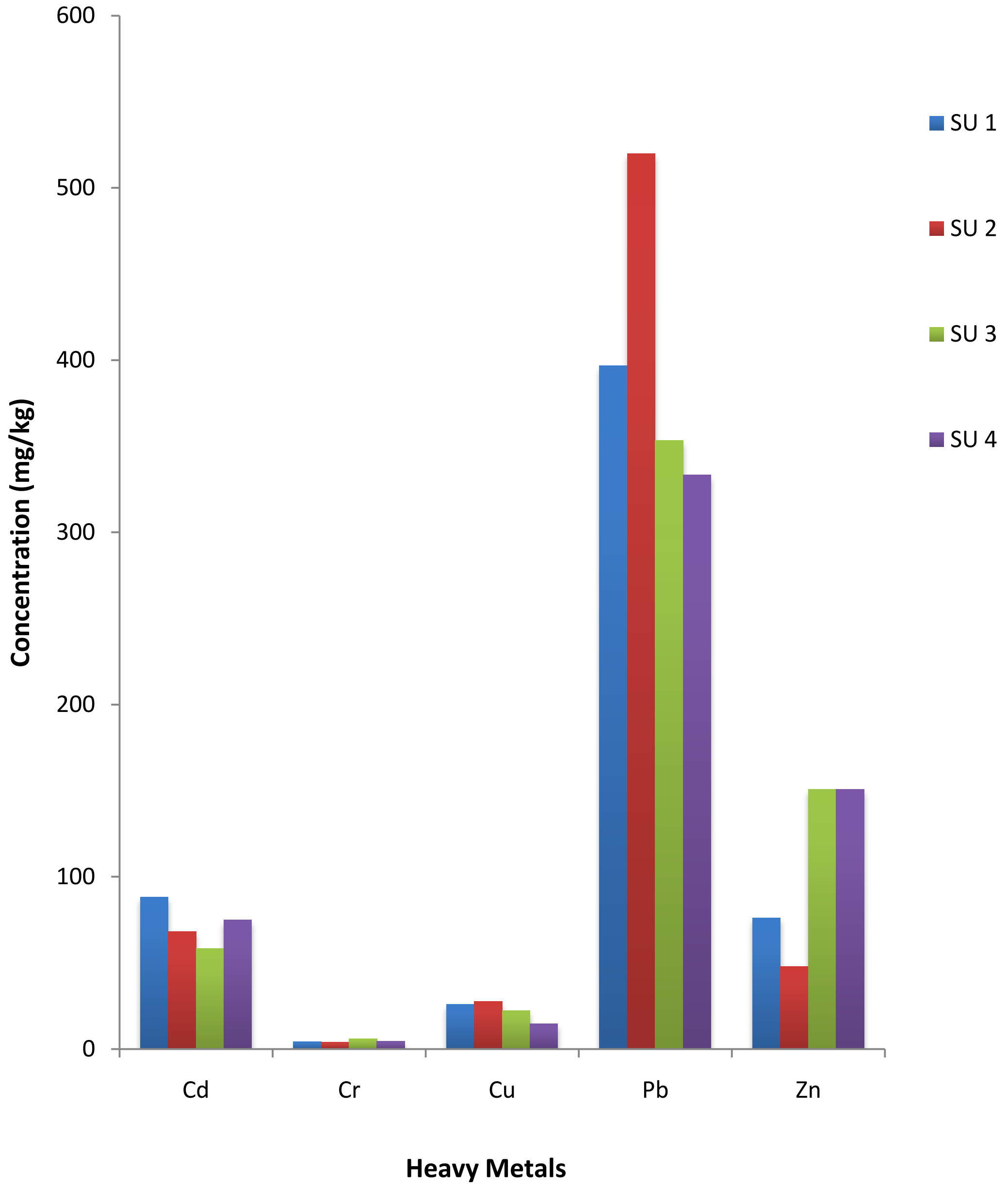

Fig 32: Mean Stem Metal Concentration (mg/kg) at the four Sampling Units

KEY
SU 1 = Doruwa Salau
SU 2 = Irrigation Research Station, Kadawa
SU 3 = Doruwa Salau
SU 4 = Irrigation Research Station, Kadawa

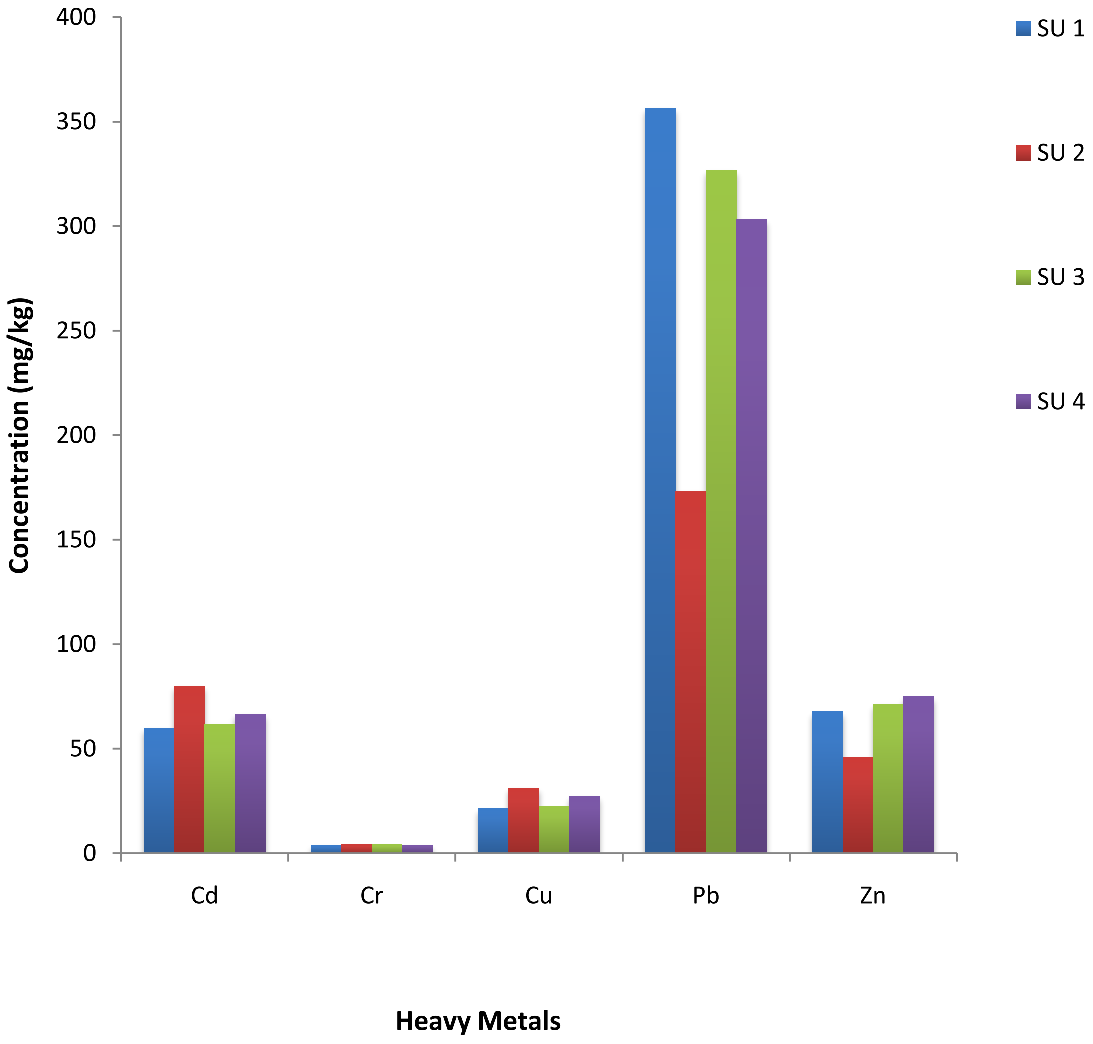

Fig 33: Mean Root Metal Concentration (mg/kg) at the four Sampling Units

KEY
SU 1 = Doruwa Salau
SU 2 = Irrigation Research Station, Kadawa
SU 3 = Doruwa Salau
SU 4 = Irrigation Research Station, Kadawa

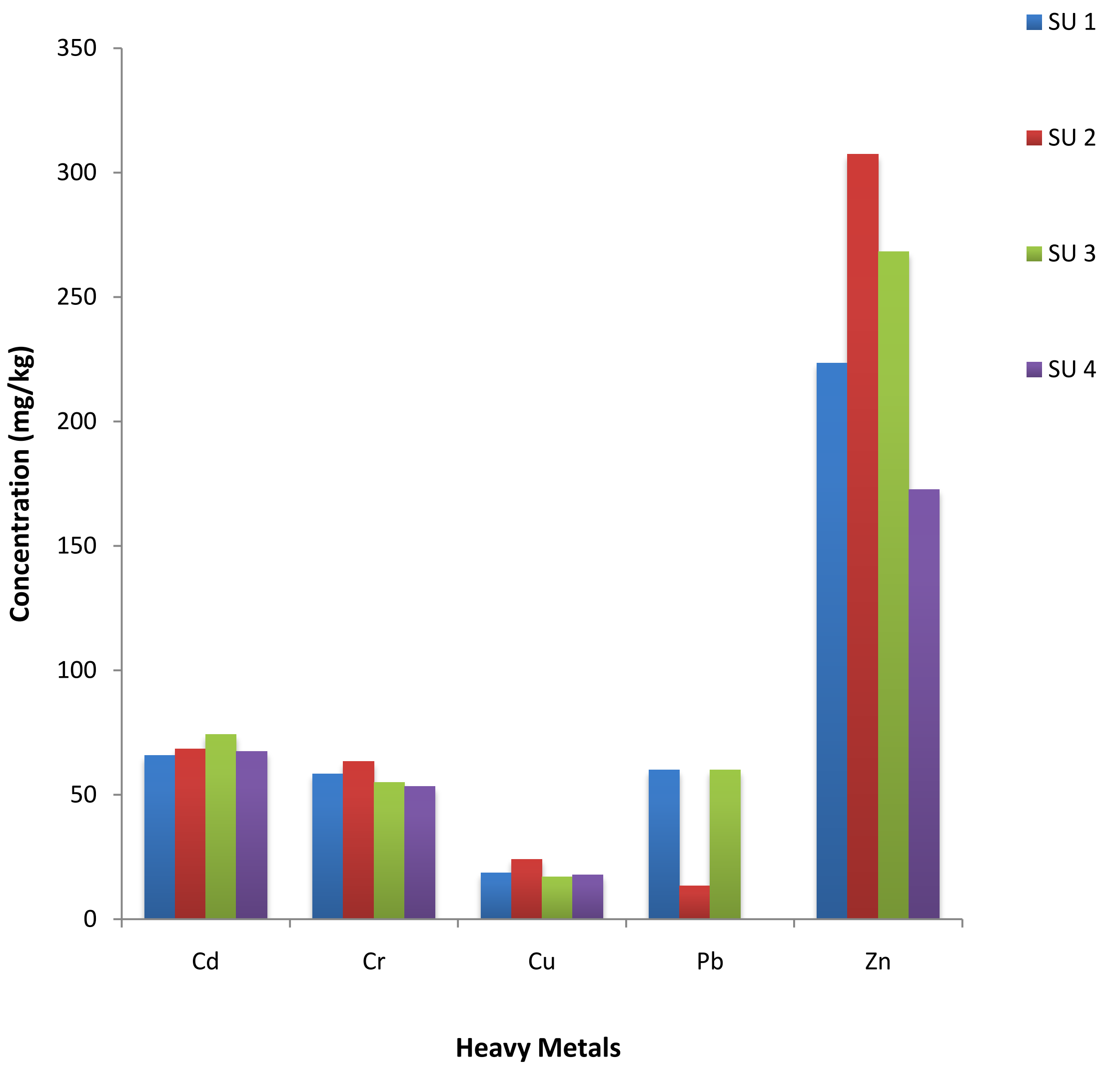

Fig 34: Mean Soil Metal Concentration (mg/kg) at the four Sampling Units

KEY
SU 1 = Doruwa Salau
SU 2 = Irrigation Research Station, Kadawa
SU 3 = Doruwa Salau
SU 4 = Irrigation Research Station, Kadawa

loam soil and seem to decrease as the growth periods increase progressively. The best Pb accumulator was Pavon-76 at the tillering (30 days) stage, while the worst was yellow maize at the shooting (45 days) stage, both at Doruwa Salau closest to the Kano – Zaria Highway. Also popcorn was among the worst accumulator on the IRS at the flowering (75 days) stage.In the case of Cd, fluctuating ratios were observed in popcorn at the tillering and shooting (45 days) stages on Doruwa Salau and siettecerros at the heading (60 days) stage on the IRS. The best accumulator of Zn were pavon 76, yellow maize and popcorn and at the germination (15 days), and shooting stages. The transfer coefficient for Zn was generally lower for all the crops investigated except popcorn at the control site which had a higher transfer coefficient (3.3876) in comparison to Korentejar 1991, 2001.

The TC for both Cr and Cu were generally below the standard soil-transfer coefficients. The TC for investigated trace metals in *Triticum aestivum* L. var. Pavon-76 and *Zea mays* L. var. yellow maize are presented in Table 4.11.2.

The transfer coefficient for both the Pavon-76 and yellow maize were generally less than one for Cd, Cr, Cu and Zn except Pb, which had a high value and greater than unity at all the growth stages except at the 45-days growth stage for Pavon-76 at theexperimental site. Popcorn had the highest TC for Pb and Zn both at the 15-days growth stage while a lower TC was observed for Cd, Cr and Cu at all the growth stages (Table 4.11.2). Similarly, the TC for Cr and Cu were below the standard soil-transfer coefficient.

Table 4.11.1 Transfer Coefficient (TC) of the Pavon-76 and YellowMaize at the Six growth stages at Doruwa Salau closest to the Kano-Zaria Highway (Experimental Site)

Growth stages, Species, Sites	Cd	Cr	Cu	Pb	Zn
	Trace Metal (mg/kg)				
A1	0. 6729	0. 0407	0. 1495	3. 2553	2. 0011
A3	0. 2999	0. 0200	0. 0658	1. 6330	0. 5504
B1	0. 4265	0. 0305	0. 1632	**6. 3222**	0. 1372
B3	0. 2086	0. 0061	0. 0815	3. 6414	0. 4586
C1	0. 3940	0. 0330	0. 1946	1. 0133	0. 8045
C3	0. 4172	0. 0297	0. 2038	0. 5216	1. 1315
D1	0. 3225	0. 0294	0. 1634	2. 6799	0. 1395
D3	0. 4062	0. 0216	0. 0541	1. 3347	0. 0741
E1	0. 4860	0. 0193	0. 1796	2. 0449	0. 6421
E3	0. 6960	0. 0328	0. 3002	2. 5523	0. 8053
F1	0. 7618	0. 0272	0. 1526	1. 2765	0. 1138
F3	0. 8267	0. 0451	0. 2210	3. 9682	0. 1088

Values > 1 indicates uptake by the test crops
Values < 1 indicates that test crops are assumed safe for consumption
(KLOKE et al., 1984; KORENTEJAR et al., 2001; KHAN et al., 2009)

KEY
A = 15 days (germination stage)
B = 30 days (tillering stage)
C = 45 days (shooting stage)
E = 75 days (flowering stage)
F = 90 days (ripening stage)
D = 60 days (heading stage)

1 = Pavon-76 at Doruwa Salau,
3 = Yellow Maize at Doruwa Salau,

Table 4.11.2 Transfer Coefficient (TC) of Siettecerros and Popcorn at the Six growth stages at the Irrigation Research Station(IRS) (Control site)

Growth stages, Species, Sites	Trace Metal (mg/kg)				
	Cd	Cr	Cu	Pb	Zn
A2	0. 1382	0. 0137	0. 1265	1. 5383	0. 5449
A4	0. 8062	0. 0370	0. 0588	**6. 3751**	**3. 3876**
B2	0. 5683	0. 0259	0. 1359	3. 9784	0. 0603
B4	1. 1942	0. 0607	0. 3545	4. 8655	0. 2666
C2	0. 4005	0. 0223	0. 1688	2. 2816	0. 4931
C4	1. 0901	0. 0421	0. 2092	2. 7253	1. 6746
D2	1. 1137	0. 0607	0. 3051	3. 7462	0. 4043
D4	0. 6440	0. 0348	0. 3001	1. 6443	0. 2240
E2	0. 8394	0. 0302	0. 2338	2. 0983	0. 7811
E4	0. 3828	0. 0299	0. 0777	0. 5615	1. 3516
F2	0. 3110	0. 0335	0. 1389	2. 1568	0. 1080
F4	0. 4678	0. 0536	0. 1321	2. 4951	0. 1634

Values > 1 indicates uptake by the test crops
Values < 1 indicates that test crops are assumed safe for consumption
(KLOKE et al., 1984; KORENTEJAR et al., 2001; KHAN et al., 2009)

KEY
A = 15 days (germination stage)
B = 30 days (tillering stage)
C = 45 days (shooting stage)
E = 75 days (flowering stage)
F = 90 days (ripening stage)
D = 60 days (heading stage)

2 = Siettecerros at the IRS,
4 = Popcorn at the IRS

4.12 Plant Uptake Factor (PUF) and Translocation Factor (TF)

The standard translocation factor used in this study is according to Baker and Brooks, 1989. The PUFand TF values for the two varieties of wheat and maize, and sites are given in Tables 4.12.1 and 4.12.2. The highest PUF value among the four sampling units was recorded for Cu(49.6) at SU 3 and at the 75 days growth stage and in the following pattern Pb (45) at SU 1>Pb (25.5) at SU 2> Cu (9.09). While, the highest TF values was observed in Pb (10.33) at SU 3>Cu (8.79) at SU 1>Pb (7.66) at SU 2. Soil Pb was also not detected at the Doruwa Salau at the 15 days, 30 days and 90 days growth stages. The PUF for Pavon-76 for all the metals examined were in the general trend of Pb>Cu>Cd>Zn>Cr while in yellow maize, the trend was in the order of Cu>Pb>Cd>Zn>Cr. Cu and Pb had extremely high PUF greater than 1.0 at Doruwa Salau (Table 4.12.1).

Pb was not detected in the soils of the IRS where popcorn and siettecerros were cultivated, except at the 45-days ad 75-days growth stages, yet Pb had the highest PUF in siettecerros than all the other metals. PUF in siettecerros among the five trace metals, decreased in the order of Pb>Cu>Cd>Zn>Cr and for popcorn in the order of Cu>Cd>Zn>Cr>Pb (Table 4.12.2).

Generally, the maximum PUF value was found in yellow maize (49.6) for Cu while the minimum was found in siettecerros (0.044) for Zn both at Doruwa Salau. The maximum and minimum PUF value for Cd was in yellow maize (5.5 and 0. 666) at Doruwa Salau.

PUF for Cr for the two varieties of wheat and maize were all less than unity or one while Zn PUF values ranged from 0.044 to 2.616 in siettecerros and pavon 76 at the IRS.

Table 4.12.1 The Plant Uptakefactor (PUF) and translocation factor (TF) of the Cereal Crops with respect to the six Growth Stages at Doruwa Salau (Experimental Site – S1).

Growth Stages, Sites, Crops	Cd		Cr		Cu		Pb		Zn	
	PUF	TF	PUF	TF	PUF	TF	PUF	TF	PUF	TF
A1	2. 357	1. 8	0. 213	**6. 535**	6. 098	**8. 796**	<u>400</u>	0. 625	**2. 616**	0. 990
A3	2. 46	**2**	0. 127	0. 944	**0. 525**	1. 214	5. 25	**0. 285**	0. 716	1. 377
B1	2. 545	**2**	0. 091	0. 583	4. 741	1. 087	**45**	1. 166	0. 127	**0. 370**
B3	**0. 666**	**0. 4**	0. 047	6	2. 518	1. 360	<u>1300</u>	0. 774	0. 401	0. 847
C1	1. 384	1	0. 134	1. 053	2. 232	0. 838	3. 5	0. 363	1. 196	1. 642
C3	1. 375	0. 8	0. 119	1. 035	7. 403	0. 849	**3**	0. 75	1. 320	0. 715
D1	1. 538	1. 333	0. 138	0. 933	5. 935	0. 864	23	3. 5	0. 180	1. 248
D3	**5. 5**	**2**	0. 148	**0. 506**	1. 887	1. 591	5. 375	**10.333**	**0. 091**	1. 121
E1	3. 636	1. 667	0. 139	1. 005	6. 725	1. 204	6. 125	0. 75	1. 010	1. 183
E3	1. 714	0. 416	0. 142	1. 049	**49. 6**	**0. 779**	9	1. 5	1. 685	**2. 537**
F1	3. 058	1. 272	0. 167	0. 823	0. 893	1. 282	5. 75	2	0. 176	1. 116
F3	1. 8	1. 142	0. 219	0. 606	2. 276	0. 987	<u>720</u>	1. 166	0. 119	0. 669

Values > 1 indicates accumulations in the test crops
Values < 1 indicates that test crops are assumed safe for consumption
(KLOKE et al., 1984; MA et al., 2001)

Underlined numbers = soil Pb was not detected, PUF not computed
Bolded numbers = Highest and lowest value

KEY

A = 15 days (germination stage)
B = 30 days (tillering stage)
C = 45 days (shooting stage)
E = 75 days (flowering stage)
F = 90 days (ripening stage)
D = 60 days (heading stage)

1 = Pavon-76 at Doruwa Salau,
3 = Yellow Maize atDoruwa Salau,

Table 4.12.2 The Plant Uptakefactor (PUF) and translocation factor (TF) of the Cereal Crops with respect to the six Growth Stages at the Irrigation Research Station IRS (Control Site – S2)

Growth Stages, Sites, Crops	Cd		Cr		Cu		Pb		Zn	
	PUF	**TF**	**PUF**	**TF**	**PUF**	**TF**	**PUF**	**TF**	**PUF**	**TF**
A2	1. 307	1. 666	0. 126	0. 955	1. 888	0. 750	880	1. 45	0. 524	0. 715
A4	3. 1	1.333	0. 134	2. 476	2. 585	0. 519	900	0. 95	**4. 748**	2. 600
B2	1. 692	2. 428	0. 123	0. 811	0. 643	0. 617	1780	5. 333	0. 044	**0. 067**
B4	3. 230	1. 5	0. 160	1. 246	9. 091	0. 305	620	0. 625	0. 343	1. 042
C2	2	0. 571	0. 109	1. 058	3. 982	0. 685	25. 5	7. 666	0. 690	3. 272
C4	2. 285	0. 33	0. 121	0. 940	3. 958	1. 567	560	1. 714	2. 548	0. 914
D2	2. 285	0. 833	0. 130	0. 894	1. 555	0. 750	660	5	1. 428	2. 636
D4	2	0. 75	0. 193	0. 858	0. 826	0. 336	400	1. 5	0. 227	0. 446
E2	3. 636	1	0. 136	0. 943	7. 606	2. 557	16	2	0. 849	0. 587
E4	1. 375	2	0. 136	1. 020	**0. 336**	0. 115	220	60	1. 959	**3. 725**
F2	1. 263	**2. 666**	0. 153	1. 108	3. 189	0. 798	880	2. 5	0. 148	0. 380
F4	2	2. 5	0. 322	1. 051	1. 505	1. 350	720	1. 666	0. 187	1. 789

Values > 1 indicates accumulations in the test crops
Values < 1 indicates that test crops are assumed safe for consumption
(KLOKE et al., 1984; MA et al., 2001)

Underlined numbers = soil Pb was not detected, PUF not computed
Bolded numbers = Highest and lowest value

KEY

A = 15 days (germination stage)
B = 30 days (tillering stage)
C = 45 days (shooting stage)
E = 75 days (flowering stage)
F = 90 days (ripening stage)
D = 60 days (heading stage)

2 = Siettecerros at the IRS,
4 = Popcorn at the IRS

and Doruwa Salau respectively. Cu PUF varied from 0.336 in popcorn at the IRS to 49.6 in yellow maize at Doruwa Salau.

4.12.1. Plant uptake factor (PUF) by varieties and growth stage

The PUF value for the two varieties of wheat and maize, at the six growth stages are also shown in Table 4.12.1 and Table 4.12.2. The shooting (45 days) stage recorded the highest PUF value for Pb in yellow Maize while siettecerros has the lowest value for Zn at the tillering (30 days) stage, than all the two varieties of wheat and maize investigated.

PUF value for Cd was observed in yellow maize at the tillering (30 days) and heading (60 days) stages as the lowest and highest values respectively. The lowest and highest Zn PUF was found in siettecerros and pavon 76 at the tillering (30 days) and germination (15 days) stages respectively. Popcorn and yellow maize have the lowest and highest PUF for Cu both at the flowering (75 days) stage.

Though none of the two varieties of the two cereals sampled were metal hyperaccumulators, they still have accumulation potentials while some interesting observations were noted. Based on the total PUFs of the two varieties each of wheat and maize sampled, the highest PUF value was observed for Cu (PUF=49.6) in yellow maize at the 75 days growth stage and Pb (45) in Pavon-76 at the 30 days growth stage respectively, both at the experimental sites.

Generally, the cereal crops showed PUF>1 for all the trace metals except for Cr and Zn. Yellow maize cultivated at SU 3 (at a distance of about 345.79m from the Kano-Zaria Highway) was evidently the highest accumulator among the heavy metals (Cu, Cd, Pb) investigated. Similarly, Pavon-76 at Doruwa Salau also showed a PUF>1 for Pb and Cu.

4.12.2. Translocation factor (TF) by varieties and site

Generally, among the two varieties of wheat and maize, those with a TF >1 are all in the same sequence with those with a TF<1. Translocation factor for the two varieties of wheat and maize, based on site are indicated in Table 4.12.1 and Table 4.12.2. Among all the two varieties of wheat and maize, yellow maize at Doruwa Salau had the highest TF of 10.333 for Pb while the lowest was found in Zn (0.067) found in siettecerros at the IRS.

Cd recorded the maximum (2.666) and minimum (0.33) TF value both at the IRS (popcorn and siettecerros respetively), while the highest and lowest TF value for Cr was found in pavon 76 (6.535) and yellow maize (0.506) both at Doruwa Salau. Similarly pavon 76 (49.6) at Doruwa Salau and popcorn (0.115) at the IRS recorded the highest and lowest TF values for Cu respectively. IRS recorded the highest and lowest TF value for Zn in popcorn and siettecerros respectively.

Here too, some interesting observations were noted. Based on the total TFs of all crop samples, the yellow maize, Pavon-76 and siettecerroswere most efficient in translocating Pb (TF=10.33), followed by Cu (8.796) and Pb (7.666) and Cd (2.666) respectively.

4.12.3. Translocation factor (TF) by varieties and growth stages

Pavon 76 and popcorn recorded the highest and lowest TF value at the germination (15 days) and shooting (45 days) stages respectively. The TF value for Cu was highest at the germination (15 days) stage in Pavon -76 and lowest in popcorn at flowering (75 days) stage. The tillering (30 days) and flowering (75 days) stages recorded the lowest and highest TF value for Zn in siettecerros and popcorn respectively (Tables 4.12.1 and 4.12.2). The maximum and minimum TF for Cd were found in popcorn at the shooting (45 days) stage and in siettecerros at the ripening (90 days) stage respectively.

On a general note, the PUF and TF were generally higher than the TC for Cd, Cr, Cu and Zn than Pb, while Pb had a higher TC than PUF and TF. Also the sampling units 1 and 3 in close proximity to the experimental site (Kano-Zaria Highway) had a higher PUF, TF and TC than at the sampling units 2 and 4 on the control site (IRS). In addition, among the four sampling units, SU 4 seems to have the lowest PUF, TF and TC values with Cd, Cu, Pb and Zn having a comparatively lower values among the three models used in this study than Cr.

4.13 Comparison of PUF, TC And TF For Cd, Cr, Cu, Pb and Zn among the Four Sampling Units at the Selected Growth Stages of Wheat and Maize.

Line graphs illustrating the variations in the PUF values and TC values of the individual trace metals in Pavon-76 at Doruwa Salau are shown in Fig. 35 and Fig. 36 respectively. There was no PUF value for Cd, Cr, Cu, Pb and Zn at sampling units 2, 3 and 4, because soil Pb was not detected at the selected growth stages. PUF for Pb at SU 1 was the highest at the 30- and 60- days growth stages followed by Cu, Cd, Cr and Zn (Fig. 35). The TC for Pb at SU 1 was highest at the 30-days and 60-days, followed by Zn at the 15-days then Cd, Cu and Cr (Fig. 36).

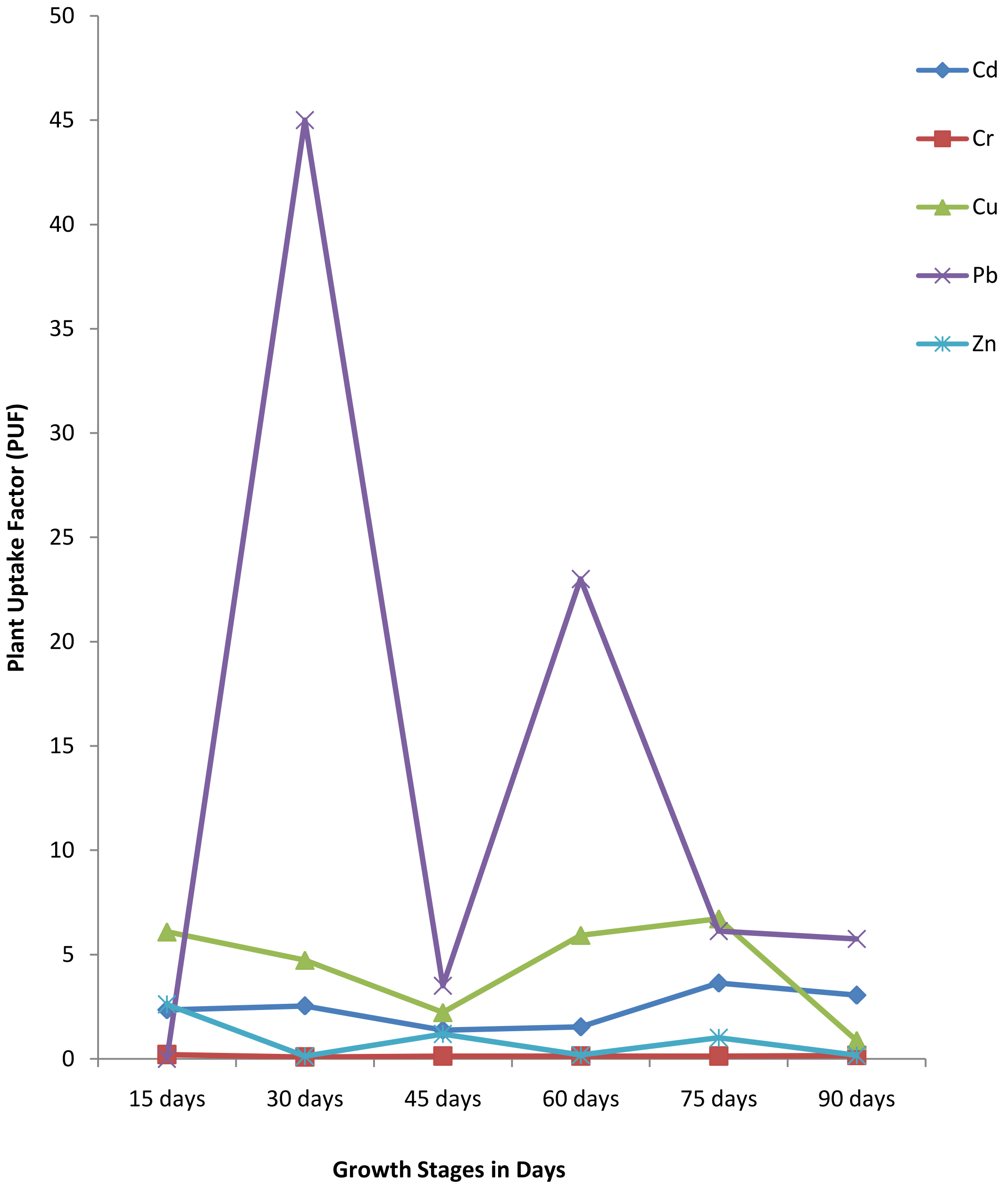

Fig 35: Plant Uptake Factor for Cd,Cr,Cu,Pb and Zn in *Triticum aestivum L.* var. Pavon-76 at sampling unit 1

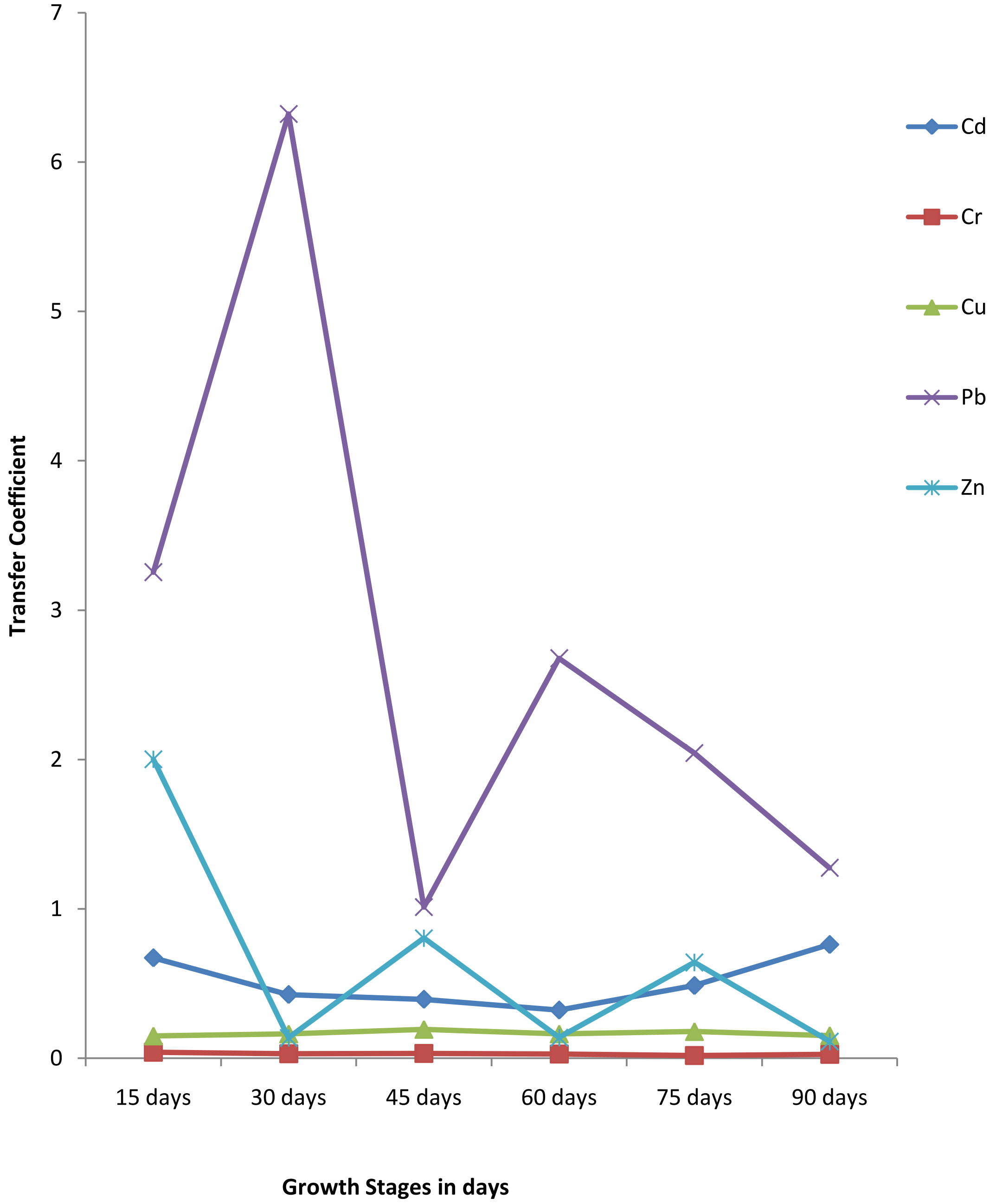

Fig 36:Transfer Coefficient for Cd, Cr, Cu, Pb and Zn in *Triticum aestivum* var. L. Pavon-76 at sampling unit 1

The variations in the values of the transfer coefficient for Cd, Cr, Cu, Pb and Zn in *Triticum aestivum* L. var. Siettecerros at IRS and *Zea mays* L. var. yellow maize at Doruwa Salau are indicated in Fig. 37 and Fig. 38 respectively.

TC for Pb at SU 2 was the highest at the 60-days with a wide variation between the other metals followed by Cd at the 60-days and Zn at the 75 days. The lowest TC was at the 15-days growth stage for Cd, Cr and Cu (Fig. 37). Sampling unit 3 recorded the highest TC for Pb at the 60-days and 90-days growth stages. Zn was the next at the 45- and 75-days growth stages. Cu and Cr had the lowest TC throughout the growth stages (Fig.38).

Comparison of TC values for Cd, Cr, Cu, Pb and Zn in *Zea mays* L. var.popcorn at IRS is shown in Fig. 39. Pb had the highest PUF at SU 4 at the 15- and 90-days growth stages, then at the 45- and 60 days growth stages. The TC for Zn was the highest in the following order of growth stages; 15-days > 45-days > 75-days and lowest at 30-, 60- and 90-days growth stages respectively. The TC for Cd was the next highest at the 30- and 45-days growth stages while the TC for Cr and Cu were reportedly the lowest (Fig. 39).

Similarly, the translocation factor (TF) values for Cd, Cr, Cu, Pb and Zn in *Triticum aestivum* L. var. Pavon-76 at Doruwa Salau is illustrated in Fig. 40. Among the five metals observed at SU 1, the 15-days growth stage recorded the highest TF for Cr and Cu. The next highest TF was for Pb at the 60-days growth stage. However, the TF values for the five metals were reportedly greater than one (Fig. 40).

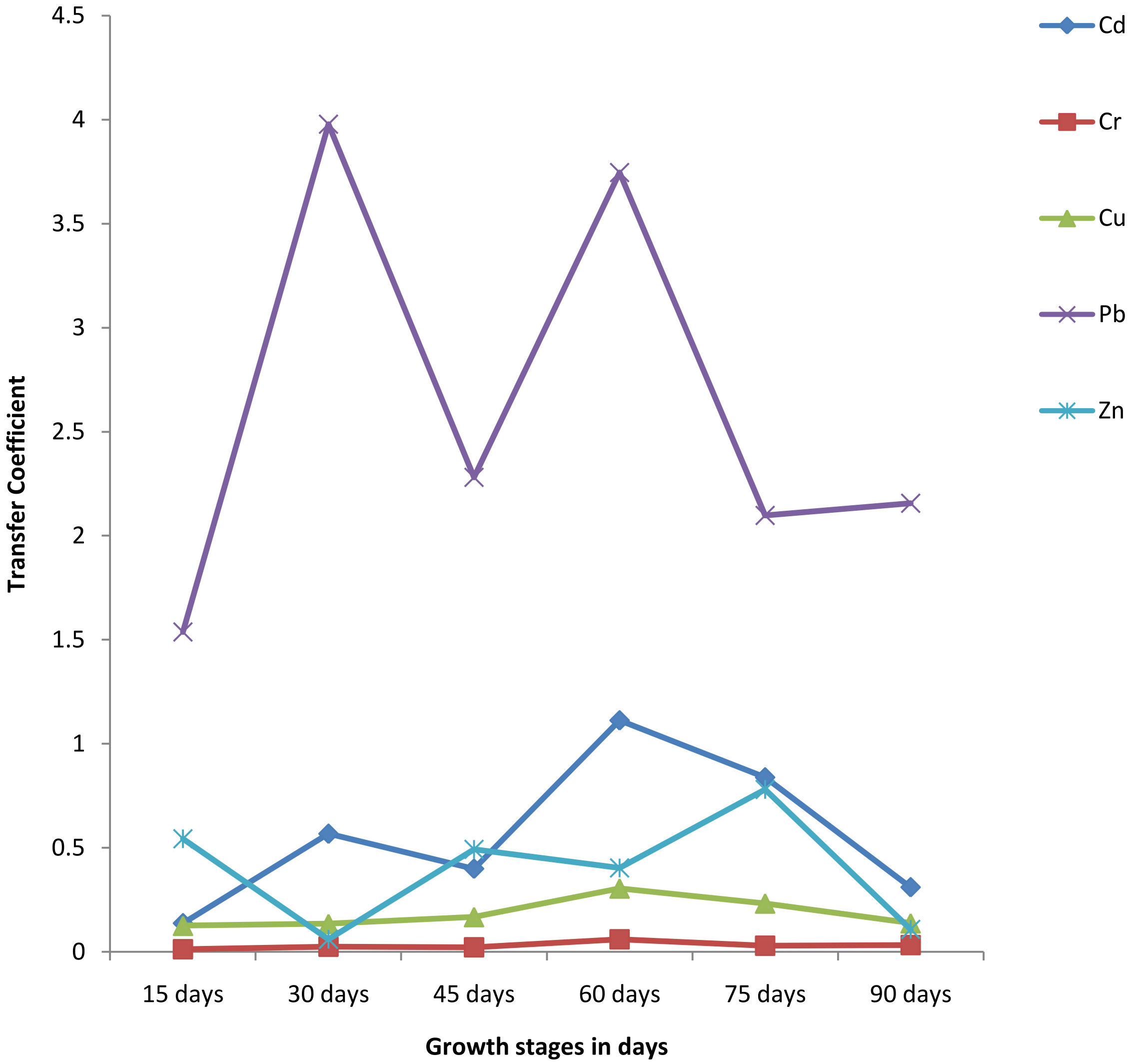

Fig 37: Transfer Coefficient for Cd, Cr, Cu, Pb and Zn in *Triticum aestivum L.* var. Siettecerros at sampling unit 2

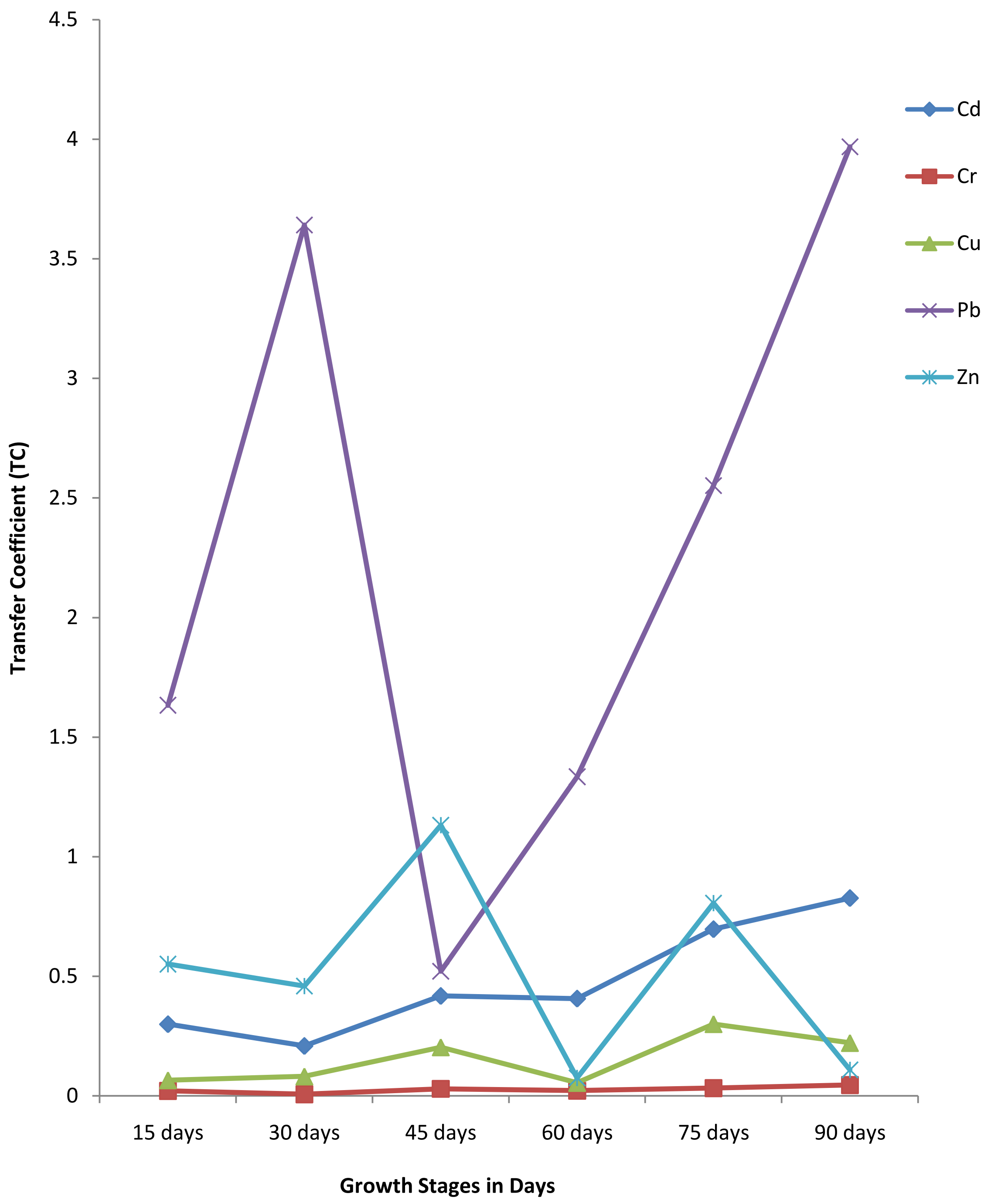

Fig 38: Transfer Coefficient for Cd, Cr, Cu, Pb and Zn in *Zea mays* L. var. TZEE-Y at sampling unit 3

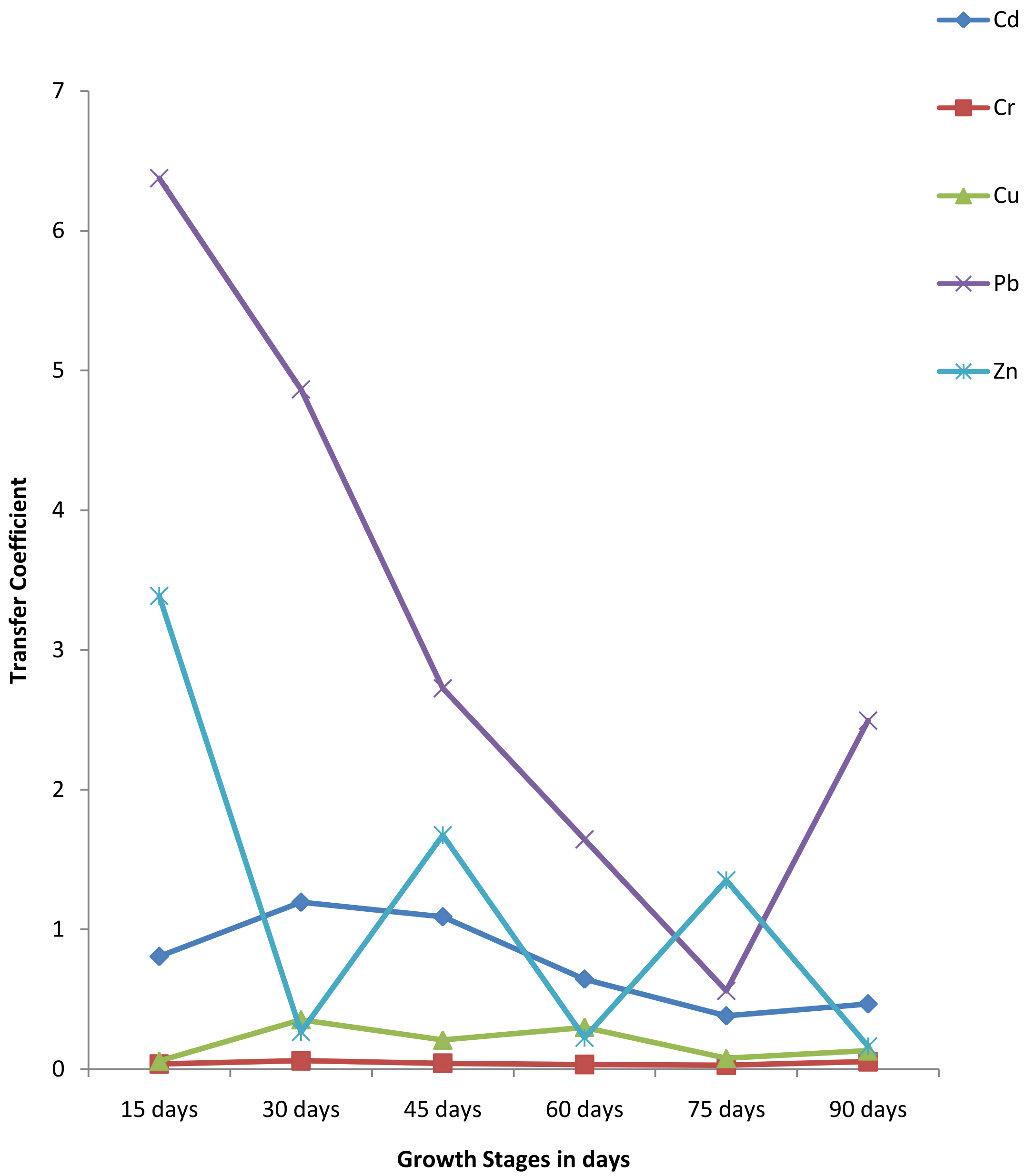

Fig 39: Transfer Coefficient for Cd, Cr, Cu, Pb and Zn in *Zea mays everta* L. at sampling unit 4

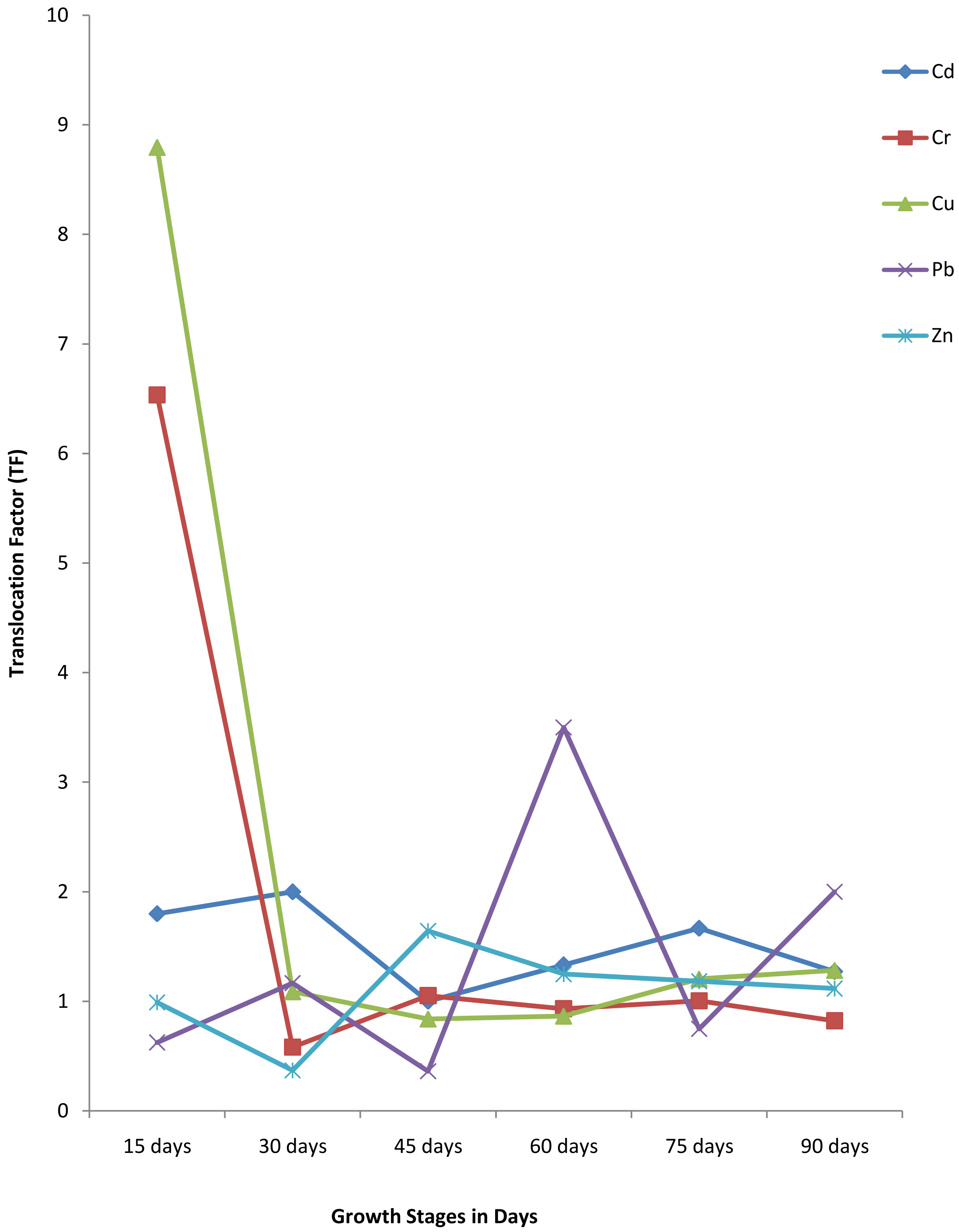

Fig 40:Translocation Factor for Cd, Cr, Cu, Pb and Zn in *Triticum aestivum* L. var. Pavon-76 at sampling unit 1

Comparison of the TF values for Cd, Cr, Cu, Pb and Zn in another variety of *Triticum aestivum* L. var. Siettecerros at IRS is demonstrated in Fig. 41. The magnitude of TF values at SU 2 for the five metals was in the following descending order; Zn at 45-days > Cd at 90-days > Cu at 75-days growth stages. The TF for Zn was also the lowest at the 30-days than all the metals (Fig. 41).

The translocation factor values for the individual trace metals in *Zea mays* L. var. TZEE-yellow maize at Doruwa Salau are compared as explained in Fig. 42. TF at SU 3 was in the following descending order; Cd at the 15-days > Pb at 60-days > Cr at 30-days while the TF for Cd was reportedly the lowest at the 30-days and 75-days growth stages (Fig. 42).

Similarly, the variations of the values among Cd, Cr, Cu, Pb and Zn in popcorn are shown in Fig. 43. TF for Pb at SU 4 was the highest at the 75-days while Cd, Cr, Cu and Zn TF were below the permissible limits. Generally, the PUF, TC and TF values for Pb, Cd and Zn at the 15-days, 30-days and 60-days growth stages had the highest occurrences than Cu and Cr at the 45-days, 75-days and 90-days growth stages. The PUF value was generally the highest than the TC and TF values (Fig. 43).

4.14 Correlation Coefficient Analysis Between The PUF, TC and TF

The correlation analyses between PUF/TF, PUF/TC and TC/TF for each of the metals (Cd, Cr, Cu, Pb and Zn) in the two varieties each of *Triticum aestivum* L. and *Zea mays* L. are presented in Table 4.14. There was significant difference between the PUF/TF for Cr in Pavon-76 and Cu in Siettecerros; between PUF/TC for Zn in Pavon-76, for Cr and Zn in *Zea mays* L. (yellow maize) and Zn in *Zea mays everta* L. and TC/TF was negatively

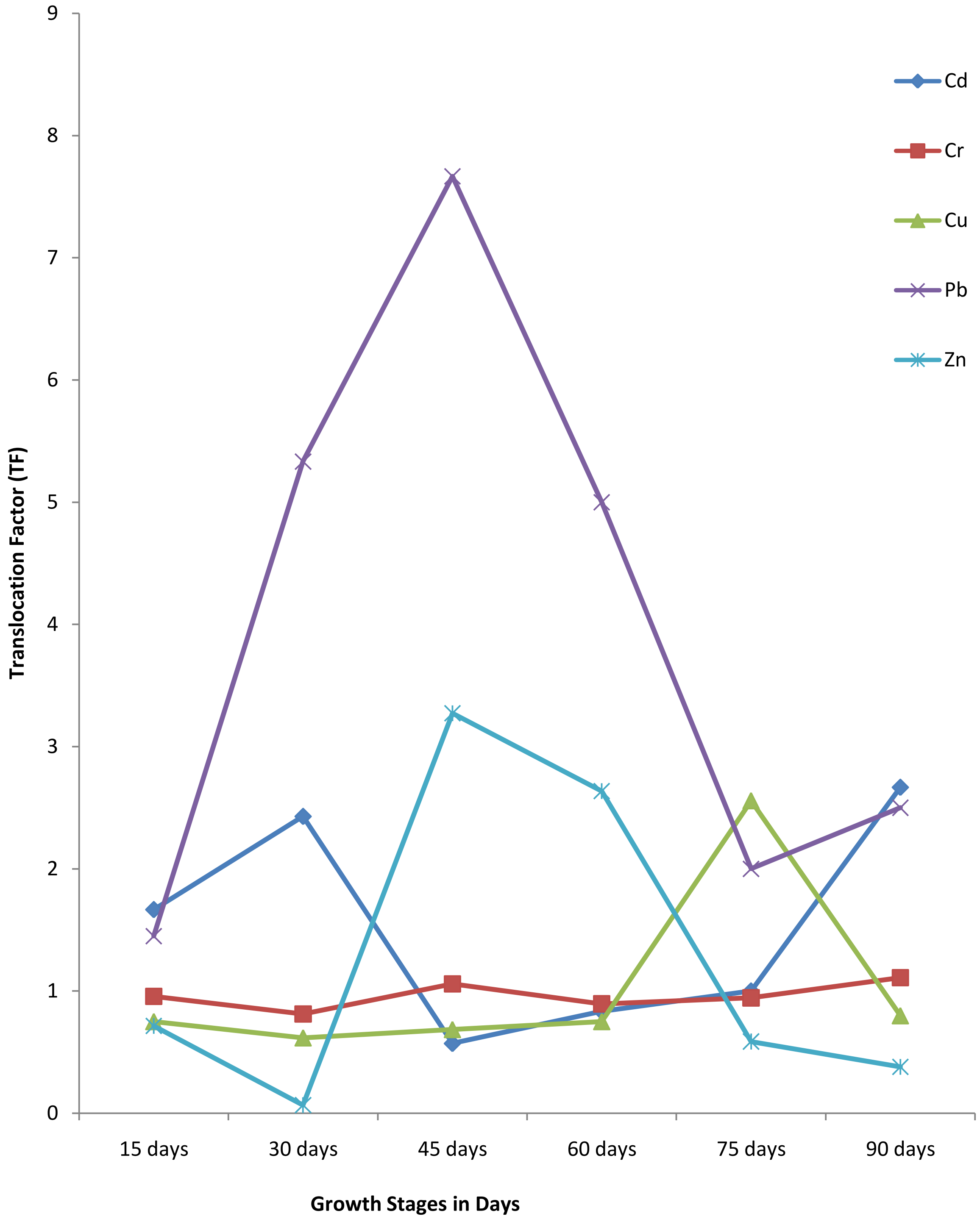

Fig 41: Translocation Factor for Cd, Cr, Cu, Pb and Zn in Triticum aesthivum var. Siettecerros at sampling unit 2

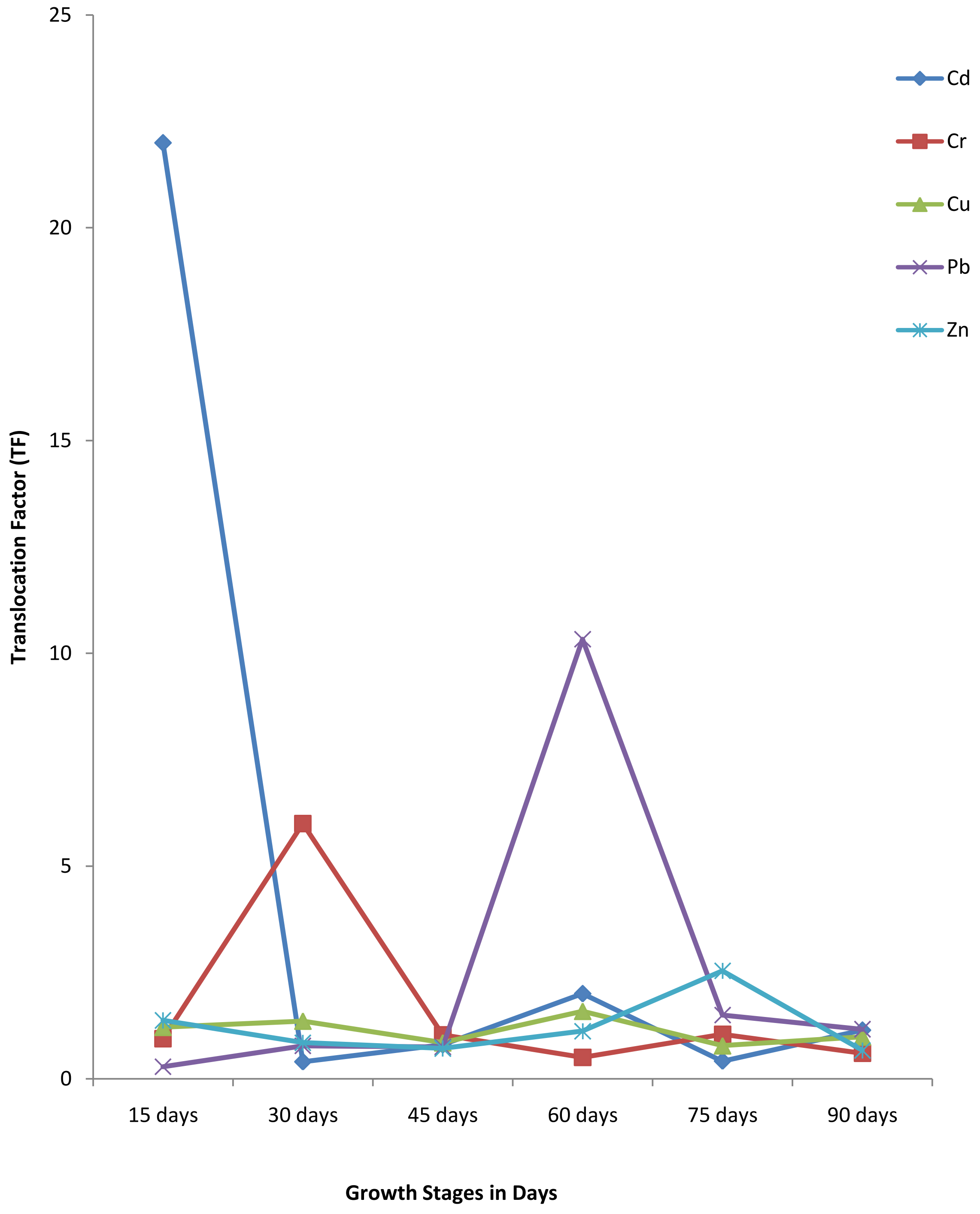

Fig 42:Translocation Factor for Cd, Cr, Cu, Pb and Zn in *Zea mays* L. var TZEE-Y at sampling unit 3

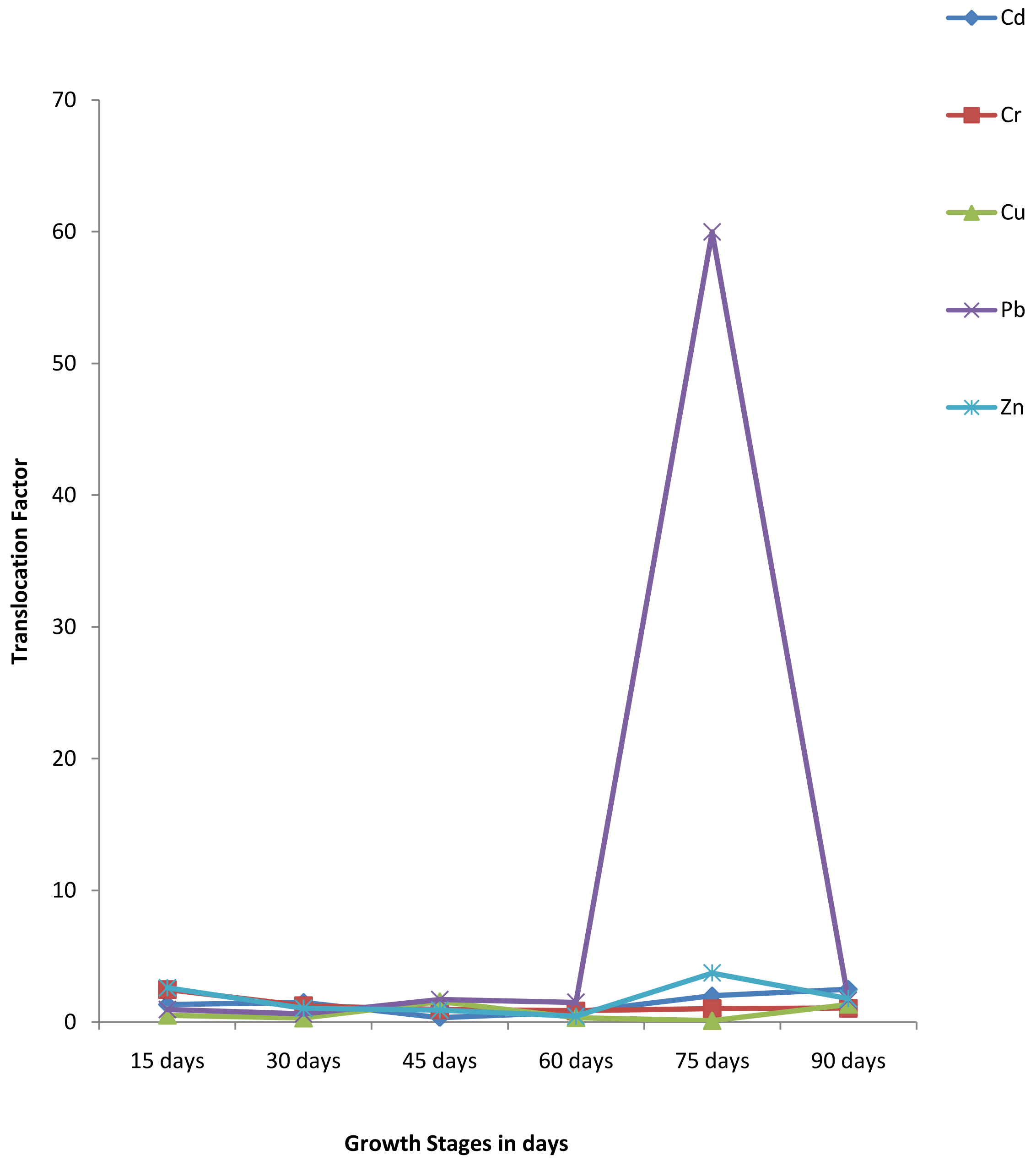

Fig 43: Translocation Factor for Cd, Cr, Cu, Pb and Zn in *Zea mays everta* L. at sampling unit 4

Table 4.14 Correlation Coefficient Analyses between PUF/TF, TC/TF and TC/PUF

Risk Assessment Techniques	Sampling Units	Trace Metals				
		Cd	**Cr**	**Cu**	**Pb**	**Zn**
PUF/TF	SU 1	0 .4737	0 .8210*	0. 3377	0. 2345	0. 2114
TC/TF	SU 1	0 .1090	0. 7204	-0. 5322	-5. 3895	0. 1473
TC/PUF	SU 1	0 .5356	0. 4695	-0. 0797	0. 9712 *	0.9958*
PUF/TF	SU 2	-0 .5926	0. 2925	0. 8909*	ND	0. 6699
TC/TF	SU 2	-0 .4537	0. 1725	0.3505	0.5206	0. 2849
TC/PUF	SU 2	0. 6858	0. 2912	0. 2336	ND	0. 6026
PUF/TF	SU 3	0. 1230	-0. 8058	-0. 6065	ND	-0. 4492
TC/TF	SU 3	-0. 3594	-0. 7316	-0. 9082*	-0. 2960	0. 2560
TC/PUF	SU 3	-0.0317	0. 9140*	0. 7534	ND	0. 8915*
PUF/TF	SU 4	-0. 2145	-0. 2675	-0. 0124	ND	0. 4699
TC/TF	SU 4	-0. 6020	-0. 0642	-0. 0985	-0. 5950	0. 4731
TC/PUF	SU 4	0. 7817	0. 4285	0. 6257	ND	0. 9986*

***0.05**

KEY
PUF = Plant Uptake Factor
TF = Translocation Factor
TC = Soil-plant transfer coefficient
SU 1 = Kano – Zaria Highway
SU 2 = Irrigation Research Station, Kadawa
SU 3 = Kano – Zaria Highway
SU 4 = Irrigation Research Station, Kadawa

significant for Cu at SU 3 only (Table 4.14). There were no values for correlations between TC/PUF and PUF/TF in Siettecerros, yellow maize and popcorn for Pb. Soil Pb was not detected during the trace metal analysis, resulting to no PUF values.

CHAPTER FIVE

5.0 DISCUSSION

It appears that metal concentration in the different samples (soil and plant samples) varied to a great extent from sample to sample, site to site and from growth stage to growth stage.

5.1 Physico-Chemical Analysis of Soil

Plant accumulation of metals from soils depends on their bio-availability and on atmospheric deposition (Haiyan and Stuanes, 2003), either directly entering the plants through stomata or taken up by plant roots after its deposition on the soil surface (Alloway 1995). Plant accumulation of metals from soils also depends on physiological processes, for instance soil factors such as CEC, organic matter content, concentrations of other cations and pH, influences the proportion of soil metal (Chan and Hale, 2004), as well as plant species, cultivar and age of plant (Jung and Thornton, 1996; Rosselli *et al.*,2003). The mobility and availability of heavy metals in soil are generally low, especially when soil is high in pH, clay and organic matter (Jung and Thornton, 1996; Rosselli *et al.*,2003) as well as the growth stages (Liu *et al.*,2005; Hatamzadeh *et al.*,2012). The optimum pH range for most plants is between 5.5 and 7.0; however, many plants have adapted to thrive at pH values outside their range. In this study, the pH values are in accordance with the acceptable range for wheat and maize cultivation at SU 1 and SU 4 but below the ranges at SU 2 and SU 3 which could have been influenced by the textural class of the soil. The high organic matter and organic contents at the SU 1 (Doruwa Salau closest to the Kano-Zaria Highway) and SU 4 (Irrigation Research Station), with the same soil type of sandy clay loamy might have also influenced the elevated levels of metals at both sites respectively. Also, the slightly acidic to moderately acidic soils reduced the mobility of trace metals in the soil (Meng and Li, 1998; Cheng, 2003). Zn concentrations were higher at pH 5.75 and pH 5.48 on the sandy loam soils of Doruwa Salau and the IRS.

The textural class of the soil and the pH could have increased the concentration of Zn as well as Cu at the control site. The high organic matter and organic content of the soil at Doruwa Salau and the same textural class (sandy clay loam) at both the experimental and control sites where Pavon-76 and popcorn were cultivated, contributed to the high metal concentration during growth, and the enrichment of the organic matter contents of the soil by the dead remains of the growing crops. The relatively high organic matter content in the top soil appeared to bind the metals in non-leachable forms thereby reducing their mobility (Amoo *et al.,* 2004).However, heavy metal behaviour still differs individually and other soil physical properties, like texture, might play an important role in heavy metal behaviour in soils. Today it is commonly accepted that soil type plays an important role in heavy metal bioavailability and toxicity (Maclean *et al*., 1987; Henning *et al., 200l*). Chaney (1973) pointed to the fact that the toxicity level of Zn, in a similar way as for Cu strongly depends on several factors which control the Zn availability in soils. These factors may differ considerably for different soils. One of the major factors controlling Zn availability is the pH. For the same Zn addition level, the yield reduction and the Zn contents of chard leaves were found to be much higher at pH 5.3 than at pH 6.4. Total Zn levels in soil are at normal conditions in the 10- 300ppm range with 30-50ppm as a rough average value (De Haan and Zwerman, 1993). The toxic effects of heavy metals are partly determined by soil pH and organic matter, high values being protective (Peredney and Williams, 2000).

The pH values in the study areas ranged from 4.66 to 6.41 suggesting that all the soils were between moderately acidic or slightly acidic in nature. Soil pH, nature of soil and climatic changes affect the rate of uptake of metals by plants (Alloway and Ayres, 1997). Metal mobility has been shown to increase with decreasing soil pH. Hence, the slightly acidic values observed in the present study could have decreased mobility of metals in the soil, thus exceeding the FAO/WHO permissible limits of metal levels in the soils of the study area.

In addition, the higher contents of heavy metals in soil can be backed up by geochemical anomalies or can be the result of air pollution (Dube *et al.*,2001; Blaha, 2004; Barna, 2005). The high levels of metals in the soil during developments of the cereal crops than in the soil before sowing were due to mechanical remobilization of the soils during the standard cultural practices of dry season irrigation farming system.

5.2 Uptake of Trace Metals in the Two Cereal Crops

Data from the four sampling units were compared with the maximum permissible levels of heavy metals from the Codex Alimentarius Commission of the Joint FAO/WHO food standards (2006) and the values used are those applicable to soils and food crops. These values have been produced to protect the food quality of the ecologically adapted food crops. In this study, levels of all the trace metals exceeded the background standard permissible limits, yet the concentrations of each trace metal varied with each site.

5.2.1 Metal concentrations in plant parts of the cereal crops

When plants die and decay, the heavy metals taken into the plants are redistributed and the soil is enriched with the pollutants. Uptake and accumulation of elements by plants may follow two different paths i.e., through the roots and foliar surface (Sawidis *et al.,* 2001) including deposition of particulate matter on the plant leaves (Reuben *et al.,* 2008).

The uptake of metals from the soil depends on different factors such as their soluble content in it, soil pH, plant growth stages, types of species, fertilizers and soil (Ismail, *et al.,*2005; Sharma *et al.,*2006). Uptake and accumulation of toxic trace metals in the different plant parts of the cereal crops varied significantly and were above the tolerable limits on all the sampling units.This suggests that the agricultural produce from these sites maybe potentially hazardous for human and livestock consumption.

Plants differ in their uptake of heavy metals and the subsequent distribution of metals within plant organs (Pal *et al*., 2013). Generally, the leaves revealed higher metal levels than the roots and stems in this research. This could be attributed to the larger exposure area of the leaves than the other parts to wind action, the surface adsorption of particulate matter and high rate of assimilation of heavy metals from the environment agreed with the findings of Pinder *et al.*, (1991), Keane *et al*., (2001) and Al-Kateeb and Leilah (2005).This result also agrees with other reports that metal concentrations in leaves are usually much higher than those in grain and other plant parts (Reuben *et al*., 2008 ; Jung, 2008). Plant characteristics that affect the rate of particle deposition and retention include the exposed surface area of the foliage and the presence or absence of leaf hairs (Collins *et al*., 2006). Earlier works by Little and Wiffen (1977) observed that rough or hairy leaf surfaces were more efficient at collecting aerosols than smooth surfaces, explained by the increased surface area and projection of roughness elements through the leaf-air boundary layer (Collins *et al*., 2006).This is also partly in agreement to Bu-Olayan and Thomas, 2009 where the leaves had higher metal levels than the shoots and roots irrespective of the sampled species. However, stem trace metal levels were determined in this study, while shoot metal concentration was determined by Bu-Olayan and Thomas, 2009. Al Jassir *et al*., (2005) reported that vegetables, especially those of leafy vegetables grown in heavy metals contaminated soils, accumulated higher amounts of metals than those grown in uncontaminated soils because of the fact that they absorb these metals through their leaves.

Leaf loss and senescence can lead to the transfer of chemicals from plant foliage to the surrounding soil, thus reducing the chemical concentration in foliage. However, edible plant parts are likely to be harvested before leaf loss and senescence which becomesignificant chemical transport pathways (Collins *et al*., 2006). However, in most cases with active deposition occurring, the foliar interception pathway is dominant over the root uptake pathway (Reed, 2003).

The root also recorded high metal levels which could be attributed to atmospheric origin through particulate deposition on the soil resulting to uptake by the plant roots.

Plant species have a variety of capacities for removing and accumulating heavy metals, so there are reports indicating that some species may accumulate specific heavy metals, causing a serious health risk to human health when such plants based foodstuff are consumed (Wenzel and Jackwer, 1999). Although the most abundant trace metal at Doruwa Salau closest to the Kano-Zaria highway was Pb, the control site-IRS also recorded the highest occurrence of Pb, which may have been dispersed from the high traffic site due to the dominant wind condition (Haiyan and Stuanes, 2003). Momani *et al.*, 2000 reported that the predominant path of atmospheric pollutants depends upon the type of chemical species and upon meteorological factors such as the intensity and distribution of rainfall. It is also a known fact that automobiles are contributors of Pb (McLaughlin *et al.*, 1999). The site that had a high Pb concentration also tended to have high Zn and Cu concentrations, which may indicate that all three metals come from similar sources of contamination (Yoon *et al*., 2006).

The leaf, stem and root trace metal levels of Pavon-76 and yellow maize at the sampling units perpendicular to the Kano-Zaria highway, were reportedly higher than at the Irrigation Research Station (Figs. 1 – 6).

Lead, being a zootoxic metal is one of the many toxic metals in the environment that needs to be monitored in plants parts used by humans and animals (Alloway, 1995). Lead occurs naturally in all plants and exists almost entirely in inorganic form (Rehman *et. al.*, 2008; Sharma *et al.*, 2010). Several studies indicated that plants have the ability to concentrate Pb (Sridhar, 1988). Leaf and root contain more Pb than stem and the contents of Pb in different plant organs were positively correlated to the Pb content in soils (Sridhar, 2001).In contrast to this study, the amounts of Pb in leaves and stems were higher than in the roots. One possible explanation of this situation is that the Pb uptake arose from the aerial deposition of Pb particulate from vehicular emission exhausts. About 80% of Pb in petrol escapes through the exhaust pipe as particulate (Ogbuagu *et al.*, 2001). Human beings, animals, vegetation and soil are the ultimate recipients of the Pb particulates. Human beings and animals inhale the airborne parts, while the rest are deposited on water bodies, vegetation and soils (Rim-Rukeh and Okokoyo, 2003).

The pH of soil and the levels of organic matter can also promote Pb uptake by the leaves. The Pb content of most plant species is normally in the range of 0.5-3ppm. For certain species however, the Pb toxicity level is very high. This may create a rather dangerous situation because such plants may show no toxic symptoms and apparently looks healthy at Pb levels which are hazardous for human consumption. Baumhardt and Welch (1972) found for corn a significant increase of Pb in the forage but not in the grain. This would indicate that the use of corn grown on Pb contaminated soils for silage could be more dangerous than use after grain harvesting. According to the Codex Alimentarius Commission of the Joint FAO/WHO Food Standards (2006), the maximum level for Pb in most vegetables is 0.1 mg kg^{-1} on fresh weight basis. Although Pb has no biological role in animals, plants, and microorganisms, it forms a bond with the sulfihydryl group of proteins, and hence can disrupt the metabolism and biological activities of many proteins and has caused cancer in kidneys of rodents. This present study revealed higher levels in the cereals above the WHO safe limits (2 mg kg^{-1}).

Cadmium is very harmful to cereals and other crops (An, 2004) and it causes many health problems in humans (Anon., 2008). Therefore, there is a dire need to investigate the critical toxic level for wheat and maize growth. Cadmium is an important heavy metal pollutant, the presence of which in agricultural soils and crops is of great concerns (Sharma *et al.*, 2010). Cadmium concentration was highest in the root at the 30-days growth stage at the control site. However the Cd levels in the cereal crops investigated were noted to be above the critical level of 0.01 mg kg^{-1} as approved by WHO and thus might be a threat for the consumers. Cd is readily accumulated by plants and may get to levels which are adverse to the plants themselves, consequently posing a significant threat to animals and humans that consume plants. Human exposure to Cd has been associated with cancers of the prostate, lungs and testes (Bertin *et al*., 2006).

The most reported illness induced by excessive Cd intake is the development of high blood pressure or hypertension and more generally vascular diseases. Awareness of the health hazards of Cd has made the uptake of Cd by vegetables and agricultural crops a subject of extensive research. It is a common finding that Cd can easily be taken up by most plants. Also in the plant uptake of Cd particularly in the leaves, an influence of Zn is found. Fathi *et al*., 2011 reported that different concentration of zinc and cadmium did not affect wheat final growth and did not see any plant height reduction due to these heavy metals.

Chromium concentrations were higher in the leaves and stems than in the roots and was found to be the least metal as compared to other metals individually in the soil. Low levels of Cr in the plant parts have been attributed to its insolubility under most soil conditions (Smith *et al*.,1992), and it did not affect the plant growth unless the concentrations were very large (Sharma and Sharma, 1996). This supported the findings of Ghani *et al* ., 2010. Our present study also showed that the yellow maize roots and popcorn leaves to be the least and highest accumulator of Cr, respectively. Necessity of Cr for plant growth has not been proved. The mobility of Cr within the plant is extremely low (De haan and Zwerman, 1993). It thus remains in that part where the uptake took place. Toxicity of Cr levels at high concentration levels has not been reported. However, it was noted that chromium concentrations in all the cases observed in this research were above permissible limits of 1.30 mg kg^{-1}(WHO, 2006).

Copper is one of the most important essential elements for plants and animals (Alloway, 1995). Copper concentration was highest in the roots and stems than in the leaves. In contrast, Farooq *et al*., (2008) reported that Cu accumulated more in the roots and leaves than those in other parts because both are the entry points of heavy metals from soils and air, respectively. Demirezen and Ahmet (2006) reported that levels of Cu (22.19-76.50 mg kg^{-1}) were higher in the leafy species than the non-leafy vegetable species from Turkey, which may be related to the richness in chlorophyll. The effects of high Cu contents of soil on the uptake of certain other micronutrients by plants are well known. High Cu levels may cause iron deficiency which is demonstrated as typical chlorosis features. With respect to crop production, it is generally reported that an adverse influence on plant growth results if the copper concentration in the soil solution exceeds 0.1ppm (De haan and Zwerman, 1993). On a general level, our study revealed that all the cereal crops parts accumulated Cu above the critical level (10.00 mg kg^{-1}, WHO), however, the concentration was very low in popcorn leaf (15-days, 45-days and 75-days), siettecerros leaf (45-days) and yellow maize leaf at the 45-days and 60-days growth stages. In normal situation zinc acts as micronutrient but at higher concentration, it becomes phytotoxic (Alloway, 1995).

The amount of Zinc was highest in the leaves and roots than in the stems. Zinc and copper are used as components of vehicle lubricating oils. They are also used in the manufacture of some components of vehicle engines (Abubakar *et al.*,2004). Zinc toxicity is usually caused by interactions in plant uptake of other essential elements like iron and phosphorus. According to Chapman (1966) Zn deficiency symptoms usually start for most plant species at Zn levels lower than 20- 25 ppm. Toxic levels are at about 400ppm and above. Most plants have been severely injured at such high Zn levels. The higher toxicity and sensitivity of plants as compared to animals serves as an automatic protection against Zn accumulation in the food chain (De Haan and Zwerman, 1993). Although Zn has relatively low toxicity to humans, studies have shown allergies and Zn poisoning could occur along the food chain (Antoniuos *et al*., 2011). Also an antagonism between Cu and Zn has been observed. Very generally, is can be said that copper is about twice as toxic as zinc, whose relative toxicity is governed by the organic matter, phosphate level and pH which are the most important conditions (De haan and Zwerman, 1993). Analysis of the cereal crops in our present study revealed the concentration of Zn to be above the set limits of international standards (5.00 mg kg^{-1}, WHO, 1996). Overall, the siettecerros roots and the yellow Maize stems both at the 30-days growth stage had the highest and least accumulator of Zn respectively.

Therefore, the high levels of trace metals than the safety limits suggest a tendency of potential contamination and this implies that these products are unsafe for consumption (Li *et al*., 2007). The input of metals into food web generates another potentially more harmful problem than agricultural systems in close proximity to areas of high traffic density (Li *et al*., 2007).

The highly significant variations for the individual trace metals among the two varieties each of *Triticum aestivum* L. and *Zea mays* L. particularly for *Zea mays* L. and *Zea mays everta* L. shows a strong selective ability of the crops to accumulate certain metals within their plant bodies. The highly significant difference of the trace metals that existed between the plant parts of the four varieties of the two cereals indicates that the concentrations of the trace metals in Pavon-76 and Siettecerros were influenced by the plant parts (leaf, stem and root) as well as proximity to the Kano-Zaria Highway. Also the high trace metal concentrations as well as the highly significant difference of the trace metal concentrations at the selected growth stages for *Zea mays everta* L.could be attributed to the broad and hairy surface of the leaves that easily attracted and allowed the deposition of SPM particles, and the transportation of small particles over longer distances. These small particles have longer atmospheric residence times than larger ones (Hutchinson and Whitby 1977; Salemaa, 2004).The rates of deposition, either dry or wet, tend to be greatest near the pollution source. Aside those of the anthropogenic factors such as climate, atmospheric deposition, plant growth stages, variation in plant species, control absorption and element characteristics, have a direct influenced on metal accumulation by plants (Lake *et al*., 1984; Scott *et al*., 1996; Vousta *et al*., 1996; Margaret, 1998; Nouri *et al*., 2009; Omoloye, 2009). The highly significant differences in the trace metal levels between the four varieties at the selected growth stages and at the interaction of plant parts, selected growth stages and sampling units refelects that the levels of the trace metals in the cereal crops were greatly influenced by a complex interplay of these parameters in determing the trace metal levels in the crops due to atmospheric pollutants. This might also be due to the ability of the cereals and their specific parts to accumulate certain metals.

Furthermore, high levels of metals in the cereal crops may also be as a result of crop breeding programmes for quicker and better yields of crops in order to meet the increasing human population. Breeders have significantly boosted the yield potential of cereals over recent decades, and the currently controversial use of genetically modified strains may do so further. However, crop-breeding programmes may also tend to select for higher values of stomatal conductance since this will increase rates of CO_2 assimilation. This may inadvertently be increasing the potential sensitivity of plants to air pollutants since the main pathway of pollutant uptake is through the stomata. This was suggested to be the reason for the greater sensitivity to O_3 of more recent wheat cultivars observed in Greece (Velissariou *et al.*,1992).

The 15- and 30-days growth stages recorded the highest levels of trace metals in the three plant parts than the 60-days growth stage. This is due to the dilution of the trace metal levels in the plant parts as growth progresses.Over the growing season the biomass of plant increases, diluting the chemical concentration within plant tissues relative to the flux of chemical uptake, and increasing the aboveground canopy for interception of aerial deposition (Collins *et al*., 2006). Plant growth has been recognised as an important variable in the plant uptake of radionuclides by root uptake and aerial deposition (Thorne *et al*., 2004).

5.3 Trace Metals in Soils

5.3.1 Preliminary Trace Metals in the soils

The high trace metal concentrations in the soils during the developments of the cereal crops could indicate that aerial trace metal deposits were taken up from the soil by plants via their root systems and translocated to other regions of the plant (Mulgrew and Williams, 2005). The high metal content of the soils at Doruwa Salau could be attributed to the proximity of the sampling units to the Kano-Zaria Highway. The low trace metal content of the soils at the IRS may be due to the location of the site in an open area usually subjected to windy conditions. In other words, it may be due to meteorological conditions such as wind direction and speed. Speed is related to low traffic movement, which produces low turbulence and re-suspension (Bisessar *et al.*,1982; Anongo *et al.,* 2005), so that significant fractions of trace metals were deposited on the roadside soil at the control site. The dominant wind direction may also be as a result of the presence of the Tiga dam around the site. Heavy metals from atmospheric deposition are potentially more mobile than those that are ultimately inherited from the geological parent material (Chlopecka *et al.*,1996; Donisa *et al.*,2000; Momani *et al*., 2001; Collins *et al*., 2006).

Higher values of soil Cd and Pb which exceeded the permissible limits suggests anthropogenic sources, while soil Cr, soil Cu and soil Zn within the permissible limits poses a potential health risks of these agricultural field lands used for crop production. The non-significant differences of the individual and combined ANOVA of soil trace metals at the six growth stages, indicates an enrichment of the soil trace metals by anthropogenic sources in this study. This suggests that the trace metals in the leaves, stems, roots and whole plant of the two varieties each of wheat and maize investigated in this study originated from polluted atmosphere by motor vehicles and not from the soils.

Several findings have reported that higher concentrations of Pb, Cd, Cu and Zn in soil samples correlated with traffic conditions and therefore, attributed it to anthropogenic effects related to motor vehicles (Momani *et al.*,2000; Uwagboe and Hymore, 2001; Anongo *et al.*,2005). According to De Haan and Zwerman (1993) the normal content of each individual metals in the soil varies in concentrations. For instance naturally occurring Cd concentrationin soils ranges from 0.001-3ppm (Alloway, 1995). Cd is widely used as a coating material. It is applied in batteries, in photography and as a fungicide. The occurrence of Cd in motor oil and in car tires explains the relative accumulation in roadside soils. Cd contents of soil in non-polluted areas are usually below 1ppm.

Chromium has its most widespread application as corrosion inhibitors. Many metals used in household, traffic and industry are chrome-plated to extend their durability. Cr is an essential element for man and animal, and it plays a major role in the so-called glucose tolerance factor i. e. the return of excess levels of glucose in the blood to normal levels. Chromium is one of those heavy metals whose environmental concentration is steadily increasing due to industrial growth, especially the development of metal, chemical and tanning industries. Other sources of chromium permeating the environment are air and water erosion of rocks, power plants, liquid fuels, brown and hard coal, and industrial and municipal waste. Although there is no risk of chromium contamination on a global scale, local permeation of the metal to soil, water or the atmosphere might result in excessive amounts of this pollutant in biogeochemical circulation (Wyszkowska, 2002). As observed by Ghosh and Singh (2005) non-biodegradability of chromium is responsible for its persistence in the environment; once mixed in soil, it undergoes transformation into various mobile forms before ending into the environmental sink (Bartlett and James, 1983; Bartlett, 1988). Although Cr toxicity in the environment is relatively rare, it still presents some risks to human health since chromium can be accumulated on skin, lungs, muscles fat, and it accumulates in liver, dorsal spine, hair, nails and placenta where it is heavyable to various heath conditions (Reyes-Gutiérrez *et al*., 2007).

Normal Cu contents of soil are around 20 ppm with variations over the range 2 – 100 ppm (De Han and Zwerman, 1993). Mobility and displacement of Cu in soils is low. It is strongly bound by organic matter and clay minerals. As a result of this bonding, downward movement of Cu in silty or clayey soils is almost nil. Even in sandy soils, such movement is very small. Peat soils are famous for their fixations. Therefore the elevated Cu concentrations in the soils during growth of the crops on both sites may also be attributed to the soil texture and aerial deposition. In addition the high Cu contents on the experimental site as well as on the control site indicate that the organic matter content also contributed to the high Cu content because of slow solubility. Organic matter plays a role in complexing and retaining metals especially Cu and Cd (Camobreco *et al.*,1996). With these high trace metal contents in the soil, crops, croplands and livestock are likely to accumulate these metals in their plant and body tissues leading to various toxic effects. The potential toxic effects may fast reach lethal levels affecting every organism along the food chain.

Lead (Pb) occurs naturally in all soils, in concentrations ranging from 1 to 200 mg/kg, with a mean of 15 mg/kg (Chirenje *et al*., 2004). Normal mean content of Pb crustal rocks is usually about 13ppm. Although the total amount of Pb used is highest in batteries, but the gasoline additives are the major Pb discharges. The accumulation of Pb in the cereal cropswas very high at Doruwa Salau both for Pavon-76 and yellow Maize and is directly related to aerial deposition.Though the soil of the experimental site was predominantly contaminated with Pb and invariably absence in the soil at the control site, both sites also contained moderate and elevated concentrations of Cu and Zn respectively (Table 4.4). This is in agreement to Yoon *et al*., 2006 that Pb, Zn and Cu seems to have the affinity of co-existing in the soils irrespective of their concentrations. However, in contrast to this study, Yoon *et al*., 2006 reported a much higher concentration of Pb (90 to 4100mg kg^{-1}), Zn (195 to 2200mg kg^{-1}) and Cu (20 to 990mg kg^{-1}) concentrations. Pb is highly toxic and could be bioaccumulated and transferred to the food chain. This is of particular relevance because of the potential adverse effects on health and food security of people in the region. Similarly, the high levels of Zn and Cu found both in soils and plants are of ecological concern. It should be noted that Cu and Zn are not considered toxic for humans but are toxic for plants and for this reason some countries have posed restrictions to their concentrations in soil (Davila *et al*., 2012). This is of particular relevance because a higher concentration of these elements hinders the development of plants and could reduce land productivity and access to food.

5.4.Compound Pollution of Trace Metals in the Soil – Plant Systems

There was no relationship in the graphical illustrations between the plant and soil trace metals (Figs. 11 to 30). Metal concentrations in the plant parts were poorly correlated with metal concentrations in the soil, which is expected since total metal concentrations have been considered poor indicators of metal availability to plants (Kabata-Pendias and Pendias,1992). This supports the works of Keller *et al*., 1998 that the uptake of metals, both by roots and leaves, was not linearly correlated to the external metal concentrations.There was no significant correlation between soil trace metals and the cereal crops, which supports that many factors other than total soil trace metals control the mobility of trace metals in the soil-plant system in most cases. Nouri *et al*., 2001 reported that the lack of correlation in some cases only implies that, in isolation, these factors are not dominant in determining metal uptake by the plant. Indeed, it may be the variation and interaction of all these factors, plus forms of heavy metals (Nouri *et al*. 2001) and organic content (Wright and Otte 1999). The non-significant relationship further indicates that the metals may have been derived from aerial routes through foliar retention and absorption from vehicular traffic as probable pollution sources (Adeniyi, 1996). In contrast to this study, Sinha *et al*., 2006 found highly positive correlations between metals accumulatedin some plants (leafy vegetables) and the available metals in soils. However, Fytianos *et al.* 2001 concluded that the correlations between metal concentrationsin soils and vegetables were generally poor for the majority of cases (Chao *et al*., 2007).

Preliminary soil trace metal was comparatively higher than soil trace metals during growth and development. This could be an indication that the elevated levels observed in the plant parts arose from vehicular exhausts.The absence of Pb in the soil on the control site (Table 4.1) strongly indicates that the metals originated from atmospheric deposition not from parent materials (Donisa *et al.*,2000).Vehicular traffics are associated with the introduction of some chemical substances into the atmosphere of which metallic elements are some of the most important. The atmosphere is an integral component of the ecosystem and plays some fundamental roles in the food chains processes of the ecosystem. As such the chemical substances introduced into the atmosphere by vehicular and other types of emissions can eventually get to humans through the food chain. Compounds containing Zn and Cu are used in the production of vehicle lubricating oils. The metals are also used in the manufacture of some components of vehicle engines (Smith *et. al*., 1992). In built-up areas where vehicular traffic is high, deposition of chemical substances, including some of the heavy metals contained in the smoke tends to occur (Kapu *et. al*., 1991). As livestock and even humans consume some components such as leaves and stems of such plants, the substances can be passed into human and livestock tissues.

The concentrations of heavy metals are higher in soils than vegetables grown on the same soils (Khan *et al*., 2009). This indicates that only a small portion of soil heavy metals is transferred to the vegetables and the root acts as a barrier to the translocation of heavy metals within plant (Davies and White, 1981; Khan *et al*., 2009). In contrast to this study, metal concentrations was reportedly higher in the plant tissues than in the soils indicating that a larger part of the growing plants were more exposed to atmospheric deposition than the soil. Heavy metal accumulation in plants can also reflect the relative extent of the burden and its dispersal (Mulgrew and Williams, 2005).

The mean increase of plant trace metals after sowing in pavon-76 and yellow maize at Doruwa Salau and siettecerros at the control site reveals a direct relationship between the concentration of the trace metals and traffic density. It also suggests that the wheat varieties and yellow maize have greater potential of accumulating trace metals than the popcorn. Similarly Baumhardt and Welch (1972) in a similar study revealed that corn accumulated higher levels of Pb, but the variety of the corn was not mentioned in their study.

Furthermore, metal levels in the leaves and roots were also comparatively higher than in the soils before and after sowing, and in the stems. This could also be as a result of traffic density. However, this phenomenon is contrary to the findings of Bu-Olayan and Thomas (2009) in desert plants of Kuwait Governorates, where the trace metal concentrations in soil were comparatively higher than in roots and shoots but lower than that of the leaves in the sampled plants. This could be attributed to the variations observed in the morphological, absorption area, phyllotaxis of the leaves and the effect of different metals concentrations analyzed to that of the present study.

Generally, metal concentrations were highest in the plant parts than in the soils and at Doruwa Salau closest to the Kano-Zaria Highway than at the Irrigation Research Station. The leaves were the highest accumulator of metal levels than the stem and roots.

Therefore, potential bioaccumulation and mobility of heavy metals from motor vehicles into growing plants could increase the potential transfer of heavy metals through crops to animals (feed crops) and humans (food crops)(Antoniuos *et. al*., 2011). Heavy metals are not biodegradable and therefore can accumulate in human vital organs (Demirezen and Aksoy, 2006) and lead to progressive toxic effects if consumed with food that has concentrations of heavy metals above the permissible levels. Heavy metals are toxic to soil microorganisms when present in excessive concentrations (Chakrabarti *et. al.*, 2005). In addition, plants themselves can also suffer from excess trace metals in soil.

The toxicity of heavy metals in the soil and their varying effects on soil organisms are dependent on several factors. Chaney (1973) pointed to the fact that the toxicity level of Zn, in a similar ways as to Cu and Ni strongly depends on several factors such as organic matter, phosphate level, of which pH is one of the major factors controlling Zn availability in the soil. These factors such as pH differ considerably for different soils and also determine the actual availability of Zn versus Cu or Ni. pH was also considered by Chumbley (1971) as the main controlling factor of the mobility of heavy metals in the soil. It can be said that Cu is about twice as toxic to plants as Zn, where as Ni is about 8 times as toxic as Zn.

5.4.1. Transfer of metals in cereal crops

The mechanism of uptake of heavy elements by plants is based on root uptake of metals and foliar absorption, including deposition of particulate matter on the plant leaves. The intensity of extent of the uptake therefore influences the actual content of an element in the plant (Reuben *et al.*, 2008)**.** The soil-plant transfer factor, expressed as the ratio of plant concentration divided by the total concentration in soil. Kloke *et al.,* (1984) reported that Cd, Ti and Zn have the highest soil to plant transfer coefficient (TC), in part because of their relatively poor sorption in the soil, while elements such as Cu, Co, Cr and Pb have low transfer coefficient (TC), and are stably board to the soil structure. This is partly in agreement to this study where Cu and Cr recorded a lower TC and in contrast where a lower and higher TC was observed for Cd and Zn, and Pb respectively. This may be an indicator of the plant accumulation behaviour (Kabata-Pendias and Pendias 1992). Lübben (1993) showed large differences in the transfer of Cd, Zn, Ni, Cu, Pb and Cr from soil to different plant parts. The lowest transfer factors of Cd were found for grains of maize, peas, oats and wheat, whereas the highest values were reported for leaves of spinach and lettuce and the roots of various plants. Low transfer factors of Zn were reported for carrot and grains of maize and pea, whereas the highest were found for leaves of spinach and roots of radish and other plants. The transfer factors in the investigated plants were reported to be similar also for Cu, Cr and Pb (Lübben ,1993).This data indicates that there is a large difference in the uptake of Pb and Zn, whereas differences in the uptake of Cu, Cr and Cd were less pronounced.

Zea mays everta L. recorded the highest TC among the metals, which might be due to its wider surface areas than the other cereal crops. This supports the works of Chao *et al*., 2007 where spinach had the highest TC probably due to the rather bigger surface areas of the leaves than celery, garlic and cole in their study. This also further conformed to the fact that garlic exhibited the lowest TC values because of the minimum surface areas than the leaves of the other vegetables. However, the slight difference between this present study and that of Chao *et al*., 2007, is the different crop species. In general, Khan *et al*., 2009 remarked that the transfer coefficient of 0.2 indicates anthropogenic contamination for leafy plants than the 0.50 by Kloke *et al.,* 1984 (Sridhara *et al*., 2008). They argued thatKloke *et al.*,1984 gave a generalized transfer coefficient for soils and plants based on the root uptake of metals.Also, *Zea mays everta* L. had generally very high transfer coefficient especially for Pb which also agree with the works of Chao *et al*., 2007, and indicating atmospheric depositions both on the aerial plant parts and on the soil which reflect that,only Pb might have accumulated into the plant from both the atmosphere and soil in this study. At the IRS and the site nearest to the Kano-Zaria Highway, it was suspected that high Pb transfer coefficient was a combined result of elevated topsoil metal concentrations (mg kg^{-1} for Pb) during growth and absorption of atmospheric metal deposits in popcorn and pavon-76 respectively which also agree with the findings of Chao *et al*., 2007. Tiller *et al*., (1987) reported that soil could be contaminated with heavy metals by aerial deposition for up to hundreds of kilometers away from the source. Cd, Cr, Cu and Zn with a TC less than one therefore indicates that the high mean metal concentrations in the plants than in the soil suggest an anthropogenic source from aerial metal deposition and could be regarded as far distance air transport of heavy metals outside their original mineral associations which requires small and easily soluble molecular compounds (aerosols of a certain maximum size), that are finally deposited on the ground (Mutsch, 1996). There, they increase the pool of the portion of easily soluble elements caused by weathering and biogenic processes (Zimmermann and Blaser, 1993; Mutsch, 1996). In addition, the concentration of heavy metals in the environment either by pollution-related depositions or by biogenic accumulation or weathering processes depends on the respective element and the parent rock of the respective site (Mutsch, 1996). The mobility of the heavy metals is also dependent on the binding strength; the greater the mobility, the lower the binding strength and vice versa. Market, 1993, Toth *et al.*,2008 and Kuklova *et al*.,2010, concluded that the relatively low TC of Pb and Hg indicates that the amounts of Pb transported to the above ground plant parts (including fruits) are low. The high accumulation of Pb in the leaves might be related to atmospheric deposition as with the findings of Chao *et al*., 2007. This is because soil Pb was generally not detected in the soils of all the four sampling units before sowing in this study. From the TC values, it could be concluded that Pb was mainly accumulated in the cereal crops through the leaves, while Cr, Cd, Cu and Zn accumulated in the cereals through the leaves and the roots. This study also reveals a high TC for Pb at the experimental site suggesting a higher input of Pb from polluted atmosphere in recent years. Also lower values of TC for Cd, Cr, Cu and Zn also suggests inputs from vehicular emissions due to absence of industrial, commercial and densely populated residential activities at the site nearest to the Kano – Zaria Highway.

Soil properties may have further influenced the soil-plant transfer coefficient of Cu and Pb. The moderately acidic nature of the soils from the Kano-Zaria Highway (mean pH of 6.41) and the IRS (mean topsoil pH of 6.21) may have increased the availability of metals for cereal crops uptake.Transfer factor could also be influenced by soil properties like soil texture. Henning *et al*., 2001, reported that the transfer coefficient of Zn in Maize grown in the sandy and clayey soils were lower than the normal transfer coefficient ranging from 1 to 2 according to Korentejar (1991).

Copper is one of the most important essential elements for plants and animals (Alloway, 1995). The normal plant transfer coefficient values for Cu in plant tissues are between 0.01 and 0.05 (Korentejar *et al*., 2001). Also, Henning *et al*., 2001 reported a higher transfer coefficient for all the soil types according to Korentejar (1991), who remarked that a higher transfer coefficient and uptake of Cu in the seedling tissue that occurred in the loamy soil is possibly due to the low soil pH which caused a higher availability of Cu in soils for plant uptake (Alloway, 1995)

Lead (Pb), being a zootoxic metal, needs to be monitored in plant parts used by humans and animals (Alloway, 1995; Korentejar *et al*., 2001). The transfer coefficient for all the crops were generally higher at all the growth stages, especially at the 15 days and 30 days growth stages, both for Pavon-76 (SU 1)and popcorn (SU 4) at the experimental and control site respectively. Also the sandy loam soil observed on both sampling units (SU 1 and SU 4) contributed to the higher transfer coefficient and uptake of Pb, resulting to higher availability of Pb for plant uptake at the early stages of growth. This is in agreement to the findings of Korentejar *et al*., 2001.

Cadmium is a very mobile and bioavailable metal which may accumulate in crops and humans (Alloway, 1995). Smith *et al*., 1996 and Henning *et al*.,2001 reported a lower bioavailability of Cd in the clayey soil due to a much higher CEC in clayey soil which resulted to the formation of stable complexes. The availability of Cd in the sandy soil could be due to the mineralisation of Cd from organic complex to an inorganic form for plant uptake (Korentejar *et al*., 2001). However, in this study, the textural class observed for all the sampling units ranged from sandy loam to sandy clay loam.

Zinc is a phytotoxic metal, but it is important as a micronutrient at the appropriate levels (Alloway, 1995). Henning *et al*., 2001 also reported that a lower pH in the loamy soil caused a higher transfer coefficient in the loamy soil and subsequent higher uptake of Zn in the maize seedling tissue, whereas in this study, a moderate pH (6.21) in the sandy loam soil caused a subsequent lower uptake of Zn in the plant tissues except in popcorn. This is in contrast to Korentejar *et al*., 2001, who observed a higher transfer coefficient and lower pH in the loamy soil and subsequent higher uptake of Zn in the maize seedling tissue.

In addition, the low organic carbon contents (Table 4.2) of soils sampled could have also enhanced soil-plant transfer of metals, which is in agreement with the works of Kachenko and Singh, 2006.

Generally the TC for all the trace metals progressively increased between the germination stage through to the flowering stage, with higher occurrences between the tillering and shooting stages.

5.4.2 Accumulation of trace metals in the cereal crops by species, sites and growth stages.

The Plant uptake Factor (PUF) is a competent technique developed to assess the level of the metal in the plant as a fraction of the soil's total. Previous studies have indicated that the uptake of metals by plants differs from one metal to another, from one plant species to another and from one site to the other (Amusan *et al*., 2005; Agyarko *et al*., 2010). The results from this study as shown in Table 4.12.1 and table 4.12.2 indicated that the uptake of each metal differs from one site to another and from one growth stage to the other. This variation might be due to the differing soil properties which may differ from one site to the other. The variations might also be related to the different physical, chemical and biological properties of the soils at the four sampling units and probably the genetic composition of each of the species and/or variety of the food crops used in this study. Plants generally function better in slightly acidic soils (pH 6.0 – 7.0) because at lower pH many of the minerals needed for optimal growth are more soluble and thus available for plant uptake (Braun, 2006). Organic matter also plays an important role in that it can act as a binder to metals and organic chemicals, but should not be considered permanent as it has a half-life of 10 years (McBride, 1995). In short, PUFs can vary significantly based on the crops cultivated, the nature of the soil, and how the gardener manages their plot (Braun, 2006).The extremely high PUF for both pavon-76 and yellow maize at Doruwa Salau could probably be through uptake from the leaves and roots. Particulate deposition represents the major pathway of contamination by the dry deposition of suspended particles with subsequent permeation into the cuticle (Collins *et al*., 2006). Reed, 2003 remarks that during active deposition in most cases, the foliar interception pathway is dominant over the root uptake pathway.Translocation, which is the transport of water within the plant, is also the major mechanism for movement of nutrients and energy-rich photosynthate (Bell, 1992). It is also the principal route by which contaminants move from the root system to stems, leaves, and storage organs (McFarlane, 1995; Collins *et al*., 2006). Hence, they could be labeled as accumulators of pollution due to the proximity of the site to the highway. This supports the works of Kalisova-Spirochova *et al.*, 2003, where corn was the highest accumulator of Pb and Zn in the leaves and in the roots and Kuklova *et al.*, (2010) remarks that, this could be caused by higher input of these trace metals from polluted atmosphere. Similarly, Chao *et al*., 2007 also reported the highest enrichment coefficient (EC) for Pb, Cu and Zn in vegetables. The PUF value of the same metal differed from one cereal crops to the other across, suggesting a selectivity of the crops in absorbing elements from the atmosphere. The great variations of the PUF exhibited by the same crop at the six growth stages probably resulted from different chemical fraction distributions of metals.

Hyperaccumulators are conventionally defined as species capable of accumulating metals at levels 100-fold greater than those typically measured in common nonaccumulator plants

(Chaney *et al*., 1994; Reeves and Baker, 1999). Hyperaccumulation is a natural ability of some plant species, normally wild species, and normally quite unusual or even rare species that grow on naturally metal-rich areas of the earth, which have evolved to take up huge amounts of metals. Although the standard has not been scientifically defined (Nazir *et al*., 2011), comparison with the present study was made as described as four rules i.e., the concentration of heavy metals in plant shoots reach hyperaccumulating level (Pb and Cu > 1000 mg/kg, Zn > 10,000 mg/kg) (Baker *et al.*,1994; Brown *et al.*,1994 and Wei *et al.*,2002; Kakar *et al.*,2011); the concentration of heavy metals in its above ground part is 10-500 times more than in plants from non polluted environments (Concentration: Pb 5 mg/kg, Zn 100 mg/kg, Cu 10 mg/kg) (Shen and Liu, 1998); the metal concentrations in shoots are invariably greater than that in roots; and enrichment coefficient > 1, showing a special ability of the plant to absorb from soils and transport metals and store in their above-ground parts (Baker *et al.*,1989; Baker *et al.*,1994; Brown *et al.*,1994; Wei *et al.*,2002). It is difficult to judge whether a plant species is a hyperaccumulator or not if the plant species do not accord with the above four rules simultaneously. So, definite use of a scientific standard for hyperaccumulator will be very necessary for hyperaccumulator choice and phytoremediation of soil polluted by heavy metals (Nazir *et al*.,2011).

In this study none of the cereal crops showed metal concentrations> 1000mg/kg in shoots, since only the metal concentration of the leaves, stems and roots were determined. Although, one of the rule of the standard for hyperaccumulator with the following concentration of heavy metals (Pb 5 mg/kg, Zn 100mg/kg, Cu 10mg/kg) ,was observed in this study, none of the cereal crops could be regarded as a hyperaccumulator. This is because according to the standard, the plant species must accord with the above four rules simultaneously. Considering the PUF for Pb, all the cereal crops at all the growth stages may possess the characteristic or potential of hyperaccumulator. With the exception of Cd in yellow maize at the tillering stage and Cu in yellow maize, siettecerros, popcorn and pavon-76 at the germination, tillering, heading and flowering stages respectively, the cereal crops may be excluders of Zn and Cr. Biological accumulation occurs when a contaminant taken up by a plant is not degraded rapidly, resulting in the accumulation in the plant. (Nazir *et al.*,2011; Khan *et al.*,2010, 2011).

Though none of the crops sampled were metal hyperaccumulators, some interesting observations were noted. Pavon-76 and yellow maize were the most efficient in taking up Pb and Cu respectively. Pavon-76 and yellow maize showed trace metal concentration higher than the normal phytotoxic levels.

Roadside soils used for agricultural activities often serve as the major sink for heavy metals released into the environment from vehicular emissions. Accordingly, plants too could become sinks for these particulate heavy metals. Therefore, monitoring trace metals in soil and edible plants due to atmospheric pollutants should be regarded as a requirement for the safe use of agricultural fields along high traffic densities.

High values of trace metals can be attributed to anthropogenic effects related to motor vehicles. Livestock that feed on pasturage and arable grown at close proximity to the highways are exposed to potential health hazards. Therefore, the study suggests that cultivation of edible crops on roadside agricultural soils should be discouraged.These also suggest that informed concerns of deliberate avoidance of crops from such sites despite the low concentrations are not misplaced (Omoloye, 2009).

5.4.3 Translocation of metals in cereal crops

Generally, the TF values were evidently higher and consistent for Cd at germination, tillering and flowering stages; Cr at the shooting and flowering stages; Pb at the shooting, heading, flowering and ripening stages and Zn at the flowering and ripening stages respectively. TF indicates a fraction of the total deposition on plant surfaces that is incorporated into the edible plant parts (Reed, 2003). TF also signifies the amount of heavy metals in the soil that ends up in the test crop (Odai *et al.*, 2008). This may imply the restriction in soil-root transfer at higher metal concentrations in the soil (Yoon *et al*., 2006; Majid *et al*., 2012). The cereal crops growing at the sites were capable of accumulating heavy metals in the roots and stems, but most of them had low TF values, although they were greater than unity indicates an aerial depositions as well as limited ability of trace metals accumulation and translocation by the plants. Also, soil reaction might have also contributed to the low TF value. The optimum soil reaction for the majority of cultivated plants is around the neutral pH value, because under neutral to weakly alkaline conditions bioavailability of some heavy metals (except As, V, Mo, Co and Cr) decreases (Mathur *et al*.,1991; Dermatas & Meng, 2003). This reduces the possibility of their translocation from roots into the plant itself (Bolan *et al*., 2003; Kisic *et al*., 2007).

Among the six growth stages and the metals tested, the cereal crops growing at the experimental site were most efficient in taking up and translocating Pb. High translocation of Pb indicates that plants were willing to transfer Pb from their roots to shoots possibly due to Pb toxicity. The elevated metal concentrations in the underground tissues and low translocation to the aboveground tissues in the cereals examined might also suggest that they are capable of rather well-balanced uptake and translocation of metals under metal polluted conditions.

5.5 Uptake of Metals in Cereal Crops at the Selected Growth Stages

Uptake of trace metals by the aerial or above ground parts of the cereal crops indicates atmospheric deposition arising from motor vehicles (Momani *et al*., 2001). According to

Collins *et al*., 2006, plant uptake of metals could be through the leaves or roots. But since soil Pb was not detected at some selected growth stages, there is a strong indication that the heavy metals levels observed in the plant parts arose from polluted atmosphere from motor vehicles, and also due to the absence of any industrial, residential and commercial activities within the study area.

5.5.3 Transfer of metals in cereal crops at the selected growth stages

The highest TC for Pb in Pavon-76 and popcorn than all the other metals at SU 2 and SU 3 is probably due to the proximity of SU 1 to the Kano-Zaria Highway even though soil Pb wasdetected at the 15-days growth stage only, while on the SU 4 at a distance of 1934.6metres might be related to meteorological conditions such as wind, mobile nature of the particulates (Mutch, 1996) resulting to wider dispersion. However, small particles are transported over longer distances, and have longer atmospheric residence times than larger ones (Hutchinson and Whitby,1977; Salemaa, 2004)).The factors that may affect the fate of atmospheric metal deposition in the receiving plant - soil systems include particle size, solubility, distance of the receiving system from the metal source, and acidity of rainfall (Ross 1994a; Salemaa, 2004).

5.5.4 Translocation of metals in cereal crops at the selected growth stages

The TF values varied among the five metals investigated and the six selected growth stages used in this study, indicating selective translocation among the growth stages and the two varieties each of the wheat and maize used in the study.

The 15-days, 30-days and 60-days growth stages had the highest occurrences of the three factors than the other growth stages. They are the vegetative stages of the cereal developmental stages before the reproductive stage. The vegetative growth cycle is the growth of the plant biomass in preparation for flowering. It is the period of growth between germination and flowering where the plants are busy carrying out photosynthesis and accumulating resources that will be needed for flowering and reproduction.

On a general note, the high value of PUF, TC and TF for Zn, Cd, Cu and Pb suggest that these metals are anthopogenic in origin, for example, from the emissions of motor vehicles, which support the findings of Momani *et al*., 2000. Values of PUF, TF and TC greater than unity indicate anthropogenic source possibly vehicular emissions, while less than unity indicate natural source (Momani *et al*., 2000). A higher PUF and TC and high TF values shows that there is higher accumulation of the trace metals in the cereal crops, while a higher TC value for Pb indicates a higher transfer or translocation of Pb from the soil to the roots, and subsequently from the roots to the stems and leaves of the cereal crops (Davila *et al*., 2011). Although, *Zea mays everta* L. at SU 4 had the highest TC, *Zea mays everta* L. had the lowest PUF, TF and TC among all the sampling units, reflects the location of the site at a very far distance of 2438.28m from SU 1 and SU 3 and at a distance of 1945.23m from the highway which explains the lower values for all the three models.

5.5.3 Correlation analyses between PUF/TC/TF

The PUF and TF signify the ability of plant to accumulate trace metals (Lou, 2012, Kumi *et al.,* 2013). Also, Baker *et al.,* 1994, Brown *et al.,* 1994, Wei *et al.,* 2002 and Sasmaz *et al.,*2008 reported that crops absorbed and transported metals from the soil, and stored them in the aerial plant parts. However, in contrast to this research, the existence of a relationship between PUF and TF for Cr and Cu (SU 1and SU 2) indicates special ability of the crop (Pavon-76 and Siettecerros) to absorb and transport Cr and Cu from the polluted atmosphere as well as storing them in the aerial plant parts resulting to higher levels.

The significant relationship between the TC/PUF for Zn and Cr in SU1, SU 3 and SU 4 suggests that the levels of Cr and Zn in *T. aestivum* var. Pavon -76, *Zea mays* L. and *Zea* *mays everta* L. came from both the atmosphere and the soil as earlier mentioned. The non – existence of a significant relationship between the TF and TC shows that a larger percentage of the stem trace metal levels in the two cultivars each of *Triticum aestivum* and *Zea mays* L. could be of atmospheric origin.

CHAPTER SIX

6.0. CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The highway induces contamination on the nearer environment by pollutant transfer via atmospheric fallouts.The trace metal input through anthropogenic activities increases the total contents of the metals, which may result in increase of potential environmental health risk.

The study of the metal concentrations and distributions in the soils and in the leaves, stems and roots at the selected growth stages for *Triticum aestivum* L. var. Pavon-76, siettecerros, *Zea mays* L. var. yellow maize and *Zea mays everta* L. var. popcorn which exceeded the allowable limits, revealed the following results:

1) Cd, Cr, Cu, Pb and Zn concentrations were found to be significant at both the experimental and control sites in the soils, even though higher at the experimental site than at the control sites. The concentration of Pb and Zn were even much higher than the other trace metals. This supports the fact that atmospheric pollutants from motor vehicle emissions is a major factor that contributed to the higher concentrations of the trace metals on both sites.

2) The trace metal concetrations in the different plant parts (leaf, stem and root) at the selected growth stages did not follow a regular pattern with variations among the cultivars. However, the general observations showed higher concentrations in the leaves and roots than in the stems, and at the experimental site than at the control. The concentration of the plant heavy metals was much higher than the soil heavy metals, before sowing and during growth of the four cereal crops.

3) From the results, the leaves and roots of the cereal crops as well as the soils were identified as the major routes of trace metals accumulation from atmospheric pollution.

4) The wheat variety (pavon-76) and maize variety (popcorn) have the potential of accumulating higher metal contents at the experimental and control sites respectively. The plant parts of these crops are considered unsuitable for consumption by livestock within the study area.

5) Also Cd, Cu, Pb and Zn except Cr had PUF greater than 1 and all the investigated heavy metals had a TF greater than 1 for pavon-76 and yellow Maize. Generally, the low TF observed in this study for the cereal crops investigated implies limited ability of heavy metal accumulation and translocation in the crops. The results of this study revealed high PUF for yellow maize and Pavon-76, high TC for popcorn and high PUF for Pb and low PUF and TC for Cr, Cd, Cu and Zn, and high TF proves the far-distance transport of pollutants which posed as a threat to food chain contamination.

6.2 Recommendation

1. Agricultural land use planning should go beyond soil fertility assessment, to integrate eco-toxicity study of the environment to achieve integrated sustainable agricultural practices and crop production, since it has been observed that atmospheric pollutants like Pb, Cd, Cu, Pb and Zn from vehicular emissions may result in higher than desired levels in the soils along the major highways.

2. Tree-planting programmes/projects should be used as shields and buffer zones to farmlands and to be conducted at some specific distances along major highways to minimize the effects of atmospheric pollutants in the soil and crops.A strategic intercropping and crop rotation techniques should also be developed to allow the use ofthe fast growing plants with high trace metals uptake ability and rapid biomass gainfirst before the use of slow accumulatorspecies. By this, accumulation of trace metals in both the soil and crops will be minimized and, will also break cycles of metal accumulation associated with continuous cropping.

3. Continuous monitoring and further studies of soil trace metal contents and edible plant parts in the cereal growing areas are recommended to ascertain long-term effects that may have not yet been reached. This will control the pollution problems of roadside soils and crops used for pasturage and arable farming.

4. Environmental scientists should intensify efforts to extend ecotoxicity studies to the entire ecological zones of Nigeria beyond the agronomy of agricultural crops, since higher plants are usually the first indicators of changes in the chemical and biological composition of natural ecosystems, where other indicators are absent. Suitable methodologies such as air pollution transport models can be developed to relate pollution to impacts, for use in risk assessment in Nigeria.

5. A National institutional frameworks to be established for monitoring and recording of pollutant concentrations in rural agricultural lands, rangelands and forested areas. Enactions of acceptable or permissible limits in accordance to world standards for the current Nigerian situation.

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APPENDIX I

Appendix I: Precision of Measurement Ranges for Elements (ppm) in IAEA-V10 (hay powder) and IAEA-359 (Cabbage)compared with Certified Values.

Metal	IAEA-V10 (Measured)	IAEA-V10 (Certified)	IAEA -359 (Measured)	IAEA-359 (Certified)
Cr	LOD	6.5± 1.5	LOD	1.30± 0.120
Mn	43± 12.0	47.0± 7	30± 3	31.9±1.200
Fe	152±14.0	186.0± 13	136±8	148.0±7.800
Ni	LOD	4.2± 1.1	LOD	1.05± 0.100
Cu	11±04.0	9.4± 0.9	6± 2	5.67± 0.360
Zn	22±04.0	24.0± 2	39± 3	38.6± 1.400
As	LOD	-	LOD	0.1±0.008
Cd	LOD	-	LOD	0.12± 0.022
Sb	LOD	0.009± 0.002	LOD	-
Pb	LOD	1.6± 1.100	LOD	-

APPENDIX II

Appendix IIa: Standard Atomic Absorption Conditions for Cd

Wavelength (mm)	Slit (mm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
228. 8	0. 7	1. 0	0. 028	1. 5	2. 0
326. 1	0. 7	0. 90	11. 0	500. 0	---

1. Recommended Flame: Air-acetylene, oxidizing (lean, blue)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 ´ Sensitivity improvement.
3.Characteristic Concentration with a N2O-C2H2 flame at 228.8 nm: 0.11 mg/L
4. Table contains HCL data. EDL sensitivity values are slightly (<10%) better.

Appendix IIb: Standard Atomic Absorption Conditions for Pb

Wavelength (mm)	Slit (mm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
283. 3	0. 7	0. 43	0. 45	20. 0	20. 0
217. 0	0. 7	1. 0	0. 19	9. 0	20. 0
205. 3	0. 7	1. 4	5. 4	250. 0	----
202. 2	0. 7	1. 8	7. 1	350. 0	----
261. 4	0. 7	0. 35	11. 0	500. 0	----
368. 3	0. 7	0. 40	27. 0	1200. 0	----
364. 0	0. 7	0. 33	67. 0	3000. 0	----

1. Recommended Flame: air-acetylene, oxidizing (lean, blue)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 □ sensitivity improvement.
3. Characteristic Concentration with a N2O-C2H2 flame at 283.3 nm: 2.7 mg/L
4.Table contains HCL data. EDL sensitivity values approximately the same.

APPENDIX III

Appendix IIIa: Soil Concentrations of Metals from the Literature ($mgkg^{-1}$)

ELEMENT	Cd	Cu	Pb	Zn	REFERENCE
World average Crust	0. 11	50	14	75	Bowen 1979
World average Crust	0. 16	68	13	76	Greenwood 1984
World average soil	0. 06	20	10	50	Bowen 1976

AppendixIIIb: Allowable Limits of Heavy Metal Concentrations in soil (mg/kg) of other countries

Heavy Metal	Austria	Germany	France	Luxembourg	Netherlands	Sweden	United Kingdom
Cd	1 to 2	1	2	1 to 3	0. 5	0. 4	3
Cr	100	60	150	100 to 200	30	60	400
Cu	60 to 100	40	100	50 to 140	40	40	135
Ni	50 to 70	50	50	30 to 75	15	30	75
Pb	100	70	100	50 to 300	40	40	300

Source: ECDGE (2010)

Appendix IIIc: Soil-plant transfer coefficient (TC) of several heavy metals (acc. to KLOKE *et al.*,1984; KORENTEJAR *et al.*,2001).
Values > 1indicate accumulations in the plant.

Element	Transfer Coefficient
Cd	1. 00 – 10. 00
Zn	1. 00 – 10. 00
Ni	0. 10 – 1. 00
Cu	0. 10 – 1. 00
Cr	0. 01 – 0. 10
Pb	0. 01 – 0. 10

APPENDIX IV

APPENDIX IVa:Analysis of Variance (ANOVA) for Cadmium in Pavon-76 at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	2452.78	1226.39	2.1526	NS
Growth Stages (G – 1)	5	14806.95	2916.39	5.1979	NS
Error (P-1)(G-1)	10	5697.22	569.72		

APPENDIX IVb:Analysis of Variance (ANOVA) for Chromium in Pavon-76 at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	0.55	0.27	0.1377	NS
Growth Stages (G – 1)	5	0.80	0.16	0.0816	NS
Error (P-1)(G-1)	10	19.60	1.96		

APPENDIX IVc:Analysis of Variance (ANOVA) for Copper in Pavon-76 at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	66.24	33.12	0.7434	NS
Growth Stages (G – 1)	5	641.19	128.23	2.8783	NS
Error (P-1)(G-1)	10	445.53	44.55		

Appendix IVd: Analysis of Variance (ANOVA) for Lead (Pb) in Pavon-76 at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	5200	2600	0.0447	NS
Growth Stages (G – 1)	5	934400	186880	3.2154	NS
Error (P-1)(G-1)	10	581200	58120		

Appendix IVe: Analysis of Variance (ANOVA) for Zinc in Pavon-76 at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN.(0.01%)
Plant Parts (P-1)	2	3802.19	1901.09	1.0034	NS
Growth Stages (G – 1)	5	95214.96	19042.99	10.0510	**
Error (P-1)(G-1)	10	18946.25	1894.62		

Appendix IVf: Analysis of Variance (ANOVA) for Cadmium in Yellow Maize at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	2211.12	1105.56	1.1944	NS
Growth Stages (G – 1)	5	6844.45	1368.89	1.4790	NS
Error (P-1)(G-1)	10	9255. 55	925.55		

Appendix IVg: Analysis of Variance (ANOVA) for Chromium in Yellow Maize at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	1.22	0.61	0.5648	NS
Growth Stages (G – 1)	5	35.78	7.15	6.6203	**
Error (P-1)(G-1)	10	10. 85	1.08		

Appendix IVh: Analysis of Variance (ANOVA) for Copper in Yellow Maize at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	377428.81	188714.40	8.5835	**
Growth Stages (G – 1)	5	104979.51	20995.90	0.9540	NS
Error (P-1)(G-1)	10	219855. 7	21985.5		

Appendix IVi: Analysis of Variance (ANOVA) for Lead (Pb) in Yellow Maize at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	2177.78	1088.89	0.0241	NS
Growth Stages (G – 1)	5	515311.11	103062.22	2.2817	NS
Error (P-1)(G-1)	10	451688. 89	45168.88		

Appendix IVj: Analysis of Variance (ANOVA) for Zinc in Yellow Maize at Doruwa Salau (close proximity to the Kano-Zaria Highway) (Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	250.99	125.49	0.1753	NS
Growth Stages (G – 1)	5	41624.13	8324.82	11.6304	**
Error (P-1)(G-1)	10	7157. 89	715.78		

Appendix IVk: Analysis of Variance (ANOVA) for Cadmium in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	808.33	404.16	0.2871	NS
Growth Stages (G – 1)	5	10029.16	2005.83	1.4251	NS
Error (P-1)(G-1)	10	14075.01	1407.50		

Appendix IVl: Analysis of Variance (ANOVA) for Chromium in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	0.32	0.16	0.4848	NS
Growth Stages (G – 1)	5	6.57	1.31	6.9696	**
Error (P-1)(G-1)	10	3.38	0.33		

Appendix IVm: Analysis of Variance (ANOVA) for Copper in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	436.43	218.21	2.1062	NS
Growth Stages (G – 1)	5	463.77	92.75	0.8952	NS
Error (P-1)(G-1)	10	1036.09	103.60		

Appendix IVn: Analysis of Variance (ANOVA) for Lead (Pb) in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	408933.33	204466.66	8.4770	**
Growth Stages (G – 1)	5	326866.66	65373.33	2.7103	NS
Error (P-1)(G-1)	10	241200.01	24120.00		

Appendix IVo: Analysis of Variance (ANOVA) for Zinc in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	10095.24	5047.62	2.1906	NS
Growth Stages (G – 1)	5	46578.13	9315.62	4.0429	NS
Error (P-1)(G-1)	10	23041.45	2304.14		

Appendix IVp: Analysis of Variance (ANOVA) for Cadmium in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	386.711	193.05	0.1936	NS
Growth Stages (G – 1)	5	4206.95	841.39	0.8444	NS
Error (P-1)(G-1)	10	9963.94	996.39		

Appendix IVq: Analysis of Variance (ANOVA) for Chromium in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	1.03	0.51	0.8306	NS
Growth Stages (G – 1)	5	25.43	5.08	8.1935	**
Error (P-1)(G-1)	10	6.23	0.62		

Appendix IVr: Analysis of Variance (ANOVA) for Copper in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	700.34	350.17	1.9463	NS
Growth Stages (G – 1)	5	1684.65	336.93	1.8727	NS
Error (P-1)(G-1)	10	1799.19	179.91		

Appendix IVs: Analysis of Variance (ANOVA) for Lead (Pb) in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	29377.78	14688.89	0.4732	NS
Growth Stages (G – 1)	5	432444.44	86488.88	2.7876	NS
Error (P-1)(G-1)	10	310355.56	31035.55		

Appendix IVt: Analysis of Variance (ANOVA) for Zinc in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	17463.47	8731.73	1.8009	NS
Growth Stages (G – 1)	5	195643.58	39128.71	8.0702	**
Error (P-1)(G-1)	10	48485.14	4848.51		

APPENDIX V

AppendixVa: Analysis of Variance (ANOVA) for Leaf Trace Metals in Pavon-76 at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	32805.75	16402.88	2.2491	NS
Growth Stages (G – 1)	5	285604.94	57120.99	7.8322	**
Error (r-1)(G-1)	10	72930.4	7293.04		

Appendix Vb: Analysis of Variance (ANOVA) for Stem Trace Metals in Pavon-76 at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN.(0.01 %)
Replication (r-1)	2	17039.54	8519.77	0.6868	NS
Growth Stages (G – 1)	5	84329.75	16865.95	1.3598	NS
Error (r-1)(G-1)	10	124032.38	12403.24		

Appendix Vc: Analysis of Variance (ANOVA) for RootTrace Metals in Pavon-76 at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	2874.16	1437.08	0.0739	NS
Growth Stages (G – 1)	5	123711.11	24742.22	1.7277	NS
Error (r-1)(G-1)	10	194396.15	19439.62		

Appendix Vd: Analysis of Variance (ANOVA) for SoilTrace Metals in Pavon-76 at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	1	3790.34	3790.34	0.0089	NS
Growth Stages (G – 1)	5	2385190.85	477038.17	1.1207	NS
Error (r-1)(G-1)	5	2128144.62	425628.92		

Appendix Ve: Analysis of Variance (ANOVA) for LeafTrace Metals in Yellow Maize at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	4497.14	2248.57	0.3491	NS
Growth Stages (G – 1)	5	114833.89	22966.78	3.5660	NS
Error (r-1)(G-1)	10	64404.62	6440.46		

Appendix Vf: Analysis of Variance (ANOVA) for Stem Trace Metals in Yellow Maize at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	9227.13	4613.57	0.2716	NS
Growth Stages (G – 1)	5	67433.55	13486.71	0.7939	NS
Error (r-1)(G-1)	10	169860.62	16986.06		

Appendix Vg: Analysis of Variance (ANOVA) for Root Trace Metals in Yellow Maize at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	16591.88	8295.94	0.5348	NS
Growth Stages (G – 1)	5	66462.03	13292.41	0.8570	NS
Error (r-1)(G-1)	10	155100.24	15510.02		

Appendix Vh: Analysis of Variance (ANOVA) for SoilTrace Metals in Yellow Maizeat Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	1	0.38315	0.38315	0.0000	NS
Growth Stages (G – 1)	5	136004.34	27200.86	1.3192	NS
Error (r-1)(G-1)	5	103089.72	20617.95		

Appendix Vi: Analysis of Variance (ANOVA) for LeafTrace Metals in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	21447.45	10723.73	1.4085	NS
Growth Stages (G – 1)	5	21710.74	4342.15	0.5703	NS
Error (r-1)(G-1)	10	76130.8	7613.08		

Appendix Vj: Analysis of Variance (ANOVA) for StemTrace Metals in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	34504.30	17252.15	1.0727	NS
Growth Stages (G – 1)	5	224529.69	44905.94	2.7921	NS
Error (r-1)(G-1)	10	160828.96	16082.89		

Appendix Vk: Analysis of Variance (ANOVA) for RootTrace Metals in Popcorn at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	14192.60	7096.3	1.1087	NS
Growth Stages (G – 1)	5	168925.65	33785.13	5.2786	NS
Error (r-1)(G-1)	10	64003.74	6400.37		

Appendix Vl: Analysis of Variance (ANOVA) for SoilTrace Metals in Popcornat the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	1	10451.26	10451.26	1.5196	NS
Growth Stages (G – 1)	5	99422.57	19884.51	2.8913	NS
Error (r-1)(G-1)	5	34385.96	6877.19		

Appendix Vm: Analysis of Variance (ANOVA) for LeafTrace Metals in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	93111.34	46555.67	3.1943	NS
Growth Stages (G – 1)	5	47412.45	9482.49	0.6506	NS
Error (r-1)(G-1)	10	145743.36	14574.34		

Appendix Vn: Analysis of Variance (ANOVA) for Stem Trace Metals in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	21537.22	10768.61	1.9342	NS
Growth Stages (G – 1)	5	71455.22	14291.04	2.5669	NS
Error (r-1)(G-1)	10	55673.48	5567.35		

Appendix Vo: Analysis of Variance (ANOVA) for Root Trace Metals in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	2	755957.52	377978.76	5.4382	NS
Growth Stages (G – 1)	5	40337.27	8067.45	0.1160	NS
Error (r-1)(G-1)	10	695037.98	69503.79		

Appendix Vp: Analysis of Variance (ANOVA) for Soil Trace Metals in Siettecerros at the IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Replication (r-1)	1	41741.32	41741.32	0.6352	NS
Growth Stages (G – 1)	5	427044.35	85408.87	1.3081	NS
Error (r-1)(G-1)	5	326439.97	65287.99		

APPENDIX VI

Appendix VIa: Combined Analysis of Variance (ANOVA) for Trace Metals in the three Plant Parts of Pavon-76 at Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	8256.73	4128.37	0.3164	NS
Replication within Plant Parts P(r-1)	6	52719.45	8786.58	0.6735	NS
Treatment (Growth Stages) (G-1)	5	284911.33	56982.27	4.3680	* *
P X G interaction (P-1)(G-1)	10	209004.82	20900.48	1.6021	NS
Error [P(r-1)(G-1)]	30	391358.93	13045.29		

Appendix VIb: Combined Analysis of Variance (ANOVA) for Trace Metals in the three Plant Parts of Yellow Maizeat Doruwa Salau(Experimental Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	5141.42	2570.71	0.1980	NS
Replication within Plant Parts P(r-1)	6	30316.15	5052.69	0.3893	NS
Treatment (Growth Stages) (G-1)	5	89745.26	17949.05	1.3829	NS
P X G interaction (P-1)(G-1)	10	158984.21	15898.42	1.2249	NS
Error [P(r-1)(G-1)]	30	389365.48	12978.85		

Appendix VIc: Combined Analysis of Variance (ANOVA) for Trace Metals in the three Plant Parts of Siettecerros on IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	137316.58	68658.29	2.2976	NS
Replication within Plant Parts P(r-1)	6	870606.08	145101.01	4.8558	* *
Treatment (Growth Stages) (G-1)	5	111783.16	22356.63	0.7481	NS
P X G interaction (P-1)(G-1)	10	47421.79	4742.18	0.1586	NS
Error [P(r-1)(G-1)]	30	896454.82	29881.83		

Appendix VId: Combined Analysis of Variance (ANOVA) for Trace Metals in the three Plant Parts of Popcorn On IRS (Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Plant Parts (P-1)	2	18409.99	9204.99	0.9175	NS
Replication within Plant Parts P(r-1)	6	70144.35	11690.73	1.1653	NS
Treatment (Growth Stages) (G-1)	5	272191.38	54438.28	5.4263	* *
P X G interaction (P-1)(G-1)	10	142974.69	14297.47	1.4251	NS
Error [P(r-1)(G-1)]	30	300963.5	10032.12		

Appendix VIe: Combined Analysis of Variance (ANOVA) for Crop or Variety Trace Metals on the four Sampling Unitsat Doruwa Salau and IRS (Experimental and Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Sampling Units (Su-1)	3	15566.7	5188.9	0.5076	NS
Replication within Samplig Units [Su(r-1)]	8	328356.43	41044.55	4.0158	* *
Treatment (Growth Stages) (G-1)	5	2238500.98	447700.19	43.8031	* *
R x G x Su interaction (R-1)(G-1)(Su-1)	30	679523.29	22650.78	2.2161	* *
Error C(r-1)(G-1)	120	1226488.83	10220.74		

Appendix VIf: Combined Analysis of Variance (ANOVA) for Soil Trace Metals on the four Sampling Unitsat Doruwa Salau and IRS (Experimental and Control Site)

SOURCE OF VARIATION	DF	SS	MS	F-RATIO	SIGN. (0.01%)
Sampling Units (Su-1)	3	177521.99	59173.99	0.4565	NS
Replication within Samplig Units [Su(r-1)]	4	55983.30	13995.82	0.1079	NS
Treatment (Growth Stages) (G-1)	5	3047662.11	609532.42	4.7030	**
R x G x Su interaction (R-1)(G-1)(Su-1)	15	622856.35	41523.75	0.3203	NS
Error Su(r-1)(G-1)	20	2592060.27	129603.01		