THE EFFECT OF VARYING METAL ION CONCENTRATION IN SOIL ON ACCUMULATION OF THE IONS IN PARTS OF SOME VEGETABLES

BY

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DECLARATION

I hereby declare that the work in this thesis entitled “The effects of varying metal ion concentration in soil on accumulation of the ions in parts of some vegetables” has been performed by me in the Department of Chemistry under the supervision of Dr. V. O. Ajibola and Prof. (Mrs.) Agbaji. The information derived from the published works of others has been dully acknowledged in the text and referred to accordingly in the list of references. No part of this thesis was previously presented for another degree in the University.

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CERTIFICATION

This thesis entitled, “The effects of varying metal ion concentration in soil on accumulation of the ions in parts of some vegetables” by **Musa Haliru (M.Sc/Sci/34110/02-03)** meets the regulations governing the award of the degree of Master of Science (M.Sc) in Analytical Chemistry of Ahmadu Bello University, Zaria and is approved for its contribution to literary presentation.

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DEDICATION

I dedicate this project work to Mr. A Musa Ciwar and Family and those that encourage and cherish the progress of humanity.

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ABSTRACT

The uptake and accumulation of lead, nickel, cadmium, chromium and arsenic in the root, stem leaves and fruits of okra (*Ablmoschus esculentus*) and pepper (*Capsicum annum*), and the leaves and root of lettuce (*Lactuca sativa*) at different metal concentrations in the soil was studied. The physio-chemical properties of the soil indicate: total nitrogen as 0.21%, organic matter 3.32%, cation exchange capacity (CEC) was 17.20 mol/kg, clay 20%, silt 46% and sand 34%. The soil pH was weakly acidic and the textural class was loam. The result obtained for uptake and accumulation showed that different plants had different preferences for each metal at the concentration used. The variation in the concentration of applied metal ion increased.

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CHAPTER ONE

1.0 INTRODUCTION

High heavy metals' contamination of soils is one of the major environmental problems. Increasing industrial pollution, urban activities, and agricultural practice lead to a build-up of toxic levels of cadmium, copper, lead, zinc, nickel (Dudka *et al,* 1996). When accumulated in excess in plant tissues, these metals cause alterations in various vital growth processes such as mineral, nutrition, transpiration, photosynthesis, enzyme activities related to metabolism and biosynthesis of chlorophyll and nucleic acids (Doncheva et *al,* 1996).

Plants and animals need specific elements for them to grow and function properly. At least 16 elements are essential for healthy growth and development of higher plants (Wild, 1988). Carbon, hydrogen and oxygen are derived from air and water while the other elements are supplied by the soil, and enter the roots. These include trace elements, which are essential to plants but may be required by animals (Brian, 1964, Jones and Clement, 1973).

Chromium availability in the soil depends on several soil conditions, such as pH, or redox potential (Bartlett and Kimble, 1976). The solubility of chromium and other metal salts can be increased or decreased depending on the presence of other elements in the soil/plant system (Smith and Demchak, 1987). When chromium is in the soil solution, it can be taken up by roots and accumulated and distributed within the plant. This fact may lead to interactions

between chromium and other essential elements, which can have a significant effect on the nutrient concentration and distribution in the plant as well as modifying some physiological processes affecting plant morphology.

It has been reported that plant grown in sludge-treated soils take up heavy metals (Bojakowska and Kochary, 1985; Adeniyi, 1996). These toxic metals taken up by plant roots and passed to stems and leaves, which are eventually consumed by animals and humans. The amount of these metals present in the different parts of a plant may depend on the amount present in the soil and the processes involved in transporting these metals from the root to the stem and fruits are controlled by the plant. For example Crump *et al*, (1980) studied seasonal variations in the lead levels of a pasture grass growing near a motorway, and found that there was a large reduction in the concentration of lead in the grass during spring. This was thought to be due to the rapid spring growth of the grass causing dilution.

1.1.0 DESCRIPTION OF THE SPECIES

Lettuce, okra and pepper belong to the class of leafy vegetables. They can be described as plants, which provide a source of food often low in calories and dry matter contents. They are consumed in addition to a starchy basic food in order to make it more palatable. Vegetables add protective nutrients especially vitamins and minerals to the diet. They also make several contributions to the tropical diets, which include:

(a) They improve digestion.

(b) They sometimes have a curative action (Gruben and Denton, 2004).

1.1.1 ORIGIN OF PEPPER (*Capsicum annuum*)

The genus capsicum originated in central and south America. The approximately 25 wild species all occur in this area. Mexico was probably the centre of origin of the sweet pepper *(Capsicum annuum).*

The aromatic hot pepper was probably introduced into West African during a later period than the chilli and bird pepper, and Africa slaves brought it back from West Africa to the Caribbean and West Indies.

1.1.2 GROWTH, DEVELOPMENT AND ECOLOGY

Seeds germinate 6-21 days after sowing. Continuous flowering starts 60-90 days after sowing. Flowers open three hours after sun rise and remain open for 1-3 days. Optimal temperatures for growth and production are between 18°C and 30°C. Seeds germinate best at 25-30°C.

Capsicum grows on almost all soil types but is most suited to well drained sandy or loamy soils, rich in lime, with a pH of 5.5 - 6.8 and a high water retention capacity.

Fruits begin to mature 4-5 weeks after flowering, and can be picked every 5-7 days. The peak harvest period is 4-7 months after sowing. In the absence of frost and diseases growth continues and plants may be become perennial.

1.1.3 USES OF CAPSICUM

1. Capsicum fruits are consumed in fresh dried or processed form. Non-pungent fruits, usually called sweet pepper, are eaten raw in salads, but more commonly cooked, fried or processed together with other foods.
2. The red pigment extracted from ripe fruits is used as a natural colouring agent for food and cosmetics.
3. It is widely used in local medicine. Pungent pepper cause strong salivation, aid digestion and are laxative. Capsacin, the active ingredient, stimulates the mucous membrane of the mouth, stomach and bowels causing strong peristalsis.
4. It is said that regular consumption is beneficial for vascular conditions and against haemorrrhoids, varicose veins, anorexia and liver congestion.
5. The leaves are used as a dressing for wounds and sores, and the leaf sap is squeezed into the eyes against headache (Ghana, Congo). Gruben and Tahir (2004). The leaves are prepared as a portion to treat cough and heart pain.
6. In Guinea a mixture including red pepper powder is used as a traditional insecticide to control kola weevil.
7. In recent years hot pepper is increasingly used in aerosol sprays replacing tear gas for crowd dispersal, police officials.

1.1.4 ORIGIN OF OKRA *(Abelmoschus esculentus)*

Origin and distribution: The genus *Abelmoschus* originated in south-east Asia. However, the cultigens are of uncertain origin. It is widely spread in tropical, subtropical and warm temperate regions, but is particularly popular in West Africa, India, Philippines e.t.c.

1.1.5 GROWTH DEVELOPMENT AND ECOLOGY OF SPECIES

Seeds germinate 5-10 days after sowing. Continuous flowering starts within 45-80 days. *Abelmoschus esculentus* needs temperatures above 20°C for normal growth and development. Germination percentage and speed of emergence are optimal at 30-35°C.

Common okra tolerates a wide variety of soils but prefers well drained sandy loams, with pH 6-7 and a high content of organic matter. For vegetable use the fruits are picked about one week after anthesis. The regular removal of young fruits permits sustained vegetative growth and flowering, prolonging the productive period. In a seed crop, it takes about one month from anthesis to fruit maturity.

Uses of *Abelmuschus esculentus*

1. Young immature fruits are important vegetable, consumed cooked or fried. In West Africa they are usually boiled in water to make slimy soaps and sauces

(2) Okra mucilage is suitable for medicinal and industrial applications. It

has been used as a plasma replacement or blood volume expander.

(3) Okra mucilage has been added as a size to glaze paper and is used in confectionery.

(4) The bark fibre has been locally used for fish lines and game traps. It is suitable for spinning into rope and for paper and cardboard manufacture.

(5) Roasted okra seeds are used in some areas as a substitute for coffee.

(6) The leaves are sometimes used as cattle feed.

1.1.6 ORIGIN OP LETTUCE *(Lactuca sativa)*

The origin of lettuce is in Turkey or the Middle East. Lettuce was known as a vegetable in the Mediterranean as early as 450 BC. At present lettuce is the world's most important salad crop. Lettuce is important in Africa as an exotic.

1.1.7 GROWTH, DEVELOPMENT AND ECOLOGY OF SPECIES (LETTUCE)

The seeds germinate within l-4days, at temperatures from 15-25°C. Growth of young lettuce plants is exponential, slow in the beginning and very vast in the last weeks before the harvest stage. The head is fully formed and ready for harvesting about two months after sowing. Plants start bolting within 2-3 months old. Lettuce grows best at moderate day temperature of 15-20°C. Lettuce is often grown on neutral sandy-loamy soils with pH 6.5-7.2. It does not tolerate acid soils (pH <5.5). In temperate countries, lettuce is partially grown in green houses.

1.1. 8 USES

Lettuce is grown for its leaves, which are usually eaten raw as a salad with a dressing of oil vinegar. Occasionally lettuce is used as a cooked vegetable, especially in low land areas. In China, a form of lettuce with a thickened stem is eaten as a cooked vegetable.

1.2 STATEMENT OF THE PROBLEM

The trace metals under investigation have been generally adjudged to be toxic to human and animals if taken in high concentrations. Vegetables take up and accumulate these metals in different concentrations depending on the concentration of the metals in the soil. These plants also accumulate these metals to a different extent in the roots, stem, leaf and fruits.

1.3 AIM AND OBJECTIVES OF THE STUDY

This study was conducted to:

1. Determine the uptake of lead, nickel, cadmium, chromium and arsenic by lettuce, okra and pepper at different concentrations in the soil.
2. To determine the distribution/accumulation of these metals in the different parts of the plants.

1.4 JUSTIFICATION FOR THE STUDY

The uptake of some of the metals lead, nickel, cadmium, chromium and arsenic in various concentrations by these vegetable plants is a source of concern, because high concentration of these metals in these vegetables plants could affect human beings, who depend on it as their source of essential minerals, vitamins and dietary fibre.

CHAPTER TWO

LITERATURE REVIEW

2.0 UPTAKE OF METALS BY PLANTS

Trace elements such as Cd, Cu, Ni, Pb and Zn are common pollutants in urban industrial soils (Dudka *et al,* 1996). These elements are often adsorbed or occluded by carbonates, organic matters, Fe-Mn oxides and primary or secondary minerals (Adriano, 1986; Ross, 1994). Since plants take up most nutrients from the soil solution, it is often assumed that the dissolved trace metals are readily available to organisms (Barber, 1984). Thus, determination of total dissolved metals and their chemical speciation may provide useful information on metal bioavailability and toxicity (Knight *et al,* 1998).

Trace metals are distributed in the soil solution as free ions (M^{n+}) in form of inorganic and organic complexes. It is generally accepted that, in the short term, plant growth and metal uptake are related to free ion activities (Sparks 1983, Me Bride 1994). In experiments conducted using soil or nutrient solution, the free ion model was able to predict metal uptake by plants (Pavan *et al* 1982; Bell *et al* 1991).

Several studies have shown that constructed wetlands are very effective in removing heavy metals from polluted waste waters (Larsen and Schierup, 1981; Nixon and Lee, 1986; Hansen *et al,* 1998).

Wetland vegetation plays a major role in the removal of toxic trace elements from waters passing through the wetland. Wetland plants remove trace elements by several processes.

(i) Uptake and accumulation in their tissues.

(ii) Phystostabilization of the element into unavailable form; and

(iii) Phytostimulation of hizosphere micro-organisms that mineralize, sequester and stabilize the elements (e.g. Se, Hg) into the atmosphere (Terry and Zayed, 1994; Rugh *et al,* 1996; Berti and Cunningham 1997).

Different wetland plants species differ however, in their abilities to take up and accumulate various trace elements in their tissues (Rai *et al,* 1995). Different plant species can have varying abilities to take up trace metals (Martin *et al,* 1996). Since some plants transfer more metals to foliage than others, the effects of bioavailability of metals could not be ascertained. More recently, Falih (1998a) reported that Cd and Pb were accumulated in bio mass of Rhodotorula minute in amounts between 4 and 5mg/g dry weight at a metal initial concentration of 400mg/l in the medium.

According to Zayed *et al,* (1998), cauliflower, collard etc accumulated Cr mostly in the roots, with concentration exceeding 160 mg/kg Dw. Application of high cadmium content in corn leaves from 0.5 to 20 mg/kg Dw. (Jones *et al,* 1975).

Leafy vegetables such as lettuce, spinach, beet greens as well as

tobacco were found to contain high cadmium levels (Dowdy and Larson, 1975; Charney and Honrich, (1978). The source of lead found in some plants is mostly from the soil (De Dolp *et al,* 1970) and it is absorbed through the roots of the plants. Half of the lead found in rye grass and radish leaves originated from the soil. Distribution of lead within the plant is variable with plant species.

Motto *et al* (1970) observed that the lead occurring in plants was more concentrated in the roots and leaves than in the fruits, gratins or tubers. Also, the concentration of lead in the leaves increased as the soil concentration of the elements increases (Motto *et al,* 1970).

Twelve leafy vegetables were planted on field plots and were treated with 356 mgkg-' Zn per acre and control (normal water). The results showed that of the crops grown, only Swiss orchards and spinach had tendency to accumulate zinc. The concentrations of zinc in Swiss orchard and spinach were 80 mg/kg and 139 mg/kg respectively in the control plants, while in the zinc treated plots (436 mg/kg Zn acre), the zinc concentrations in Swiss orchard and spinach were 862 mg/kg and 340 mg/kg respectively. (Boawn, 1971).

Analysis for Cd, Cu, Mn, Ni and Zn were carried out at different field conditions by Devries and Tiller (1978) who concluded that sludge application brought about a sharp increase of the concentration of the metals in the plant materials.

Corn irrigated with municipal sewage effluent at application rate of 7.5cm^3/week was found to accumulate Cu, Zn, Cd and Pb more than the control experiment, (Sidle *et al*, 1976). Vegetable crops were grown on sandy soils treated with sludge from still water in Minnesota at application rate of 450 mg/kg. The report show that in the corn area, the concentration of trace elements in corn leaves were 9 mg/kg for boron, 1.32 mg/kg for cadmium, 77 mg/kg for manganese, 4 mg/kg for lead and 293 mg/kg for zinc. The trace elements concentrations in the corn grains were 3 mg/kg for boron, 0.05 mg/kg for cadmium, 9 mg/kg for manganese, less than 0.2 mg/kg for lead and 65 mg/kg for zinc (Dowdy and Larson, 1975). Similar observations were made by Hinesly *et al* (1972) when corn was grown on silty loamy soil treated with sludge fro Chicago at application rate of 70 mg/kg. The corn leaf indicated trace elements concentrations of 43.6 mg/kg boron, 11.6 mg/kg Cd, 116 mg/kg, Mn, 6.3 mg/kg Pb and 212 mg/kg Zn. The corn grain showed 6.6 mg/kg B, 1.03 mg/kg Cd, 18.3 mg/kg Mn, 0.03 mg/kg Pb and *152* mg/kg Zn (Motto *et al*., 1970)

Also, corn grown on a silty clay soil sludge disposal field in Dayton Ontario at a sludge application rate of 980 mg/kg, the concentration of some trace elements (Cd, Mn, Pb and Zn) in the roots, were 448.7 mg/kg Cd, 467 mg/kg Mn, 542 mg/kg Pb, and 1350 mg/kg Zn (Motto *et al*., 1970).

In stems, the concentration of 13.9 mg/kg Cd, 99 mg/kg Mn, 11 mg/kg Pb and 196 mg/kg Zn. Finally, the concentration in the corn train were 0.9

mg/kg Cd, 5 mg/kg Mn less than 5 mg/kg and 79 mg/kg Zn (Kirkcham, 1975).

2.1 VARIATION IN TRACE ELEMENT UPTAKE AND ACCUMULATION IN PLANT TISSUES

2.1.1 CADMIUM (Cd)

Floating plants water hyacinth and duckweed are very good accumulators of Cd. They accumulated up to 6 and 13 g/kg Dw, respectively, when supplied with 10 mg/l (Zayed *et al* 1998a; Zhu *et al,* 1999). These same species were also found to accumulate Cd ion in a different work (Muramoto *et al.*, 1989; Huebert and Shary, 1993).

2.1.2 NICKEL (Ni)

High Ni concentrations have been found in roots of parrot's feather and water, however, Ni concentrations in both roots and shoots of smartweed were found to be much higher in these wetland plant species (Sela and Garty, 1989; Srivastav *et al,*1994). Duckweed was reported to accumulate Ni to high levels (Jain *et al,* 1990; Sharrna and Gaur, 1995; Zayed *et al,* 1998a). Some wetland plant species, however, show low Ni accumulation, for example, cattail had low root and shoot concentrations (Taylor and Crowder, 1983; Leeeta,1981).

2.1.3 CHROMIUM (Cr)

Chromium was analyzed in different parts of Smartweed and the results showed that the highest concentration was observed in the plant roots and least in plant shoots. (Sinha *et al,* 1993). Chromium has also been found to concentrate in shoots of water (Zayed *et al,* 1998a: Zhu *et al,* 1991). High concentrations of Cr accumulation by wetland plant species such as, bacopa and bulrush plants supplied with 5 mg/dm^3 Cr in solution culture (Sinha *et al,* 1993; Gupta *et al,* 1994). Like Cu and Ni, floating submerged plant species were more efficient than rooted emergent species in accumulating Cr from contaminated waters. (Srivastav *et al,* 1994; Jana 1988; Viapayel *et al,* 1995).

2.1.3 LEAD (Pb)

Lead uptake and accumulation by most wetland plant species (e.g. *Potamogeton crispus* L.P., *Perfoliatus bennett, Myriophythum alterniforum, Lithorellla uniflora* (L.), *Salicornia virginical,* etc have been found not to exceed 40-fold the external Pb supply level (Welsh and Deny, 1980; Chigbo *et al*., 1982; Galleaher and Kibby, 1980).

Several floating wetland plant species however, were shown to accumulate appreciable amounts of Pb, for instance, water hyacinth treated with 8 mg dm^3 Pb (Muramoto and Oki, 1983). Giant duckweed *(Lem.rn.na polyriza* L.) accumulated high concentration of Pb (on whole plant tissue basis) when supplied with l0mg/dm^3 Pb in solution culture (Sharma and Gaur, 1995)

and water velvet accumulated higher concentration of Pb after 14 days of exposure (Jain *et al.*, 1990). Monkey flower, sedge, smooth cord grass, Iris - leaved rush, and mares tail were found to be the least accumulators of Pb in the same study.

2.1.4 ARSENIC (As)

Water lettuce was found to be a poor accumulator of As it accumulated 44mg As kg^{-1} in shoot tissues when exposed to l0 mg/kg in solution culture (Zhu *et al,* 1999). Higher levels of As accumulation in plant tissues (200 to 500mg/kg DW As) have been previously reported for several submerged and floating aquatic species growing in pond water containing 4 to 46 ug/dm^3 As including water lettuce, *Nettlia* Sp., water gentian *(Nymphoides Indica* (L.) Kuntze), bladder wort (*Ultri cullria* Sp). Hydrilla, Muskgrass (*Chara* Sp) and water spinach *(Ipomoea aquotica* Forsk) (Lee *et al.,*1991). Similarly submerged species of *Potamogeton pectinatus* L. exposed to As in contaminated gold mine effluent accumulated much more As (5000 mg/kg As) than emergent species (e.g. *Typha latifolia* accumulated 41mg/kg and 98mg/kg in shoots and roots respectively (Dushenko *et al.,* 1995). Submerged and floating aquatic species differ markedly from rooted emergent species in that their foliage is exposed to the surrounding water. Leaf uptake of trace elements from water may be a significant path way in submerged and floating species and may account for the higher As levels detected in these species. In

the current study, however, only plant roots were in contact with the nutrient solution and no element uptake occurred through leaf tissues.

2.2 FACTORS AFFECTING THE UPTAKE OF TRACE ELEMENTS

Any factor that affects the availability of trace elements in the soil also affects the accumulation in plants. The soil pH affects the availability of trace elements in plants. Increased soil pH commonly reduces the uptake of trace elements (Davies, 1980). According to Chaney (1973) the trace elements are much more available at soil pH of below 6.5 - 7.0. Zimdhal and John (1974) reported on the influence pH on uptake of lead by some plant roots treated with lead nitrate solution at concentration of l0 ug/ml. They concluded that the lead uptake was reduced as the solution approached pH 7.0 in Soya bean and field bean.

However, uptake by barley and radish remained nearly constant. Lagewatt *et al,* (1973) reported a similar effect of pH for maize except that the suppressive effect of pH on lead accumulation in the *maize* plant was relatively minor or absent at higher soil lead concentration.

Organic matter may lower the susceptibility of plants to injury. This action is enhanced by the formation of chelate of trace elements, which protects the roots of the plant from severe injury, and stunting (Chaney, 1973).

The reports of Mortvedt and Giodarno (1975) and of Cunningham *et al,* (1975) established that trace elements added to sludge in the form of inorganic

salts or trace elements in sludges are taken up less readily than are trace elements added directly to soil in the same concentrations as was present in the sludges.

Haghiri (1974) determined the effects of added organic matter on the cadmium concentrations in Oat shoots and on the exchangeable cadmium in soil. He observed that neither cadmium concentrations in oat hoots nor soil exchangeable cadmium was significantly affected by the addition of organic matter. He concluded that the retaining power of organic matter for cadmium was predominantly through its cation exchange capacity property rather than chelating ability. The cation exchange capacity of soil to some extent affects the uptake of trace elements by plants.

Korte *et al*. (1975) found that the cation exchange capacity is unimportant in predicting the quantity of trace elements leached from soil. However, Singh (1974) determined the effect of cation exchange capacity of soil on the uptake of cadmium by adding a constant amount of cadmium at five cation exchange capacity levels. The cadmium concentrations in oat shoots were decreased by increasing the cation exchange capacity of the soil.

The species and varieties of plants differ greatly in toxic metal accumulations. Peterson (1977) studied cadmium uptake between crop species and varieties. His experimental results showed that cadmium uptake by several barley varieties, cultivated in Sweden, and were not significantly different statistically. However, data reported by the Council of Agricultural

Science Technology (CAST 1980) showed the contrary.

Also, John and Van Laerhoven (1976) found significantly different levels of cadmium accumulation in nine varieties of lettuce grown by sand culture, with cadmium concentrations of the nutrient solution ranging from 0.10 to 50ug/l.

The uptake of some elements by plants is also controlled by synergistic and antagonistic interaction with other elements. Mitchell *et al,* (1978) and Bingham *et al,* (1975) studied the interactive effects of Cd, Cu, Ni and Zn on phytotoxicity to lettuce when sludge, spiked with the salts of the metals, was added to the soils. All these metals according to these authors may interact both synergistically and antagonistically in affecting the yield of lettuce. They concluded that generally, the elements interacted synergistically to reduce yield. Root *et al,* (1975) have also reported an interaction between zinc and cadmium in solution culture. As cadmium concentrations of maize leaves and roots increased, that of zinc decreased. In the same experiment and contrary to the results of John (1976), iron concentration in leaves and roots of maize plant increased as that of cadmium increased. It was concluded that cadmium reduced the uptake of zinc and that this in turn caused an increase in the uptake of iron. Chancy (1973) observed a lower at pH 5.5 -6.6 than at pH 6.5 - pH 7.0. He suggested that this observation was due to the presence of other toxic metals, which can interfere with zinc transport.

2.3 TRACE ELEMENTS AND HUMAN HEALTH

As a result of waste water re-use in irrigation, men and animals are being increasingly subjected to exposure to toxic chemicals including heavy metals. When these chemicals are absorbed in large amounts, severe toxic effects upon the consumers can result unless effective control measures are introduced and maintained.

It has been well established that certain elements such as cadmium, lead, manganese, zinc and boron present in trace concentrations in human tissues are essential to health, while others have no apparent physiological functions (Harry, 1974). Elements in either category may be extremely toxic at unnaturally high concentrations (Maugh, 1973). Individual responses to given exposure may vary significantly from person to person. So a designation of a tolerable level of exposure is frequently difficult (Maugh, 1973).

Cadmium is toxic to virtually every system in the body whether ingested, injected or inhaled. According to Underwood (1979) pathological changes have been observed in the kidneys, liver, gastro intestinal tract, heart, testes, pancreas and bones of man and animals affected with chronic cadmium toxicity.

Chronic lead poisoning is characterized by neurological defects, kidney dysfunction and anaemia. Damage to the brain and central nervous system is a marked feature in children, and includes behavioural problems,

intellectual impairment and hyperactivity (David, 1974).

Manganese toxicity in man arising from excessive intakes in food plants has never been reported, except where industrial contamination occurs (Underwood, 1979). Manganese poisoning is characterized by a severe psychiatric disorder resembling schizophrenia, followed by a permanently crippling neurological disorder (Underwood, 1979).

Zinc is relatively non-toxic to mammals. Underwood (1979) observed that men exhibit considerable tolerance to high zinc intakes. According to him the relatively low toxicity of zinc among the divalent cations, coupled with efficient homeostatic control mechanisms make chronic zinc toxicity from dietary sources an unlikely hazard to man.

2.4 LEAD IN THE SOIL, PLANT AND HUMAN BEINGS

Alloway and Jackson 1991 analysed washed samples of vegetable from several parts of Wales and found that the contents of copper, lead and zinc to be higher where soil has been heavily contaminated by mine waste.

Mitchell and Reith in 1966 concluded that plants grown directly on contaminated soils contained between 0.3 to 1.5 ppm lead (dry matter). Ingram in 1987 reported that the toxicity of cadmium (Cd) lead (Pb) and organic solvent can be measured by measurement of chemiluminescence (Cl) of white blood cells of human beings, which often decreases.

World Health Organization (WHO) gave a provisional tolerable level of

lead for weekly intake as 3mg person or 0.05mg/kg body weight. 0.01-0.3 is found in animal tissues and 0.005-0.3mg for plant tissues (Russle, 1961). John *et al,* (1992) found that much of the lead absorbed by a plant is retained in the roots so that upward movement is restricted.

2.4.1 NICKEL (Ni)

Nickel (Ni) exist in + 2, +1, and + 4 valence states with the two later states unstable in aqueous solutions. No function has been ascribed to Ni in the human body, although when applied in vitro, it activates *enzymes.* The most toxic of all Nickel compounds is [Ni $(CO)_4$] (Nickel carbonyl) which is a highly volatile, colourless and flammable liquid with a musty odour (Sittig, 1979) which decomposes above room temperature to yield carbon monoxide and finely divided Nickel.

Ni and compounds especially Ni $(CO)_4$ are carcinogens. Ni is present in the Lung, liver, kidney and intestine of still born infants. Measurement of Nickel in serum, urine faeces and hair are used as measures of environmental exposure to Nickel.

Symptoms of acute nicked, toxicity in man include severe gastroenteritis, tremor, cholera, movement paralysis and possibly heart failure and death. Chronic symptoms include degenerative changes in heart, muscle brain, lung, liver and kidney tissues and also growth retardation and impairment of reproductive capacity, sarcoma of the bone nerves etc.

2.4.2 LEAD (Pb)

Lead (Pb) exhibits +2 and +4 valence state with + 2 being most stable. It is present in all living organisms and widely distributed in the environment and food. Pb is about 5ppb of seawater. After absorption of Pb by the body, it is carried to soft tissues like brain, lung, spleen and heart by the blood and finally deposited in the bone where about 90% of total body Pb is found. Symptoms of acute Pb poisoning include abdominal pain, constipation or diarrhea, passing of blood, heart circulation, kidney or liver failure and death. Pb poisoning can lead to asthmatic attacks (Reidl, 1941; Spuhler, 1940).

Lead tetra alkyls are more dangerous than in organic Pb compounds because of their affinity for lipids in the central nervous system (Brain, spinal cord e.t.c.). High levels of Pb in pregnant women may lead to abortion or still birth (Lenihan and Fletcher, 1977) virtually all compounds of Pb are toxic. In addition to the Pb tetra alkyls, others are powdered Pb metal, PbO, PbO_2, $PbSO_4$ e.t.c.

2.4.3 Chromium (Cr)

Chromium exhibits 5 valences, + 2, to +6. Cr^{2+} is basic, Cr^{+3} amphoteric and Cr^{+5} is acidic. Cr is about 1 -2 ppb of seawater and the normal human body contains about 6mg of Cr. Cr^{+6} compounds are most toxic of Cr and are typically corrosive in anionic form. Cr^{3+} is one of the least toxic of all trace metals (Schroeder *et al,* 1962). Toxic Cr compounds include chromium

(VI) oxide (CrO_4), chromic acid (H_2CrO_4), chromium carbonyl, Cr $(CO)_4$, calcium chromate (Ca CrO_4) zinc and potassium chromates, lead chromate e.t.c. The last three being confirmed carcinogens.

Inhalation of Cr^{+6} leads to inflammation of and ulceration of the nasal mucosa in humans and pulmonary cancer has been found in people working in Cr references and related industries. Both Cr^{3+} and Cr^{+6} compounds are regarded as active inducing bronchial cancer.

However, chromium is regarded, as an essential metal in human body especially in enhancing insulin activity, which is of crucial importance to diabetics and also important in the membrane transport of human cell metabolites. In 1980 the recommended safe and adequate intake of Cr was established at 50-200 g/kg for adults (National Research Council, 1980). In a separate study, Cr intake of a well balanced diet designed by nutritionist was only 9ug/1,000 calories. Therefore 3,000 to 5,000 calories may need to be consumed to achieve a daily intake equal to the suggested minimum safe and adequate intake (Bunker *et al,* 1984).

2.4.4 ARSENIC (As)

Some foods contain arsenic but mainly in the less toxic pentavalent form (Underwood, 1979). Arsenic exhibits the following valences -3, +3 or + 5 in its various compounds and can form both ionic and cationic salts. Thus, arsenic gets into the air via industrial processes and also burning of coal and

smelting of metal ores. It gets into the soil by use of fertilizer, pesticides etc and it has been found to reduce soil fertility. Man and animals ingest it by eating contaminated food.

However, as stated earlier, arsenic is present in some foods in small amounts. (Beef, l.5mg/g; cocoa, 0.6mg/g; Table salt 2.7 mg/g; Sugar 0. mg/g; Rice 0.l mg/g (Underwood 1979). Pentavelent arsenic is less toxic than the trivalent form. Chronic arsenic poisoning leads to growth retardation, general weakness, nausea, loss of appetite with possibly vomiting and diarrhoea, ulceration of gastrointestinal tract, tremors, chronic hepatitis and liver cirrhosis. Inhaled arsenic liberates hemoglobin from the red blood cells, which blocks the kidney and the liver resulting in pains in the loins, general collapse and possibly anemia.

2.4.5 CADMIUM (Cd)

It is generally agreed that Cd doesn't occur free in nature. The only Cd ore, cadmium sulphide (Greenockite) which is about 78% Cd, is rare and usually occurs as a coating on sphalerite (zinc sulphide ore). Small amounts of Cd are in zinc, copper and lead ores and as such Cd is obtained during the refining of these ores. Cd is a bluish-white metal that is insoluble in water but soluble in acids. Cd ranks 67^{th} of the 97 most common elements in the earth Crust (0.05ppm).

Cd is very resistant to corrosion and is used as protective coating for iron, copper and steel, Cu-Cd alloy wires are used in telephone lines, Ni-Cd are used in rechargeable batteries, Cd oxide is used in alkaline storage batteries, Cd and CdF_2 are used as neutron absorbers in nuclear reactors, Cd is used as stabilizer for polyvinyl chloride plastics, in Nickel plating, as an amalgam in dentistry, in manufacture of fluorescent lamps, semi-conductors, photocells, jewelry, automobile and aircraft manufacture etc. Small amounts of Cd are in sea water and sea food (especially Oysters) in wheat/rice proteins and in the human body (the main storage site being the kidney). Cd enters the environment through contamination from all these process. It easily vaporizes like mercury and gets into the air easily. Cigarette smoking adds cadmium to the air at the rate of 15 to 18g/20 cigarettes (Venugopal and Luckey, 1978). Disposal of waste from processes using Cd allow the contamination in phosphate fertilizers and gets into the soil via addition of fertilizers.

Cd usually exists in the divalent state. It resembles zinc in its electronic configuration and can form complexes especially with organic ligands. It has particular affinity for sulphydryl groups and also for hydroxyl groups and ligands containing Nitrogen. Toxic compounds of Cd include cadmium Oxide (CdO), cadmium chloride ($CdC1_2$). CdF_2, $CdS0_4$, Cd_3 ($P0_4$),. Cd is toxic to all man and animal tissues and has no known beneficial effect (Fox, 1976). Acute Cd toxicity is usually caused by

inhalation of Cd dust or fumes easily produced when Cd is heated and symptoms include irritation of upper respiratory tract, excessive salivation, abdominal pains, diarrhea, vertigo, cough, general weakness and loss of consciousness. Chronic Cd toxicity symptoms include growth retardation, impaired kidney function, poor reproductive capacity, hypertension, tumor formation, hepatic dysfunction, lung damage, poor lactation etc. One of the classical examples of chronic Cd poisoning is the Itai-itai byo disease, which happened in Fuchu, Toyama province of Japan in 1968. This was caused by people eating rice grown on fields irrigated with water from a river contaminated by a mine several miles up stream. The disease was first seen in women above 45 years (past menopausal) and was characterized by Osteo malacia, severe pain caused by softened bones, sever renal dysfunction and increased excretion of protein, glucose and amino acids. The daily intake of Cd was about 10 times that in most parts of the world.

High levels of zinc in diet attenuates the toxic effect of Cd. Cd interferes with the metabolism of Zn, Cu and Fe in the body and above normal levels of these reduces Cd toxicity. Frieberg (1957) examined autopsy specimens of four workers who died of Cd poisoning and found deposition of CD in kidneys, liver, pancreas and thyroid and that one of them dies 9 years after exposure which means that elimination of absorbed Cd is extremely slow.

Christie et al. (1957) showed that Cd can be quantitatively determined in sewage and industrial wastes by colorimetry after complexation with biphenyl carbazide.

CHAPTER THREE

3.0 EXPERIMENTAL

3.1 SAMPLE COLLECTION AND TREATMENT

3.1.1 COLLECTION OF THE SOIL

Soil sample was collected from a location around the Department of Crop production, Ahmadu Bello University, Zaria in March, 2005 before the commencement of the rainy season.

3.1.2 COLLECTION OF THE SEEDS

The lettuce seeds *(Lactuca satiuaty,* okra seeds *(Abelmoschus esculentum)* and pepper seeds *(Caspicum annum)* were of improved variety purchased from an Agro-Allied Shop in Zaria.

3.1.3 SOIL TREATMENT/ANALYSIS

Soil samples were collected from a virgin land close to the Department of Crop Protection, A.B.U. Zaria, before the commencement of the rainy season. The soil was thoroughly mixed to ensure homogeneity and composite samples were taken for the analysis of the physicochemical properties.

Two kilograms each of the soil was weighed into 48 plastics containers and soaked with distilled water and allowed to stand for three days in the Biological Gardens in Federal College of Education, Zaria.

The seeds were initially planted in a nursery in biological gardens in F.C.E, *Zaria* for about two weeks after which they were carefully transplanted

into the 48 plastics containers and safely transported into the glass house in the Biological Sciences Department of A.B.U, *Zaria*. The plants were allowed to stabilize for one week in the well-aerated biological gardens with sunshine of 9 hours approximately per day. After which different solutions containing of 10ug/g, 50ug/g and 100 ug/g of Lead (Pb), Nickel (Ni), cadmium (Cd), chromium Cr and arsenic (As) were prepared using analytical grade reagents. When the plants were already stabilized, each solution containing these metals ions were used to wet one plant in each case. About $10cm^3$, $15cm^3$ and $20cm^3$ of each solution was used to wet three (3) different vegetable plants that is lettuce, okra and pepper each day, and this continued for complete two (2) months i.e. eight weeks. Control experiments were also performed in which the plants received only $20cm^3$ of water daily.

When the plants were adjudged to be matured at the end of the eighth week, they were uprooted and separated into the root portion, stem and leaves using a sharp knife. These different parts were air-dried separately ground into powder and stored in air-tight plastic container.

3.2 REAGENTS

All the reagents used were of analytical grade except otherwise stated. Distilled water was used in the preparation of all solutions. Glasswares were properly washed with liquid soaps, rinsed with water soaked in dilute nitric acid overnight and then rinsed thoroughly with distilled water before use.

3.3 DETERMINATION OF THE PHYSICO-CHEMICAL PARAMETERS OF THE SOIL USED

3.3.1 DETERMINATION OF SILT, CLAY AND SAND

Reagent

Calgon (Sodium hexametaphosphate)

Procedure

50.0g of 2mm sieved soil was weighed into a 250 cm^3 plastic bleaker. 100. cm^3 of calgon and 100.0cm^3 of distilled waster were added and strived. The mixture was left to stand for 30 minutes with occasional stiring.

The mixture was then transferred into a mixing cup. The beaker was washed with 20. cm^3 of distilled water and the washing added to the mixing cup and stirred for 10 minutes. After the stirring the mixing cup content was transferred to a 1000 cm^3 measuring cylinder. Distilled was added to make it to the mark. Complete mixing was achieved by using long handled plunger.

Hydrometer readings were taken for 40 seconds, 4 minutes, 2 hours, 8 hours and 24 hours, according to the Bonyoucos method for 20Ulm and 2Um fractions respectively.

Blank readings were also taken by transferring 100.0 cm^3 of the 50% colgon solution into 1000 cm^3 measuring cylinder and making it up to the mark with distilled water. The blank readings were taken for the 40 seconds, 4 minutes, 2 hours, 8 hours and 24 hours respectively.

Temperatures of the various suspensions and blanks were recorded respectively.

After the last reading was taken for each portion, the suspension was poured through a 0.2mm sieve. The sand grains retained on the sieve was washed with distilled water, and the washing together with filtrate were transferred into a large beaker and dried in an oven at 105^0C.

The sand left on the sieve was also weighed to give the coarse sand fraction.

Calculations

The corrected hydrometer readings C (g/L) were obtained by subtracting the blank reading RL (g/L) from the hydrometer. Readings in the soil suspensions R(g/L) and 0.36g/L was added for every degree above 20°C.

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

Where T= Room Temperature minus 20

The percentages by weight of the SILT + CLAY and SAND fractions were given by:

$$\%Clay = \frac{\text{Corrected 8 hrs reading-Blank x 100}}{\text{wt of soil taken}}$$

$$\% Silt = \frac{\text{Corrected 40 Sec Reading -Blank x 100-\% Clay}}{\text{wt of soil taken}}$$

% Sand =100 -% Clay +% silt.

The samples was then be classified according to the USDA or International systems of Textural classification.

3.3.2 pH Determination

Reagents

1. Distilled water and 0.01 M ($CaCl_2$)
2. 1.47g of the salt was dissolve in distilled water and made to I Litre.
3. 1M KC1 74.56g of the salt was dissolved in distilled water and made to
4. Standard buffer solution pH 4, 7, 9.

Soil to water ratio:

pH in soil was determined in the following soil to water ratio:

1:1 – l0.0g of soil to l0 cm^3 of distilled water.

1:2.5 – l0.0g of soil to 25 cm^3 of distilled water

Procedure

To l0.0g of 2mm sieved air dried soil in a 50 cm^3 plastic beaker, 25.0cm^3 of distilled water was added and stirred for 30 minutes. The suspension was then left to stand for 30 minutes undisturbed.

The pH meter was calibrated using buffer 4, 7 and 9. The electrode was immersed into the soil suspension, but it was made sure that the electrode did not touch the bottom of the beaker. The pH was read after 30 seconds.

The above procedure was repeated using 0.0IM $CaCl_2$ and 1.0MKCL solutions. The readings were recorded as pH in distilled water and 0.0Im CalCl2 and 1.0MKCl.

3.3.3 ORGANIC CARBON – (WALKLEY – BLACK)

Reagents

1. Potassium dichromate ($K_2Cr_2O_7$)

   ($K_2Cr_2O_7$) analar grade was dried at 105^0C and corted in a dessicator. 40.04g was weighed into a 1000cm^3 volumetric flask and made up to the mark.

2. Concentrated H_2S0_4

3. O-phenanthrolein ferrous sulphate indicator

4. Ammonium ferrous sulphate (0.5M)

   196.0g of ammonium ferrous sulphate was dissolved in distilled water to which 10.0 cm^3 of concentrated H2SO4 has been previously added. The mixture was vigorously shaken to achieve dissolution and then made to the mark in a 1000 cm^3 flask.

5. O-phenanthrolien – ferrous complex (0.025M)

6. Concentrated phosphoric acid

PROCEDURE

1.0g of soil was weighed into 250 cm^3 Erlenmeyer Hark. 10.0 cm^3 of the $K_2Cr_2O_7$ was added using a pipetter, and the mixture swirled gently to disperse the soil. 10.0 cm^3 of concentrated H_2SO_4 was rapidly transferred from a measuring cylinder into the flask and swirled again for 1 minute. The flask content was then allowed to stand on an asbestor sheet for 30 minutes.

100.0 $cm^{3\ of}$ distilled water was added, allowed to cool and then suspension filtered on a fitter paper.

5.0 cm^3 of phosphoric acid and 5 drops of the indicator were added, then titrated with ferrous sulphate solution on a white background. The colour changed for blue – green – dark green – red.

A blank determination was made in the same manner as above but without soil.

$$\text{Org. C \%} = \frac{(\text{meg } K_2Cr_2\ 0?\text{- meg Fe SO4.1 x 0.003 x 100 xF}}{\text{wt of air dry soil taken}}$$

Where f = Correction factor 1.33 OR

$$\text{Org. C /\%} = \frac{(\text{blank titre - actual titrel x 0.3 x m x f}}{\text{wt of air dry soil taken}}$$

Where M = CONC of ferrous ammonium sulphate

F = correction factor.

% Organic carbon X 1.729 = % Organic Matter

3.3.4 Total Nitrogen in Soils

Reagents

1. Boric acid 2%
2. Kjeldahl Catalyst mixture (mix 500g of $NaSO_4$ + 50g of $CuSO_4$ + 0.5g of selenium catalyst ground to fine powder.

3. IOM NaOH

4. Granulated zinc chips or anti-bump granules.

5. Concentrated sulphuric acid

6. Mixed indicator

7. Standard acid 0.005M $H_2 SO_4$

Procedure

1.0g of 100μM mesh soil was weighed into a 500 cm^3 Kjeldahl flask. Few drops of distilled water was added and allowed to stand for 30 minutes. 5.05 of Kjeldahl catalyst mixture and 20.0 cm^3 of concentrated sulphuric acid were added too. The flask content was heated cautiously on a block digestor until frothing ceased. The heat was increased until digest cleared and the heating continued for another 2 hours.

The flask content was cooled and little distilled water added before flask content was washed into a 100cm^3 volumetric flask, and then more distilled water was added to the mark.

10.0 cm^3 from the digest was pipetted into a distillation flask 20.0 cm^3 of 2% Boric Acid was measured into a 100 cm^3 conical flask and the conical flask introduced to the bottom of the distillation condenser. 10.0 cm^3 of 10M NaOH was added to the digest was then quickly distilled and 50.0 cm^3 distillate collected.

The distillate was then titrated with 0.01N H_2SO_4 from, green to purple end point to Purple end point.

Calculation

$$\% = \frac{0.014 \times (T - B) \times NA \times \text{Vol of digest} \times 100}{\text{wt of soil} \times \text{Aliquote distilled}}$$

3.4 PREPARATION OF SOLUTIONS APPLIED TO SOIL

3.4.1 LEAD STOCK SOLUTION

Standard lead solutions were prepared by dissolving 0.063g, 0.15g ands 0.31g of pure Pb $(NO_3)_2$ in three (3) different 250cm^3 volumetric flasks and diluting to the mark with distilled water. 0.lcm^3, 10cm^3 and 20cm^3 of the stock solutions above were then placed separately into three (3) 50cm^3 volumetric flasks and made to mark with distilled water to give 10 ug/g, 50 ug/g and 100 ug/g respectively.

The volume of stock solution used in preparing the working standards for lO ppm, 50ppm and l00 ppm used in watering the lettuce, okra and pepper (L.O.P) was obtained by using the equation. $Ci\ Vi = C_2\ V_2$

Where Ci = Concentration of the stock solution.

Vi = Volume of the stock solution

Ca = Concentration of the solution required

V_2 = Volume of solution required.

3.4.2 NICKEL STOCK SOLUTION

Standard Nickel solutions were prepared by dissolving 0.032g, 0.05g and 1.61g of pure Ni (Ni $SO_4.6H_2O$) in three (3) different 250 cm^3 volumetric flasks

and diluted it to the mark with distilled water. 0.lcm^3, 10cm^3 and 20cm^3 of the stock solutions above were then placed separately into three (3) 50cm^3 volumetric flasks and made to the mark with distilled water to give 10 ug/g, 50 ug/g and l00 ug/g respectively, which were used in wetting the three vegetable plants (viz Lettuce, okra and pepper).

3.4.3 CHROMIUM STOCK SOLUTION

Standard chromium solutions were prepared by dissolving 0.052g, 0.13g and 0.26g of pure Cr (K_2Cr0_4), in three (3) different 250cm^3 volumetric flasks and diluting to the mark with distilled water. 0.lcm^3, 10cm^3 and 20cm^3 of the stock solution above was then placed separately into three (3) 50cm^3 volumetric flask and made to the mark with distilled water to give l0ug/g, 50ng/g and 100ng/g respectively which were used in wetting the three (3) vegetable plants.

3.4.4 CADMIUM STOCK SOLUTION

The standard cadmium solution were prepared by dissolving 0.048g, 0.119g and 0.238g of pure Cd ($CdSO_4.8H_2O$), in three (3) different 250cm^3 volumetric flask and diluting to the mark with distilled water. 0.lcm^3, 10cm^3, and 20cm^3 of the stock solutions above were then placed separately into three (3) 50cm^3 volumetric flasks and made to the mark with distilled water to give 10 ug/g, 50ng/g and 100ng/g respectively, which were used in wetting the three (3) vegetable plants.

3.4.5 ARSENIC STOCK SOLUTION

The standard Arsenic solution was prepared by dissolving 0.061g, 0.152g and 0.305g of pure As (NaASO2J, in three (3), different 250cm^3 volumetric flasks and diluting to the mark with distilled water. 0.lcm^3, 10cm^3 and 20cm^3 of the stock solutions were then placed separately into three (3) 50cm^3 volumetric flasks and made to the mark with distilled water to give 10 ug/g, 50 ug/g and 100 ug/g respectively which is used in wetting the three (3) experimental vegetable plants.

3.5 DIGESTION OF SOIL (Allen *et al* 1974)

The finely ground soil (1g) was weighed into an evaporating dish. 5cm^3 of 73% trioxonitrate(s) acid was added and was heated at 80°C for 10 minutes using a thermostated heating mantle. When the brown fume of NO_2 was noticed, 5cm^3 of (98%) H_2SO_4 was added and the digestion temperature was increased to 120°C. The mixture was heated for 20 minutes with addition of a total of 15cm^3 of HNO_3 over the digestion period adding 5cm^3 each time. The digest was allowed to cool and stored in screw capped plastic buttons. The metals were determined using atomic absorption spectrophotometer (Pye Unicam, Model SP 969).

3.6 DIGESTION OF PLANT SAMPLES (Alien *et al*, 1974)

The finely ground plant sample (1g) was weighed into an evaporating dish and 15cm^3 of 73% trioxonitrate (V) ($HN0_3$) was added and the evaporating

dish was placed on a hot plate in a fume cupboard and 5cm^3 of 36% of Hydrochloric acid (HC1) were added and the temperature of the hot plate was gradually increased to 100°C.

The solution was put aside after 30 minutes heating, then allowed to cool and the digest was diluted with 10cm^3 of distilled water. The resulting solution was boiled again, set aside to cool, filtered and made up to 50cm^3 in a volumetric flask. The metals were also determined using atomic absorption spectrophotometer (Pye Unicam, model SP 969) equipped with automatic background corrector from National Research Institute for Chemical Technology (NARICT) Zaria.

3.7 PRINCIPLE AND APPLICATIONS OF ATOMIC ABSORPTION SPECTROMETRY

Atomic Absorption Spectrometry (AAS) is a common technique for detecting and measuring concentration of metals and metalloids in biological, environmental and geological samples. AAS can be used to analyze the concentration over 62 different elements in solution (Wikipedia, 2006). An indirect determination of phosphate, silicate and niobium by AAS using chemical amplification procedure has also been described (Thompson and Reynolds, 1978).

According to Royal Society of Chemistry, RSC (2006), atomic absorption spectrometer has the following three components: a light source

which is capable of producing light of characteristic wavelength, a device for producing an atomic vapor of the element from the compounds present in the sample solution, and a device for measuring the specific light absorbed. The light source is usually a lamp having a hollow cathode made of the element to be determined. The production of free atoms occurs in an atomizer and the process is called atomization. Most of atomic absorption equipments use flames for the atomization process; other devices for atomizing the elements in the sample matrix are electrothermal atomizer, carbon rod analyzer and tantalum boat analyzer (Ma and Gonzalez, 1997). A photomultiplier is usually used to measure the amount of light absorbed.

In AAS, a solution containing metallic species is aspirated into a suitable flame and an atomic vapor of the metal will generally be formed. If irradiated with light of their own characteristic resonance wavelength, the ground state atoms will absorb some of the radiation. The absorbance being proportional to the population density of atoms in the flame. From a calibration curve prepared from standard solutions of the element to be determined, the concentration of the element in a sample matrix can be obtained.

3.8 ANALYTICAL TECHNIQUES

3.8.1 PREPARATION OF CALIBRATION CURVES.

The standard solutions prepare for each metal were aspirated into the

flame system of the atomic absorption spectrometer and the absorbance corresponding to the concentration in each standard solution measured. These absorbance's were plotted against the concentrations of metal in various standard solutions. The calibration curves obtained for Pb, Ni, Cd, and Cr are shown in appendices.

3.9 DETERMINATION OF METAL CONCENTRATIONS IN THE SAMPLES

To determine the concentration of each metal contaminant in the samples, the blank reagent was first aspirated into the flame system of the AA spectrometer and the absorbance measured. Thereafter, the absorbance of each sample solution was measured in a similar manner and the concentration of the particular metal obtained from the calibration curve corresponding to the particular metal under determination. This was done by interpolation on the calibration curve with the aid of computer coupled with the atomic absorption spectrometer.

3.10 DETERMINATION OF ARSENIC USING X-RAY FLUORESCENCE (ED- XRF)

The samples were ground manually with an agate mortar and pestle to grain size of less than 125pm. Pellets of 19mm diameter were prepared from 0.3-05g powder mixed and pressed after wards at l0 tons with a hydraulic press.

Measurements were performed using an annular 25mci 109 Cd as the

excitation source, that emits Ag-K X-Rays (22.1kev) in which case all elements with lower characteristics excitation energies were accessible for detection in the samples. The system consists of a Si (Li) detector, with a resolution of 170 eV for the 5.90 KeV line, coupled to a computer controlled ADC-card. Quantitative analysis of the samples was carried out using the emission Transmission (E-T) method, for which a number of quantification methods have been developed and applied (Leroux and Mahamoud *et al,* 1996).

This quantification methods provide different approaches to correct the matrix absorption as well as enhancement effects. In this work quantification was carried out using a modified version of E-T method as suggested by (Kump, 1996 and Funtua 1999a&b) and it involves the use of pure target material (Mo) to measure the absorption factors in the sample.

The Mo target serves as a source of monochromatic x-rays, which are excited through the sample by primary radiation and then penetrate the sample on the way to the detector. In this way the absorption factor is experimentally determined which the program uses in the quantification of concentration of the elements. In addition, the contribution to the Mo-K peak intensity by the Zr-K is subtracted for each sample. Sensitivity calibration of the system was per formed using thick pure metal foils (Ti, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb) and stable chemical compounds (K_2CO_3 and $CaCO_3$). The spectra for the samples were collected for 3000s with the ^{109}Cd source. The spectra were then evaluated using the AXIL-QXAS program (Benasconi, 1996).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 PHYSICO-CHEMICAL ANALYSIS OF THE SOIL USED

The physicochemical properties of the soil were carried out in the soil science laboratory in Ahmadu Bello University Zaria, before planting the three (3) vegetable plant (viz, lettuce, okra and pepper) as shown in Table 4.1. The soil test value suggested that the pH values were weakly acidic, and the textural class is loamy with average organic matter content. The above classes of soil are suitable for the growing of the three (3) vegetable plants (Gruben and Tahir, 2004).

TABLE 4.1 RESULT OBTAINED FOR THE PHYSICO-CHEMICAL ANALYSIS OF THE SOIL USED

CHARACTERISTICS	
pH (H_2O)	6.10
pH (0lM $CaCl_2$)	5.20
% Total Nitrogen	0.21%
% Organic matter	3.32%
% EXCHANGEABLE IONS	
Cation exchange capacity	17.20%
Lead (Pb)	0.983
Nickel (Ni)	0.005
Cadmium (Cd)	0.021
Chromium (Cr)	0.339
Arsenic (As)	0.095
Particle size analysis (%) Particle size distribution corrected to 20°c	
Sand	20
Silt	46
Clay	20
Textural class	Loam
Colour	Dull brown

4.2 UPTAKE OF METALS BY PLANTS

Plant roots penetrate into the subsoil from, which they take up metal ions, but different plant species can have varying abilities to take up trace metals (Martin *et al.,* 1996). The uptake of the metal ions (Pb, Cd, Ni, Cr and As) is controlled by pH or organic matter content as well as synergistic and antagonistic interactions with other nutrients. (Bartiett and Kimble, 1976). The results obtained for the various metal uptake by the different plants used are shown in Tables 4.2– 4.9 and pictorially in Figures

4.10– 4.12

4.2 LIST OP TABLES

Table 4.2. Metal ions concentration of lettuce leaves

Concentration of metal ions applied (µg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	As	(% Rsd)
Control	0.019	30.7	0.064	11.4	0.009	0.9	0.016	10.9	0.055	0.0
10	0.411	1.7	1.188	3.6	0.029	0.8	0.915	3.9	0.075	3.8
50	37.100	5.9	6.692	3.2	0.045	0.2	0.711	0.2	0.089	6.6
100	39.530	3.0	19.620	26.3	0.141	0.1	0.839	6.0	0.099	9.0

Table 4.3. Metal ion concentration of lettuce roots

Concentration of metal ion applied (μg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	As	(% Rsd)
Control	0.103	9.0	0.111	26.0	0.006	9.4	0.212	0.9	0.045	0.0
10	18.06	11.2	5.867	5.8	0.030	0.1	0.323	1.6	0.052	4.2
50	34.56	0.9	23.440	5.1	0.113	0.3	0.342	1.6	0.049	4.0
100	35.07	1.4	17.900	6.9	0.137	0.0	0.022	7.9	0.048	5.7

Table 4.4. Metal ion concentration of okra leaves

Concentration of metal ion applied (µg/g)	Pb	(%Rsd)	Ni	(%Rsd)	Cd	(%Rsd)	Cr	(%Rsd)	As	(%Rsd)
Control	0.097	56.6	0.009	9.0	0.002	84.1	0.008	9.0	0.047	0.0
10	0.267	18.4	0.039	17.3	0.002	0.5	0.001	1.5	0.047	0.0
50	0.261	8.7	0.139	3.8	0.004	1.0	0.010	73.6	0.043	0.0
100	0.348	1.6	0.089	0.9	0.002	7.0	0.003	0.1	0.044	0.0

Table 4.5 Metal ion concentration of okra fruits

Concentration of metal ion applied (µg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	As	(% Rsd)
Control	0.053	28.7	0.007	33.1	0.002	33.0	0.007	9.0	0.040	0.0
10	0.263	21.0	0.29	35.5	0.001	57.2	0.016	57.2	0.039	0.0
50	0.222	15.2	0.032	10.9	0.005	4.9	0.012	39.1	0.054	0.0
100	0.319	8.2	0.033	26.4	0.005	20.9	0.001	12.5	0.043	0.0

Table 4.6 Metal ion concentration of okra roots

Concentration of metal ion applied (µg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	As	(% Rsd)
Control	0.007	31.0	0.003	13.6	0.004	3.5	0.012	9.0	0.078	0.0
10	0.192	11.6	0.043	10.8	0.001	12.4	0.006	23.8	0.066	0.0
50	0.187	11.8	0.060	2.1	0.002	2.8	0.004	39.8	0.061	0.0
100	0.283	5.2	0.066	14.9	0.001	1.0	0.004	9.5	0.078	2.0

Table 4.7 Metal ion concentration in pepper leaves

Concentration of metal ion applied (µg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	As	(% Rsd)
Control	0.018	9.0	0.011	35.2	0.001	21.0	0.017	2.4	0.045	0.0
10	0.188	0.5	0.022	25.1	0.011	11.4	0.017	17.1	0.058	0.0
50	0.239	6.0	0.052	3.7	0.012	2.2	0.011	29.7	0.045	0.0
100	0.411	22.3	0.062	14.7	0.014	0.1	0.003	7.4	0.059	0.0

Table 4.8. Metal ion concentration in pepper fruits

Concentration of metal ion applied (µg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	*As*	(% Rsd)
Control	0.104	2.5	0.055	10.8	0.001	4.8	0.012	6.5	0.056	0.0
10	1.610	4.6	2.685	9.7	0.037	0.8	0.151	2.6	0.065	4.0
50	8.96	62.3	4.396	7.6	0.031	0.4	0.418	0.8	0.027	0.0
100	25.74	1.0	7.792	51.5	0.043	0.8	0.767	1.1	0.065	9.7

Table 4.9. Metal ion concentration in pepper roots

Concentration of metal ion applied (µg/g)	Pb	(% Rsd)	Ni	(% Rsd)	Cd	(% Rsd)	Cr	(% Rsd)	As	(% Rsd)
Control	0.128	2.9	0.040	41.2	0.001	57.1	0.007	17.9	0.043	0.0
10	0.130	58.1	0.660	3.2	0.005	1.2	0.011	3.1	0.044	0.0
50	0.180	0.4	0.110	10.4	0.001	0.0	0.002	4.5	0.048	0.0
100	0.250	9.2	0.081	10.8	0.004	0.0	0.033	24.6	0.071	0.0

FIG 4.1 HEAVY METAL CONCENTRATION CHARTS OF ROOTS, LEAVES AND FRUITS OF OKRA

FIG 4.2 HEAVY METAL CONCENTRATION CHARTS OF ROOTS AND LEAVES OF LETTUCE

FIG 4..3 HEAVY METAL CONCENTRATION CHARTS OF ROOTS, LEAVES AND FRUITS OF PEPPER

4.3 LEAD IN LETTUCE, OKRA AND PEPPER

Lead is essential for plant growth (Hewith and Smith, 1975) and therefore the uptake by plant is controlled by the soil organic matter content and the pH. Increase in pH and organic matter levels in the soil commonly reduce the uptake of the lead by plants (Largewerf and Speltch, 1970). The concentration of lead in lettuce roots for the control experiments is 0.103ug/g, which increases to 35.07ug/g when the concentration of the solution used to wet the plant increase to l00 ug/g. As shown in Table 4.3 above. It can then be concluded that, the concentration of metals ion is highest in the roots, and the uptake of the metal ion is proportional to the concentration of the solution used to wet the plant. This is same as observed in the leaves of the lettuce as shown in Table 4.2.

This result agrees with Motto *et al.*, (1970) who observed that the lead occurring in plants was more concentrated in the roots and leaves than in the fruits, grains or tubers. While in okra (vegetable crops) the concentration of lead from the control increases from the roots, leaves and fruits in proportion with the increase of the concentration of solution used to wet the plant as can be seen on Tables 4.4, 4.5 and 4.6.

The highest concentration in the roots is 0.283µg/g, leaves = 0.348 µg/g and fruits - 0.31µg/g all at l00 µg/g, the concentration used to wet the plant. Here the highest concentration was observed in the leaves, which are contrary to the report of (Jones and Clement (1973) which revealed that, the highest concentration of lead is found in the root of lettuce and cabbage.

While, the concentration of lead in the pepper plants for the controls increases in the roots as the concentration of solution used to wet the plant increase as can be seen on the Tables 4.7, 4.8 and 4.9.

The concentration for the control increases in the roots as 0.28µg/g, 0.130ug/g, 0.180µg/g and 0.250µg/g as increases from control to 100µg/g in the roots respectively as shown on Table 4.7, 4.8 and 4.9.

These results indicate that fruits have the highest concentration compare with the roots which have been reported earlier by Motto *et al.*, (1970) who observed that the lead occurring in plants was more concentrated in the roots and leaves than in the fruits, grains or tubers.

It has been observed that lead is converted into $PbSO_4$ and occasionally to PbO - or PbS. And that those conversions occur either during transport or after deposition in the soil. Therefore, this deviation of the result might be unconnected to the soil pH, temperature and the varieties of the sample used.

4.4 NICKEL IN LETTUCE, OKRA AND PEPPER

Nickel is a heavy metal considered as an environmental pollutant. The level of Nickel in the soil depends on the natural occurrence and incorporation of metal-containing substances (Tiller, K.G. 1989). The concentration of nickel in the lettuce plants for the control increases in the roots as the concentration of solution used to wet the plant increases as shown on Tables 4.2 and 4.3. The concentration of control in the roots increases from 0.11l µg/g, 5.865 µg/g, 23.44

µg/g to 17.90 µg/g respectively.

The highest concentration in the leaves at l00ppm is 0.348ppm as shown on table 1. These results agreed with the reports of Mortved and Giodarno (1975) and of Cunningham *et al,* (1975) who established that trace elements in sludges are taken up less readily than are trace elements added to sludge in the form of in organic salts or trace elements added directly to soil in the same concentration as was present in the sludges. When compared to the report of (Jain *et al.,* 1990) who reported that Duckweed accumulate Nickel (Ni) from root to shoot to high level ranging from 2000 to 5500mg/g (DW.).

In okra plant crops, the concentration of Nickel in the control increases in the roots as follows, 0.003, 0.043, 0.060, 0.66 µg/g as the concentration of the solution used to wet the plant increases to 100µg/g as shown on the Tables 4.4 4.5 and 4.6. This shows an increase in the concentrations in the roots. While, the leaves and fruits have the highest concentration of 0.089µg/g and 0.33 µg/g respectively this is contrary to the report of Jones and Clement (1997).

While, in pepper plants, the concentration of Nickel in control and the roots is as follows; 0.040, 0.660, 0.110 and 0.081 as the concentration of the solution used to wet the plant increases up to l00µg/g as shown on Tables 4.7, 4.8 and 4.9 showing an increase and decrease at various concentrations. The highest concentrations in the leaves and fruits are 0.062 µg/g and 7.792 µg/g respectively.

The results agreed with what several authors suggested that important proportions of the metal Nickel was precipitated as carbonates or forming organic complexes page A.C and Chang 1982.

4.5 CADMIUM IN LETTUCE, OKRA AND PEPPER

Cadmium has long been recognized as a toxic element, but its importance as an environmental contaminant increases when the relationship between the Itai-itai disease in Japan and cadmium concentration in rice was identified (Kobayashi, 1978). Most of the cases of soil pollution of Cd are due to mining and refining of zinc ores (Elinder, 1986).

The concentration of cadmium in lettuce for the control experiment increases from the root to the leaves and this is proportional to the increase in the concentration of the metal ions used to wet the plants as can be seen on Tables 4.3 and 4.3. And this result agrees with the report of (Jones *et al*, (1975) who reported that, the application of high cadmium sludge increases the cadmium content in corn leaves from 0.5 to 20µg/g, while leafy vegetables such as, lettuce, Spinach, beet greens as well as tobacco contained the highest cadmium levels (Dowdy and Larson, 1975).

The concentration of cadmium in okra for the control experiment is quite different in the roots, leaves and fruits, respectively with highest concentration of 0.004|ig/g in roots, 0.004µg/g in leaves and 0.005µg/g fruits respectively at highest concentration 100ug/g of solution that wet the

samples. The result obtained for cadmium in okra as shown on Tables 4.4, 4.5 and 4.6.

The report of the result obtained in okra for the analysis of cadmium has agreed with the report of Devries and Tiller (1978) who analyzed for Cd, Cu, Mn, Ni and Zn under the different conditions has concluded that sludge application brought about a sharp increase in the concentration of the metals in the plant material.

Furthermore, the concentration of cadmium in the pepper crop for the control experiment increases from the root, leaves and fruits as the concentration used to wet the solutions increases as can be seen on the Tables 6, 7 and 8 for pepper which also agrees with the result of Van Noorwijk *et al.* (1995). Showing that the relative cadmium uptake of maize was roughly proportional to the fraction of total root length in the contaminated layer in an experiment with an un polluted top layer of marine clay on polluted habour slugged. Zayed *et al* (1998a) reported that floating plant water hyacinth and duckweed were very good accumulators of cadmium. They accumulated up to 6 and 13g/kg DW respectively, when supplied with l0g/kg.

4.6 CHROMIUM IN LETTUCE, OKRA AND PEPPER

Chromium is a heavy metal with a potential risk to human health. Its presence in agricultural soils could be due to several practices, as a fertilizers and use of wastewater for irrigation (Baxter *et al.*, 1983).

Chromium availability in soil depends on several soil conditions, such as pH or redox potential (Bartlett and Kimble, 1976). If chromium is in the soil solution, it can be taken up by roots and accumulated and distributed within the plant. This fact may lead to interaction between chromium and other essential elements, which can have a significant effect on the nutrient concentration and distribution in the plant.

The concentration of chromium in lettuce for the control experiment in the root is 0.212ug/g, which is even higher than 0.022ug/g when the solution used to wet the plant is at l00µg/g as shown on table 4.3 for the lettuce. This report agrees with Sidle *et al.,* (1976) who irrigated corn with municipal sewage effluents and control (normal water) at application rate of 7.5 cm/week. These authors analyzed for Cu, Zn, Cd and Pb, and found that the total uptake of these metals by the corn in the control was usually higher than in the sewage effluent treated areas. While, in the leaves of the lettuce there was an increase from control down to 100µg/g as the concentration of solutions used to wet the plant increases as can be seen in Table 4.2. This agrees with report of Motto *et al.,* (1990). Cr is essential for chloroplast membrane system (Rasheed, 1998).

Okra

The concentration of chromium in okra for the control experiment increases from the roots to the fruits, as shown in Table 4.4, 4.5 and 4.6. The concentrations increases in proportions as the concentration of solution used

to wet the plant increases and this result agrees with the report of Devries and Tiller (1978) who analysed for Cd, Cu, Mn, Ni and Zn under different conditions and concluded that sludge application brought about a sharp increase of the concentrations of the metals in the plant material from the glass house, where as there was little increase in the concentrations of the metals in the field plants.

Pepper

The concentration of chromium in pepper for the control experiment in roots and fruits increases in proportion with the increase in concentration of solution used to wet the plant. While there was a change in the concentration in relation to the change in the concentration of solution used to wet the plant in the leaves as can be seen in Tables 4.7, 4.8 and 4.9. Chromium accumulated preferentially in roots. The aerial parts of the plants accumulated little chromium probably due to the slow transport of chromium from the roots.

(Zayed *et al*, 1998a; Zhu *et al*, 1999) reports that chromium (Cr) accumulated the greatest concentration in plant roots and to the least levels in plant shoots, Smartweed acquired the highest concentrations of Cr chromium of 298mg/kg in its roots; while the highest Cr concentration of 24mg/kg was in water lettuce.

4.7 ARSENIC IN LETTUCE, OKRA AND PEPPER

Arsenic can be considered to be toxic especially when it is methylated by biological process. The presence of methylated arsenic in the environment will affect the plant uptake as well as human beings that consume the plant.

The concentration of arsenic in lettuce for the control experiment increases from the root in proportion with the increase of the concentration of solution used to wet the plant in which the root has a highest concentration of 0.048 at 100ug/g; while the leaves shows a highest concentration of 0.099 at 100μg/g. This shows that, at highest concentration of 100 μg/g the leaves have absorbed more than, that of the roots as shown in Tables 4.2 and 4.3. This result agrees with Peterson (1977), who reported that the species and varieties of plants differ greatly in toxic metal accumulations. Which experimental results showed that cadmium uptake by several barley varieties, cultivated in Sweden, and were not significantly different statistically.

Zhu *et al,* (1999) reported that all the plant species tested in their studies were poor accumulators of arsenic, as water lettuce accumulated the highest concentration of Arsenic in both roots (177mg kg^{-1}) and shoots (34mg kg^{-1}).

Okra

The concentration of Arsenic in okra for the control experiment increases from the roots to fruits then to the leaves as the concentration of solution used to wet the plant increases. But there is exception in the roots, fruits and leaves as can be seen in the Tables 4.4, 4.5 and 4.6. The highest concentration in the roots is 0.078 when the concentration of solution used to wet the plant is 100µg/g, while the highest concentration in leaves is 0.047µg/g, when the concentration of solution used to wet the plant is l0µg/g, and the highest concentration in the fruits is 0.054µg/g, when the concentration of solution used to wet the plant is 50µg/g They analysed for Cu, Zn, Cd and Pb, and found that the total uptake of these metals by the corn in the control was usually as high as or higher than in the sewage effluence treated areas.

While the concentration of Arsenic in pepper for the control experiment in the roots has the highest concentration of 0.043µg/g, when the concentration of solution used to wet the plant is l00µg/g. Leaves have the highest concentration of 0.059µg/g, when the concentration of solution used to wet the plant is 100µg/g, and fruits have the highest concentration of 0.065ug/g, when the concentration of the solution used to wet the plant is 100µg/g.

The result shows that increase in the concentration of solution used to wet the plant leads to the increase in the concentrations of the metal ions in

the roots, leaves and fruits. This agrees with Jones *et al*, (1975) who reported that, application of high cadmium sludges increases the cadmium content in corn leaves from 0.5 to 20ug/g. Zhu *et al,* (1999) reported that, all the plant species tested in this study were poor accumulators of Arsenic with the exception of water lettuce. Water lettuce accumulated the highest concentration of Arsenic in both roots (mg/kg) and shoots (34 mg/kg).

4.8 CORRELATION STUDIES

The relationship between each of the applied heavy metal in soil and the corresponding metal uptake in each of the different parts of the plants were studied. This was done by computing the Pearson correlation coefficient (r values). Table 4.13 shows the Pearson correlation coefficient between applied metal in soil and the metal uptake in okra. The results show that Pb metal uptake is positively correlated with the applied Pb concentrations in the soil. Cd has a low negative association in the roots (r = -0.012) and leaves(r = -0.012) of this crop. However, Cd has a positive association (r = +0.786) in fruits of okra. Cr has a high negative association in the roots(r = -0.860) and fruits ((r = -0.993) of okra, but a low positive correlation (r = +0.200) in the leaves of this plant. As has a positive association in the roots (r = +0.695) and fruits (r = 0.117), but a negative association in the leaves (r = -0.712) of okra.

The correlation studies show that (Table 4.14) Pb uptake and the applied

Pb in the soil are positively related in the roots (r = + 0.996), leaves (r = + 0.958) and fruits (r = 0.997) *of pepper vegetable. Ni correlated* positively and significantly (r = +0.999) with applied Ni in the fruits of pepper. Ni also correlate *positively in the leaves* (r = +0.984) but negatively in the roots (r = -0.882) of pepper plant. Cr correlate negatively and significantly in the leaves (r = -0.998) and, positively and significantly in the fruits (r = +0.998) of pepper. A high positive association (r = +0.931J of As is observed in the roots of pepper. There is a weak positive association of As in the leaves (r = +0.076) and fruits(r = +0.143) of pepper.

The correlation studies on the roots and leaves of lettuce plant are shown on Table 4.12 Pb is positively correlated in the root(r = +0.873) and leaves(r = +0.887) of lettuce plant. Ni has a positive association in roots (r = +0.661) and leaves(r = +0.977) of lettuce. There is a high positive correlation of Cd in the roots (r = +0.949) and leaves(r = +0.929) of lettuce. Cr correlated negatively in the roots and leaves of lettuce. As correlate positively (r = +0.994) and negatively (r = -0.957) in the leaves and roots of lettuce respectively.

The different metals uptakes at the various parts of the plants were studied. In this study Pb uptake is greatest at the applied 0.50 μg/g, concentration, and has its highest values on the leaves of okra and lettuce (Fig 4.1 and 4.2). However, Pb is virtually absent in the roots and leaves of pepper but found mostly on the fruits with the highest value on the applied

0.50 μg/g concentration (Fig 4.2).

Ni uptake is greatest at the 0.25 μg/g concentration in the leaves of okra (Fig 4.1), but has its greatest value in (Fig 4.2) on the roots and leaves of lettuce (0.25 μg/g). The distribution of Ni is very low in the roots of pepper, but distributes progressively on the fruits with highest value at the 0.50 μg/g (Fig 4.3).

Fig 4.1 shows that Cd has its greatest uptake values on the control of roots, 0.25 μg/g of leaves; 0.25 μg/g and 0.50 μg/g of fruits of okra. Overall, the distribution is highest on the fruits. The roots and leaves of lettuce at the applied ion metal concentration of 0.50 μg/g have the greatest uptake (Fig 4.2). In pepper, Cd is highly concentrated on the fruits with the highest value at the 0.50 μg/g level of the applied metal. Cr like Cd has the greatest value in the control of the roots of pepper. The leaves of lettuce have higher Cr concentration with the highest value at the 0.10 μg/g (Fig 4.2). However, this heavy metal is found distributed in increasing order of applied metal concentration on the fruits of pepper.

As uptake decreases in the order of roots, leaves and fruits of okra, with highest values on the roots of 0.50μg/g applied concentration and the control (Fig 4.1). However, As has higher uptake value in the leaves of lettuce compared to the roots, with the greatest value on the applied 0.50 μg/g of the leaves. As is found almost evenly distributed at the 0.50 μg/g of roots, 0.10 μg/g and 0.50 μg/g of both the leaves and fruits of pepper (Fig 4.3).

Table 4.10. Pearson correlation coefficient between applied metal and metal uptake in okra

Metal	Pearson correlation coefficient (r)		
	Roots	Leaves	Fruits
Pb	0.848	0.840	0.686
Ni	0.961	0.490	0.911
Cd	-0.012	-0.012	0.786
Cr	-0.860	0.200	- 0.993
As	0.695	-0.712	0.117

Table 4.11. Pearson correlation coefficient between applied metal and metal uptake in pepper

Metal	Pearson correlation coefficient (r)		
	Roots	Leaves	Fruits
Pb	0.996	0.958	0.997
Ni	-0.882	0.957	0.999
Cd	-0.229	0.984	0.619
Cr	0.698	-0.998	0.998
As	0.931	0.076	0.143

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

Table 12. Pearson correlation coefficient between applied metal and metal uptake in lettuce

Metal	Pearson correlation coefficient (r)	
	Roots	Leaves
Pb	0.873	0.887
Ni	0.661	0.977
Cd	0.949	0.929
Cr	-0.845	-0.358
As	-0.957	0.994

4.9 CONCLUSION

The conclusion drawn from this study is that, of all the vegetable plants studied (Lettuce, Okra and pepper) lettuce accumulated the highest concentration of Lead (35.07µg/g) in the Roots, followed by Okra (0.28µg/g) in the roots and pepper (0.25µg/g) in the roots. The absorptions of other metals in these vegetable plants are relatively lower. It is known fact that cadmium exists mainly as free ions at acidic pH, where as the other four metals occur mostly as either organic or inorganic complexes.

Results obtained for Lead, Nickel, Cadmium, Chromium and Arsenic on the tables of lettuce, okra and pepper, indicate that the vegetable plants have a way of controlling metal uptake from the soil to root, stem, Leaves and to the fruits. It is also a clear fact with the result that the concentration of these metals in soils does not necessarily determine the concentration in the vegetable plant.

The vegetable plant took what it needed for its metabolic activities irrespective of the level or concentration of the metals in the soil.

4.10 RECOMMENDATION

1. Generally, all the vegetable plants lettuce, okra and pepper, has accumulated

little or much of this trace element Pb, Ni, Cd, Cr and As in their roots, leaves or fruits, and this trace metals at high concentrations becomes dangerous to the human health. Therefore, it is recommended that care should be taken to properly investigate where this vegetable plants are grown, since soil polluted with this metals may accumulate it.

(ii) In this study the analysis of the metal concentration in the different parts of the vegetable plants was carried out using Atomic Absorption Spectrometric method (A. A. S) and Energy dispersive x-ray fluorescence. (ED-XRF) other methods of analysis of the metal concentration such as differential pulse poloragraphy, (DPP). Neutron activation analysis and induction coupled plasma atomic emission spectrophotometry (ICP - AES) e.t.c could be employed.

(iii) The present study is limited to only a few metals and crops. Therefore, the study should be extended to cover other toxic metals and other different vegetable plants.

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APPENDIX

CALIBRATION CURVES FOR LEAD, (Pb), NICKEL (Ni), CADMIUM (Cd) AND CHROMIUM (Cr)

Calibration curve for Lead (Pb)

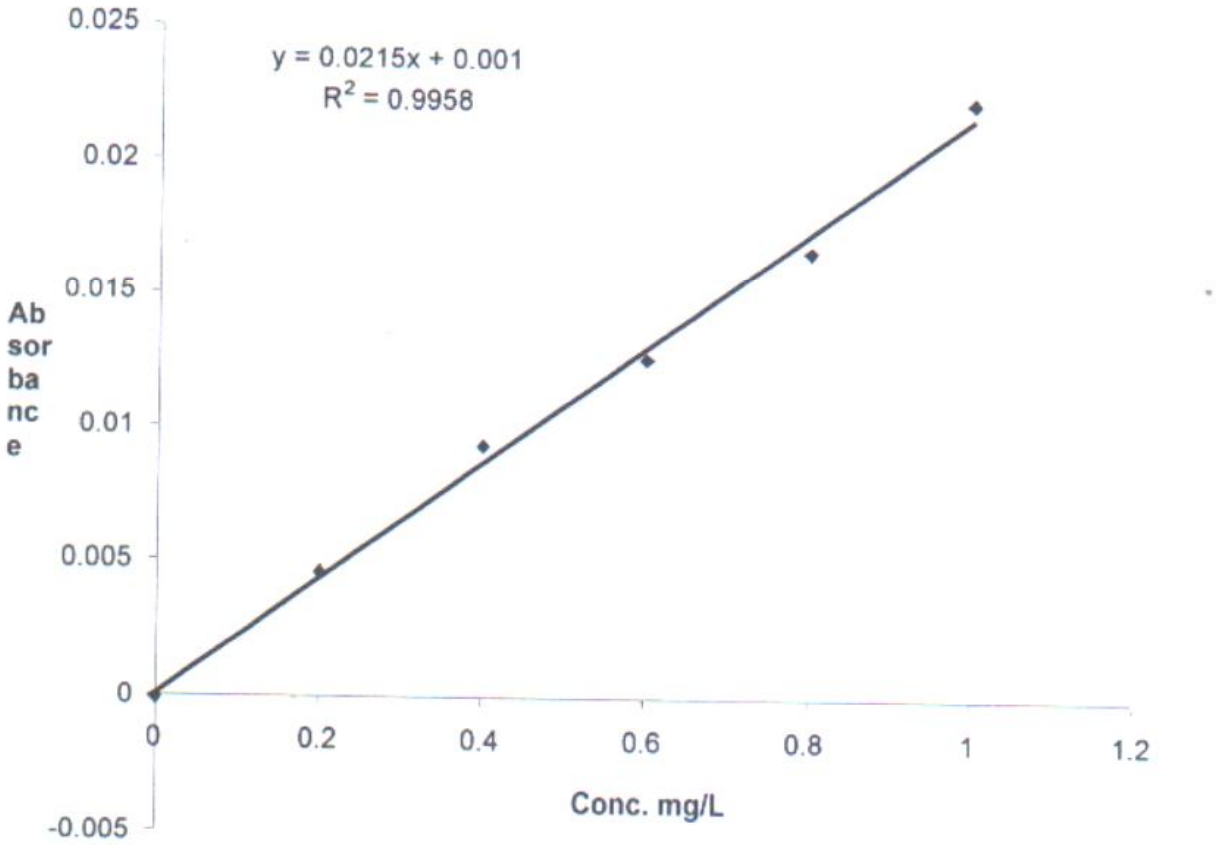


Figure A: Calibration curve for Lead (Pb)

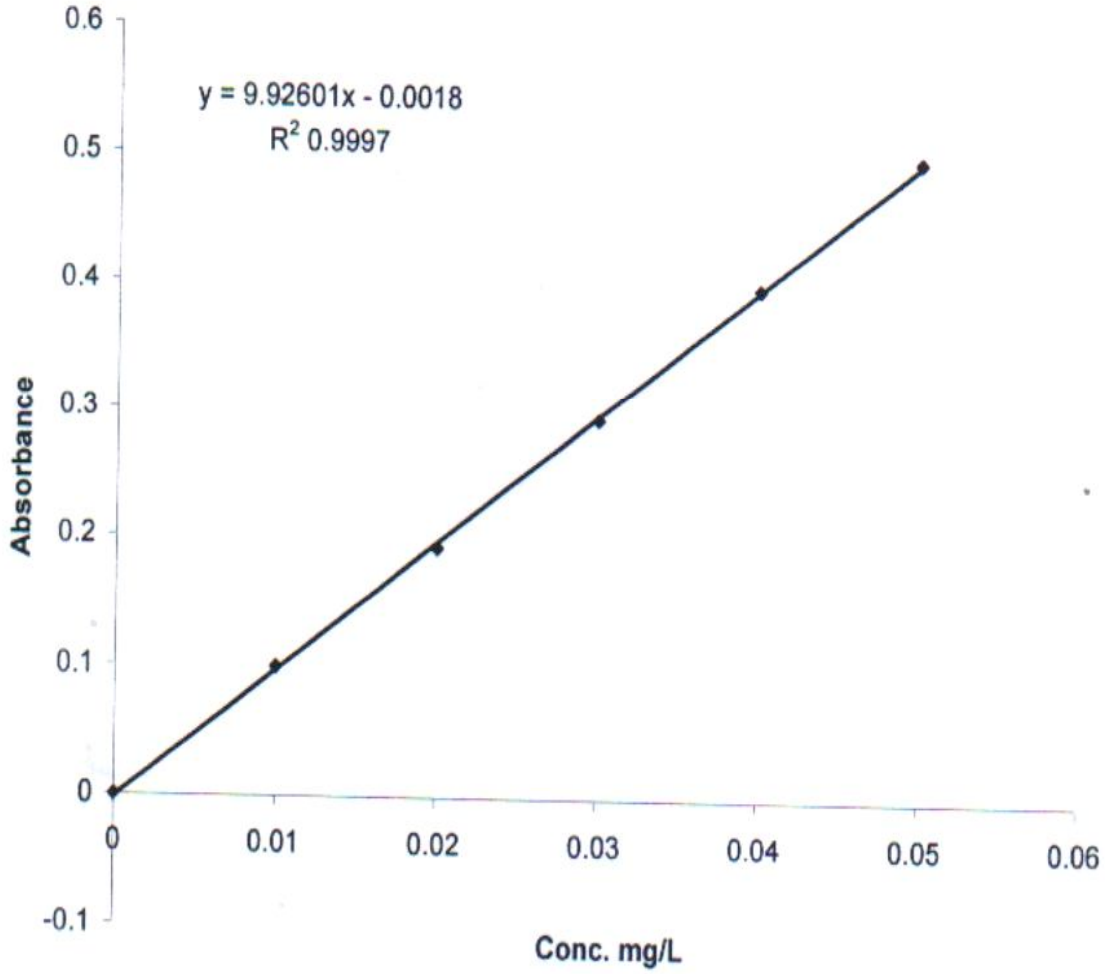


Fig C: Calibiration curve for Cadmium (Cd)

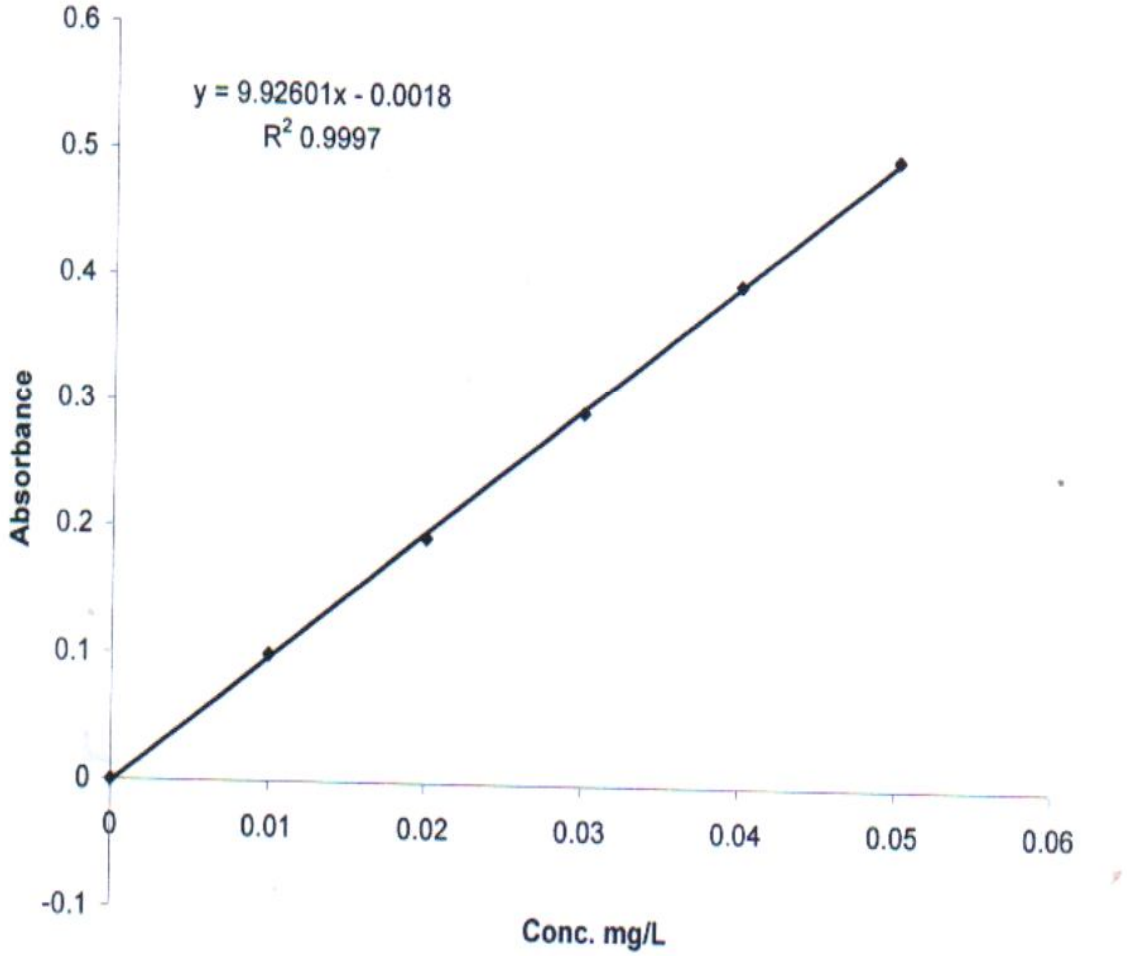


Fig C: Calibiration curve for Cadmium (Cd)

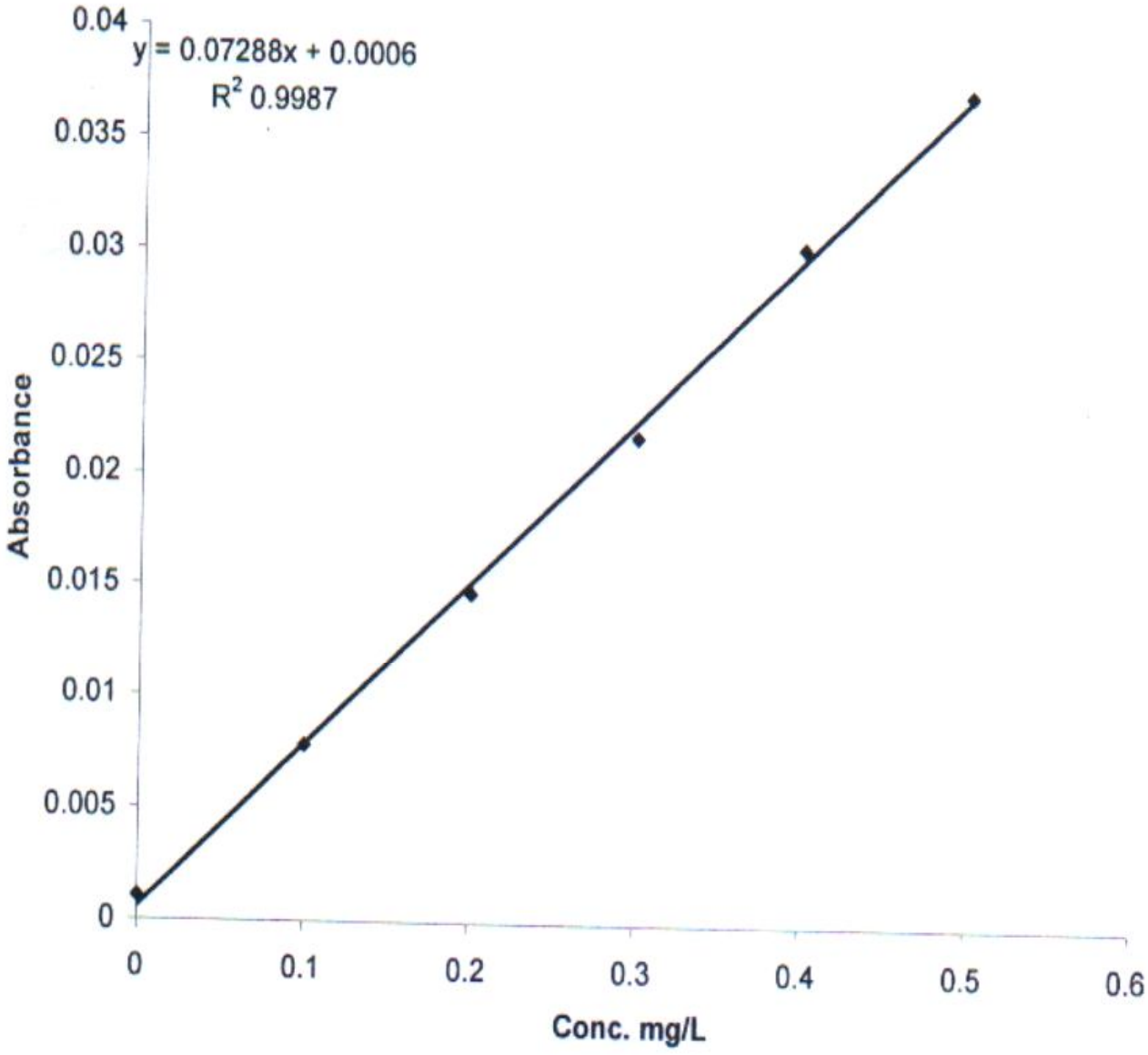


Figure D: Calibration curve for Chromium (Cr)