TRACE METAL RISK ASSESSMENT IN VEGETABLE CROPS IRRIGATED WITH SEWAGE WATER AND SLUDGE ALONG KUBANNI RIVER DRAINAGE BASIN IN ZARIA METROPOLIS, NIGERIA.

BY

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DECLARATION

I hereby declared that the work reported in this thesis entitled ‘‘Trace Metal Risk Assessment in Vegetable Crops Irrigated with Sewage Water and Sludge Along Kubanni River Drainage Basin in Zaria Metropolis, Nigeria’’, has been conducted by me in the Department of Chemistry under the supervision of Dr. A. Uzairu, Prof. G. F. S. Harrison and Mr. P. A. P. Mamza.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

_____ _____

Name of Student and Signature Date

CERTIFICATION

The Thesis entitled ‘‘Trace Metal Risk Assessment in Vegetable Crops Irrigated with Sewage Water and Sludge Along Kubanni River Drainage Basin in Zaria Metropolis, Nigeria’’, by Adamu Haruna meets the regulations governing the award of Masters of Science of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my parents, Malam Adamu Iliyasu and Malama Aisha Adamu (Lami), for all their parental guidance, care, prayers and protection which have gone a long way in bringing me to this milestone. May God bless them both and give them peace in this world and hereafter.

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ABSTRACT

The concentration levels of trace metals in spinach and lettuce irrigated with sewage water on agricultural lands in metropolitan Zaria were determined in a 3-month monitoring programme (February − April, 2008). The investigation was carried out in the biggest sewage water - irrigated vegetation in the city, which is a *fadama* land (flood plain) along river Kubanni drainage basin. Samples of spinach, lettuce, sewage water, sewage sludge and soil from the study area, as well as samples of tube-well water, soil, spinach and lettuce from a control area were analysed for five trace metals (Zn, Ni, Cu, Pb and Cd) using atomic absorption spectrophotometry (AAS). The physico-chemical characteristics of the sewage water, tube-well water, sewage sludge and soil samples, and the fertility of the sewage sludge were also evaluated. The results obtained showed that sewage water quality characteristics were mostly beyond the permissible limits as recommended by the Food and Agriculture Organisation (FAO) and United State Environmental Protection Agency (USEPA). The levels of Cd, Cu, Pb, Cl^- and NO_3^- in sewage water samples analysed were also found to be higher than the respective reference values for irrigation water.

Furthermore, the results indicated a substantial build-up of trace metals in soil and vegetables that were grown with sewage water. The levels of Cd, Cu and Ni in soils, as well as the levels of Cd and Pb in vegetables were beyond the permissible limits recommended by FAO, USEPA and EU, suggesting that irrigation with sewage water resulted in an obvious increase of trace metal content in soil ($P > 0.05$). In fact, metal transfer factors from soil to spinach and lettuce were found significant for Pb, Ni and Cu. The mobility and bioavailability of the five metals in sewage sludge and soil samples were also assessed using a six step selective sequential extraction scheme for partitioning the metals into different chemical forms.

The results obtained showed that the residual fractions of both sewage sludge and soil samples were the most abundant pool for all the trace metals examined. The mobility and the potential bioavailability of the metals investigated were in the order: Pb > Zn > Cu > Ni > Cd and Ni > Zn > Pb > Cd > Cu for soil and sewage sludge samples, respectively.

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CHAPTER ONE

1.0 INTRODUCTION

1.1. Background

Rapid population growth and extensive damage from natural disasters have intensified the worldwide struggle for adequate food supplies. Thus, the urgency of increasing food production becomes patently obvious while one of the basic inputs required for achieving this still remains water. If adequate supply and control of water are not ensured, it is very difficult to grow crops and vegetables more than once a year. Conversely, to achieve optimum production of these farm produce, adequate use of available natural resources or development of new natural resource becomes necessary if starvation and malnutrition and their related problems, are to be minimized.

Many parts of the world where rainfall is not adequate have so far developed new methods of harnessing natural resources, which may be either surface dams or reservoirs for their domestic, irrigation and livestock activities. Similarly, places where rainfall is seasonal and the aforementioned facilities are also not available, sewage water from drainage basins or ponds (pools of stagnant water) have been put to use for small-scale irrigation to supplement rainy season farming. The use of this facility for irrigating farm lands has long been noted in northern Nigeria where rainfall is seasonal.

The use of sewage water on farmlands provided copious resource products (e.g. carrot, lettuce, onion and other vegetables) and a sustainable livelihood to several number of people in Northern Nigeria. On the other hand, use of this delicate resource can result into numerous health and environmental problems. Obviously, the chemical status of this delicate resource would have its influence on the receiving lands, which might possibly reflect on the produce

cultivated on such lands and subsequently ends up within the inner system of humans and becomes a danger to life.

The possibility of trace metal transfer from sewage water and sludge to humans through the food chain in many cities in Northern Nigeria is of great concern. The toxic trace metals entering the ecosystem may lead to geoaccumulation, bioaccumulation, and biomagnifications. Trace metals like Fe, Cu, Zn, Ni and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Ward, 1995). Food chain contamination by trace metals has become a burning issue in recent years because of their potential accumulation in bio-systems through contaminated foods, water, soil and air. Therefore, a better understanding of trace metal sources, their accumulation in the soil and the effect of their presence in water, soil and plant systems seem to be particularly important issue of present-day research on risk assessments (Rajesh *et al*., 2004).

Most of our water resources are gradually becoming polluted due to the addition of foreign materials from the surroundings. These include organic matter of plant and animal origin, land surface washing, and industrial effluents and domestic sewage (KSPCB, 2002). Rapid urbanization with improper environmental planning often leads to discharge of domestic sewage into lakes and rivers. The lakes and rivers have a complex and fragile ecosystem, as they do not have self-cleaning ability and therefore readily accumulate pollutants. River Kubanni drainage basin is no exception being one of the drainage basins that drain Southern Zaria, through which domestic sewage, refuse and wastes from abattoir find their ways into the river basin. Trade wastes (from auto-mechanics, hotels, and road side car-wash operators) are also directly or indirectly drained into the river basin.

Fadama land (Flood plain) along Kubanni River basin in Zaria city is noted for agricultural irrigation practices both for subsistence and small scale farming during dry seasons for many years. The River is a seasonal river, with intermittent flows occurring in flashes mainly during rainy season (Eigbefo, 1978; KDSG, 2000) and, thus chiefly becoming sewage - bearing river in dry seasons. This has eventually forced the farmers to be using the raw sewage water for irrigation due to dearth of fresh water from the River during dry seasons.

However, it has been reported that sewage water of municipal origin contains appreciable amount of major essential plant nutrients and therefore the fertility levels of soil are improved considerably under sewage irrigation of vegetables (Rajesh *et al.*, 2004). But the application of raw sewage water in soil may give rise to accumulation of trace metals such as Pb, Cd, Ni, Cu, Zn, Hg and Cr in the top soil (Williams *et al*., 1980) and hence in the tissues of plants grown on them (Day *et al*., 1979). As such, this may become important pathways of human exposure to metal contamination. It is with this consideration that it becomes necessary to investigate the level of trace metals in vegetable crops grown with sewage water. Although water is commonly employed as a pollution indicator of trace metals, sewage sludge can also provide deeper insight into threat to water contamination. Indeed sewage sludge is ready sink or reservoir of pollutants including trace metals where they accumulate to pollution level (Onyari *et al*., 2003).

1.2 **The Research Problem**

The Kubanni River is one of the most important rivers draining Zaria and its environ. Much considerations and attention have been given to this river because of the numerous

farming and irrigation activities that take place seasonally along its course, as well as its economic importance to the inhabitants. A great number of Zaria peasants have farms along the course of the River, from which they obtain their food stuffs (such as maize, rice, sugarcane and vegetables such as tomato, garden egg, carrot, lettuce, cabbage, onions etc). Many of the farming activities take place during dry season by irrigation. Unfortunately, the River is prone to pollution due to all forms of human activities that take place around it.

Environmental pollution is one of the most investigated subjects of research at present time. Most industrial and municipal wastes end up in rivers, lakes and sea. Hence, the idea of having continuous survey of water quality receives wide spread attention. In recent years, because of industrialization and increasing population, water pollution has become an important problem all over the world (USEPA, 1984). Inorganic materials have proved to be much more persistent than organic matter as sewage pollutants, since the former are not readily removed by *in situ* oxidation, and, may render the water unsuitable for irrigation. Thus, it is important to investigate the state and quality of sewage and its sludge in terms of trace metal load and its influence on the receiving vegetation along the river course, as well as the vegetables that are grown with the sewage water. The human activities that are likely to cause pollution of the Kubanni River include:

(i) Disposal of domestic wastes

(ii) Food processing

(iii) Biological wastes from Zango Village and the abattoir

(iv) Domestic and artisenal/micro industrial intrusion, e.t.c.

These entire wastes eventually drained into the Kubanni River. There is, therefore, the need to monitor periodically the Kubanni waterway for trace metals. It is for this reason that

the sewage water, which is being put to use for irrigation during dry seasons, its sludge, soil of the irrigated sewage vegetation and the vegetables that are grown with sewage water would be screened for trace metal content.

Although there is some information on the levels of trace metals on soil and some vegetables grown on the bank of River Kubanni in the literature, there are no comprehensive studies at one time on the levels of trace metals in sewage water, soil, sewage sludge and vegetables from the River bank. Thus, there is need to carryout such a comprehensive investigation on the sewage water, sludge, soils and vegetables grown on the river bank, so as to evaluate the trace metal health status of the vegetables and to have some insight into the impact of sewage water used for irrigation activities in the area.

1.3 **Justification**

Studies have shown that uptake and accumulation of metals by different plant species depend on several reasons (Lokeshwari and Chandrappa, 2006). Unlike other pollutants that are visible, trace metals may bioaccumulate in vegetable crops to toxic levels unnoticed.

Because the Kubanni River is a sewage-bearing river in the dry season and is used for growing vegetable crops, it becomes imperative to periodically screen all the compartments of the River bank, most especially crops, for their trace metal status. Thus, it is important to investigate the state and quality of sewage water and its sludge in terms of metallic load and its influences on the receiving vegetation along the bank of the River. Considering the production level and consumption of the vegetables, significant level of trace metals in the vegetables may lead to ingestion of toxic metals by consumers at unacceptable levels.

1.4 **Aim and Objectives**

The aim of this study is to investigate the trace metal health status of vegetable crops grown with sewage water along Kubanni River bank, Zaria, Nigeria. This will be achieved by pursuing the following objectives:

a. Determination of the physico-chemical parameters of sewage water and sludge from the study area as well as tube-well water, which is also used by the farmers that are not close to the River to grow vegetables as control.

b. Determination of the physico-chemical parameters of the River bank soil on which the vegetable crops are grown with sewage water as well as the soil on which tube well water is used as control.

c. Determination of the concentrations of Zn, Ni, Cu, Pb and Cd in sewage water, sludge, soils and vegetables (spinach and lettuce) in the study area.

d. Determination of the same metals in tube-well water, soils and vegetables (spinach and lettuce) in the control area.

e. Assessment of fertilizer capacity of sewage sludge of the study area.

f. Determination of chemical fractionation of Zn, Ni, Cu, Pb, and Cd in sewage sludge and soils in order to assess the mobility/availability of the metal from soils to vegetables.

g. Determination of water and soil contamination risks based on the individual and global trace metal contamination factors.

h. Establishment of trace metals pollution status of sewage water, sludge, soils and vegetables (spinach and lettuce) by comparison of results to international limits for trace metals.

1.5 **Scope and Limitation of the Study**

The study concentrates on the sewage water irrigation of *fadama* land along Kubanni River basin and is aimed at determining concentration levels of trace metals in the four environmental compartments of the study area namely, sewage water, sewage sludge, soil and vegetables (spinach and lettuce). Physico-chemical parameters of sewage water, sewage sludge and soils were also analyzed. Cost was the majr factor in limiting length of investigation and sample size in the study. Thus, samples of the four compartment of the study area were collected during the dry season only. The AAS analysis was done at the price of fifty naira (N50.00) per element per sample. This limited the number of sampling points as well.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Trace Metals

The term trace metals, trace elements, toxic metals and heavy metals are used interchangeably and this sometimes causes confusion (Jannett *et al*., 1980; and Thornton *et al.*, 1981). According to USEPA (1984), the heavy metals are oftentimes referred to as trace elements or trace metals. According to Passow *et al.* (1991), the term heavy metals is not rigidly defined and is generally held to refer to those metals having a density greater than five, about forty (40) elements in all. However, more precisely, IUPAC (2002) defined trace metals as metals found in low concentration, in mass fractions of ppm or less, in some specified sources, e.g. soil, plant, tissue, ground water, etc. Some of these metals may be important trace elements in the nutrition of plants, animals or humans (e.g Zn, Cu, Mn, Cr, Ni and V), while others are known to have negative nutritional effects (e.g. Cd, Pb and Hg); all of these trace metals may cause toxic effects if they occur excessively (Spiegel, 2002).

2.2 Trace Metal Pollution of Sewage Water

Sewage or wastewater is the used water supply of a community. It consists of outflow from domestic and industrial premises and run-off from roads. The sewage water is composed of domestic-borne waste such as human excrement, wash water and industrial water-borne wastes like oils, animal and vegetable wastes. It also consists of ground, surface and atmospheric water (Ojeka, 2007).

There is a lot of literature outlining the benefits and risks of using sewage (Furedy and Chowdhury, 1996). Sewage has provided an invaluable input into development. For instance

peri-urban aquaculture alone sustains several thousand jobs (Lewcock, 1995). Using sewage for irrigation enables farmers to produce vegetable crops during dry season. For example, in Kano (Nigeria) and Hubli Dharwad (India), most sewage-bearing streams carry water all year round, thus enabling farmers to cultivate their plots of land even during dry season and sell them at a higher wholesale price (Lewcock, 1995). However, since the wastewater (sewage) is heavily polluted with faecal matter and trace metals there are some risks attributed to its use (Furedy and Chowdhury, 1996). The application of sewage can contaminate agricultural products, externally and internally with coliform bacteria and other pollutants, putting not only the farmers but also the consumers at risk when the produce is eaten raw.

In many areas of the world urban agriculture depends on water supplies for irrigation. Water is often extracted from rivers, and these may be contaminated with wastewater (sewage), discharged into rivers with little or no prior treatment. In some areas, untreated wastewater is used for irrigation directly (Blumenthal *et al*., 2004). The use of little treated or untreated sewage water on vegetation has the potential to create environmental pollution because of the likely high contents of toxic trace metals and thus, can increase the risk of chemical attack to consumers of the vegetable crops that were raised with sewage water. Pollution problems may arise if toxic trace metals are metabolized into the soil solution and then taken up by plants and later consumed by humankind. Therefore, trace metals are being transferred along the water – soil – plant – animal – human chain. It has been reported that domestic wastewater contains considerable amount of trace metals, of which has been put to use for irrigation (Shomar *et al*., 2003). Besides, even the treated sewage water also contains variable amounts of trace metals such as Pb, Ni, Cd, Cu, Hg, Zn, and Cr, which have the potential to contaminate vegetation under such irrigation (Lokeshwari and Chandrapa, 2006).

It has also been reported that sewage effluents of municipal origin contain appreciable amount of major essential plant nutrients and therefore the fertility levels of the vegetable crop fields are improved considerably when sewage water is used to grow crops (Rajesh *et al*., 2004). However, studies on the sewage water revealed that the presence of toxic trace metals like Fe, Pb and Hg reduce agricultural output (Lakhande and Kelkar, 1999). In addition, application of raw sewage water in soil may give rise to accumulation of trace metals in the top soils (Williams *et al*., 1980). Thus, the chemical composition of sewage can be a good indicator of trace metal induced pollution of vegetation irrigated with sewage water.

2.3 **Bioavailability of Trace Metals in Sewage Water**

Even though a number of literature reports have confirmed the presence of trace metals in domestic wastewater, their ability to enter into the ecosystem depends on their bioavailability (water solubility) (Lokeshwari and Chandrappa, 2006). The bioavailability of trace metals in wastewater depends on the concentration of anions and chelating ligands present in water, pH and redox status and the presence of adsorbent sediments (Mido and Satake, 2003). If the bioavailability of metals with respect to total metal content occurs, then the metals will be readily available for plant uptake (Lokeshwari and Chandrappa, 2006). It is with this consideration that some metals may be much more readily bioavailable than the other(s) for plants. In addition, water acidity is known to influence the solubility and, therefore, the availability and toxicity of metals in the aquatic ecosystem (Awofolu *et al*., 2005).

2.4 **Trace Metals in Sewage Sludge**

Sludge is the insoluble residue from sewage water that separates out during *in situ* sedimentation process or when sewage water is subjected to treatment (Servinc *et al*., 2002). Sludge comprises resistant organic compounds (60% organic matter), nitrogen, phosphorus, other macronutrients (such as K_2O, CaO, MgO), a wide range of macronutrients and nonessential trace metals. It may also contain organic micro-pollutants, micro-organisms and eggs of parasitic organisms (Servinc *et al*., 2002). Farmers have for long discovered the nutritional potential of sewage sludge to plants and have been applied on soil as a source of nutrients for crops production (Garcia *et al*., 1991). However, this practice has the potential to create environmental pollution problems because of the likely high contents of toxic trace metals that are present in sludge (Chakraborty *et al*., 1987; Petruzzelli *et al*., 1995; Berrow and Burridge , 1990; Evans *et al*., 1995; Karpati, 1994).

Pollution problems may arise if toxic trace metals are metabolized into soil solution and subsequently are either taken up by plants or transported in drainage waters to associated water supplies (Zufiaurre *et al*., 1998). Although water is commonly employed as a pollution indicator by trace metals, sewage sludge, being the sediment of sewage, can also provide a deeper insight into the long-term pollutants' state of the water-body. Sediment has been described as a ready sink or reservoir of pollutants, including trace metals (Becker *et al*., 2001; Onyari *et al*., 2003). Sewage sludges act as sediments and is therefore a sink and constant source of supply of pollutants that enter sewage water and receiving river or water body depending on physical, biological and chemical factors such as oxidation – reduction, sorption-desorption processes, etc (Jannett *et al*., 1980; Lee *et al*., 2003;). Thus, the chemical

composition of sewage sludge can be a good indicator of trace metal status of sewage-bearing river (Binning and Baid, 2001).

Agronomic benefits of sludge application to crops are well documented (Lindsay and Logan, 1998). However, Berti and Jacobs (1998) reported that sewage sludge may contain trace metals such as Cd, Cr, Cu, Hg, Ni, Pb and Zn that are of environmental concern. In addition, when soil is amended with sewage sludge a new source of trace metals is introduced (Shrivastava and Banerjee, 2004). Sewage sludge is composed of different phases (fractions) and metal ions partition between these fractions which include water soluble, Exchangeable, Carbonatic, Reducible (bound to oxides), Oxidizable (bound to organic matter) and residual fractions. It is with the aid of these phases (fractions); the bioavailability index of trace metals in sewage sludge is usually indicated and used to predict their mobility when sewage sludge is discharged into the environment (Zufiaurre, *et al.*, 1998).

2.5 **Trace Metals in Soil**

Trace metal concentration in the soil of urban areas cannot be attributed solely to geological factors alone. Human inputs also play a predominant role in the development and modification of the soil from these areas. Although non-urban soils have been reported to also be polluted by trace metals, urban soils have higher concentration of trace metal pollutants (Chirenje, *et al.*, 2003; Oluwole, *et al.*, 1994). When soil is amended with sewage sludge a new source of trace metals is introduced. Unless the retaining properties of the resulting amended soil are increased in accordance with this, trace metals may spread to the surrounding environment (Shrivastava and Banerjee, 2004). The anthropogenic deposition of trace metals in agricultural soil will either become detrimental to plant growth or to the consumers of the

harvested crops depending on the chemical form of the metals present in the soils (Chaney and Giordano, 1977; Latterell *et al*., 1978; Mahler *et al*., 1980). Plants are known to take up and accumulate trace metals from contaminated soils (Singh and Narwal, 1984; Bojakowska and Kochany, 1985; Pulford and Watson, 2003; Madejon *et al*., 2003). A major part of trace metals is taken up by crops from soil via roots (Lokeshwari and Chandrappa, 2006).

Several studies have indicated that vegetables, particularly leafy crops, grown in trace metal contaminated soils have higher concentrations of trace metals than those grown in uncontaminated soils (Guttormsen *et al*., 1995; Dowdy and Larson, 1975). Another major route of soil contamination is through atmospheric deposition of trace metals from point sources such as metaliferous mining, smelting and industrial activities. Other non point sources of contamination affecting predominantly agricultural soils include inputs such as fertilizers, pesticides, sewage water, sewage sludge, organic manures and composts (Singh, 2001).

2.6 **Bioaccumulation of Trace Metals in Soil**

Soils are particularly important in the attenuation of trace metals in the environment because they contain surface-active mineral and humic constituents that are involved in metal retention and accumulation (Rudd *et al*., 1986). The global concern about trace metals in the environment arose from their persistence, toxicity and bioaccumulation in the food chain, i.e. water-soil-plant-animal-human chain (Welch, 1980; Shrivastava and Banerjee, 2006). In terms of soil, bioaccumulation is the deposition and storage of toxic trace metals in soil such that soil concentrations continue to rise with prolonged exposure to the metals (Mattley *et al*., 2003). Beside the surface-active mineral and humic constituents, soil texture and soil activity can also

influence retention and bioaccumulation of trace metals in soils (Francis, 2005). The rate at which trace metals are mobilized into soil solution and taken up by plants is a major factor determining the level of bioaccumulation of trace metals in soil (Francis, 2005).

2.7 **Bio-mobility of Trace Metals in Soil**

The problems of pollution of trace metals from soil arise if toxic metals are mobilized into soil solution and are either taken up by plant or transported in drainage waters to associated water supplies. Whether the plant uptake or transportation in drainage waters, it all depends on the bio-mobility of trace metals in soils. A major part of trace metals is taken up by crops from the soil through roots. Trace metal transportation from soil to the roots largely depends on the type and genetic features of soil, granuliometric soil composition, amount of organic matter, pH of the soil, sorption capacity and amount of $CaCO_3$, anthropogenic load and other chemical and physical properties of the soil (Olaniya *et al*., 1998; Baltrenaite and Butkus, 2004). Adsorption of trace metals onto the oxide phase of soils has been found to be important factor for many trace metals that significantly affects their mobility in soils (Baltrenaite and Butkus, 2004). Laboratory experiments have demonstrated that titanium oxides (TiO_2) are strong sorbents for trace metals (Gao *et al*., 2004). Hence, presence of TiO_2 and aluminium (in combined form) in soil may have an influence on the uptake of trace metals by plants. According to Mido and Satake (2003), high concentration of trace metals are found in vegetables when their adsorptive nature in soil is weak. Another study revealed that the biomobility of trace metals is regulated by pH, particle size and cation exchange capacity of soils as well as by root exudation and other physico-chemical parameters (Lokeshwari and Chandrappa, 2006).

The soil pH is of paramount importance in controlling the plant absorption of trace metals since it conditions their mobility in soil. According to Pluquet (1984), an increase of one unit in pH reduces trace metals absorption by plant by 14%. Previous studies have shown that if the pH of soils is maintained at neutral or slightly alkaline then the toxic metals present are relatively immobile (Evans *et al*., 1995). Therefore, soil pH is the key parameter regulating metal behaviour in soil systems (McBride, 1994).

The soil organic matter is another parameter that plays important role in water retention, aggregation and soil structure. It is a measure of soil fertility and could also affect the mobility of metals from soil to plants. Organic matter is known to form complexes with trace metals, which influences the availability and mobility of the latter (Sauve *et al*., 1998). For instance, Cu and Pb form very stable complexes with dissolved organic matter, and only a very small fraction of these metals exists as free hydrated metal ions, when soil pH is not strongly acid (Aualiitia and Pickering, 1986; Sauve *et al*., 1998). Moreover, Kretzchmar and Voegelin (2001) reported that trace metals that are released into soil from anthropogenic load would in long term be subsequently immobilized by re-adsorption to the soil solid phases or by the formation of new solid products such as hydroxides, hydrotalcite, or phyllosilicate structures.

2.8 **Trace Metals in Vegetables**

Several studies have indicated that vegetables, particularly leafy crops, grown in trace metal contaminated soils have higher concentration of trace metals than those grown in uncontaminated soil (Guttormsen *et al*., 1995; Dowdy and Larson, 1975). Additionally, foliar uptake of atmospheric trace metal has also been identified as an important pathway of trace

metal contamination in vegetable crops (Bassuk, 1986; Salim *et al*., 1992). Therefore, the main source of trace metals to vegetable crops are their growth media (soil, air, nutrient solutions) from which these are taken up by the roots or foliage. In addition, plants are known to take and accumulate trace metals from contaminated soils (Singh and Narwal, 1984; Bojakowska and Kochany, 1985; Pulford and Watson, 2003; Madejon *et al*., 2003). According to Sanders *et al*. (1986); and Omran and Waly (1988), trace metal accumulation in the plant tissues did occur when agricultural soils are amended with sewage sludge or irrigated with sewage water.

Furthermore, accumulation of trace metals by vegetable crops in sewage irrigated soils has been reported by Malla *et al*. (2007) and recorded high levels of Zn, Pb, Ni, Cu and Cd in the leaves of vegetable crops harvested from sewage water irrigated soils. The average mean concentrations of Zn and Ni were 144.22 and 76.63 mg/kg, respectively. The concentrations of Cu, Pb and Cd were 111.75, 24.47 and 4.10 mg/kg, respectively. In a similar study, Arora *et al. (*2008) reported a substantial build-up of trace metals in vegetables irrigated with wastewater. The range of various metals in wastewater – irrigated plants was 16-378, 12-69, 5.2-16.8 and 22-46 mg/kg for Fe, Mn, Cu and Zn, respectively.

Rattan *et al*. (2005) also reported the presence of Zn, Cu, Ni, Fe and Pb in the vegetables grown on the sewage water- irrigated soils, but only Zn exceeded the phyto-toxicity limit. Abdel-hady (2007) studied plant uptake of trace metals from soils irrigated with polluted water and found that trace metals accumulated in the vegetables that grew on the polluted water – irrigated soils. Specifically, 52.1, 6.0, 50.0, 21.8 and 1.3 mg/kg levels for Zn, Cu, Ni, Pb and Cd, respectively, were obtained for crop studied.

However, studies have revealed that trace metals do not readily accumulate in the fruiting part of vegetable crops; higher concentrations are more likely to be found in leafy vegetables (Rose, 2002). Leafy vegetables rose with sewage water and contaminated with Cu, Pb, Zn, Ni, Co and Cd have also been reported in Poland, India, Russia, Taiwan and China (Flynn, 1999).

2.9 **Mechanism of Trace Metal uptake by Vegetables**

Most of the laboratory researches on biosorption (uptake) of trace metals indicate that no single mechanism is responsible for metal uptake (Lokeshwari and Chadrappa, 2006). In general, two mechanisms are known to occur, viz. 'adsorption', which refers to binding of materials onto a surface and 'absorption', which implies penetration of metals into the inner matrix of plant body (Ramraj *et al*., 2000). Either one of these or both the mechanisms might take place in the transportation of metals into the plant body. Different vegetable species accumulate different metals depending on environmental conditions, metal species and available forms of the metals. Studies have shown that uptake and accumulation of metals by different plant species depend on several factors, and various researchers have identified several reasons (Bingham *et al*., 1975; Dowdy *et al*., 1978). These factors include pH, texture as well as particle size and cation exchange capacity of soil (Harrison, and Chirgawi, 1989). The soil pH is of paramount importance in controlling the plant absorption of trace metals since it conditions their mobility in soil (Servinc *et al*., 2002). Another factor which influences the uptake of trace metals by vegetable plants through root cells is the valency nature of toxic cations (Francis, 2005). For instance, univalent cations enter root cells at faster rate than bivalent and multivalent ones (Francis, 2005). Besides, the uptake of trace metals by vegetable

plants is also plant-species dependent (Oyedele *et al*., 1995; Hooda *et al*., 1997; Rasheed and Awadallah, 1998). For example, a study revealed that the order of toxic trace metals contamination in vegetables is as follows: spinach>radish>brinjal>beans (Lokeshwari and Chandrappa, 2006).

2.10 **Studies of Trace Metals in Vegetables in Nigeria**

Vegetables are very important part of diet. In Nigeria, general public awareness on the safety of vegetables, fruits and other food crops is on the increase (Chiroma *et al*., 2003). In fact, the tradition of growing vegetable crops on contaminated soils or sewage sludge and/or waste solid amended soils has attracted the attention of many environmental scientists. For example, Audu and Lawal (2005) investigated the variation in metal content of plant grown in some garden sites in Kano metropolis. They found the relative abundance of metals found in the plants to follow the sequence Fe > Zn > Mn > Cu > Ni > Pb > Co > Cr. In addition, the vegetables analysed generally showed higher retention capacity for essential metals (Zn, Mn and Cu) than for the toxic ones (Ni, Pb, Co and Cr).

Similarly, Hart *et al*. (2005) investigated crops harvested from some oil prospecting locations in Rivers state, Nigeria. They found that crops from industrialized locations, especially green vegetables, had the highest metal content. Dike *et al*. (2005) reported the levels of Pb, Fe, Cu and Cd (0.799, 0.944, 0.632 and 0.039 mg/kg, respectively) in spinach harvested from wastewater – irrigated soils along banks of River Jakara in Kano, Nigeria. In another study, high concentrations of Cu, Pb, Cd, Fe and Cr in spinach grown along the banks of River Kaduna in Kaduna have also been reported (Ojeka and Achi, 2004).

Chiroma *et al*. (2003) studied trace metal contamination of vegetables and soils irrigated with sewage water and reported high concentration of the metals (Fe, Zn, Cu, Mg, Mn and Pb) suggesting trace metal contamination of soil irrigated with sewage water and their accumulation in different parts of vegetables cultivated in the soil. Similar work by Abdullahi *et al*. (2008) who studied the levels of Zn, Ni, Mn and Cu in tomatoes and onions reported high concentrations of these metals. In addition, Awode *et al*. (2008) also reported the presence of Zn, Ni and Cd in the peppers grown on polluted water-irrigated soils, but only Cd was found beyond allowed limit.

2.11 **Toxicity of the Trace Metals**

Trace metals are natural components of earth's crust. Although at trace levels some trace metals (e.g. Selenium and Zinc) are essential for the human body, most of them are toxic or poisonous even at low concentrations (Ardelt *et al*., 2005). Trace metals include the elements arsenic, cadmium, chromium, lead, mercury, copper and thallium. Typically they enter the body via the food chain, ambient air or drinking water. Unfortunately, ever since the start of the industrial revolution, waterways and coastal waters have been polluted. Likewise, contaminants have been introduced into the soil with negative consequences for the food chain and thus, human health is at risk (Ardelt *et al*., 2005). Similarly, plant uptake is one of the major path ways by which metal from soils enter the food chain (Rasheed and Awadallah, 1998). The food chain plants might absorb enough amounts of trace metals to become a potential health hazard to consumers (Francis, 2005). Also, deposition of trace metal in agricultural soil, through amendment will either become detrimental to plant growth or to the

consumer of the harvested crops depending on the chemical form of metals present in the soils (Chaney and Giordano, 1977; Latterell *et al*., 1978; Mahler *et al*., 1980).

The presence of toxic metals such as Pb and Cd in the environment has been a source of worry to environmentalists, government agencies and health practitioners. This is mainly due to their health implications since they are non-essential metals of no benefit to human (Tyler, 1981; Borgman, 1983).

Toxicity of trace metals is dependent on dosage (Oladimeji, 1983 and Eichler *et al*., 2006). The toxicity of trace metals may sometimes be acute or chronic. Acute toxicity is as a result of large doses of a metal toxicant and symptoms appear rapidly and may result in death. Chronic toxicity is as a result of prolonged exposure to small doses and symptoms appear gradually and may also lead to death (Venugopal and Luckey, 1978). Factors that determine the toxicity of trace metals in water include concentration, speciation, hardness, temperature, dissolved oxygen content, pH, physiochemical form (ionic or complex) and presence of other metals or substances. Toxicity tends to increase as dissolved oxygen and hardness decrease and as temperature increases.

The effect of trace metals on man and animals can be additive, antagonistic or synergistic (Underwood, 1979; Ellis *et al*., 1989). For instance, the metal, together with other elements, e.g. Zn form a toxic "soup" that often acts synergistically. Trace metals are known to induce all kinds of diseases in man and animals, of which will be subsequently discussed when dealing with individual element of trace metals. Virtually all trace metals, including the essential ones (Iron, Copper, etc) are toxic if safe limits are exceeded.

Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering *et al*., 1994). It accumulates mainly in the kidney and liver and high

concentrations have been found to lead to chronic kidney dysfunction. It induces cell injury and death by interfering with calcium (Ca) regulation in biological systems. It has been found to be toxic to fish and other aquatic organisms (Woodworth and Pascoe, 1982). Cadmium has been implicated in endocrine disrupting activities, which could pose serious health problems. In addition, health effects of cadmium include proteinuria, bone lesions, prostate and lung cancer. It is also embryotoxic and teratogenic (Frieberg and Elinder, 1988).

Lead is potentially hazardous and toxic to most forms of life (USEPA, 1986a). It has been found to be responsible for quite a number of ailments in humans such as chronic neurological disorders especially in foetuses and children (Awofollu *et al.*, 2005). Lead is a well known toxic metal and it has been reported to account for about 50% of the total inorganic Pb absorbed by human beings (Mohan and Hosetti, 1998). After absorption by the body, it is carried to soft tissues like the brain, lung, spleen and heart by the blood and finally deposited in the bone where about 90% of the total body lead is found. Lead damages the liver, kidneys, brain, central nervous and reproductive systems (Lovei *et al*., 2000) causing all kinds of diseases.

Zinc, although found to have low toxicity to man can cause some health complications such as fatigue, dizziness and neutropenia (Hess and Schmid, 2002). Some literature sources have also revealed that Zn could be toxic to some aquatic organisms such as fish (Alabaster and Lloyd, 1980). Acute Zn toxicity causes diarrhoea, depression of central nervous system leading to tremors and paralysis etc while chronic Zn toxicity causes growth retardation, faulty reproduction anemia in man (Luckey and Venugopal, 1977).

Copper is classified as essential to life due to its involvement in certain physiological processes. Elevated levels of it, however, have been found to be toxic (Spear, 1981).

Symptoms of acute copper toxicity include hypotension, anemia and cardiovascular collapse while chronic toxicity leads to sporadic fever, vomiting, diarrhoea and jaundice. It is suspected that copper is carcinogenic due to high incidence of cancer among copper smiths (Luckey and Venugopal, 1978).

Nickel is a naturally occurring element found in a number of mineral ores including nickel phosphate, oxides and silicates. It is present in the enzyme urease and as such is considered to be essential to plants and some domestic animals (Awofolu, *et al*., 2005). However, the essentiality of Ni to health has not been demonstrated, but Ni related health effects such as renal, cardiovascular, reproductive and immunological effects have been reported in animals. Also, its toxicity in man are related to dermal, lung and nasal sinus cancer (Holynska *et al*., 1996)

Table 2.1 Trace metals and their effects on plants and human health

Metal	Sources	Agronomic effects	Effect on human health
Cd	Washing powders as an impurity in phosphates, impurity in zinc steel industry, paint and plastic	Toxic to beans, beats and turnips at low concentrations as how as 0.1mg/L in nutrient solutions. Risk of accumulation in plants and soils	very harmful cumulative, poison. food chain source of intake

Pb	Lead-acid batteries, Solder, alloy	Decreases respiration of soil organism and inhibit plant Cell growth at very High concentrations.	Accumulate in skeleton, harmful for children for Children and pregnant Women.
Cu	Plumbing, animal wastes, pesticide, Earth crust	Toxic to Number of plant at 0.1mg/L In nutrient solutions.	Liver cirrhosis. Food main source of intake Uncertain toxicity to humans.
Ni	Industrial effluents	Toxic to a number of plants at 0.5mg/L to 1 mg/L.	Carcinogenic, lack of data on carcinogenic by the oral route.
Zn	Plumbing, animal wastes Pesticide	Toxicity to many plants at widely varying concentrations.	Not a major hazard to Health.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 List of Apparatus and Equipment

1) Conical flask – 125ml, 250ml
2) Beaker – 50ml, 100ml
3) Volumetric flask – 50ml, 100ml, 250ml, 500ml, 1000ml
4) Measuring cylinder – 10ml, 100ml
5) Plastic bottles for samples and digests – 50ml, 120ml
6) Plastic jerry can for samples – 2.0 litres
7) Plastic jerry can for distilled and deionized water – 25 litres
8) Polythene bags
9) Big bowls for washing
10) Plastic buckets
11) Reagent bottles
12) Funnels – small and big ones
13) Stainless steel knives
14) Plastic cutting sheet
15) Filter paper – Whatman no 40 and 42 and grades 1, 934AH,
16) Mortar and pestle
17) Nose guard
18) Eye goggles
19) Drying Oven (Gallenkamp, ov – 160)

20) Dessicator – big (with recharged silica gel)

21) Dessicator – small (with recharged silica gel)

22) Hot plates (Bibby sterling U.K, HC 500)

23) Analytical balance (A and D instrument, GR – 200 – EC)

24) Fume cupboard

25) Thermometer

26) pH/conductivity meter (Hanna, H 1991000)

27) Spectrophotometer (Hach, DR – 2000)

28) Photometer (Perkin-elmer, 6420)

29) Lovibond comparator

30) Steam bath (Gallenkamp, WF 455)

31) Crucibles – small and big ones

32) Burettes

33) Flask shaker

34) Teflon cups

35) Extraction bottles

36) Hydrometer (Perkin-elmer R-200)

37) Glass rod

38) Pipette – 1ml, 5ml, 10ml, 25ml

39) Centrifuge machine (Bard and Latlock auto bench)

40) Centrifuge tubes

41) Retort stand and clamp

42) Pipette pump

43) Watch glasses

44) Foil paper

45) Erlenmeyer flask

46) Kjedahl flask – 500ml

47) Spatula

48) Test tube brushes

49) Buchner funnel

50) Porcelain evaporating dishes

3.2 List of Reagents and Chemicals

1) $AgNO_3$ = Silver nitrate(99% assay, laboratory reagent made by BDH, England)

2) $BaCl_2$ = Barium chloride(AnalaR, made by May and Baker, England)

3) $CaCO_3$ = Calcium carbonate(99% assay, laboratory reagent made by BDH, England)

4) $CaCl_2$ = Calcium chloride(99% assay, laboratory reagent made by BDH, England)

5) Cd $(NO_3)_2$ = Cadmium nitrate(98% assay, laboratory reagent made by BDH, England)

6) Pb $(NO_3)_2$ = Lead nitrate(99% assay, laboratory reagent made by BDH, England)

7) Cu $(NO_3)_2$ = Copper nitrate(98% assay, laboratory reagent made by BDH, England)

8) Ni $(NO_3)_2$ = Nickel nitrate(98% assay, laboratory reagent made by BDH, England)

9) Zn $(NO_3)_2$ = Zinc nitrate(96-103% assay, laboratory reagent made by BDH, England)

10) HCl = Hydrochloric acid(36.5-38% assay, laboratory reagent made by BDH, England)

11) HNO_3 = Nitric acid(70% assay, laboratory reagent made by BDH, England)

12) $HClO_4$ = Perchloric acid(65% assay, laboratory reagent made by BDH, England)

13) HF = Hydrofluoric acid(70% assay, laboratory reagent made by BDH, England)

14) H_2SO_4 = Sulphuric acid(98% assay, laboratory reagent made by BDH, England)

15) KCl = Potassium chloride(AnalaR, made by May Baker, England)

16) K_2CrO_4 = Potassium Dichromate(AnalaR, made by May Baker, England)

17) KH_2PO_4 = Potassium Hydrogen Phosphate(AnalaR, made by May Baker, England)

18) KNO_3 = Potassium Nitrate(99% assay, laboratory reagent made by BDH, England)

19) K_2SO_4 = Potassium Sulphate(AnalaR, made by May Baker, England)

20) Na_2CO_3 = Sodium Carbonate(99% assay, laboratory reagent made by BDH, England)

21) NaCl = Sodium Chloride(AnalaR, made by May Baker, England)

22) NaOH = Sodium hydroxide(97.5% assay, laboratory reagent made by BDH, England)

23) NH_3 = Ammonia(35% assay, laboratory reagent made by BDH, England)

24) NH_4Cl = Ammonium chloride(AnalaR, made by May Baker, England)

25) NH_4F = Ammonium fluoride(AnalaR, made by May Baker, England)

26) NH_4OH = Ammonium hydroxide(AnalaR, made by May Baker, England)

27) EDTA = Ethylenediamiume tetraacetic acid(AnalaR, made by May Baker, England)

28) H_2O = Water (distilled and deionized ones, prepared in the department laboratory)

29) H_2O_2 = Hydrogen peroxide(30-31% assay, laboratory reagent made by BDH, England)

30) Mg $(NO_3)_2$ = Magnesium nitrate(99% assay, laboratory reagent made by BDH, England)

31) CH_3 $COONH_4$ = Ammonium acetate(95% assay, laboratory reagent made by Pharmacos, England)

32) Na_2 EDTA = Disodium ethylenediamine tetracetic acid98% assay, laboratory reagent made by BDH, England)

33) $NH_2OH.HCl$ = Hydroxyl amine hydrochloride(AnalaR, made by May Baker, England)

3.3 **Description of study Area**

Zaria is a city situated in the North central Kaduna State of Nigeria (Fig 3.1) and is located on a plateau at a height of about 570. 56m above sea level in the center of Northern Nigeria, and more than 644 km away from the sea. Zaria is located at latitude11^{o}3'N and longitude 7^{0} 40'E, 128km South-East of Kano and 64km North-East of Kaduna City. Two out of 23 Local Government areas in Kaduna state are in Zaria (Zaria and Sabon Gari LGAs), Fig 3.2.

It is characterized by a tropical climate with two distinct seasons; a rainy season (May – October) and a dry/Harmattan season (November – April). Based on the classification of geographical regions of Nigeria, Zaria falls into the Guinea Savanna Climate (Udo, 1978). The study area is the *Fadama* lands (flood plains) along the Kubanni River basin which is located within the city (Fig.3.3). The Kubanni drainage basin is one of the drainage basins that drain southern Zaria. The Ahmadu Bello University, Zaria, the Institute for Agricultural Research, Samuru, and Nigeria College of Aviation Technology, Zaria, are located at the northern side of the Kubanni River basin which flows to form a natural frontier between Tudun Wada on one hand and Sabon Gari on other. It also flows through the back of Nigeria military School, the Nigerian Army Depot and the Advanced Teachers College before emptying into the Galma River (also another river that passes through the city).

The Kubanni River is relatively a seasonal river with intermittent flows occurring in flashes mainly during rainy season (Eigbefo, 1978; KDSG, 2000). Thus, the river is mainly sewage – bearing river in the dry season.

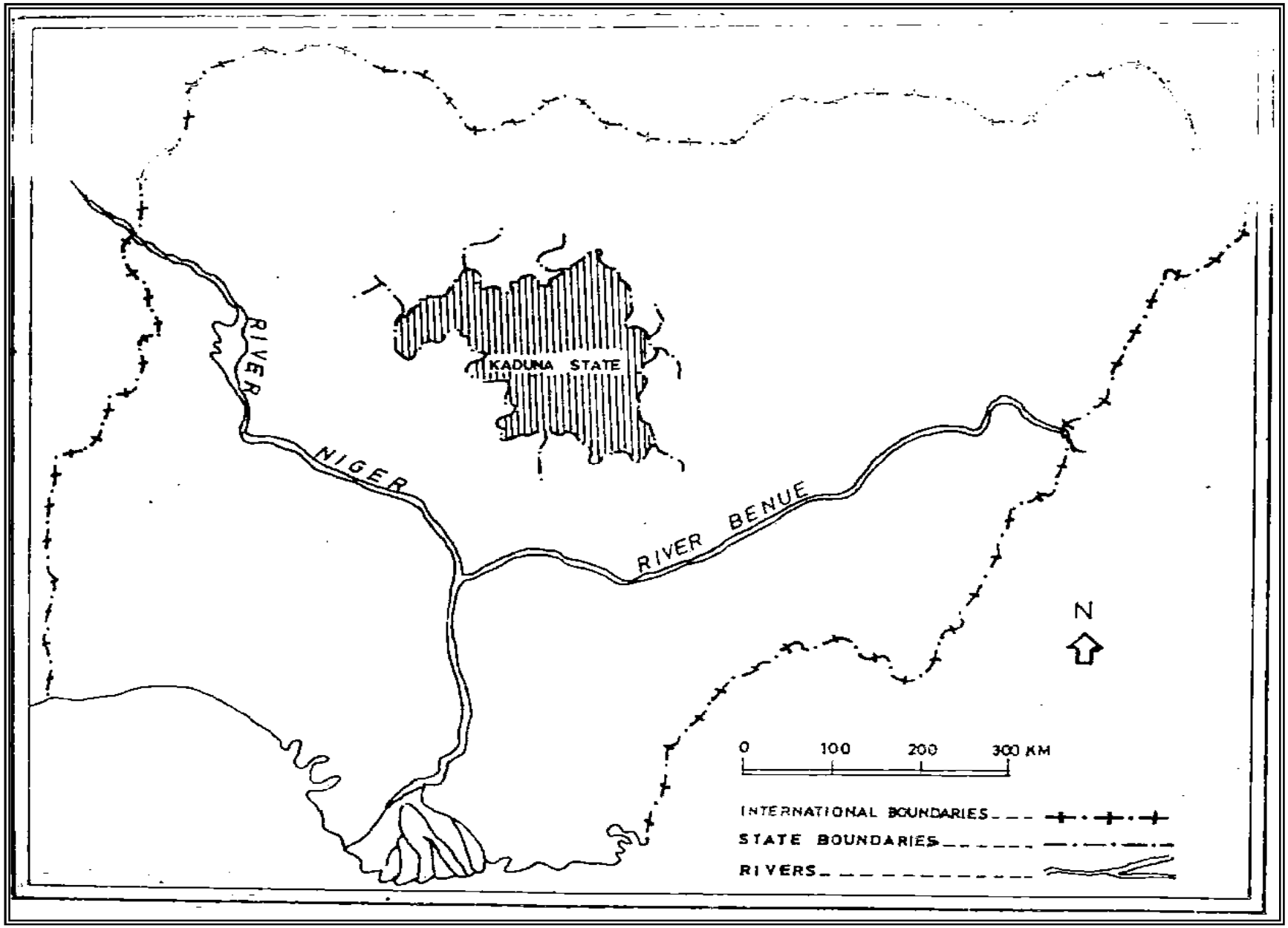


FIG 3.1: NIGERIA SHOWING KADUNA STATE

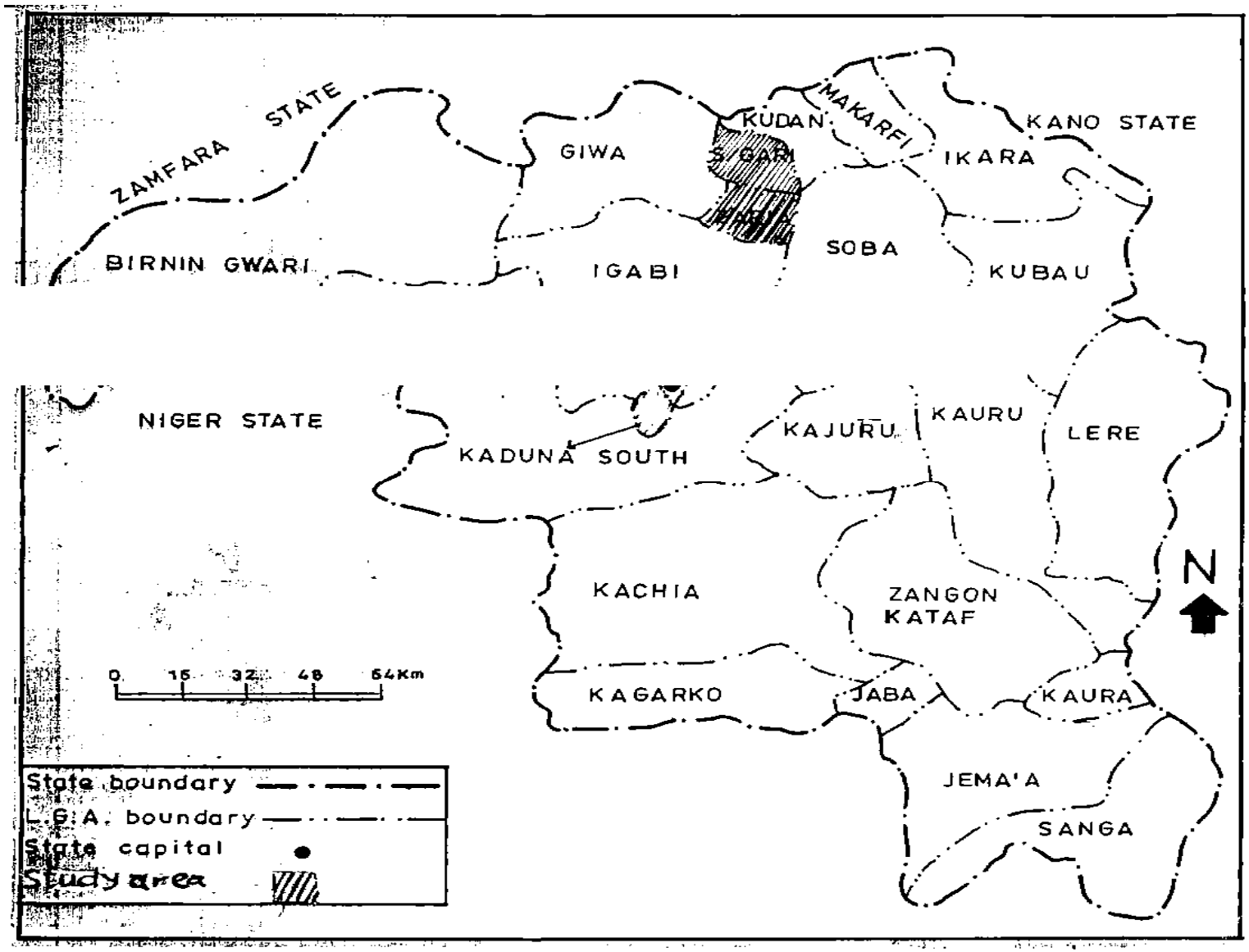


FIG 3. 2: KADUNA STATE SHOWING LOCAL GOVERNMENT AREAS

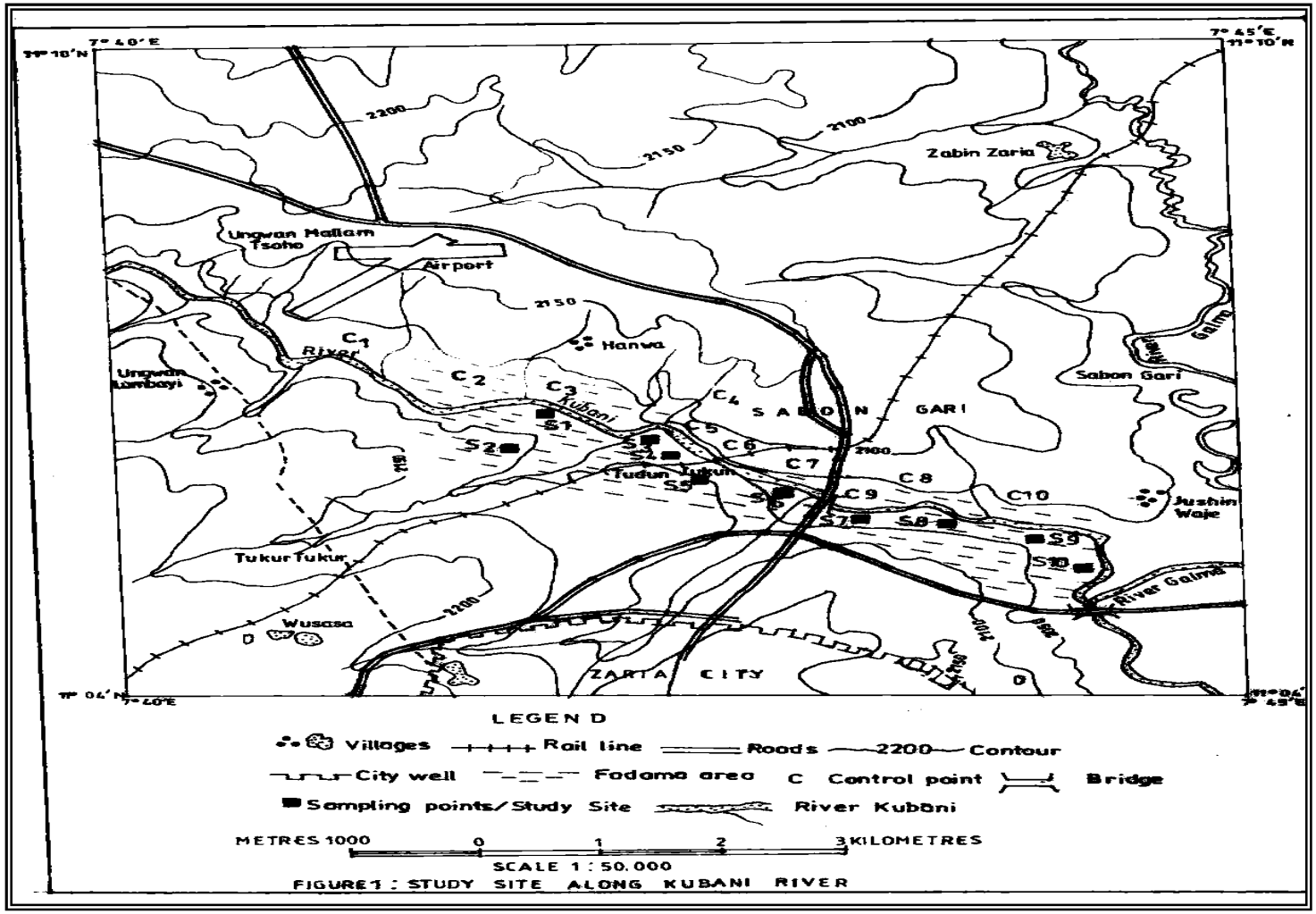


FIG 3.3: STUDY AREA ALONG KUBANNI RIVER BASIN

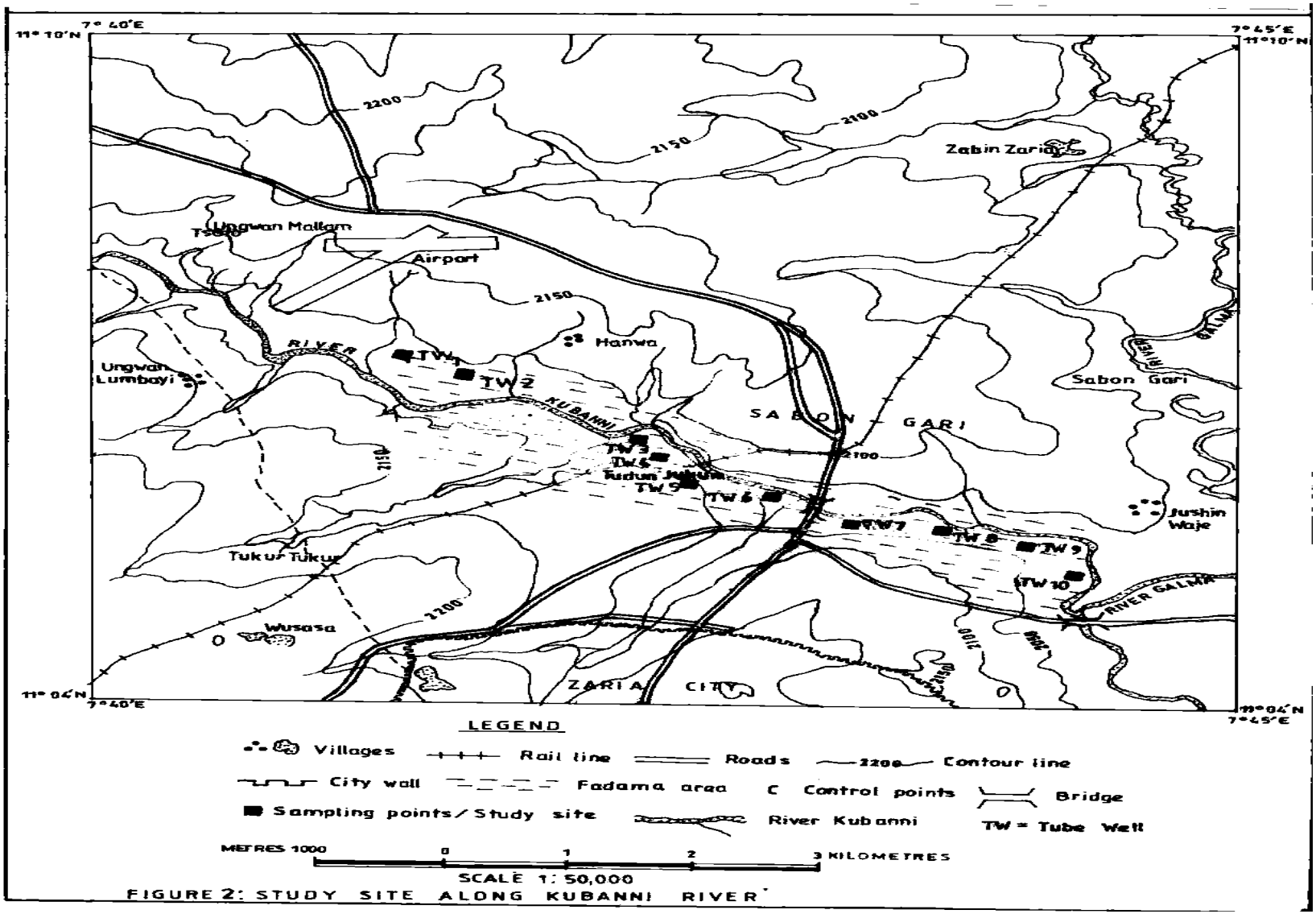


FIGURE 2: STUDY SITE ALONG KUBANNI RIVER

FIG 3.4: LOCATIONS OF TUBE-WELLS ALONG KUBANNI RIVE BASIN

3.4.0 **Sampling and Preservation**

3.4.1 **Number of Samples**

The number of samples was determined using t – distribution as follows:-

$$n \geq \frac{[ts]^2}{d}$$

Where t at 95% level of confidence for 3 replicate measurements = 3.18

s = Standard deviation

d = distance of sample mean from population mean

n = number of samples to be drawn for investigation

$$S = \sqrt{\frac{\sum\left(x - \bar{x}\right)^2}{n}}$$

x = measurement

$\bar{x}$ = mean of measurements

n = number of measurements

The number of samples was determined based on the work of Awofolu *et al* .(2005), who investigated the trace metals level in water and sediment from Tyume River and its effects on an irrigated farmland in South Africa. The mean values for lead in soil for four sampling dates were 0.046, 0.038, 0.019 and 0.017. The mean of these values, $\bar{x}$, is 0.03.

$$s = \sqrt{\frac{(0.046-0.03)^2 + (0.038-0.03)^2 + (0.019-0.03)^2 + (0.017-0.03)^2}{4}}$$

$$s = \sqrt{\frac{0.00061}{4}} = \sqrt{0.0001525} = 0.0123$$

$d \geq y - \mu = \frac{ts}{\sqrt{n}}$ where y = sample mean and

μ = population mean

$\therefore$ d is estimated as 0.0124, i.e. the distance of sample mean from population mean

So therefore,

$$n \geq \left(\frac{3.18X0.0123}{0.0124} \right)^2 \geq 9.95 \cong 10 \text{ samples.}$$

Thus, a total of 10 samples each of sewage, sludge, soil and vegetables were collected from the study area and similarly, 10 samples each of water (shallow tube-well water), soil and vegetables from the control area were also collected.

3.4.2 **Sampling points**

10 sampling points each were chosen in the study area (points 1 to 10), Fig 3.3 and control area (Points 1 to 10), Fig 3.4. In choosing the points for sampling sewage water and sludge, preference was given to such factor as points at which sewage water is being pumped onto the vegetation for irrigation. However, in the control area, points were chosen at Tudun Jukun bridge, after Kubanni bridge and Maje where shallow tube-wells are available for irrigation, Fig. 3.4.

3.4.3 **Sample Collection and Preservation**

Sewage water and sludge samples were collected from the river-bank closest to where sewage is being pumped onto the vegetation. Vegetables (spinach and lettuce) were purchased directly from farmers, requesting vegetable stalks from different areas of the farmlands.

Sewage and its sludge were collected following a standard procedure (APHA, 1992). Sewage water and sludge samples were kept cooled *en route* the laboratory and stored at 4^0C while sludge samples at – 18^0C until finally analyzed. Sewage water samples were acidified with 1.5ml concentrated HNO_3/litre of sample (APHA, 1992), after pH, conductivity and temperature measurement, before storage at 4^0C. Sludge samples when frosted, they were allowed to defrost, then air-dried in a circulating oven at 30^0C and thereafter ground and sieved mechanically using a 2mm sieve (Awofolu *et al*., 2005). All determinations were based upon the fine sludge particles obtained since metals are known to adhere to these fine particles.

Vegetable samples were collected and placed in polythene bags, labeled and taken to laboratory. For soil samples, the sampling area was subdivided into grids of 20 x 20m and samples taken from the centre of each grid (0-10cm depth), 10 soil samples were collected from each site. To obtain composite samples of each site, bulking procedure was adopted to standardize the samples. A conning and quartering method was applied repeatedly to reduce the sample volume (Jackson, 1958). Each representative site sample was prepared by mixing the whole 10 samples from different grids of the same site to overcome spatial variability.

Vegetable samples were thoroughly rinsed with water and then with distilled water to remove any attached soil particles, allowed to drain, and then oven dried at 60^0C over night (Awofolu *et al*., 2005). The dried vegetables were then ground in an acid washed mortar. A portion of the homogeneous soil samples were also air-dried by circulating air in the oven over night and thereafter ground and sieved mechanically sing 2mm sieve. All metal determination were based on these fine soil particles (Awofolu *et al*., 2005)

3.4.4 **Sample Labeling**

The samples were given specified labels to avoid misrepresentation in the course of sample processing, digestion and analysis. Thus, the samples were labeled as follows:

Sewage water:	SW_1 - SW_{10}
Tube-well water:	TW_1 – TW_{10}
Sewage sludge:	SL_1 – SL_{10}
Soil (Study area):	SS_1 – SS_{10}
Soil (Control):	CSS_1 – CSS_{10}
Spinach (Study area):	SP_1 – SP_{10}
Spinach (Control):	CSP_1 – CSP_{10}
Lettuce (Study area):	LT_1 – LT_{10}
Lettuce (Control):	CLT_1 – CLT_{10}

3.5 **Samples Pre-treatment**

(a). Drying: - Sludge and soil samples for metal analysis were placed in porcelain crucibles and dried in oven at 80^0C for 24hrs (Bining and Berd, 2001) while the vegetable samples were dried in an oven at 100^0C for 10hrs (Francis, 2005).

(b). Grinding: – Dried soil, sludge and vegetable samples were grinded into fine powder with the aid of mortar and pestle, which was acid washed prior to use. The processed samples were then stored in desiccators to attain constant weight before being stored in airtight plastic bottles.

(c). Sieving:– The dried – grinded soil, sludge and vegetable samples were sieved with the aid of 2mm and 1mm (for vegetables) sieves before being used for analysis.

(d). Washing – Glassware, plastic containers, crucibles, mortar, pestle, and watch glasses were all washed with liquid soap, rinsed with distilled water and soaked in 10% HNO_3 solution for 24hrs. They were then washed with distilled water and then dried in an oven at 80^0C for 5hrs.

3.6.0 **Analysis of Physico-Chemical Parameters**

3.6.1 **Physico-chemical Analysis of Water Samples**

a) ***pH, conductivity and temperature measurement***

i) Calibration of pH meter – Buffer solutions were prepared by dissolving buffer 4, 7 and 9 tablets in 100ml distilled water separately. A pH/temperature/conductivity meter (Hanna, H1991000) was calibrated with these buffer solutions. The calibrated meter was then left standing in distilled water for at least 12 hours before measuring pH of water samples (Mendham, 2000).

ii) Calibration of conductivity meter – 0.7455g of oven dried KCl (105^0C) was dissolved in 1 litre of distilled water giving 0.01 $moldm^{-3}$ solution. This was used to calibrate the conductivity meter (conductivity of this solution is $1412\mu scm^{-1}$).

iii) Measurement – pH of water samples was measured by inserting the calibrated pH meter into the water sample immediately after collection. It was always rinsed and left standing in distilled water before being used for further pH measurements. Temperature and conductivity readings were also taken at the same time as pH measurements.

b) ***Total Solids (APHA, 1992)***

A clean evaporating dish was heated for 1hour in an oven, stored and cooled in desiccators. 100ml of water sample was then pipetted into a pre-weighed dish and evaporated to dryness on steam bath. The dish and evaporated sample were oven-dried at 105^0C for 1 hour, cooled in a desiccator and weighed. The process of drying, cooling, desiccating and weighing was repeated until constant weight was achieved. Duplicate determinations agreed within 5% of their average.

$$\text{mg total solid/litre} = \frac{(A-B) \times 1000}{\text{ml of sample}}$$

A = weight of dried residue +dish (mg)

B = weight of dish (mg)

c) ***Total dissolved solids (APHA, 1992)***

A clean evaporating dish was heated to 180^0C for 1 hour in a drying oven and cooled in a desiccator. The water samples were stirred with magnetic stirrer and 50ml pipetted into a glass fiber filter (Whatman grade 934AH) with applied vacuum. It was washed with three 10ml volumes of distilled water, allowing complete drainage between washings and continued suction for 3 minutes after complete filtration. The total filtrate was transferred into a cooled evaporating dish and evaporated to dryness on a steam bath. The dish and sample were oven-dried at 180^0C for 1 hour, cooled in desiccator and weighed. The process of drying, cooling, desiccating and weighting was repeated until constant weight was attained.

mg total dissolved solid/litre = $\frac{(A-B) \times 1000}{\text{ml of sample}}$

A = weight of dried residue + dish (mg)

B = weight of dish (mg)

d) ***Total suspended solids (TSS)***

TSS = Total solids – total dissolved solids

e) ***Total alkalinity (Allen, 1974)***

3g of anhydrous Na_2CO_3 was heated for 16 minutes at moderate heat with continuous stirring in a clean crucible, cooled in a desiccator and weighed. The process was repeated until constant weight is attained. 1.325g of Na_2CO_3 was then dissolved in a little quantity of hot distilled water in a beaker and transferred into a 250ml volumetric flask. The beaker was washed into the flask and flask made up to mark with distilled water giving 0.05 $moldm^{-3}$ Na_2CO_3. 2ml of concentrated HCl was dissolved in 250ml of distilled water and was standardized with the Na_2CO_3 solution (methyl orange as indicator).

100ml of water sample was measured into a conical flask and 3 drops of methyl orange was added. This content was titrated with 0.01 $moldm^{-3}$ HCl until faint orange color appeared (methyl orange end – point).

Total alkalinity (mg/litre $CaCO_3$) = $\frac{\text{total titre (ml)} \times 500}{\text{ml of sample}}$

f) ***Total hardness (APHA, 1992)***

Buffer solution was prepared by dissolving 1.179g of the disodium salt of EDTA dihydrate and 780mg $MgSO_4.7H_2O$ in 50ml distilled water. This content was added to a solution of 16.9g NH_4Cl dissolved in 143ml concentrated NH_4OH. Both were well mixed and diluted to 250ml with distilled water. 25ml of water sample was diluted to 50ml with distilled water; 2ml of buffer solution and 2 drops of Eriochrome black-T indicator were added and the resultant reddish solution was titrated with standard EDTA titrant slowly with constant stirring until the last reddish tinge disappeared. Few drops of titrant were added at 5 second intervals until a blue colour appeared (end-point)

$$\text{EDTA hardness as mg } CaCO_3 \text{ /litre} = \frac{A \times B \times 1000}{\text{ml of sample}}$$

A = ml titration for sample

B = mg $CaCO_3$ equivalent to 1.00ml EDTA titrant.

g) ***Nitrate - Nitrogen, NO_3^- – N (APHA, 1992)***

2g of KNO_3 was oven dried at 105^0C for 24 hours and 0.7218g dissolved in distilled water, transferred into a 1000ml volumetric flask giving nitrate stock solution (1ml = 0.05mg NO_3^{--}). Nitrate calibration standards were prepared in the range 5 – 25mg NO_3^{--} - N/litre. The absorbance was read with a spectrophotometer and a calibration curve of absorbance against concentration was plotted (Appendix I).

100ml of water sample was evaporated to dryness and 2ml phenoldisulphuric acid was added to the residue and left for 10 minutes. 15ml of distilled water and 5ml concentrated NH_3 solution were added. The yellow mixture that resulted was stirred and allowed to cool. The

absorbance was measured with the colorimeter at 410nm using distilled water as blank. NO_3^- - N concentration was read from the calibration curve.

$$\text{mg } NO^-_3 \text{ - N/litre} = \frac{\text{mg } NO_3^{--} \text{ - N from curve x 1000}}{\text{ml of sample}}$$

h) ***Phosphate – Phosphorus, PO_4^{3-} - P (APHA, 1992; Lind 1979)***

0.2197g of KH_2PO_4 was oven dried at 105^0C for 1 hour and then dissolved in distilled water and diluted to 1000ml in a volumetric flask giving phosphate stock solution (1ml = 0.05mg P). Working standards of 0.025, 0.05, 0.1, 0.2 and 0.25 mg PO_4^{3--} – P/litre were prepared. Absorbances were read with colorimeter at 690nm and a calibration curve of absorbance against concentration was plotted (Appendix II).

100ml of water sample was taken and 4ml of ammonium molybdate reagent (Deniges reagent) and 0.5ml (10 drops) of stannous chloride were added. Absorbance was measured after 11 minutes for all samples at 690nm and concentration read from the curve.

$$\text{mg } PO_4^{3--} \text{ - P/litre} = \frac{\text{mg } PO_4^{3--} \text{ -- P/litre from curve x 1000}}{\text{ml of sample}}$$

i) ***Sulphate – Sulphur, SO_4^{2-} – S (APHA, 1992)***

0.5434g of anhydrous K_2SO_4 was dissolved in 1 litre of distilled water in a volumetric flask giving 1000ppm SO_4^2 – S stock solution (1ml = 100µgS). 100ml of the stock solution was withdrawn and diluted to 1 litre giving an intermediate solution (1ml = 10mg S). This was

used to prepare working standards of 50, 100, 150, 200 and 250mg. Transmittances were measured with photometer and calibration curve of transmittance against concentration was plotted (Appendix III).

100ml of water sample was measured and transferred to Erlenmeyer flask. 50ml of glycerol was measured and 30ml of concentrated HCl, 30ml distilled water, 100ml of 95% ethyl alcohol and 55g NaCl were added (conditioning reagent) and the mixture was stirred on a magnetic stirrer. While the solution was being stirred, a spoonful of $BaCl_2$ crystals was added and began timing immediately. Stirring continued for exactly 1 min. at constant speed and thereafter the solution was immediately decanted into a cell of photometer. The transmittance of the turbidity formed in the solution was measured with 2 – 4 min. for all the samples at 420nm and the concentration was read from curve.

$$\text{mg } SO_4^{2-} - \text{S/lit} = \frac{SO_4^{2-} \text{ - S from curve x } 1000}{\text{ml of samples}}$$

j) ***Chloride (APHA, 1992)***

100ml of water sample was measured and transferred into a 250ml conical flask. This was directly titrated in triplicate with standardized $AgNO_3$ solution of molarity 0.01 using 1ml K_2CrO_4 as indicator, to a pinkish yellow end point. The volume of standardized $AgNO_3$ solution used for the titration was noted and recorded.

$$\text{mg Cl/lit} = \frac{\text{A x M x } 35,450}{\text{ml of samples}}$$

A = Average ml of titration for sample

M = molarity of silver nitrate solution (M = 0.01)

k) ***Ammonia (Ademoroti, 1996)***

50ml of water sample was measured and transferred into a beaker. 5 drops of potassium sodium tartrate tetrahydrate, $KNaC_4H_4O_6.4H_2O$ (Rochelle salt) was added into the water sample and mixed. 2ml of alkaline potassium iodomercurate (Nessler's reagent) was also added and allowed to stand for 10 minutes for colour development and thereafter the mixture was filled into the Nessler cell and inserted inside Lovibond comparator through which colour intensity was determined by comparing the cell with the colour discs and best visual match selected.

3.6.2 Physico-chemical Analysis of Sewage Sludge Samples

a) ***pH (Agbenin, 1995)***

15g of air dried sewage sludge sample was weighed into a 50ml beaker and 20ml of distilled water was added. It was stirred with the aid of glass rod and allowed to stand for 30 minutes. A pre-calibrated pH meter was inserted into the mixture and pH was taken.

b) ***Electrical conductivity (Agbenin, 1995; Allen, 1974)***

Three small bottles were cleaned and dried and nearly filled with distilled water, stoppered and equilibrated. A pre-calibrated conductivity meter was rinsed in the first two and conductivity of the third measured. 50g of air-dried sewage sludge sample was then shaken in 50ml of distilled water in an extraction bottle with mechanical shaker for 1 hour. The suspension was then filtered twice to remove turbidity and two drops of 0.1% $(NaPO_3)_6$ added

to the filtrate. The pre-calibrated conductivity meter was then inserted and reading taken in μScm^{-1}.

c) ***Organic matter (Allen, 1974; Elith and Garwood, 2001)***

An acid washed crucible was dried at 105^0C in an oven for 1 hour, cooled in desiccator and weighed. The process of drying, cooling and weighing was repeated until a constant weight was attained. 1g of oven-dried (dried at 105^0C) sewage sludge sample was transferred into the crucible. 3 drops of 50% solution H_2O_2 was added to promote oxidation and crucible was ignited at 500^0C in a CARBOLITE furnace for 4 hours and cooled in desiccator to achieve constant weight.

$$\% \text{ Organic Matter} = \frac{(W_1 - W_2) \times 100}{\text{Sample weight.}}$$

W_1 = Weight of crucible + sample before ignition

W_2 = Weight of crucible + sample after ignition ‘

d) ***Textural Analyses (based on the proportion of different particle size***)

50g of sieved sewage sludge sample was placed in a 250ml plastic beaker. 100ml of 50% sodium hexametaphosphate (calgon) solution was added and stirred with glass rod. 100ml of distilled water was added, stirred and allowed to stand for 30 minutes with occasional stirring. It was then transferred to a 250ml plastic container and shaken on mechanical shaker for 10 minutes and then into a 1000ml measuring cylinder and made up to mark with distilled water. The suspension was thoroughly mixed with a hand plunger and hydrometer/temperature readings were taken after 40 seconds and 8 hours respectively. A blank consisting of 50%

calgon in 100ml of distilled water was made, diluted to 1000ml in a measuring cylinder and hydrometer/temperature readings were taken.

$$\% \text{ clay} = \frac{(\text{Corrected 8 hours reading} - \text{Blank}) \times 100}{\text{Weight of soil taken}}$$

$$\% \text{ Silt} = \frac{(\text{Corrected 40 seconds reading} - \text{Blank}) \times 100}{\text{Weight of soil taken}} - \% \text{ clay}$$

$$\% \text{ Sand} = 100 - (\% \text{ clay} + \text{silt})$$

$$\text{Corrected readings (g/litre)} = R - R_{L+}(0.36T)$$

R = Hydrometer readings of soil suspension; T = room temperature ($20^{O}C$)

R_L = Blank readings.

0.36 g/litre is added to soil suspension readings for every degree above $20^{0}C$.

Based on the values got above, the sewage sludge samples were classified according to international systems of textural classification (Allen, 1974).

e) ***Phosphate – Phosphorus, PO_4^{3-} – P (Agbenin, 1995)***

15ml of 1.00moldm^{-3} NH_4F and 25ml of 0.5moldm^{-3} KCl were mixed with 460ml of distilled water and the mixture stored in a glass bottle giving the extraction solution. 0.2197g of KH_2PO_4 was oven dried at $105^{0}C$ for 1 hour, dissolved in distilled water and diluted to 1000ml in a volumetric flask giving phosphate stock solution (1ml = 0.05mg P). Phosphate Calibration standards were prepared in the range 2 – 8mg PO_4-P/litre. Absorbances were read with spectrophotometer at 690nm and a calibration curve of absorbance against concentration was plotted (Appendix IV). 5g of sludge sample was weighed into an extraction bottle and

35ml of extraction solution was added. The bottle was shaken for 1 minute and filtered into a dry beaker. Filtration was repeated until filtrate was cleared. 10ml of the filtrate was taken for the determination of PO_4^{3-} - P as it was done in water samples (section 3.6.1 h).

$$\text{mg } PO_4^{3-} \text{ - P/kg} = \frac{PO_4^{3-} \text{ - P from curve x Extractant volume}}{\text{Aliquot of sample x weight of sample}}$$

f) ***Cation exchange capacity (CEC) (Agbenin, 1995)***

10g of sewage sludge sample was weighed into a 100ml plastic beaker. 40ml of 1.00 $moldm^{-3}$ ammonium acetate solution (pH 7) was added and the suspension stirred with glass rod and was left overnight. It was filtered with light suction using 55mm buchner funnel (coning size No. 40). The residue from filtration was leached with four 25ml portions of 1.00$moldm^{-3}$ NH_4Cl solution (pH 7) and one 25ml portion of 0.25 $moldm^{-3}$ NH_4Cl (pH 7). The solution was discarded and electrolyte washed out of the sample with 150ml ethanol. The sample was allowed to drain completely and leached gradually with acidified NaCl to a volume of 250ml. 50ml of 2% boric acid was measured into a 250ml conical flask and 3 drops of methyl orange was added as an indicator. The acidified NaCl leachate was poured into 500ml Kjeldahal flask and 10ml of concentrated NaOH plus anti – bumping granules were added. The leachate was distilled over the boric acid. 150ml of the NH_4 – borate distillate was titrated with standard 0.1 $moldm^{-3}$ HCl.

$$\text{CEC (C mol/kg)} = \frac{\text{(titre – blank) x M x 100}}{\text{weight of sample}}$$

M = Molarity of boric acid.

g) ***Cation Exchangeable Bases (Agbenin, 1995)***

10g of sewage sludge sample was weighed and taken into a funnel fitted with fitter paper (Whatman no. 40) over 100ml volumetric flask. The sewage sludge sample in the funnel was leached with 1.00 mol/dm3 ammonium acetate (pH 7) to a volume of 100ml. The leaching was done for about 2 hours with about 10ml of ammonium acetate (pH 7) at each washing. After the leaching, the funnel with the filter paper was removed and the flask stoppered, which was then shaken very well. The leachate was transferred into plastic bottles and taken for the determination of Na, K, Ca and Mg. Na and K were determined on flame Emission and their calibration curves are in Appendix VII and V respectively, while Ca and Mg were determined by AAS and their calibration curves are in Appendix VI and VIII respectively. The proportions of the stock solutions of these metals were described in section 3.7.2.

h) ***Total Nitrogen (Agbenin, 1995)***

1g of sewage sludge sample was weighted and transferred into 500ml Kjeldahl flask. Few drops of distilled water was added and left to stand for about 30 min. 5g of Kjeldahl catalyst mixture was added to the content and followed by 20ml concentrated sulphuric acid. The content in the flask was cautiously heated until frothing ceased. The heat was then increased until digest cleared for about 2 hours. Thereafter, the flask was allowed to cool, little distilled water added with care before washing the content into 100ml volumetric flask, and then made up to the mark. 10ml of the digest was pipetted into a distillation flask. 20ml of 2% boric acid was measured into a 100ml conical flask and introduced to the bottom of the distillation condenser. 10ml of 10 mol/dm^3 NaOH was then added to the 10ml pipetted digest in the distillation flask and was immediately introduced to the distillation unit and the digest

distilled off. The distillate was titrated with 0.01 mol/dm^3 H_2SO_4 until an end point was attained from green to purple.

$$\text{Total nitrogen \%} = \frac{0.014x\ (titre - blank)\ x\ M\ \ x\ vol.\ of\ \ digest}{Weight\ of\ \ soil\ \ x\ \ Aliquot\ distilled} \text{ x } 100$$

M = Molarity of the acid.

3.6.3 **Physico-chemical Analysis of Soil Samples**

Soil pH and electrical conductivity were determined based on the procedure described for treating sewage sludge samples (section 3.6.2), respectively. Similarly, soil organic matter was also determined based on the procedure described in section 3.6. 2c. Exchangeable cations and exchangeable bases were also determined by employing the same procedure described in sub-section 3. 6. 2 f and g. Finally, textural analyses were determined by the same method employed in section 3. 6. 2 d.

3.7.0 **Analysis Using Flame Atomic Absorption Spectrophotometry**

3.7.1 ***Principles***

Atomic absorption spectrophotometry is the most common method for determination of trace metals in Africa and flame atomization is used in AAS for most metals (Biney *et al.*, 1994). FAAS involves the atomization of solution of a sample containing a metallic salt (or some other metallic compound) and measurement of the amount of radiation absorbed by atoms of interest when placed in the path of an incident radiation which has been passed through a monochromator to isolate characteristic wavelength of absorption of the element of

interest. Concentration of atoms is then related to the amount of radiation absorbed according to Beer – Lambert's law. The incident radiation is produced by a source lamp (usually Hollow cathode Lamp) with the cathode made of the element of interest in order to reduce interferences and make instrument more sensitive.

3.7.2 **Preparation of Stock Solutions**

i) Cadmium solution was prepared by dissolving 2.7435g $Cd(NO_3)_2$. $4H_2O$ in distilled deionized water and the solution was made up to 1 litre with distilled water in a volumetric flask giving 1000mg/L cadmium solution

ii) Lead solution was prepared by dissolving 1.5895g $Pb(NO_3)_2$ in distilled deionized water and making up to 1 litre giving 1000mg/L lead solution.

iii) Nickel solution was prepared by dissolving 4.9542g of $Ni(NO_3)_2$. $6H_2O$ in distilled deionized water and making up to 1 litre giving 1000mg/L nickel solution.

iv) Copper solution was prepared by dissolving 3.8031g of $Cu(NO_3)_3$. $3H_2O$ in distilled deionized water and making up to 1 litre giving 1000mg/L copper solution.

v) Zinc solution was prepared by dissolving 4.5486g of $Zn(NO_3)_2$. $6H_2O$ in distilled deionized water and making up to 1 litre giving 1000mg/L zinc solution.

vi) Calcium solution was prepared by dissolving 2.775g of $CaCl_2$ in distilled deionized water and making up to 1 litre giving 1000mg/L calcium solution

vii) Magnesium solution was prepared by dissolving 6.167g of $Mg(NO_3)_2$ in distilled deionized water and making up to 1 litre giving 1000mg/L magnesium solution.

viii) Sodium solution was prepared by dissolving 2.543g of NaCl in distilled deionized water and making up to 1 litre giving 1000mg/L sodium solution

ix) Potassium solution was prepared by dissolving 1.909g of KCl in distilled deionized water and making up to 1 litre giving 1000mg/L potassium solution

3.7.3. **Calibration Curves**

Five working standards were prepared in triplicate for each metal by serial dilution of stock solution. These and blank solutions were aspirated into a *Shimadzu* (model AA-650) double beam digital atomic absorption spectrophotometer. A calibration curve of absorption against concentration was prepared for each metal and used in the determination of the metal concentration in the samples (Appendices V – XIII).

The actual concentration of the metal in sewage sludge and plant samples was determined as follows:

Amount of metal in volume of digested solution =

$$\frac{Vol.\ of\ \ sample\ solution \times conc.\ of\ \ sample\ \ from\ calibration\ curve}{1000}$$

$$= Xmg$$

$$Amount\ of\ metal\ in\ mg/kg\ of\ sample = \frac{Amount\ of\ \ metal\ in\ vol.\ of\ \ digested\ \ solution}{weight\ \ of\ \ sample\ digested\ (kg)}$$

$$= \frac{X}{Weight\ of\ \ sample\ digested\ (kg)}$$

3.7.4 Digestion of Samples

a) ***Digestion of Water Samples***

Water samples were digested according to APHA (1992). 100ml of sample was transferred into a 125ml conical flask. 5ml of concentrated HNO_3 and few boiling clips were added. The solution was boiled slowly and evaporated on a hot plate to about 20ml, before precipitation occurs. Heating and addition of concentrated HNO_3 was continued until a light coloured, clear solution was obtained (digestion complete). The sample was not allowed to dry during digestion. The wall of the flask was washed with distilled water and solution filtered. The filtrate was transferred into a 50ml volumetric flask with two 5ml portions of water, cooled and diluted to mark and mixed thoroughly. Portions of this solution were used for metal determination.

b) ***Digestion of Soil and Sewage Sludge Samples***

Soil and sewage sludge samples were digested in accordance with the method used by Francis (2004). One gram of the finely ground dried soil and sewage sludge samples were mixed with $20cm^3$ (1: 1) HCl/ HNO_3 acid mixture and the content was heated until dryness. The residue was extracted using $2moldm^{-3}$ HCl and brought to $50cm^3$ with distilled water.

c) ***Digestion of Vegetable Samples***

Two grams of each vegetable sample was ashed in a Teflon beaker using $20cm^3$ of 1: 1 $HNO_3/HClO_4$ acid mixture and this was followed by the addition of 3 drops of HF. This was heated to clear solution and continued until dryness. The cooled residue was dissolved in $5cm^3$

concentrated HCl and the liquor was made up to 50cm^3 using distilled water (Francis, 2004). Portions of this solution were used for metal determination.

3.7.5 **Method Validation (Spiking Experiment)**

(a). ***Preparation of Multi-Element Standard Solution***

0.00055g of $Cd(NO_3)_2.4H_2O$ was weighed and dissolved in 2ml distilled water in a beaker and transferred into 1 liter volumetric flask. The beaker was rinsed thoroughly with distilled water into the flask. 0.0076g of $Cu(NO_3)_2.3H_2O$ was also weighed, dissolved in 2ml distilled water in a beaker and transferred into the same 1 liter volumetric flask. The beaker was also rinsed with distilled water into the volumetric flask. 0.0099g of Ni $(NO_3)_2.6H_2O$ was dissolved in 2ml distilled water in a beaker and transferred into the volumetric flask. This was followed by separate weighing out of 0.0008g of $Pb(NO_3)_2$ and 0.0091g of Zn $(NO_3)_2.6H_2O$, dissolving them in distilled water in separate beaker and transferring them into the same volumetric flask. The beakers were thoroughly rinsed in each case. The flask was made up to mark with distilled water giving the Multi-element Standard Solution (MESS). The concentration of the metals in MESS is shown in Table 3.1. Aliquots of this solution were used in the spiking experiment.

Table 3.1: Metals and their concentrations in Multi-Element Standard Solution

Metal	Concentration mg/L
Cd	0.5
Pb	0.5
Cu	2
Ni	2
Zn	2

(b). ***Digestion of Unspiked Sample***

One sample each of sewage water, tube-well water, sewage sludge, soil and vegetables from a representative sampling point and blanks were digested in triplicate as in section 3.7.4 (a) – (c) and run on the AAS machine. The amount of each metal present in each sample was determined from the calibration curve. This gave the amount of metal in unspiked sample and provided the basis for the spiking experiment.

(c). ***Spiking Experiment***

20ml of the multi-element standard solution was drawn with the aid of graduated pipette and was used to spike sewage water, tube-well water, sewage sludge, soil and vegetable sub-samples from the same original samples as was the unspiked samples. These were digested as in sections 3.7.4 (a) – (c) and run on the AAS machine. Each spiked sample was digested in triplicate alongside blank digests. Concentrations of metals in spiked samples were then

determined from calibration curves. Concentrations of metals in spiked and unspiked samples were used to calculate percentage recovery in order to validate the method as follows:

Percentage Recovery

Amount of metal used to spike a sample

$$= \frac{\text{vol. of MESS used x conc. of metal in MESS}}{1000}$$

= X mg of metal used to spike a sample (calculated)

Amount of metal in unspiked sample

$$= \frac{\text{vol. of digest of unspiked sample x con. of metal in digest of unspiked sample}}{1000}$$

= Y_o mg of metal in Zg or ml of unspiked sample

Amount of metal in spiked sample

$$= \frac{\text{vol. of digest of spiked sample x con. of metal in digest of spiked sample}}{1000}$$

= Y_1 mg of metal in Zg or ml of sample spiked

Estimate of amount of metal used to spike a sample determined

= amount of metal in spiked sample determined (Y_1) – amount of metal in unspiked sample determined (Y_O)

= $X^{/}$ mg of metal used to spike a sample (determined)

= recovery of metal

$$\% \text{ recovery (of metal)} = \frac{\text{amount of metal used to spike a sample determined}}{\text{amount of meted used to spike a sample calculated}} \times 100$$

$$= \frac{X'}{X} \times 100$$

3.8 **Sequential Extraction**

An experimental approach commonly used for studying the mobility, transport and bioavailability of metals in sewage sludges is the use of selective sequential extraction procedures (Forstner *et al*., 1989). Although some of the sequential extraction schemes were originally developed for sediment analysis (Tessier *et al*., 1979), their use has been extended to soil and sewage sludge analysis (Hickey and Kittrick, 1984; Jardo and Nickless, 1989; Li *et al*., 1995). Selective extraction procedure provides information on the chemical forms of the metals. Several sequential extraction scheme for extraction of metals have been presented by many research workers from time to time, such as by McLaren and Crawford (1973), Tessier *et al*. (1979), Forstner (1985), Solomon and Forstner (1984), Meguellati (1982), Emmerich *et al*. (1982), Shuman (1985), Ure *et al*. (1993), Maiz *et al*. (1997). The procedure of Tessier *et al*. (1979) is one of the most thoroughly researched and widely used procedures to evaluate the efficiency of decontamination treatements (Pardo *et al*., 1990; Calvet *et al*., 1990; Rauret *et al*., 1988). The selective extraction scheme used here is based upon operationally defined fractions: water soluble, exchangeable, oxidizable (bound to organic matter), acid soluble (bound to carbonate), reducible (bound to oxide and hydroxide) and residual (bound to silicates and detrital materials) to investigate the chemical fractionation of selected metals in sewage sludge and soil and evaluate the effect of total metals concentration on metal partitioning into different fractions.

The Sequential extraction was carried out on the basis of selective extraction in order to extract metals that are in different phases, proposed by Testier *et al.* (1979). $Mg(NO_3)_2$ was used instead $MgCl_2$ to extract exchangeable fractions because the chloride ion can complex metals (Shuman, 1985) and increase the solubility of several trace metals within sewage sludge added to soil (Evan *et al*., 1995).

The extraction of oxidizable phase was under taken after the extraction of the exchangeable phase. This method will allow the destruction of organic matter, which entraps the mineral materials and then provides a better extraction of the following phases (Meguellati, 1982).

For the residual fraction, a combination of aquaregia/hydrofluoric acid $HCl/HNO_3/HF$) was used instead of the $HF/HClO_4$ (Sanchez *et al*., 1994; Maiz *et al*., 1997).

Three sub samples (one gram each) for sludge and soil were subjected to sequential extraction separately. The extraction was aimed at differentiating fractions in six stages as follows:-

1. Water soluble phase: Soil or sewage sludge was extracted with 15ml of deionized water for 2 hours. This was centrifuged and decanted. The extracted solution was then made up to 40 ml with double distilled water.
2. Exchangeable phase: Residue from 1 was shaken at room temperature with 16ml of $1moldm^{-3}$ $Mg(NO_3)_2$ at pH 7.0 for 1hr, centrifuged and supernatant decanted and made up to 40ml with double distilled water prior to analysis.
3. Oxidizable phase (bound to organic matter):- Residue from 2 + 10ml H_2O_2 8.8 $moldm^{-3}$ + 6ml HNO_3 $0.02moldm^{-3}$, was shaken for 5 + 1 hr at 98^0C, 10ml CH_3COONH_4

3.5moldm^{-3} was added as an extracting agent, centrifuged and supernatant made up 40ml with double distilled water prior to analysis.

4. Acid soluble phase (Bound to carbonate):- 25ml of 0.05moldm^{-3} Na_2 EDTA was added to the residue from 3 shaken for 6 hr. and centrifuged. The supernatant was decanted and made up to 40ml with double distilled water prior to analysis.

5. Reducible phase (Bound to Fe/Mn oxide and hydroxides):- residue from 4 + 17.5ml $NH_2OH.HCl$ 0.1moldm^{-3} + 17.5ml CH_3COONH_4 3.5moldm^{-3} , was shaken for 4 + 1 hr at 98^{o}C, was extracted with 10ml CH_3COONH_4 3.5moldm^{-3}, shaken for 1hr, centrifuged, the supernatant decanted and made up to 40ml with double distilled water prior to analysis.

6. Residual fraction (Bound to silicate and detrital materials):- Residue from 5 was digested by using a mixture of (1:3:1 v/v) of $HCl/HNO_3/HF$ (0.35: 12 W/V soil/solution ratio) in acid digestion Teflon cup. This was dry ashed for 2hr. and evaporated to dryness. The residue was diluted to 40ml with double distilled water, centrifuge and the supernatant decanted, which was made up to 40ml with double distilled water prior to analysis

Note that, each sample was centrifuged at 4500rpm for 15min after each successive extraction (Legret *et al.*, 1988). The supernatants were removed with pipette and filtered with Whatman No. 42 filter paper. The residue was washed with deionized water followed by vigorous hand shaking and then followed 15 minutes centrifugation before next extraction.

3.9 **Statistical Analysis**

The results were analyzed using Pearson correlation analysis and single factor analysis of variance (ANOVA). Pearson correlation coefficient, r, is a dimensional index that ranges from – 1.0 to 1.0 inclusive and shows the degree of linear relationship between two sets of data, {X} and {Y}. If there is perfect linear relationship with positive slope between the two variables, we have a correlation coefficient of 1, if there is positive correlation, whenever one variable has a high (low) value, so does the other. If there is a perfect linear relationship with negative slope between the two variables, we have a correlation of -1; if there is negative correlation, whenever one variable has a high (low) value; the other has a low (high) value. A correlation of 0 means that there is no linear relationship between the variables.

An ANOVA is an analysis of the variation present in an experiment. It is a test of the hypothesis that the variation is an experiment is not greater than that due to normal variation of individuals' characteristics and error in their measurement. The tests in an ANOVA are based on the F – ratio (Variance ratio): the variation due to an experimental treatment or effect divided by the variation due to experimental error. ANOVA puts all the data into one number (F) and gives us one P (significance level) for the null hypothesis.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 QUALITY ASSURANCE

The validity of the digestion procedures used for sample treatment and the precision and accuracy of the AAS analysis were tested by spiking experiment. The mean percentage recoveries of metals used to spike water, sewage sludge, soil and vegetable samples are presented in Table 4.1. For sewage and tube-well water samples, the mean percentage recoveries of metals ranged from 87.1±0.2 – 95.7±0.5 and 79.2±0.2-95.5±0.3, respectively while mean percentage recoveries of meals in soil and sewage sludge samples varied from 86.4±0.2 – 96.2±0.4 and 88.7±0.5 – 96.7±0.4, respectively. For spinach and lettuce, the recovery values ranged from 85.4±0.3 – 92.8±0.2 and 82.4±0.2 – 96.2±0.3, respectively.

The trend of metal recovery efficiency for sewage and tube-well water samples was found to follow the decreasing orders: Pb> Ni> Zn> Cd> Cu and Zn> Cd> Pb> Ni> Cu, respectively. The patterns in soil and sewage sludge were also found to follow the decreasing orders: Zn> Cd> Ni> Cu> Pb and Ni> Pb> Cd> Cu> Zn, respectively, while Cu> Pb> Cd> Ni> Zn and Zn> Cd> Cu> Pb> Ni were the trends for spinach and lettuce, respectively.

Sewage sludge gave, in general, the highest metal recoveries while tube-well water sample gave the least. The efficiency of trace metal recoveries in the matrices subjected to the spiking experiment was found to follow the trend: sewage sludge> sewage water> soil> spinach> lettuce> tube-well water. Amongst the metals, Ni in sewage sludge had the highest recovery overall and Cu in tube-well water had the least recovery overall. The metal recoveries

for all the matrices overall varied from 79-96%, which is similar to the 86-98% range reported for the same metals in similar matrices by Awofolu *et al.* (2005).

Overall the recovery results were in good agreement with expected values. Therefore, the reproducibility of the methods and the precision and accuracy of the AAS machine were adjudged reliable.

4.2 **Physico-Chemical parameter of sewage and tube-well water samples**

The results of physico-chemical parameters of water samples from study and control areas are presented in Tables 4.2 – 4.7. There was progressive temperature increase at each sampling point in the study area from February – April, while in the control area, the temperature of the tube-well water samples generally decreased in the same period. In fact, the highest temperature value recorded for the tube-well water samples was 25.4^0C in the month of February, 2008. This trend was as a result of seasonal variation from cool/harmattan extremely hot season, in which the tube-well water was warmer than sewage water in cool/harmattan season and cooler than the sewage water during hot season.

The pH of the sewage water samples in the study area varied sharply in the months of investigation. It ranged from 7.39-7.93, 8.03 – 8.38 and 8.14 – 8.49 for the months of February, March and April, respectively. Therefore, the sewage waters were alkaline during the period of study. It was reported that the alkaline nature of sewage waters is due to the presence of ammonia and that sewage waters are usually alkaline as a result of the presence of ammoniacal compounds (Khaiwal *et al.*, 2000). During the investigation it was observed that the pH values generally increased as the temperature increased, showing temperature dependency. This may be due to increase in levels of ammonia in the sewage water as could be

Table 4.1: Mean % recoveries (± SD) of trace metal standards added to pre - digested vegetables, soil, sewage water, tube-well water and sewage sludge samples.

Metals	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
Spiked conc. (mg/l)	2	2	2	0.5	0.5
Spinach	85.4 ± 0.3	87.9±0.6	92.8±0.2	90.4±0.2	88.3±0.4
Lettuce	96.2± 0.2	82.4±0.4	89.2±0.2	88.6±0.5	91.7±0.6
Soil	96.2± 0.2	91.6±0.3	89.8±0.5	86.4±0.4	93.8±0.4
Sewage sludge	88.7± 0.5	96.7±0.4	89.9±0.3	92.9±0.4	90.3±0.4
Sewage water	95.7± 0.4	93.2±0.3	87.1±0.2	95.7±0.5	88.6±0.4
Tube-well water	95.5± 0.3	87.0±0.15	79.2±0.2	89.3±0.2	90.0±0.15

seen from Tables 4.2-4.7 from February to April:

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_{3(aq)}$$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}{}_{aq)}$$

The last step is temperature dependent. Thus, pH values increased with the increase in temperature as observed and might be responsible for the alkaline pH of the waters. However, the pH values of water samples, in control area ranged from 7.24 – 7.48, 7.10 – 7.26 and 7.08 – 7.16 for the months of February, March and April, respectively. These values were below those of the study area, even though the tube-well waters too tended to be slightly alkaline.

Similar results were reported by Das and Acharya (2003) for wastewater, as 7.38 – 7.81 and Akan *et al*. (2008) for wastewater, as 8.94 – 10.34. Although the sewage water pH was alkaline throughout, it was within the range of 6.5-8.4, with the exception of 8.49 at SW9, recommended for irrigation by FAO (1985) and Landon (1991). Therefore, the pH values were normal and safe for irrigation.

The electrical conductivity (EC) and total dissolved solids (TDS) ranged from 1090 – 1483, 1357 – 1924, 1675 – 2030μScm^{-1} and 533 – 752, 648 – 986 and 849 – 1013mg/L, respectively, for the months of February, March and April. The values of EC and TDS were again found to be higher in April, which might be attributed to greater solubility of ions at higher temperature. Similar observation was reported by Akan *et al*. (2008) for wastewater, where they recorded 1021 – 1534 μScm^{-1} and 1131 – 2673 mg/L for EC and TDS, respectively.

For control area, EC and TDS from the control area ranged from 426 – 568, 380 – 496, 346 – 448μScm^{-1} and 206 – 278, 186 – 242 and 168 – 216 mg/L, respectively, for the months

of February, March and April. This indicated that the tube-well water samples had lower values of EC and TDS than the sewage water samples. As for total suspended solid (TSS), the sewage water samples found to carry 124-167 mg/L, while tube-well water samples had TSS ranging from 1 -2 mg/L only throughout the period of study. The values of TSS are usually taken as an index of contamination of a water body (Ibrahim, 2005). Thus, in this case, the sewage water, which carried TSS more than 100 times than tube-well water, was contaminated.

The total hardness of sewage water samples ranged from 285.12 – 320.03, 318.73 – 358.03 and 335.18 – 382.15 mg/L for the months of February, March and April, respectively. The result indicated that the sewage water was very hard, since water with hardness of 201-500 mg/L is very hard water (Sawyer and MacCarty, 1967). Alkalinity values of sewage water were higher in April, followed by the values in March and then February. The values in tube-well water samples varied between 30-44mg/L throughout the period of study. Alkalinity serves as pH reservoir for inorganic carbon. It is usually taken as an index of productive potential of water (Manahan, 1994). The high values obtained during the months of study revealed that sewage water had ability to support algal growth, which further indicated that the sewage water samples were truly wastewater, while the results obtained from the control area, had no ability to support algal growth due to lower values of alkalinity.

The anionic concentrations of sewage and tube-well water samples are also presented in Tables 4.2 – 4.7. The Cl^- content of the sewage water was quite higher throughout the period of investigation. The results indicated that the sewage water samples were polluted, since excess of Cl^- in water is usually taken as an index of pollution (Khaiwal *et al*., 2000). In a similar work, Das and Acharya (2003) also reported very high content of Cl^- in the range of 294 – 311 mg/L. The Cl^- content in tube-well water samples from the control area however,

varied between 1.6 – 3.6, 1.8 – 3.4 and 1.7 – 3.4 mg/L for the months of February, March and April, respectively.

Available literature suggested that irrigation water with (mg/L) 5(NO_3^-), 300 (SO_4^{2-}) and 0 – 2 (PO_4^{3-}) are safe (FAO, 1985). The SO_4^{2-} and PO_4^{3-} values (with some few exceptions in PO_4^{3-}) for all the sewage water samples fell within the recommended limits throughout the period of investigation. Similarly, the SO_4^{2-}, NO_3^- and PO_4^{3-} levels in tube-well water samples fell within the recommended limits, although the values were quite lower than those found in sewage water from the study area.

However, the nitrate levels obtained in all the sewage water samples were, in general, above the recommended limits for irrigation water. The NO_3^- levels in the sewage water varied from 4.4 – 14.2, 7.3 – 15.2 and 8.1 16.9 mg/L, while those of tube-well water samples were in the range 1.4 – 6.2, 1.3 – 5.6 and 1.9 – 5.7 mg/L for February, March and April, respectively. High NO_3^- levels were found in the tube-well water samples also, which might be attributed to excess application of manure, refuse dump and sometimes sewage sludge on the surface soil of the control area and the possible leaching of these fertilizers down the soil profile. The nitrate content in water is taken as a warning and excess of it in surface water is taken as a warning for alga blooms and besides, it is usually taken also as a pollution indicator (Khaiwal *et al*., 2007). With this consideration, therefore, the sewage water was quite polluted compared with the tube-well waters.

Another pollution indicator in water is ammonia content. The values of ammonia content in sewage water samples ranged from 0.05 – 0.16, 0.05 – 0.18 and 0.08 – 0.19 mg/L for the months of February, March and April, respectively, while the values obtained from the tube-well water samples were quite lower than those found in sewage water samples.

In general, all the physico-chemical parameters of sewage water from the study area were higher in values than the corresponding ones from the control area. This revealed that the sewage water was quite polluted and might be attributed to the fact that the river basin received pollutants since it is the main basin that drains Southern Zaria, Samaru/ABU area inclusive.

4.3 **Metal Content of Sewage and Tube-well water Samples**

The results for metal concentrations in water samples from both the study and control areas for different sampling points are presented in Table 4.8 – 4.13. The composition of metals in the sewage water samples ranged from 0.454 $\pm$ 0.008 – 1.382$\pm$0.03mg/l for Zn; 0.624$\pm$0.007 – 1.813$\pm$0.01 mg/L Ni; 0.139$\pm$0.008 – 0.438$\pm$0.009 mg/L Cu; 0.056$\pm$0.004 – 0.193$\pm$0.04 mg/L Pb and 0.053$\pm$0.001 – 0.124$\pm$0.008mg/L Cd for the whole period of investigation.

The concentration of trace metals in the sewage water samples were found to be in the following order Ni> Zn> Cu> Pb> Cd. This indicated that Ni had the highest concentration (1.813 mg/L) while the least was Cd (0.124 mg/L).

TABLE 4.2: The physicochemical characteristics of sewage water (SW) for the month of February, 2008.

	Temp (^{0}C)	pH	Cond µScm^{-1}	Alkalinity (mg/l)	Total Hardness (mg/l)	Total suspended solid (mg/l)	Total dissolved solids (mg/l)	Total solids (mg/l)	Chloride (mg/l)	Sulphate (mg/l)	Phosphsate (mg/l)	Nitrate(mg/l)	Ammonia (mg/l)
SW_1	18.1	7.67	1280	94	293.21	155	624	779	45.93	230	0.05	8.1	0.08
SW_2	18.8	7.59	1332	112	304.82	168	642	810	32.51	290	0.06	4.4	0.05
SW_3	18.4	7.87	1090	169	302.52	145	533	673	46.03	310	0.04	12.6	0.08
SW_4	18.5	7.39	1261	124	324.08	137	622	759	36.32	240	0.03	8.5	0.12
SW_5	18.9	7.76	1310	119	317.42	162	643	805	49.10	350	0.06	14.2	0.16
SW_6	18.7	7.72	1440	158	285.12	124	702	826	34.08	220	0.08	12.9	0.05
SW_7	18.9	7.79	1094	108	310.73	152	553	705	31.79	225	0.02	5.8	0.07
SW_8	19.2	7.88	1423	133	299.05	135	723	858	33.14	270	0.04	4.4	0.06
SW_9	19.4	7.93	1483	127	313.09	140	752	892	39.03	235	0.05	6.7	0.09
SW_{10}	19.1	7.52	1202	98	320.03	154	624	778	37.57	220	0.09	9.2	0.06
FAO Limit for irrigation waters		6.5-8.4							4	300	0 - 2	5	

TABLE 4.3: The physicochemical characteristics of sewage water (SW) for the month of March, 2008.

	Temp (^{0}C)	pH	Cond µScm^{-1}	Alkalinity (mg/l)	Total Hardness (mg/l)	Total suspended solid (mg/l)	Total dissolved solids (mg/l)	Total solids (mg/l)	Chloride (mg/l)	Sulphate (mg/l)	Phosphsate (mg/l)	Nitrate(mg/l)	Ammonia (mg/l)
SW_1	25.8	8.02	1456	121	324.41	145	698	843	58.02	280	0.09	15.2	0.08
SW_2	26.2	8.24	1562	132	332.04	152	751	903	35.13	320	0.12	13.3	0.06
SW_3	26.6	8.38	1357	153	318.73	156	661	817	39.27	330	0.18	8.7	0.09
SW_4	27.2	8.12	1670	141	330.58	144	805	945	53.04	275	0.14	14.1	0.09
SW_5	27.1	8.22	1594	126	337.16	137	776	913	32.43	344	0.07	13.1	0.14
SW_6	27.8	8.20	1940	152	326.09	109	954	1063	48.82	255	0.08	14.7	0.07
SW_7	29.1	8.19	1343	128	343.14	142	648	790	36.06	286	0.16	6.3	0.18
SW_8	29.4	8.10	1875	137	322.54	126	929	1056	39.84	308	0.09	13.9	0.05
SW_9	29.8	8.34	1924	124	351.63	128	986	1114	44.59	289	0.11	8.1	0.08
SW_{10}	30.2	8.09	1718	113	358.03	162	878	1040	49.73	268	0.21	4.5	0.08
FAO Limit for irrigation waters		6.5-8.4							4	300	0 - 2	5	

Table 4.4: The physicochemical characteristics of sewage water (SW) for the month of April, 2008

	Temp (^{0}C)	pH	Cond µScm^{-1}	Alkalinity (mg/l)	Total Hardness (mg/l)	Total suspended solid (mg/l)	Total dissolved solids (mg/l)	Total solids (mg/l)	Chloride (mg/l)	Sulphate (mg/l)	Phosphsate (mg/l)	Nitrate(mg/l)	Ammonia (mg/l)
SW_1	28.8	8.14	1685	113	337.53	164	853	1017	53.70	320	0.11	16.9	0.10
SW_2	29.2	8.34	1782	128	351.06	148	902	1050	61.04	375	0.16	14.2	0.08
SW_3	29.7	8.42	1870	152	335.18	167	922	1089	52.15	365	0.23	13.8	0.13
SW_4	30.2	8.21	1910	147	361.42	132	963	1095	67.63	290	0.18	14.9	0.17
SW_5	30.5	8.32	1882	122	364.13	124	967	1091	55.09	370	0.08	15.6	0.19
SW_6	30.7	8.33	2010	149	358.23	136	995	1131	72.17	306	0.07	13.1	0.08
SW_7	30.6	8.36	1675	131	372.54	135	849	984	51.21	308	0.12	8.1	0.09
SW_8	30.9	8.24	2011	153	349.17	146	1026	1172	47.01	340	0.24	16.2	0.08
SW_9	31.4	8.49	2030	116	379.10	154	1031	1185	39.19	315	0.16	9.5	0.09
SW_{10}	31.8	8.22	2024	121	382.15	148	1024	1172	57.44	302	0.26	14.3	0.09
FAO Limit for irrigation waters		6.5-8.4							4	300	0 - 2	5	

Table 4.5: The physicochemical characteristics of Tube-well water (TW) for the Month of February, 2008

	Temp (^{0}C)	pH	Cond µScm^{-1}	Alkalinity (mg/l)	Total Hardness (mg/l)	Total suspended solid (mg/l)	Total dissolved solids (mg/l)	Total solids (mg/l)	Chloride (mg/l)	Sulphate (mg/l)	Phosphsate (mg/l)	Nitrate(mg/l)	Ammonia (mg/l)
TW_1	24.2	7.27	486	37	128.22	2	232	234	1.6	23	0.003	3.1	0.03
TW_2	24.1	7.24	462	36	122.53	2	222	224	2.1	36	0.005	2.4	0.02
TW_3	24.6	7.31	514	40	130.15	1	248	249	2.3	55	0.004	1.9	0.02
TW_4	25.1	7.42	527	41	132.58	2	256	258	3.2	21	0.003	3.6	0.03
TW_5	24.8	7.34	623	32	130.42	2	249	251	2.1	19	0.002	5.6	0.04
TW_6	24.9	7.36	426	33	119.23	1	206	207	1.9	18	0.004	1.4	0.01
TW_7	25.4	7.47	459	39	113.09	2	219	221	2.8	11	0.003	2.2	0.02
TW_8	24.2	7.48	568	42	159.26	2	278	280	3.5	32	0.004	6.2	0.04
TW_9	24.3	7.26	438	36	120.16	1	210	211	3.2	14	0.002	2.7	0.03
TW_{10}	24.4	7.24	464	38	118.58	2	229	230	2.2	31	0.002	3.9	0.04
FAO Limit for irrigation waters		6.5-8.4							4	300	0 - 2	5	

TABLE 4.6: The physicochemical characteristics of tube - well water (TW) for the Month of March, 2008

	Temp (^{0}C)	pH	Cond µScm^{-1}	Alkalinity (mg/l)	Total Hardness (mg/l)	Total suspended solid (mg/l)	Total dissolved solids (mg/l)	Total solids (mg/l)	Chloride (mg/l)	Sulphate (mg/l)	Phosphsate (mg/l)	Nitrate(mg/l)	Ammonia (mg/l)
TW_1	22.4	7.16	414	34	113.61	2	196	198	1.8	31	0.002	2.8	0.02
TW_2	22.2	7.10	436	32	118.54	2	206	208	2.3	28	0.002	2.6	0.02
TW_3	22.3	7.14	494	42	126.84	1	238	239	2.2	39	0.005	1.6	0.01
TW_4	22.5	7.18	488	43	130.16	2	242	244	3.2	23	0.004	2.9	0.02
TW_5	22.8	7.15	486	31	124.21	2	231	233	2.5	18	0.003	5.1	0.04
TW_6	22.4	7.18	380	30	111.52	1	186	187	2.2	20	0.001	1.8	0.01
TW_7	22.8	7.22	422	34	116.68	2	230	205	3.1	13	0.001	2.6	0.02
TW_8	22.9	7.24	496	44	122.88		224	226	3.2	26	0.003	5.6	0.05
TW_9	22.3	7.26	408	38	116.06	1	202	203	3.4	17	0.002	1.3	0.01
TW_{10}	22.6	7.20	439	33	120.54	2	212	214	2.6	24	0.002	2.4	0.02
FAO Limit for irrigation waters		6.5-8.4							4	300	0 - 2	5	

TABLE 4.7: The physicochemical characteristics of tube - well water (TW) for the Month of April, 2008

	Temp (^{0}C)	pH	Cond µScm^{-1}	Alkalinity (mg/l)	Total Hardness (mg/l)	Total suspended solid (mg/l)	Total dissolved solids (mg/l)	Total solids (mg/l)	Chloride (mg/l)	Sulphate (mg/l)	Phosphsate (mg/l)	Nitrate(mg/l)	Ammonia (mg/l)
TW_1	21.2	7.13	388	33	107.02	2	188	190	1.7	26	0.001	2.1	0.02
TW_2	20.6	7.08	393	30	108.55	2	190	192	2.4	31	0.001	3.1	0.03
TW_3	21.3	7.14	436	39	120.29	1	211	212	2.9	42	0.003	2.4	0.02
TW_4	20.8	7.10	402	43	110.51	2	196	198	3.1	19	0.003	3.2	0.03
TW_5	20.6	7.08	434	34	119.52	2	210	212	2.4	21	0.004	4.8	0.04
TW_6	20.8	7.12	346	36	103.41	2	168	170	2.6	22	0.002	3.3	0.03
TW_7	20.9	7.14	408	32	111.59	1	199	200	3.0	10	0.003	1.9	0.01
TW_8	21.4	7.16	448	40	121.33	1	216	217	3.4	28	0.002	5.7	0.04
TW_9	21.6	7.09	393	41	109.72	2	192	192	3.3	13	0.004	3.7	0.03
TW_{10}	22.2	7.08	414	30	115.69	1	204	204	2.7	21	0.004	3.4	0.03
FAO Limit for irrigation waters		6.5-8.4							4	300	0 - 2	5	

From the results, the distribution patterns of Ni concentrations amongst the sampling points was in the order SW_2> SW_1 SW_5> SW_8> SW_4> SW_3> SW_9> SW_{10}> SW_7> SW_6, whereas for Cd the trend was SW3> SW_8> SW_7> SW_6> SW_2> SW_9 SW_5> SW_1> SW_4> SW_{10}. These trends could be attributed to the anthropogenic influence within the vicinity of these sampling points. For example, every close to some of these sampling points are some activities like automobile repair workshops, refuse dump and car-wash sites, apart from the direct discharge of wastewater from the nearby residences might be adduced to the trends. The high levels of Ni obtained in this study might be as a result of the presence of old battery wastes, components of automobiles and many other items containing stainless steel and other Ni alloys.

The predominance of Ni amongst the metals analysed was in agreement with the report of Adakole (1995), who concluded that Ni was the most predominant metal in the stretch of River Kubanni. The average values of metals analysed (Zn, Ni, Cr, Pb, Cu and Cd) in Kubanni River water by Uzairu *et al*. (2008), who carried out the investigation in 2006 reported the following values (Pb, 6.54; Zn, 106.38; Cu, 73.51; Cr, 37.46; Ni, 11.83 and Cd, 0.82 mg/L), which are higher than the levels found in this study. Similarly, levels of Zn, Ni, Cu, Pb and Cd found in this study were lower than the corresponding values reported for Jakara wastewater channel (Zn, 7.45, Ni, 20.91, Cu, 3.58; Pb, 5.23 and Cd, 2.87 mg/L, Akan *et al*., 2008) and River Jakara (Pb, 1005-1818; Cu, 285 – 1390 and Cd, 290 – 310 mg/L; Dike *et al*., 2004) both in Nigeria as well as those for Tyume (Pb, 21-35; Zn, 97-431; Cu, trace – 387; Ni, 201-1777 and Cd, 30-44 mg/L; Awofolu *et al*., 2005) and Umtata (pb, 240 – 1110; Zn, 20-120; Cu, 100 – 530 and Cd, 10-260 mg/L; Fatoki et al., 2002, 2004) Rivers in South Africa. The level of these metals (Zn, 132; Ni, 3.0; Cu, 12.0; Pb, 9.0 and Cd, 0.7 mg/L) for Ballandure Lake (which

is a sewage-bearing lake) in India (Lokeshwaric and Chandrappa, 2006), were higher than the mean levels for Kubanni River basin.

Irrigation water with (mg/L) 0.01, Cd; 0.065, Pb; 0.017 Cu; 1.4, Ni and 2.0, Zn is considered safe for irrigation (FAO, 1985; USEPA, 2001). Therefore, Cd, Pb and Cu concentrations in all the sewage water samples were above the permissible limits for irrigation water and thus, the sewage water was polluted and not safe for irrigation throughout the period of investigation. The high levels of these metals in sewage water might be attributed to, apart from the natural sources, the indiscriminate discharge of wastes from nearby mechanic workshops, which could be from motor battery of Ni – Cd base, car paints, car panel beating wastes and solder for soldering car components as well as run-off from roadside car-wash sites. But in contrast, the amount of Zn in all the samples was within the permissible limits in irrigation water and again, Ni content was also within the permissible limits, but with some few exceptions. The few exceptions obtained might be attributed to anthropogenic activities mentioned. Therefore, in general, high concentrations of Cd, Pb, Cu and Ni (in some cases) rendered the sewage water from the study area unsuitable for irrigation.

For tube-well water samples from the control area, the metal concentrations varied between 0.024 $\pm$ 0.002 – 0.125 $\pm$ 0.002 mg/L for Zn; 0.061 $\pm$ 0.001 – 0.688$\pm$0.003 mg/L Ni; 0.024$\pm$0.001 – 0.096 mg/L Cu; 0.026$\pm$0.001 – 0.066 $\pm$ 0.002 mg/L Pb and 0.018$\pm$0.001 – 0.058$\pm$0.001 mg/L Cd for the whole period of investigation.

The profile of mean metal concentrations in tube-well water samples were in the sequence Ni> Zn> Cu> Pb> Cd. As it was in sewage water samples, Ni had the highest levels (0.688 mg/L) whereas Cd was also the least (0.058 mg/L). The trend of Ni distribution amongst the sampling points was in the order TW8> TW7> TW5> TW10> TW4> TW9>

TW2> TW3> TW6> TW1> while for Cd the pattern was TW8> TW4> TW1> TW10> TW9> TW7> TW2> TW5> TW3> TW6. From the results it was observed that tube-well water samples assumed similar trend of metal concentration distribution as sewage water samples. This might be as a result of percolation from nearby sewage water sources, which perhaps contaminated the ground waters in a similar trend.

The levels of Pb, Zn and Ni in all water samples from the control areas were within the permissible limits. However, Cd and Cu contents were above the permissible maximum levels for irrigation water. The high levels of these metals in all the tube-well water samples might be attributed to the excess application of phosphate fertilizers (which contained trace amounts of Cd), refuse dump and sewage sludge for soil fertility amendment. The metals from the contaminated soils might move out of the surface layer by percolation and probably contaminated the tube-well waters furthermore.

The mean values for all the metals in sewage samples were higher than those of the tube-well water samples from control sites. Therefore, this strengthened the observation made mention earlier that the sewage waters from the study area were quite polluted, since sewage water source points were more vulnerable to all sorts of water disposure than the tube-well water source points, which are confined environmental compartments.

4.4 **Physico-chemical parameters of sewage sludge samples**

Tables 4.14 – 4.16 present the physico-chemical parameters of sewage sludge from February – April, 2008, for all the sampling points. The pH values of the sewage sludge samples varied between 6.39 – 7.08, 6.44 – 6.95 and 6.73 – 7.10 for the months of February, March and April, respectively. The results revealed that the sewage sludge was slightly acidic

except at sampling point SL8 in February and sampling points SL3, SL10 and SL5 in April, which were neutral. It was observed that the highest pH value was found in April sampling, reached 7.10 at sampling point SL5. The lowest pH value was detected in SL9, during February sampling, 6.39. Furthermore, the results indicated that pH values were highest in April and lowest in February. This temporal variation was clear, since sampling was done from cool/harmattan to extremely hot season, in which temperature values were progressively increased.

Acidic pH of the sewage sludge samples might be attributed to the decomposition of organic matter by sewage sludge micro-organisms, since humus in the sewage sludge are not stable and decay over time to carbon dioxide. Therefore, under this condition the sewage sludge samples could become acidic due to formation of carbonic acid as a result of the reaction between the already formed carbon dioxide and water. The reaction pathway could be:

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)} \longrightarrow HCO^-_{3(aq)} + H^+_{(aq)}$$

Similar pH values (6.86-7.08) were reported by Servinc *et al*. (2002) for sewage sludge and Shomar *et al*. (2003) 6.43 – 7.04 for sewage sludge. In another similar study, Toory *et al*. (2003) reported 6.32 – 6.94 for sewage sludge. Thus, the results of pH values obtained in this work are similar to values reported in the literature.

The electrical conductivity (EC) of the sewage sludge samples ranged from 0.94 – 2.31, 0.94 – 2.20 and 1.03 – 2.18 dSm^{-1} for the months of February, March and April, respectively. The high values of EC obtained are indication of heavy presence of metallic ions. In fact, highest EC value was found in February sampling, reached 2.31dSm^{-1} at sampling point SL4, while the lowest EC in the sewage sludge samples was observed at sampling points SL8 and

TABLE 4.8: Mean ± SD of the metal concentrations (mg/l) in sewage water (SW) for Feb, 2008.

Element	Zn	Ni	Cu	Pb	Cd
SW_1	0.732± 0.020	1.641± 0.009	0.194± 0.007	0.056± 0.004	0.066± 0.003
SW_2	0.810± 0.009	1.724± 0.010	0.275± 0.010	0.075± 0.007	0.082± 0.010
SW_3	1.061± 0.030	0.964± 0.005	0.362± 0.040	0.128± 0.006	0.122± 0.020
SW_4	0.452± 0.008	1.054± 0.006	0.243± 0.006	0.093± 0.008	0.058± 0.006
SW_5	1.222± 0.007	1.375± 0.030	0.177± 0.009	0.069± 0.002	0.074± 0.006
SW_6	0.934± 0.007	0.624± 0.007	0.302± 0.010	0.107± 0.004	0.095± 0.008
SW_7	0.523± 0.010	0.781± 0.020	0.391± 0.007	0.131± 0.010	0.103± 0.002
SW_8	0.864± 0.040	1.286± 0.070	0.423± 0.010	0.086± 0.009	0.116± 0.007
SW_9	0.981± 0.050	0.832± 0.005	0.139± 0.008	0.113± 0.006	0.077± 0.006
SW_{10}	1.323± 0.030	0.804± 0.008	0.235± 0.020	0.132± 0.005	0.053± 0.001
RANGE	0.452-1.323	0.624- 1.724	0.139-0.432	0.056- 0.132	0.053-0.122
FAO and USEPA limits	2.0	1.4	0.017	0.065	0.01

TABLE 4.9: Mean ± SD of the metal concentrations (mg/l) in sewage water (SW) for March 2008

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SW_1	0.823± 0.020	1.284± 0.040	0.218± 0.008	0.061± 0.005	0.057± 0.001
SW_2	0.941± 0.009	1.561± 0.030	0.191± 0.020	0.093± 0.007	0.076± 0.007
SW_3	0.902± 0.010	0.784± 0.010	0.287± 0.002	0.098± 0.010	0.085± 0.004
SW_4	0.647± 0.005	1.311± 0.005	0.253± 0.010	0.065± 0.002	0.072± 0.003
SW_5	1.382± 0.030	1.328± 0.009	0.214± 0.006	0.084± 0.006	0.104± 0.003
SW_6	0.784± 0.007	0.963± 0.020	0.326± 0.007	0.136± 0.007	0.112± 0.007
SW_7	0.832± 0.010	1.086± 0.008	0.378± 0.030	0.148± 0.010	0.083± 0.010
SW_8	1.204± 0.008	1.204± 0.008	0.438± 0.009	0.103± 0.005	0.124± 0.008
SW_9	1.081± 0.050	0.941± 0.007	0.153± 0.004	0.129± 0.008	0.825± 0.009
SW_{10}	1.142± 0.006	0.635± 0.004	0.194± 0.020	0.114± 0.005	0.059± 0.005
RANGE	0.647-1.382	0.635- 1.561	0.153-0.438	0.061- 0.148	0.057-0.124
FAO and USEPA limits	2.0	1.4	0.017	0.065	0.01

TABLE4.10: Mean ± SD of the metal concentrations (mg/l) in sewage water (SW) for April, 2008

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SW_1	1.103± 0.020	1.327± 0.008	0.183± 0.010	0.173± 0.007	0.062± 0.008
SW_2	0.875± 0.040	1.813± 0.010	0.301± 0.005	0.188± 0.030	0.088± 0.010
SW_3	0.943± 0.009	0.752± 0.009	0.249± 0.020	0.106± 0.009	0.074± 0.005
SW_4	0.528± 0.010	1.433± 0.020	0.316± 0.007	0.193± 0.040	0.081± 0.007
SW_5	1.094± 0.008	0.859± 0.007	0.143± 0.009	0.159± 0.008	0.095± 0.006
SW_6	0.861± 0.050	1.025± 0.008	0.259± 0.030	0.121± 0.006	0.073± 0.004
SW_7	0.856± 0.007	0.976± 0.040	0.318± 0.009	0.110± 0.009	0.097± 0.020
SW_8	1.012± 0.008	1.316± 0.005	0.391± 0.004	0.189± 0.004	0.102± 0.004
SW_9	1.303± 0.010	1.014± 0.009	0.184± 0.006	0.095± 0.005	0.068± 0.010
SW_{10}	1.224± 0.008	0.771± 0.030	0.166± 0.040	0.098± 0.009	0.071± 0.009
RANGE	0.528-1.303	0.752- 1.813	0.143-0.391	0.095- 0.188	0.062-0.102
FAO and USEPA limits	2.0	1.4	0.017	0.065	0.01

TABLE 4.11: Mean ±SD of the metal concentrations (mg/l) in shallow tube - wells (TW) for the month of February, 2008.

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
TW_1	0.024+ 0.002	0.084± 0.002	0.073± 0.002	0.060± 0.002	0.049± 0.003
TW_2	0.052± 0.001	0.257± 0.001	0.053± 0.001	0.026± 0.001	0.033± 0.001
TW_3	0.074± 0.001	0.174± 0.002	0.024± 0.001	0.058± 0.001	0.019± 0.001
TW_4	0.103± 0.002	0.336± 0.002	0.039± 0.003	0.053± 0.001	0.052± 0.001
TW_5	0.125± 0.002	0.517± 0.1002	0.051± 0.002	0.048± 0.001	0.028± 0.002
TW_6	0.044± 0.002	0.103± 0.001	0.046± 0.001	0.034± 0.001	0.019± 0.001
TW_7	0.028± 0.001	0.521± 0.003	0.087± 0.003	0.063± 0.001	0.035± 0.002
TW_8	0.012± 0.002	0.688± 0.003	0.062± 0.001	0.052± 0.001	0.052± 0.002
TW_9	0.083± 0.002	0.293± 0.002	0.043± 0.002	0.046± 0.002	0.038± 0.002
TW_{10}	0.034± 0.002	0.034± 0.002	0.092± 0.001	0.055± 0.002	0.042± 0.003
RANGE	0.012-0.125	0.034- 0.521	0.024-0.092	0.026- 0.063	0.019-0.052
FAO and USEPA limits	2.0	1.4	0.017	0.065	0.01

TABLE 4.12: Mean ±SD of the metal concentrations (mg/l) in shallow tube - wells (TW) for the month of March, 2008.

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
TW_1	0.046± 0.02	0.061± 0.001	0.036± 0.001	0.046± 0.001	0.023± 0.001
TW_2	0.032± 0.001	0.196± 0.003	0.044± 0.002	0.034± 0.002	0.053± 0.002
TW_3	0.057± 0.003	0.203± 0.001	0.041± 0.001	0.061± 0.001	0.018± 0.001
TW_4	0.098± 0.002	0.281± 0.002	0.073± 0.001	0.063± 0.001	0.042± 0.001
TW_5	0.061± 0.003	0.683± 0.001	0.069± 0.003	0.028± 0.002	0.036± 0.001
TW_6	0.036± 0.001	0.210± 0.002	0.039± 0.003	0.054± 0.001	0.028± 0.002
TW_7	0.069± 0.003	0.359± 0.003	0.064± 0.002	0.043± 0.001	0.044± 0.002
TW_8	0.106± 0.001	0.412± 0.002	0.096± 0.002	0.063± 0.001	0.036± 0.002
TW_9	0.029± 0.003	0.163± 0.001	0.028± 0.002	0.051± 0.002	0.026± 0.003
TW_{10}	0.046± 0.001	0.509± 0.003	0.052± 0.001	0.037± 0.003	0.038± 0.001
RANGE	0.029-0.106	0.061-0.683	0.028-0.094	0.028-0.063	0.018-0.053
FAO and USEPA limits	2.0	1.4	0.017	0.065	0.01

TABLE 4. 13: Mean ±SD of the metal concentrations (mg/l) in shallow tube - wells (TW) for the month of April, 2008.

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
TW_1	0.032± 0.001	0.093± 0.001	0.031± 0.001	0.039± 0.002	0.034 ±0.001
TW_2	0.048± 0.002	0.154± 0.002	0.066± 0.002	0.029± 0.001	0.041± 0.002
TW_3	0.042± 0.001	0.143± 0.001	0.033± 0.001	0.051± 0.001	0.026± 0.001
TW_4	0.089± 0.003	0.293± 0.001	0.049± 0.003	0.043± 0.002	0.053± 0.001
TW_5	0.028± 0.002	0.406± 0.002	0.028± 0.001	0.034± 0.002	0.029± 0.002
TW_6	0.046± 0.002	0.188± 0.003	0.057± 0.002	0.028± 0.002	0.022± 0.001
TW_7	0.032± 0.001	0.291± 0.002	0.052± 0.002	0.048± 0.002	0.036± 0.002
TW_8	0.094± 0.002	0.424± 0.002	0.037± 0.002	0.036± 0.001	0.047± 0.002
TW_9	0.053± 0.001	0.197± 0.002	0.034± 0.001	0.043± 0.001	0.030± 0.001
TW_{10}	0.029± 0.002	0.458± 0.003	0.067± 0.002	0.038± 0.003	0.033± 0.001
RANGE	0.028-0.094	0.093- 0.458	0.028-0.067	0.029- 0.051	0.022-0.053
FAO and USEPA limits	2.0	1.4	0.017	0.065	0.01

SL10, during February and March samplings, respectively. The EC variation amongst the sampling points might be due to the difference in precipitation and settling of soluble salts in the subsurface layer of sewage sludge samples, of which are usually influenced by inundation, flow rate and channel fragmentation imposed by impoundments. The results of EC found in this study were similar with the values reported by Servinc *et al*. (2002) (1.76 – 2.10 dSm^{-1}) for sewage sludge. But in contrast, the values of EC reported by Shrivastava and Banerjee (2004) (0.56 dSm^{-1}) is lower than the values obtained in this work.

The results of organic matter content of sewage sludge samples varied between 24.6 – 51.1% in February sampling, 23.4 – 52.6% in March and 25.9 – 48.7% in April, 2008. The highest organic matter content in the samples of 52.6% was recorded for sampling point SL4, during March sampling, and the lowest was (23.4%) also found in March sampling point SL10. Diffuse pollution source from a refuse dump site near the sampling point SL4 might be the reason for the high organic matter content of sampling point.

The relevance of organic matter to this study is its influence on the nutrient storage capacity as well as mobility and flux of trace metals. The very significant amount obtained in this study signified that organic matter could be in charge of stocking nutrients and in case of pollution, storing persistent substances, such as trace metals. This is because organic matter has more adsorption power than even clay (Jayashree, 2006). The amounts of organic matter content obtained in this research were higher than the value reported by Servinc *et al*. (2002) and Shrivastava and Banerjee (2004), whose highest values were 25.0% and 36.2%, respectively, for sewage sludge.

Apart from the rich organic matter content, sewage sludge contained nitrogen, phosphates and relatively small amounts of potassium and in addition, micronutrients (Petrik

and Ing, 1957). The total nitrogen values of the sewage sludge samples were found to range from 2.4 – 4.9, 2.7 – 4.4 and 2.5 – 4.2% for the months of February, March and April, respectively. The highest nitrogen content was 4.9%, observed for SL3, while sampling point SL6 had the lowest nitrogen content of 2.4%. Phosphorus content of the sewage sludge samples also varied between 1.1 – 2.8, 1.3 – 2.7 and 1.3 – 2.6% for the same months in the same order. The highest value of 2.8% was detected in SL5, and the lowest of 1.1% for sampling point SL6. The potassium content of the samples ranged from 0.6 – 1.3, 0.5 – 1.6 and 0.5 – 1.3% for the same months of February, March and April, respectively. Sampling point SL1 had the highest potassium content while sampling point SL8 and SL10 had the lowest potassium levels. The nitrogen, phosphorus and potassium contents obtained in this work were higher than the values reported by Toory *et al*. (2003) for sewage sludge, whose highest values of nitrogen, phosphorus and potassium were 2.62%, 0.61% and 0.06%, respectively. But in contrast, the values obtained in this investigation were lower than the values reported by Servinc *et al.* (2002) for sewage sludge, whose highest values of the nutrients were 5.28%, 3.08 and 1.91% for the same elements in the same order. Therefore, the sewage sludge samples were quite rich with significant percentages of nitrogen, phosphorus and potassium, and besides, the agronomic parameters of the sewage sludge samples agreed with the data presented in Table 4.17. Thus, the sewage sludge from Kubanni River basin was appropriate for use in agricultural application for soil fertility amendment.

Tables 4.14 – 4.16 also contain the particle size distribution; texture classes of sewage sludge at each sampling point. Clay content ranged from 14 – 38, 16 – 39 and 15 – 39% for the months of February, March and April, respectively, while the silt content varied between 31 – 52, 44 – 50 and 43 – 53% for the same months in the same order. The sand content also ranged

from 16 – 53, 17 – 38 and 16 – 38% for the same months in the same order. All the samples were in the texture class clay loam with the exception of sampling points SL6 and SL10, which were classified as silt loam. This partial variation was due to their higher silt/sand content. However, the high clay/silt content of the samples might be attributed to the flow rate of the sewage water in the river basin, which was moved slowly and thus, high deposit of sludge enriched with these materials occurred. The textural class obtained for sewage sludge samples in this work corresponded with the sewage sludge textural class observed by Servinc *et al*. (2002).

Results of the cation exchange capacity (CEC) of the samples are also presented in Tables 4.14 – 4.16, which ranged from 49.2 – 80.6, 46.5 – 74.4 and 51.3 – 78.8 cmol/kg for the months of February, March and April, respectively. The results indicated that calcium was the dominant exchangeable cation (20.57 – 68.24 cmol/kg) in all the samples. The cation concentration in the sewage sludge samples were in the following descending order: Ca> Mg> K> Na. The obtained results agreed with those obtained by Shrivastava and Banerjee (2004) and Toory *et al*. (2003) for sewage sludge.

The ability to exchange cations is one major sewage sludge property that controls the fate of ionically charged contaminant in the sewage sludge. Besides, the storage capacity of sewage sludge is determined by its cation cxchange capacity. Furthermore, the fertility of sewage sludge also is expressed by CEC (Jayashree, 2006). The greater the CEC value the more fertile is the sewage sludge (Zufiaurre *et al*., 1998). With the values obtained, therefore, this supports the observation made earlier that the sewage sludge samples were rich with agronomic parameters and, the sewage sludge samples were actually filled with plant nutrients. Soil fertility is not only influenced by the cation exchange capacity (CEC), but also by how

much of the CEC is actually filled with plant nutrients (Jayashree, 2006). Each exchange site can be filled by members of either of two groups of cations. One group consists of H^+ and Al^{3+}, which are not plant nutrients at all. Their primary contribution is to acidify the sludge. The other cations are called exchangeable base and include elements such as Ca, Mg, K and Na. Except for sodium, the other bases are plant nutrients. Hence, the results of these exchangeable bases obtained signified the potential fertility of the sewage sludge from the Kubanni River basin.

4.5 **Metal content in sewage sludge samples**

Tables 4.18 – 4.20 show the concentrations of the five metals examined in sewage sludge samples collected from February – April, 2008. The Zn Content of the sewage sludge samples ranged from 334.5±8.2 – 445.8±6.4, 315.7±6.8 – 442.8±5.6 and 373.6±5.6 – 479.3±7.1 mg/kg for the months of February, March and April, respectively, while Ni concentrations varied between 118.6±6.2 – 258.5±7.2, 146.4±6.2 – 276.3±5.6 and 175.8±6.7 – 243.9±5.7 mg/kg for the same months in the same order. The levels of Cu ranged from 253.2±6.3 – 346.5±8.3, 252.9±5.6 – 349.2±8.4 and 242.2±5.1 – 338.1±8.3 mg/kg for the same order of the months as above. The Cd and Pb concentrations varied from 8.8±2.7 – 24.7±3.9, 8.2±2.1 – 23.6±4.1, 8.5±2.6 – 25.9±3.3 mg/kg and 89.6±5.3 – 155.5±5.8, 95.3±3.8 – 151.3±4.9, 86.3±4.4 – 193.3±5.2 mg/kg, respectively for the same months in the order. Among the trace metals examined in the sewage sludge samples, Zn levels was found to be highest followed by Cu and Cd concentration was the least. The high concentration of Zn found in this study might be as a result of anthropogenic deposition influence in the river basin. The profile of the average metal concentration in the sewage sludge samples was: Zn> Cu> Ni> Pb> Cd.

The high levels of Zn in the Kubanni River basin could be attributed to Zinc – galvanised materials such as remnant of roofing sheets and the dumping of Le Chalanche cells or R20 and AA-size batteries with Zn cathode amongst the sampling points. In fact, at sewage sludge sampling station SL2, heavy presence of such R20 and AA-size Tiger brand materials were observed. As for Ni concentrations, the highest concentration was 276.3mg/kg in SL1, and the lowest was 118.6 mg/kg at sampling point SL7. This variation might be attributed to the difference in the settlement of nickel containing materials in the basin as it was hypothesized in sewage water samples. In the case of Cu and Pb, the highest Cu concentration was recorded at SL2 (349.2 mg/kg), SL4 (193.3 mg/kg) for Pb and the lowest Cu and Pb concentrations were at SL9 (242.2 mg/kg) and SL10 (86.3 mg/kg), respectively. This might be as a result of the variation in the levels of organic matter content amongst the sampling stations, as Cu and Pb form very stable complexes with dissolved organic matter which influences their availability (Sauve *et al.*, 1998). The sampling station SL5 had the highest Cd concentration (25.9mg/kg), while SL3 had the lowest Cd concentration (8.2 mg/kg).

The significant concentration of these metals observed was not surprising, as it was reported that sewage sludge is a ready sink or reservoir of pollutant including trace metals where they concentrate according to the level of pollution (Onyari *et al.*, 2003). In addition, sewage sludge is in charge of stocking nutrient and, in case of pollution, storing persistent substances such as trace metals, for instance (Zufiaurre *et al.*, 1998). According to Nilsson *et al.* (2005), this accumulation is as a result of physical, chemical and biological processes (e.g.

TABLE 4.14: Basic physicochemical and agronomic characteristics of sewage - sludge (SL) for the month of Feb. 2008.

Char.	pH	EC (dsm^{-1})	Organic Matter (%)	Total Nitrogen (%)	Available phosphorus (%)	Potassium (%)	Clay (%)	Silt (%)	Sand (%)	Textural Class	CEC (cmoi/kg)	Ex-Na^{+} (cmoi/kg)	Ex - K^{+} (cmoi/kg)	Ex - Ca^{2+} (cmoi/kg)	Ex - Mg^{2+} (cmoi/kg)
SL_1	6.82	2.12	42.8	3.8	2.4	1.3	36	46	18	Clay Loam	67.8	8.22	15.41	42.77	16.52
SL_2	6.54	1.78	49.3	4.3	2.2	0.9	33	44	23	Clay Loam	72.7	6.12	10.62	53.33	18.27
SL_3	6.91	1.28	36.9	4.9	2.6	0.6	32	52	16	Clay Loam	80.6	3.89	8.57	68.24	15.60
SL_4	6.87	2.31	51.1	3.3	1.7	1.1	34	48	18	Clay Loam	64.6	4.06	9.28	48.25	10.88
SL_5	6.77	1.58	39.4	3.1	2.8	1.2	38	42	20	Clay Loam	56.8	5.74	10.90	34.23	13.36
SL_6	6.84	1.24	24.6	2.4	1.1	0.7	16	31	53	Silt Loam	49.9	6.18	8.07	31.66	15.69
SL_7	6.67	1.05	32.4	3.4	1.4	0.8	32	46	22	Clay Loam	63.7	8.27	7.17	49.08	16.78
SL_8	7.08	0.94	35.7	3.8	1.6	0.6	32	47	21	Clay Loam	64.8	11.02	10.43	32.84	17.06
SL_9	6.39	2.09	37.2	3.4	2.3	0.8	36	44	20	Clay Loam	56.3	5.92	10.81	29.45	15.22
SL_{10}	6.46	0.97	26.8	2.6	1.2	0.9	14	50	36	Silt Loam	49.2	12.11	10.55	20.57	16..11

CEC, Cation exchange capacity; Ex, exchangeable; EC, electrical conductivity

TABLE 4.15: Basic physicochemical and agronomic characteristics of sewage - sludge (SL) for the month of March. 2008.

Char.	pH	EC (dsm^{-1})	Organic Matter (%)	Total Nitrogen (%)	Available phosphorus (%)	Potassium (%)	Clay (%)	Silt (%)	Sand (%)	Textural Class	CEC (cmoi/kg)	Ex-Na^{+} (cmoi/kg)	Ex - K^{+} (cmoi/kg)	Ex - Ca^{2+} (cmoi/kg)	Ex - Mg^{2+} (cmoi/kg)
SL_1	6.48	2.20	38.7	4.1	2.7	1.6	36	44	20	Clay Loam	70.2	6.88	13.52	45.18	22.41
SL_2	6.63	2.11	44.2	3.6	1.8	1.1	31	46	23	Clay Loam	68.6	3.19	8.24	43.21	20.53
SL_3	6.88	1.68	38.2	4.4	2.3	0.9	34	48	18	Clay Loam	74.4	2.79	11.58	52.02	18.82
SL_4	6.74	2.06	52.6	3.4	1.9	0.8	33	50	17	Clay Loam	68.9	3.11	9.22	49.33	15.76
SL_5	6.56	1.75	40.9	3.3	2.1	1.2	34	46	20	Clay Loam	52.7	4.26	7.92	38.20	13.44
SL_6	6.92	1.62	28.2	2.7	1.3	0.6	18	50	32	Silt Loam	55.1	2.04	10.36	36.62	14.34
SL_7	6.44	1.43	35.3	3.6	1.4	0.9	32	44	24	Clay Loam	71.2	2.93	12.03	54.37	19.25
SL_8	6.95	1.18	30.9	3.0	1.9	0.5	35	46	20	Clay Loam	66.3	3.07	8.44	48.78	14.72
SL_9	6.58	1.56	39.7	3.2	2.4	1.3	39	44	17	Clay Loam	58.8	5.12	9.47	36.56	18.06
SL_{10}	6.79	0.94	23.4	2.8	1.6	0.7	16	46	38	Silt Loam	46.5	4.57	9.82	73.43	10.61

CEC, Cation exchange capacity; Ex, exchangeable; EC, electrical conductivity

TABLE 4.16: Basic physicochemical and agronomic characteristics of sewage - sludge (SL) for the month of April. 2008.

Char.	pH	EC (dsm^{-1})	Organic Matter (%)	Total Nitrogen (%)	Available phosphorus (%)	Potassium (%)	Clay (%)	Silt (%)	Sand (%)	Textural Class	CEC (cmoi/kg)	Ex-Na^{+} (cmoi/kg)	Ex - K^{+} (cmoi/kg)	Ex - Ca^{2+} (cmoi/kg)	Ex - Mg^{2+} (cmoi/kg)
SL_1	6.88	2.14	40.3	4.2	2.3	0.8	35	49	16	Clay Loam	78.8	8.26	16.83	46.21	20.13
SL_2	6.73	2.16	46.4	4.0	2.6	1.3	30	49	21	Clay Loam	68.3	6.94	12.07	41.38	19.06
SL_3	7.01	1.88	41.2	3.7	1.9	0.7	31	50	19	Clay Loam	76.2	9.16	7.56	57.92	21.51
SL_4	6.92	2.18	48.7	3.8	1.5	0.6	29	53	18	Clay Loam	66.7	11.1	10.19	43.12	18.10
SL_5	7.10	1.77	43.5	3.6	2.4	1.1	36	43	21	Clay Loam	60.8	7.22	13.20	39.33	16.41
SL_6	7.04	1.92	25.9	2.5	1.3	0.9	17	45	38	Silt Loam	53.4	6.55	9.17	34.11	13.87
SL_7	6.78	1.85	34.4	3.7	1.6	0.8	30	50	20	Clay Loam	69.1	3.89	12.32	40.52	18.95
SL_8	6.69	1.69	36.8	3.2	1.8	0.7	31	52	17	Clay Loam	76.5	12.44	8.05	52.08	20.49
SL_9	6.96	2.06	34.1	3.6	2.2	1.2	32	48	20	Clay Loam	62.9	4.31	11.42	41.82	15.74
SL_{10}	7.03	1.03	27.2	2.7	1.4	0.5	15	49	36	Silt Loam	51.3	5.83	7.57	37.64	14.68

CEC, Cation exchange capacity; Ex, exchangeable; EC, electrical conductivity

Table 4.17: Recommended Levels of nutrient content (% dry weight) of sewage sludge for agricultural purposes

Nutrients	Sewage Sludge
N	1.5
P	1.3
K	0.4

Source: http://www.uky.edu/Agriculture/Horiticulture/comveggie.html

settling, precipitation, complexation, and bioaccumulation) some of which are influenced by flow manipulation and channel fragmentation. Therefore, the concentrations of these metals found in sewage sludge were much higher than those of sewage waters; hence the sewage sludge could be an influential contributor to the level of these metals in sewage water column. This could further be strengthened with the fact that positive correlations ($p>0.05$) were found between sewage water and sludge (Appendices XVIa – XVIc). Furthermore, the acidic pH and significant organic matter of the sewage sludge could also be influential factors which influenced the availability of these metals in the sewage sludge.

The levels of the trace metals found in this study are similar to the values (Zn, 408; Ni, 127.2; Cu, 321.3; Pb, 109.3 and Cd, 15.3 mg/kg) reported by Shrivastava and Banerjee (2004) for sewage sludge. In a similar work, Zufiaurre *et al*. (1998) analysed sewage sludge for levels of these metals and obtained: Zn, 1635; Ni, 232.1; Cu, 298.1; Pb, 137.1 and Cd, 11.5mg/kg. Their values are also almost the same with those reported here except that their Zn concentration was higher than any of the values found in this study. In their study also, Zn had the highest concentration and Cd had the least. The pattern of distribution of these metals in their work was: Zn> Cu> Ni> Pb> Cd, which is the same with the trend obtained in this investigations. In another study, Shomar *et al.* (2003) reported (Zn, 897 – 2281; Ni, 24 – 60; Cu, 110 – 251; Pb, 49 – 92 and Cd, 0.9 – 2.0 mg/kg) for sewage sludge which were lower than the mean levels obtained in this research, with the exception of Zn concentration which is higher than the corresponding one obtained.

However, all the mean values found in this investigation were below the EU (1986) sewage sludge standard for agricultural uses. Therefore, from the agricultural point of view, the

sewage sludge from the Kubanni River basin could be used as fertilizer for soil fertility amendment, as the trace metal concentrations had not exceeded the EU permissible limits.

4.6 **Physico-chemical Parameters of Soil Samples**

Tables 4.21 – 4.22 show the physico-chemical parameters of soil of study and control areas, respectively. The pH values of soil samples from the study area were found to be in the range 5.83 to 7.32, whereas those for control area varied from 5.87 to 7.32. In the study area, the highest pH value was 7.32 at sampling point SS10 and the lowest was found to be 5.83 at site SS8. For the control area, the highest pH value was 7.12 at CSS10, while the least value was 5.87 at site CSS7. This revealed that the soil samples from both study and control areas were slightly acidic to slightly alkaline in nature. The electrical conductivity (EC) varied from 0.38 – 0.66 dSm^{-1} for soil samples from study area and 0.20 – 0.33 dSm^{-1} for those from control area. The higher values obtained in the study area than those of the control area might be attributed to the secondary addition of soluble salts as a result of irrigation with sewage water, from which more ions got into the soils of the study area. In fact, studies have shown that sewage water irrigated soils become enriched with soluble salts from sewage water when used for irrigation (Ibrahim *et al*., 1992).

The typical amount of organic matter in soil varies from < 1% in ordinary soil to 90% in mineral soils (Rodojevic and Bashkin, 1999). Therefore, the values obtained in this work were within this range and the relevance of organic matter to this study is its influence on mobility and flux of trace metals in the soils. The normal range of organic matter obtained signified that the trace metals in soils of both the study and control areas would be available

TABLE 4.18 the total metal content (mg/kg±SD, dry weight) in sewage - sludge (SL) for the month of Feb. 2008.

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SL_1	344.5± 8.2	258.5± 7.2	346.5± 8.3	155.5± 5.8	17.4± 3.1
SL_2	411.8± 7.4	134.5± 7.8	321.7± 7.8	134.7± 6.3	13.1± 2.8
SL_3	369.2± 6.2	214.8± 5.3	259.2± 5.8	126.4± 5.6	10.7± 3.3
SL_4	457.2± 6.8	128.5± 6.8	283.4± 5.3	93.4± 4.2	15.8± 4.2
SL_5	382.5± 5.9	142.3± 5.7	302.6± 7.5	137.3± 7.3	10.3± 2.6
SL_6	404.6± 7.3	201.7± 9.4	314.8± 5.4	142.6± 8.4	20.4± 4.7
SL_7	362.8± 5.7	118.6± 6.2	291.2± 6.2	113.4± 6.5	9.7± 2.1
SL_8	423.2± 8.4	223.4± 8.4	277.3± 8.4	89.6± 5.3	15.3± 3.8
SL_9	445.8± 6.4	183.2± 5.9	253.2± 6.3	128.1± 6.9	24.7± 3.9
SL_{10}	363.1± 8.2	158.9± 5.7	326.7± 8.6	102.8± 2.7	8.8± 2.7
RANGE	344.5-457	128.5-258.5	253.2-346.5	89.6-155.5	8.8-24.7
EU limits for Agric. purpose	2,500-4,000	300-400	1,000-1,750	750-1200	20-40

TABLE .4.19: The total metal content (mg/kg±SD, dry weight) in sewage - sludge (SL) for the month of March. 2008.

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SL_1	413.2± 7.4	296.3± 5.6	339.6± 6.9	123.8± 6.2	10.6± 2.3
SL_2	356.5± 8.3	229.1± 7.1	349.6± 6.9	149.2± 5.9	23.6± 4.1
SL_3	354.8± 6.2	185.3± 5.2	283.7± 5.1	133.7± 4.8	8.2± 2.1
SL_4	387.1± 8.7	131.5± 6.4	252.9± 5.6	102.3± 5.1	14.3± 2.8
SL_5	418.3± 9.1	211.8± 7.8	284.5± 7.5	118.9± 6.7	9.8± 1.9
SL_6	315.7± 6.8	173.9± 5.6	306.4± 5.3	151.3± 4.9	18.2± 3.3
SL_7	424.5± 5.5	146.4± 6.2	276.7± 6.2	107.5± 5.2	21.7± 3.7
SL_8	382.3± 7.3	210.4+ 5.7	314.5± 7.8	128.4± 6.1	18.9± 2.8
SL_9	343.9± 8.4	163.7± 8.2	296.3± 5.8	95.3± 3.8	15.5± 3.6
SL_{10}	442.8± 5.6	221.6± 6.5	341.8± 6.3	119.4± 5.3	12.7± 2.4
RANGE	315.7-442.8	131.5-296.3	252.9-349.6	95.3-151.3	8.2-23.6
EU limits for Agric. purpose	2,500-4,000	300-400	1,000-1,750	750-1200	20-40

TABLE 4.20: The total metal content (mg/kg±SD, dry weight) in sewage - sludge (SL) for the month of April. 2008.

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SL_1	392.4± 6.3	243.9± 5.7	327.2± 5.4	116.9± 4.6	13.7± 2.3
SL_2	479.3± 7.1	213.7± 7.6	252.3± 8.1	130.8± 5.6	16.6± 3.4
SL_3	408.9 ±6.4	226.4± 6.7	319.4± 5.8	101.5± 4.9	12.7± 4.1
SL_4	387.6± 5.8	175.8± 6.1	295.7± 5.4	193.3± 5.2	8.5± 2.6
SL_5	422.4± 6.9	236.3± 5.3	313.5± 6.2	137.4± 6.2	25.9± 3.3
SL_6	391.8± 7.1	218.7± 4.9	328.4± 5.8	144.8± 4.8	14.4± 2.9
SL_7	373.6± 5.6	181.4± 5.5	301.6± 4.9	125.6± 5.2	10.1± 2.2
SL_8	443.8± 6.7	209.4± 6.3	283.5± 6.3	112.7± 4.5	13.3± 3.1
SL_9	385.7± 5.6	194.9± 4.7	311.2± 5.1	123.8± 4.6	20.1± 3.2
SL_{10}	411.6± 8.1	231.3± 8.3	338.1± 4.4	86.3± 4.4	9.3± 2.5
RANGE	343.8-479.3	175.8-243.9	252.3-388.1	86.3-193.3	9.3-25.9
EU limits for Agric. purpose	2,500-4,000	300-400	1,000-1,750	750-1200	20-40

since trace metals are known to form complexes with organic matter which influences their availability (Sauve *et al.*, 1998). However, the availability of these metals would be less in the soils of control area since the organic matter contents there were less than those of the study area. This is further supported with the fact that there will be less availability of trace metals in soil, provided there is no enough organic matter present to facilitate metal binding (Jacob and Otte, 2003).

The results of particle size distribution and texture classes of soils at each sampling point in the study and control area are also presented in Tables 4.21 – 4.22. The clay content of soil samples from study area ranged from 7 – 14%, while the silt content varied between 38 – 56% and the sand content was between 32 – 57%. All the soil samples from of the study area were classified as loam with the exception of soil samples from sampling points SS8, SS9 and SS10, which were classified as silt loam. Similarly, clay content of soil samples collected from the control area varied from 8 – 17%, silt content from 38-48% and sand content from 39-50%. Without exception, all the soils of the control area were in the texture class loam. Nyles and Ray (1999) reported that soil with low clay content has high pollutant leaching potentials. From the obtained results, it could therefore be deduced that the soils of both study and control areas have high potentials of leaching trace metals due to their low clay contents, which could easily penetrate into the subsurface layer of the soils. For example, Ericksson (1989) found that for a given total Cd concentration, Cd was more soluble and plant available in soils that are not clay in nature. This further indicated that the soil solution in this study might be enriched with trace metals, thus making them available for plant uptake. Thus, plants in these soils may accumulate high concentration of trace metals.

The results of cation exchange capacity (CEC) for the soil samples from both study and control areas are also shown in Tables 4.21 and 4.22, respectively, and revealed that the CEC of the soils of the study area were higher than those of the control area. For the study area soil samples, the CEC values ranged from 17.6 – 28.4 cmol/Kg, while the CEC values for control area soil samples varies from 8.3 – 16.8 cmol/kg. Calcium was the dominant exchangeable cation (20.92 and 12.29 cmol/kg) in all the samples of both the study and control areas. The results indicated that the soils of the study area were more fertile than the soils of the control area. This might be due to the influence of the type of water used for irrigating the soils of the study area, as it was earlier reported that sewage water of municipal origin contained appreciable amount of major plant nutrients and possibly, supplies additional nutrients to sewage water – irrigated soils (Rajesh *et al*., 2004). Regarding the cation exchangeable bases, it is clear from the results obtained that the exchangeable bases K^+, Na^+, Mg^{2+} and Ca^{2+} followed the trend as $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. This is in accordance with the result obtained by Mapanda *et al*. (2005) in a similar study. However, in contrast, Abdel-Hady (2007) reported a different trend, of which the exchangeable bases were in the following order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$.

In general, values of physico-chemical parameters of soils from the study area were higher than those from the control area. This indicated that soil basic characteristics such as cation exchange capacity (CEC), exchangeable bases and organic matter in sewage water irrigated area obviously increased. Therefore, sewage water irrigation had influenced soils quality/property in the soils of the study area.

TABLE 4.21: Basic physicochemical characteristics of soils from sewage water - irrigated lands.

Char.	pH	EC (dsm^{-1})	Organic Matter (%)	Clay (%)	Silt (%)	Sand (%)	Textural Class	CEC (cmoi/kg)	Ex-Na^{+} (cmoi/kg)	Ex - K^{+} (cmoi/kg)	Ex - Ca^{2+} (cmoi/kg)	Ex - Mg^{2+} (cmoi/kg)
SS_1	6.72	0.39	4.55	10	34	56	Loam	22.8	0.26	1.24	18.48	5.45
SS_2	6.31	0.51	5.14	10	40	50	Loam	25.5	0.39	0.99	18.21	6.56
SS_3	6.44	0.38	7.07	8	42	50	Loam	19.8	0.18	1.03	19.16	3.69
SS_4	6.78	0.43	8.28	12	40	48	Loam	20.4	0.48	2.01	13.14	5.09
SS_5	6.83	0.49	7.45	7	38	55	Loam	17.6	0.22	0.76	13.83	4.81
SS_6	7.25	0.59	4.89	10	40	50	Loam	28.4	0.78	1.52	20.92	6.76
SS_7	6.94	0.38	8.04	13	30	57	Silt Loam	17.9	0.24	0.32	17.36	6.25
SS_8	5.83	0.66	9.82	9	54	37	Silt Loam	21.5	0.33	2.23	15.14	4.09
SS_9	6.11	0.40	6.76	12	56	32	Silt Loam	24.5	0.51	1.59	17.25	6.76
SS_{10}	7.32	0.62	10.21	14	52	34	Silt Loam	20.5	0.61	0.88	16.04	4.55

CEC, Cation exchange capacity; Ex, exchangeable; EC, electrical conductivity

TABLE 4.22: Basic physicochemical characteristics of soils from control area

Char.	pH	EC (dsm^{-1})	Organic Matter (%)	Clay (%)	Silt (%)	Sand (%)	Textural Class	CEC (cmoi/kg)	Ex-Na^{+} (cmoi/kg)	Ex - K^{+} (cmoi/ kg)	Ex - Ca^{2+} (cmoi/kg)	Ex - Mg^{2+} (cmoi/kg)
CSS_1	6.92	0.30	2.21	8	38	44	Loam	12.8	0.15	0.98	18.94	2.29
CSS_2	6.85	0.23	1.87	14	44	42	Loam	16.8	0.18	0.48	10.21	1.94
CSS_3	6.30	0.26	2.43	16	40	44	Loam	10.8	0.12	1.01	7.67	1.47
CSS_4	6.72	0.22	2.69	13	48	39	Loam	10.6	0.26	1.47	8.01	2.05
CSS_5	6.88	0.20	2.83	10	42	48	Loam	8.3	0.17	0.88	8.25	1.99
CSS_6	6.10	0.29	1.86	9	43	48	Loam	13.2	0.29	0.83	12.29	3.21
CSS_7	5.87	0.25	1.73	17	40	43	Loam	10.4	0.09	0.23	6.05	2.87
CSS_8	5.96	0.31	3.02	12	38	50	Loam	11.3	0.18	1.60	9.12	1.88
CSS_9	6.68	0.27	3.21	12	40	48	Loam	15.3	0.12	0.78	11.48	2.97
CSS_{10}	7.12	0.33	2.74	15	40	46	Loam	14.9	0.27	0.43	9.74	3.13

CEC, Cation exchange capacity; Ex, exchangeable; EC, electrical conductivity

4.7 **Metal Content of Soil Samples**

The results of total metal content of soil samples from both the study and control areas are presented in Tables 4.23 and 4.24, respectively. For soil samples from study area, Zn content varied from 117.2± 5.4 – 296.8 ± 9.8 mg/kg, while Ni concentration ranged from 62.3 ± 5.1 – 143.4 ± 5.7 mg/kg and Cu level was from 76.8 ± 3.7 – 204.7 ± 10.4 mg/kg. Lead and Cd levels ranged from 29.8 ± 3.2 – 83.4 ± 4.6 kg/kg and 8.5 ± 2.3 – 46.6 ± 4.3 mg/kg, respectively. The distribution pattern of the metals in the soil samples was in the following sequence: Zn > Cu > Ni > Pb > Cd. Similarly, for soil samples from control area, Zn and Ni concentrations varied between 31.2 ±2.8- 92.9 ± 4.6 mg/kg and 33.2 ± 4.0 – 96.5±5.3 mg/kg, respectively, whereas the Cu level ranged from 49.8 ± 3.8 – 98.1 ± 5.2 mg/kg. The Pb and Cd contents varied from 11.1 ± 1.8 – 38.4 ± 6.3 and 1.2 ± 0.2 – 3.9 ± 0.9 mg/kg, respectively. The profile of mean metal content of soil samples from the control area was also: Cu > Ni > Zn > Pb > Cd.

The trace metal data obtained from the soil samples of the study area revealed that Zn had the highest concentration, while Cd had the least. The predominance of Zn in the sols might be attributed to the stabilization of Zn oxides in the soils, as it was reported that Zn oxides in soil have high stability constant (Lena and Rao, 1997), while in the case of Cd might be due to weak adsorptive nature of Cd in the soils (Mido and Satake, 2003). In the control area, Cu had the highest concentration amongst the metals examined and the least was also Cd. The reason might be as a result of Cu-organic complexes intrusion from the animal manure and sometimes soil of refuse dump were usually applied on the soil of the area as fertilizers for soils fertility improvement. In fact, Francis (2005) reported the presence of trace metals in

animal wastes and Uba *et al*. (2008) also reported the presence of trace metals in the refuse waste soils of some dumpsites in Zaria metropolis.

The highest Zn concentration was 296.8mg/kg recorded for soil sample collected at site SS7 and lowest was found to be 117.2 mg/kg in SS8, while control area soils have the highest Zn concentration at sampling point CSS5 (92.9 mg/kg) and the lowest concentration was found at CSS1, 31.2 mg/kg. As for Ni concentrations, the highest level in the soils of study area was 143.4 mg/kg, detected in SS5, and the lowest was 62.3 mg/kg in CSS9, whereas in control area the highest value recorded was 96.5 mg/kg (CSS8) and the lowest value was 33.2 mg/kg (CSS4). For Cu and Pb, the highest concentrations were 204.7 mg/kg (SS8) and 83.4 mg/kg (SS6), while the lowest concentrations were 76.8 mg/kg (SS6) and 29.8mg/kg (SS3) respectively. For the control area, the highest Cu and Pb concentrations were 98.1 mg/kg (CSS9) and 38.4 mg/kg (CSS6) and the lowest values were 49.8 mg/kg (CSS9) and 11.1 mg/kg (CSS4), respectively. The highest Cd level was 46.6 mg/kg, detected in SS5, and the lowest level was 8.5mg/kg at SS6, while in the soils of the control area the highest value recorded was 3.9 mg/kg (CSS2) and the lowest concentration was 1.2 mg/kg (CSS4).

The obtained results indicated that the mean values for all the metals examined in the soils of the study area were higher than those of the soils from the control area. The reason might be inclined towards the type of water used for irrigating the soils, as the soils of the study area received polluted water as irrigation water. It was established that irrigation water sources were found to affect trace metal distribution in soils (Rattan *et al*., 2005). This could further be supported with the correlation calculations performed between levels of metals in sewage waters and that of the soils of study area (Appendices XVa – XVc) which gave large and positive correlation ($P > 0.05$). This implies that sewage water used for irrigation coiuld be

responsible factor for elevating the level of metal concentration in the soils of the study area. Similarly, correlation analysis between metal concentrations in tube-well waters and that of the soils of control area (Appendices XVIIIa – XVIIIc) showed positive correlation ($P > 0.05$), with the exception of sampling points 4 and 9, which showed negative correlation. This implies that apart from tube-well water, significant contributions were likely came from other sources such as emission through combustion from automobile exhausts, for instance, the sampling point CSS4 is close to high traffic roads.

The average values of the metals analysed in the soils of our study area were higher than the values (Cu, 207.50; Pb, 143.30 and Cr, 230.00 mg/kg) reported by Awode *et al*. (2008) for Challawa river bank soil samples used for irrigation, but lower than the values (Pb, 2 – 15; Cu, 0.5 – 2.0 and Cd, 0.1 – 0.25 mg/kg) reported by Dike *et al*. (2005) for Jakara river bank soil samples also used for irrigation. The levels of trace metals found in the soil samples of study area in this work were also lower than those (Cu, 798; Pb, 649 and Zn, 3019 mg/kg) found by Marisa and John (2006) for contaminated soils used for irrigation. Furthermore, trace metal concentrations (Cd, 10; Pb, 120; Cu, 150; Ni, 165 and Zn, 235 mg/kg) obtained by Lokeshwari and Chandrappa (2006) for soil samples contaminated by Bellandur Lake were also higher than the corresponding values obtained in this investigation except for Zn and Cu. Furthermore, the metal levels obtaineds in soil samples of study area were lower than the metal levels (Pb, 128.62; Zn, 768.21; Cu, 234.40 and Ni, 319.42 mg/kg) reported by Rattan *et al*. (2005) for contaminated soil used for growing vegetable crops in India.

However, the soil mean metal concentration levels obtained in this work were above the recommended permissible limits in soils by EU (1986), except for Zn and Pb. Although the maximum concentrations of Zn and Pb fell within the range of standard, it was found that their

concentrations in the surface soils were higher than the natural concentration, 25 and 0.5 mg/kg, respectively, (Ward, 1995). This suggests that the soils accumulated trace metals excessively. Therefore, in general, the soils of the study area were truly contaminated with the five metals studied, which might be due to water sources that were used for irrigating the soils.

4.8 **Metal Content of Vegetable Crops**

The trace metal content of vegetables (spinach and lettuce) from both study and control areas are presented in Tables 4.25 – 4.28. The mean concentrations of the metals in spinach from the study area ranged from 29.3 $\pm$ 4.3 – 54.5 $\pm$ 3.6, 3.4 $\pm$ 0.9 – 8.9 $\pm$ 1.4, 9.5 $\pm$ 0.9 – 18.7 $\pm$ 3.1, 6.2 $\pm$ 2.1 – 15.4 $\pm$ 1.3 and 1.1 $\pm$ 0.6 – 3.3 $\pm$ 1.2 mg/kg for Zn, Ni Cu, Pb and Cd, respectively. The mean concentration of the same metals in the spinach of the control area varied from 11.4 $\pm$ 2.8 – 24.2 $\pm$ 5.1, 1.6 $\pm$ 0.08 – 4.8 $\pm$ 0.9, 4.2 $\pm$ 0.3 – 9.2 $\pm$ 2.2, 2.5 $\pm$ 0.9 – 5.1$\pm$ 1.4 and 0.3 $\pm$ 0.04 – 1.3 $\pm$ 0.8 mg/kg in the same order as for study area. The profiles of mean metal contents in the spinach of both the study and control areas were found to follow the same sequence: Zn > Cu > Pb > Ni > Cd.

Similarly, the mean metal concentrations in lettuce of the study area ranged from 31.9 $\pm$ 4.2 – 57.3 $\pm$ 5.3, 3.9 $\pm$ 1.2 – 9.3 $\pm$ 1.8, 9.4 $\pm$ 0.7 – 18.1 $\pm$ 2.3, 5.1 $\pm$ 1.8 – 19.6 $\pm$ 1.2 and 2.1 $\pm$ 0.6 – 4.8 $\pm$ 1.4 mg/kg for Zn, Ni, Cu, Pb and Cd, respectively. For lettuce from the control area, the concentration levels of the metals in the same order varied between 12.6 $\pm$ 2.8 – 24.5 $\pm$ 3.5, 2.3 $\pm$ 0.4 – 4.9 $\pm$ 0.9, 3.9 $\pm$ 1.1 – 9.6 $\pm$ 1.9, 2.9 $\pm$ 0.4 – 6.3 $\pm$ 0.8 and 0.3 $\pm$ 0.08 – 1.4 $\pm$ 0.7 mg/kg, respectively. The profile of metal levels in the lettuce of the study area was: Zn > Cu $\approx$ Pb > Ni > Cd, whereas the distribution pattern of the metals in the lettuce of the control area was: Zn > Cu > Pb > Ni > Cd.

TABLE 4.23: The total metal content (mg/kg ± SD, dry weight) in contaminated soil samples (SS)

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SS_1	217.8± 4.60	103.1± 8.20	121.2± 5.60	72.6± 7.20	25.7± 3.60
SS_2	223.6± 6.20	137.9± 6.40	167.8± 9.3	44.6± 4.30	12.4± 2.10
SS_3	148.3± 7.30	68.9± 4.40	143.5± 8.20	29.8± 3.20	17.4± 2.20
SS_4	183.5± 6.60	86.2± 5.30	176.4± 5.90	48.7± 3.70	35.4± 3.20
SS_5	162.5± 4.60	143.4± 5.70	84.5± 4.20	36.4± 2.80	46.6± 4.30
SS_6	214.5± 8.60	98.6± 4.60	76.8± 3.70	83.4± 4.60	8.5± 2.30
SS_7	296.8± 9.40	76.7± 5.50	133.8± 6.40	68.5± 4.60	44.6± 4.1
SS_8	117.2± 5.40	134.4± 6.20	204.7± 10.40	39.2± 5.70	11.2± 1.8
SS_9	156.1± 7.40	62.3± 5.1	127.3± 5.30	40.8± 4.20	28.8± 2.7
SS_{10}	132.6± 4.80	83.9± 4.3	116.9± 7.80	30.3± 2.60	10.7± 2.2
RANGE	117.8-296.8	62.3-137.9	76.8-204.7	29.8-83.4	8.5-44.6
EU and Ewers limits	150-300	30-75	50-140	50-100	1-3

TABLE 4.24: The total metal content (mg/kg ± SD, dry weight) in control soil samples (CSS)

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
CSS_1	31.2± 2.80	59.3± 3.30	92.4± 4.50	28.3± 4.70	2.8± 0.60
CSS_2	64.3± 3.0	88.1± 6.40	71.3± 3.80	24.2± 3.30	4.9± 0.90
CSS_3	71.5± 4.20	49.3± 3.2	84.5± 5.60	15.7± 2.90	1.5± 0.40
CSS_4	32.5± 3.10	33.2± 4.1	88.3± 4.1	11.1± 1.8	1.2± 0.2
CSS_5	58.4± 4.40	52.3± 4.40	50.3± 3.7	25.7± 4.30	2.1± 0.4
CSS_6	42.9± 4.60	44.1± 4.60	58.3± 4.7	85.4± 6.3	3.9± 0.8
CSS_7	43.8± 5.1	38.5± 5.0	67.9± 5.5	33.3+ 4.2	2.4± 0.9
CSS_8	69.1± 4.7	96.5± 5.30	77.5± 3.9	18.8± 2.2	2.3± 1.2
CSS_9	89.5± 5.3	41.4± 3.70	98.1± 5.3	23.3± 2.4	4.3± 1.2
CSS_{10}	79.4± 4.9	52.7± 3.80	49.8± 3.8	19.1+ 1.8	2.3± 0.5
RANGE	31.2-89.5	33.2-96.5	49.8-98.1	11.1-85.4	1.2-4.9
EU and Ewers limits	150-300	30-75	50-140	50-100	1-3

For spinach from the study area, Zn had the highest concentration of 54.5 mg/kg at sampling point SP10 and the lowest value of 29.3 mg/kg in SP7. Similarly, the spinach from control area had the highest Zn level at CSP10 (24.2 mg/kg) and the lowest was found at CSP1 (11.4 mg/kg). For Ni concentrations, SP3 had the highest value (8.9 mg/kg) and the lowest value was detected at SP5 (3.4 mg/kg). For the spinach from control area Ni level was highest at CSP10 (4.8 mg/kg) and lowest was recorded at CSP6 (1.6 mg/kg). For mean concentrations of Cu and Pb in spinach of study area, SP8 (18.7 mg/kg) and SP3 (15.4 mg/kg) had the highest values respectively, and SP10 had the least. The highest Cd concentration of 3.3 mg/kg was recorded at SP7 and the lowest was found to be 1.1 mg/kg (SP5). For spinach samples from the control area, the highest Cd level (1.3 mg/kg) was found at CSP3 and the lowest (0.3 mg/kg) at CSP10.

In the case of lettuce samples from the study area, the highest Zn concentration was 57.3 mg/kg at sampling point LT 9 and the lowest was found to be 31.9 mg/kg at LT8. For lettuce from control area the highest Zn concentration was at CLT9 (24.5 mg/kg) and the lowest level was found at CLT3 (2.6 mg/kg). For Ni concentrations, the highest was 9.3 mg/kg at LT8 and the lowest was 3.9 mg/kg at LT2, whereas in control area the highest value recorded was 4.9 mg/kg (CLT4) and the lowest value was 2.3 mg/kg (CLT3). As for Cu and Pb levels, the highest concentrations were 18.1 mg/kg (LT1) and 19.6 mg/kg (LT4), while the lowest levels were 9.4 mg/kg (LT6) and 5.1 mg/kg (LT8), respectively, but in the control area the highest levels were 9.6 mg/kg (CLT7) and 6.3 mg/kg (LCT5) and the lowest values were 3.9 mg/kg (CLT1) and 2.9 mg/kg (CLT8) for the same metals in the same order, respectively. The highest Cd level in lettuce of study area was 4.8 mg/kg recorded at LT8, and the lowest

level was 2.1 mg/kg at LT2, while in the lettuce of control area the highest recorded was 1.4 mg/kg (CLT7) and the lowest value was 0.3 mg/kg (CLT1).

The results indicated that the mean metal levels in spinach and lettuce from study area were higher than the mean metal levels in the same vegetables from the control area. In fact, the soils of the study area were more contaminated with these metals than the soils of the control area. This was attributed to the increase in the amount of trace metals in the soils of study area due to contamination from the irrigation water source (sewage water) and thereafter absorbed by the vegetables. It can therefore be inferred that with an increase in the content of trace metals in soils due to contamination from the irrigation water sources, the uptake of trace metals by vegetables also increased. This could evidently be supported with the fact that irrigation water sources were found to influence the trace metal distribution in soils and subsequently in vegetables (Rattan *et al*., 2005). Furthermore, correlation calculations between trace metals in soils and vegetables of the study area (Appendices XVIIa – XVII b) gave high significant positive correlation coefficients and similarly, high significant positive correlation coefficients between metals in soils and vegetables of the control area (Appendices XVIIId – XVIIIe) were also found. In another report, the positive relationships amongst the soils and the vegetables metal content may be a cause of trace metals contamination to both plants and animals through their entry into food chain (Awofolu *et al*., 2005).

The levels of the metals in vegetables of the study area were not within the normal range, except Zn and Cu which were within the normal range (Cd, 0.1 – 2.4; Pb, 5.10; Cu, 5 – 20, Ni, 0.02 – 5 and Zn, 1 – 400 mg/kg; Bowen, 1979) for metals in plant leaves. However, the levels of metals in vegetables of the control area were all within the normal range for metals in plant leaves. This generally indicated that the presence of the analysed metals in vegetables of

the study area might be absorbed from the contaminated soils and thus, contribution to the metal levels in vegetables of the study area from the sewage water is highly probable since the soils of the area were irrigated with sewage water and had enriched the soils with the trace metals.

Plants are known to take-up and accumulate trace metals from contaminated soils (Singh and Narwal, 1985; Bojakowska and Kochany, 1985; Pulford and Watson, 2003; Madejon *et al*., 2003), hence detection of elevated metal levels in the vegetables of the study area was not surprising. Although concentrations of Zn and Cu in the vegetables of the study area were within the normal range in plant leaves, continual consumption could lead to accumulation with adverse health implications. The presence of Zn and Cu within the normal range in the vegetables, even though the soils were contaminated, might be attributed to the high stability constant of Zn oxides and high formation constant of Cu – organic complexes in the soils (which were slightly acidic and alkaline) and thus, reducing their availability to the vegetables. Apart from these reasons, availability to plants of trace metals depends also on a number of physical and chemical factors in the soil. These include soil pH, redox potential of metals, cation exchange capacity (CEC), anions concentrations, soil texture and organic matter (Lokeshwari and Chandrappa, 2006). In addition, metal absorption by plants is also influenced by the characteristics of the plants themselves (Mapanda *et al*., 2005). In this regard, for example, lettuce accumulated more of these metals than the spinach in this work. An earlier study on metal contents of vegetables showed that accumulation of trace metals by lettuce surpassed other leafy vegetables, and this is particularly the case with leafy vegetables grown in farmlands that are irrigated with wastewater (Itanna, 2002).

The mean concentrations of the metals analysed in the vegetables of the study area

were higher than the values (Cd, 0.059; Cu, 2.263 and Pb, 7.918 mg/kg) reported for spinach by Dike *et al*. (2005), but lower than the values (Zn, 76.63; cu, 24.47 and Pb, 22.59 mg/kg) reported by Chiroma *et al*. (2003), in the similar works. Furthermore, metal levels obtained in this work were higher than metal levels reported by Mapanda *et al*. (2005) (Zn, 60 – 228; Ni, 9 – 19; Cu, 20 – 94; Pb, 22 41 and Cd, 2 – 4.3 mg/kg) for vegetables grown in the wastewater in Harare, Zimbabwe.. But in contrast, trace metal levels obtained for spinach in this work were higher than (Zn, 25; Ni, 0.5; Cu, 8.0; Pb, 0.5 and Cd, 4.0 mg/kg) obtained by Lokeshwari and Chandrappa (2006) except for Cd concentration. Lastly, the metal levels obtained in this work were lower than the levels of metals (Zn, 59.1; Cu, 6.00 and Ni, 50.0 mg/kg) reported by Abdel-Hady (2007) for leafy vegetables irrigated with Nile water, except for Cu level.

In general, the mean metal concentrations obtained in this investigation were below the recommended maximum levels in vegetables as recommended by Codex (FAO/WHO) (2001), except for Cd and Pb. Although the maximum concentrations of Zn, Ni and Cu fell within the recommended standards, it was found that their concentrations in the vegetables of the study area were 2, 9 and 4.5 – fold higher than the natural concentrations (Zn, 25; Ni, 1.0 and cu, 4.0 mg/kg; Ward, 1995). This suggested that the excessive accumulation beyond the natural levels in the vegetables might be inclined towards the irrigation water sources, which was the source of contamination of the soils of the study area and thereafter absorbed by the vegetables.

Surprisingly, the Cd and Pb concentrations in the vegetables of the control area were also above the recommended maximum levels, as recommended by Codex (FAO/WHO) (2001). This observation might be attributed to the secondary addition through foliar uptake of atmospheric trace metals emission from the automobile exhausts, as some of the sampling points of the control area are close to major roads where there is high flow of traffic. It is

established that foliar absorption of atmospheric deposits on plant leaves is identified as an important pathway of trace metal contamination in vegetable crops, and this is particularly the case with vegetables growing in areas that is near sources of atmospheric deposits and thus have an elevated risk of potential contamination (Bassuk, 1986; Mido and Satake, 2003). Besides, it is established fact that Cd and Pb are found in fuels, which are emitted into the environment in particulates from automobile exhausts (Rattan, 2007). Therefore, the elevated levels of the two metals found in the vegetables of the control area might be due to foliar absorption from the atmospheric deposits, as the soils of the control are were not contaminated with the metals except for Cd levels at sampling points CSS2, CSS6 and CSS9.

4.9. **Chemical Fractionation of Metals in Sewage Sludge**

Table 4.29 shows the results obtained for the six steps sequential extraction of Zn metal for each sampling point along the Kubanni River basin. The concentrations found for Zn in the six fractions ranged from 2.8-7.1, 4.2-14.3, 9.7-50.7, 11.6-66.6, 17.4-60.6 and 278.4-295.4mg/kg for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual, respectively.

In SL1 sewage sludge, the greatest percentage of Zn (83.8%) was associated with residual fraction. The reducible fraction was the next most abundant fraction for this sewage sludge (SL1) (5.8%), followed by the organic (4.8%), Carbonate (3.3%), exchangeable (1.6%), and water soluble fraction (0.7%). As a result, the distribution profile of Zn in this sewage sludge decreased in the sequence: residual > reducible > organic > carbonate> exchangeable> water soluble. The residual fraction was also the most abundant pool for Zn in SL2 (75.3%). As it was in SL1, the reducible was the next most concentrated fraction for this metal (12.3%), followed by the organic (6.7%), carbonate (4.2%), exchangeable (3.3%), and water soluble

TABLE 4.25: The total metal content (mg/kg ± SD, dry weight) in spinach (SP)

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
SP_1	42.9± 3.2	5.7± 1.6	12.5± 2.1	13.8± 1.6	2.5± 0.8
SP_2	35.7± 4.2	4.8± 0.8	11.1± 2.4	8.3± 1.2	1.7± 0.4
SP_3	46.1± 2.9	8.9± 1.4	17.7± 1.8	15.4± 1.3	3.1± 0.9
SP_4	31.4± 3.4	6.4± 1.2	16.3± 2.2	10.1± 2.5	2.2± 0.9
SP_5	42.2± 5.2	3.4± 0.9	9.5± 0.9	9.4± 1.3	1.1± 0.6
SP_6	50.6± 3.6	5.6± 1.1	13.2± 1.4	14.8± 2.4	2.5± 0.7
SP_7	29.3± 4.3	6.8± 1.3	10.8± 2.5	12.8± 1.7	3.3± 1.2
SP_8	32.8± 3.7	8.1± 2.1	18.7± 3.1	7.2± 2.5	2.7± 0.5
SP_9	49.1± 5.5	7.8± 2.4	15.7± 1.1	13.1± 2.3	1.9± 0.8
SP_{10}	54.5± 3.6	5.9± 1.6	11.8± 1.9	6.2± 2.1	2.8± 0.9
RANGE	29.3-50.6	3.4-8.1	9.5-18.7	7.2-15.4	1.1-3.3
FAO/WHO limits	99.4	67.9	73.3	0.3	0.2

TABLE 4.26: The total metal content (mg/kg ± SD, dry weight) in spinach of the control area (CSP)

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
CSP_1	11.4± 2.8	1.8± 0.08	4.2± 0.3	3.8± 0.8	0.4± 0.06
CSP_2	18.2± 3.4	2.1± 0.07	9.1± 1.6	3.6± 0.5	0.9± 0.08
CSP_3	19.9± 2.7	2.6.± 0.1	7.4± 0.9	4.2± 1.1	1.3± 0.8
CSP_4	22.5± 2.1	1.7± 0.05	5.6± 1.1	4.7± 1.2	0.8± 0.9
CSP_5	20.4± 3.1	3.1± 0.09	4.8± 1.4	5.1± 1.4	0.6± 0.07
CSP_6	16.4± 2.5	1.6± 0.08	9.2± 2.2	3.1± 0.9	0.5± 0.08
CSP_7	14.8± 2.6	2.9± 0.3	6.1± 1.7	3.3± 0.6	1.2± 0.6
CSP_8	13.1± 4.2	3.7± 0.2	7.4± 1.3	4.1± 1.2	0.6± 0.04
CSP_9	18.5± 3.7	3.3± 0.4	8.8± 2.1	2.8± 0.7	0.7± 0.05
CSP_{10}	24.2± 5.1	4.8± 0.9	5.9± 0.8	2.5± 0.9	0.3± 0.04
RANGE	11.4-24.2	1.6-4.8	4.2-9.2	2.5-5.1	0.3-1.3
FAO/WHO limits	99.4	67.9	73.3	0.3	0.2

TABLE 4.27: The total metal content (mg/kg ± SD, dry weight) in lettuce (LT)

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
LT_1	38.7± 3.3	6.4± 1.4	18.1± 2.3	11.2± 2.8	2.3± 0.7
LT_2	54.4± 5.2	3.9± 1.6	13.5± 1.6	16.6+ 3.3	2.1± 0.6
LT_3	32.4± 4.7	9.1± 1.8	12.2± 2.2	18.2± 3.1	2.8± 0.7
LT_4	44.3± 3.8	7.6± 2.1	10.9± 1.9	19.6± 1.2	3.1± 0.9
LT_5	38.1± 3.4	4.3± 1.8	16.9± 2.1	12.4± 2.7	3.6± 0.6
LT_6	37.5± 4.7	6.8± 1.3	9.4± 0.7	13.2± 2.5	3.5± 1.1
LT_7	49.7± 4.3	5.2± 0.9	11.7± 2.9	19.4± 1.8	3.3± 0.9
LT_8	31.9± 4.2	9.8± 1.8	14.2± 1.2	5.1± 1.8	4.8± 1.4
LT_9	57.3± 5.3	8.9± 2.2	17.9± 3.1	10.7± 2.4	2.6± 0.6
LT_{10}	55.5± 3.9	6.5± 1.3	14.8± 2.7	14.6± 3.3	4.2± 1.5
RANGE	31.9-57.3	3.9-9.1	9.4-18.1	5.1-19.6	2.1-4.8
FAO/WHO limits	99.4	67.9	73.3	0.3	0.2

TABLE 4.28: The total metal content (mg/kg ± SD, dry weight) in lettuce of the control area (CLT)

Element	**Zn**	**Ni**	**Cu**	**Pb**	**Cd**
CLT_1	14.7± 3.2	4.5± 1.6	3.9± 1.1	4.3± 1.2	0.3± 0.08
CLT_2	17.8± 3.7	3.6± 0.7	8.5± 1.8	3.4± 1.1	0.8± 0.6
CLT_3	12.6± 2.8	2.3 ± 0.4	6.2± 0.9	5.8+ 1.6	0.5± 0.04
CLT_4	21.3± 3.4	4.9± 0.9	7.8± 1.2	5.2± 1.4	1.3± 0.6
CLT_5	15.3± 2.6	3.7± 0.8	5.4± 1.7	6.3± 0.8	0.7± 0.5
CLT_6	22.1± 3.6	2.8± 0.5	7.5± 1.8	3.8± 0.9	0.9± 0.7
CLT_7	20.4± 2.9	3.2± 0.8	4.4± 1.1	3.7± 0.6	1.4± 0.7
CLT_8	16.4±. 2.2	6.9± 1.4	4.7± 0.6	2.9± 0.4	1.2± 0.3
CLT_9	24.5± 3.5	2.8± 0.9	7.2± 1.5	4.9± 1.2	0.6± 0.2
CLT_{10}	18.3± 3.7	3.6± 0.7	8.7± 1.4	3.3± 0.7	0.9± 0.8
RANGE	12.6-24.5	2.3-6.9	3.9-8.7	2.9-6.3	0.3-1.3
FAO/WHO limits	99.4	67.9	73.3	0.3	0.2

(1.2%) fraction. The distribution pattern of Zn in this sample was found to be in the order: residual > reducible> organic > carbonate > exchangeable > water soluble.

Similarly, SL3 had the highest percentage of Zn (69.7%) associated with the residual fraction. The organic fraction was the next (13.4%), followed by the carbonate (9.9%), reducible (4.6%), exchangeable (1.6%), and then water soluble fraction (0.8%). The observed trend for the concentration of Zn in this sample was found to be residual > organic > carbonate > reducible > exchangeable > water soluble fraction. Another different pattern was also observed for SL4, in which the greatest percentage of Zn (72.4%) was found to be associated with residual fraction, followed by the carbonate fraction (14.2%), then reducible (7.1%), organic (4.8%), exchangeable (0.9%), and water soluble fraction (0.6%). The trend found for distribution of Zn in SL4 was: residual> Carbonate> reducible> organic> exchangeable> water soluble fraction.

Of the ten sewage sludge samples studied, five of them (SL5, SL6, SL7, SL9 and SL10) had their highest percentage of Zn (67.6, 65.7, 81.4, 79.1 and 72.9 %, respectively) associated with the residual fraction. The reducible fraction was then the next most concentrated fraction for this samples (15.3, 13.9, 7.2, 8.6 and 14.6%), followed by the carbonate (7.3, 10.8, 4.3, 6.6 and 5.1 %), organic (4.4, 6.0, 4.1, 3.5 and 3.1 %), exchangeable (3.6, 2.8, 2.1, 1.5 and 2.9%) and then water soluble fraction (1.8, 0.8, 0.8, 0.7 and 1.4%) in the same order as above. The trend for the concentration of Zn at the five sampling points was residual > reducible >carbonate > organic > exchangeable > water soluble fraction.

Lastly, SL8 was found to have 78.8% its Zn content associated with residual fraction. The reducible fraction (8.1%) was the next most abundant fraction, followed by the organic (4.7%), carbonate (3.7%), exchangeable (3.3%), and water soluble fraction (1.4 %). The

distribution profile of Zn concentration in SL8 was in the following order: residual > reduciable> organic> carbonate> exchangeable > water solution fraction. Overall, the average distribution of Zn in the sewage sludge samples collected from the river basin was found to be: residual > reducible> acid soluble> oxidizable > exchangeable > water soluble.

The highest percentage of Zn in the residual fraction reflected the greater tendency to become unavailable to the environment or when the sludge is used in soils for soil fertility amendment. This might be attributed to the fact that residual fraction represents metals largely embedded in the crystal lattice of the sewage sludge fractions and therefore, are rarely released to the environment under natural conditions, except under very harsh conditions (Ikem *et al*., 2003, Osakire and Egharevba, 2008). Similar results were reported by other workers (Jordao and Nickless, 1989; Zufiaurre *et al*., 1998). Among the non-residual fractions, the reducible fraction (bound to Fe/Mn oxides) contained the greatest amount of Zn in all the sewage sludge samples. The reason might be due to the high stability constant of Zn oxides (Shrivastava and Banerjee, 2004). Several other researchers have also found Zn to be associated with reducible fraction (Zufiaurre *et al*., 1998, Shrivastava and Banerjee, 2004).

Table 4.30 gives the results obtained for the six steps sequential extraction of Ni metal for each sampling point of the study area. The amounts found for Ni in the six fractions varied between 0.7-1.4, 1.2-3.3, 4.1- 9.4, 3.0-6.3, 7.6-16.6 and 65.8 –80.2 % for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fractions, respectively. The highest percentage of Ni (74.6%) in SL 1 was found to be associated with residual fraction. The oxidizable fraction was the second most abundant fraction (12.2%), followed by the reducible (6.1%), acid soluble (3.0%), exchangeable (2.8%) and water soluble (1.3%) fraction. From the result, the SL1 had the following trend for Ni: - residual > oxidizable> reducible >

acid soluble > exchangeable > water soluble. Sample SL2 also had the greatest percentage of Ni (80.2%) in the residual fraction. The second most concentrated fraction (7.6%) in this sample was the reducible fraction, followed by the oxidizable fraction (5.8%), acid soluble (4.2%), exchangeable (1.4%) and then water soluble fraction (0.8%). The observed trend of Ni distribution in this sample was: residual > reducible > oxidizable > Acid soluble > exchangeable > water soluble.

Samples SL3, SL4, SL5, SL6, SL9 and SL10 had the same distribution pattern, in which the highest concentrations of Ni (68.4, 70-6, 79.4, 65.8, 73.3 and 69.5%, respectively) were mainly associated with the residual fraction. The oxidizable fraction was the next most abundant fraction (14.9, 11.7, 10.2, 14.6, 9.4 and 16.6% for the same samples in the same order), followed by reducible fraction (8.3, 7.1, 4.1, 9.4, 5.8 and 5.4%), acid soluble (4.6, 6.3,3.2, 5.5, 4.3 and 3.9%), exchangeable (2.7, 3.1, 2.4, 3.3, 1.2 and 3.2) and water soluble (1.1, 1.2, 0.7, 1.4, 1.0 and 1.4%) fraction. The distribution pattern for Ni in these samples was found to be: residual > oxidizable > reducible > acid soluble > exchangeable> water soluble. However, SL7 and SL8 had showed a slightly different pattern, in which the highest Ni concentrations (75.7% and 71.2%, respectively) were associated with the residual fraction. The oxidizable fraction was the next most concentrated fraction for this metal in these samples (11.3 and 15.1% for the same samples in the same order), followed by the acid soluble (6.3 and 6.1 %), reducible (3.7 and 4.0%), exchangeable (2.1 and 2.8%) and then water soluble fraction (0.9 and 0.8%) all for the same samples in a similar order as above. The trend was found to be: residual >Oxidizable > acid soluble > reducible > exchangeable > water soluble. In general, the average distribution of Ni in the sewage sludge samples was found to be: residual > oxidizable > reducible > acid soluble > exchangeable > water soluble. The residual fraction was by far the

TABLE 4.29: The chemical fractionation of Zn metal in sewage – sludge (mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SL_1	2.5±0.4 0.7%	5.6±1.4 1.6%	16.9±2.4 4.8%	11.6±1.6 3.3%	20.5±3.7 5.8%	295±7.1 83.8%	57.1 16.2%	352.6
SL_2	5.1±1.7 1.2%	14.1±1.2.9 3.3%	28.6±4.1 6.7%	17.9+2.1 4.2%	52.5±5.0 12.3%	321.2±6.3 75.3%	105.4 24.7%	426.6
SL_3	3.0±0.6 0.8%	6.1±1.7 1.6%	50.7±3 13.4%	37.5+3.4 9.9%	17.4±2.7 4.6%	263.7±8.3 69.7%	114.7 30.3%	378.4
SL_4	2.8±0.8 0.6%	4.2±1.1 0.9%	22.5±3.6 4.8%	66.6+4.3 14.2%	33.3±2.4 7.1%	339.7±10.2 72.4%	129.4 27.6%	469.2
SL_5	7.1±1.3 1.8%	14.3±2.6 3.6%	17.4±2.4 4.4%	28.9±3.1 7.3%	60.6±4.7 15.3%	267.9±7.7 67.6%	128.4+ 32.4%	396.3
SL_6	3.6±0.7 0.8%	11.9±1.8 2.8%	25.4±2.7 6.0%	45.8±3.3 10.8%	58.9±4.6 13.9%	278.4±8.5 65.7%	145.4 34.3%	423.8
SL_7	3.4±0.5 0.8%	7.9±1.4 2.1%	15.3±2.4 4.1%	16.1±2.6 4.3%	26.9.±2.8 7.2%	304.7±10.6 81.4%	69.6 18.6%	374.3
SL_8	6.0±1.0 1.4%	14.2±2.7 3.3%	20.2±4.0 4.7%	15.9±2.5 3.7%	34.9±3.1 8.1%	339.4±9.4 78.8%	91.3 21.2%	430.7
SL_9	3.2+0.6 0.7%	6.8±1.8 1.5%	16.0+2.4 3.5%	30.1±3.1 6.6%	39.2±4.3 8.6%	360.8±8.3 79.1%	95.3 20.9%	456.1
SL_{10}	4.4+0.8 1.4%	9.0±2 2.9%	9.7+2.3 3.1%	15.9±2.6 5.1%	45.5±3.7 14.6%	227.2±7.9 72.9%	84.4 27.1%	311.6

most important fraction for Ni in all the sewage sludge samples. This might be due to the presence of acid resistant minerals and the co-operation of Ni with various silicate species which resulted into the co-option into the mineral lattice of the sewage sludge samples and thus may not be available for remobilization into the environment, except under very harsh conditions (Asagba *et al*., 2007). The result obtained result is in agreement with what was reported by Tessier *et al*. (1980) and Shrivastara and Banerjee (2004). The reducible and oxidizable fractions contained most of the Ni in the non-residual fractions, although their percentages were not substantial and consequently the Ni may not be potentially available when exposed to the environment (Ure and Davidson, 1995). In addition, Ni removal from these fractions required strong acid condition and may not therefore, be available for remobilization into environment since the sewage sludge samples were slightly acidic. The presence of Ni in the acid soluble, exchangeable and water soluble was poor. This suggested that Ni in these sewage sludge samples might not be available for plant uptake when soil is amended with sewage sludge from the basin, as the bioavailability index from these fractions was low.

For Cu, the results of six steps sequential extraction of Cu metal for each sampling point is presented in Table 4.31. The levels found for Cu in the six fractions ranged from 0.6-1.4, 0.8-2.4, 2.5-6.2, 2.0-4.8, 1.4-3.9 and 83.4-92.9% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

The residual fractions for samples (90.4, 89.3, 91.2 and 83.4%) SL1, SL4, SL6, and SL8 were the most important fractions for Cu followed by the oxidizable 93.1, 3.1, 2.5 and 6.2% for the same samples in the same order), then the acid soluble (2.3, 2.8, 2.0 and 4.3%), reducible (1.6, 2.6. 1.8 and 3.9%), exchangeable (1.4, 1.2, 14 and 1.4%) and water soluble

fraction (1.2, 1.0, 0.9 and 0.8%) fractions. The observed distribution trend of Cu amongst these samples was in the order: residual > oxidizable > acid soluble> reducible > exchangeable > water soluble fraction. However, SL5 had a slightly different distribution of Cu; the highest Cu concentration (92.9%) was found to be associated with residual fraction. The acid soluble fraction (2.8%) was the next most concentrated fraction, followed by the oxidizable (2.2%), reducible (1.4%), exchangeable (0.8%) and water soluble (0.6%) fractions. The profile of Cu distribution in the SL5 sample was: residual > acid soluble > oxidizable > reducible > exchangeable > water soluble. Similarly, the residual fractions (89.6, 91.0, 87.1, 87.4 and 85.5%) of SL2, SL3, SL7, SL9, and SL 10, respectively were the dominant in these sewage sludge samples. The oxidizable fraction was the next most abundant pool for this metal (3.4,2.8, 3.6, 3.7 and 4.0%) in the same, followed by the reducible (2.6, 2.3, 3.3, 3.2, and 3.5%), acid soluble (2.3, 2.2, 2.9, 3.0 and 3.3%), exchangeable (1.2, 0.9, 2.2, 1.7 and 2.4%) and then water soluble (0.9, 0.8, 1.4, 1.0 and 1.3%) fractions. The profile of the Cu disrtribution amongst these samples was: residual> oxidizable > reducible> acid soluble > exchangeable > water soluble. This type of trend, on the overall, was the predominant amongst the sampling points.

Like Zn and Ni, most of the Cu content of the sewage sludge samples was in the residual fraction, which is an inert phase, and corresponds to the part of Cu which cannot be remobilized (Zufiuarre *et al*., 1998) and thus, the metal may not be available when the sewage sludge from the river basin is used for soil fertility amendment. This result is consistent with the findings of Shrivastava and Banerjee (2004) who found most of the Cu content of the sewage sludge samples they studied to be associated with the residual fraction. High presence of Cu in the oxidizable fraction has been reported (Tessier *et al*; 1980; Jordao and Nickless,

TABLE 4.30: The chemical fractionation of Ni metal in sewage - sludge (mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SL_1	3.5±1.1 1.3%	7.5±1.8 2.8%	32.5±3.4 12.2%	8.0±1.6 3.0%	16.2±2.3 6.1%	198.6±6.3 74.6%	67.6 25.4%	266.2
SL_2	1.2±0.6 0.8%	2.1±0.9 1.4%	8.6±1.8 5.8%	6.2±1.3 4.2%	11.3±2.4 7.6%	119.3±5.8 80.2%	29.4 19.8%	148.7
SL_3	2.5±0.9 1.1%	6.2±1.6 2.7%	34.2±3.7 14.9%	10.6±2.2 4.6%	19.0±2.9 8.3%	156.9±4.2 68.4%	72.5 31.6%	229.4
SL_4	1.5±0.6 1.2%	3.8±1.4 3.1%	14.5 ±2.3 11.7%	14.1±2,5 6.3%	8.8±1.6 7.1%	157.9±5.0 70.6%	36.4 29.4%	123.7
SL_5	1.1±0.5 0.7%	3.8±1.0 2.4%	16.2±2.4 10.2%	5.1±1.0 3.2%	6.5±1.2 4.1%	125.7±4.7 79.4%	32.6 20.6%	158.3
SL_6	3.0±1.2 1.4%	7.0±2.2 3.3%	31.2±3.4 14.6%	11.7±2.6 5.5%	20.1±2.5 9.4%	140.4±4.4 65.8%	73.0 34.2%	213.4
SL_7	1.1±0.6 0.9%	2.6±1.4 2.1%	14.1±2.6 11.3%	7.9±2.2 6.3%	4.6±1.3 3.7%	94.5±4.9 75.7%	30.3 24.3%	124.8
SL_8	1.7±0.5 0.8	6.1±1.8 2.8%	33.0±3.6 15.1%	13.3±2.0 6.1%	8.7±1.7 4.0%	155.6±5.3 71.2%	62.9 28.8%	218.5
SL_9	1.9±0.7 1.0%	2.4±0.8 1.2%	18.5±2.4 9.4%	8.4±2.3 4.3%	11.4±2.5 5.8%	153.9±4.8 73.3%	42.6 21.7%	196.5
SL_{10}	2.2±0.09 1.4%	5.0±1.6 3.2%	25.8±3.1 16.6%	6.1±1.6 3.9%	8.4±1.4 5.4%	108.0±5.4 69.5%	47.4 30.5%	155.4

1989; Zufiaurre *et a*l.; 1998). The reason might be attributed to the high stability constant of Cu-organic complexes (Stumm and Morgan, 1981). A small percentage of Cu was also associated with reducible fraction, which was nearly of equal importance for non-residual fractions. The high surface area and adsorbing capacity of Fe/Mn oxides coupled with the ability of Cu^{2+} to replace Fe^{2+} in some Fe- oxides might be responsible for the small adsorption of Cu in this fraction (Taylor, 1965). Copper removal required strong acid condition, hence was poorly associated with acid soluble, exchangeable and water soluble fractions, because the observed pH of the sewage sludge was slightly acidic which could not favour the release of Cu from these fractions. This indicated that the metal might not be available for plant uptake when the sewage sludge is applied to soil for fertility improvement.

Table 4.32 shows the result of six steps sequential extraction of Pb metal for each sampling point. The concentrations of Pb in the six fractions varied from 0.7-1.1, 0.9-1.6, 1.6-6.5, 1.7-9.8, 3.3-6.8 and 77.5-85.8% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

The residual fractions (85.7, 85.8 and 83.6%) were the predominant fractions for Pb in SL1, SL5 and SL7, respectively. The oxidizable fraction was the next most concentrated fraction (5.8, 5.8 and 6.5%) for the same samples in the same order as above), followed by the reducible (4.1, 4.4 and 4.6%), acid soluble (2.7, 1.7 and 2.7%), exchangeable (1.0, 1.3 and 1.6%) and then water soluble (0.7, 1.0 and 1.0%) fractions. The profile of Pb distribution amongst these samples was in the order: residual > oxidizable > reducible >acid soluble > exchangeable > water soluble fraction.

For sewage sludge samples SL2, SL3, SL4, SL6, SL8, SL9 and SL10 also, for the same metals in the same order was the most abundant pool for Pb. Acid soluble fraction was the

second most abundant pool (6.5, 9.8, 5.7, 9.2, 6.8, 8.2 and 9.8%) for similar samples in the same order as above), followed by the reducible (5.0, 5.7, 3.3, 5.7, 4.8, 5.2 and 6.8%), oxidizable (3.5, 2.9, 1.6, 2.5, 2.2, 3.0 and 3.9%), exchangeable (1.2, 1.4, 1.2, 1.4, 0.9. 1.0 and 1.2%) and then water soluble fraction (0.9, 1.1, 0.8, 0.9, 0.7, 0.9 and 0.8%) fractions for the same samples in the same order. The observed trend of distribution of Pb in the six fractions for these samples was in the following sequence: residual> acid soluble > reducible > oxidizable > exchangeable> water soluble fraction.

As the Pb concentration in the residual fraction was the predominant, this study indicated that the metal might not be readily available to the environment. Similar observations have been reported (Zufiaurre *et al.*; 1998; Shrivastava and Banerjee, 2004). The amount of Pb found in acid soluble fractions of the sewage sludge (bound to carbonates) was reasonable when compared with the other fractions of non-residual. This might be due to co-precipitation of Pb into carbonates in the sewage sludge samples. The carbonate fraction is influenced by acidic pH and the observed slightly acidic condition of the sewage sludge samples could not favour the release of Pb from this fraction and thus, cannot be remobilized into soil when sewage sludge is applied as fertilizer. The small presence of Pb also found in reducible and oxidizable fractions might be inclined towards the scavenging effect of Fe/Mn oxides and the affinity for organic matter by Pb, as the slightly acidic condition in the sewage sludge samples could not affect the sorption of Pb by organic matter. Lead concentration was also found in very small amounts in exchangeable and water soluble fractions. The operationally defined extraction sequence follows the order of decreasing solubility of chemical forms of the metals,

TABLE 4.31: The chemical fractionation of Cu metal in sewage - sludge (mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SL_1	4.1±1.2 1.2%	4.8±1.4 1.4%	10.7±2.7 3.1%	7.9±2.4 2.3%	5.5±1.3 1.6%	311.5±10.4 90.4%	33.1 9.6%	344.6
SL_2	3.1±0.9 0.9%	4.1±1.3 1.2%	11.5±2.1 3.4%	7.8± 1.1 2.3%	8.8±1.6 2.6%	304.1±8.9 89.6%	35.3 10..4%	339.4
SL_3	2.0±0.7 0.8%	2.2±0.9 0.9%	7.0±3.4 2.8%	5.5±0.9 2.2 %	5.7 ±1.7 2.3%	226.2±4.3 91.0%	22.4 9.0%	248.6
SL_4	2.9±0.5 1.0%	3.6±1.2 1.2%	9.2± 2.1 3.1%	8.3±1.8 2.8%	7.7±1.5 2.6%	264.4±5.5 89.3%	31.7 10.7%	296.1
SL_5	1.9±0.7 0.6%	2.5±0.8 0.8%	6.9± 1.8 2.2%	6.6±1.2 2.8%	4.4±1.3 1.4%	292.2±6.3 92.9%	22.3 7.1%	314.5
SL_6	2.8±0.8 0.9%	4.3±1.1 1.4%	7.7± 2.0 2.5%	6.2± 1.8 2.0%	5.6±1.5 1.8%	283.1±8.1 91.2%	27.3 8.8%	309.7
SL_7	4.4±1.4 1.4%	6..9±1.7 2.2%	11.4±2.8 3.6%	9.1±2.4 2.9%	10.4±3.1 3.3%	274.6±7.7 87.1%	40.7 12.7%	315.3
SL_8	2.2±0.9 0.8%	3.8±1.5 1.4%	16.9±3.6 6.2%	11.8±2.0 4.3%	10.7±2.9 3.9%	228.3±5.8 83.4%	45.5 16.6%	273.8
SL_9	2.7±0.8 1.0%	4.5±1.9 1.7%	9.9±2.7 3.7%	8.0±5.13 3.0%	8.5±2.6 3.2%	232.8±7.2 87.4%	33.6 12.6%	266.4
SL_{10}	4.2±1.0 1.3%	7.8±2.4 2.4%	12.9±3.2 4.0%	10.6±2.4 3.3%	11.3±2.1 3.5%	276.8±8.7 85.5%	46.7 14.5%	323.8

TABLE 4.32: The chemical fractionation of Pb metal in sewage - sludge (mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SL_1	1.1±0.5 0.7%	1.6±0.8 1.0%	9.4±2.1 5.8%	4.4±1.4 2.7%	6.6±1.3 4.1%	138.2±4.9 85.7%	23.1 14.3%	161.3
SL_2	1.3±0.6 0.9%	1.8±0.9 1.2%	5.2±1.3 3.5%	9.6± 3.8 6.5%	7.4±2.1 5.0%	122.6±5.7 82.9%	25.3 17.1%	147.9S
SL_3	1.4±0.8 1.1%	1.7±0.8 1.4%	3.6±1.7 2.9%	12.2±3.3 9.8%	7.1±2.8 5.7%	98.8± 4.6 79.1%	26 .1 20.9%	124.9
SL_4	0.8±0.5 0.8%	1.2±0.9 1.2%	1.7±0.6 1.6%	5.9±1.6 5.7%	3.4±1.4 3.3%	90.7±3.9 87.4%	13.1 12.6%	103.8
SL_5	1.5±0.7 1.0%	1.9±1.0 1.3%	8.5±2.7 5.8%	2.5±1.3 1.7%	6.4±1.5 4.4%	125.4±42 85.8%	20.8 14.2%	146.2
SL_6	1.4±0.7 0.9%	2.2±0.7 1.4%	3.9±1.0 2.5%	14.2±2.4 9.2%	8.8±1.8 5.7%	124.2±5.2 80.3%	30.5 19.7%	154.7
SL_7	1.1±0.8 1.0%	1.7±0.8 1.6%	7.1±1.6 6.5%	2.9±0.8 2.7%	5.0±1.6 4.6%	90.7±4.1 83.6%	17.8 16.4	108.5
SL_8	0.7±0.5 0.7%	0.9±0.7 0.9%	6.6±1.6 6.8%	6.6±1.6 6.8%	4.6±0.8 4.8%	81.8±4.8 84.6%	14.9 15.4%	96.7
SL_9	1.2±0.6 0.9%	1.4±0.7 1.0%	4.1±1.7 3.0%	11.1±2.2 8.2%	7.0±1.8 5.2%	110.5±4.3 81.7%	24.8 18.3%	135.3
SL_{10}	0.9±0.5 0.8%	1.3±0.9 1.2%	4.3±1.1 3.9%	10.9± 2.7 9.8%	7.6±1.6 6.8%	86.3±5.3 77.5%	25.1 22.5%	111.4

hence the water soluble and exchangeable fractions may indicate which metals are most available for plant uptake and could affect human health via food chain (Hlavay *et al*; 2004). By this criterion, Pb must not be considered quite mobile and biologically available from these sewage sludge samples.

Table 4.33 presents the results obtained for the six steps sequential extraction of Cd metal for each sampling point. The amount of Cd in the six fractions ranged from 0.8-1.8, 1.3-2.5, 1.2-4.5, 1.6-6.4,1.4-4.1 and 82.7-91.8% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

Of the ten sewage sludge samples examined, six (SL1, SL3, SL4, SL5, SL7 and SL8) exhibited the same trend of Cd distribution amongst the six fractions. The greatest percentages of Cd (91.8, 86.4, 87.7, 90.1, 91.3 and 82.7%), respectively for these samples in the same order were associated with residual fraction. The acid soluble was the next abundant fraction (2.9, 4.5, 3.3, 3.2, 2.9 and 6.4%), followed by the reducible (1.9, 3.4, 3.0, 2.1, 1.4 and 4.1%), oxidizable (1.4, 3.0, 2.2, 1.9, 1.2 and 3.0%), exchangeable (1.2, 1.5, 2.5, 1.6, 1.8 and 2.2%) and water soluble (0.8, 1.2, 1.8, 1.1, 1.4 and 1.6%) fraction. The distribution profile of Cd amongst these six samples was in the decreasing order: residual > acid soluble > reducible > oxidizable > exchangeable > water soluble.

However, SL2, SL6, SL9, and SL10 had the same but slightly different distribution of Cd. As for the other samples, the residual fraction (88.9, 93.4, 84.3 and 83.2%) for the same samples in the same order, was the most abundant pool for this metal but then the acid soluble was the second most concentrated fraction (3.7, 1.6, 4.5 and 5.9%), followed by the oxidizable (3.1, 1.5, 3.9 and 4.5%) reducible (2.0, 1.4, 3.8 and 3.3%), exchangeable (1.2, 1.3, 2.0 and 1.8%) and then water soluble fraction (1.1,0.9 2.0, and 1.8%) fraction. This result indicated

that these sampling points had a trend in the following sequence: residual> acid soluble> oxidizable> reducible> exchangeable>water soluble. Overall, the average distribution of Cd in the sewage sludge was found to be: residual > acid soluble > reducible>oxidizable>exchangeable>water soluble.

Like the other four metals, Cd was predominantly in the residual fraction. This revealed that the content of Cd in these sewage sludge samples could be considered more sluggishly mobile and poorly available for remobilization into environment/soil when exposed. The reason might be due to the entrapment of Cd within the sedimentary matrix of the sewage sludge samples and thus, made the metal less mobile. This result is in agreement with the result reported by Hlavay *et al*. (2004) and Shrivastava and Banerjee (2004). The acid soluble fraction amongst the non-residual fractions was the most important for Cd association. Similar observation of Cd association with acid soluble fraction has been reported (Shrivastva and Banerjee, 2004). The very low percentage of Cd found in the reducible fraction indicated that Cd was much less soluble, since the metal could change with variation in redox conditions becoming more soluble under reducing conditions and less under oxidizing ones (Horsfall and Spiff, 2005). This further suggested that Cd might not be available for plant uptake when the sewage sludge is used as fertilizer. The unavailability of Cd for remobilization into environment when exposed was further signified by the insignificant amount of Cd in the oxidizable, exchangeable and water-soluble fractions.

Overall, the results obtained in the fractionation of the examined metals indicated that all the metals were mainly associated with the residual fraction, with which suggesting that these trace metals are immobile in the Kubanni river basin. With very small percentages of the

metals in the non-residual fractions extracted, it could be said that the bioavailability index of the examined metals was low.

4.10. **Chemical Fractionation of Metals in Contaminated Soils**

The result of six steps sequential extraction of Zn metal for each sampling point is presented in Table 4.34. The contents found for Zn in the six fractions varied between 0.1-0.8, 0.3-12.8, 0.3-7.0, 0.5, 24.9, 1.5-17.7 and 54.2 –97.3% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fractions, respectively.

The greatest percentages of Zn (64.0 and 87.0%) were associated with residual fraction in SS1 and SS8, respectively. The reducible fraction was the next most abundant pool in these samples (14.8 and 9.6%), followed by the exchangeable (12.8 and 1.9%), acid soluble (6.2 and 0.9%), oxidizable (1.5 and 0.4%) and then water soluble (0.7 and 0.2%) fractions for the same samples in the same order. As the result revealed, the distribution profile of Zn in these samples was in the following sequence: residual > reducible> exchangeable > acid soluble > oxidizable> water soluble. However, in SS2, the greatest portion of Zn was in the residual fraction (75.5%). The reducible fraction was the next most abundant (11.8%), followed by the acid soluble (8.4%), exchangeable (2.4%), oxidizable (1.8%) and then the water soluble fraction (0.1%). The trend was: residual > reducible> acid soluble> exchangeable>oxidizable> water soluble. SS3 soil sample had yet a different Zn distribution pattern: the highest percentage of Zn was associated with the residual fraction (70.9%). The exchangeable was the second most concentrated fraction (10.9%), followed by the reducible (8.9%), acid soluble (7.5%), oxidizable (1.3%) and water soluble fraction (0.5%).

TABLE 4.33: The chemical fractionation of Cd metal in sewage - sludge (mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SL_1	0.2±0.02 0.8%	0.3±0.02 1.2%	0.4±0.0 3 1.4%	0.7±0.0 6 2.9%	05±0.08 1.9%	20±73.3 91.8%	1.9 82.2%	22.6
SL_2	0.2±0.04 1.1%	0.2±0.01 1.2%	0.6±0.05 3.1%	0.7±0.09 3.7%	0.4±0.08 2.0%	16.3±2.6 88.9%	2.0 11.1%	18.3
SL_3	0.2±0.05 1.2%	0.3±0.06 1.5%	0.5±0.08 3.0%	0.7±0.09 4.5%	0.6±0.0.5 3.4%	14.1±3.3 86.4%	2.2 13.6%	16.3
SL_4	0.4±0.1 1.8%	0.6±0.02 2.5%	0.6±0.03 2.2%	0.8±009 3.3%	0.7±0.04 3.0%	20.0±3.0 87.7%	2.8 12.3%	22.8
SL_5	0.2±0.01 1.1%	0.3±0.01 1.6%	0.4±0.03 1.9%	0.6±0.05 3.2%	0.5±0.04 2.1%	16.1±2.9 90.1%	1.8 9.9%	17.9
SL_6	0.2±0.03 0.9%	0.2±0.01 1.3%	0.3±0.05 1.5%	0.3±0.05 1.6%	0.3±0.06 1.4%	17.6±2.7 93.4%	1.2 6.6%	18.8
SL_7	0.2±0.03 1.4%	0.3±0.05 1.8%	0.2±0.0 7 1.2%	0.4±0.08 2.9%	0.2±0.3 1.4%	13.6±2.6 91.3%	1.7 18.7%	14.9
SL_8	0.4±0.02 1.6%	0.5±0.09 2.2%	0.7±0.04 3.0%	1.5±0.6 6.4%	1.0±0.02 4.1%	19.9±3.8 82.7%	4.2 17.3%	24.1
SL_9	0.4±01 1.5%	0.5±0.08 2.0%	0.9±0.04 3.9%	1.1±0.3 4.5%	0.9±0.04 3.8%	19.9±3.2 84.3%	3.7 15.7%	23.7
SL_{10}	0.2±0.05 1.3%	0.3±0.02 1.8%	0.7±0.06 4.5%	0.9±0.05 5.9%	0.5±0.03 3.3%	12.3±2.4 83.2%	2.5 16.8%	14.8

The distribution profile was in the order: residual > exchangeable >reducible > acid soluble > oxidizable > water-soluble. SS4 and SS5 had the same but yet a different trend, in which the residual fraction had the major portion of Zn concentration (55.8 and 64.3%, respectively). The reducible fraction was the next most concentrated fraction (17.7 and 15.2%, respectively), followed by the acid soluble (13.9 and 9.4%), oxidizable (6.8 and 7.2%) exchangeable (5.5 and 3.7%) and water soluble fraction (0.2 and 0.2%) for the same samples in the same order. The trend was in the order: residual > reducible > acid soluble > oxidizable > exchangeable > water-soluble.

In the SS6 soil sample, the residual fraction had the highest percentage of Zn (97.3%,. the reducible was the next fraction most abundant pool for Zn (1.5%), followed by the acid soluble (0.5%), oxidizable and exchangeable, which was in equal amount (0.3%) and then water soluble fraction (0.1%). The distribution trend was: residual > reducible > acid soluble > oxidizable ≈ exchangeable > water-soluble. However, in SS7 soil sample, residual fraction had the major amount (63.5%). The reducible was the next fraction (15.4%), followed by the oxidizable (7.0%), acid soluble (6.8%), exchangeable (6.7%) and then the water soluble fraction (0.6%). The trend was residual > reducible> oxidizable> acid soluble> exchangeable> water soluble.

SS9 soil sample had yet a different Zn distribution pattern. The highest percentage of Zn was associated with the residual (54.2%). The acid soluble was the next fraction in this sample (24.9%), followed by reducible (17.3%), exchangeable (1.7%), oxidizable (1.4%) and water soluble fraction (0.5%). The trend of the Zn distribution in this sample was: residual > acid soluble > reducible > exchangeable> oxidizable > water soluble. Finally, SS10 soil sample was found to be associated more with the residual fraction (62.4%). The acid soluble was the

next fraction (18.6%), followed by the reducible (10.4%), oxidizable (5.7%), exchangeable (2.1%) and then water soluble fraction (0.8%). The profile of the Zn distribution in this sample was in the order: residual> acid soluble> reducible> oxidizable> exchangeable> water soluble

The greatest percentage of Zn in the residual fraction probably indicated the greatest tendency for Zn to become unavailable. This is because the residual fraction represented metals that are largely embedded in the sedimentary matrix of the soil and may not be available for remobilization except under very harsh conditions (Lena and Rao, 1997). Similar result was reported for a soil from tailing dumps (Jordao and Nickless, 1989). The reducible fraction amongst the non-residual fractions contained the highest amount of Zn in all the soil samples except SS3 and SS9 soil samples, in which the exchangeable and acid soluble fractions, respectively, had the highest amount of Zn concentration. The highest amount of Zn in the reducible fraction might be attributed to the high stability constant of Zn oxides (Lena and Rao, 1997). Several other researchers such as Ramos *et al*. (1994) and Xian (1989) have also found Zn to be associated with the reducible fraction.

Xian (1989) found that the sums of the exchangeable and acid soluble fractions were strongly correlated with Zn uptake by cabbage. Therefore, the sum of Zn in the exchangeable and acid soluble fractions in this study was significant in some soils and thus, Zn in some of these soils might be available for plant uptake. The concentration of water soluble and oxidizable fraction in these soils was relatively low. The low concentration of Zn in the soils might be due to the low organic matter content, since organic matter content provides high surface adsorption capacity for metals in soils (Osakwe and Egharevba, 2008). Overall, although large percentage of total Zn was in the residual fraction in the soil samples, the amount of Zn present in the non-residual fraction was also appreciable. Therefore, from the

environmental point of view Zn was relatively mobile and bioavailable. Table 4.35 presents the result of six steps sequential extraction of Ni metal for each sampling point of the sewage water-irrigated soils. The concentrations found for Ni in the six fractions ranged from 0.4-1.2, 2.2-30.0, 1.0-7.5, 1.2-21.8, 1.8- 19.8 and 29.8-91.8% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

Of the ten soil samples studied, four (SS1, SS2, SS3 and SS7) had similar trend of Ni distribution amongst the six fractions. The majority of the Ni concentration was in the residual fraction (90.9, 89.3, 91.8 and 87.2%, respectively). The exchangeable was the second most concentrated fraction (3.6, 4.1 3.4 and 4.7%), followed by the reducible (2.3, 2.5, 1.8 and 3.4%) acid soluble (1.3, 1.8, 1.2, and 2.5%), oxidizable (1.1, 1.3, 1.0 and 1.3%) and then the last was water soluble (0.8, 1.0, 0.8 and 0.9%) fractions for the same samples in the same order. The distribution pattern was in the following order: residual> exchangeable> reducible> acid soluble> oxidizable> water soluble. However, in SS4 and SS5, the residual fraction of these samples had the highest concentrations (29.8 and 40.6%, respectively). The exchangeable was the next most abundant fraction (30.0 and 29.7%, respectively), followed by the acid soluble (21.8 and 16.2%), reducible (14.9 and 11.3%), oxidizable (2.6 and 1.8%) and then the water soluble (0.9 and 0.4%) fraction for the same samples in the same order. The distribution trend was in the decreasing order: residual > exchangeable > acid soluble > reducible > oxidizable > water-soluble. For SS6 soil sample also, the residual was the predominantly fraction (71.0%). The reducible was the next most abundant fraction (13.2%), followed by the oxidizable (7.5%), exchangeable (5.7%), acid soluble (3.4%) and then the water soluble (1.2%) fractions. The distribution pattern was in the following order: residual > reducible > oxidizable > exchangeable > acid soluble > water-soluble.

TABLE 4.34: The chemical fractionation of Zn metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SS_1	1.2±0.08 0.7%	22.1±3.6 12.8%	2.6±0.9 1.5%	10.7±2.8 6.2%	25.6±3.3 14.8%	110.6±6.1 64.0%	62.2 36.0%	172.8
SS_2	0.2±0.01 0.1%	5.7±1.6 2.4%	4.3±1.2 1.8%	19.8±2.6 8.4%	27.9±3.4 11.8%	178.3±5.7 75.5%	57.9 24.5%	236.2
SS_3	0.8±0.3 0.5%	17.1±2.5 10.9%	2.0±0.7 1.3%	11.8±2.8 7.5%	14.0±2.6 8.9%	111.5±6.3 70.9%	45.8 29.1%	157.3
SS_4	0.5±0.09 0.2%	9.9±2.1 5.5%	12.2±2.8 6.8%	25.0±3.7 13.9%	31.8±4.1 17.7%	100.2±5.9 55.8%	79.3 44.2%	179.5
SS_5	0.5±0.2 0.2%	5.8±1.3 3.7%	11.3±1.9 7.2%	14.7±2.3 9.4%	23.8±2.7 15.2%	100.8±6.2 64.3%	55.9 35.7%	156.7
SS_6	0.2±0.0.4 0.1%	0.7±0.3 0.3%	0.7±0.3 0.3%	1.1±0.6 0.5%	3.3±1.1 1.5%	215.8±8.4 97.3%	6.0 2.7%	212.8
SS_7	1.8±0.8 0.6%	20.3±2.4 6.7%	21.2±2.7 7.0%	20.6±3. 6.8%	46.6±4.2 15.4%	192.0±5.9 63.5%	110.4 36.5%	302.4
SS_8	0.3±0.08 0.2%	1.9±0.7 1.9%	0.5±0.2 0.4%	1.2±0.9 0.9%	12.3±2.6 9.6%	111.9±4.8 87.0%	16.7 13.0%	128.6
SS_9	0.8±0.3 0.5%	2.8±1.0 1.7%	2.3±0.7 1.4%	41.1±4.2 24.9%	28.5±3.2 17.3%	89.3±4.4 54.2%	75.5 45.8%	164.9
SS_{10}	1.2±0.3 0.8%	3.0±1.2 2.1%	8.2±2.2 5.7%	26.9±3.4 18.6%	15.0.±2.4 10.4%	90.2±4.9 62.4%	54.4 37.6%	144.6

Like the first four soil samples, SS8, SS9, and SS10, had a similar trend, in which the residual fraction contained the major proportion of the Ni concentration (68.1, 58.0 and 64.6%, respectively). The reducible phase was the second most abundant fraction (15.2, 19.8 and 14.9%, respectively), followed by the acid soluble (9.8, 12.4 and 9.7%), oxidizable (4.1, 4.7 and 6.1%), exchangeable (2.2, 3.5 and 3.8%) and then the last was water soluble fraction (0.6, 1.6 and 0.9%) for the same sample in the same order. The profile of the Ni distribution amongst the six fractions in these samples was: residual > exchangeable >reducible > acid soluble > oxidizable > water-soluble. In the overall, the average distribution of Ni in the soil samples was in the following sequence: residual > reducible > acid soluble > oxidizable > exchangeable s> water-soluble.

Although the major percentage of the total Ni was in the residual fraction, the amount of Ni present in the non-residual fraction was also appreciable with the exception of SS1, SS 2, SS3, and SS7 samples. The appreciable percentage of Ni in the non-residual fraction in the majority of the soil samples indicated the bioavailability of Ni. Amongst the non-residual fractions the exchangeable fraction was found highest. Metals present in the exchangeable fraction are usually thought to be readily available for plant uptake (Xian, 1989), because exchangeable fraction of soil consists of metal species found in soil solution. The reducible fraction was also found important for non-residual fractions in the soils. This might be due to the ability of Fe^{2+} and Fe^{3+} species to scavenge metals from soil solution that would normally not precipitate (Asagba *et al*., 2007). A significant amount of Ni was also found in the acid soluble fraction of the SS4, SS5 and SS9 soil samples. The reason might be due to co-precipitation of the metal into carbonates in these soils. A similar result was reported by Lena and Rao (1997), who found Ni highly associated with exchangeable, reducible and acid soluble

fractions. A very small amount of Ni was also found in the oxidizable and water soluble fractions. In general, the Ni metal was found relatively mobile and bioavailable in the majority of the soil samples.

Table 4.36 shows the results found for the six steps sequential extraction of Cu metal for each sampling point. The concentration of Cu in the six fractions varied between 0.5-1.4, 1.2-4.1, 2.6-17.3, 1.2-13.8, 1.8-14.9 and 55.8-90.7% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

Of the ten soil samples studied, seven (SS1, SS2, SS3, SS4, SS5, SS6, and SS10) showed the same pattern of Cu distribution amongst the six fractions. In these samples, the highest amounts of Cu concentration (79.5, 68.4, 81.0, 59.8, 57.9, 89.7 and 80.4%, respectively) were chiefly associated with the residual fraction. The oxidizable fraction was the second phase that contained the next highest amount of Cu concentration (8.4, 11.3, 6.4, 15.0, 17.3, 3.2 and 7.6%, respectively), followed by the acid soluble (5.6, 9.7, 5.1, 11.2, 12.1, 2.7 and 4.8%), reducible (4.5, 6.9, 4.7, 10,9, 8.5, 2.2 and 3.3%), exchangeable (1.2, 2.4, 1.9, 2.3, 3.3, 1.4 and 2.8%) and then water soluble (0.8, 1.3 0.8,0.8, 0.9, 0.8 and 1.1%) fractions for the same samples in the same order. The trend of Cu distribution was in the order: residual > oxidizable > acid soluble > reducible > exchangeable > water-soluble. However, soil sample SS7 had a slightly different trend of distribution for Cu: the residual fraction (58.1%) was the dominant amongst the fractions. The reducible was the next most abundant fraction (16.0%), followed by the oxidizable (13.0%), acid soluble (10.3%), exchangeable (2.1%) and then water soluble fraction (0.5%). The profile of distribution was in the decreasing order: residual > reducible >oxidizable > acid soluble > exchangeable> water-soluble.

TABLE 4.35: The chemical fractionation of Ni metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SS_1	0.9±0.09 0.8%	4.3±1.1 3.6%	1.3+0.5 1.1%	1.5±0.6 1.3%	2.7±0.8 2.3%	107.8±6.8 90.9%	10.9 9.1%	118.6
SS_2	1.4±0.5 1.0%	5.9±1.6 4.1%	1.9±0.6 1.3%	2.6±0.8 1.8%	3.6±1.0 2.5%	128.1±5.7 89.3%	15.4 10.7%	143.5
SS_3	0.5±0.08 0.8%	2.1±1.0 3.4%	0.7±0.2 1.0%	0.8±0.3 1.2%	1.2±0.7 1.8%	60.3±4.4 91.8%	5.4 8.2%	65.7
SS_4	0.9±0.2 0.9%	29.2±3.1 30.0%	2.5±0.9 2.6%	21.2±4.2 21.8%	14.5±2.8 14.9%	29.0±3.7 29.8%	68.3 70.2%	97.3
SS_5	0.6±0.1 0.4%	41.2±4.6 29.7%	2.5±1.1 1.8%	22.5±4.1 16.2	15.7±2.6 11.3%	56.3±3.5 40.6%	82.3 59.4%	138.6
SS_6	1.1±0.3 1.2%	3.3±1.0 5.7%	6.6±2.1 7.5%	3.0±0.9 3.4%	11.6±3.3 13.2%	62.6±5.7 71.0%	25.6 29.0%	83.2
SS_7	0.8±0.09 0.9%	3.9±1.7 4.7%	1.1±0.7 1.3%	2.1±0.8 2.5%	2.9±1.2 3.4%	73.2±4.3 87.2%	10.7 12.8%	83.9
SS_8	0.9±0.2 0.6%	3.3±1.1 2.2%	6.1±1.8 4.1%	14.6±2.8 9.8%	22.6±3.7 15.2%	101.2±4.8 68.1%	47.4 31.9%	148.6
SS_9	1.2±0.7 1.6%	2.6±0.9 3.5%	3.5±1.2 4.7%	9.3±2.6 12.4%	14.8±2.8 19.8%	43.4±3.9 58.0%	31.4 42.0%	74.8
SS_{10}	0.9±0.1 0.9%	3.7±1.7 3.8%	5.9±2.2 6.1%	9.4±2.4 9.7%	14.4±2.7 14.9%	62.3±4.8 4.6%	34.1 35.4%	96.4

Soil sample SS8 was found to have yet another different kind of Cu distribution amongst the soil phases: the residual fraction (90.7%) had the highest portion of the Cu concentration. The exchangeable was the second largest (3.1%), Followed by the oxidizable (2.6%), reducible (1.8%), acid soluble (1.2%) and then the water soluble fraction (0.6%). The profile was in the following sequence: residual > exchangeable > oxidizable > reducible > acid soluble > water-soluble. Finally, the distribution of Cu in SS9 soil sample was found to be in the following decreasing order: residual > reducible > acid soluble > oxidizable > exchangeable > water-soluble. Overall, the trend for Cu distribution was: residual > oxidizable > acid soluble > reducible >exchangeable> water-soluble.

The amount of Cu was mostly concentrated in about 1:1 ratio in non-residual and residual fractions of SS4, SS5, SS7 and SS9 soils. Again, appreciable amount of Cu was found in the non-residual fraction of SS1, SS2, SS3 and SS10 soil samples. The high percentage of Cu in the non-residual fraction reflected the high tendency to become bioavailable in these soils. The oxidizable fraction amongst the non-residual fraction was found the highest. The major association of Cu with organic fraction in the soil samples might be due to the high formation constant of the Cu-organic complexes (Stumm and Morgan, 1981). The acid soluble fraction was the next important fraction for the soil samples. This result is consistent with that of Harrison (1981), who found significant amount of Cu associated with organic and acid soluble fractions. Although Cu was in appreciable amount in the non-residual fraction with the exception of SS6 and SS8 soils it was predominantly in the residual fraction. Osakwe and Egharevba (2008) and Hickey and Kittrick (1984) also found a majority of the Cu in soils and sediments to be associated with the residual fraction. Apart from the oxidizable and acid soluble fractions of non-residual portion, percentage of reducible fraction was also found

significant, more especially in SS2, SS4, SS5, SS7 and SS9 soil samples. A small percentage of Cu was associated with exchangeable and water soluble fractions. The poor presence of Cu in the exchangeable and water soluble fractions might be attributed to the high stability of Cu in the Cu-organic complexes, immobility caused by the carbonates through the provision of adsorbing/nucleating surface (Ramos *et al*; 1994) and Fe/Mn oxides scavenging effect, since the Cu concentration in the non-residual portion was in these fractions. In general, the result suggested that as the extent of Cu contamination in the soils increased, more Cu was associated with the non-residual fractions, which increased the potential of Cu mobility and bioavailability in these soils.

The result of six steps sequential extraction of Pb metal for each sampling point is presented in Table 4.37. The concentration of Pb obtained in the six fractions ranged from (BDL).-0.9, BDL-3.4, 2.8-6.9,8.4-12.4,14.7-33.1 and 50.6-67.8% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

In all the ten soil samples studied, the Pb distribution amongst the six fractions was throughout similar. Lead was predominantly in the residual fraction (50.6, 58.9, 62.6, 63.9, 56.7, 67.8, 60.1, 66.9, 61.1 and 66.6%) for SS1, SS2, SS3, SS4, SS5, SS6, SS7, SS8, SS9 and SS10, respectively. The reducible fraction had the second highest concentration of Pb (33.1, 21.8, 17.3, 15.4, 29.3, 14.7, 23.4, 18.3, 20.3 and 22.7%), followed by the acid soluble (8.56, 11.6, 10.5, 10.2, 10.8, 8.8, 12.1, 9.4, 12.4 and 8.4%), oxidizable (6.9, 6.4, 6.7, 6.5, 3.2, 5.2, 4.4, 3.1, 4.6 and 2.8%), exchangeable (BDL, 1.3, 2.9, 3.4, BDL, 2.6, BDL, 2.6, 1.2% and BDL) and then water soluble (0.8, BDL, BDL, 0.6, BDL, 0.9, BDL, 0.7, 0.4% and BDL) fractions for the same samples in the same order. From the result, the distribution trend of Pb amongst the

six fractions was in the following decreasing order: residual > reducible > acid soluble > oxidizable > exchangeable > water-soluble.

Even though Pb was predominantly in the residual fraction, however, a significant amount of Pb was in the non-residual portion. The high percentage of Pb in the non-residual fraction indicated the greatest tendency to become available. The highest Pb content found in the residual fraction in this study is in agreement with the findings of Osakwe and Egharevba (2008) and Asagba *et al*. (2007). Among the non-residual fractions, reducible and acid soluble fractions were found the highest. Some other workers have also found Pb to be highly associated with reducible form (Ramos *et al.*; 1994; Shrivastava and Banerjee, 2004). The high percentage Pb in the reducible form might be due to the ability of Fe/Mn oxides to scavenge metals from the soil solution that would normally not precipitate (Asagba *et al.*; 2007).

However, small percentage of Pb content was also found in the oxidizable fraction. Exchangeable and water soluble fractions of Pb were found in a very small percentage and not even detected in the SS1, SS2, SS3, SS4, SS7 and SS 10 soil samples (detection limit was 0.5mg/l). This suggested that Pb in these soil samples may not be bioavailable because the exchangeable and water soluble fractions consist of metal species found in the soil solution. They are the most labile and may easily be absorbed into the plant matrix or leached into the ground water sources (Asagba *et al*., 2007). Overall, upon all the ten soil samples studied were contaminated with Pb and may be available as the amount of the metal was significantly present in the non-residual forms.

TABLE 4.36: The chemical fractionation of Cu metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SS_1	1.1±0.2 0.8%	1.6±0.8 1.2%	11.1±3.1 8.4%	7.4±2.7 5.6%	6.0±2.3 4.5%	105.3±5.3 79.5%	27.1 20.5%	132.4
SS_2	2.0±0.9 1.3%	3.7±1.0 2.4%	17.6±3.2 11.3%	15.1±2.3 9.7%	10.7±2.4 6.9%	106.5±4.9 68.4%	49..2 31.6%	155.7
SS_3	1.2±0.1 0.8%	2.6±0.8 1.9%	8.8±2.6 6.4%	7.1±2.2 5.1%	6.5±2.1 4.7%	111.9±4.7 81.0%	26.3 19.0%	138.2
SS_4	1.5±0.3 0.8%	4.3±1.2 2.3%	27.9±2.6 15.0%	20.9±3.4 11.2%	20.3±3.2 10.9%	111.5±3.8 59.8%	74.9 40.2.2%	186.5
SS_5	0.9±0.3 0.9%	3.2±1.1 3.3%	17.0±1.6 17.3%	11.9±2.5 12.1%	8.4±1.4 8.5%	56.9±2.7 57.9%	41.4 42.1%	98.3
SS_6	0.7±0.2 0.8%	1.3±0.8 1.4%	2.9±0.8 3.2%	2.5±0.9 2.7%	2.0±0.7 2.2%	82.3±4.1 89.7%	95. 10.3%	91.8
SS_7	1.6±0.2 0.5%	2.7±0.8 2.1%	16.7±2.4 13.0%	13.3±2.9 10.3%	20.6±3.1 16.0%	74.8±4.2 58.1%	54.0 41.9%	128.8
SS_8	1.2±0.7 0.6%	6.3±1.8 3.1%	5.3±1.2 2.6%	2.4±1.0 1.2%	3.6±1.8 1.8%	183.6±6.2 90.7%	18.8 9.3%	101.4
SS_9	1.9±0.8 1.4%	5.6±1.4 4.1%	13.6±2.3 10.0%	18.7±2.6 13.8%	20.2±3.4 14.9%	75.7±2.7 55.8.8%	59.9 44.2%	135.6
SS_{10}	1.4±0.6 1.1%	3.4±0.9 2.8%	9.3±1.3 7.6	5.9±1.5 4.8%	4.1±1.4 3.3%	98.7±4.4 80.4%	24.1 19.6%	122.8

Table 4.38 presents the result of six steps sequential extraction of Cd metal for each sampling point. The percentage concentration of Cd in the six fractions varied between 0.5-1.2, 1.9-29.7, BDL-2.6, BDL –21.8, BDL-14.9 and 30.2-96.5% for water soluble, exchangeable, oxidizable, acid soluble, reducible and residual fraction, respectively.

Of the ten soil samples examined, six (SS1, SS3, SS6, SS7, SS8 and SS9 showed similar trend of Cd distribution amongst the six fractions. The highest percentage of Cd concentrations (83.5, 87.9, 92.6, 90.5, 91.3 and 94.2%, respectively) was chiefly associated with the residual fraction. The exchangeable was the next most concentrated fraction (7.7, 3.8, 2.0, 2.9, 2.7 and 1.9%, respectively), followed by the reducible (3.4, 2.7, 1.8, 2.6, 2.2 and 1.5%), oxidizable (1.6, 1.8, 1.2, 1.3, 1.2 and 0.7%) and then water soluble (1.2, 1.4, 0.9, 0.8, 0.8 and 0.5%) fractions for similar samples in the same order. The trend of Cd distribution in these soil samples was in the order: residual > exchangeable >reducible > acid soluble > oxidizable > water-soluble.

However, SS2, SS4, and SS5 had slightly different but the same trend, in which the highest of Cd concentrations in these soils was in the residual fraction (55.6), 30.2 and 40.5%, respectively). The exchangeable fraction was the second largest contained the Cd concentration (19.5, 29.6 and 29.7%), followed by the acid soluble (13.3, 21.8 and 16.2%), reducible (8.4, 14.9 and 11.3%), oxidizable (2.1, 2.6 and 1.8%) and then water soluble fraction (1.1, 0.9 and 0.5%) all for the same sample in the same order. The profile of Cd distribution amongst these soils was in the order: residual > exchangeable > reducible > acid soluble > oxidizable > water-soluble. Finally, the residual was the major fraction containing the Cd concentration (96.5%) in SS10 soil sample, exchangeable fraction was the next most abundant (2.7%), followed by the water soluble fraction (0.8%). No Cd was detected in the reducible, acid soluble and

TABLE 4.37: The chemical fractionation of Pb metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SS_1	0.6±0.09 0.8%	BDL	5.4 ± 1.1 6.9%	6.7±1.3 8.6%	25.9±2.9 33.1%	39.6±3.2 50.6%	38.7 49.4%	78.3
SS_2	BDL	0.7±0.3 1.3%	3.3 ± 0.8 6.4%	6.0±1.4 11.6%	11.3±2.0 21.8%	30.5±3.4 58.9%	21.2 41.1%	51.7
SS_3	BDL	1.1± 0.5 2.9%	2.4 ± 0.7 6.7%	3.8±1.0 10.5%	6.3±1.5 17.3%	22.8±2.7 62.6%	13.6 37.4%	37.4
SS_4	0.3±0.0 0.6%	2.0 ± 0.5 3.4%	3.7 ± 0.8 6.5%	5.9.±1.4 10.2%	8.9±2.1 15.4%	36.7±3.6 63.9%	20.8 36.1%	57.5
SS_5	BDL	BDL	1.4±0.6 3.2%	4.8±1.3 10.8%	13.1±2.4 29.3%	25.3±2.6 56.7%	19.3 43.3%	44.6
SS_6	0.8±0.2 0.9%	2.3± 0.6 2.6%	4.6±1.4 5.2%	7.7±1.1 8.8%	12.9±2.2 14.7%	59.5±4.2 67.8%	28.3 32.2%	87.8
SS_7	BDL	BDL	3.3±0.8 4.4%	8.9±1.7 12.1%	17.3±2.7 23.4%	44.4+3.8 60.1%	29.5 39.9%	73.9
SS_8	0.3±0.03 0.7%	0.7+0.3 1.6%	1.4±0.8 3.1%	4.3±1.3 9.4%	8.3±1.3 18.3%	30.4±3.3 66.9%	15.0 33.1%	45.4
SS_9	0.2±0.0 0.4%	0.6 ± 0.3 1.2%	2.3±0.6 4.6%	6.1±1.1 12.4%	10.0±2.4 20.3%	30.0±2.8 61.1%	19.1 38.9%	49.1
SS_{10}	BDL	BDL	1.0±0.3 2.8%	3.1±0.8 8.4%	8.4±2.2 22.7%	24.6±2.3 66.6%	12.6 33.9%	37.2

BDL - Below detection limit for Pb, the detection limit for Pb was 0.05 mg/l

oxidizable fractions of this soil sample (detected limit was 0.03mg/l). In the overall, the average Cd distribution amongst the soil samples was in the following decreasing order residual > exchangeable >reducible > acid soluble > oxidizable > water-soluble.

More than 83% of the total Cd in all the soils excluding SS2, SS4 and SS5 was associated with the residual fraction. Cadmium concentration in SS2, SS4 and SS5 soils was mostly presented in the non-residual phase. Fifty two percent of the Cd in SS2, 66% in SS4 and 57% in SS5 soil was associated with the exchangeable, acid soluble and reducible fractions, with the exchangeable fraction being the highest. This suggested that Cd in these three soils was potentially bioavailable for plant uptake (Xian, 1989; Asagba *et al*., 2007). These findings are in agreement with the earlier observations of Harrison (1981), Lena and Rao (1997) and Kuo *et al*. (1983).

The residual fraction was the most abundant pool for all the metals in the soil samples studied. However, a significant percentage of the total metals was associateds with the non-residual fractions. The order of contamination was Pb> Zn> Cu> Ni> Cd. Amongst the ten soil samples tested, SS1, SS2, SS4, SS5, SS7 and SS9 soil samples were the most contaminated with the five trace metals studied.

4.11 **Transfer and Contamination Factors for Trace Metals**

One approach to assess the mobility of metal from soil to plants is to calculate transfer factor (TF), as defined in the following equation (Chojnacka *et al*., 2005):

$$TF = \frac{C_{plant}}{C_{soil}}$$

where C_{plant} is the concentration of an element in the plant material (dry weight basis) and C_{soil} is the concentration of the same element in the soil (dry weight basis) in which plant was grown. The higher the value of the TF, the more mobile/available the metal is for plant absorption.

The transfer factor of metals from soil to vegetation is one of the key routes of human exposure to metal through the food chain (Lokeshivari and Chandrappa, 2006). According to Rasheed and Awadallah (1998), plant uptake is one of the major pathways by which metals from soils enter the food chain. The food-chain plants might absorb enough amounts of trace metals and become a potential health hazard to consumers (Francis, 2005).

The transfer factors (TF) of the metals studied are presented in Table 4.39. Transfer factors were determined for Zn, Ni, Cu, Pb and Cd to quantify the relative difference in bioavailability of the metals to plants or to identify efficiency of plant species to accumulate a given metal. These factors were based on the root uptake of metals and discount the foliar absorption of atmospheric metals deposits. For spinach, the TF values ranged from 0.099-0.411, 0.013-0.129, 0.066-0.172, 0.171-0.517 and 0.024-0.294 for Zn, Ni, Cu, Pb and Cd, respectively.

From the result, the highest TF value of Zn was found in site 10 and the lowest was in site 7, while for Ni and Cu, the highest values were obtained in site 3 and site 6, whereas the lowest were in site 9 and site 2, respectively. However, for Pb and Cd, the highest values were found in site 3 and site 6, while the lowest values were obtained in site 6 and site 5, respectively.

As for lettuce, the TF values varied between 0.167-0.419, 0.028-0.143, 0.062-0.149, 0.154-0.611 and 0.077-0.412 for Zn, Ni, Cu, Pb and Cd, respectively. It was observed that the

highest TF value of Zn was found to be in site 10 and the lowest value was obtained in site 7. The highest TF values of Ni and Cu were found in site 9 and site 1, while the lowest values were obtained in site 2 and site 4, respectively. For Pb and Cd, however, the highest values were observed in site 3 and site 6, where as the lowest were obtained in site 1 and site 5, respectively.

Generally, TF values were high in site 3, 6 and 10. This suggested that vegetables that were grown on these soils absorbed enough amounts of the metals studied. The TF values obtained in these soils might be attributed to the physico-chemical properties of the soils which might have enhanced soil-plant transfer of the metals. For instance, low clay content and high sand content may have influenced the soil-plant transfer of the metals, as it was reported that soils with high sand content have poor metal retention capacity (Asagba *et al*; 2007). The sequence of the mobility of the metals was: Pb> Zn> Cd> Cu> Ni. The low TF of Ni found in this study is in accordance with the findings that accumulation of Ni is comparatively less, while that of Zn, Cd and Cu is more in plants (Olaniya *et al*., 1998). In addition, Cd occurs with the Zn in nature and Cd (II) is retained less by the soil (Lokeshwari and Chandrappa, 2006).

Upon comparison, the TF values of lettuce were higher than those found for the spinach. This suggests that the metals were more in the lettuce samples than the spinach samples, as it was earlier mentioned and further revealed by TF value. Therefore, the lettuce harvested from the study area exposed consumers more to ingestion of toxic metals than spinach. The TF values found in this work are similar to the TF values observed by Awode *et al*. (2008), Osakwe and Egharevba (2008) and Lokeshwari and Chandrappa (2006), but lower than the values reported by Francis (2005).

TABLE 4.38: The chemical fractionation of Cd metal in the contaminated soil sample (Mean ± SD, mg/kg dry weight)

Fractions	Water soluble phase	exchangeable phase	oxidizable phase (Bound to organic)	Acid soluble phase (Bound to carbonate)	Reducible phase (Bound to oxides)	Residual phase (Bound to silicates)	Non - residual phase	Total extractable (∑T)
SS_1	0.3±0.5 1.2%	2.2±0.8 7.7%	0.5±0.2 1.6%	0.6±0.4 2.2%	1.0±0.6 3.4%	23.5±3.8 83.5%	4.5 16.5%	28.2
SS_2	0.2±0.04 1.1%	3.7±1.2 25.5%	0.3±0.02 2.1%	2.2±0.8 15.3%	1.7±0.7 11.6%	6.5±2.1 44.4%	8.1 55.6%	14.6
SS_3	0.3±0.01 1.4%	0.7±0.4 3.8%	0.3±0.01 1.8%	0.5±0.2 2.4%	0.5±0.1 2.7%	17.0±3.2 87.9%	2.3 12.1%	19.3
SS_4	0.3±0.05 0.9%	11.5±1.8 29.6%	1.0±0.4 2.6%	8.4±2.1 21.8%	5.8±1.2 14.9%	11.7±2.9 30.2%	27.0 69.8%	38.7
SS_5	0.2±0.06 0.5%	12.6±3.1 29.7%	0.8±0.5 1.8%	6.9±1.8 16.2%	44.8±1.6 11.3%	17.2±3.4 40.5%	25.2 59.5%	42.4
SS_6	0.1±0.0 0.9%	0.3±0.06 2.0%	0.2±0.04 1.2%	0.2±0.04 1.5%	0.3±0.0 1.8%	12.9±3.2 92.6%	1.0 7.4%	13.9
SS_7	0.4±0.1 0.8%	1.3±0.6 2.9%	0.6±0.2 1.3%	0.7±0.3 1.5%	1.2±0.5 2.6%	43.3±4.7 90.5%	4.5 9.5%	47.8
SS_8	0.1±0.0 0.8%	0.4±0.03 2.7%	0.2±0.07 1.2%	0.3±0.06 1.8%	0.3±0.03 2.2%	13.0±2.7 91.3%	1.2 8.7%	14.2
SS_9	0.1±0.0 0.5%	0.5±0.1 1.9%	0.2±0.03 0.7%	0.3±0.04 1.2%	0.4±0.1 1.5%	24.8±3.8 94.2%	1.5 5.8%	26.3
SS_{10}	0.1±0.0 0.8%	0.3±0.04 2.7%	BDL	BDL	BDL	9.5±2.9 96.5%	0.3 3.5%	9.8

BDL - Below detection limit for Cd, the detection limit for Cd was 0.03 mg/l

Furthermore, the transfer factors as suggested by Klode *et al*. (1984) for Cu and Pb (0.01-0.1), Zn and Cd (1-10) and Ni (0.1-1) were used as a generalized range for comparison/standards. Both the lettuce and spinach samples exceeded the suggested factor range of Cu and Pb, but Ni was within the range. This revealed that Pb, Cu and Ni posed the greatest threat amongst the metals studied in relation to human health.

Table 4.40 shows the individual (C^i_f) and global ($C_f = \Sigma\, C^i_f$) contamination factors for five metals in the sewage sludge samples analyzed. The individual contamination factors (ICF) for the various sampling sites were calculated from the result of the chemical fractionation study for each sampling site. The global contamination factor (GCF) for each site was calculated by summing the ICF for all the five metals obtained for a site (Ikem *et al*., 2003). The ICF reflects the risk of contamination of sewage water body and soils by a pollutant, while the GCF reflects the overall potential risk that may be posed by metals to the river basin, soils environment and indeed to biota. The higher the levels of the mobilizable fractions (i.e. the water soluble, exchangeable, oxidizable, acid soluble and reducible) in the sewage sludge and soil, the greater the potential risk to sewage water contamination by sludge and to vegetation contamination by soil.

The individual contamination factor values obtained for sewage sludge ranged from 0.2 – 0.5, 0.2 – 0.5, 0.1 – 0.2, 0.1 – 0.3 and 0.1 – 0.2 for Zn, Ni, cu, Pb and Cd, respectively. From the results obtained, Zn has the highest ICF values, amongst the metals studied, followed by Ni, then Pb, Cu and Cd had the lowest ICF values. It could be seen that all the sampling sites had very low individual and global contamination factors. Therefore, all the metals did pose very low risk to sewage water contamination, since the chemical forms of the trace metals is

Table 4.39: *Metal transfer factor for each metal from soil to vegetation.

Metals	Zn	Ni	Cu	Pb	Cd
$Site_1$	0.240 (0.217)	0.055 (0.062)	0.103 (0.149)	0.190 (0.154)	0.097 (0.089)
$Site_2$	0.160 (0.243)	0.035 (0.028)	0.066 (0.080)	0.186 (0.372)	0.137 (0.169)
$Site_3$	0.311 (0.218)	0.129 (0.132)	0.123 (0.085)	0.517 (0.611)	0.178 (0.161)
$Site_4$	0.171 (0.241)	0.074 (0.088)	0.092 (0.062)	0.207 (0.402)	0.062 (0.088)
$Site_5$	0.260 (0.234)	0.024 (0.030)	0.112 (0.200)	0.258 (0.341)	0.024 (0.077)
$Site_6$	0.236 (0.175)	0.057 (0.049)	0.172 (0.122)	0.171 (0.158)	0.294 0.412)
$Site_7$	0.099 (0.167)	0.089 (0.068)	0.081 (0.087)	0.187 (0.283)	0.074 (0.072)
$Site_8$	0.280 (0.272)	0.060 (0.029)	0.091 (0.069)	0.184 (0.385)	0.241 (0.429)
$Site_9$	0.315 (0.367)	0.013 (0.143)	0.123 (0.141)	0.321 (0.262)	0.066 (0.090)
$Site_{10}$	0.411 (0.419)	0.075 (0.077)	0.102 (0.127)	0.205 (0.482)	0.262 (0.393)

*Values in parentheses are for lettuce.

one of the factors that can influence the remobilization of metals from sewage sludge into sewage water column.This further suggested that the metals analyzed in the sewage sludge might only pose very low risk to soil contamination when used as fertilizer for soil fertility amendment.

Site 3,4,5,6, and 10 generally had higher individual and global contamination factors when compared to other sites, even though very low values were recorded. The high trend for these sites might be due to the increased levels of mobilizable fractions in the sludge of these sites. However, in the overall, very low ICF and GCF values were detected in all the sampling sites. The very low trend might be as a result of the entrapment of the contaminants into the sedimentary matrix of the sewage sludge.

Also, the result of the individual and global contamination factors for soil samples are presented in Table 4.41. The individual contamination factors found ranged from 0.1 – 0.8, 0.1 – 2.4, 0.1 – 3.4, 0.5 – 1.0 and 0.1 – 2.3 for Zn, Ni, cu, Pb and Cd, respectively. The values revealed that Cu had the highest ICF values and Ni was the next highest, followed by Cd, Pb and then Zn had the lowest values.

Sampling sites 4,5, and 9 generally had the highest individual and global contamination factors, followed by sites 2 and 7 when compared to other sites. The remobilization of metals from the soil into the soil solution is usually influenced by factors such as pH, chemical forms of the trace metals and physico-chemical characteristics of the soils. Therefore, the high trend observed in these sites might be inclined towards the chemical forms of the trace metals in the soils of these sites, of which were significantly present in the modifiable fractions. Consequently, this reflected the risk of contamination of the soils of these sites by the metals

Table 4.40: Individual (C^i_f) and global (C_f) contamination factors of five metal in sewage sludge

Site	Individual contamination factors (C^i_f)					Global contamination factor
	Zn	Ni	Cu	Pb	Cd	$C_f = \Sigma C^i_f$
Site 1	0.2	0.2	0.1	0.2	0.1	0.8
Site 2	0.4	0.2	0.1	0.2	0.1	1.0
Site 3	0.4	0.5	0.1	0.3	0.2	1.5
Site 4	0.4	0.4	0.1	0.1	0.2	1.2
Site 5	0.5	0.3	0.1	0.2	0.1	1.2
Site 6	0.5	0.5	0.1	0.2	0.1	1.4
Site 7	0.2	0.3	0.2	0.2	0.1	1.0
Site 8	0.3	0.4	0.2	0.2	0.2	1.3
Site 9	0.3	0.2	0.1	0.2	0.2	1.0
Site 10	0.4	0.4	0.2	0.3	0.2	1.5

analyzed and also, the overall potential risk posed by these toxic metals to the vegetation and to humans by extension.

Amongst the metals analyzed, Cu and Ni posed the highest risks to vegetation contamination, followed by Cd and Pb, while Zn posed the lowest risk. Generally, risk to vegetation contamination was highest in sites 4, 5 and 9, followed by sites 2 and 7 based on the calculated global contamination factors.

Upon comparison between sewage sludges and soils, soils posed the greatest threat based on the calculated individual and global contamination factors. This showed that the accumulation of the five toxic metals in the soils was a threat to both plants and humans in terms of exposing them to metal contamination, since soil-plant is an important pathway of metal contamination in the ecosystem. Therefore, assessment of the impact of sewage water irrigation on the irrigated farming areas should be periodically monitored.

Table 4.41: Individual (C^i_f) and global (C_f) contamination factors of five metal in soil

Site	Individual contamination factors (C^i_f)					Global contamination factor
	Zn	Ni	Cu	Pb	Cd	$C_f = \Sigma C^i_f$
Site 1	0.6	0.1	0.2	0.1	0.2	1.2
Site 2	0.3	0.1	0.5	0.7	0.8	2.4
Site 3	0.4	0.1	0.2	0.6	0.1	1.4
Site 4	0.8	2.4	3.4	0.6	2.3	9.5
Site 5	0.6	1.5	2.7	0.8	1.5	7.1
Site 6	0.1	0.4	0.1	0.5	0.1	1.2
Site 7	0.6	0.1	0.7	0.7	0.1	2.2
Site 8	0.1	0.5	0.1	0.5	0.1	1.3
Site 9	0.8	0.7	3.2	0.6	0.1	5.4
Site 10	0.6	0.6	0.2	0.5	0.1	2.0

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The findings of this study revealed that the physico-chemical parameters of sewage waters were not suitable for irrigation but that those control area waters (tube-well waters) were suitable for irrigation. Trace metal contents were generally more in study areas and thus, it can be concluded that the study areas received more pollution load of trace metals than the control areas. Trace metal contents in the sewage sludge have not accumulated beyond the permissible limits as recommended by EU. The soils from the study area were contaminated with the trace metals. However, there was an increase in the trace metal contents in the vegetables harvested from sewage water-irrigated soils as compared to tube-well water-irrigated ones. The levels of Cd, Pb and Ni in the vegetables of the study area exceeded the permissible limits of metals and are, therefore, not fit for human consumption. The study further showed that growing vegetables in sewage water containing variable amounts of trace metals led to increase in concentration of trace metals in the soils and vegetation. The results show that the distribution profile of the metals in the four environmental compartments studied for study areas was as follows: sewage sludge > soil > vegetation > sewage water. In all of the samples analysed Zn had the highest mean values relative to other metals followed in some cases by Cu and in other cases by Ni, while Cd had the lowest values. Therefore, Zn was the most prevalent metal in the samples while Cd was the least.

5.2 **Recommendations**

Since irrigation with sewage water or wastewater is an attractive solution to the problem of both wastewater disposal and the scarcity of irrigation water, soil, plant and water quality monitoring and evaluation should periodically be carried out in order to prevent potential health hazards to consumers of vegetables from such areas. As such, alternative source of irrigation water should be explored like sinking of enough tube-wells in the area through government and non-governmental aid, so as to minimize the extent of trace metal contamination to the soils and vegetation in turn. The use of sewage sludge as fertilizer should be monitored to ensure that the trace metal content do not pose threat to safety of the vegetables that will be grown with it.

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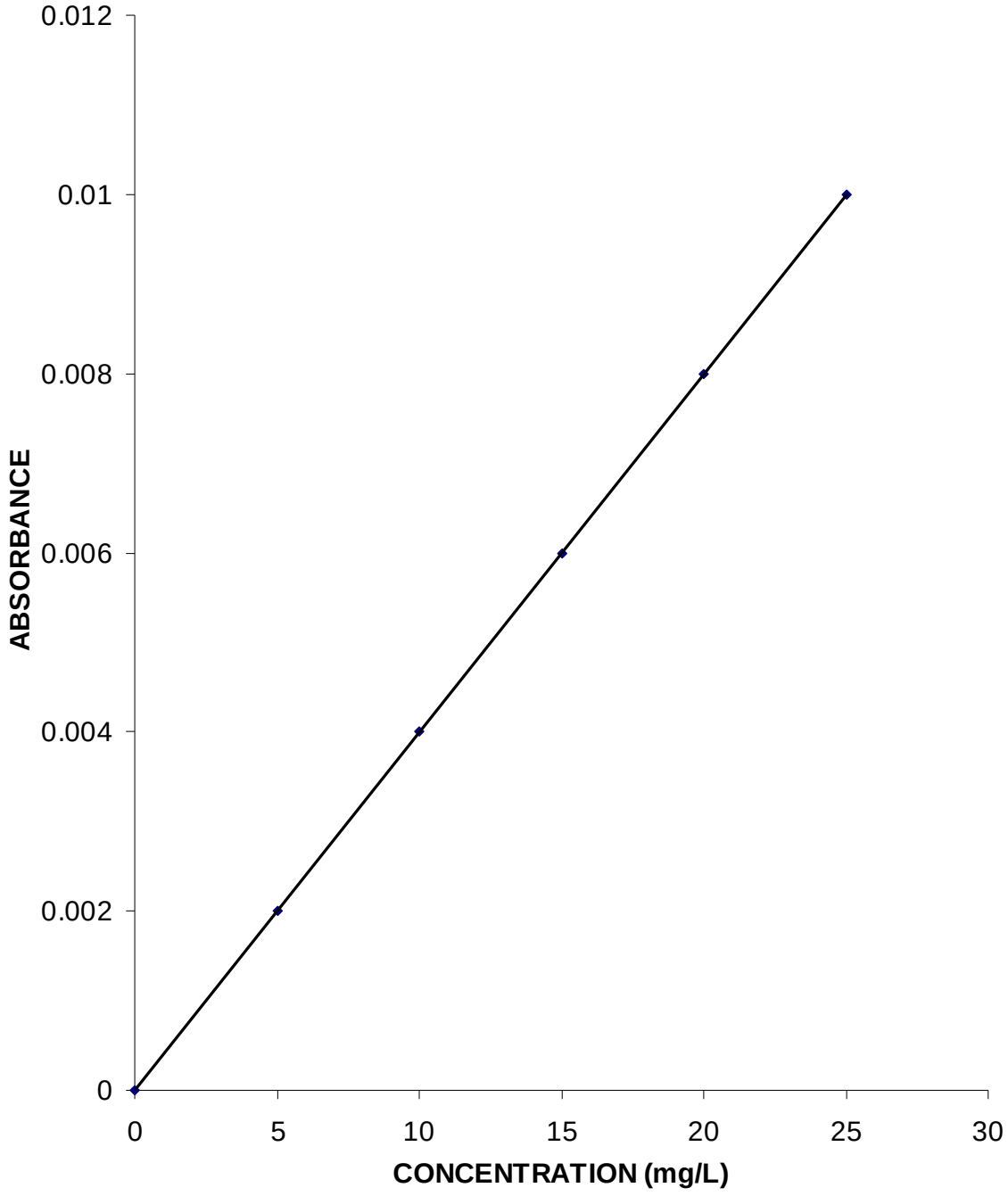
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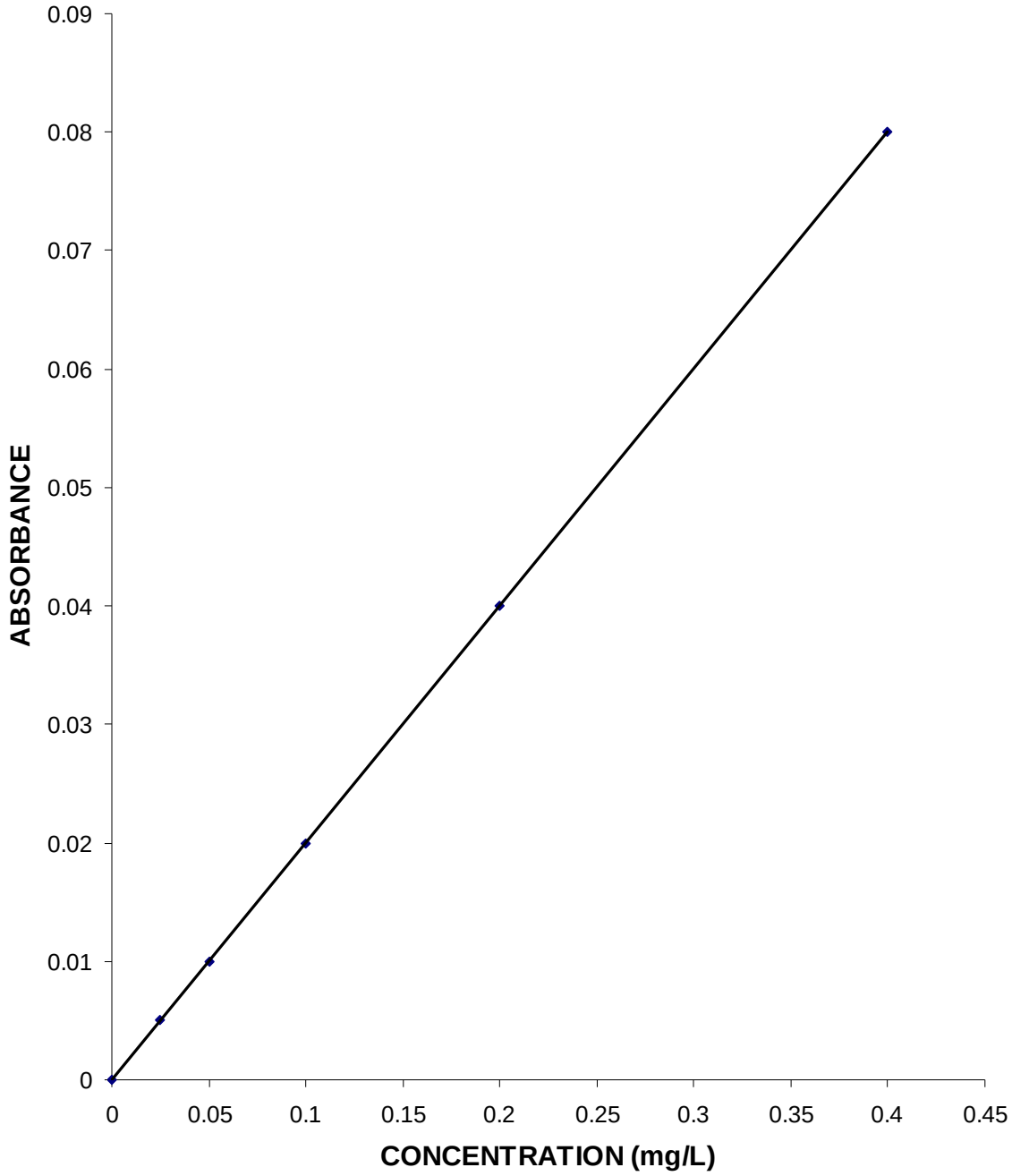
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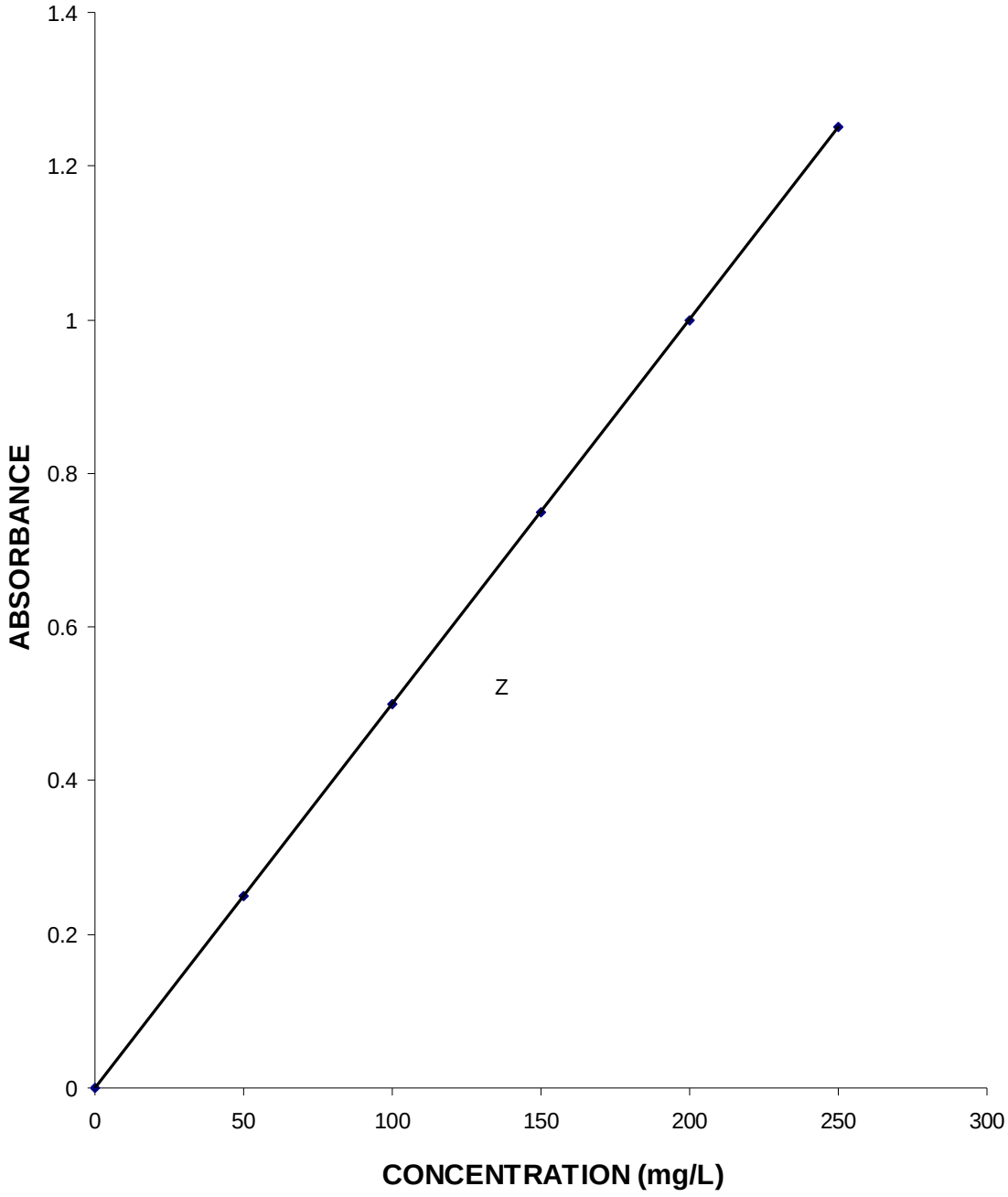
APPENDIX I : CALIBRATION CURVE FOR NITRATE



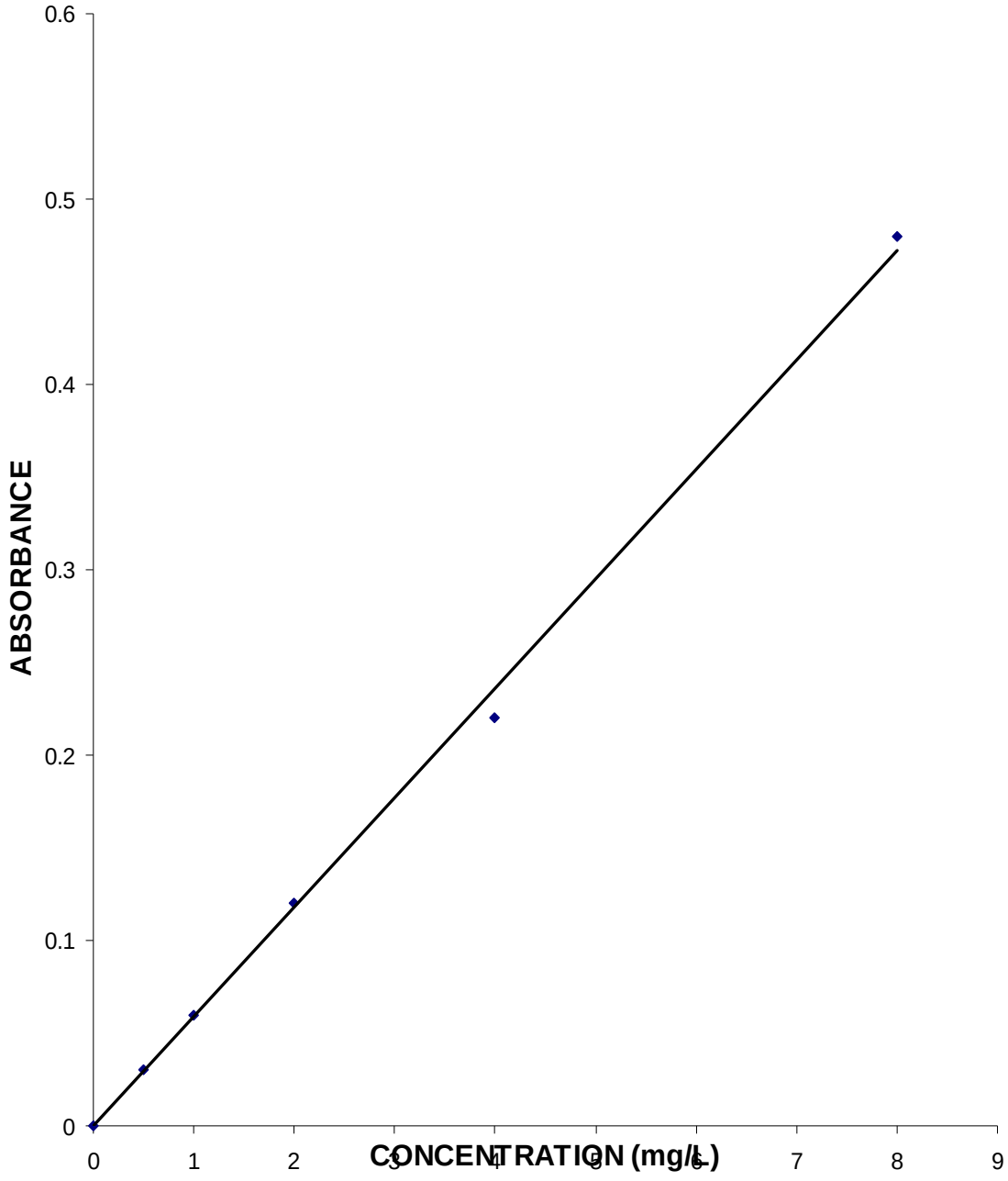
APPENDIX II : CALIBRATION CURVE FOR PHOSPHATE



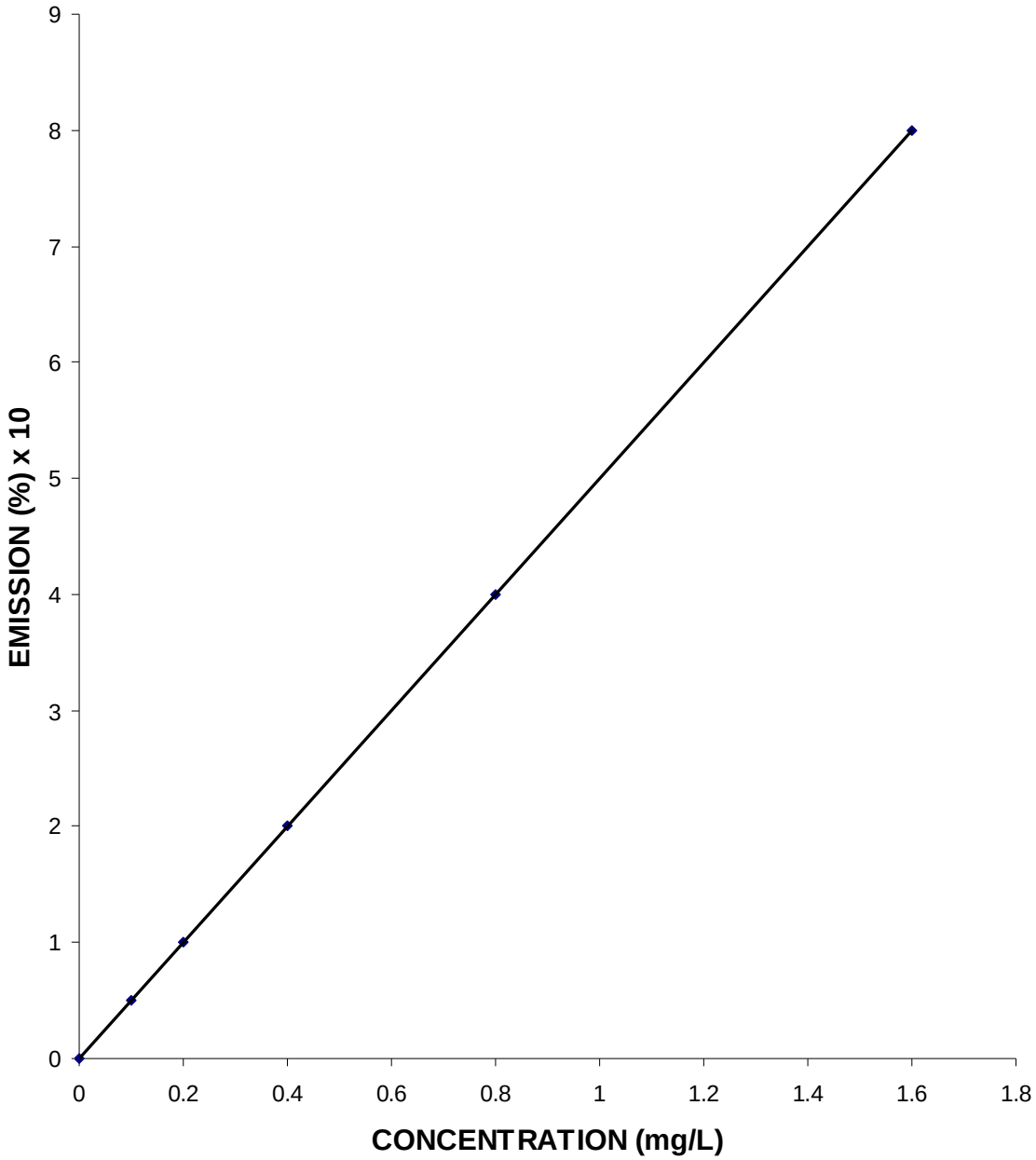
APPENDIX III : CALIBRATION CURVE FOR SULPHATE



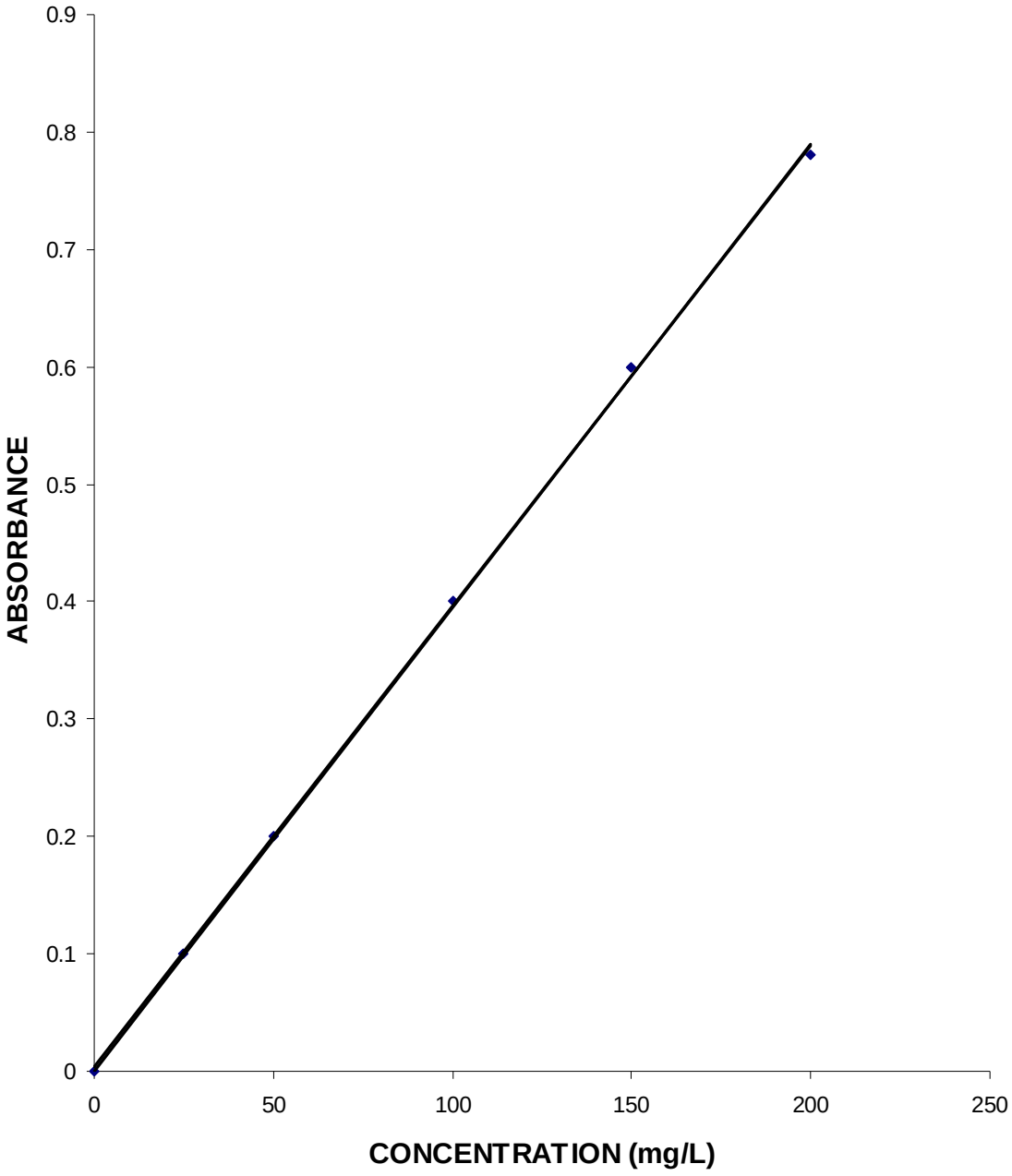
APPENDIX IV:CALIBRATION CURVE FOR PHOSPHATE (SLUDGE)



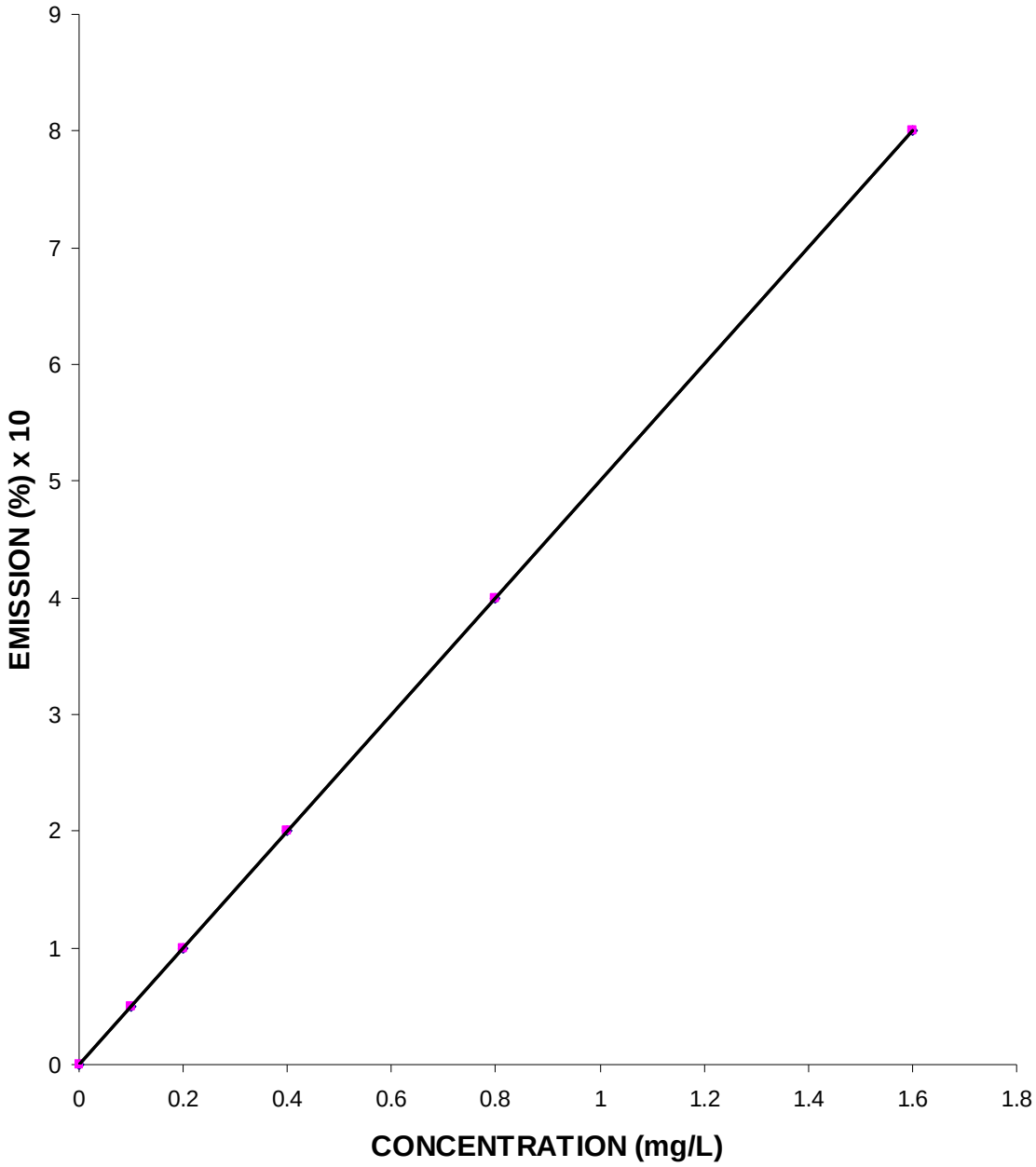
APPENDIX V : CALIBRATION CURVE FOR POTASSIUM



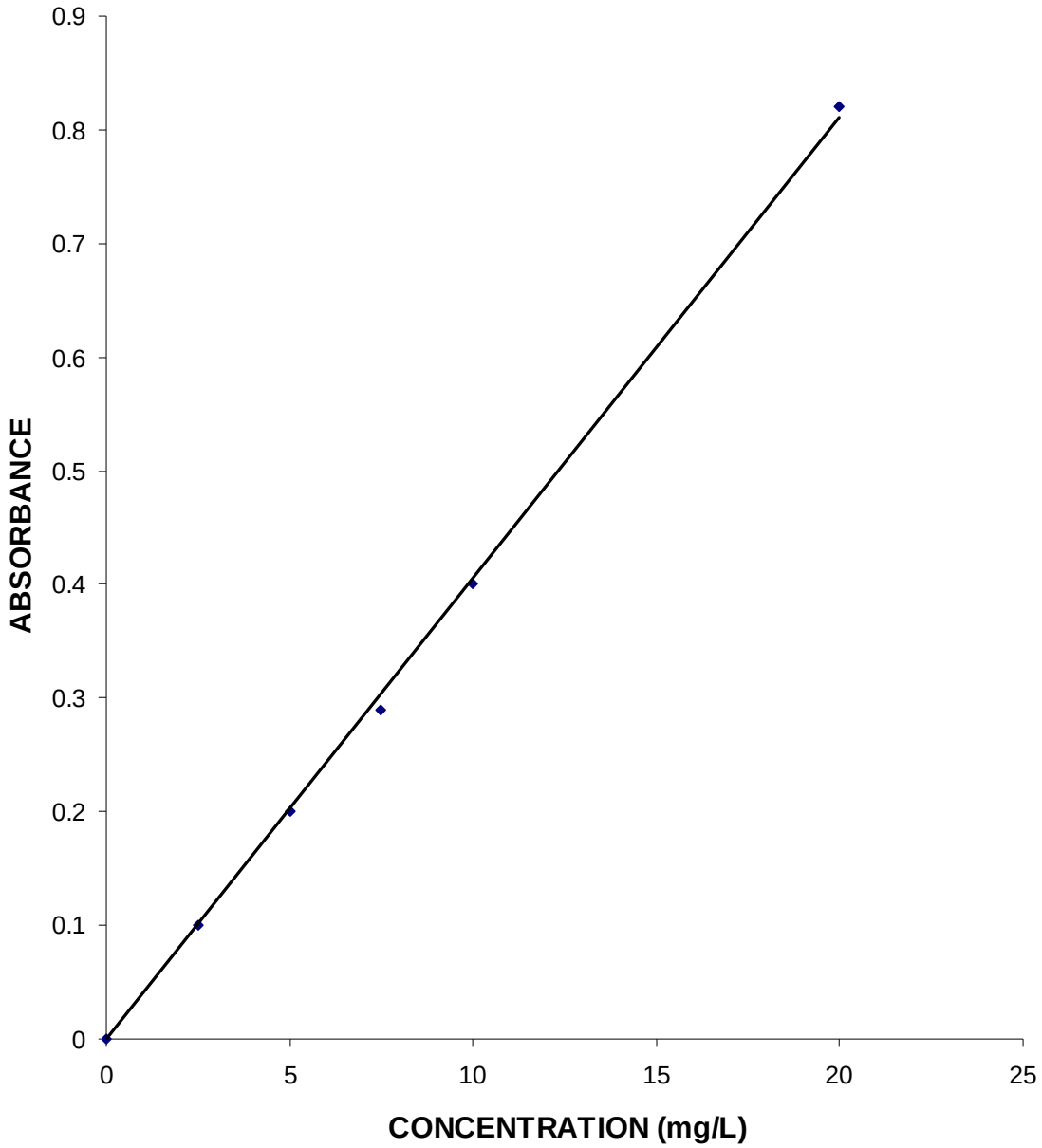
APPENDIX VI : CALIBRATION CURVE FOR CALCIUM



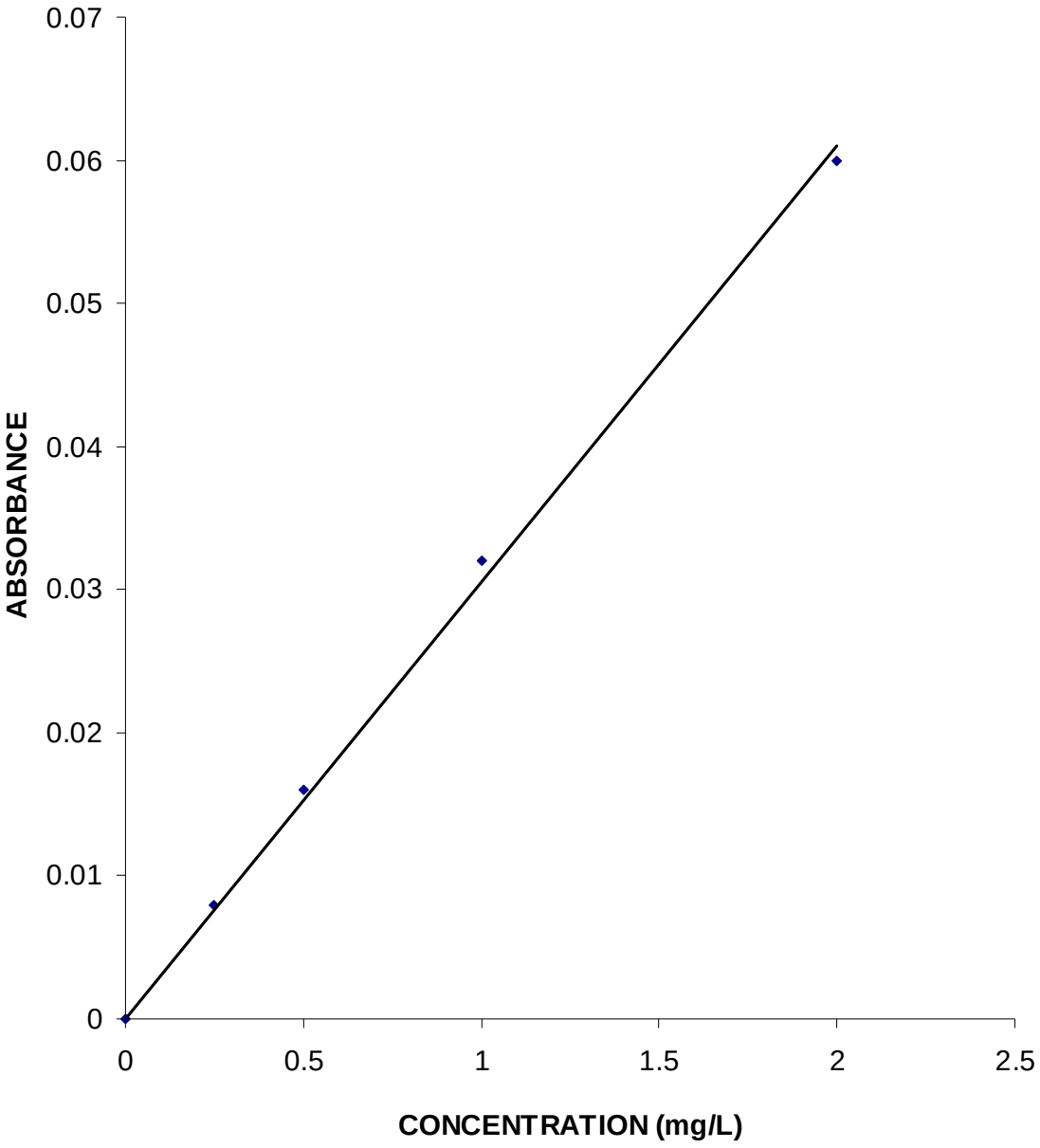
APPENDIX VII : CALIBRATION CURVE FOR SODIUM



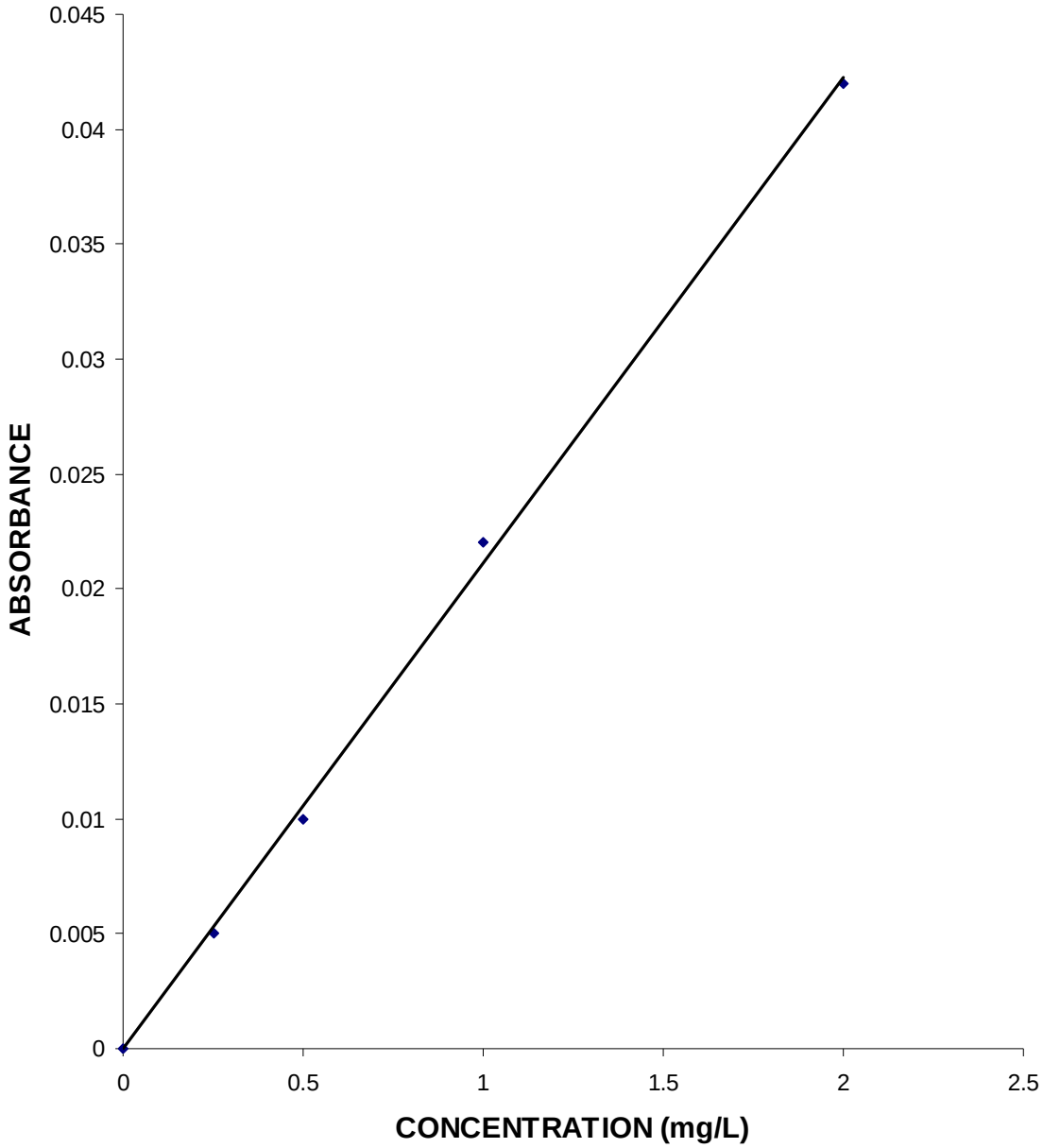
APPENDIX VIII:CALIBRATION CURVE FOR MAGNESIUM



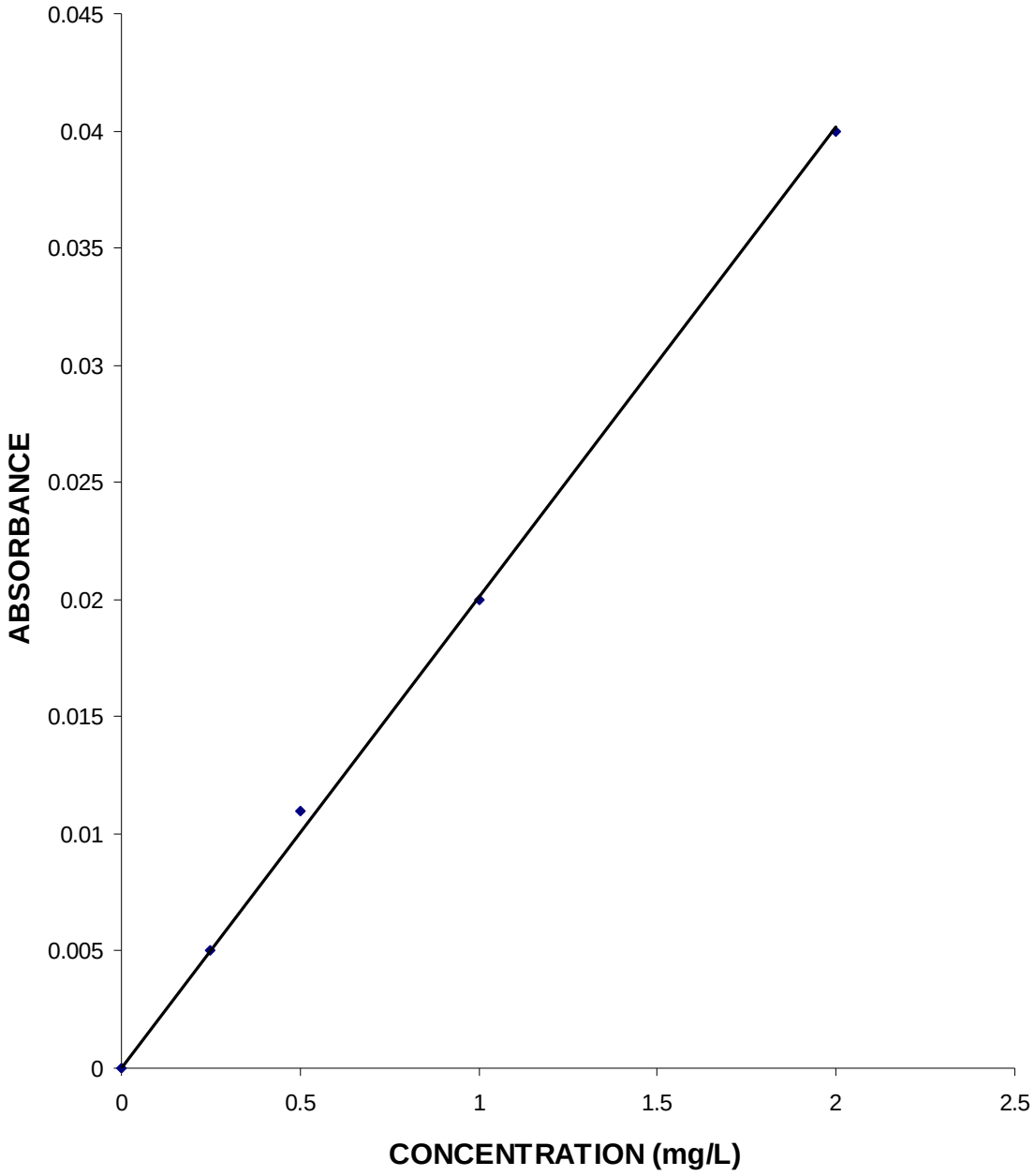
APPENDIX IX: CALIBRATION CURVE FOR CADMIUM



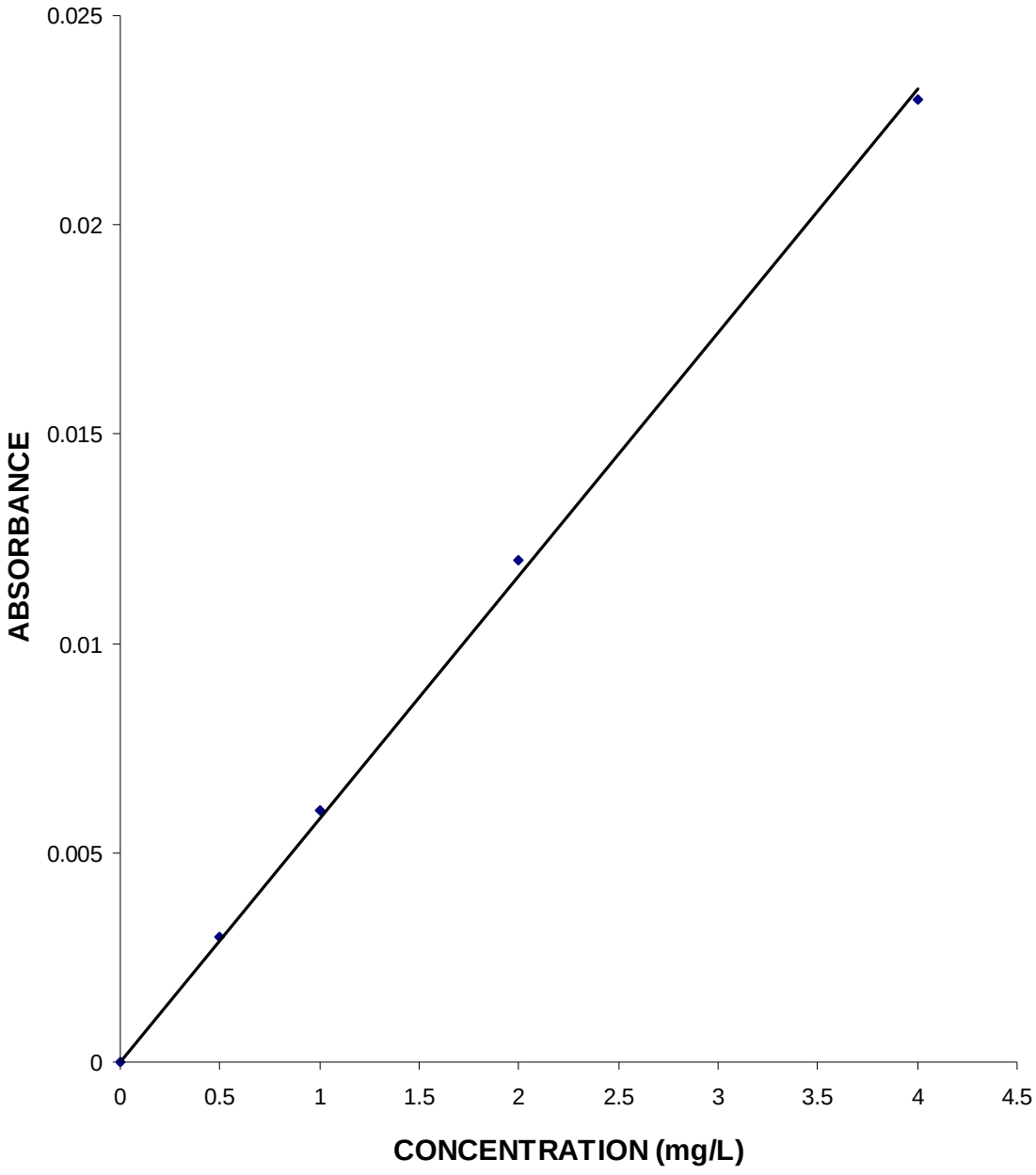
APPENDIX X : CALIBRATION CURVE FOR COPPER



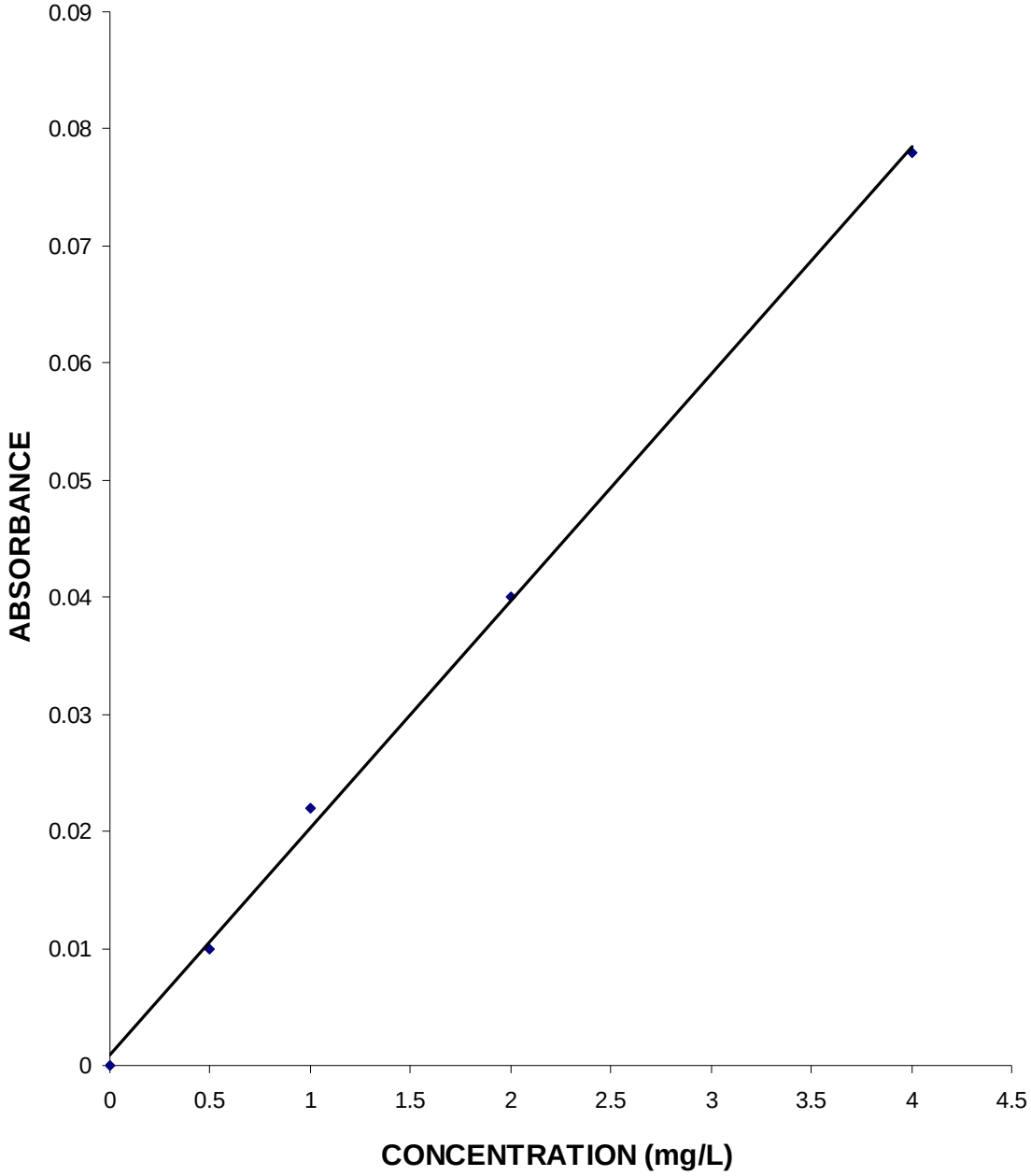
APPENDIX XI : CALIBRATION CURVE FOR LEAD



APPENDIX XII : CALIBRATION CURVE FOR NICKLE



APPENDIX XIII : CALIBRATION CURVE FOR ZINC



Appendix XIVa: Test of significant difference between metal concentrations in February, March and April of sewage water at 95% confidence.

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
F calculated	0.022	0.018	0.096	0.091	0.085	0.030	0.128	0.010	0.199	0.032
F critical	5.05	5.05	5.05	5.05	5.05	5.05	5.05	5.05	5.05	5.05
P value	0.978	0.982	0.909	0.914	0.919	0.970	0.881	0.990	0.822	0.969

Appendix XIVb: Test of significant difference between metal concentrations in February, March and April of sewage sludge at 95% confidence.

Factor	SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10
F calculated	0.010	0.019	0.030	0.062	0.056	0.053	0.024	0.275	0.045	0.061
F critical	5.05	5.05	5.05	5.05	5.05	5.05	5.05	5.05	5.05	5.05
P value	0.990	0.981	0.970	0.940	0.946	0.948	0.976	0.764	0.956	0.941

Appendix XVa: Correlation coefficients between metal concentrations (February) in sewage waters and soils.

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
SS1	0.388									
SS2		0.497								
SS3			0.593							
SS4				0.189						
SS5					0.946*					
SS6						0.891*				
SS7							0.361			
SS8								0.527		
SS9									0.525	
SS10										0.731

Key

* Correlation is significant at the 0.05 level.

Appendix XVb: Correlation coefficients between metal concentrations (March) in sewage waters and soils.

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
SS1	0.540									
SS2		0.552								
SS3			0.602							
SS4				0.224						
SS5					0.965**					
SS6						0.664				
SS7							0.454			
SS8								0.509		
SS9									0.158	
SS10										0.728

Key

* Correlation is significant at the 0.01 level.

Appendix XVc: Correlation coefficients between metal concentrations (April) in sewage waters and soils.

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
SS1	0.625									
SS2		0.490								
SS3			0.597							
SS4				0.118						
SS5					0.947*					
SS6						0.689				
SS7							0.534			
SS8								0.509		
SS9									0.574	
SS10										0.695

Key

* Correlation is significant at the 0.05 level.

Appendix XVIa: Correlation coefficients between metal concentrations in Sewage water and sludge (February).

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
SL1	0.397									
SL2		0.139								
SL3			0.783							
SL4				0.169						
SL5					0.408					
SL6						0.782				
SL7							0.408			
SL8								0.633		
SL9									0.714	
SL10										0.645

Appendix XVIb: Correlation coefficients between metal concentrations in Sewage water and sludge (March).

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
SL1	0.585									
SL2		0.382								
SL3			0.685							
SL4				0.254						
SL5					0.674					
SL6						0.468				
SL7							0.510			
SL8								0.730		
SL9									0.696	
SL10										0.760

Appendix XVIc: Correlation coefficients between metal concentrations in Sewage water and sludge (April).

Factor	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10
SL1	0.583									
SL2		0.397								
SL3			0.759							
SL4				0.154						
SL5					0.695					
SL6						0.573				
SL7							0.583			
SL8								0.439		
SL9									0.646	
SL10										0.714

Appendix XVIIa: Correlation coefficients between metal concentrations in Soils and spinach (study area).

Factor	SS1	SS2	SS3	SS4	SS5	SS6	SS7	SS8	SS9	SS10
SP1	0.915*									
SP2		0.941*								
SP3			0.874							
SP4				0.914*						
SP5					0.780					
SP6						0.906*				
SP7							0.512			
SP8								0.865		
SP9									0.981**	
SP10										0.946*

Key

* Correlation is significant at the 0.05 level

** Correlation is significant t the 0.01 level.

Appendix XVIIb: Correlation coefficients between metal concentrations in Soils and Lettuce (study area).

Factor	SS1	SS2	SS3	SS4	SS5	SS6	SS7	SS8	SS9	SS10
LT1	0.773									
LT2		0.963*								
LT3			0.762							
LT4				0.862						
LT5					0.769					
LT6						0.451				
LT7							0.761			
LT8								0.939*		
LT9									0.845	
LT10										0.956*

Key

* Correlation is significant at the 0.05 level.

Appendix XVIIIa: Correlation coefficients between metal concentrations in Tube-well water and soils in February (Control area).

Factor	TW1	TW2	TW3	TW4	TW5	TW6	TW7	TW8	TW9	TW10
CSS1	0.213									
CSS2		0.744								
CSS3			0.081							
CSS4				-0.003						
CSS5					0.340					
CSS6						0.064				
CSS7							0.074			
CSS8								0.643		
CSS9									-0.082	
CSS10										0.228

Appendix XVIIIb: Correlation coefficients between metal concentrations in Tube-well water and soils in March (control area).

Factor	TW1	TW2	TW3	TW4	TW5	TW6	TW7	TW8	TW9	TW10
CSS1	0.512									
CSS2		0.301								
CSS3			0.088							
CSS4				-0.008						
CSS5					0.253					
CSS6						0.095				
CSS7							0.074			
CSS8								0.669		
CSS9									-0.079	
CSS10										0.248

Appendix XVIIIc: Correlation coefficients between metal concentrations in Tube-well water and soils in April (control area).

Factor	TW1	TW2	TW3	TW4	TW5	TW6	TW7	TW8	TW9	TW10
CSS1	0.312									
CSS2		0.437								
CSS3			0.092							
CSS4				-0.012						
CSS5					0.410					
CSS6						0.085				
CSS7							0.109			
CSS8								0.711		
CSS9									-0.094	
CSS10										0.236

Appendix XVIIId: Correlation coefficients between metal concentrations in Soil and spinach (control area).

Factor	CSS1	CSS2	CSS3	CSS4	CSS5	CSS6	CSS7	CSS8	CSS9	CSS10
CSP1	0.577									
CSP2		0.945*								
CSP3			0.812							
CSP4				0.355						
CSP5					0.879*					
CSP6						0.807				
CSP7							0.515			
CSP8								0.992**		
CSP9									0.924*	
CSP10										0.929*

Key

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level.

Appendix XVIIIe: Correlation coefficients between metal concentrations in Soil and Lettuce (control area).

Factor	CSS1	CSS2	CSS3	CSS4	CSS5	CSS6	CSS7	CSS8	CSS9	CSS10
CLT1	0.652									
CLT2		0.955*								
CLT3			0.763							
CLT4				0.457						
CLT5					0.790					
CLT6						0.694				
CLT7							0.830			
CLT8								0.923*		
CLT9									0.794	
CLT10										0.946*

Key

* Correlation is significant at the 0.05 level.