CHAPTER ONE

INTRODUCTION

1.1 General Introduction

Heavy metals or trace metals are terms applied to a large group of trace elements which are both industrially and biologically important. Although not completely satisfactory from a chemical point of view, heavy metal is the most widely recognized and used term for the large group of elements with an atomic density greater than 6 gcm^{-3} (Holgate, 1979). In this section , essential information on sources, uses and toxicity metals (Zn, Co, Mn, Cd, Cu, Pb, and Cr) are presented.

Heavy metals tend to cause a lot of concern with regard to human health, agriculture and ecotoxicology. Agricultural productivity on large areas of land in many parts of our country can be limited by deficiencies of essential trace elements or heavy metals (often called micronutrients). These elements can easily cause pollution of the agricultural land. Pollution is the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate uses of the environment (Holgate, 1979).

Studies of heavy metals in ecosystems have indicated that many areas near urban centres and rivers, metalliferous mines or major road systems contain anomalously high concentrations of these elements. Soils in such regions have been polluted from a wide range of sources with Pb, Cd, Cu, Mn, Cr and other heavy metals. Humans may be experiencing a silent epidemic of environmental metal poisoning from ever increasing amounts of metals released into the biosphere. The mining, manufacture and disposal of heavy metals inevitably cause environmental pollution (Nriagu, 1988).

Heavy metals occur naturally in soils, usually at relatively low concentrations, as a result of the weathering and other pedogenic processes acting on rock fragments on which soils develop. Soil protection and the sustainability of agricultural production have become increasingly important topics of discussion and research and the heavy metal contamination of soils features prominently in many aspects of the subject as a result of their potentially toxic effects and long-term persistence (Alloway, 1995).

Main agricultural activity in Yala swamp is rice growing which also involves harvesting and processing. Other minor farming activities include; horticulture, banana growing, fish and poultry farming. The activities are carried out by Dominion Farm Limited, Kenya Agricultural activities in the area could introduce pollutants to the soil and water bodies since over application of fertilizers and pesticides can lead to retention of some heavy metals in soils and water bodies.

There is increasing awareness of the potential hazards that exist due to contamination of fresh water impoundments by toxic metals, phosphates and nitrates associated with agricultural activities, urbanization and the mining industry (Dupreez *et al.*, 2003).

The heavy metals are widely distributed in the environment, in soils, in plants and animals and in most of their tissues. The concentrations of individual metals in living tissues are ordinarily very low and must be maintained within narrow limits to permit the optimum biological performance of most organisms. Some heavy metals are essential in trace amounts, namely Co, Cu, Fe, Mn, Mo, Zn for plants and, in addition, Cr, Ni, Sn for animals; Cd, Hg, and Pb, have not been shown to be essential for either plants or animals.

Presence of heavy metals in water and soils can be from natural or anthropogenic sources. Currently, anthropogenic inputs of the metals exceed the natural inputs. Excess metal levels in surface water may pose a health risk to humans and to the environment. Toxic heavy metals constitute one of the most formidable groups of environmental pollutants known today. Some heavy metals have found wide use in industrial, agricultural and pharmaceutical applications. It is therefore, necessary to monitor their concentrations in the environment. Natural sources of heavy metals include; chemical and physical weathering of igneous and metamorphic rocks and soils, decomposition of plant and animal detritus, precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke, plant exudates, and oceanic spray. Anthropogenic sources are; surface runoff from mining operations, combustion of fossil fuels, urban storm water runoff, domestic wastewater effluent, corrosion of water pipes and consumer products. Heavy metals are present in all uncontaminated soils as the result of weathering from their parent materials (WHO, 1992a).

Although in some circumstances there are direct atmospheric inputs to plants, addition to the soil and subsequent transfer from soil to plants is for most heavy metals the major route of entry into the living tissues of plants, animals, and man. The fate of heavy metals added to soils, including their mobility and reactions in the soil and their subsequent uptake and distribution in plants, is therefore of critical importance to man’s health.

1.2 Background of the study

Signs of environmental pollutions are present from time immemorial and have been documented in many parts of the country by various researchers, both as a major problem in water bodies and terrestrial ecosystems. This is specifically in many urban centres where pollutants find their way into the system through industrial activities, agriculture, urbanization and motor vehicles wastes. Heavy metal pollution is significant among pollutants owing to less attention it is receiving from environmental lobbyists in relations to other forms of environmental pollutions (Scheren *et al*., 1994).

Soil is both a source of metals and also a sink for the metal contaminants. Factors controlling the total and bioavailable concentrations of heavy metals in soils are of great importance with regard to both human toxicology and agricultural productivity. The major consequences of environmental contamination by heavy metals, nitrates and phosphates are their toxicity to humans after entering the food chain. Toxicity of these metals has been investigated and it has been reported that; Zn, Cu, Cr and Mn have chronic poisoning effect on animals if acceptable daily intake levels are exceeded. Lead can impair intellectual capacity at levels of 50 µg/dl of blood (Alloway, 1995).

Heavy metals are toxic to living organisms when present in excess. However, some metals such as Co, Cr, Cu, Mn, Mo, and Zn are essential in small amounts for the normal healthy growth of either plants, animals or both, although they are toxic at high concentrations. Monitoring of heavy metals in the environment is therefore of great concern because they are being added to the soil, water and air in increasing amounts. The pollution by heavy metals and fertilizers being witnessed in many areas in Kenya can be controlled if there is monitoring on the concentrations of these pollutants in the global environment. Previous studies in other urban areas in Kenya showed wide variation of heavy metal contamination in drinking water, soil and flora (Hamza, 1996).

When using chemicals one must be fully aware of their environmental impact where they are applied. In order to put in place the remedy or prevent pollution arising from the use of the agrochemicals (fertilizers and pesticides), reliable data on their quantity in water, food and working environment is needed (Wandiga and Onyari, 1987).

Most commonly used pesticides in Yala swamp include insecticides, herbicides, fungicides and acaricides. Use of fertilizers and pesticides has contributed greatly to the increase in food production worldwide and this has improved human and animal health. However, side effects such as toxicities to non target species have been observed, for instance Cu used as fungicide caused inactivity and mortality in larval clams. This toxicity can extend to human beings since some of the pesticides persist in soils and sediments (La-Breche *et al*., 2002).

Preparation of land for farming in Yala swamp started in the year 2003. However, the actual rice growing was established in 2006. Agricultural systems and agronomic activities in the region have undergone major changes particularly in the last four years leading to greater dependence on artificial fertilizers and pesticides. Global problems such as soil pollution, soil erosion, other forms of land degradation and eutrophication are posing serious threats to the sustainability of modern agricultural systems. Appropriate use of fertilizers and pesticides based on recommendations is generally expected to cause little adverse impact on the environment (Getenga *et al*., 2000).

Proper management of human environment can thus be under taken if there is up to date data on the intrinsic heavy metal concentration and also nitrogen and phosphorus concentrations in water and soil. Lack of data on this makes the management to be very difficult should health problems resembling other common diseases occur. The present study would provide a baseline data that will contribute to the current knowledge on the heavy metal dynamics within the Yala swamp. This will form the bedrock for future management of the farm and formulation and implementation of agricultural policies.

1.3 Statement of the problem

Environment is frequently sacrificed for the sake of economy in our society. This policy is shortsighted because destruction of the environment undermines future economic resources (MacKenzie, 1988). Thus, the trade off is not between economy and environment, but between economic prosperity now and in the future. Abundance between economic development and production of resources has been found. Unless corrective measures are implemented soon, the world will be facing overpopulation, energy and food shortages, and a general decline in the standard of living (Global 2000, 1980).

Some heavy metals are important in lower quantities both in plants and animals, as well as humans. Yala swamp is an important agricultural area since it hosts a rice growing farm (Dominion Farm) which supplies its produce to many areas in Kenya. Many industries deposit their wastes into the water of River Yala as it emerges from its source and other tributaries. These pollutants of which most are heavy metals end up in the swamp. As a result, transport agents can redistribute these pollutants via the running water into the aquatic systems, soils and crops.

When the heavy metals and pesticide residues accumulate in water, soils and crops reach maximum threshold safety levels, humans can also be in grave danger due to consumption of water and food crops planted within the swamp. This creates a major problem to the humans as a result of heavy metals and pesticides residue poisoning. Yala swamp is a densely populated area with the rural inhabitants relying heavily on locally grown rice and food crops for constituent diet. Due to high demand for greater yields, the use of commercial fertilizers and pesticides is imminent on the farm. This coupled with poor methods of domestic waste disposal poses a serious health to inhabitants in the region and Kenyans as a whole. Water from river Yala which gets into the swamp contains industrial effluents and domestic wastes which contribute heavy metals from the area.

Environmental problems have assumed dimensions of global magnitude. What happens in remote corners of the world concerns all of us, the best example being the nuclear power plant accident in Chenobyl in the USSR. The Yala swamp ecosystems have supported and nurtured human communities for years. The restoration, protection and management of the swamp guarantees the survival and well being of the surrounding community. The management of the swamp is increasingly noticing a reduction in water volume. Proper management of the environment will improve the health of the surrounding community and the country at large, improves the food security and economic development. Baseline data obtained from the research will help in addressing the challenges facing the management of the Yala swamp.

1.4 Justification of the study

Wastes from mines and industries are deposited into rivers and this causes the contamination of water and hence pollution. In particular, soils in such areas or regions have been polluted from a wide range of sources with heavy metals. The mining, manufacture and disposal of metals and metal-containing materials inevitably cause environmental pollution (Nriagu, 1988).

Kenya is an agricultural and industrially developing country. Its agricultural sector heavily depends on fertilizers and pesticides. The water courses draining into Lake Victoria traverse this agricultural land. The pollutants are introduced into the water system from various sources such as industrial effluents, agricultural run-off, chemical spills, domestic run-off, and municipal wastes (Barlas, 2002). Hence, in order to develop and maintain an adequate level of environmental protection, there is an urgent need to develop a robust monitoring program for the continued surveillance of the pollutants in Yala swamp, hence, water and fish quality of river Yala and lake Victoria. This is important because it causes massive kills of fish and contamination of aquatic animals and plants which are eventually consumed by human beings and enter their body tissues and hence pose a health risk (Karanja, 2002).

In Kenya, heavy dependency on fertilizers and pesticides for food production has led to the death of fish in lake Victoria through river Yala and the swamp. This in turn has led to the ban of exportation of fish to the European Union. The need for baseline data on pollution studies along the swamp is therefore, of utmost importance (Ntiba *et al*., 2001).

1.5 Rationale

Many cases of severe heavy metal pollution of soils and the environment have been reported in the former communist countries, of central and eastern Europe and Russia. Some of the problems are associated with abandoned military bases and training grounds but most are due to inadequate pollution control in metal mining and smelting operations and metallurgical industries. The 1999 Environmental Management and Co-ordination Act, (EMC Act, 1999) bestowed everyone living in Kenya with the responsibility to create and protect the environment. The act also seeks the establishment of standards and enforcement review committee under National Environment Management Authority (NEMA) is charged with the responsibility of carrying out environmental audit and monitoring of all activities that are likely to have significant effect on the environment. Therefore, there is need for continuous monitoring of the heavy metal levels in river Yala swamp (Dominion Farm).

1.6 Objectives of the study

1.6.1 General objectives

The general objective of this study was to assess the spatial and temporal variation of selected heavy metals, nitrogen and phosphorus in water and soil of Yala swamp (Dominion Farm), Kenya. This research intended to come up with recommendations that will convince the management of the farm and government to institute remedial measures so as to control their use within the swamp.

1.6.2 Specific objectives

1. To analyze the levels of heavy metals; Zn, Co, Mn, Cd, Cu, Pb and Cr in water and soil samples collected from Yala swamp using Atomic Absorption Spectroscopy.
2. To assess the spatial and temporal variation of heavy metals, total nitrogen and total phosphorus in water and soil of Yala swamp.

1.7 Hypotheses

1. There is difference in levels of contaminants before and after the swamp
2. There is no variation in contaminants in both seasons of the year.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This section deals with essential information on sources, uses and toxicity of the following heavy metals; Zn, Co, Mn, Cd, Cu, Pb and Cr. Fertilizers and the importance of phosphates and nitrates to plants are also discussed.

Heavy metals are defined as a large group of metal elements with an atomic density greater than 6 g/cm^3 (Wild, 1993). This definition captures the following elements; Zn, Pb, Ni, Mn, Hg, Fe, Cu, Cr, Co, Al, Cd and As.

Heavy metals are widely distributed in the global environment. They are partitioned among the various aquatic environmental compartments, that is, water, suspended solids, and soils. The majority of most heavy metals fulfill essential functions in all living things (Adamo, 2005).

2.2 Zinc

Zinc is an essential trace element for humans, animals and higher plants. Although the beneficial effect of Zn on the growth of *Aspergillus niger* was discovered by Raulin in 1869-1870, the discovery of the essentiality of Zn for higher plants in 1926 is generally attributed to Sommer and Lipman (Alloway, 1995)

2.2.1 Sources of zinc

In recent years, Zn concentrations in some soils have gradually increased, particularly in industrialized countries as a consequence of human activities. The main sources of Zn in soils are metalliferous mining activities, agricultural use of sewage sludge and compost materials, and the use of agrochemicals such as fertilizers and pesticides. Mining and smelting of Zn containing ores is a major source of Zn pollution. High Zn concentrations are found in soils polluted by metal processing industries (Asami, 1981).

Total Zn content in soil is largely dependent on the composition of the parent rock materials (Sillanpaa, 1972). The common range for total Zn concentrations in soils is 10-300 mg/kg with an average of 50 mg/kg. Zinc was found to be uniformly distributed in most soils in Europe, the lowest being 28 mg/kg in podzols, 35 mg/kg in luvisols, histosols had 50 mg/kg and fluxions had 60 mg/kg. Zinc concentrations in most soils are consistent with levels considered as background values, with exception for mined areas (Kabata-Pendias *et al.*, 1992).

The burning of coal and other fossil fuels and the smelting of non-ferrous metals are the major Zn sources contributing to air pollution. An estimation of the global release of Zn as a contaminant into the environment may be based on the world minerals and energy consumption demand. Natural sources such as volcanic eruptions and Aeolian dusts may also contribute to Zn pollution (Kabata-Pendias *et al.*, 1992).

Sewage sludges usually applied in soil as source of plant nutrient often contain appreciable amounts of Zn, which can affect crop plants. Zinc in sewage tends to be associated with suspended solids and is partitioned into the sludges during treatment. Conventional sewage treatment removes 40-74 % of Zn from the effluents (Davis, 1980). Sludges exhibit a wide range of Zn concentrations which are generally higher than the background levels found in soils. Uncontrolled utilization of sewage sludge on agricultural farms will therefore lead to accumulation of Zn and other heavy metals in the soil and consequently a permanent risk for plants and crops. Efforts have been made to minimize these risks by regulating the amount of sewage sludge applied on agricultural land. Guidelines for sludges have been adopted in many countries (Webber *et al*., 1984).

Fertilizers and pesticides also increase the concentration of Zn in the soil. All fertilizers, minerals as well as organic and soil amendments contain Zn, most often as impurities. Zinc concentrations in inorganic phosphate fertilizers ranges from 50 – 1450 mg/kg, in limestone from 10 – 450 mg/ kg while in manures from 15 – 250 mg/kg have been reported. Some pesticides contain Zn concentrations up to 25 % and therefore may increase its concentrations in soils (Adriano, 1986).

The richest sources of Zn are oysters (which may contain over 1000 ppm Zn) and to a lesser extent other sea foods and the muscle meats and nuts, which usually lie within the range of 30 – 50 ppm of the edible portion. The poorest sources are white sugar, pomes and citrus fruits, nonleafy vegetables and tubers, and vegetable oils, which generally contain less than 1 ppm Zn. Whole cereal grains are relatively rich in total Zn, with small differences among the species (Spencer *et al*., 1988). Zinc concentration in wheat grown soil with aid of Zn containing fertilizers was found to be twice that of wheat grown on the same soil, without Zn applications (Underwood, 1972).

Total Zn input to the soil is a major factor affecting Zn concentration in plant tissue. Differences in Zn inputs induced marked differences in Zn behaviour in soils and plants. Soil total Zn contents of up to 1748 mg/kg in areas which had received heavy application of sewage sludge were noted. Prolonged periods of irrigation are associated with significant increases in the total and available forms of Zn (Elhassanin, 1993).Zinc is normally the most abundant heavy metal in crops, and in sewage sludges of both domestic and industrial origin. Its concentration in crops is increased substantially, as a result of addition of sludges. The figures for the total recovery of Zn in four successive crops averaged 0.65 % of an addition of 180 kg per ha in sludge (Kelling *et al.*, 1977).

2.2.2 Uses of zinc

A deficient intake of Zn consistently results in an impairment of a function from optimal to sub-optimal and supplementation with physiological levels of this element, but not others, prevents or curbs this impairment. The recommended safe and adequate dietary intake for adults is around 15 mg/day (Mertz, 1981).

Zinc acts as a catalytic or structural component in numerous enzymes involved in energy metabolism and in transcription and translocation. Zinc deficiency symptoms in humans and animals are failure to eat, severe growth depression, skin lesions and sexual immaturity. For humans depression of immuno-competence and change of taste acuity also occurs (Marschner, 1986)

Higher plants predominantly absorb Zn as a divalent cation (Zn^{2+}), which acts either as a metal component of enzymes or as a functional structural or regulatory cofactor of a large number of enzymes. Four enzymes containing bound Zn are; carbonic anhydrase, alcohol dehydrogenase, Cu-Zn superoxide dismutase and RNA polymerase (Marschner, 1986). Zinc is required for activity of various enzymes such as dehydrogenises, aldolases, isomerases, and transphosphomylases and DNA polymerases. Because of these functions, Zn is involved in carbohydrate and protein metabolism (Chapman, 1972).

Zinc is also required for the synthesis of tryptophan, a precursor for the synthesis of indolacetic acid (IAA). Most pronounced Zn deficiency symptoms, namely stunted growth and 'little leaf' rosette of trees are related to the latter physiological function of Zn. Crops particularly sensitive to Zn deficiency are the cereals maize and sorghum, flax, hops, cotton, legumes, grapes, citrus and fruit trees (peach, apple). The most permanent symptoms of Zn deficiency are inter-veinal chlorosis, stunted growth, malformation of stems and leaves, and violet-red points on leaves. Typical names for Zn deficiency are white bud (corn and sorghum), little leaf (fruit trees), mottle leaf (citrus) and sickle leaf (cacao) (Chapman, 1972).

2.2.3 Toxic effects of zinc

Zinc belongs to a group of trace metals potentially most hazardous to the biosphere. Most of the concern about excessive Zn concentration in soils relates to possible uptake by crops and subsequent adverse effects on the crops themselves and on livestock and humans along the food chain. Together with Cu, Ni and Cr, Zn is principally phytotoxic, so the concern about the metal is mainly directed at effects on crop yield and soil fertility (Chapman, 1972).

Zinc is more toxic to plants than animals. Thus, a concentration of 400 – 500 μgg^{-1} in the foliage has been reported as toxic to plants whereas diets containing concentrations of this order have been fed to animals with very little effects. It therefore, appears reasonable to assume that the phytotoxicity of Zn provides a safeguard against toxicity to animals or man (Underwood, 1977).

Inhalation of Zn fumes causes fever, depression, vomiting, excess salivation and headache. Zinc unlike Pb, Cd, As and Sb, does not accumulate in the biological systems including man. It has been found that Zn concentrations below the maximum EU guidelines (< 300 mg/kg) caused significant toxic effects in *R. leguminosum bv trifolii (*Marschner, 1986).

When Zn salts or compounds are given orally in large doses over prolonged periods, as in the treatment of chronic leg ulcers or the prophylaxis of cardiovascular disease, possibilities of toxic effects cannot be dismissed. Doses of 150 mg Zn/day which are equivalent to about 200 – 300 ppm of the total daily dry matter intake of an adult are enough to interfere with Cu and Fe metabolism since Zn is a metabolic antagonist of both metals (Miller *et al.*, 1970).

2.3 Cobalt

Cobalt is hard, lustrous, silver – grey ferromagnetic metal. Pure Co is not found in nature, but its compounds occur naturally in many forms. It has a density of 8.99 g/cm^3, a melting point of 1495 ^0C and a boiling point of 2927 ^0C. Cobalt has an atomic number of 27 and a standard atomic weight of 58.93 g/mol (Alloway, 1995).

Cobalt ore minerals include (CoAsS – FeAsS) and akutterudite ($CoAs_3$ – $NiAs_3$). Apart from these deposits, it is most abundant in relatively unstable ferromagnesium minerals such as olivine, pyroxenes, amphibole and biotite, which are concentrated in basic igneous rocks (Aubert and Pinta, 1977). These minerals contain as their principal cations Mg^{2+} (ionic radius 7.8 nm) and Fe^{2+} (ionic radius 8.3 nm), and ions such as Co^{2+} are incorporated into the crystal lattice by isomorphous substitution. In contrast, silica rich acidic igneous rocks such as granite, which do not contain ferromagnesium minerals, are low Co (Mitchell, 1964).

2.3.1 Sources of cobalt

Ultra basic rocks such as dunite and peridotite and the product of their metamorphism, serpentinit, contain 100 – 200 mg/kg of Co. Basic rocks such as basalts and andesite contain 30 – 45 mg/kg, whereas acid or neutral types such as granite and rhyolite contain only 5 – 10 mg/kg. Cobalt contents of sedimentary rocks reflect the composition and the material from which they were originally derived. Thus shales formed from the easily weathered ultra basic and basic rocks are relatively rich in Co: 10 – 50 mg/kg while sand stones originating from silica-rich acidic rocks have much lower concentrations (Sanders, 1983).This is illustrated in Figure 1.

	IGNEOUS	SEDIMENTARY	METAMORPHIC
High Co Conc.	Ultra-basic and basic rocks	Argillaceous rocks, e.g. shales	Metamorphic rocks containing ferromagnesian minerals, e.g. serpentine
Low Co Conc.	Acidic rocks, e.g. granite	Arenaceous rocks, e.g. sandstones	Metamorphic silica-rich rocks, e.g. gneiss

Figure 1: **General relationships between rock types and total Co content**.

(Adapted from Alloway 1995)

Significant Co sources in soils are the parent materials from which the soils are derived and the deliberate applications of Co salts or Co-treated phosphate fertilizers to top soils to overcome deficiencies which are causing problems with ruminant nutrition or the cultivation of legumes. Total Co contents vary widely from 0.05 to 300 mg/kg, with an average content in the range 10 – 15 mg/kg. The contents vary mainly in relation to the parent materials from which they were derived even though there are also differences with depth in the soil profile and between different soil types derived from a common parent material due to pedagogical processes Soil drainage status has a major influence on the amount of Co available for plants uptake. In poorly drained soils, the amount of extractable Co is generally greater than in adjoining areas which are well drained and plant uptake is significantly increased (Aubert and Pinta, 1977).

Within a given soil profile, Co is generally concentrated in those horizons rich in organic materials and clays. The oxides, hydroxides and carbonates of Co are insoluble in alkaline conditions. In acidic conditions, on the other hand dissolution and leaching are most likely to occur. These result in generally greater concentrations of total Co in alkaline than acid soils. Uptake of Co increases with a decrease in soil pH (Sanders, 1983). In cases where herbage has low concentration of cobalt, Co can be top dressed on the pastures or administered orally (Corner and Smith, 1983).

2.3.2 Uses of cobalt

Cobalt is important to our industrial civilization, and also to the maintenance of life within it. Cobalt, although much less abundant (and correspondingly more expensive than Mn) is used for the manufacture of special steels, and has been used for centuries in the manufacture of blue pigments and glass. Cobalt has essential role in the living organisms (microorganisms and animals). The primary interest in Co as a constituent of soils lies in its essential roles in ruminant animals and microorganisms, and because of deficiencies rather excesses. For centuries, farmers in different parts of the world had found some pastures to be unsuitable for grazing sheep and cattle. Even on apparently rich pastures, these animals lost appetite, because of being weak and emaciated, suffered severe anaemia and eventually died. These symptoms were attributed to low concentrations of Co in the herbage, and both top dressing of the pastures with Co salts and oral administration of Co were used to alleviate the condition (Underwood and Filmer, 1972).

In 1948, an ‘anti-pernicious-anaemia factor’ containing 4 % Co was isolated from liver. This substance became known as vitamin B_{12}, and was shown to cure pine in lambs

(Smith *et al*, 1972). Vitamin B_{12} and its coenzymes are complex molecules containing Co (III) at the centre of tetrapyrrole macrocyclic structure, which are synthesized by micro organisms in the rumen (Purcell and Kotz, 1977).

Cobalt has an essential role in biological N-fixation in plant biology stems. A requirement for the element was demonstrated both for rhizobium bacteria forming symbiotic associations with legume roots and for free – living N fixing bacteria such as *azotobacter ssp* (Iswaran and Sundara, 1960).

Cobalt appears to be essential for blue – green algae. Although to date it has not been conclusively demonstrated that there is a comparable essential requirement by higher plants, evidence has been obtained of growth benefits resulting from an enhanced supply of the element which leads to increased cereal yields (Young, 1979).

Cobalt occupies a very restrictive place in the treatment of human anaemia. It has been used as a nonspecific stimulant in the treatment of nephritis and infection, and several reports of responses to Co, in addition to Fe, in the treatment of iron deficiency anaemia in children and pregnant women have been made (Hamilton, 1956).

Cobalt therapy is used in the treatment of human hypertension. Since vasodilatation with flushing has been observed following the injection of Co salts, Perry and Schroeder treated nine hypertensive patients with 50 mg cobalt chloride per day for 10 – 65 days. Marked lowering of blood pressure to normal was also observed in the patients (Perry and Schroeder, 1983).

2.3.3 Toxic effects of cobalt

Cobalt is an essential element necessary for the formation of vitamin B_{12} (hydroxocobalamin); however, excessive administration of this trace element produces goitre and reduced thyroid activity. Exposure to Co produces an allergic dermatitis and occupational asthma. Clinical experience and epidemiogical studies shows that Co exposure may lead to severely impaired lung infection, that is, hard metal lung disease and occupational Co related asthma, contact dermatitis and cardiovascular effects. Most frequently, exposure to Co occurs simultaneously with exposure to other elements known to pose a health risk. The importance of Co as a sole casual agent in hard metal lung diseases, cardiomyopathy and cancer are still a matter of controversy (McLaren, 1987).

For the general population, the diet is the main source of exposure to Co. In the occupational setting, exposure to Co occurs during the production of cobalt powders. Under certain circumstances, Co intakes substantially lower than 20 – 30 mg/day as producing toxic manifestations, when used as an erythropoietic stimulant, can be toxic to man. Cobalt has been incriminated as the precipitating factor in several outbreaks of severe cardiac failure in heavy beer drinkers. Cobalt was suspected because of the high incidence of polycythemia, thyroid epithelial hyperplasia, and colloidal depletion noted in their fatalities, in addition to congestive heart failure (Anonymous, 1983).

Cobalt salts had been added to beer to improve its foaming qualities at concentrations of 1.2 – 1.5 ppm. At such concentrations the reported formidable consumption of 24 pints (approximately 5 litres/day) of beer would supply about 8 mg of cobalt sulphate, an amount well below that which can be taken with impunity by normal individuals. High Co and high alcohol intakes are both necessary to induce the distinctive cardiomyopathy (Grinvalsky and Fitch, 1969).

2.4 Manganese

Manganese is grey – white metal resembling Fe. It is a hard metal and is very brittle, fusible with difficulty, but easily oxidized. It has a density of 7.2 g/cm^3, a melting point of 1246 ^{0}C and a boiling point of 2016 ^{0}C. Manganese has atomic number of 25 and a standard atomic weight of 54.93 g/mol (Alloway, 1995)

2.4.1 Sources of manganese

Soils derive their Mn content from parent materials, and the concentrations found in mineral soils reflect the composition of these parent materials. In soils, Mn commonly occurs as the oxide minerals birnessite and vernadite. Non-stoichiometric oxides of mixed valency are the normal outcome of oxidation of Mn (II) or reduction of Mn (IV). The various oxides of Mn show a strong tendency to form mixed crystals with other transition metals, including Co (Gilkes and McKenzie, 1988).

Manganese can exist in all oxidation states from Mn (II) to Mn (VII), of which the (II), (III) and (IV) states occur in combination with oxygen, carbonate and silica. The divalent manganese ion is the main form of Mn in soil and water. Examples are the ore minerals pyrocusite (MnO_2), rhodochrosite ($MnCO_3$) and rhodonite ($MnSiO_3$), and many other oxides and oxhydroxides in which substitution of Mn (II) for Mn (IV) occurs extensively (Gilkes and McKenzie, 1988).

Birnessite is the first oxidation product of weathered carbonate rocks and occurs in concentrations as well as in more finely divided material. In a well aerated soil, in neutral or slightly alkaline conditions, the Mn (IV) oxidation state is the most stable, and the composition of these manganese oxides ranges from Mn_3O_4 to MnO_2, but in reducing conditions the Mn (II) state is favoured. The oxides vary in their solubility and ease of reduction and this has a relationship with their relative capacities to supply Mn to plant roots (Jarvis, 1984).Apart from the natural mineralogical sources, other significant source of Mn in soils is the result of application of the element to deficient crops normally in the form of $MnSO_4$, MnO, or as an addition to macronutrient fertilizers (Walter, 1988).

2.4.2 Uses of manganese

Manganese finds applications in products such as engineering steels and electrical storage batteries. It also has essential role in living organisms. $MnSO_4$ and MnO are added to the soils deficient of the element Mn applied in range from 10 – 100 kgs of Mn per hectare. This is because Mn is a micronutrient in higher plants (Masagni and Cox, 1985).

Manganese is added to gasoline engines to boost their performance. It is also used in strengthening steel and aluminium metal and in the production of disinfectants ($KMnO_4$). Often it is also used in the glass industry as a decolourizer of glass, or as a colouring material in glass, pottery, and bricks (Marschner, 1988).

The role of Mn as a micronutrient in higher plants was first found in oats, soya beans and tomatoes. Manganese (II) activates enzymes and is also involved in the synthesis of glycoprotein in mammalian system and is present in metalloenzymes such as arginase and pyruvate carboxylate (Bowen, 1979).

Manganese is involved in fatty acid synthesis and in bone development in poultry. There are a number of important functions for which Mn is essential in plants. It is present in the NAD malic enzymes system found in leaves of C4 plants. It is also a specific constituent of the photosynthetic oxygen-evolving system in chloroplasts (Leach, 1968).

Main manifestations of Mn deficiency, namely, impaired growth, skeletal abnormalities, disturbed or depressed reproductive function, ataxia of the newborn, and defects in lipid and carbohydrate metabolism are displayed in animals. Their actual expression varies with the degree and duration of the deficiency, its rate of development and with the age and stage of growth of the animal (Doisy, 1974).

2.4.3 Toxic effects of manganese

Most common biological toxicities of Mn are found in plants exposed to excess natural Mn in the soil particularly in flooded conditions. Plants take up Mn as Mn (II). Manganese toxicity symptoms have been found in a wide range of crops including soya beans, cotton, tobacco and upland rice grown in soils with high levels of Mn. Reported toxic concentrations for these and other species range from 80 to 5000 mg/kg. The toxicity is commonly associated with acidic soils and warm climates (Page, 1962).

Preparing a baby formula already containing Mn with water containing Mn may make the infant get higher dose than other family members. Young children absorb more and excrete less Mn than older age groups. Research work has found that early childhood and parenthood exposure to Mn can have effects on behaviour and learning. Therefore, it is important to know the Mn level in drinking water before using it to make baby formula.

Chronic Mn poisoning occurs among miners following prolonged working with its ores. Excess Mn enters the body mainly as oxide dust via the lungs and also via the gastrointestinal tract from the contaminated environment. The lungs apparently act as a depot from which the Mn is continuously absorbed (Walter, 1988).

Manganese poisoning is characterized by a severe psychiatric disorder (locura manganica) resembling schizophrenia, followed by a permanently crippling neurological disorder similar to Parkinson’s disease. Comparative studies of a population of “healthy” Mn miners and patients suffering from chronic Mn poisoning revealed faster losses of injected Mn from the whole body and from the area representing the liver and higher tissue Mn concentration in the former group than in those suffering from chronic Mn poisoning (Mena *et al*., 1967).

Large amounts of soluble Mn in water cause Mn toxicity in plants, since it is needed only as a micronutrient. If it is used for household purposes, water containing Mn may stain clothes and bathroom fixtures (Tisdale and Nelson, 1993).

Pneumonia and coughs have been observed in workers exposed to Mn and recently in Japan where respiratory illnesses were observed in students near a factory emitting Mn. It has also been observed that, men exposed to Mn have impaired fertility as well as impotence and loss of libido (Bowen, 1979).

2.5 Cadmium

Cadmium belongs to the group IIB of the periodic table and is relatively a rare metal, being 67th in orders of elemental abundance. It has a density of 8.65 g/cm^3 and it melts at 321.0 ^{0}C and boils at 767.0 ^{0}C. It has an atomic number of 48 and a standard atomic weight of 112.4 g/mol. It is soft, malleable, ductile, toxic, bluish white bivalent metal (Alloway, 1995).

2.5.1 Sources of cadmium

Cadmium pollution of the environment has been rapidly increasing as a result of rising consumption of Cd by industry. Environmental pollution is an inevitable consequence of metal mining, manufacture and disposal. Sources of soil contamination by Cd are mining and smelting of Pb and Zn; atmospheric pollution from metallurgical industries, the disposal of wastes containing Cd such as the incineration of plastic containers and batteries; sewage sludge application to the land; and burning of fossil fuels. Even before Cd was used commercially, contamination was occurring from a wide range of materials containing Cd as an impurity. The deposition of aerosol particles from urban and industrial air pollution also affects the soils in most industrialized countries, and Cd from this source can also be absorbed directly into plants through foliage (Bowen, 1979).

Soils derived from igneous rocks have Cd contents of 0.1 – 0.3 mg/kg, those on metamorphic rocks contain 0.1 – 1.0 mg/kg and those derived from sedimentary rocks 0.3 – 11 mg/kg Cd. Most soils can be expected to contain < 1 mg/kg, except those contaminated from discrete sources or developed on parent materials with anomalously high Cd contents, such as black shales (Holmgren *et al.*, 1993).

Phosphatic fertilizers are widely regarded as being the most ubiquitous source of Cd contamination of agricultural soils. Relatively high concentrations of Cd (< 500 mg/kg) can be found in phosphorites (rock phosphates) used for the manufacture of fertilizers. Cadmium concentrations found in phosphate fertilizers can vary widely depending on the origin of the phosphorite raw material (Alloway, 1995).With the increasing awareness of this source of Cd contamination of soils, some major manufacturers have changed to sources of phosphorite raw material with lower Cd concentrations and this has resulted in a reduction of the concentration in phosphatic fertilizers in some countries or regions (Hutton, 1982). Large annual application of farmyard manure is a significant source of Cd than the combined inputs from phosphatic fertilizers and atmospheric deposition (Jones *et al*., 1987).

The major sources of atmospheric pollution emissions are non-ferrous metal production, fossil fuel combustion refuse incineration and iron and steel production. The relatively high volatility of Cd when heated above 400 ^{0}C accounts for the significance of atmospheric emissions from these sources. The average annual emission rates from global anthropogenic sources have been increasing from 3400 t to 7400 t from 1951 to 1980. Cadmium concentration on top soil is also high due to atmospheric deposition in industrial and metropolitan regions (Sposito and Page, 1984).

Composition of sewages vary and contain Cd from various sources, including human excretion, domestic products containing Zn, storm waters containing particles of rubber tyres and various industrial effluents. Cadmium accumulates in the insoluble sludge produced during sewage treatment and a wide range of Cd concentrations in sewage sludges has been reported from around the world (Merington and Alloway, 1994).

The other major sources of Cd which can cause contamination of soils are mining, ore-dressing and smelting of Cd-containing sulphide ores which can contain up to 5 % Cd. Dispersion of particulates from these sources can be by gravity from spoil tips, by wind, and by water through the erosion and fluvial transport of tailings from old mines and mineral dressing floors. Soils severely polluted Pb-Zn mining and smelting have been found to contain up to 750 mg/kg. Higher Cd content occur at sites near metallurgical works emitting Cd or where sewage sludge is applied to land (Fergussion, 1990).

Soils developed on parent materials with anomalously high Cd content, especially black shales, can have significantly elevated total Cd concentrations even in the absence of marked contamination from anthropogenic sources. Cadmium concentration reported for soils on black shales include < 22 mg/kg on out crops. Within soil profiles, Cd is normally found concentrated in the surface horizon which is due to a combination of factors: it is the zone with the highest organic matter content and metals may be retained in this strongly adsorptive horizon after reaching it as a result of cycling through vegetation, or from application of Cd containing fertilizers and manures, or from the wet and dry deposition from the atmosphere (Merington and Alloway, 1994). Unlike Cu and Pb, Cd (together with Zn and Ni) has the tendency to move down the profile through the extent, and the rate depends on various soil and factors (Kabata- Pendias *et al.*, 1992).

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2.5.2 Uses of cadmium

Cadmium has been widely used in the 20th century. More than half of the Cd used in industry was produced in the last 25 years (Hutton, 1987). It is obtained as a by-product of the smelting of Zn and other metals, and no ores are used primarily as a source of Cd. Its principal uses are: as a protective plating on steel, in various alloys, in pigments (for plastics, enamels and glazes), as a stabilizer for plastic, in Ni-Cd dry cell batteries and other minor uses, including photovoltaic cells and control rods for reactors (WRI, 1992).

2.5.3 Toxic effects of cadmium

Cadmium is highly toxic to plants and animals. However, the concentrations of Cd encountered in the environment do not cause acute toxicity. The major hazard to human health from Cd is its chronic accumulation in the kidneys where it can cause dysfunction if the concentration in the kidney cortex exceeds 200 mg/kg fresh weight (Fassett, 1980).

Food is the main route by which Cd enters the body. Tobacco smoking and occupational exposures to CdO fumes are also important sources of the metal. FAO/WHO recommended maximum tolerable intake of Cd to be 400 - 500 µg/week, which is equivalent to a 70 µg/day. Average dietary intake of Cd ranges between 25 and 75 µg/day and there is clearly a problem where the intake is near the top of the range. People who smoke add an extra 20 to 35 µg Cd/day to their intake (Page *et al.*, 1981).

Considerable concern about Cd as an environmental pollutant has risen from the suggestion that increased intake of this metal result in hypertension and from the finding that itai-itai disease in Jingu Valley in Japan was associated with elevated concentrations of Cd in some foods. Elevated concentrations were traced to contamination of the river and soil by waste from metal mine upstream (Fleischer *et al*., 1974).

It is well established from studies with experimental animals that Cd is highly toxic under conditions of chronic, long-term exposure as well as with short-term exposure to a relatively large dietary load. Once absorbed, Cd is tenaciously retained in the body and accumulates with increasing intakes and age. Because of this accumulation and the possible adverse effects of increased intakes in animals and man there has, in the recent years, probably been more research on Cd than on other heavy metal in sewage sludges.

Cadmium has a half-life of between 15 and 1100 years in soils and this is obviously a long-term problem and pollution needs to be prevented or minimized wherever possible. Long term occupational exposure results to severe chronic effects in lungs and kidneys. Although Cd toxicity can occur in plants on severely polluted soils, its accumulation in food crops at sub-phytotoxic levels is a greater cause for concern due to the risk of increased dietary exposure in consumers. Even slightly elevated Cd concentrations in foods can have significant effect in the long-term (Kabata – Pendias *et al*., 1992).

Cd interacts or competes with metals such as Cu, Zn, Fe, Mn and Ca for ligand sites on bimolecular systems hence interfering with homeostasis. Inhalation of fumes or dust containing Cd and its compounds affects the respiratory track. Long term occupational exposure results to severe chronic effects in lungs and kidneys (WHO, 1994).

Acute Cd toxicity is manifested by leaf chlorosis, wilting and stunted growth. The order or toxicity to wheat and lettuce plants on soils is Cd > Ni > Zn (Mitchell et al., 1978). Most municipal waters contain less than 1-3 µg Cd/litre, which is well below the upper limit for drinking water of 10 µg/liter set by WHO (WHO, 1993).

2.6 Copper

Copper, with an atomic number of 29, is the first element of sub-group IB of the Periodic Table. It is one of the most essential elements for plants and animals. In metallic state, it is reddish in colour, takes on a bright metallic lustre, and is malleable, ductile and a good conductor of heat and electricity. It has a density of 8.96 g/cm^3, a melting point of 1084.6 ^{0}C and a boiling point of 2562.0 ^{0}C.

2.6.1 Sources of copper

The availability of Cu is related to the chemical potentials of the respective species in the soil solution. The distribution of total and extractable Cu in the soil profile varies with soil type and parent material. Copper is specifically adsorbed or ‘fixed’ in soils, making it one of the heavy metals which move the least. Higher concentrations of Cu in the surface of soil is an indication of soil additions from smelter, fertilizers, sewage sludges, fungicides or bactericides or manures from swine and poultry fed with selected Cu containing compounds for increased feed efficiency and greater growth rates (Nriagu, 1979).

The average Cu concentration in the earth’s crust ranges from 24 – 55 mg/kg and the average Cu range for soils is 20 – 30 mg/kg. The abundance of Cu in basaltic rocks is greater than for granitic rocks, and is very low in carbonate rocks. Gabbro and basalt rocks have the highest Cu contents and granodiorite and granite the lowest. The abundance of Cu in igneous rocks is partly controlled by the process of differentiation during crystallization. Crystals formed separate from silicate melts and settle to the lower part of the magma chamber (Cox, 1979).

Soil management of Cu for crop production has beneficial results. This is obtained by application of a wide range of materials and compounds containing Cu to soils. The usual Cu fertilizer source is $CuSO_4.5H_2O$ (blue-stone), although other compounds, mixtures and chelates are also used. Hydrated $CuSO_4$ is compatible with most fertilizer materials. Anthropogenic inputs of Cu to land are very diverse. Soil levels of Cu are affected by soil and crop treatments including fungicides, fertilizers, livestock manures, sewage sludges and atmospheric deposition (Follett *et al*., 1981).

Atmospheric inputs of Cu to soils from both rains and dry deposition varies considerably according to the proximity of industrial emissions containing Cu and the type and quantities of wind-blown dust. The total quantity of Cu that has been emitted to the atmosphere since 3800 BC has been estimated at 3.2×10^6 tones (Nriagu, 1979). This amount is about three orders of magnitude greater than the present- day atmospheric Cu burden. Because of the relatively short residence time for airborne Cu aerosols, it is doubtful if there can be any substantial build- up of Cu in the atmosphere. Most of this enormous quantity of Cu is apparently wasted on land even though the turnover time of artifacts may be considerable. The total production of 3.07×10^8 tonnes is about twice the Cu content of the top 2 cm layer of soils of the world and is about an order of magnitude greater than the annual Cu demand for all living land biota (Nriagu, 1979).

Sewage sludges should be analyzed and used as fertilizers because of the relatively high concentrations of Cu and other metals compared to non-polluted soils. While sewage sludges are capable of substantially increasing the soil levels of Cu, there have been no reports of plant toxicities to sludge Cu when grown in fertile, limed soils. Soil organic matter appears to be the dominant factor controlling Cu retention. The rate of decomposition of sludge organic matter is a prime consideration for sludge treated soils. While toxicity to higher plants is of major concern, soil biological activity may be much more sensitive to sludge Cu inputs (Mathur and Sanderson, 1980).

Natural sources of Cu include wind-blown dust, forest fires and decaying vegetation. It is widely distributed in free state in sulphides, arsenide, chlorides and carbonates. It is commonly present in natural surface water in trace amounts. It may be released to water as a result of natural weathering of soil and discharge from industries and sewage plants. The major source of Cu is the related mines and sewage sludge. Burning of coal, oil and wood contribute to pollution of the environment with Cu (Stevenson, 1981).

2.6.2 Uses of copper

The main uses of Cu are in the production of wire and of brass and bronze alloys. It is used in electrical industries in the manufacture of generators, light bulbs, telephone wires, telegraph cables, rods cooking utensils and for light and power lines. Copper is also used in making agricultural chemicals such as fungicides, algaecides, fertilizers, bactericides, animal feed additives and growth promoters as well as for the disease control in livestock and poultry (Thorton and Webb, 1980).

The quality of crop products is affected by Cu deficiency. Some examples of adverse effects of Cu deficiency include unattractive appearance and smaller size for citrus fruits; discolouration and spongy texture in onions; discolouration in carrots; chlorosis and wilting in lettuce; reduced protein, altered proportions of amino acids and Cu content of wheat barley; high concentrations of amino acids in juice extracted from sugar beets; high incidence of cork spot and superficial cork in pears; and low Cu content of grass resulting in Cu deficiency in ruminant animals especially where the soil has an elevated Mo level (Kubota, 1983).

In sheep, the process of pigmentation and keratinization of wool are the first to be affected by a lowered Cu status, so that at certain levels of Cu intake these defects can develop without any other signs of Cu deficiency being apparent. Neonatal ataxia occurs readily in lambs from Cu-deficient ewes in some areas (Braude, 1981).

In many areas of the world, pig manure slurries and poultry manures are enriched with Cu resulting from feeding $CuSO_4$ to improve rates of grain and feed efficiency. What has been considered to be high levels of supplemental Cu in swine ratios increases both rates of weight gain and feed efficiency (Thorton and Webb, 1980). Copper in plants function as part of the prosthetic groups of enzymes and as a facultative activator of enzyme systems (Arnon and Stout, 1939).

2.6.3 Toxic effects of copper

In all animals continued ingestion of Cu in excess of requirements leads to some accumulation in the tissues, especially in the liver. The capacity for hepatic Cu storage varies greatly among species, and differences among species in tolerance to high-Cu intakes are also great. Ruminant animals, especially sheep, are highly susceptible to Cu toxicity and may be adversely affected by even slight increases in concentrations in forage crops caused by applications of sludge. Tolerable levels of Cu and of other heavy metals will depend on the extent to which interacting elements are present in the diet. In the case of Cu they are so important that a particular concentration of this metal in the diet can lead to either Cu toxicity or deficiency depending on the relative contents of Mo, Zn and Fe (Boyden *et al*., 1993).

Copper in forage and pasture crops depends on soil availability of Cu, plant species, stage of growth, time of year and lime and fertilizer applications. Legumes tend to take up larger amounts of Cu than grasses (Kubota, 1983). Water from wells and other sources for human consumption is always below the 1 mg/kg interim Cu limit, which is based on the taste considerations. Because of Cu contamination of domestic water supplies by plumbing, several approaches are used by various countries to establish standards for Cu in drinking water. Daily intake of Cu by humans is almost always above the recommended daily requirement of 2 mg/day (Braude, 1981).

Hereditary Cu toxicosis is known as Wilson’s disease. It is an expression of an inborn error of metabolism that affects Cu homeostasis. Copper accumulates in the liver, brain, kidneys and cornea as affected infants grow, and evidence of histological damage can be seen in early infancy. However, clinical illness is usually not observed before the age of five years. Wilson’s disease is rare and can be arrested and prevented by drug therapy, which mobilizes Cu from the tissues and promotes its excretion in the urine. For most individuals homeostatic mechanism for Cu prevents excessive accumulations (Baker and Bowers, 1988). An excessive amount of Cu and Zn interferes with certain enzyme systems for example; it interferes with membrane adenosine triphosphate and pyruvic acid-pyruvate oxidative systems (Gupta, 1979).

2.7 Lead

Lead is a member of Group IVB of the Periodic Table of the elements. It is a transition metal with an atomic number of 82 and standard atomic weight of 207.2 g/mol. It has a density of 11.3 g/cm^3, a melting point of 327 ^{0}C and a boiling point of 1744 ^{0}C. It is bluish in colour when freshly cut but tarnishes to a dull greyish colour when exposed to air and is shiny chrome silver when melted into a liquid. Two oxidation states (Pb (II) and Pb (IV)) are stable but the environmental chemistry of the element is dominated by the plumbous ion, Pb^{2+} (Alloway, 1995).

2.7.1 Sources of lead

Soil is a sink for anthropogenic Pb and there are several well recognized major sources, namely, mining and smelting activities, manures, sewage sludge usage in agriculture and contamination from vehicle exhausts. Lead arsenate ($PbHAsO_4$) has been applied to orchard trees to control insects, pests and orchard soils may, therefore, contain elevated concentration of Pb (Merry *et al*, 1983). Commercial use of these sprays is now infrequent since they have been replaced by organic pesticides.

As the internal combustion engine developed, there was a growing demand for petrol of higher octane ratings to avoid the problem of uneven combustion in the engine cylinders, that is, knocking or pinking. In the early 1920s it was discovered that Pb alkyls (tetraethyl and tetra methyl Pb) when added to petrol helped overcome the problem. The first leaded petrol was sold in 1923 and was rapidly used. This was found to be polluting the environment and is being done away with (Greninger *et al.*, 1974). It was reported that soil and vegetation samples collected near roads contained unusually high Pb content from petrol fumes (Warren and Delavault, 1960). This suggests that there is a zone of about 15 m wide on either side of most roads in which the concentration of Pb exceeds local background levels and contamination of the roadside environment is a worldwide consequence of the use of leaded petrol.

The large scale of modern Pb industry inevitably leads to accumulations of Pb in soils despite strict environmental controls. Some of the modern mines and smelters are located on sites of older, dirtier works which have a legacy of environmental contamination. Maximum Pb accumulations occur close to the stack. Within 3 km of a well- established smelter, soils are likely to contain about 1500 – 2200 mg/kg of Pb (Kobayashi, 1972). Accumulations of Pb may also be expected in the soils around secondary smelters and other Pb using industries.

Surface waters used for domestic vary greatly in Pb content. The upper limit of safety Pb given by the WHO is 100 µg of Pb/litre. Many domestic water supplies can exceed this limit where the water is soft and comes from lead-lined tanks and water pipes. Survey carried out on three groups of households: those with a lead-lined storage tank and Pb piping, those with no Pb tank but Pb piping in excess of 60 feet, and those with less than

60 feet of Pb piping. The mean Pb contents of the cold tap water for the three groups were approximately 1000, 220, and 100 µg/litre, respectively (WHO, 1992b).

Lead aerosols emitted to the atmosphere from vehicle exhausts or general industrial fumes can be carried over long distances (Kral *et al.*, 1992). Its compounds tend to accumulate in soils and sediments and due to their solubility and relative freedom from microbial degradation they remain accessible to food chain and human metabolism far into the future. Lead is a wide spread soil contaminant in all areas except those remote from populous regions or where human settlement is very recent. In many areas Pb concentrations in the environment are sufficiently high as to pose a potential risk to health, especially near major Pb using industries and in major cities (Alloway, 1995).

Sewage sludge has undesirable high content of heavy metals. The typical concentration of Pb in human faeces is 11 mg/kg dry solid whereas the medium content of sludge from non-industrial area is 121 mg/kg. The extra Pb is derived from Pb water pipes and road run-off. This was not realized until metal contamination of soil following long-term application of high rates of sewage sludge was reported (Merry *et al.*, 1983).

2.7.2 Uses of lead

The low melting point of Pb has allowed it to be smelted, melted and worked even in primitive societies. The metal is very soft and tends to creep or flow under sustained pressure. It is therefore, readily cut and shaped and has long been used on roofs or as pipes. Metallic Pb is relatively opaque to ionizing radiation, and makes a valuable shield material in X-ray and radioisotope work (Alloway, 1995).

It readily alloys with other metals: the Pb/Sb alloy is chiefly used to make battery plates but is also used in shotgun pellets and often used as solder. Lead metal, in combination with PbO_2, is used to fabricate the lead-acid accumulator battery. Other inorganic compounds are widely used, that is, the yellow chromate is used in road markings, and many paints contain Pb oxides or Pb soaps to promote polymerization (Alloway, 1995).

2.7.3 Toxic effects of lead

Lead is known for being poisonous to mammals. Chronic Pb poisoning is characterized particularly by neurological defects, renal tubular dysfunction, and anaemia. Damage to the central nervous system causing Pb encephalopathy and neuropathy, is a marked and common feature, especially in children with low Pb tolerance. In children, chronic Pb poisoning involves physical brain damage, with permanent sequelae, including behavioural problems, intellectual impairment, and hyperactivity (David, 1974).

The anaemia that is a common feature of chronic Pb poisoning arises from effects on heme synthesis and red blood cells, and perhaps also from an effect of Pb on Fe and Cu metabolism. Lead affects fragility of red cells which have a shortened life-span. These effects of lead are the main cause of the anaemia, but there are also reports of synergistic effects of Pb and Fe deficiency on impairment of hematopoiesis (Karamanos, 1976).

Chronic Pb toxicity is manifested further by the occurrence of renal tubular dysfunction with aminoaciduria and glycosuria. Impairment of energy metabolism may be responsible for the reduced transport function of the kidney and therefore the aminoaciduria and glycosuria in Pb toxicity, and that the respiratory abnormalities in renal mitochondria may result from their reduced cytochrome content (Rhyme and Goyer, 1971).

In the biochemical effects, Pb inhibits lipoamide dehydrogenase, an enzyme crucial to cellular oxidation and the enzyme aminolevulinic (ALA) acid dehydrase, which governs the condensation of two molecules of ALA to form porphobilinogin and requires the presence of reduced glutathione for its activation. The function of endocrine glands was found to be affected in a small series of lead-intoxicated through drinking “moonshine” whiskey. In many environments concentrations are sufficiently high as to pose risk to health, especially lead-using industries and major cities (Wixson and Davies, 1994).Lead can inhibit nitrogen mineralization and nitrification rates in an acid soil. Although Pb is not especially toxic to plants, high substrate concentrations do result in stunted growth or death (Atkins *et al*., 1982).

2.8 Chromium

Chromium is a d-block transition metal of Group VIB of the Periodic Table with an atomic number of 24 and an atomic weight of 51.996 g/mol. It has a high melting point of 1907 ^{0}C and a boiling point of 2671 ^{0}C with a density of 7.19 g/cm^3. It is grey and brittle and can be highly polished. It occurs in Cr (III) and Cr (VI) oxidation states in the environment, though Cr (III) (Cr^{3+}) is the most stable; ionic radii are 0.052 – 0.053 nm for Cr^{6+} and 0.064 nm for Cr^{3+} (Alloway, 1995).

2.8.1 Sources of chromium

Chromium is produced from the ore chromite, which is a mixed oxide with the general formula FeO. Cr_2O_3 but also contains variable amounts of Mg and Al. Chromium is found in igneous rocks, where it readily substitutes for Fe. Mafic and ultramafic rocks are richest in Cr containing up to 3400 mg/kg of Cr.

The largest total amounts of Cr released to the atmosphere by human activities are from metallurgical industries in the form of particles such as from electric furnaces (GCA, 1973). Other important sources of atmospheric Cr are refractory brick production, combustion of coal, and steel production. Iron and steel industry is the largest anthropogenic source of Cr emissions globally (Nriagu, 1988).

Chromium-containing effluents are released by the following activities; metal plating, anodizing, ink manufacture, dyes, pigments, glass, ceramics, glues, tanning, wood preserving, textiles and corrosion inhibitors in cooling water. Both Cr (III) and Cr (VI) can be present in these waters. However, many effluents either treated on site to decrease the potentially toxic load in waste water, or at the sewage treatment works, where Cr (VI) is reduced by organic matter and consequently the Cr in sludge exhibits the chemistry of Cr (III) compounds (Beszedits, 1988).

Disposal of fly-ash on land is the largest single input of Cr to soils. Fly-ash is enriched in Cr, and as a result, soils around coal-fired electricity generators may be slightly enriched with Cr (Wilkins, 1991). Other smaller sources of Cr include wear of Cr-containing asbestos brake linings in vehicles and aerosols produced from Cr catalysts used in emission reduction systems for treating exhaust fumes. Both of these have greatest impact on roadside soils. Emissions of Cr in the waste from chromate smelters bring about large increases in soil Cr (NRCC, 1976).

2.8.2 Uses of chromium

Chromium has been used in alloy steels, and chrome plating. It is resistant to attack by oxidation, which leads to its use in alloys that are resistant to attack by corrosion. The presence of Cr in alloys also increases hardness and resistance to mechanical wear. Alloy steels contain 10 – 26 % Cr. Chromium compounds such as (Cr_2O_3) and chromate (VI) are used as pigments for colouring glass and in leather tanning, textiles, as oxidizing agents and in refractory (Sharp, 1990).The refractory properties of Cr are used in the production of bricks for lining furnaces and kilns. Chromate ore is used in chemical industries such as chrome alum (Cr (III)) for tanning leather, pigments and wood preservatives (sodium dichromate) (Alloway, 1995).

Severe Cr deficiency in human causes weight loss, peripheral neuropathy, impaired glucose tolerance, and subnormal blood and hair Cr concentrations. Chromium deficiency in human causes glucose intolerance, inability to utilize glucose for energy, neuropathy with normal insulin levels and no impairment of insulin action on amino acids uptake (Anderson, 1981). Countries with high levels of soil Cr have low death rates due to cardiovascular diseases (Guthrie, 1982).

2.8.3 Toxic effects of chromium

Chromium ingestion can cause severe toxicity through ingestion of contaminated food and water. Ingestion causes vomiting, diarrhoea, and cardiac abnormalities. The presence of abundant Cr anions in the water is generally a result of industrial wastes. The chronic adverse health effects are respiratory and dermatologic (Pohl *et al*., 1993).

Chromium low level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of Cr (Jarup, 2003).

Chromium (VI) compounds are irritating and corrosive and are absorbed through digestive track, skin or alveoli of the lungs. Body deposits of Cr are principally the lungs, muscles, fat, and the skin. Cell function studies reveal that half of the body Cr is within the cell nucleus. Inhalation of dust/ mist of Cr are irritating to upper respiratory parts and causes sneezing, nasal discharge and vascular congestion (Palko and Yli-Halla, 1988).

Hexavalent chromium, (Cr^{6+}) is more toxic than trivalent chromium, (Cr^{3+}). Trivalent Cr has such a low order of toxicity that a wide margin of safety exists between amounts ordinarily ingested and those likely to induce deleterious effects. Chromium is a chemical carcinogen connected with long-term occupation exposures that produces bronchogenic carcinomas. Chronic exposure to chromate dust is correlated with increased incidence of lung cancer (Anonymous, 1993).

2.9 Phosphates

2.9.1 Sources of phosphates

Phosphorus in soils exists as organic and inorganic compounds. Humus, manure, and other types of non-humified organic matter are the major sources of organic P in soils. Some of the compounds in the soil organic fraction considered potential sources of P are phospholipids, nucleic acids and inositol phosphates. Bones, teeth, and muscle tissue in animals are rich in P (Tisdale and Nelson, 1993).

Inorganic P is derived mostly from the apatite minerals, which are accessory minerals in all types of rocks. During the natural process of weathering, the rocks gradually release P as phosphate ions. Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate in which each compound contains P in a different chemical environment. These forms of phosphate occur in living and decaying plant and animal remains, as free ions or weakly and chemically bonded in aqueous systems, chemically bonded to sediments and soils, or as mineralized compounds in soil, rocks, and sediments (Oram, 2003).

The inorganic P content in soils is higher than the organic P content. Orthophosphate forms are produced by natural processes, but the major man-influenced sources include; partially treated and untreated sewage runoff from agricultural sites and application of some fertilizers. The organic phosphate is the phosphate that is bound in plant tissue, waste solids, or other organic material. Phosphates enter surface streams from natural sources of decaying biomass and weathering of soluble inorganic minerals and from anthropogenic sources such as fertilizers and domestic water containing phosphate detergents (Jeschofnig, 2003).

In solution, P is present in the inorganic form, as either the primary, $H_3PO_4^-$, or the secondary, HPO_4^{2-} orthophosphate ion. The concentration of these ions in soil solution depends on soil pH. Large amounts of P ions are detrimental to the environment. The use of household detergents, and the over use of phosphate fertilizers are the reasons for accumulation of phosphate in soil. In lakes and rivers, excessive amounts of P results in excessive growth of unwanted plants, a phenomenon called eutrophication (Oram, 2003).

2.9.2 Importance of phosphorus to plants

Phosphorus is a plant nutrient and an essential component of deoxyribonucleic acid (DNA), the seat of genetic inheritance in plants as well as animals, and of various forms of ribonucleic acid (RNA) needed for protein synthesis. Other uses include; cell division and fat and albumin formation, flowering and fruiting, including seed formation, crop maturing, in which P counteracts the effects of excess N applicants, root development, particularly of the lateral and fibrous rootless strength of straw in cereal crops, thus helping to prevent lodging and improvement of crop quality (Larsen, 1967).

Phosphorus is an important element in practical agriculture. It is a component of two compounds involved in the significant energy transformation in plants, adenosine diphosphate (ADP) and adenosine triphosphate (ATP). Adenosine triphosphate is synthesized from ADP through perspiration and photosynthesis. It contains a high energy phosphate group that drives most biochemical processes requiring energy. Uptake of some nutrients and their transport within the plant as well as synthesis of different molecules are processes requiring energy facilitated by ATP (Donahue *et al.*, 1983).

2.9.3 Toxic effects of phosphorus

Phosphorus is very poisonous, and inhaling the fumes of white P may cause necrosis of the bones in the jaw and nose, and may also cause death. It has been used in the past for making matches, but since the fumes are very toxic, the match heads today contain tetraphosphorus trisulphide, P_4S_3, a less toxic substance. Phosphorus is still used today as rat poison and in the making of explosives, fireworks, chemicals, fertilizers, and as spoil retardants in food substances.

2.10 Nitrates

2.10.1 Sources of nitrogen

Nitrogen occurs in soils in both cationic (ammonium, NH_4^+) and anionic (nitrate, NO_3^- and nitrite, NO_2^-) forms, the greater part by far occurs in organic forms. Of the 5 % or so in the inorganic form, nitrite, which is phytotoxic, is negligible. Ammonium tends to be held on cation-exchange sites. Nitrate is a highly mobile anion, and is substantially adsorbed by soil mineral components at any pH. However, unless the soil contains a large pool of readily available N, nitrate tends to be taken up by the soil microbial biomass or by plants during the active growth period. Nitrogen availability tends to depend upon the rate at which organic N is converted to inorganic N, a process known as mineralization. Mineralization rate is temperature and pH dependent and bacterial oxidation of ammonium to nitrate is reduced under acidic conditions (Freney and Galbally, 1982).

Fertilizers supply N as ammonium-, nitrate-, or amide-N (urea or cyanamide); organic fertilizers or manures supply N combined with organic matter, often in protein-like materials. Nitrate ions are mobile in soil and are readily taken up by plants. Ammonium-N is quickly nitrified in all slightly acid and neutral soils by bacteria; amides are hydrolyzed to ammonium salts which are then nitrified. Organic sources of N are also converted to nitrate by bacteria. While most plants take up both ammonium- and nitrate-N, in practice uptake of nitrate is important since this ion is mobile in soil and is transported to the roots in mass flow of water (Fox and Hoffman, 1981).

Nitrates form when microorganisms break down fertilizers, decaying plants, manures or other organic residues. Usually plants take up these nitrates, but sometimes rain or irrigation water can leach them into groundwater. Although nitrates occur naturally in some groundwater, in most cases higher levels are thought to result from human activities. Common sources of nitrate include; fertilizers and manure, animal feedlots, municipal wastewater and sludge, septic systems, and N-fixation from atmosphere by legumes, bacteria, lightning and plant residues (Soltanpour *et al*., 1999).

In natural waters, N is found in combined form as nitrate and is leached into the ground water. Most crop plants require large quantities to sustain high yields. The formation of nitrates is an integral part of the N cycle in our environment. In moderate amounts, nitrates are a harmless constituent of food and water. Plants use nitrates from the soil to satisfy nutrient requirements and accumulate them in leaves and stems. In soil water, nitrates are stable in the absence of organic compounds. These organic compounds may act as biological catalysts, which induce the reduction of nitrates (US – EPA, 1992).

Nitrate ions, whether derived from ammonium added as nitrate fertilizer, or formed by mineralization of organic materials, are not retained in soils by electrostatic or chemical bonding. Nitrate is not, however, leached as rapidly as the front of percolating water moves down a soil. Most of the water moves through cracks and large pores whereas much nitrate is formed and released to water stored in small pores within soil aggregates; nitrate in small pores is partially protected from leaching as it must diffuse out of the pores before joining the main stream of percolating water. Many investigators have shown that nitrates are retained by soil even in wet periods when much water passes through the soil (Jacobsen and Westerman, 1991).

2.10.2 Importance of nitrogen to plants

Nitrate is a naturally occurring form of N found in soil. Nitrogen is essential to all life. This is because the amount of the element in available forms in the soil is small, while the quantity withdrawn annually by crops is comparatively large. At times, there is too much N in readily soluble form and it is lost in drainage and may even become water pollutant. At other times, it is lost from the soil by volatilization; at all times, most of the soil N is unavailable to higher plants. Moreover, its effects on plants usually are very marked and rapid. Thus, over application, which may be harmful, sometimes occur (Nyle, 1984).

Some plants such as legumes have been associated with their roots soil organisms that fix atmospheric N into forms that they can use. Others such as grasses are largely dependent upon outside sources either through non-symbiotic fixation or through the addition of fertilizers or other combined forms of N. All in all, N is a potent element that should be not only conserved but carefully regulated (Burns and Hardy, 1975).

Nitrogen is an integral component of many compounds essential for plant growth processes including chlorophyll and many enzymes. It is an essential component of proteins and related amino acids, which are critical not only as building blocks for plant tissues but in the cell nuclei and protoplasm in which the hereditary control is vested. It is essential for carbohydrate utilization within plants and stimulates root growth and development as well as uptake of other nutrients of the macronutrients usually applied in commercial fertilizers. Nitrogen seems to have the quickest and most pronounced effect. It encourages above the ground vegetation growth and in parts deep green colour to leaves. With cereals, it increases the plumb-ness of the grain and percentage of protein. With plants, N is a regulator that governs to a considerable degree, the utilization of K, P and other constituents. There are three major forms of N minerals in the soil; organic N associated with the soil humus, ammonium N fixed by certain clay minerals and soluble inorganic ammonium and nitrate compounds (Nyle, 1984).

Deficiency of N in plants leads to stunted growth and restricted root system. The leaves turn yellow or yellowish green and then drop off. When N is applied in excess, the leaves become dark green in colour and excess vegetative growth occurs. The stems are not stable upright and they lodge and fall over with the slightest wind. It may also adversely affect the grain and fruit quality as in barley, apples and peaches. It also affects sugar levels in sugarcane or sugar beets. Excess N also delays the crop maturity and the plants become more susceptible to diseases and insect pests (Nyle, 1984).

2.10.3 Toxic effects of nitrogen

The presence of nitrate in amounts above 30 mg/l is considered hazardous to human health by WHO standards and particularly to babies. When consumed, nitrate may not only be carcinogenic, it will also be reduced into nitrite in the anaerobic environment of the digestive system. The nitrite reacts with hemoglobin and interferes with its function as an oxygen carrier, causing blue colouring in babies, a condition known as methaemoglobinemia, especially found in infants less than six months. This results in reduced oxygen supply to vital tissues such as brain (Stanton, 1992).

Methaemoglobin in infant blood cannot change back to hemoglobin, which normally occurs in adults. Severe methaemoglobin can result in brain damage and eventually death. Pregnant women, adults with reduced stomach acidity, and people deficient in enzyme that changes methaemoglobin back to normal hemoglobin are all susceptible to nitrite-induced methaemoglobin (Kendall, 1992). The most common symptom of methaemoglobin is a bluish color of the skin, particularly around the eyes and mouth. Other symptoms are headache, dizziness, weakness or difficulty in breathing. If detected early, methaemoglobin is treated with an injection of methylene blue (Stanton, 1992).

Prolonged intake of high levels of nitrate is linked to high levels of nitrosamines. Ruminant animals (cattle and sheep) are susceptible to nitrate poisoning because bacteria present in the rumen convert nitrate to nitrite. Non-ruminant animals rapidly eliminate nitrate in their urine. Horses are monogastric, but their large cecum acts much like rumen. This makes them more susceptible to nitrate poisoning than other monogastric animals. It is difficult to determine the toxicity of nitrate in animals because it depends on the rate at which the substance is consumed. Common symptoms include abdominal pains, diarrhoea, muscular weakness or poor coordination. Affected animals will have blood that is chocolate-brown in colour. If the problem is diagnosed in time, they can fully recover with a treatment of methylene blue (Kendall, 1992).

2.11 Fertilizers

Fertilizers are any materials applied to soils to increase yield to improve quality and nutritive value of crops. The bulk of fertilizers are artificially produced by chemical companies and oil industries. These fertilizers contain one or more of the elements essential for plant growth. The elements are carried out in forms available to plants. Among the many nutrients required by plants, the elements, N, P and K, are three major components of inorganic fertilizers. Based on these major elements, the artificial fertilizers can be distinguished to; nitrogen fertilizers, phosphate fertilizers, and potash (potassium) fertilizers. The three groups of fertilizers are considered single element fertilizers, in contrast to a fourth group called mixed fertilizers. The mixed fertilizers contain two or all three of the major fertilizer elements, and may also have other plant nutrients, such as the micronutrients (Brady, 1990).

Fertilizers that decrease soil pH are called acid forming fertilizers. All ammonium fertilizers are acid forming fertilizers. In contrast, nitrate fertilizers, such as sodium nitrate are basic forming fertilizers. The growth of fertilizer industry was propelled to its current dimension after the discovery of the production of ammonia by the Haber-Bosch process (Tisdale and Nelson, 1993). As the use of inorganic fertilizers increases, the potential hazard for contamination of surface and ground water increases considerably. Therefore, new techniques have to be developed to control contamination on environmental quality. The use of fertilizers has been shown to increase yield and prolong the period of good yield (Somasiri and Edwards, 1992).

Organic fertilizers include animal and green manure, fish and bone meals and compost. Microorganisms in the soil decompose organic material, making its elements available for use by plants. Use of manure and compost as fertilizers is almost as old as agriculture. They enhance the natural fertility of the soil or replace the chemical elements taken from the soil by previous crops. Manure from animal wastes (cattle, swine, chickens, horses, sheep, and other types of animals) vary considerably in chemical composition. Poultry litter is the highest in N, P and Mg contents (Encyclopedia, 2006).

Nitrogen, P and K are macronutrients or primary fertilizer elements, which are required in greatest quantity. Sulphur, Ca and Mg are called secondary elements, are also necessary to the health and any growth of vegetation but are required in fewer amounts compared to macronutrients. The other elements of agronomic importance called micronutrients and provide for plant ingestion in small amounts include; Mn, Co, B, Mo, Hg, Na and Zn. All these fertilizer elements, with other chemical elements occur naturally in agricultural soils in varying concentrations and mineral compositions, which may or may not be in forms readily accessible to plant roots (Whiting *et al*., 2005).

Compound fertilizers are produced in two distinct ways, either as chemically distinct forms (true chemical compounds, such as potassium nitrate) or by mixing the individual chemicals together. Compound fertilizers containing various proportions of N, P and K are available to suit majority of crop types and situations. Advantages of compound fertilizers lie in the need for only a single application which reduces labour costs and minimizes soil structural deterioration through unnecessary trafficking. Nitrogen fertilizers are produced by various industrial processes through the chemical combination of atmospheric N with either oxygen (nitrate) or hydrogen (ammonia) (Goss *et al*., 1991).

Application of manure on land is done to increase soil organic matter and more so N and P contents. It is also used as a method of disposal of wastes. Mineralization and nitrification of organic N may contribute substantially to total pollutant load to adjacent drainage waters. Organic N in agricultural soil may be a number of times greater than the fertilizer N typically added by farmers. Although in some areas heavy precipitation immediately following application of highly soluble ammonium nitrate may lead to nitrate pollution episode, this is only a minor component of the total problem. The bulk of the applied ammonium is retained on the cation exchange sites (Cresser et al., 1993).

Nitrogen is the nutrient responsible for much of the recent increase in agricultural production. Nitrogenous fertilizers are used in extremely large quantities by both developed and developing countries. The need for high fertilizer N inputs is then much more readily apparent. The total amount of N in a soil profile often tends to decrease as a result of cultivation. The economic returns from efficient N fertilizer use are very favourable, explaining why relatively large amounts of N are applied and also why possible controls on N use are difficult to implement. Studies done in UK indicate average responses from many fields and years show the yield of wheat increasing by 24 kg with every kg of N fertilizer applied until the stage where the N versus yield response curve begins to reach a plateau (Goss *et al*., 1991).

Nitrates increase in soil and water is as a result of direct use of low efficiency nitrogenous fertilizer application. The main goal in best management practices approach is the utilization of N-fertilizer in a most effective manner. The quality of nitrates derived from fertilizer that leaches below the root zone is subject to some degree of control by fertilizer management practices. Various management practices may be adopted to improve N use efficiency and minimizing nitrate leaching into ground water. Because of problems of over fertilization, it is recommended that the knowledge of nutrient content of the soil and nutrient requirement of the crop are carefully balanced with application of nutrients in organic fertilizers (Ntiba *et al*., 2001).

One of the main problems relating to N fertilizer use is a lack, in many parts of the world, of suitable advisory test methods for evaluating N fertilizer requirements. In consequence considerable emphasis must be placed upon such factors as previous cropping history, yield and fertilizer use all of which reduce the likely precision of predictions made of fertilizer requirement. There is considerable concern over potential risks to public health caused by nitrate concentrations in both ground and surface waters. Nitrate is toxic particularly to young children and drinking water standards have been set in various jurisdictions (Lee and Nielsen, 1987).

The reactions and interactions involving fertilizer N in soil are complicated. Except under specific conditions (for example, heavy rainfall immediately after application), N fertilizer added early in the growing season has been shown to be present at relatively low extractable amounts in the soil at the end of the season. The nitrate in crops is therefore primarily mineralized from soil organic N (Vanloon and Duffy, 2005).

Phosphates are generally insoluble and react readily with most metals present in soils. Acid soils contain large amounts of Al, Fe and Mn, which form complexes or insoluble metal-phosphate compounds. The reaction is called *phosphate fixation*. Phosphate fixation occurs at high pH values. Many aridosols with high pH contain large amounts of Ca, which can form insoluble calcium phosphate and /or other Ca phosphate compounds in the apatite group. When phosphates dissolve, most of it is leached down the soil profile, and is fixed by adsorption by soil mineral components. Phosphates and nitrates are key nutrients limiting the plants growth in oligotrophic lakes (Anonymous, 1993).

Chemical fertilizers are synthetic and are a mixture of primary elements, which are identified by N-P-K code. N denotes elemental nitrogen; P denotes the anhydride of phosphoric acid (P_2O_5); K denotes the oxide of potassium (K_2O). All are expressed numerically in percentage composition. Thus, the formula 8 – 32 – 16 contains a mixture of eight weight percent N, thirty two weight percent (P_2O_5) in some form of phosphates and sixteen weight percent K_2O in form of potassium compounds to give a total of fifty six fertilizer units. The commercial formula N – P – K rarely totals to 100 % plant nutrient because the formula indicates only the nutrient portions of the primary compound and not account for any other materials present (Whitting *et al*., 2005).

Farmers in the Yala swamp and Lake Victoria catchments experience problems of over-fertilization and thus it is recommended that the knowledge of nutrient content of the soil and nutrient requirement of the crop are carefully balanced with application of nutrients in organic fertilizers. High input of nutrients entering the lake affects the aquatic systems and water quality (Swallow *et al*., 2002).

2.12 Some past studies of heavy metals, nitrogen and phosphorus in soils

(Theodore *et al*., 2005) analyzed trace elements in Kenyan soils in Kiambu and Mbeere districts and found that concentration of Fe was the highest and that of Cu was the least concentrated. The order was found to be Fe > Mn > Zn > Cu. Cu levels were found to be lower in Kiambu while Mn levels were higher. The Fe levels were found to be varied in the two areas, while Zn levels were lower in Mbeere.

(Nyingi, 2005) conducted studies in Port Reitz Creek, Mombasa and it was found that through-ways appeared to contain elevated levels of certain elements known to be emitted by traffic, such as Al, Ba, Ca, Cu, Pb, Ni, Mn and Si.

(Meso *et al.,* 2004) determined and analyzed fish pond soils in Sagana (Kenya) for total P and total N and found that P levels had been elevated due to fertilizers, manures and feeds.

(Nzula *et al.,* 2004) carried out a research in Lake Naivasha, Kenya to analyze the total P and N and found a loading of 1.4 g/m^2 during a normal wet-dry season. (Gichuki, 1995) determined trace elements in surface and ground waters of Njoro in Nakuru district using

XRF. The results showed that areas with high traffic density, industrial and agricultural activities had higher levels of metal concentration.

Kirugaru (1996) found that large plantations of tea, sugar, coffee together with associated agro industries in the Lake Victoria basin is a source of heavy metal pollution. Elevated levels of Al, Mn, Fe and Zn were due to agricultural activities. Research conducted in some selected areas in Kenya found that concentration levels of Pb, Cd, Cr; Zn and Cu were below WHO/ FAO and KEBS recommended permissible limits.

2.13 Atomic absorption spectroscopy

2.13.1. Principles of atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) is a technique for determining the concentration of a particular element in a sample. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It relies therefore, heavily on Beer – Lambert law. The electrons of the atoms in the atomizer can be promoted to higher orbital for instance by absorbing a set of quantity of energy, that is, light of a given wavelength. This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity. As the quantity of energy put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured. It is possible, from Beer – Lambert law to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured (Alloway, 1995).

The technique of AAS requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 ^{0}C. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths. The characteristic wavelengths are element specific and accurate to 0.01 – 0.1 nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photomultiplier can detect the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample (Alloway, 1995). This is shown in figure 2 below

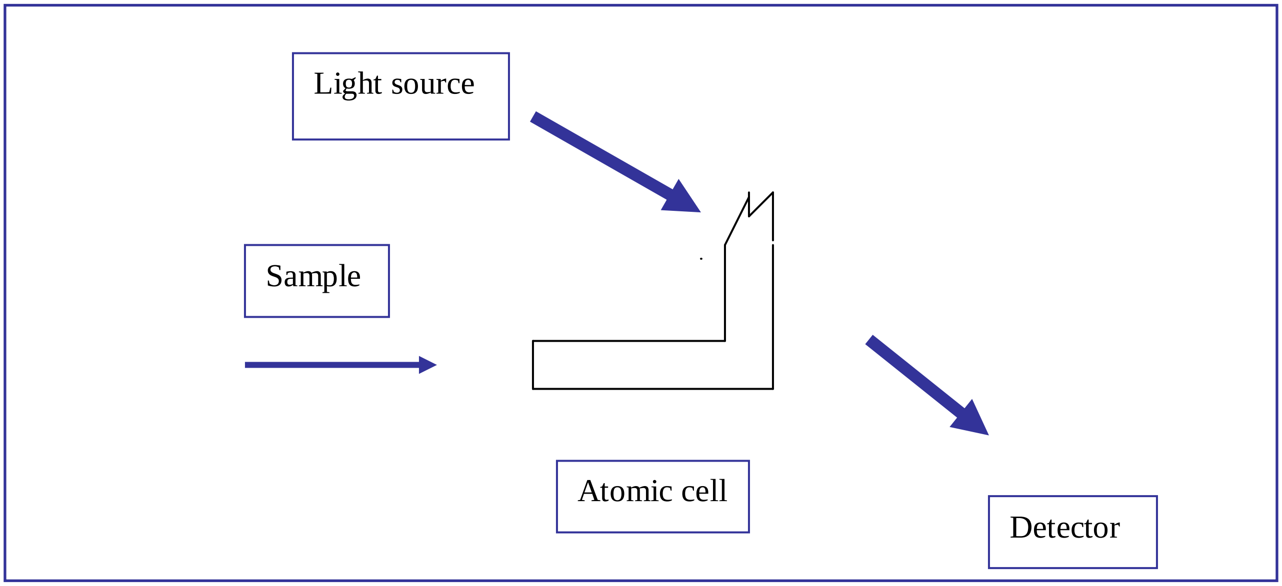

Figure 2: Operation principle of an atomic absorption spectrometer.

(Alloway, 1995)

2.13.2 Instrumentation

In order to analyze a sample for its atomic constituents, it has to be atomized. The sample should then be illuminated by light. The light transmitted is finally measured by the detector. This is illustrated in Figure 3 below.

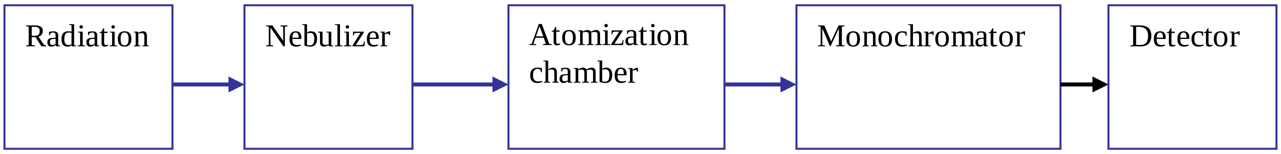

Figure 3: Block diagram of instrumentation of AAS

(Alloway, 1995)

A sharp source in form of a hollow cathode lamp is used as a source of radiation. It uses a cathode made of element of interest with low internal pressure of an inert gas. A low electrical current of approximately 10 mA is imposed in such a way that the metal is excited and emits a few spectral lines characteristic of that element. The light is emitted directionally through the lamp's window which is made of glass transparent in the UV and visible wavelengths. The hollow cathode lamp (HCL) provides analytical light for the element of interest (Chasteen, 2000).

Nebulizer is the mechanism by which a sample solution is converted into an atomic vapour. The sample is drawn up the capillary of the nebulizer and on reaching the end of the capillary, the supersonic gas flow emerging from the annulus around the end of the capillary reduces the sample to a fine mist of aerosol. These droplets travel along a spray chamber where larger droplets fall out of the gas /aerosol mixture and run to waste. The remaining fine droplets are carried to the flame by oxidant and fuel gas mixture. When the droplets reach the flame the solvent evaporates and the solid droplet is formed. This droplet then melts, volatilizes and finally atomization occurs. The nebulizer thoroughly mixes acetylene (the fuel) and oxidant air or nitrous oxide, and this creates a negative pressure at the end of the small diameter, plastic nebulizer tube. The negative pressure sucks liquid sample up the tube and into the nebulizer chamber a process called aspiration.

In most commercial AAS, a flame is used for sample atomization. The most recent year’s non-flame atomization has become increasingly important. However, these do not cover the same range of element as flame atomic absorption spectroscopy. Atomic absorption cannot be observed until atomization has occurred and free atoms are present.

Monochromator’s purpose is to isolate a particular emission line from a number of characteristic lines emitted by the HCL. It is tuned to a specific wavelength and with a specific width slit. Since the basis of the AAS process is atomic absorption, the monochromator seeks to only allow the light not absorbed by the analyte atoms in the flame to reach the photomultiplier tube (PMT). Before an analyte is aspirated, a measured signal is generated by the PMT as light from hollow cathode tube (HCT) passes through the flame. When analyte atoms are present in the flame while the sample is aspirated, some of the light is absorbed by those atoms. This causes a decrease in PMT signal that is proportional to the amount of analyte.

2.14 Spectrophotometer / colorimetric analysis

2.14.1 Principles of spectrophotometers

In absorption spectrometry, energy in the form of light excites the substrate to measurably higher levels. It has been widely employed in the field of quantitative and qualitative elemental analyses. Atomic absorption, ultraviolet and visible spectrophotometers are common laboratory instruments used for quantitative analysis and structural elucidation that uses the principles of absorption. A colorimeter is used for measuring absorption in the visible region of the spectrum (Okalebo *et al*., 1998).

When light is incident upon a homogenous medium, a part of it is reflected, a part of it is absorbed and the remainder is allowed to transmit. Quantification is achieved through the use of Beer's law that states A = abc where, A is absorbance, a is absorption coefficient, b is path length and c is concentration of substrate that is analyzed. Both a and b are constants for a given element and set instrument conditions, therefore, the equation may be simplified as A = Kc. Where K is a constant and is equal to ab. Thus a direct relationship exists between absorbance measured by the instrument and the amount of substrate responsible for that property (Okalebo *et al*., 1998).

2.14.2 Instrumentation

Spectrometric equipment consists of the following parts; a light source, a monochromator, a sample cell, a detector and a read out system. The light source can be a simple tungsten lamp suitable for the visible part of the spectrum. The lamp contains a 3 mm wide strip of tungsten which is heated by an electric current to above 2500 ^{0}C. A hydrogen discharge lamp is filled with hydrogen gas at a pressure of about 1 kpa (0.01 atm). At wavelength shorter than 350 nm this lamp produces a continuous spectrum of medium intensity by excitation of hydrogen molecules. The intensity increases when hydrogen is replaced by deuterium (Okalebo *et al*., 1998).

There are two basic spectrometer designs: single- beam and double- beam operations. Single- beam instruments are particularly suitable for quantitative measurements at fixed wavelengths. Double-beam instruments are expensive, because they contain more optical components and they can scan an absorption spectrum. There are two cuvettes, one with sample solution and one with reference solution (preferably the solvent blank). The ratio I/I_0 are measured many times per second, that is, there is nearly continuous measurement of transmittance. Variations like lamp intensity and detector response do not influence the sample signal, since I_0 is measured at virtually the same conditions (Okalebo *et al*., 1998).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

In order to obtain valid analytical results, analytical procedures were followed. Use of standard apparatus and materials as well as proper handling procedures was adhered to at all stages.

3.2 Equipment and glassware

3.2.1 Glassware

The glassware used comprised of beakers, volumetric and conical flasks, measuring cylinders, pipettes, digestion flasks, test-tubes, and separation funnels. Most of the glassware was mainly pyrex made in Germany. The glassware was thoroughly washed with hot soapy water, then rinsed in distilled water and finally rinsed in aqua regia (a mixture of concentrated nitric and hydrochloric acid in the ratio 1:3). This was done to dissolve any remaining particles in the glassware.

3.2.2 Analytical balance

The analytical balance was an XP series electronic type, a model made by Sartorious handy company, Germany; it could measure the masses up to accuracy of four decimal places.

.3.2.3 Equipment and / other apparatus

These included UV/visible spectrophotometer Model Spectroscan 30, CTA- 2000 Atomic Absorption Spectrophotometer, colorimeter, furnace, refrigerator, electrical fume chamber, water distiller, plastic reagent bottles, crucibles, spatulas, stickers, Whatman no. 1 filter papers, cheesecloth, pestle and mortar, rotary evaporator, weighing dish, clamp and stand, thermometer, cork and gloves. Before analysis, all the glass apparatus were cleaned with 50 % nitric acid and sulphuric acid. Others were cleaned with acidified potassium permanganate solution. Washing detergent and de-ionized water were used to wash and rinse the apparatus.

3.3 Study area

Determination of the levels of heavy metals (Zn, Co, Mn, Cd, Cu, Pb and Cr), total nitrogen, total phosphorus and their temporal variability was studied in Yala swamp.

Yala swamp, is in Siaya District within Siaya County in Nyanza Province with central coordinates of 34^0 10’ 26’’ to 35^0 08’ 32’’ E longitude and 0^0 01’ 27’’ to 0^0 05’ 41’’ N latitude. A map of Kenya showing the location of the swamp is given in Figure 4. It is a catchment of lake Victoria covering approximately 300 Ha that has already been reclaimed, although reclamation is still on course targeting 2000 Ha in future. The swamp has been devoted mainly for rice growing for nearly a period of 10 years. The land was reclaimed from the swampy water by the Dominion Farm. It boarders Lake Kanyaboli to the northern side. The area receives the runoff from river Yala which drains into lake Victoria. This is shown in Figure 5.

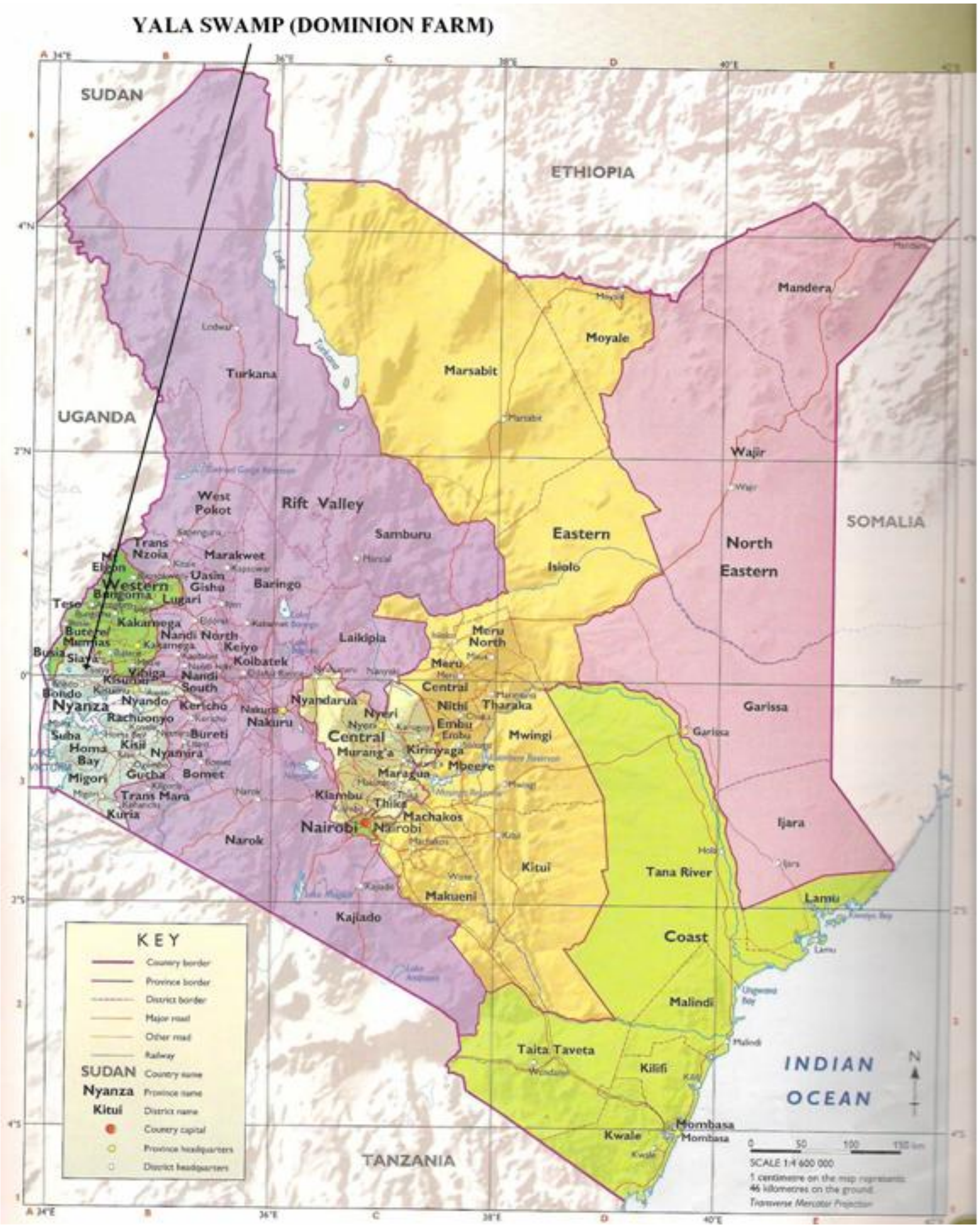

Figure 4: Map of Kenya

(**Source**: Oxford University Press, East Africa Limited 2010)

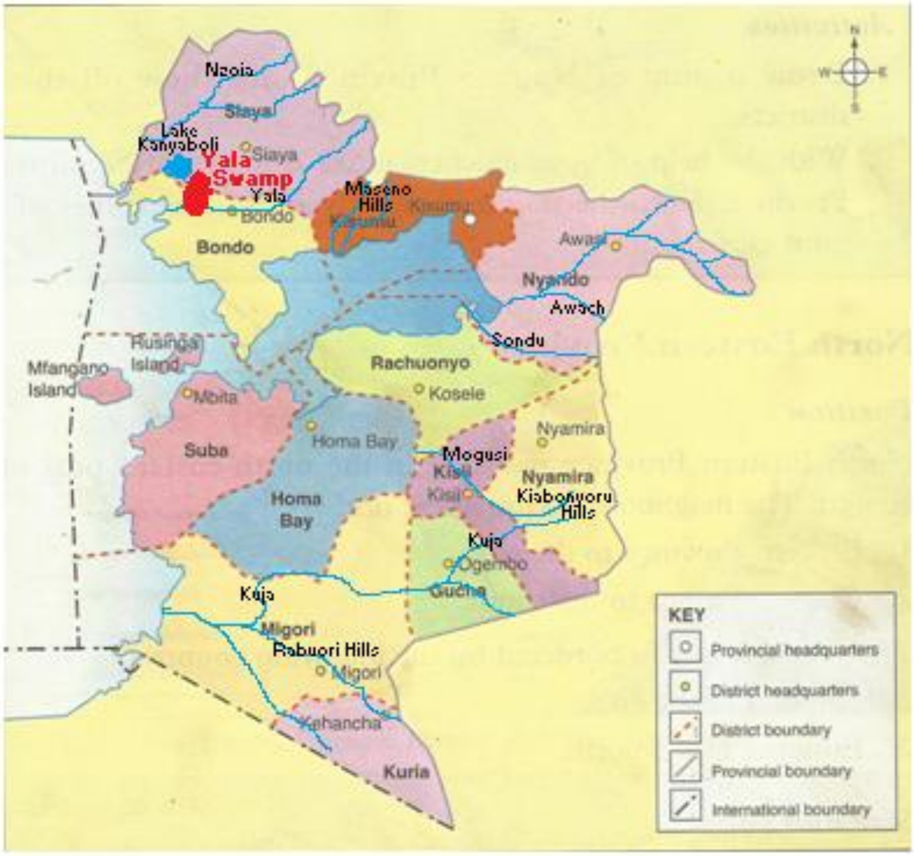

Figure 5: Map of Nyanza Province showing Yala Swamp (Dominion Farm)

(Source: Oxford University Press, East Africa Limited 2010)

3.3.1 Fielding of the sampling area

The area considered for sampling was divided into four major fields as A, B, C and D with approximated surface area of 300 m^2, 500 m^2, 400 m^2 and400 m^2 respectively since they appear on different sides of the roads in the swamp. These rice fields were further subdivided into plots as; A1, A2, A3 and A4; B1, B2, B3, B4, B5, B6 and B7; C1, C2, C3, C4, C5 and C6; D1, D2, D3, D4, and D5. The plots divided into small quadrants from which soil samples were collected in duplicates. The plots were chosen randomly depending on the size of the swamp used for cultivation. From each field, sampling of water and soil for analysis was done by simple random sampling. A map of the study area showing the sampling plots is shown in Figure 6.

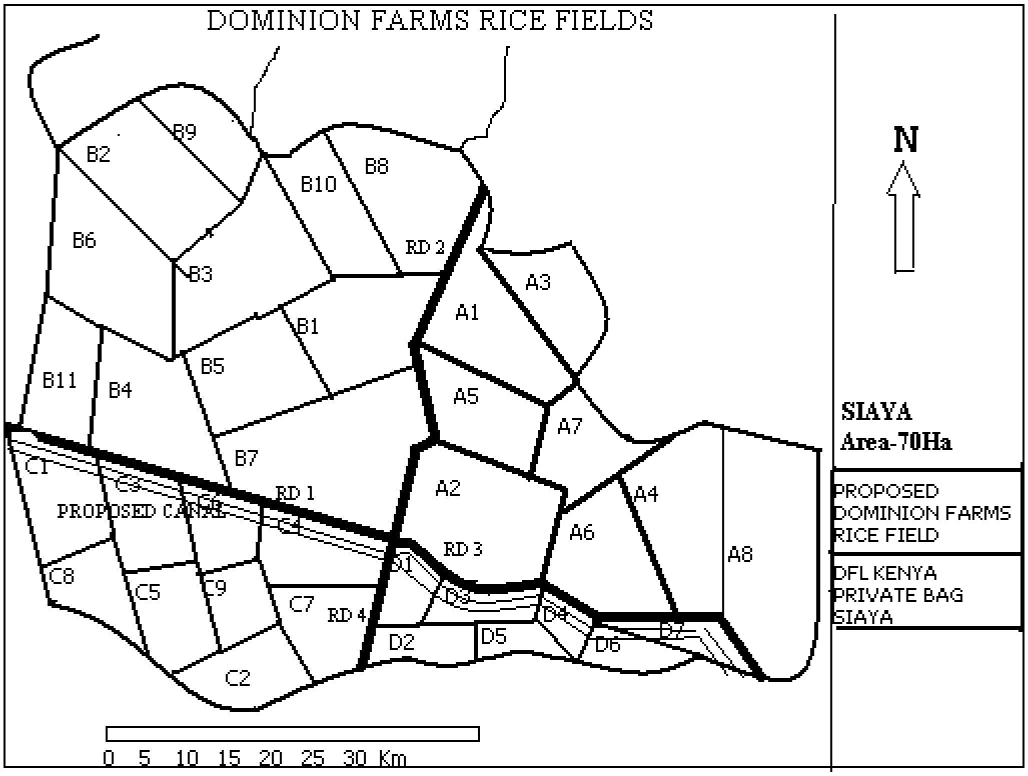

Figure 6: Yala Swamp Dominion Farm Rice Fields and Sampling plots

(Source: Dominion Farm Limited, Kenya 2010)

3.4 Sampling

The swamp was subdivided into smaller plots and thus resulted in smaller sampling areas. Sampling was done during the months of February and June 2010 comprising the dry and wet seasons.

3.4.1 Sampling of water

Sampling of water was done using half-litre plastic bottles which were previously washed thoroughly with detergents to remove grease and dirt, and then washed with tap water and 10 % nitric acid. The bottles were then cleaned thoroughly with double distilled water and rinsed with de-ionized water. The bottles were further rinsed with water to be sampled before collection of the samples. The water samples were kept in refrigerator at 4 ^{0}C awaiting analysis (Alloway, 1995).

3.4.2 Sampling of soil

Sampling plan relied on taking sample units from the field and combining them to form a bulk sample representative of that plot. The swamp was subdivided into smaller sampling areas. A total of 22 soil samples were taken from the swamp. The samples were collected in polythene bags to avoid contamination. Sampling tools were made from carbon/ steel or aluminum since these materials would not contaminate the elements of interest in the samples (Alloway, 1995).

3.4.2.1 Drying and storage of soil samples

Soil samples were prepared for drying by breaking down aggregates, spreading the soil on polythene sheets in aluminium trays and drying to constant weight at 25 ^{0}C. The dry soil samples were then ground using a pestle and mortar and then passed through aluminium sieve with a 2 mm mesh. The soil particles of less than 2 mm were stored in polythene bags awaiting digestion and analysis (Alloway, 1995).

3.5 Reagents

In all cases analytical grade chemical reagent used were procured from Chemtech Analytical Company. These include: lead (II) nitrate ($Pb(NO_3)_2$; copper (II) nitrate ($Cu(NO_3)_2.3H_2O$); chromium (II) nitrate ($Cr(NO_3)_2.9H_2O$); cadmium (II) chloride ($CdCl_2.2H_2O$); zinc chloride ($ZnCl_2$); manganese (IV) oxide (MnO_2); cobalt (II) chloride ($CoCl_2.2H_2O$); sodium hydroxide (NaOH); sodium salicylate ($C_6H_4(OH).COONa$); sodium citrate ($Na_3C_6H_5O_7.2H_2O$); sodium tartate ($[CHOH.COONa]_2.H_2O$); sodium nitroprusside ($Na_2[Fe(CN)_5NO].2H_2O$); sodium hypochlorite (NaOCl); ammonium molybdate ($NH_4MoO_{24}.4H_2O$); ascorbic acid ($C_6H_8O_6$); potassium antimony tartrate ($KSb.C_4H_4O_6$); hydrochloric acid (HCl) and double distilled water (prepared at University of Eldoret Chemistry laboratory). Gases used for AAS were compressed air and acetylene from British Oxygen Company – Kenya (BOC).

3.5.1 Reagents for digestion and actual digestion of samples

Chemical reagents used for digestion of samples were of analytical grade. They include; lithium sulphate ($Li_2SO_4.H_2O$); selenium powder and concentrated sulphuric acid (H_2SO_4) (18 M, purity of 99 % and s.g. of 1.84), concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl).

3.6 Digestion of samples

3.6.1 Digestion of samples for colorimetric analysis

To prepare the digestion mixture, 0.42 g of selenium powder and 14 g of lithium sulphate were added to 350 ml 30 % hydrogen peroxide and mixed thoroughly. A 420 ml of 18 M sulphuric acid was added slowly and with care while cooling in an ice bath. The digestion mixture was stored at 2 ^{0}C. The mixture was allowed to be stable for 4 weeks. About 0.3 ± 0.001 g of the ground soil samples was weighed, and then transferred into digestion tubes. About 4.4 ml of digestion mixture was added to each tube and also to 2 reagent blanks for each batch of samples. Digestion was done at 360 ^{0}C for two hours in the block digester until the solution became colourless. The remaining mixture was cooled then 25 ml of distilled water added and mixed thoroughly until no more sediments dissolved. This was made up to 100 ml with more distilled water in a volumetric flask. It was allowed to settle for a clear solution to form which was then taken for analysis (Okalebo *et al*., 1998).

3.6.2 Wet digestion of soil samples for heavy metals analysis

Acid digestion was carried out on the ground soil samples using concentrated nitric and hydrochloric acids as follows. A 1 g sample was measured into a 50 ml conical flask and 5 ml of concentrated nitric acid added. The sample was shaken for 2 minutes after which 2 ml of concentrated hydrochloric acid was added while shaking. The conical flask was then transferred into a hot plate and covered with a watch glass. This mixture was then heated for 2 hours until no more fumes evolved while controlling the temperature at 70 ^{0}C. The sample was not let to run dry hence nitric acid was added whenever necessary. Heating was continued until a pale brown colour appeared (digestion complete). The sample was cooled, filtered and diluted to 50 ml, then taken for AAS analysis.

3.7 Colorimetric analysis

The content of total nitrogen and total phosphorus was determined by the colorimetric method. Standards were prepared for calibration of the spectrophotometer. Reagents were prepared for total nitrogen (reagents N_1 and N_2). For total phosphorus the reagents prepared were 2.5 M sulphuric acid and ammonium molybdate/ antimony potassium tartrate. The two solutions were mixed with ascorbic acid to form ascorbic acid reducing agent used in the analysis. This was prepared as required on the day of the analysis.

3.7.1 Analysis of phosphorus

Standards for the calibration of the instrument were prepared into 50 ml volumetric flasks using a prepared working solution. The standards contained 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 ppm. The absorbance was measured at 880 nm in the spectrophotometer.

3.7.1.1 Preparation of reagents and standards

A one litre clean beaker was placed on asbestos material or in cold water in a sink. About 500 ml distilled water was poured into the beaker, 148 ml of concentrated sulphuric acid was added to the water slowly while stirring and then diluted to 1litre with distilled water.

A 12 g ammonium molybdate was dissolved in 250 ml of distilled water (warmed to 50 ^{0}C). A 0.291 g of potassium antimony tartrate ($KSb.C_4H_4O_6$) was also separately dissolved in 100 ml distilled water. The two solutions were added to 1000 ml of 2.5 M sulphuric acid previously prepared. This was mixed thoroughly and diluted with distilled water to 2 litres. The mixture was then transferred to a reagent bottle and stored in a dark cool place. This could be kept for up to 2 months.

About 2.108 g of ascorbic acid ($C_6H_8O_6$) was dissolved in 400 ml of ammonium molybdate/ potassium antimony tartrate solution (above) and mixed well. This was prepared as required on the day of analysis and could be kept only for 24 hours.

3.7.1.2 Colorimetric procedure for total phosphorus

A 5 ml of the supernatant clear wet-ashed digest solution was pipetted into a 50 ml volumetric flask. About 20 ml of distilled water was added to each flask, after which 10 ml of the ascorbic acid reducing agent was added again starting with the standards. This was made up to 50 ml mark with distilled water, stoppered then shaken well. This was let to stand for 1 hour to permit full colour development. The standards and sample absorbance (blue colour) was measured at 880 nm wavelength in a colorimeter (spectrophotometer).

A graph of absorbance against concentration of standards was plotted to aid in getting the value of m

$y = m\mathrm{c}$

Where y = absorbance of each sample – absorbance of blank.

$$\frac{y}{m} = \mathrm{c}$$

c = corrected concentration.

With a 5 ml digest aliquot and a 50 ml final solution used for colour intensity (absorbance) measurement, the following formula was used.

$$\text{P in sample \%} = \frac{c \times 0.05}{w}$$

w = weight of sample taken

c = corrected concentration

3.7.1.3 Preparation of standards plot for phosphorus

Absorbance values of the seven phosphorus standards were used to make a plot of absorbance (y-axis) versus the concentration of the standard (x-axis). A best-fit line was drawn through the data points and used to interpret the results of the samples. The calibration graph was typically linear, with correlation coefficient being R = 0.9962 over all the points of absorbance versus concentration (mg/l) of all the standard solutions.

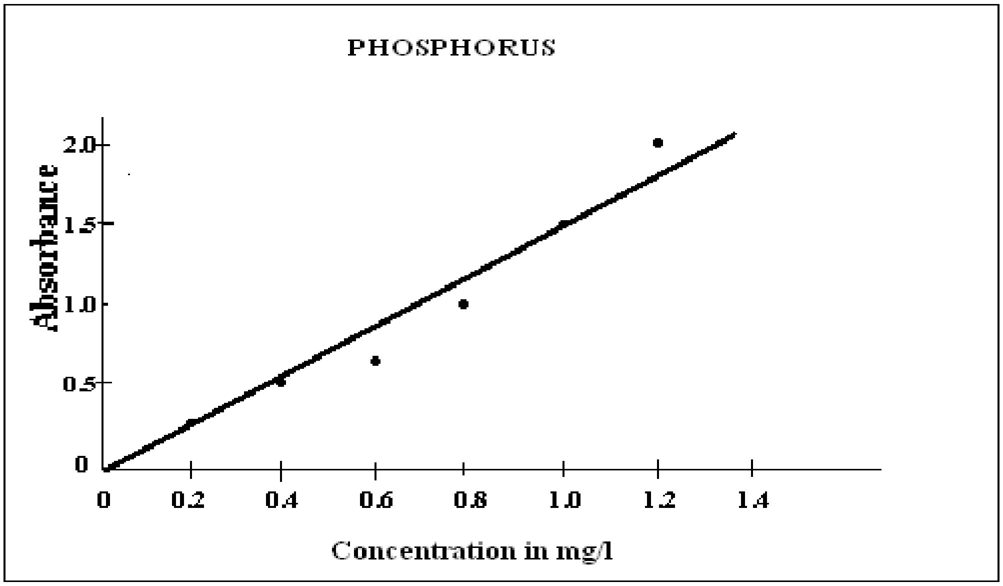

Figure 7: Calibration curve for phosphorus

3.7.2 Analysis of nitrogen

The standards containing 0, 5.0, 10.0, 15.0, 20.0 and 25.0 µg/ml of NH_4^+ was used for the calibration of the instrument. The absorbance was measured at 655 nm in a spectrophotometer.

3.7.2.1 Preparation of reagents and standards

N_1 was prepared by dissolving together 34 g of sodium salicylate, 25 g of sodium citrate and 25 g of sodium tartrate in about 750 ml of distilled water. About 0.12 g of sodium nitroprusside was added and when dissolved made up to 1000 ml with distilled water and mixed thoroughly. N_2 was prepared by dissolving 30 g of sodium hydroxide in about 750 ml distilled water and the solution allowed to cool. A 10 ml sodium hypochlorite was then added and made up to 1000 ml with distilled water and mixed thoroughly. The two reagents were prepared at least 24 hours before use.

3.7.2.2 Colorimetric procedure for total nitrogen

A micropipette was used to transfer 0.2 ml of the sample extract, the blanks and the standard into clearly labeled test tubes. A 5.0 ml of reagent N_1 was then added to each test-tube, mixed thoroughly and left for 15 minutes. This was followed by addition of reagent N_2 to each test-tube, mixed thoroughly and left to stand for one hour for full colour development (the blue colour was stable for at least 10 hours). The absorbance was read at 655 nm using a spectrophotometer.

A graph of absorbance against standard concentrations was plotted using Microsoft Excel. This gave the value of m, from, y = mc. A table was constructed and from the table the c value was found. This was used to calculate the percentage of nitrogen using the formula shown below.

$$\text{N in sample \%} = \frac{c \times 0.05}{w}$$

Where c = corrected concentration

w = weight of sample taken

3.7.2.3 Preparation of standards plot for nitrogen

A graph of absorbance against standard concentration was plotted. The concentration for each sample and blank were then determined using the graph. The calibration curve was typically linear, with the correlation coefficient being R = 0.9957 over all the points of absorbance versus concentration (mg/l) of all the standard solutions.

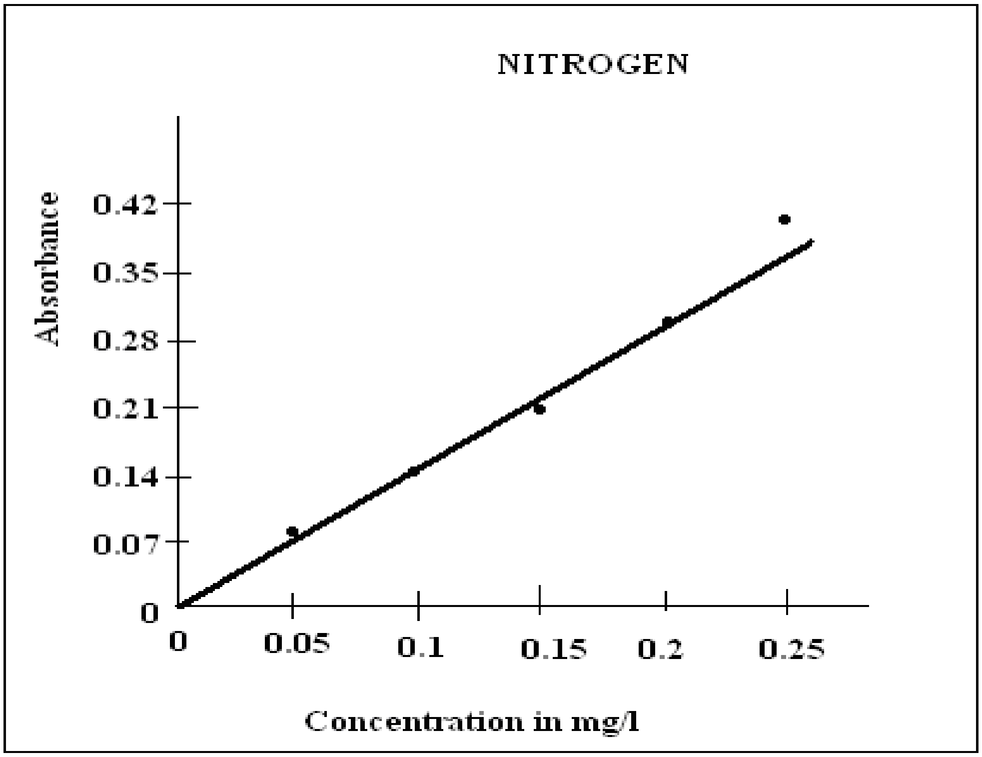

Figure 8: Calibration curve for nitrogen

3.8 Preparation of stock and working solutions

3. 8.1 Zinc stock solution

Zinc standard stock solution was prepared by dissolving 2.085 g of zinc chloride ($ZnCl_2$) in 12 % hydrochloric acid and made up to one litre. The solution had a density of 1.01 g/cm^3 and contained 1.000 µg/ ml (1000 ppm) of zinc ions. A stock solution of 100 ppm was prepared by pippeting 10.0 ml from 1000.0 ppm stock solution, transferring it in a 100.0 ml volumetric flask and making it up to the mark with deionised water. Zinc standard stock solutions of 0.0 ppm, 0.5 ppm, 1.0 ppm, and 1.5 ppm were prepared by pippeting 0.0 ml, 0.5 ml, 1.0 ml, and 1.5 ml, respectively from 100.0 ppm zinc stock solution, transferring each into a separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.8.2 Cobalt stock solution

Cobalt standard stock solution was prepared by dissolving 4.963 g of cobalt (II) chloride, ($CoCl_2.2H_2O$) in 12 % hydrochloric acid and making it up to one litre. The resulting solution had a density of 1.05 g/cm^3 and contained 1.000 µg/cm^3 (1000 ppm) of cobalt (II) ions. A stock solution of 100 ppm was prepared by pippeting 10 ml of stock solution in 100.0 ml volumetric flasks and making it up to the mark with deionised water. Cobalt standards of 0.0 ppm, 2.0 ppm, 4.0 ppm and 6.0 ppm were prepared by pippeting 0.0 ml, 2.0 ml, 4.0 ml and 6.0 ml, respectively from 100.0 ppm stock solution and transferring each into a separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.8.3 Manganese stock solution

Manganese standard stock solution was prepared by dissolving 1.582 g of manganese (IV) oxide (MnO_2) in 12 % hydrochloric acid, boiling to remove chlorine and making up to 1000 ml mark of a one litre volumetric flask. The solution had a density of 1.02 g/cm^3 and contained 1.000 µg/ml (1000 ppm) of manganese (II) ions. A stock solution of 100 ppm was prepared by pippeting 10.0 ml from the 1000 ppm stock solution, putting it in a 100.0 ml volumetric flask and making it up the mark using deionised water. Working solutions of 0.0 ppm, 2.0 ppm, 4.0 ppm and 6.0 ppm were prepared by pippeting 0.0 ml, 2.0 ml, 4.0 ml and 6.0 ml, respectively from 100.0 ppm stock solution and transferring each in to separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.8.4 Cadmium stock solution

Cadmium stock solution was prepared by dissolving 1.6875 g of cadmium (II) chloride ($CdCl_2.2½H_2O$) in 12 % nitric acid and making the solution to 1000 ml. The resulting solution had a density of 1.02 g/cm^3 containing 1.000 µg/ml (1000 ppm) of cadmium (II) ions. A stock solution of 100 ppm was prepared by pippeting 10.0 ml from the 1000 ppm stock solution, putting it in a 100.0 ml volumetric flask and making up to the mark with deionised water. Cadmium working solutions of 0.0 ppm, 1.0 ppm, 2.0 ppm and 3.0 ppm were prepared by pippeting 0.0 ml, 1.0 ml, 2.0 ml and 3.0 ml, respectively from 100 ppm stock solution, transferring each into separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.8.5 Copper stock solution

Copper standard stock solution was prepared by dissolving 3.802 g of copper (II) nitrate ($Cu(NO_3)_2.3H_2O$), in 12 % nitric acid and making it up to 1000 ml mark of a 1000 ml volumetric flask. The solution had a density of 1.04 g/cm^3 and contained 1.000 µg/ml (1000 ppm), of copper (II) ions. A stock solution of 100 ppm was prepared by pippeting 10.0 ml from 1000 ppm stock solution, transferring it into a 100.0 ml volumetric flask and making it up to the mark with deionised water. Working solutions of 0.0 ppm, 2.0 ppm, 4.0 ppm and 6.0 ppm were prepared by pippeting 0.0 ml, 2.0 ml, 4.0 ml and 6.0 ml, respectively from 100.0 ppm stock solution and transferring each into separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.8.6 Lead stock solution

A stock solution of lead was prepared by dissolving 1.599 g of lead (II) nitrate ($Pb(NO_3)_2$) in 12 % nitric acid and making it up to 1000 ml. At 25 ^{0}C, this solution had a density of 1.02 g/cm^3 and contained 1.000 µg/ml (1000 ppm), of lead (II) ions. A stock solution of 100 ppm was prepared by pippeting 10.0 ml from 1000 ppm stock solution, transferring it into a 100.0 ml volumetric flask and making up to the mark with deionised water. Standard solutions of 0.0 ppm, 2.0 ppm, 4.0 ppm and 6.0 ppm were prepared by pippeting 0.0 ml, 2.0 ml, 4.0 ml and 6.0 ml, respectively from 100 ppm stock solution and putting each into a separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.8.7 Chromium stock solution

Chromium standard stock solution was prepared by dissolving 7.695 g of chromium (II) nitrate ($Cr(NO_3)_2.9H_2O$), in 12 % nitric acid and making the solution to the mark in a 1000 ml volumetric flask. The solution had a density of 1.06 g/cm^3 and contained 1.000 µg/ml (1000 ppm) of chromium (II) ions. A stock solution of 100 ppm was prepared by pippeting 10.0 ml from the 1000 ppm stock solution into a volumetric flask and making it up to 100.0 ml mark with deionised water. Chromium standard working solutions of 0.0 ppm, 2.0 ppm, 4.0 ppm and 6.0 ppm were prepared by pippeting 0.0 ml, 2.0 ml, 4.0 ml and 6.0 ml, respectively from the 100.0 ppm stock solution, transferring each into separate 100.0 ml volumetric flasks and making each up to the mark with deionised water.

3.9 AAS analysis of heavy metals

The chemtech analytical 2000 (CTA 2000) and atomic absorption spectrophotometer (SpectrAA 100/ 200) models were used.

3.9.1 Instrument operating conditions

Before the actual analysis was carried out, the atomic absorption spectrophotometer was optimized by setting all the parameters following the manufacturer's recommendations (Chemtech Analytical Company Ltd UK). The instrument optimized conditions included the wavelength (nm), lamp current (mA), slit size, fuel and oxidant flow rates and burner heights. Fuel and oxidant flow rates were adjusted to attain maximum transparency of the mixture flame. The wavelengths (nm) were selected from maximum signal for each element by the help of the CTA 2000 programme. The optimized conditions for the AAS during analysis are depicted in Table 1.

Table 1: Atomic absorption optimized conditions for determination of zinc, cobalt, Manganese, cadmium, copper, lead and chromium

Element	**Zn**	**Co**	**Mn**	**Cd**	**Cu**	**Pb**	**Cr**
Wavelength λ (nm)	213.9	240.7	279.5	228.8	324.8	217	357.9
Lamp Current (mA)	5.0	7.0	5.0	4.0	4.0	10.0	7.0
Slit Width (nm)	1.0	0.2	0.2	0.5	0.5	1.0	0.2
Fuel Flow Rate (l/min)	2.0	2.0	2.0	2.0	2.0	2.0	2.90
Oxidant Flow Rate (l/min	13.5	13.5	13.5	13.5	13.5	13.5	13.5
Burner Height (BH) (nm)	13.5	13.5	13.5	13.5	13.5	13.5	13.5

(Alloway, 1995)

These are the standard operational conditions set for the AAS during analysis in this study. Background correction was done by the use of an Automatic Background Correction (ABC) mode. The ABC conditions were also set to optimize the instrument operations.

Table 2: The ABC optimized conditions for determination of zinc, cobalt manganese, cadmium, copper, lead, chromium

Element	**Zn**	**Co**	**Mn**	**Cd**	**Cu**	Pb	**Cr**
Wavelength	213.9	240.7	279.5	228.8	324.7	217.0	359.4
Lamp Current (mA)	5	4	5	2	3	6	8
Slit Width (nm)	4	3	3	3	4	3	4
D_2 Lamp Current (mA)	20	16	12	12	20	8	18
Gain	7-8	5±1	7±1	8±1	5±1	10	6±1

(Alloway, 1995)

All conditions were set correctly and hence led the gain condition to be automatically set. It was necessary to check whether the detection limit, sensitivity and the element specific absorbance was in agreement with the provided operating parameters described for the instrument.

3.9.2 Calibration working curves

The standard stock solutions (1000 ppm) were used to get the standard solutions. Dilution was done according to the manufacturer's recommendation for optimum working concentration for each element. The absorbance and the corresponding concentrations of the standard solutions were used to draw the calibration working curves. Working solutions of lead, chromium, copper and cobalt were 0.0 ppm, 2.0 ppm, 4.0 ppm and 6.0 ppm; cadmium and manganese were of 0.0 ppm, 1.0 ppm, 2.0 ppm, and 3.0 ppm and for zinc it was 0.0 ppm, 0.5 ppm, 1.0 ppm and 1.5 ppm. The concentration levels of all the blanks were 0.0 ppm and this value was incorporated in plotting the working curves.

The standard curves were drawn with the absorbance on the vertical axis and concentration on the horizontal axis and are shown in the appendices. The calibration curves were typically linear with the correlation coefficient being $R \geq 0.9$ over all the calibration points of absorbance versus concentration (ppm) of all the standard solutions. This shows that the Beer-Lambert's law was obeyed. Standard concentrations for each element were analyzed three times and mean absorbance calculated in each case.

3.9.3 Analysis of samples

The standards for each of the heavy metals were prepared before the actual analysis. A hollow cathode lamp for each element was also inserted. A low electric current was imposed in a way that the metal was excited and able to emit a few spectral lines characteristic of the element. The hollow cathode lamp was able to provide analytical light line for the element of interest. After atomization in the nebulizer, the monochromator was able to isolate the analytical lines of the hollow cathode lamp. The monochromator only allowed the light not absorbed by the analyte atoms in the flame to reach the PMT. Before the analyte was aspirated, a measured signal was generated by the PMT as the light from the HCT passed through the flame. In case analyte atoms were present in the flame while the sample was aspirated, then some of the light could be absorbed by the atoms leading to a decrease in PMT signal proportional to the amount of analyte. These signals led to a decrease in the measured light, which depends on concentration of the analyte. Each sample was duplicated and therefore analyzed twice; the mean concentration was then determined and subtracted from the concentration of the blank.

The standard curves were drawn with the absorbance on the vertical axis and concentration on the horizontal axis and are shown in the appendix. The calibration curves were typically linear, with the correlation coefficient found to be approximately 0.9 over all the calibration points of absorbance versus concentration, in ppm, of all the standard solution.

3.9.4 Recovery Tests

The reliability of the AAS method in the determination of the elements studied was assessed by carrying out recovery studies. A standard soil and water sample collected from the swamp was used for the recovery studies. Known quantities of each metal standard solution were added to the samples prior to the digestion step. Sample soil weighing 3.0 g were obtained and to each was added separately standards of between 1.0 – 4.0 ppm, 0.2 – 0.8 ppm, 0.25 – 1.50 ppm, 0.1 – 0.40 ppm and 0.10 – 0.4 ppm of zinc, cobalt, manganese, cadmium, copper, lead and chromium, respectively. These samples were then digested. Standard solution of 10.0 ppm, 2.0 ppm, 1.0 ppm, 2.0 ppm, 10.0 ppm, 10.0 ppm and 1.0 ppm were digested using the same process for comparison. The samples and standard solutions were analyzed for the respective elements. Percentage recoveries were worked out using the expression below.

$$\text{Percentage recovery} = \frac{\text{Recovered analyte}}{(\text{Original} + \text{Added})\ \text{analyte}} \times 100\%$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter the results from fields and plots are presented in form of tables (see appendices) and figures.

4.2 Mean concentration (ppm) of some heavy metals, total nitrogen and total phosphorus in water

Mean concentration levels of Zn, Co, Mn, Cd, Cu, Pb and Cr in ppm, total N and total P in water were obtained from various fields within Yala swamp. The results are summarized in tables (appendices 17 – 29) and in Figures 9 – 12. The graphs are drawn using Excel programe. For standard error (error bars) the maximum and the minimum values for a particular pollutant were considered for plotting. The values of total N and total P were calculated in percentage using specific formula hence the values did not include standard error.

4.2.1 General trend in field A

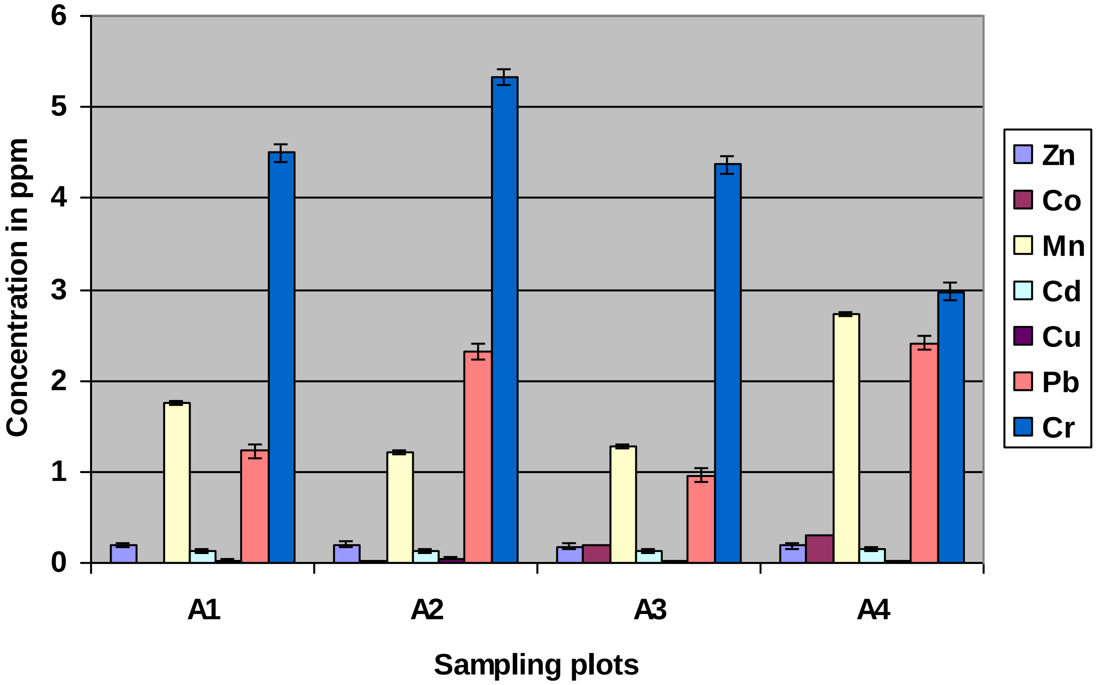

Figure 9: Concentration of heavy metals (ppm) in water in field A

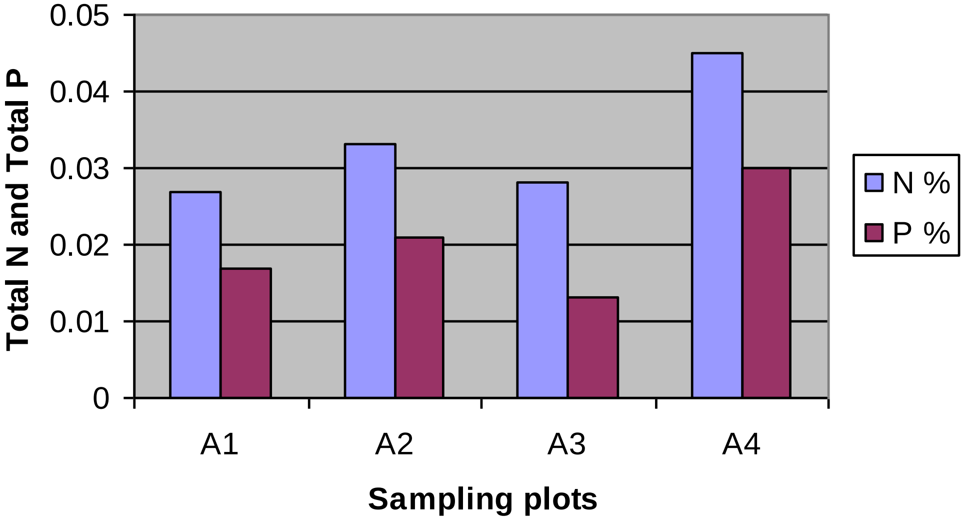

Figure 10: Concentration of total phosphorus and total nitrogen in water in field A

The concentration of heavy metals (ppm), total N and P in field A are illustrated in a table (Appendix 17) and Figures 9 and 10. The mean concentration of Zn was on average constant in the four sampling plots at a minimum value of 0.181±0.004 and a maximum value of 0.204 ±0.005. These values were far much lower than the maximum limits prescribed by both WHO/FAO and KEBS (Appendix 4). The low concentrations imply that Zn compounds are not used much in this area. This area is not exposed to municipal wastes and waste water as a major source of Zn in the environment. However, the available Zn could be due to the use of agrochemicals such as fertilizers and pesticides.

There was a general increase in the mean concentration of Co. The values increased from a minimum value of 0.007 ± 0.000 in plot A1 to a maximum value of 0.307±0.280 in plot A4. Although Co levels increased, some were, however, lower than the WHO/ FAO and KEBS in plots A1 and A2. The values in plots A3 (0.185 ± 0.109) and A4 (0.307±0.280) were two and three times, respectively higher than the maximum limits set by the WHO/FAO of 0.1 ppm. The availability of Co is as a result of industrial wastes deposited into river Yala from its tributaries in the highland regions. The presence of basic rocks such as basalts and andesite, which are known to contain Co, along the river beds, may be contributing to the presence of Co in the swamp.

There was a decrease then followed by increase in the concentration of Mn. The decrease was noted in plot A1 (1.759± 0.003) to plot A2 (1.217 ± 0.011) while increase was noted from A2 to A4 (2.730± 0.002). These values were, on average fifteen times higher than the maximum limit of 0.100 ppm recommended by WHO/FAO and KEBS. The high concentration of Mn could be as a result of parent material in the surrounding area including rocks. In the earlier chapters it was noted that Mn commonly occurs as mineral oxides birnessite and verndite (Gilkes and McKenzie, 1988). Apart from the natural mineralogical sources, the other important source of Mn in the soil (Yala swamp) is its application to deficient soils. Application to the soil is normally in the form of $MnSO_4$, MnO or as an addition to macronutrient fertilizers which are highly used in the swamp.

High concentrations of Cd were detected in all the four plots (A1, A2, A3, and A4) in this field. The values were almost constant in all plots with the highest concentration recorded in plot A4 (0.145± 0.011) while the lowest value in plot A1 (0.121± 0.007). These values were approximately fifty times higher than the WHO/FAO recommended maximum limit of 0.003 ppm. The high Cd levels in the water could be attributed to the runoff into R. Yala from volcanic activities associated with landforms in the Rift Valley region and also from the industrial effluent discharge into the river. The use of phosphate fertilizers in the farm and surrounding areas could also contribute to the presence of Cd in water in the swamp. Phosphate rock normally contains Cd and thus its level depends on the origin of the rock (WHO, 1998). When applied fertilizers from the farms are washed into the river, the water is enriched with Cd.

Mean concentration levels of Cu noted were fluctuating with the highest level recorded in plot A2 (0.049± 0.002) and the lowest level in plot A4 (0.013± 0.001). These values were almost twenty times lower than the WHO/FAO recommended maximum limits of 1.000 ppm and 2-3 times lower than the KEBS maximum limits of 0.100 ppm (Appendix 4). High levels of Cu could be attributed to the use of Cu as a component in most pesticides. This is then carried and distributed as the water flows into the swamp.

The mean concentration levels of Pb were fluctuating. It increased from plot A1 (1.230± 0.088) to plot A2 (2.320± 0.087) then decreased in plot A3 (0.960 ± 0.033) and finally increased in plot A4 (2.410± 0.022) as illustrated in Figure 9. These concentrations were, however, higher than the WHO/FAO and KEBS maximum limits of 0.01 ppm and 0.100 ppm, respectively (Appendix 4). The high levels of Pb could be attributed to Pb related compounds washed into river Yala from farms, roads and the atmosphere which ends into the swamp. It could also be increased by vehicles that move round the plots in the rice fields. High concentration levels of Pb in water from the river makes it unsuitable for drinking as it could lead to Pb poison.

The concentration levels of Cr detected in the four plots in this field were also fluctuating with the highest level noted in plot A2 (5.335 ± 0.009) and the lowest level in plot A4 (2.976±0.004). Plots A1 and A3 had average values of 4.495 ± 0.009 and 4.367 ± 0 respectively. These high levels of Cr in water samples could mean that its compounds are used much in the surrounding areas. It could also be as a result of industrial waste deposits into the river from the highlands.

The concentration levels of total N and total P noted in field A are as shown in Figure 10 (also see appendix 17). There was a general increase in the concentration levels of N with the lowest level recorded in plot A1 (0.027) and the highest level recorded in plot A4 (0.045). The increase was slight and could be attributed to washing of nitrogenous fertilizers from the farms into the surface water. Washing of fertilizers into surface water could eventually promote the growth of aquatic vegetation, which degrades water quality and eventually cause eutrophication. The use of inorganic N suppresses nitrogen-fixing soils bacteria making agriculture dependent on artificial fertilizer (Whiting et al.., 2005). The levels of P recorded in this field were slightly lower than those of N. The lowest level was noted in plot A3 (0.013) while the highest level noted in plot A4 (0.030). High levels of P are dangerous to the aquatic system because it would stimulate the growth of planktons and aquatic plants, which provide food for larger animals. Very high levels may lead to growth of algae and finally eutrophication.

4.2.2 General trend in field B

This field was divided into seven plots. The most concentrated heavy metal was Cr while the least was Co. These results are illustrated in a table (Appendix 18) and in Figures 11and12

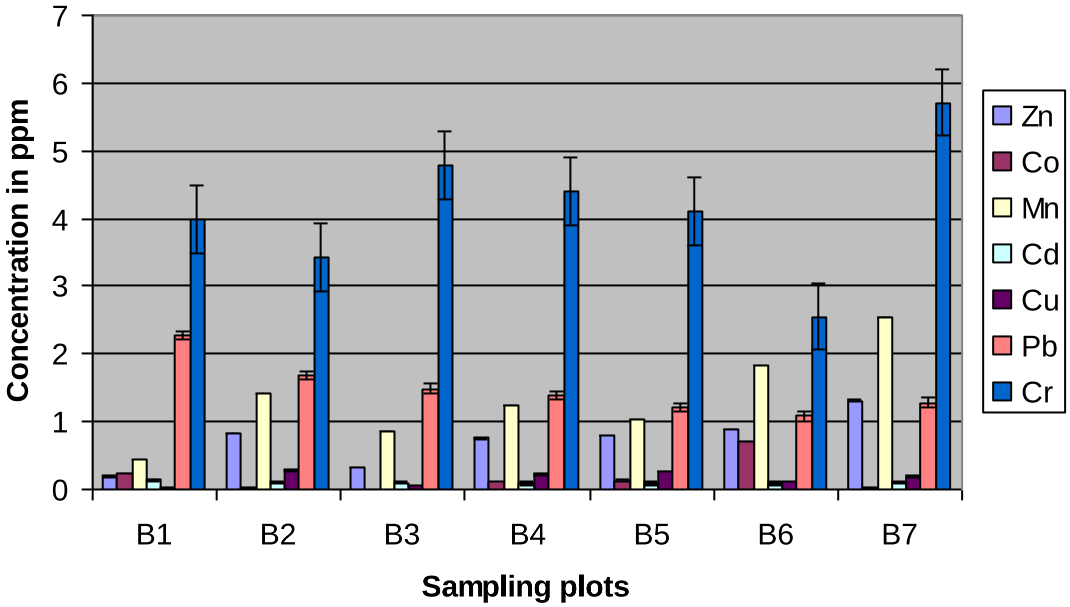

Figure 11: Concentration of heavy metals (ppm) in water in Field B

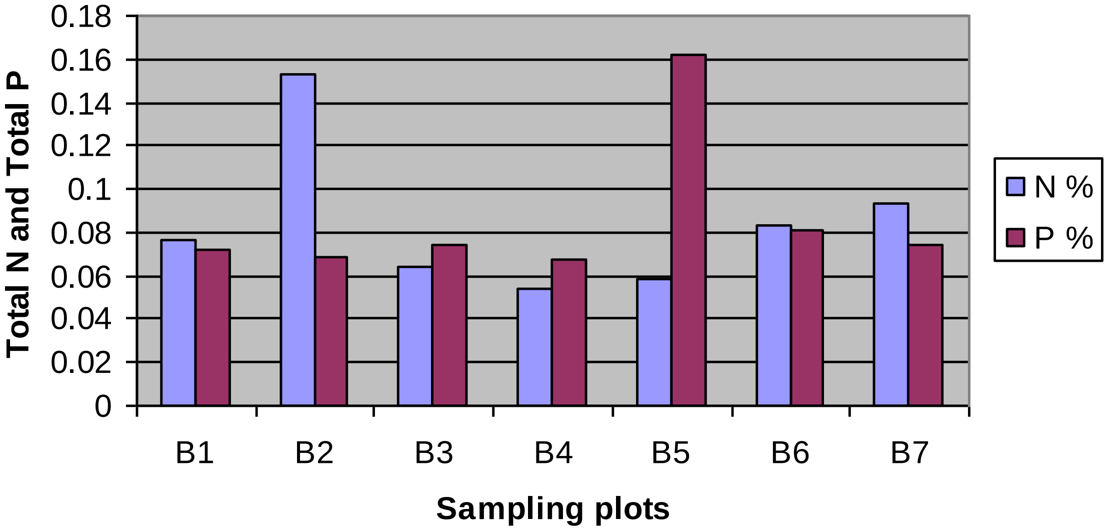

Figure 12: Concentration of total phosphorus and total nitrogen in water in field B

The mean concentration of Zn was fluctuating between the lowest level recorded in plot B1 (0.190 ± 0.005) and the highest level in plot B7 (1.311 ± 0.003). These levels were lower than the maximum limit recommended by the WHO/FAO and KEBS of 5.000 ppm. The levels in the remaining plots were also below this recommended value. The low levels of Zn in water in this field means that the area in not exposed to much Zn compounds like municipal sewage and waste water pollutants, which are the major sources of Zn in the environment.

There was no particular trend in the mean concentrations of Co because the levels either increased or decreased within the field. The lowest level of Co was noticed in plot B3 (0.005 ± 0.000) while the highest value in plot B6 (0.714 ± 0.182). Nearly half of the plots in this field had Co values less than the maximum acceptable limits recommended by WHO/FAO of 0.100 ppm while the rest had values higher than the recommended one.

Concentrations of Mn fluctuated between the lowest level of plot B1 (0.437 ± 0.003) and the highest level of plot B7 (2.538± 0.002). These values were averagely fifteen times higher than the value recommended by both WHO/FAO and KEBS as 0.100 ppm.

There was a general decrease in the mean concentration values of Cd in this field. The highest value was obtained in plot B1 (0.136± 0.016) while the lowest value was detected in plot B6 (0.084 ±0.015). All the values obtained were slightly higher than that recommended by WHO/FAO of 0.003 ppm. These high levels could be attributed to the use of phosphatic fertilizers in the farm. Phosphate rocks are naturally known to contain Cd whose level depends on the origin of the rock.

Mean concentration levels of Cu fluctuated in this field as illustrated in Figure 11. The lowest value was recorded in plot B1 (0.025± 0.004) while the highest value was recorded in plot B2 (0.281± 0.016). These values were lower than the maximum recommended limits set by WHO/FAO of 1.000 ppm but higher than that set by KEBS of 0.100 ppm. The low concentrations of Cu in water could be due to the fact that most Cu compounds are insoluble hence precipitate out in soil and sediments. Many inhabitants have been conducting sand mining activities along river Yala despite the existence of county council by laws prohibiting such mining activities (Kondoro and Mikidadi, 1998). Seepages of the natural Cu levels from these mining sites could find their way into the water and encourage increased levels of Cu.

There was a general decrease in the mean concentration levels of Pb in this field. The highest level was recorded in plot B1 (2.271± 0.055) while the lowest value was in B6 (1.085 ± 0.014). Although there was a decrease in Pb concentration in plot B6, these values were over one hundred times higher than maximum limits set by WHO/FAO but only ten times higher than that set by KEBS (Appendix 4). These high levels of Pb could be attributed to the pollution by motor vehicle emissions around the plot. The rice fields are widely exposed to air polluted with Pb. The high levels of Pb in water should be checked because it can poison the consumers of water and farm products in the area.

There was a general increase in the concentration of Cr with the highest level recorded in plot B7 (5.715±0.654) while the lowest in plot B6 (2.554± 0.206). These values were almost over ninety times higher than the maximum limits set by WHO/FAO of 0.050 ppm. The high level of Cr in water samples suggests that Cr related compounds are much used in the areas around river Yala and the swamp.

Nitrogen had highest concentration in plot B2 (0.153) and the lowest in B4 (0.054) while P had the highest level in B5 (0.162) and the lowest in B4 (0.068). The presence of these nutrients could be attributed by the fact that nitrogenous and phosphate fertilizers are applied in the farm. It could also be attributed to leaching from waste dumps and municipal runoffs, which contain detergents.

4.2.3 General trend in field C

This field was divided into six plots. The highly concentrated heavy metal was Cr while the lowly concentrated was Co as illustrated in and Figures 13 and 14 and in the table (see appendix 19).

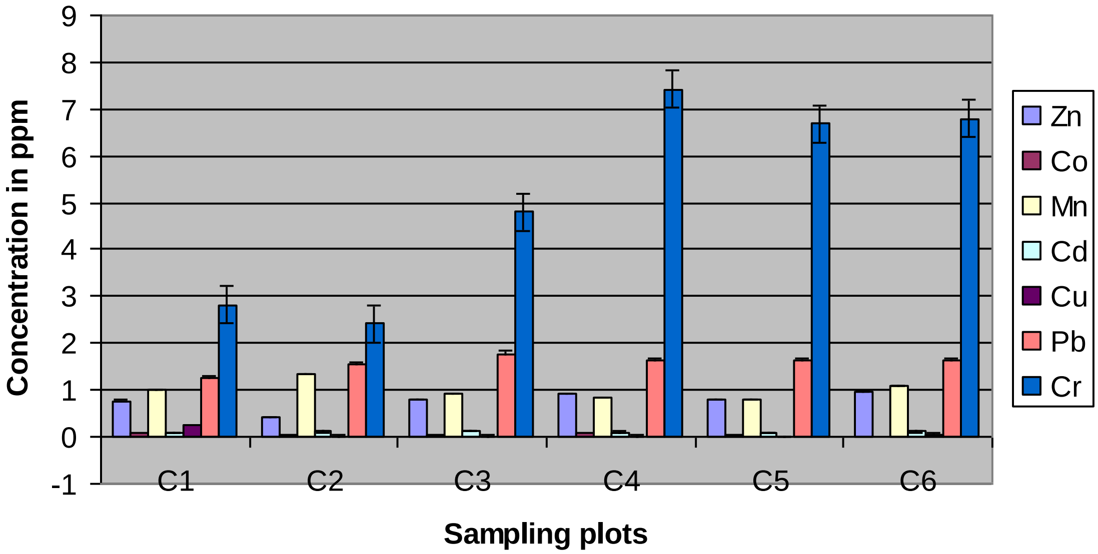

Figure 13: Concentration of heavy metals (ppm) in water in field C

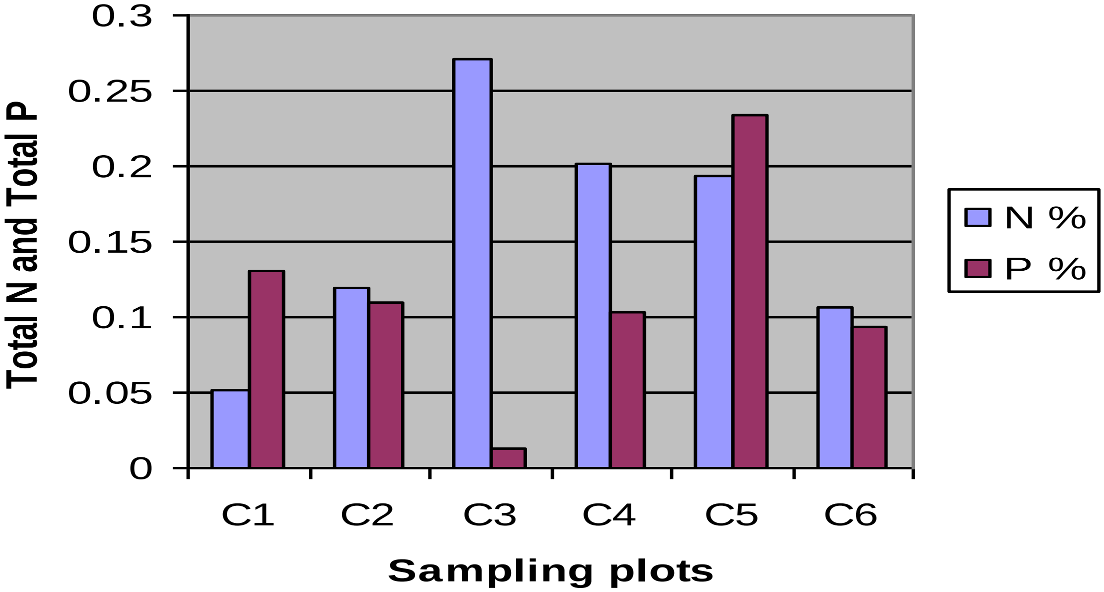

Figure 14: Concentration of total phosphorus and total nitrogen in water in field C

The mean concentration of Zn decreased from plot C1 (0.776 ± 0.004) to C2 (0.423 ± 0.003). This was followed with an increase in plot C3 (0.805 ± 0.009) then another increase in plot C4 (0.929 ± 0.003). The highest value was recorded in plot C6 (0.971 ± 0.009). The values were approximately five times lower than the recommended maximum value set by both the WHO/FAO and KEBS of 5.000 ppm. The low level of Zn in water in this plot could mean that the area is not exposed much to Zn compounds like municipal sewage and waste water pollutants, which are major sources of Zn in the environment.

The mean concentration level of Co fluctuated between the highest value in plot C1 (0.085 ± 0.003) and the lowest value in C6 (0.008 ± 0). These values were far much lower than the maximum limit set by the WHO/FAO at 0.100 ppm. These values were lower than those in soil because of the precipitation of Co compounds.

From Figure 13 it is seen that there was a general increase in the concentration level of Mn in field C with the highest level recorded in plot C2 (1.347 ± 0.034) while the lowest value was recorded in plot C5 (0.805 ± 0.006). These values were approximately thirteen times higher than the WHO/FAO and KEBS recommended values of 0.100 ppm (Appendix 4).

There was an increase in the mean concentration level of Cd from plot C1 (0.090 ±0.016) to plot C3 (0.121± 0.015). This was then followed by decrease in plot C4 (0.107±0.009), another decrease in plot C5 (0.095±0.025) and finally an increase in plot C6 (0.109± 0.001). These values were much higher than the maximum limit set by the WHO/FAO of 0.003 ppm. The high Cd levels in water could be attributed to weathering of rocks in the highland regions of Rift Valley washed down into river Yala and the use of phosphatic fertilizers in the farms. Phosphatic rocks are naturally known to contain a lot of Cd.

The mean concentration level of Cu generally decreased with the highest value recorded in plot C1 (0.258± 0.003) while the lowest value was noted in plot C5 (0.003± 0.001). These values were on average four times lower than the values set by WHO/FAO of 1.000 ppm but three times higher than maximum limit set by KEBS of 0.100 ppm (Appendix 4). The low level of Cu in water could be due to the precipitation of its compounds and finally corporation into soil and sediments.

A general increase in the mean concentration level of Pb was noted in this field with the highest value recorded in plot C3 (1.782 ± 0.086) while the lowest value was in plot C1 (1.250 ± 0.130). These values were over one hundred times higher than maximum limit set by WHO/FAO of 0.010 ppm but seventeen times higher than that set by the KEBS of 0.100 ppm (Appendix 4). These high Pb concentrations are attributed to pollution by motor vehicles emissions within the farm.

The mean concentration of Cr was fluctuating between the highest value in plot C4 (7.419± 0.249) and the lowest value in plot C2 (2.420± 0.000) as in the table (Appendix 19) and Figure 13. These values were far much higher than the set value of 0.050 ppm by the WHO/FAO (Appendix 4). This could be due to the fact that most Cr compounds are insoluble in water and therefore incorporated into soil and sediments.

The highest mean concentration of N in field C was noted in plot C3 (0.271) and the lowest in plot C1 (0.052). The lowest level of P was in plot C3 (0.013) and the highest in plot C5 (0.234). The high level of P and N could be due to the application phosphate and nitrogenous fertilizers and also due to agricultural runoffs from the surrounding farms.

4.2.4 General trend in field D

This field was divided into five plots. The results are summarized in Figures 15 and 16 and in the table (Appendix 20)

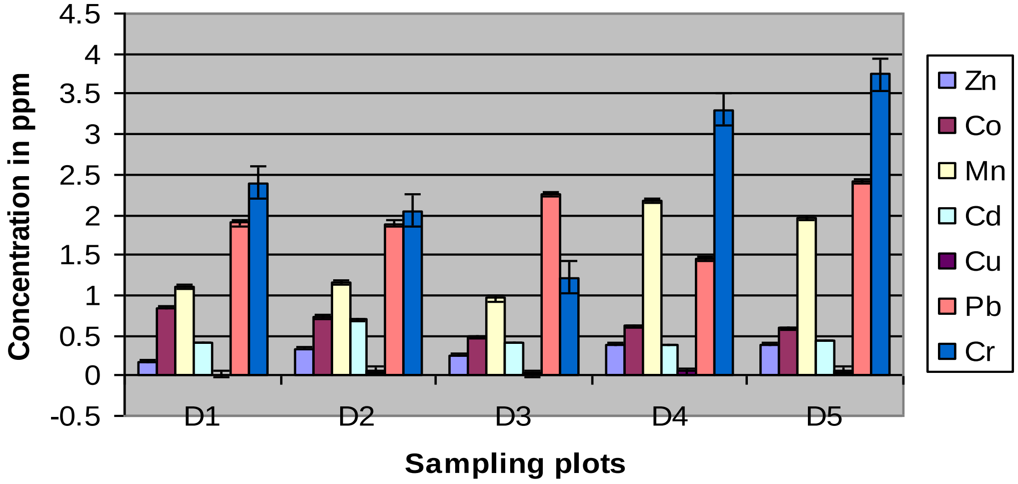

Figure 15: Concentration of heavy metals (ppm) in water in field D

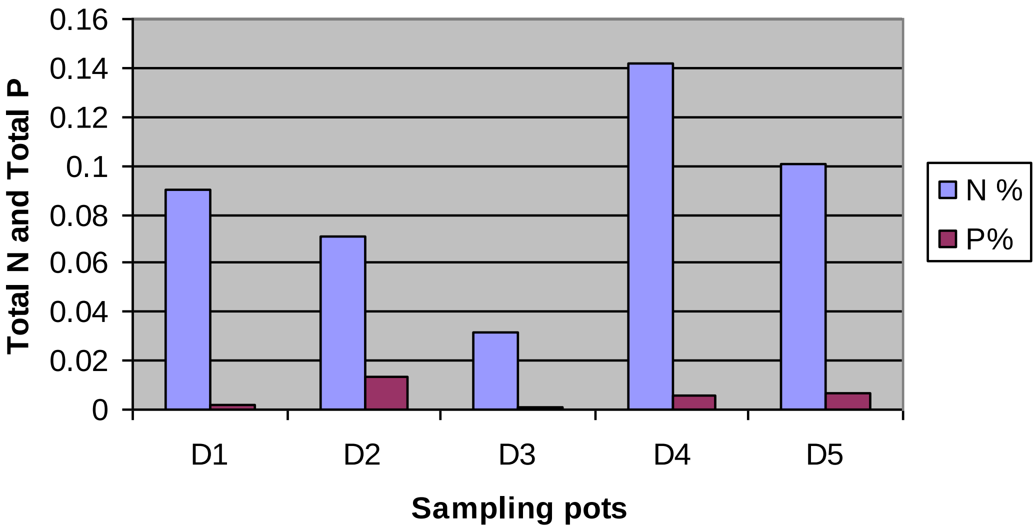

Figure 16: Concentration of total phosphorus and total nitrogen in water in field D

There was a general increase in the mean concentration level of Zn in field D. The highest value was recorded in plot D5 (0.387 ± 0.002) while the lowest value was in plot D1 (0.180 ± 0.011). These values were approximately sixteen times lower than the maximum recommended limit set by the WHO/FAO and the KEBS (Appendix 4). The presence of effluents from sugar factories and settlement wastes are necessary for the dissolution of Zn compounds. There are also numerous non- point sources of pollutions that can provide Zn above the natural background levels like metamorphosis of rocks which are numerous along river Yala. The concentration of Zn in natural surface waters is below 10 µg/l (Alloway, 1990). The acceptable Zn level in water is quite flexible but more than 3 mg/l may be undesirable (WHO, 1996).

There was a general decrease in the mean concentration values of Co in field D. The highest level was recorded in plot D1 (0.849 ± 0.000) while the lowest level was noted in plot D3 (0.477 ± 0.049) as in Figure 15 and in the table (Appendix 20). These values were, on average, seven times higher than that recommended by WHO/FAO of 0.100 ppm, but were lower than that in soil because of the precipitation of Cu compounds. The mean concentration values of Mn fluctuated between the highest level in plot D4 (2.179 ± 0.021) and the lowest level in plot D3 (0.958 ± 0.049). The concentrations were far much higher than the recommended limits by WHO/FAO and KEBS.

The mean concentration values of Cd fluctuated between the highest level in plot D2 (0.691 ± 0.003) and the lowest in plot D4 (0.380 ± 0.035) as in Figure 15. These values were over one hundred times higher than that set by WHO/FAO of 0.003 ppm (Appendix 4). The high levels could be attributed to the use of phosphatic fertilizers in the farm and also dissolution of minerals and ores from industrial effluents.

Copper levels fluctuated between the highest mean concentration in plot D5 (0.068 ± 0.022) and the lowest value in plot D1 (0.021±0.005) as illustrated in Figure 15. The values were, however, almost fifteen times lower than the maximum limit recommended by WHO/FAO of 1.000 ppm but almost three times lower than the value set by the KEBS of 0.100 ppm. This low level in water could be attributed to the precipitation of Cu compounds and eventual incorporations into soil and sediments.

Lead concentration levels generally increased in field D. The highest concentration was recorded in plot D5 (2.417 ± 0.019) while the lowest concentration was noted in plot D4 (1.451 ± 0.031) as in Figure 15. These values are over one hundred times higher than the set value by WHO/FAO of 0.010 ppm but almost twenty times higher than the recommended value of 0.100 ppm by KEBS (Appendix 4). The high levels of Pb could be due to Pb related compounds being washed into river Yala from farms, roads and atmosphere. Pollution by motor vehicle emissions within the farm roads could also lead to high Pb concentrations.

Mean concentration level of Cr generally increased in field D with the highest value found in plot D5 (3.743± 0.237) and the lowest value in plot D3 (1.219± 0.214) as illustrated in the table (Appendix 20) and Figure 15. These values were averagely seventy times higher than the recommended value of 0.050 ppm by WHO/FAO (Appendix 4). The high Cr concentrations could be due to water logging nature of the swampy soil. In waterlogged soils, aeration of organic matter is lacking and therefore, humic acid formed in the process of decomposition during long periods of water logging resulting in increased level of adsorption of Cr.

Total N in water samples in field D showed a general increase with a minimum value noted in plot D3 (0.032) and the maximum in D4 (0.142). These values are fairly low and generally lower than the values recorded in soil samples, though some plots had higher levels of N in water than in soil. This is due to the high solubility of nitrates in water, hence remaining in the surface water.

4.2.5 Mean concentrations of the elements from the four fields

The average mean concentration of the contaminants in the four major fields A, B, C and D was worked out from the concentrations of the contaminants in the plots. Field A comprised of plots A1, A2, A3 and A4. Similarly, fields B, C, and D also comprised of their respective plots. This is shown in Figures 17 and 18 and in the table (Appendix 21).

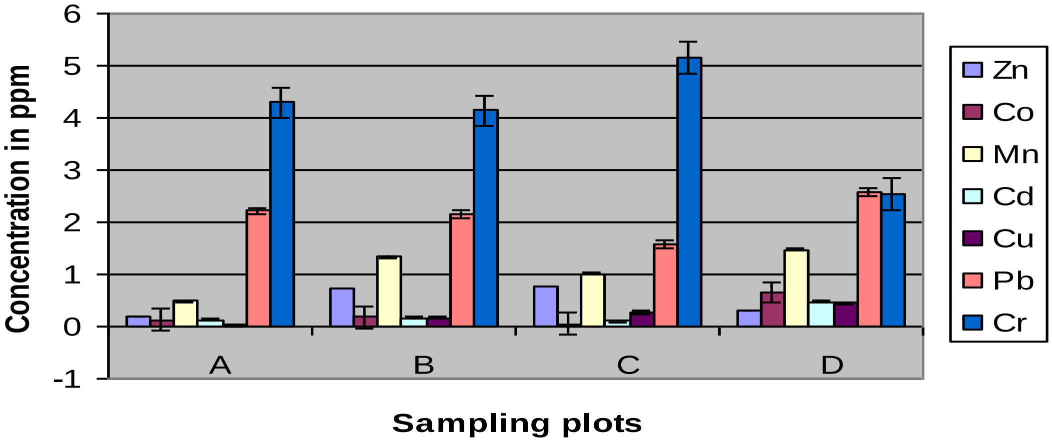

Figure 17: Mean concentration of heavy metals in different fields in water

As seen in Figure 17, it can be noted that the levels of Co, Mn, Cd, Cu and Pb were highest in field D which is closer to lakes Victoria and Kanyaboli, compared to the other fields. All these heavy metals had their values higher than maximum recommended limits by the WHO/FAO and KEBS.

From the previous studies of Zn adsorption, it has been found that clays and organic matter may adsorb quite strongly. The variation in the concentration of Zn could be explained by the adsorption of Zn in hydrolysed form and precipitation of zinc salts in the clay soils (Kirugaru, 1996).

Increase in Co is due to poor soil drainage status. This has major influence on the amount of available Co. In poorly drained soils the amount of extractable Co is generally greater than in the adjoining areas which are well drained. (Mitchel *et al.*, 1978) attributed this effect to differences in the rates of weathering of ferromagnesian minerals and difference in types of clay minerals and organic complexes formed under different drainage conditions.

Variation in the concentration of Mn is due to the fact that Mn is mainly present as a substitute for Fe^{2+} in octahedral sites in the structures of ferromagnesian silicate minerals. Contents vary widely in acidic igneous rocks and metamorphic rocks such as schists which are found near the swamp (Gilkes and McKenzie, 1988).

It has been reported that phosphate fertilizers contain high amount of Cr which is responsible for its high concentration (NRCC, 1976). The variation in concentrations is due to influences of geology and soil forming processes. Soil levels of Cu are affected by soil and crop treatments including fungicides, fertilizers, live stock manures, sewage sludges and atmospheric deposition. This varies considerably according to the proximity of industrial emissions and the quantities of wind-blown dust.

Lead in soil could be derived from vehicle fumes, abraded tyre materials, plastics and rubber factories, insecticides and car batteries. Close to buildings, old paints could also provide a source of Pb (Adamo, 2005).

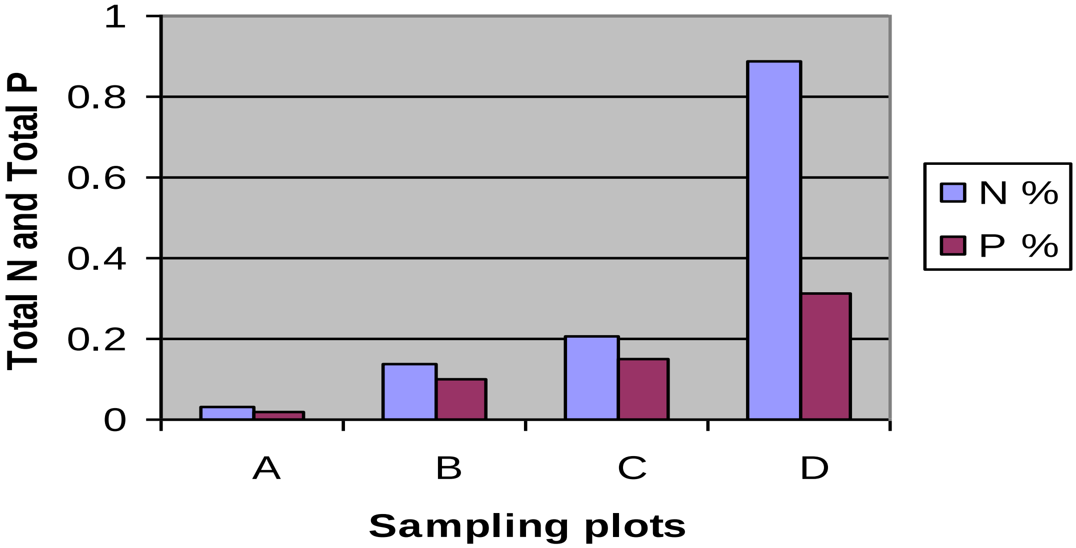

Figure 18: Mean concentration of total P and total N in different fields in water

The mean concentration of Zn was 0.310 ± 0.011, which is sixteen times lower than the maximum set value of 5.000 ppm by KEBS and WHO/FAO. Even though Cr also had lower concentration of 2.541 ± 0.284 than the rest of the fields, its value was approximately fifty times higher than the recommended value of 0.050 ppm by WHO/FAO. The low concentrations of Cr and Zn could be due to the dilution effect in field D and precipitation of their compounds and incorporation into soil and sediments.

The order of the heavy metal distribution in the four fields was as follows;

Cr >Pb >Mn >Zn > Co > Cu > Cd

Chromium was highest in concentration in all the four respective fields A, B, C and D with a mean value of (4.293 ± 0.508), (4.137 ± 0.391), (5.161 ± 0.332) and (2.541 ± 0.284). This gave an average value of 4.033 ± 0.379 for Cr level which is eighty one times higher than the recommended value of 0.050 ppm by WHO/FAO. The high concentration of Cr could be linked to water logging nature of the surrounding soils, which accounted for much of increased Cr levels. It could also be linked to the high density of metal workshops near the farm and extensive use of Cr related products such as fungicides, which are used in the farm and in wood preservatives. Chromium is also found in igneous rocks. Mafic and ultramafic rocks found in the swamp are richest in Cr. Fertilizers are found to contain a lot of Cr, with phosphates being the richest in the element (Ntiba *et al.*, 2001) The levels of Cr in natural water vary between 1 and 2 µg/l but can be elevated in areas with natural sources (WHO, 1996).

Lead was the second metal after Cr in concentration. Its average value was 2.133 ± 0.213 ppm which exceeded the maximum value of 0.01 and 0.100 ppm set by WHO/FAO and KEBS respectively. The high Pb values could be attributed to the use of tetraethyl lead additives in petrol and uses in farm machinery and also from factory effluents into river Yala. Lead could also be introduced into the environment or water through exposure of airborne Pb as reported earlier (WHO, 1992a).

Manganese was third with a mean value of 1.078 ± 0.032 ppm. It exceeded the maximum value of 0.100 ppm set by WHO/FAO and KEBS. This could be attributed to the presence of parent material in the surrounding area such as rocks and also the application of elements to deficient soils in the form of $MnSO_4$, MnO or as an addition of macronutrient fertilizers.

Zinc was fourth with a mean value of 0.478 ± 0.002 ppm. This was lower than the maximum value of 5.000 ppm set by WHO/FAO and KEBS. The low level could be attributed to the fact that the area is not exposed too much Zn compounds such as municipal sewage and waste water pollutants.

Cobalt and Cu were in positions fifth and sixth with mean values of 0.225 ± 0.001 and 0.226 ± 0.002 respectively. Concentration of Co was approximately two times higher than the maximum value of 0.100 ppm recommended by WHO/FAO. However, for Cu, the concentration was approximately four times lower than the maximum recommended value of 1.000 ppm by WHO/FAO but two times higher than value of 0.100 ppm recommended by KEBS. Seepages of natural Cu from the sand mining sites could contribute to its high level.

The least concentrated metal was Cd with an average value of 0.218 ± 0.046 ppm though approximately seventy three times higher than 0.003 ppm set by WHO/FAO. Most heavy metals were higher in soil because once they are discharged they rapidly become associated with particles and are incorporated in soil and sediments (Hanson *et al*., 1983). The accumulation of heavy metals from the overlying water into soil is dependent on a number of environmental factors such pH, ionic strength, androgenic input, the type and concentration of organic and inorganic ligands and available surface area for adsorption caused by variation in grain size distribution (Davis *et al*., 1991).

Similar work was carried out on analysis of heavy metals in water in five Rift valley lakes in Kenya, for example, lakes Nakuru, Elementaita, Naivasha, Bogoria and Baringo, by Ochieng and others (2007). The results reported dissolved mean concentration levels in µg/L for the heavy metals in water to be Zn (29.0 – 235.0), Co (5.0 – 316.0), Mn (50.0 – 282.0), Cd (2.0 – 43.0), Cu (4.7 – 100.0), Pb (25.0 – 563) and Cr (25.0 – 188.0). These values were much higher than those obtained in this present research since the lakes are within the Rift valley which is associated with deposition from highlands.

Another similar work on variations of concentrations of some heavy metals in the infiltration ponds at Olkaria, Kenya was carried out (Simiyu and Tole, 2000). They found out that generally, Zn, Cd and Pb concentrations in fluids were lower than the WHO standards in drinking water at 5, 0.05 and 0.005 ppm, respectively. However, Zn and Pb concentrations tended to increase in water in some sites due to evaporative concentrations. The highest concentrations in sediments reported were Zn 137.5, Cd 0.92 and Pb 23.9 ppm. These values are found to be much higher than those obtained in the current research possibly due to high rate of evaporation which leads to the variation of pH.

4.3 Mean concentrations (ppm) of heavy metals, total nitrogen and total phosphorus in soil.

Mean concentrations of Zn, Co, Mn, Cd, Cu, Pb, Cr, total N and total P in soil samples were obtained in various plots within the swamp (Dominion Farm). The results are summarized in Figures 19 to 28 and in tables (Appendix 22 – 26). The farm was divided into various plots to establish a trend within a particular field. The sampling of soil was done according to field A, B, C and D.

4.3.1 General trend in field A

There was a general increase in the mean concentrations of Zn in soil in field A. The lowest value was noted in plot A1 (0.327 ± 0.003) while the highest value was in plot A3 (0.412 ± 0.003) as illustrated in the table (Appendix 22) and Figure 19. These values were twelve times lower than the maximum value of 5.000 ppm set by WHO/FAO and KEBS.

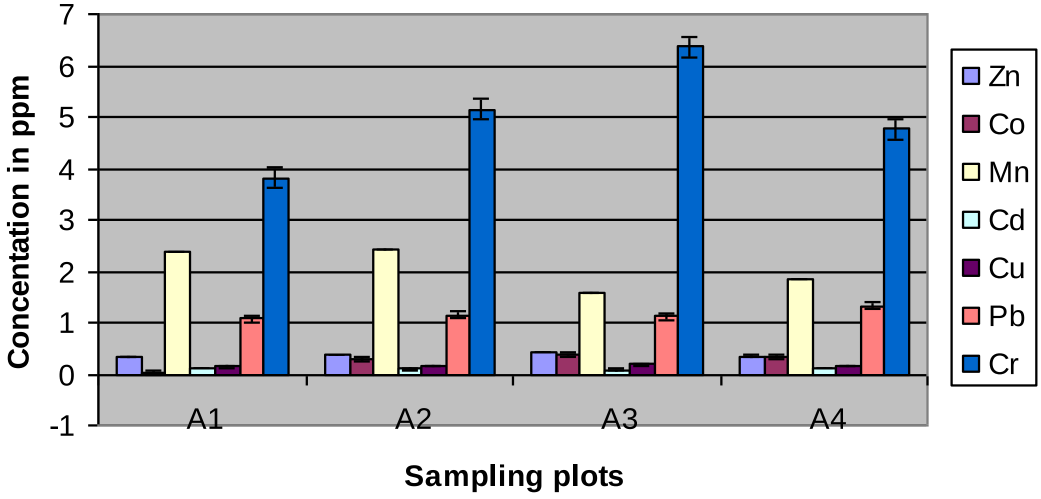

Figure 19: Concentration of heavy metals (ppm) in soil in field A

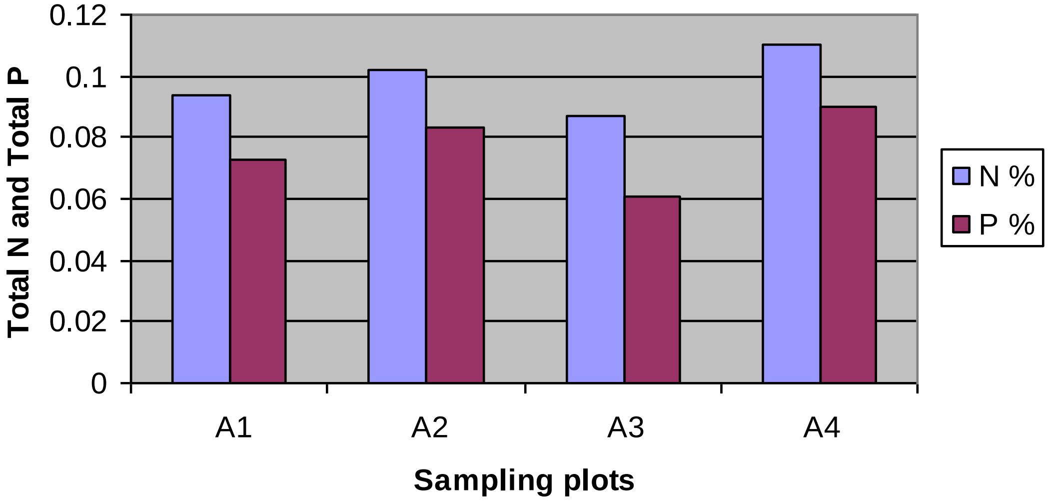

Figure 20: Concentration of total phosphorus and total nitrogen in soil in field A

This means that Zn products are not available in this field or the field is not exposed to municipal sewage and waste water, which are major sources of Zn in the environment.

Mean concentration level of Co in field A increased, with the highest level recorded in plot A3 (0.372 ± 0.057) while the lowest was in plot A1 (0.023± 0.000). The values were on average three times higher than the recommended value of 0.100 ppm by WHO/FAO. The decrease in Co level in plot A1 could be due to dilution by water getting into the plot. It could also be because Co products are not commonly used in this area; hence Co detected could be from the parent rock.

Mean concentration levels of Mn fluctuated between the highest value of 2.430 ± 0.002 in plot A2 and the lowest value in plot A3 (1.565 ± 0.002) as illustrated in Figure 19 and in the table (Appendix 22) . The values were approximately twenty two times higher than the maximum recommended value of 0.100 ppm by WHO/FAO and KEBS. High values could be due to natural mineralogical sources such as parent material and also application to the soil of compounds containing Mn, which is normally in the form of $MnSO_4$, MnO or as an addition to macronutrient fertilizers. Fluctuation in concentration could be due to dilution as water from the river floods the swamp.

The mean concentration of Cd was averagely constant in the soil in field A. The highest value was in plot A4 (0.092 ± 0.003) while the lowest was in plot A3 (0.088 ± 0.002). The values were approximately thirty times higher than the maximum limit prescribed by WHO/FAO of 0.003 ppm. These levels in river waters vary between 1 and 2 µg/l but can be elevated in areas with natural sources (WHO, 1996).

There was a general increase in the mean concentration of Cu in field A. The highest value was noted in plot A3 (0.188± 0.016) while the lowest was in plot A1 (0.151± 0.004). These values were approximately 0.2 times lower than maximum limit of 1.000 ppm by WHO/FAO but 1.5 times higher than that set by KEBS of 0.100 ppm. High Cu level could be due to the use of Cu as a component of most pesticides in farms around the swamp and also as a result of natural weathering of rocks and discharge into river Yala from sewage treatment plants. Other sources could be surface water and soil solutions from the area as Cu is known to be relatively abundant in free state as sulphides, arsenides, chlorides and carbonates in the environment as observed and reported earlier (WHO,1998).

Mean concentration levels of Pb generally increased in the plot in field A. The highest recorded value was in plot A4 (1.326 ± 0.105) while the lowest was in plot A1 (1.070 ± 0.076). These values were averagely one hundred and ten times higher than the maximum limit of 0.01 ppm set by WHO/FAO but almost eleven times higher than 0.100 ppm set by KEBS. High levels of Pb could be attributed to its natural availability in soils as a result of weathering of rock fragments on which soil develops (Omoga and Kagwanja, 1999). It could also be due to motor vehicles operating in the farm area which still use leaded petrol and also exposure of soil to contamination and precipitation of Pb compounds. Lead in the soil could be mobilized to water bodies and hence rendering the water unsafe for drinking due to Pb poisoning.

The mean concentration level of Cr fluctuated between the highest value of 6.373 ± 0.194 in plot A3 and the lowest in plot A1 (3.821 ± 0.415). The values were however, far much higher than maximum limit recommended by WHO/FAO of 0.050 ppm. These high levels could be due to availability of the metal and its related compounds in the environment and the use of Cr related products such as seed protectants and wood preservatives.

There was a general increase in total N and P in field A. The highest level of N was noted in plot A4 (0.110) and the lowest in plot A3 (0.087). The highest level of P was noted in plot A4 (0.090) while the lowest in plot A3 (0.061). These high levels in plot A4 could be attributed to washing of nitrogenous and phosphate fertilizers from farms into surface water.

4.3.2 General trend in field B

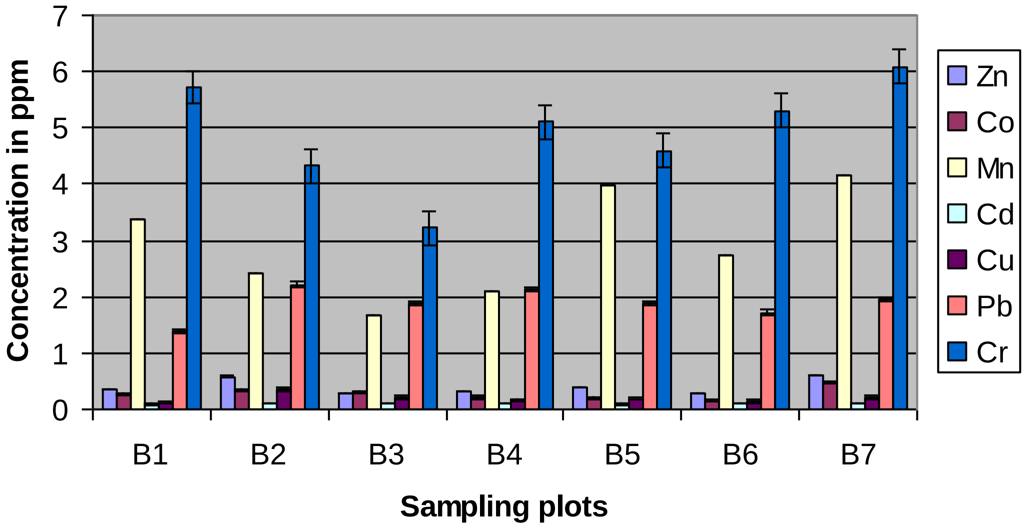

Figure 21: Concentration of heavy metals (ppm) in soil in field B

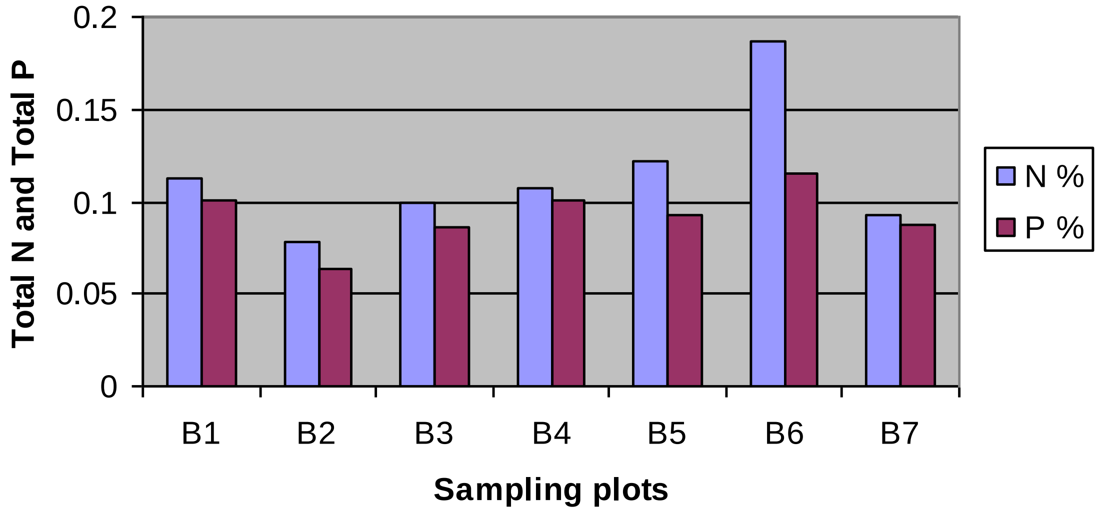

Figure 22: Concentration of total phosphorus and total nitrogen in soil in field B

The highest mean concentration level of Zn in soil in field B was noted in plot B7 (0.592 ± 0.006) while the lowest value in plot B3 (0.276 ± 0.002). These values were lower than the maximum limit of 5.000 ppm recommended by WHO/FAO and KEBS (Appendix 4). The mean concentration of Co ranged between the highest value of B7 (0.466 ± 0.128) and the lowest value of B6 (0.154 ± 0.000). The values were, however, higher than the recommended value of 0.100 ppm by WHO/FAO and also higher than those in water because of the precipitation of Co compounds.

Recorded mean concentration of Mn in soil in field B was highest in plot B7 (4.144± 0.017) and lowest in B3 (1.668± 0.002). The values were, on average, forty one times higher than the recommended maximum limit of 0.100 ppm by WHO/ FAO and KEBS. This high concentration could be because of the natural sources since Mn commonly occurs as mineral oxides birnessite and vernadite. The other significant source of Mn in soil is its application to deficient soil in the form of $MnSO_4$, MnO or as an addition to macronutrient fertilizers.

Mean concentration of Cd was highest in plots B2 and B7 (0.106 ± 0.008) and lowest in B5 (0.093± 0.010). The values were higher than the recommended maximum of 0.003 ppm by WHO/FAO. The values of Cu fluctuated between the highest value in B2 (0.356 ± 0.005) and lowest in B1 (0.120 ± 0.010), which was lower than the maximum value of 1.000 ppm set by WHO/FAO but higher than 0.100 ppm set by KEBS.

Mean concentration values of Pb in soil fluctuated between the highest value recorded in plot B2 (2.220 ± 0.046) and the lowest in plot B1 (1.391± 0.043). These values were higher than the maximum recommended limit set by WHO/FAO and KEBS of 0.010 ppm and 0.100 ppm, respectively. This could be attributed to exhaust emissions from vehicles and also effluents from factories discharged into river Yala. Fluctuation in levels could be due to dilution as water flows into the swamp.

The mean concentration of Cr was the highest recorded in soil in field B. The highest value was recorded in plot B7 (6.093 ± 0.247) while the lowest was in plot B3 (3.219 ± 0.081) exhibiting a general increase in concentrations. The values were, however, much higher than 0.050 ppm recommended by WHO/FAO. This high level of Cr could be from Cr related products such as fungicides which are used in the farm.

There was a general increase in the concentration of N in field B. The highest and lowest levels were B6 (0.187) and B2 (0.078) respectively. It was also noted that this level was higher than that recorded in field A. Since field B is closer to the lake, it implies that there is a possible accumulation in amounts of this nutrient towards the lake. This trend is dangerous because high levels of nitrogen can cause eutrophication with subsequent algal blooms and oxygen depletions. The concentration of P fluctuated between the highest level in plot B6 (0.115) and the lowest in plot B2 (0.064). The highest level in plot B6 could be attributed to the closeness of the plot to the lake since the runoff tends towards the lake. The presence of P in the field could be due to use of household detergents and over use of phosphate fertilizers. In lakes and rivers, excessive amounts of P results in eutrophication (Oram, 2003).

4.3.3 General trend in field C

Mean concentration level of Zn in soil in field C was highest in plot C6 (0.605 ± 0.010) and lowest in plot C4 (0.261 ± 0.014) thereby giving a general increase within the plots as shown in Figure 23. The values were, however, lower than the maximum limits set by the WHO/FAO and KEBS of 5.000 ppm.

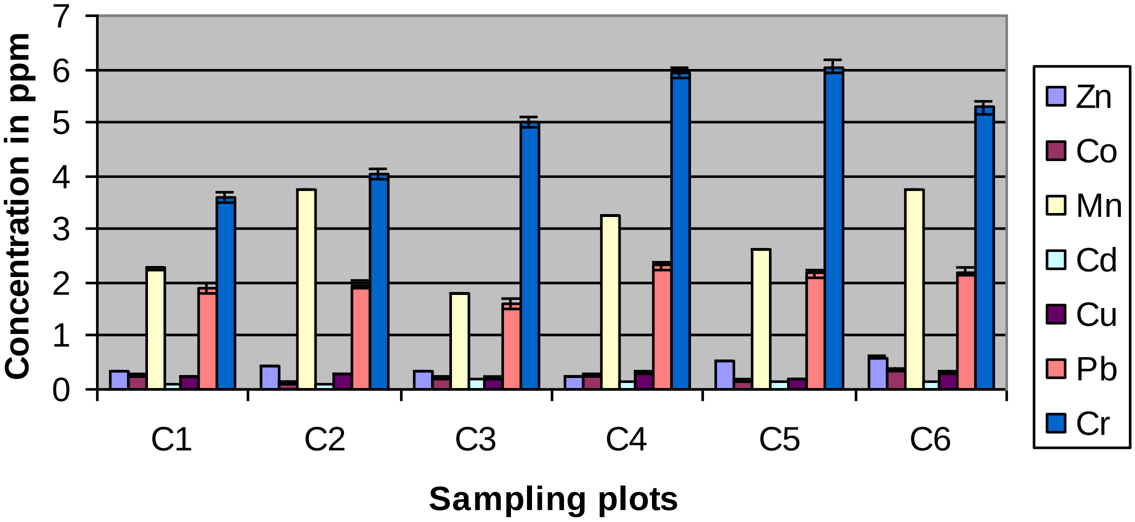

Figure 23: Concentration of heavy metals (ppm) in soil in field C

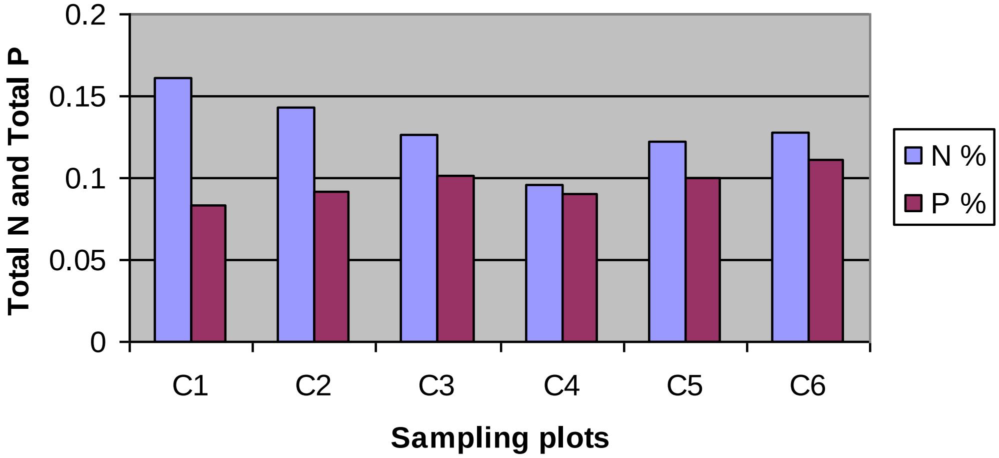

Figure 24: Concentration of total phosphorus and total nitrogen in soil in field C

Cobalt showed fluctuating concentrations with the highest being noted in plot C6 (0.378 ± 0.031) while the lowest in plot C2 (0.139 ± 0.074). These were averagely two and half times higher than maximum values set by WHO/FAO of 0.100 ppm. The mean values of Mn in soil recorded in field C was highest in plot C2 (3.762 ± 0.004) and lowest in plot C3 (1.791± 0.005). The values were higher than maximum limit set by the WHO/FAO and KEBS of 0.100 ppm. Concentration of Cd showed average values ranging between the highest in plot C3 (0.192 ± 0.006) and the lowest in C1 (0.104 ± 0.005). They were fifty five times higher than the WHO/FAO maximum limits of 0.003 ppm. The values in water were lower than those in soil due to precipitation of Co compounds.

The values of Cu in soil fluctuated between the highest value in plot C4 (0.327± 0.049) and the lowest value in plot C5 (0.194± 0.017). These values were lower than the WHO/FAO maximum limits but higher than the KEBS values (Appendix 4). Seepages of the natural Cu from the mining sites find their way into the soil which encourages increased levels in soil. This could also be attributed by the fact that Cu compounds precipitate more in soil than in water.

Significant increase was noted in the mean concentration of Pb in soil in field C. The highest value was in plot C4 (2.321 ± 0.064) while the lowest in plot C3 (1.600 ± 0.070). These values were higher than the recommended WHO/FAO and KEBS values (Appendix 4). The highest mean value of Cr was recorded in plot C5 (6.050±0.154) and the lowest in plot C1 (3.590 ± 0.097) in which they were found to be higher than the WHO/FAO and KEBS values (Appendix 4).

The highest concentration of N was in plot C1 (0.161) and the lowest in plot C4 (0.096) while for P, the highest was in plot C6 (0.111) and the lowest in plot C1 (0.083) as illustrated in Figure 24. The values were far much lower than the maximum allowable limits for domestic water (Appendix 1).The mean concentrations of total N and P in field C were noted to be slightly higher than those in field B. There existed a general increase in concentration of the elements towards the lake and this could lead to over enrichment of lake water which could disturb the ecosystem.

4.3.4 General trend in field D

There was a significant increase in the concentration of Zn in field D with the highest level noted in plot D5 (0.541± 0.017) and the lowest level in plot D2 (0.357 ± 0.004). The values were lower than that set by the WHO/FAO and KEBS of 5.000 ppm. Zinc concentrations increased probably evaporative concentrations since water was stationery in some fields. It is also possible that weeds in the fields when they die or are burnt, may have contributed to Zn concentration rise (Etherington, 1982). The highest concentration of Co was noted in plot D5 (0.360 ± 0.063) and the lowest in plot D2 (0.175 ± 0.012). These values were slightly higher than the maximum set limits of 0.100 ppm by WHO/FAO. This could be due to the water logging nature of the surrounding soils, which accounted for much of increased Co levels.

The highest concentration of Mn was recorded in plot D5 (4.120 ± 0.036) and the lowest in D3 (2.224 ± 0.006), these being higher than the maximum values set by WHO/FAO and KEBS (Appendix 4). The values increased with decreasing distance from the trench.

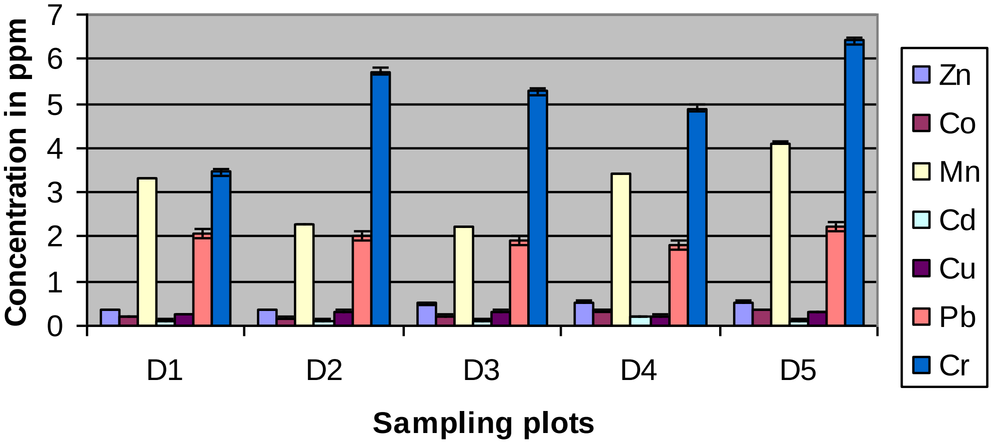

Figure 25: Concentration of heavy metals (ppm) in soil in field D

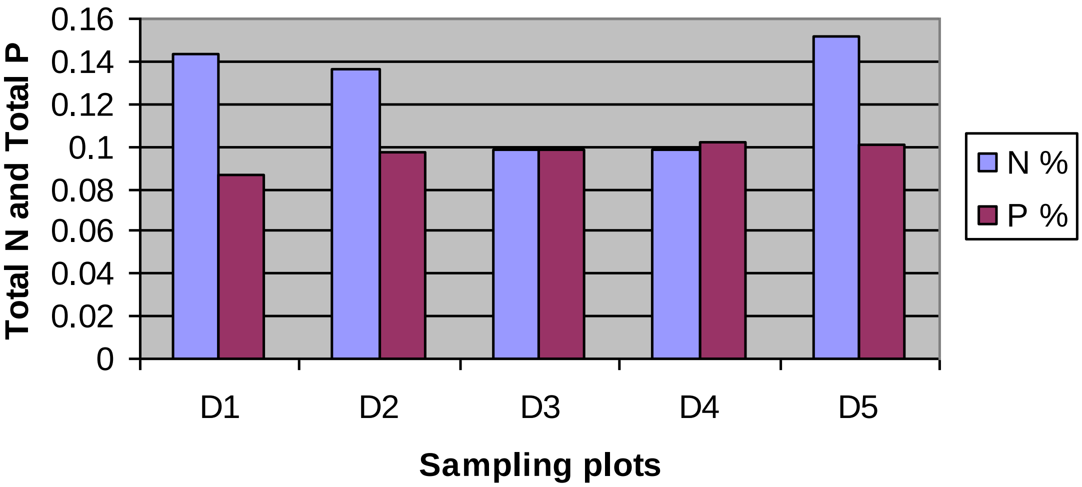

Figure 26: Concentration of total P and total N in soil in field D

However, the concentration of Cd fluctuated between the highest in D4 (0.211± 0.012) and the lowest in D3 (0.113± 0.026) these being averagely seventy times higher than the maximum limit recommended by WHO/KEBS of 0.003 ppm. This could be due to the dissolution of minerals and ores from industrial effluents into river Yala from its source.

Cadmium concentrations were generally low. The values varied progressively indicating that Cd concentration least depended on evaporation and enrichment from dead plant materials. According to Stumm and Morgan (1984), the elements Pb, Cd and Zn were expected to precipitate out.

The concentration of Cu fluctuated between the highest value in D3 (0.328 ±0.194) and the lowest in D1 (0.260 ± 0.061). The values were higher than the maximum set limit of 0.100 ppm by KEBS but lower than that by WHO/FAO of 1.000 ppm. The high values could be due to industrial effluents and runoff containing Cu transported in river Yala. Seepages of Cu from sand mining sites around the river increase its level in the soil. The concentration of Pb fluctuated between the highest value in D5 (2.224± 0.098) and the lowest in D4 (1.811 ± 0.168) which were higher than the values by WHO/FAO and KEBS of 0.010 and 0.100 ppm respectively.

The concentration of Cr was significantly higher than those of all other heavy metals in this field. The highest value was recorded in plot D5 (6.415 ± 0.015) and the lowest in plot D1 (3.453 ± 0.048) which were much higher than 0.050 ppm recommended by WHO/FAO. The values in soil samples were, however, higher than those in water samples. This could be due to the fact that most Cr compounds are insoluble and therefore incorporated into soil and sediments. The high level of Cr could mean that Cr related compounds are used much in the surrounding areas.

Moderately high values of total N and P were recorded field D since the field is also located towards the lake causing more accumulation of the elements. The highest value of N was in D5 (0.152) while the lowest was in D3 and D4 both recording same value of (0.098). Phosphorus ranged between the highest in D4 (0.102) and the lowest in D1 (0.086).

4.3.5 Mean concentration of the elements in the four fields

The average mean concentration of the contaminants in soil in the four major fields A, B, C and D was worked out from the concentration of the contaminants in the plots. This is illustrated in the table (Appendix 26) and Figures 27 and 28.

From the values recorded in the table and in the figures, it is seen that field D had the highest mean concentrations of most of the elements analyzed. It had the highest values of Zn (0.462 ± 0.010), Mn (3.071 ± 0.012), Cd (0.136 ± 0.014), Cu (0.289 ± 0.107), Cr (5.151 ± 0.061) and P (0.097 ± 0.002 %). However, field B recorded the highest concentration of Co (0.280 ± 0.076) while field C had the highest in Pb (2.027 ± 0.064) and N (0.129 ± 0.010). All the four fields A, B, C and D, had high value of Cr of 5.028, 4.909, 4.986 and 5.151 ppm respectively. This translates into an average value of 5.017 ppm, which is far much higher than the recommended value of 0.050 ppm by WHO/FAO.

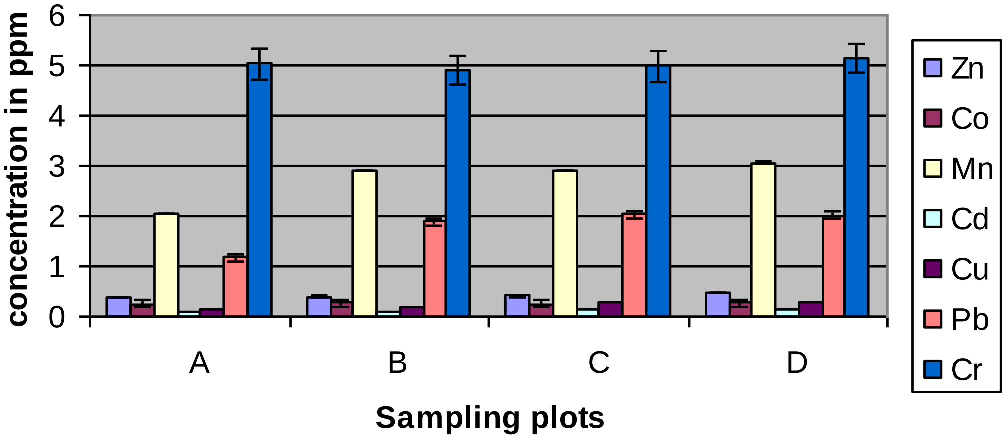

Figure 27: Mean concentration of heavy metals in different fields in soil

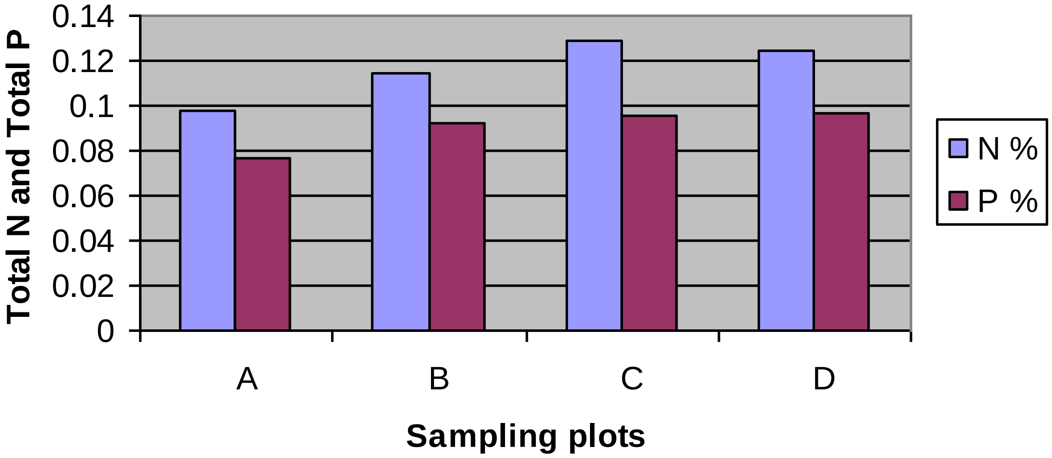

Figure 28: Mean concentration of total P and total N in different fields in soil

This high concentration could be attributed to water logging nature of the surrounding soils, which accounted for much of increased Cr levels. It could also be linked to the high density metal workshops near the farm and extensive use of seed protectants and Cr related products such as fungicides which are used in the farm and in wood preservatives. These levels of Cr should be checked as they are readily mobilized into solution.

The concentration of Zn was relatively constant in all the fields. Probably this may be attributed to contamination from the metal works and paints, which are eventually washed to the fields. The washout is particularly influenced by the acidic conditions and the diffused discharge caused by corrosion (Ohnesorge and Wilheim, 1991).

Manganese was the second highest in concentration giving an average value of 2.740 ppm, which is higher than the recommended value of 0.100 ppm by WHO/FAO and KEBS. This could be attributed to the parent material since the concentration found in mineral salts could reflect the composition of the parent material. All the rocks of the Earth's crust contain Mn in concentrations which are generally much higher. High levels of Mn in the soil pose a risk because it can be released into the water system, hence its bioavailability.

The order of the heavy metal distribution in all the fields was as follows;

Cr > Mn > Pb > Zn > Co > Cu > Cd

The least concentrated metal was Cd with an average mean value of 0.114 ppm, which is thirty eight times higher than the recommended 0.003 ppm by WHO/FAO. These concentrations could be mainly from natural sources. Field D had the highest concentration of most of the heavy metals among the four fields. Since the field is bordering lakes Kanyaboli and Victoria, it means that the elements are being washed from the farms towards the lakes causing their accumulation. This field also holds the industrial processing unit for the harvested rice and therefore, it receives more of the pollutant emissions from the factory.

Similar analysis was done on heavy metals in surface sediments on the five lakes in Rift valley, lakes Nakuru, Elementaita, Naivasha, Bogoria and Baringo (Ochieng *et al.*, 2007). These researchers reported mean sediment concentrations in µg/g dry weight to be, Zn (96.2 – 229.6), Mn (667.7 – 3946.8), Cu (1.46 – 20.95) and Pb (10.92 – 38.98) which were much higher in some sites due to anthropogenic additions. However, Cd (0.05 – 1.18), Co (0.17 – 1.38) and Cr (1.94 – 4.91) had low concentrations probably due to solubility of their compounds.

Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania was also analysed (Kishe and Machiwa, 2003). The values in ppm of Cu (26.1 ± 4.8), Pb (30.7 ± 5.6) and Zn (45.4± 13.1) were higher, approximately 25 m from the shoreline. Generally, heavy metal concentrations in the sediments decreased with increasing distance from the shoreline except for Cd (7.0± 2.10 and Cr (12.9± 1.0) whose highest concentrations were found at approximately 2,000 m from the shoreline due to the runoff. Areas around Mwanza (urban area) showed elevated levels of Pb (54.6± 11.1) and Zn (83.7± 21.5) due to emissions from motor vehicles and sewage sludges deposition, respectively. The values were, however, much higher than those reported in this present research due to proximity of Mwanza town to the lakeshore.

In another related study, heavy metals in sediments from Makupa and Port- Reitz Creek systems in Kenyan Coast were analysed by Muohi and others in 2003. The levels of Zn, Cu, Cd and Pb were determined. Higher metal concentrations in sediments were obtained in Makupa Creek sediments as follows Cu (102± 46.0), Zn (1017± 840), Pb (103± 35.8) and Cd (51± 14.3) as compared to Port-Reitz Creek Cu (21.6± 7), Zn (57.1± 17.9), Pb (26.2± 11.6) and Cd (1.38± 0.7). Industrial activities and a nearby municipal dumpsite were associated with the higher elemental concentrations particularly in Makupa. This also made the values to be higher than those obtained in this current research.

Further work had also been done on mean total dissolved heavy metals in Winam Gulf (Lalah et *al*., 2008). The concentrations in µg/L obtained were Cd (nd – 8), Co (nd – 23.3), Cr (5 – 50), Mn (50 – 3276), Cu (5 – 157.5), Pb (7 – 93.6), and Zn (25 – 219.5). These values were, however, higher than those obtained in the present study due to industrial activities taking place next to the gulf. Rivers were found to be non- polluted in terms of sediment loads. However, the rivers were polluted because of elevated levels of Pb, Mn, Cu and Zn.

Research on heavy metal analysis was also done in street and house dust in Bahrain (Akhter and Madany, 1993). Dust samples contained significant levels of the metals studied compared with the control values. The mean values for Pb, Zn, Cd, Ni and Cr in street dust were 697.2, 151.8, 72.0 125.6 and 144.4 μgg^{-1}, respectively while household dust contained 360.0, 64.4, 37.0, 110.2 and 144.7 μgg^{-1}. This suggests that motor vehicles form a major source of heavy metal just like in Yala swamp. The values of heavy metals in dust samples were not in agreement with the values found in this study and were found to be higher.

The average values of total N concentration were 0.117 and that of P was 0.091. Nitrogen was highest in field C while P was highest in field D. This is as a result of the leaching effect in soil.

4.3.6 Comparison of the concentration levels of the elements in water and soil

The average concentration levels of the contaminants, heavy metals, total N and total P in both water and soil were compared for fields A, B, C and D to determine the medium with the highest level. The results obtained are illustrated in Figures 29 and 30

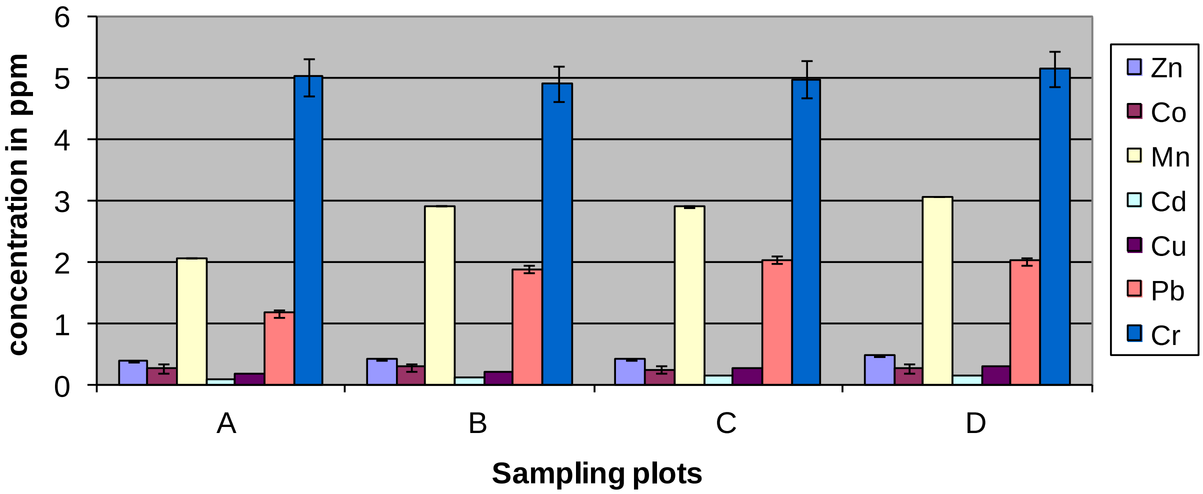

Figure 29: Comparison of levels of heavy metals in water and soil in field A

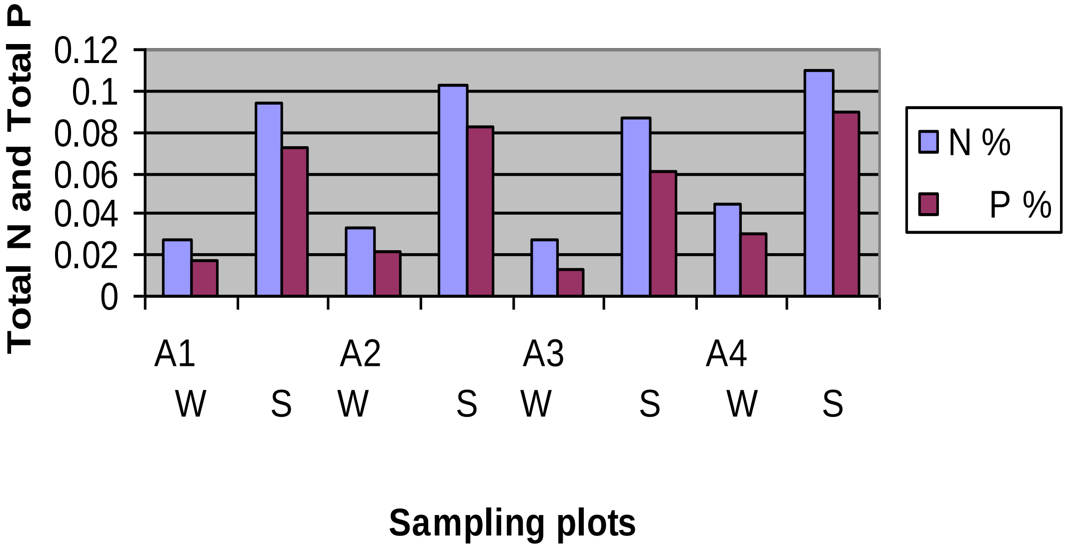

Figure 30: Comparison of levels of total N and total P in water and soil in field A

Figures 29 and 30 and the table (Appendix 20) show the results of comparison of the levels of heavy metals, total N and total P in water and soil taken from same sampling field A. From the table it can be noted that Zn and Co had higher values in soil than in water. This is attributed to the precipitation of their compounds from municipal sewage and waste water pollutants. Both Cd and Cu had higher concentrations in water than in soil. Manganese, Cr and Pb had their higher concentrations fluctuating between water and soil which could be attributed to solubility and precipitation of some of their compounds.

The mean concentration of Cu was found to be higher than 0.100 ppm set by KEBS, but lower than 1.000 ppm set by WHO/FAO. These high levels could be attributed to natural weathering of rocks and discharge from sewage treatment plants. Other sources could be agricultural farms, where Cu compounds are used as fungicides. Copper is also known to be relatively abundant in free states such as sulphides, arsenides, chlorides and carbonates in the environment (WHO, 1998).

The mean concentration values of Mn fluctuated within field A. The highest mean in soil was in plot A2 (2.430 ± 0.002) and the lowest in plot A3 (1.565 ± 0.002) which are higher than the maximum set limit by WHO/FAO and KEBS (Appendix 4).

The mean concentration values of Zn in soil and water fluctuated by increasing and then decreasing within field A. The levels were, however, higher in soil than in water. The fluctuation in the levels could be attributed to dilution, while the high levels in soil could be due to precipitation of Zn compounds, hence, incorporated into the soil. Low values in water may also be due to few soluble Zn compounds. The highest concentration in soil was in plot A3 (0.417 ± 0.003) while the lowest was in plot A1 (0.327 ± 0.003). The highest level in water was in plot A2 (0.204 ± 0.005) while the lowest in A3 (0.181 ± 0.004). These concentrations were lower than the maximum limit set by WHO/FAO and KEBS of 5.000 ppm. Zinc levels were, therefore, low and do not pose any danger to human life. Lead and Zn tended to increase. This could probably be due to varying dilution in the fields.

Mean concentration of Cr and Pb were higher in soil than in water in almost half of the plots in field A. The highest concentration of Cr in soil A3 (6.378 ± 0.194) was over one hundred times higher than the maximum limit of 0.050 ppm by WHO/FAO while that of Pb was in water A4 (2.410 ± 0.022) The high level of Cr could be due to increased use of its related products such as fungicides, seed protectants and also wood preservatives in the farm. In general there was more Pb in water than in soil in this field. This could be attributed pH and temperature variations of water in the farm. Lead compounds formed are soluble and are therefore not precipitated and incorporated in soil and sediments.

The concentration of Cd was higher in water than in soil. Its highest value in soil was noted as A4 (0.092 ± 0.003) and the lowest as A3 (0.088 ± 0.021). These were however higher than the maximum limit set by WHO/FAO of 0.003 ppm. This could be due to high levels of Cd in the surrounding soils since it is a component of phosphate fertilizers and the phosphate rock (WHO, 1998). Other sources could be due to forest fires, which may lead to the release of Cd related oxides in the environment and metal particles enrichment from terrestrial vegetation (ILZS Group, 1983).

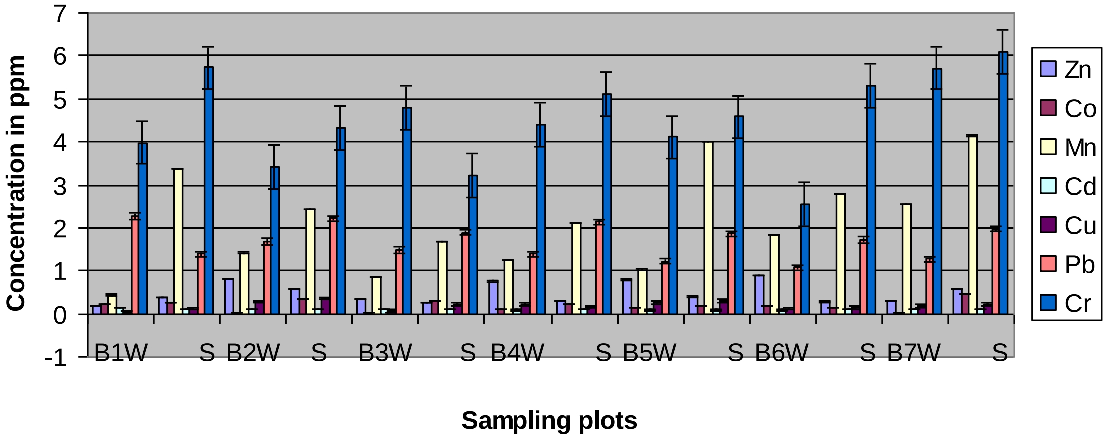

Figure 31: Comparison of levels of heavy metals in water and soil in field B

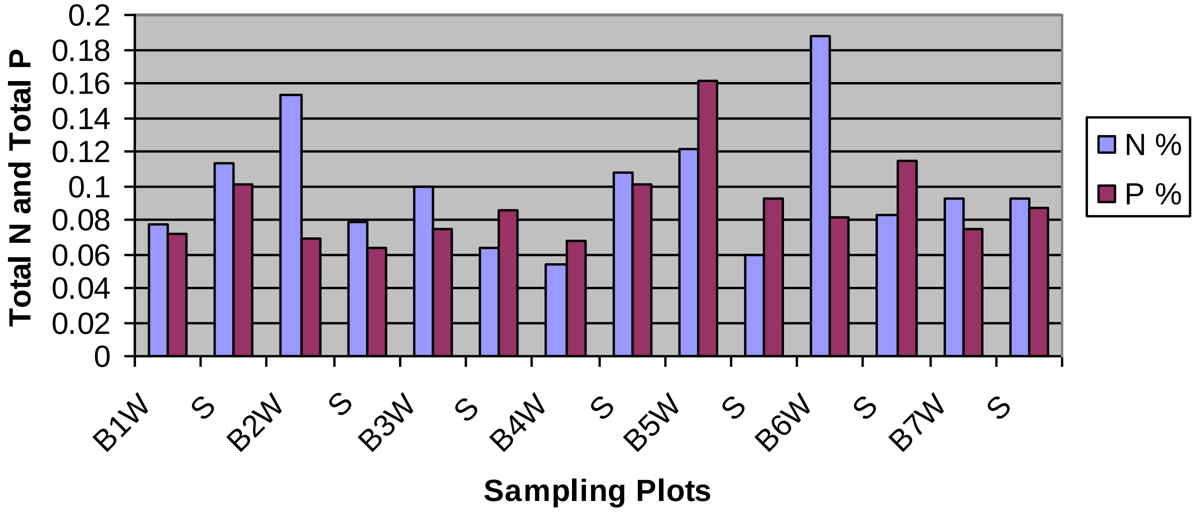

Figure 32: Comparison of levels of total N and total P in water and soil in field B

The concentration of Zn was mostly higher in water than in soil even though the values were lower than the recommended value of 5.000 ppm by WHO/FAO and KEBS (Appendix 4).Cobalt, Mn, Cu, Pb and Cr had higher concentrations in soil than in water except in a few cases. This could be attributed to the insoluble nature of most of their compounds. High level of Cr could be due to increased use of its related products such as fungicides, seed protectants and wood preservatives in the surrounding area. Half of the plots in this field had higher concentration of Cd in water than in soil which could be attributed to dilution by incoming water which causes water logging.

Awofolu et al., 2005 carried out a research work on levels of trace metals in water and sediment from Tyume River in vegetables and soil from nearby farmland. Higher levels of Cd (0.038± 0.004 to 0.044± 0.001 mg/l) and Pb (0.021± 0.004 to 0.035± 0.001 mg/l) were found in water most probably due the use of Cr related compounds and tetraethyl lead motor vehicle fumes.

Most of the plots had more N in water than in soil except in plot B1 and B4 which had higher N in soil than in water, which could be due to solubility of nitrates. Plot B7 had equal concentration of N in water and soil at 0.093. Total P was mostly higher in soil than in water because phosphate compounds form precipitates which are available in soil and sediments. These levels should be checked because during anaerobic conditions phosphates may be released back into water.

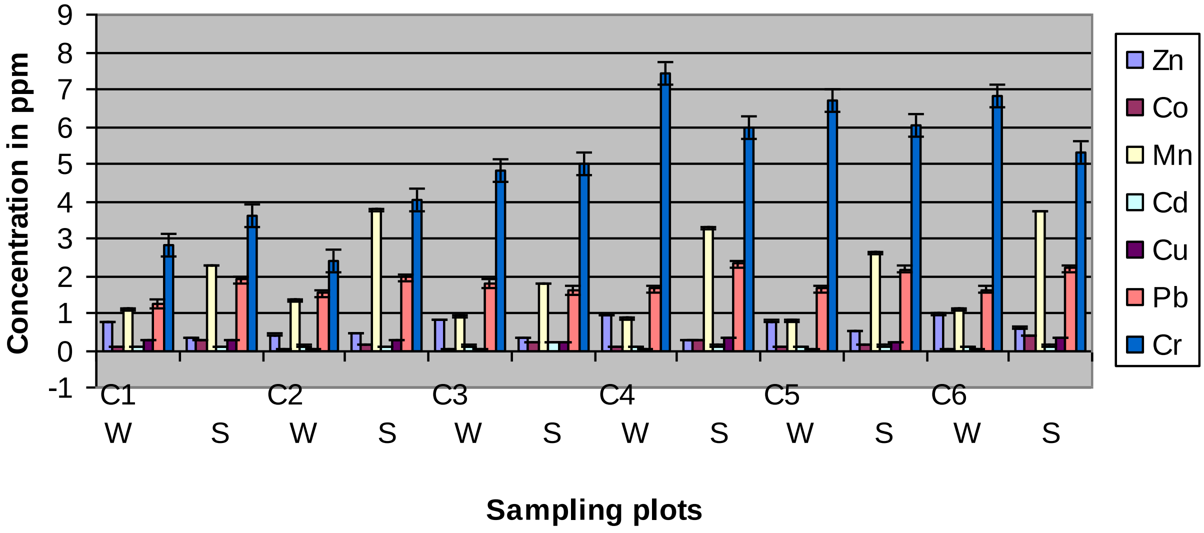

Figure 33: Comparison of levels of heavy metals in water and soil in field C

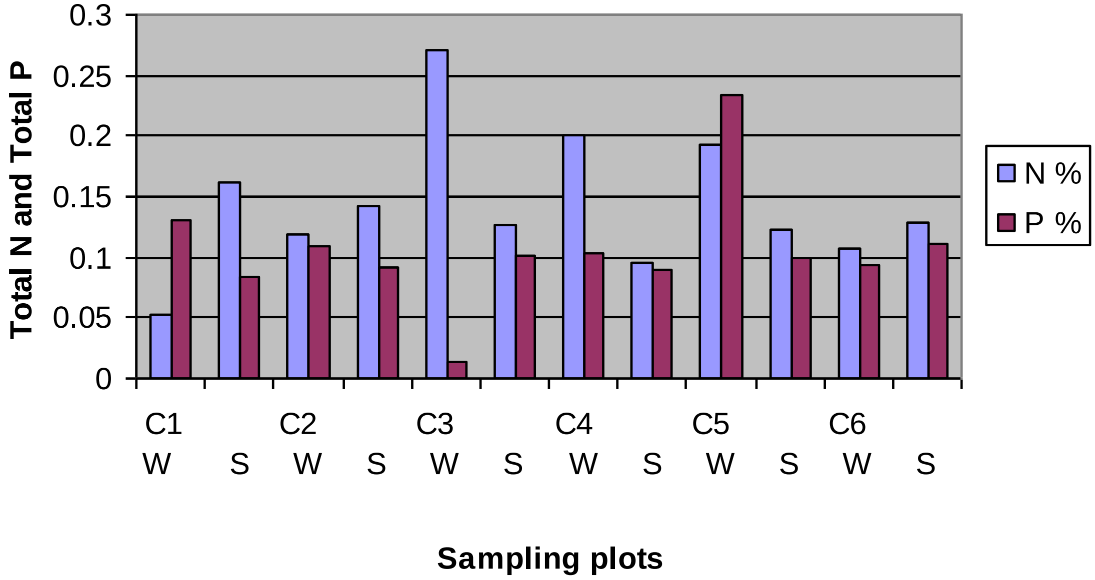

Figure 34: Comparison of levels of total N and total P in water and soil in field C

Zinc had generally higher concentrations in water than in soil which could be attributed to dilution by the incoming water and also as a result of more soluble Zn compounds. Its presence in soil could be due to precipitation of some of its compounds hence incorporated into soil. The concentrations in water were between C2 (0.423 ± 0.003) ppm and C6 (0.971 ± 0.009) ppm which were lower than the maximum limits set by WHO/FAO and KEBS (Appendix 4).

Half of the plots in this field had higher concentrations of Cr in soil. The values were moderate and could be attributed to its natural abundance in the environment. Cobalt, Mn, Cd, Cu and Pb mostly had higher concentrations in soil than in water which could be attributed to precipitation of their compounds and incorporation into soil. High levels of Cd in soil could be due to its high levels in the surrounding soils, since it is a component of phosphate fertilizers and phosphatic rock and also due to its possible availability in Cd related residues.

Concentration of N in water fluctuated between a maximum value of C3 (0.271) and a minimum of C1 (0.052) while in soil it was between C1 (0.161) and C4 (0.096). Concentration of P in water was between a maximum of C5 (0.234) and a minimum of C3 (0.013) while in soil it was between C6 (0.111) and C1 (0.083). These values are considered low compared to a value of 10 mg/l for quality standard domestic water (Appendix 1).

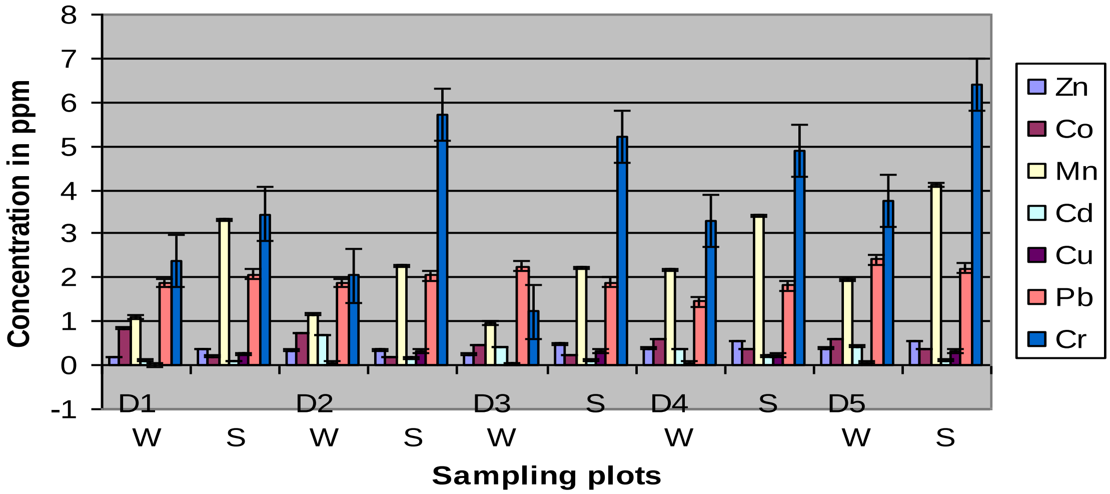

Figure 35: Comparison of levels of heavy metals in water and soil in field D

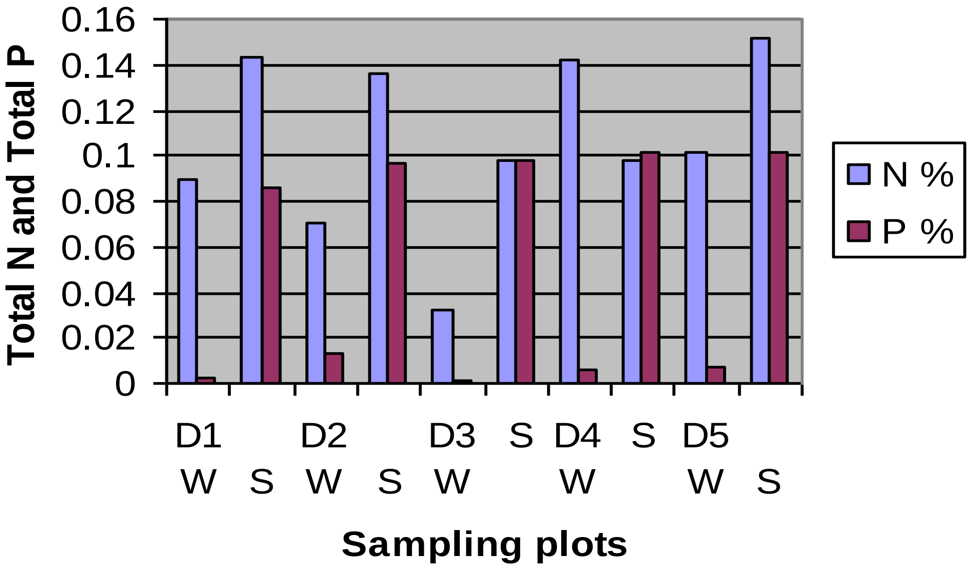

Figure 36: Comparison of levels of total N and total P in water and soil in field D

Zinc, Mn, Cu and Cr had higher concentrations in soil than in water. This could be attributed to the insoluble nature of most of their compounds, which leads to precipitation and availability into soil and sediments. Copper is also known to be relatively abundant in free states such as sulphides, arsenides, chlorides and carbonates in the environment High values of Mn could be due to its application to the soil in form of $MnSO_4$, MnO or as an addition to macronutrient fertilizers.

Cobalt and Cd had higher concentrations in water than in soil. A higher level of Cd in water could be probably due to pH, temperature and hardness of water in the area, which are not favorable for precipitation of Cd. High concentrations of Pb varied between water and soil, which could be due to pH and temperature variations of the water flowing into the swamp. Its high values in soil could also be because Pb compounds formed are insoluble and are therefore precipitated out and found in soil.

There were higher N and P concentrations in soil than in water in field D. Phosphate compounds form precipitates which are found in soil and sediments. Excessive N and P has been the main cause of eutrophication. In the presence of oxygen there is excess algal growth with some being blocked from the sun and die at lower levels. Due to lack of sunlight, bacteria, which try to decompose organic wastes, consume oxygen and release more phosphates.

4.3.7 Overall Mean concentration of the elements in water and soil from fields A, B, C and D

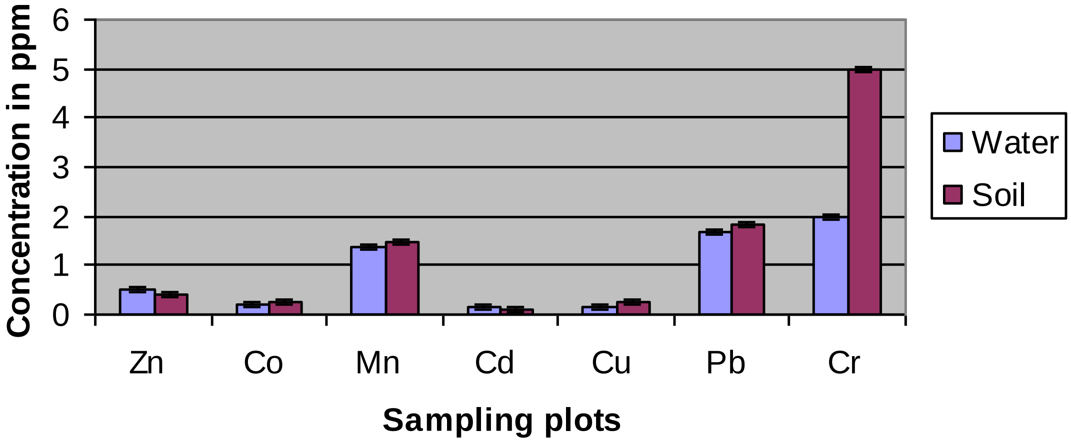

Figure 37: Overall Mean concentration of the heavy metals in water and soil

From the table (Appendix 20) and figures 37 and 38, it can be seen that Co, Mn, Cu, Pb, Cr and total P had their mean concentrations higher in soil than in water. The mean value of Co in all water samples analyzed was 0.219 ± 0.016 ppm, while that in soil was 0.262 ± 0.036 ppm.

Thus the mean value in soil was almost 1.2 times higher than that in water. This could be attributed to the formation of Co compounds which are insoluble like $CoCO_3$, hence precipitation takes place and the particles eventually get incorporated into soil and sediments.

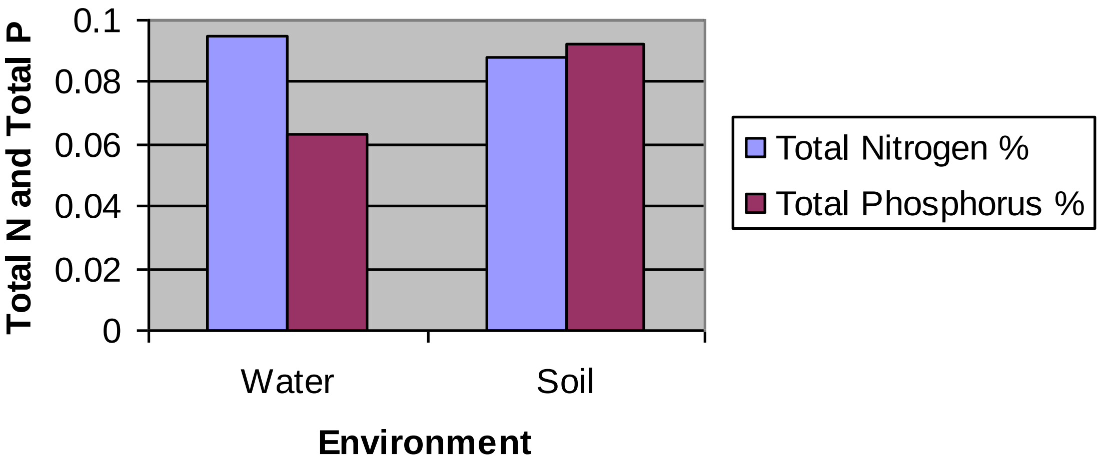

Figure 38: Overall Mean concentration of total P and N in water and soil

The value of Cu in water was 0.129 ± 0.049 ppm while that in soil was 0.237 ± 0.059 ppm. Thus the mean in soil was approximately 1.8 times higher than the value in water. This could be attributed to the precipitation of Cu compounds and then incorporation into soil and sediments. High value of Mn in soil could be attributed to the parent rock and fertilizers and also to the prevailing conditions in the swamp which favour the precipitation of Mn and incorporation into soil and sediments. Total P was higher in soil possibly due to the precipitation of P compounds.

The values of Zn, Cd, and total N were higher in water than in soil. The high levels of Cd in water could be due to the fact that it is a component of phosphate fertilizers and the phosphatic rock. High level of Zn could be due its more soluble compounds in water. Solubility of N compounds could have led to its high value in water.

The mean concentrations of Pb, Cd, Cr, Co and Mn in water and soil were higher than the maximum values recommended by the WHO/FAO and KEBS while for Zn and Cu were lower than those of WHO/FAO and KEBS (Appendix 4).

4.4 Temporal variations in the concentration of selected heavy metals, total nitrogen and total phosphorus

The concentration of the pollutants was determined during the dry season (January/ February) and rainy seasons (May/ June) to find the temporal variation of the pollutants in both water and soil. The results are summarized in the tables (Appendices 28 and 29 and also in Figures 39 to 42.

4.4.1 Temporal variations in the concentrations of selected heavy metals, total nitrogen and total phosphorus in water

Temporal variations in the concentration of elements in water are shown in Figures 39 and 40. All the elements had higher values in water during rainy seasons than in dry seasons. Concentration of Zn was significantly higher during the rainy (0.593 ± 0.016) than in dry seasons, while that of Co was (0.317 ± 0.064) in rainy season and (0.219 ±

0.061) in dry season. That of Mn was (1.776 ± 0.032) in rainy season and (1.352 ± 0.017) in dry season.

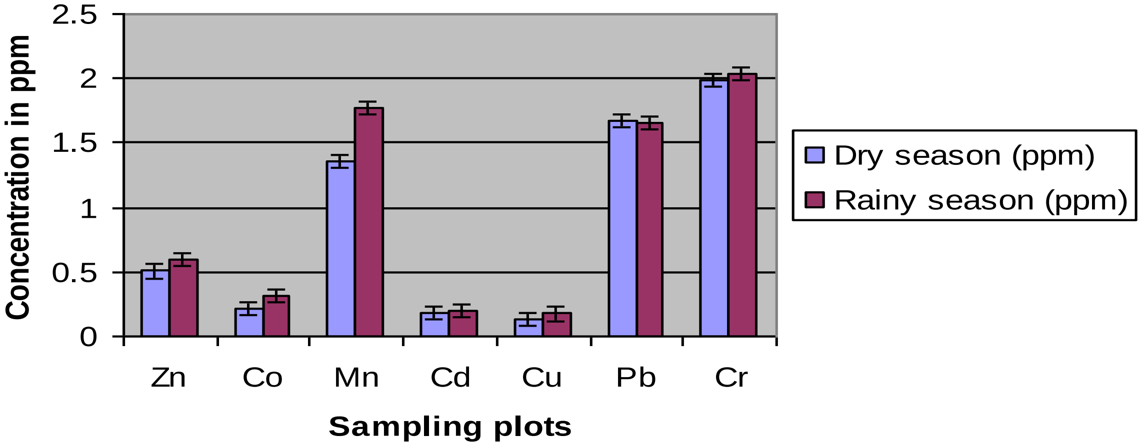

Figure 39: Temporal variation in the concentration of heavy metals in water

No significant difference in concentration was recorded for Pb between rainy season (1.654 ± 0.006) and dry season (1.668 ± 0.068). Likewise concentrations of Cr were higher in rainy seasons (2.030 ± 0.034) than in dry seasons (1.984 ± 0.372). Significant differences were also recorded for Cd and Cu with Cd having (0.203 ± 0.007) in rainy season and (0.176 ± 0.008) in dry season while Cu had (0.174 ± 0.050) in rainy season and (0.129 ± 0.049) in dry season

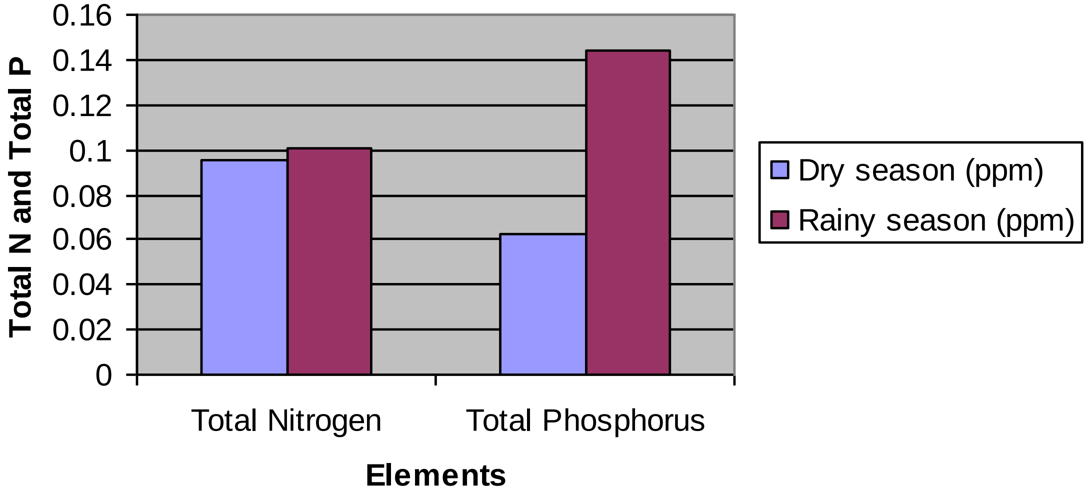

Figure 40: Temporal variation in concentration of total N and total P in water

Higher concentrations observed in rainy seasons compared to dry seasons could be attributed to enhanced runoff during rainy seasons which transport more elements into the swamp. Concentrations of Pb and Cr did not change much probably because these elements have the highest residence time in water than all the other elements analyzed. The values of Cu were quite low during both seasons possibly due to minimal use.

The value of N was (0.101) in rainy season and (0.095) in dry season while that of P was (0.144) in rainy season and (0.063) in dry season. These could be attributed to the runoff from diffuse sources which include urban effluents, factory effluents and agricultural runoffs which contain nitrate and phosphate fertilizers. High phosphate levels could also be due to leachates from waste dumps and municipal runoffs which contain detergents.

4.4.2 Temporal variations of heavy metals, total nitrogen and total phosphorus in soil

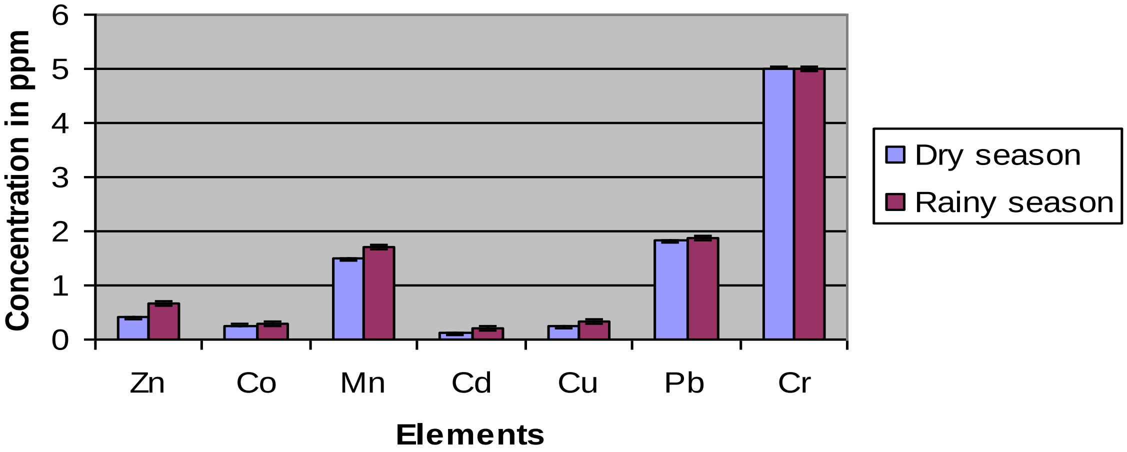

Figure 41: Temporal variation in concentration of heavy metals in soil

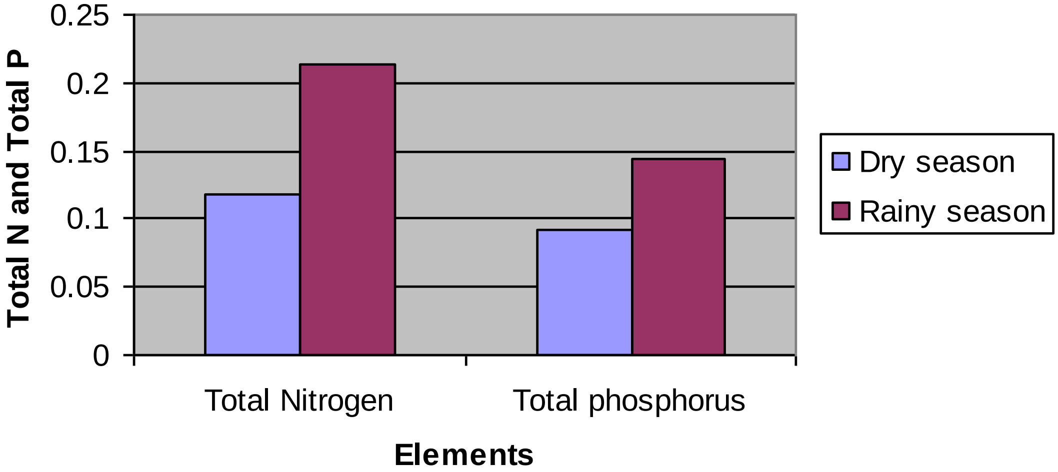

Figure 42: Temporal variation in concentration of total N and total P in soil

Zinc, Mn, Cu and Cd in soil recorded significantly higher values in rainy season than in dry season. No significant differences in concentrations recorded for Co, Pb and Cr between rainy and dry season in the soil samples. Generally the metals analyzed showed an increase in concentrations in rainy seasons compared to dry seasons. This could be due to enhanced runoff from storm water during the rain season which washed away all the heavy metals from municipal areas, paints, garages, lead gasoline or fuel from roads and other non-point sources into river Yala which finally ends up into the Yala swamp.

Seasonal variation in N and P levels showed an increase during the rainy season compared to the dry season. This could be attributed to heightened runoff and the fact that most farmers in the surrounding areas wait for the rainy season which usually coincides with the planting season for annual crops to start applying the nitrate and phosphate fertilizers.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Most contaminants showed variation in concentration between water and soil. Cobalt, Mn, Cu, Pb and Cr all had their concentrations higher in soil than in water while Zn and Cd were the only pollutants with concentrations higher in water than in soil. Among the water and soil samples analyzed, Cr was the most polluting element with a mean value of 1.984 ± 0.372 ppm in water and 5.005 ± 0.403 ppm in soil samples. These values were thirty nine times and one hundred times, respectively higher than the maximum limits set by WHO/FAO. This was followed by Pb with mean levels of 1.668 ± 0.068 ppm in water and 1.820 ± 0.086 ppm in soil samples. These values were sixteen times and eighteen times, respectively higher than KEBS maximum limit and one hundred and sixty times and one hundred and eighty times, respectively higher than the WHO/FAO maximum limits.

Manganese had values of 1.352 ± 0.017 and 1.491 ± 0.007 ppm in water and soil samples respectively. These values were approximately thirteen times higher than the maximum limit set by WHO/ FAO and KEBS. Concentration of Co in water was 0.219 ± 0.016 ppm while in soil was 0.262 ± 0.036 ppm. These values were approximately two times higher than WHO/ FAO maximum limits.

Zinc was the only heavy metal whose mean concentration in water and soil was below the maximum permissible limits set by WHO/ FAO and KEBS. Its mean concentration in water was 0.505 ± 0.006 ppm and in soil was 0.415 ± 0.006 ppm; however, the maximum set limit is 5.000 ppm.

The least polluting heavy metal in water samples was Cu with a mean value of 0.129 ± 0.049 ppm while for soil samples it was Cd with a mean value of 0.117 ± 0.013 ppm. All these concentrations were higher than the maximum permissible limits set by WHO/FAO and KEBS.

Total N and total P also showed a similar pattern with soil exhibiting higher levels than water. The mean concentration of N in water was 0.095 while in soil was 0.088 ppm. That of P in water was 0.063 while in soil was 0.092 ppm. The values were lower than those permissible by the NEMA of 10 ppm (Appendix 1)

Heavy metals, nitrates and phosphates end up in the water of river Yala and finally settle in water and soil of the swamp. Plots with higher levels should be viewed with caution as it implies that the elements can be preferentially released into the products from the farm making them bioavailable.

It was also established that the contamination of soils and water within the swamp is affected by temporal variations which was particularly higher during rainy season compared to the dry season.

5.2 Recommendations

On the basis of the findings of this study after the analysis, the following recommendations are made:

1. Proper treatment of industrial discharge should be carried out using modern techniques to reduce the concentration of pollutants in water and soil.
2. Controlled use of fertilizers should be done to avoid excessive application of nutrients in the water and soil.
3. Natural compost manure such as animal dung, ash, natural phosphates should be used to avoid soil becoming impoverished and to obtain abundant harvest.
4. Further research should be carried out to identify crops or vegetation that can take up heavy metals, nitrates and phosphates from water and soils since these can be planted within the swamp to purify water by removing these contaminants. This can help reduce chances of poisoning humans and animals through ingestion of heavy metals.
5. There should be continued monitoring of the status of heavy metal contamination of river Yala and its surrounding. Present and past baseline information should be used to monitor the levels and improve management practices.

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LIST OF APPENDICES

Appendix I: Quality standards for sources of domestic water

PARAMETER	GUIDE VALUE (MAXIMUM ALLOWABLE)
Nitrate-NO_3	10 mg/l
Phosphate-PO_4	10 mg/l
Total suspended solids	1200 mg/l
Cadmium	0.01 mg/l
Lead	0.05 mg/l
Copper	0.05 mg/l
Zinc	1.5 mg/l
Chromium	0.1 mg/l

Source: Environment management and co-ordination (water quality) regulations.

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Appendix II: Standards for recreational water

PARAMETER	MAXIMUM PERMISSIBLE VALUE
Cadmium	0.01 mg/l
Lead	0.05 mg/l
Copper	0.05 mg/l
Chromium	0.1 mg/l
Zinc	1.5 mg/l

Source: Environment management and co-ordination (water quality) regulation.

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Appendix III: Standard effluent discharge into the environment

PARAMETER	MAXIMUM ALOWABLE LIMITS
Cadmium	0.01 mg/l
Chromium	0.05 mg/l
Copper	1.0 mg/l
Lead	0.01 mg/l
Zinc	0.5 mg/l

Source: Kenya Bureau of Standards, KEBS, first revision, 1996

Appendix IV: WHO /FAO and KEBS recommended concentration limits of heavy metals in foodstuffs and drinking water

METAL	WHO /FAO MAXIMUM LIMITS (ppm)	KEBS MAXIMUM LIMITS
Pb	0.01	0.100
Cd	0.003	NA
Cr	0.050	NA
Cu	1.000	0.100
Zn	5.000	5.000
Co	0.1	NA
Mn	0.100	0.100

NA – Data not available

Source: KEBS, 1996

Appendix V: Agricultural land use in the catchment area

CROP	AREA (Ha)	%
Maize	550,000	48.2
Beans	200,000	17.5
Sugarcane	110,000	9.6
Sorghum	60,000	5.2
Cassava	40,000	3.5
Bananas	35,000	3.0
Cotton	30,000	2.6
Millet	25,000	2.2
Sweet Potatoes	20,000	1.7
Others	15,000	1.3
TOTAL	1,140,000	100

Adapted from Kangethe, 2001

Appendix VI: Rectified amounts of fertilizers applied per crop in the catchment area

CROP	AREA 10^3 ha	N – NITROGEN (tones)	P_20_5 – P (tones)
Maize	550	4,070	11,495
Beans	200	1,480	4,180
Sugarcane	110	5,484	2,640
Sorghum	60	444	1,254
Bananas	35	126	63

Adapted from Boit, C. 2004

KEY
DAP - Diammonium phosphate
CAN - Calcium Ammonium Phosphate
ASN - Ammonium Sulphate Nitrate
TSP - Triple Suprephosphate
NPK - Nitrogen Phosphate Potassium Compound 20:20:0
SSP - Single Superphosphate

Appendix VII: Maximum amounts of total nitrogen and phosphorus inputs from fertilizers in the catchment area

CROP	AREA 10^3 Ha	FERTILIZER	N-NITROGEN (Tones)	P_20_5 – P (Tones)	K_2O- K (Tones)
Maize	550	DAP	7,700	26,400	-
		CAN	11,165		-
		ASN	18,282		-
Beans	200	DAP	-	200	-
		TSP	5,600	26,460	-
Sugarcane	110	DAP	770	-	-
		ASN	5,484	2,640	-
		CAN	2,233	-	-
Sorghum	60	CAN	609	-	-
		NPK	1,200	1,200	-
Bananas	35	TSP	-	1,200	-
		SSP	710	1,249	-
		CAN	-	-	-

Adapted from Okungu, J. 2005

Appendix VIII: Total load of Nitrogen and phosphorus into the water courses of the catchment area

NUTRIENT	RECOMM. MAXIMUM (Tones/yr)	RECOMM. MINIMUM (Tones/yr)	RECTIFIED MAXIMUM (Tones/yr)	RECTIFIED MINIMUM (Tones/yr)
N-input in the field	35,552	18,665	14,880	4,370
N- input river (Method 1)	10,365	5,599	4,464	4,311
N- input river (Method 2)	-	2,525	-	-
P_2O_5-P input on field	60,392	53,083	22,075	5,326
P- input river (Method 1)	7,850	6,900	2,896	692
P- input river (Method 2)	-	303	-	-

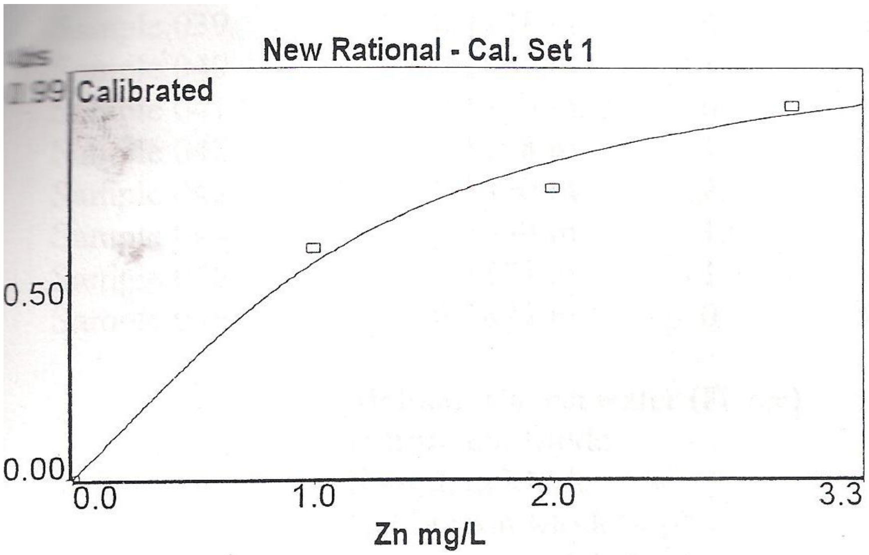
Adapted from LVEMP, 2005

Appendix IX: Pesticide application in relation to crops in the catchment area

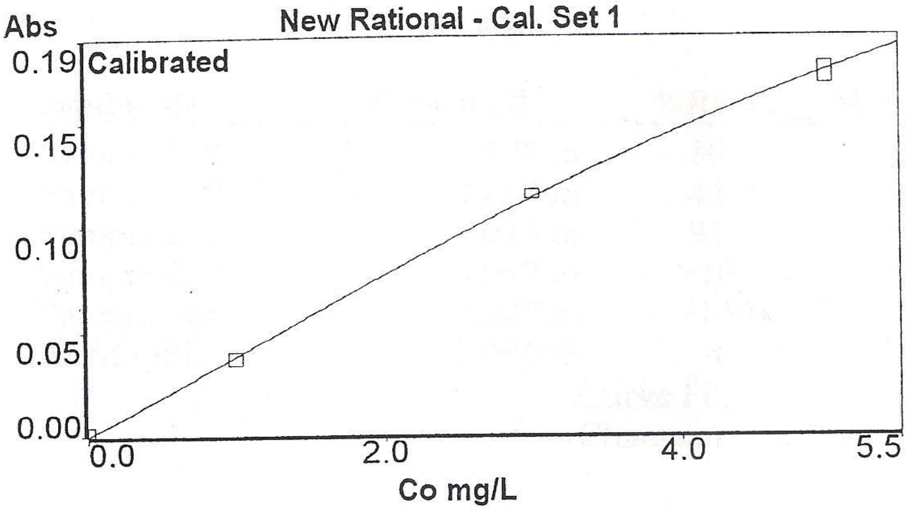
CROP	TYPE OF PESTICIDE	RECOMM. APPLICATION RATE	NO. OF APPLICATION PER YEAR
Sugarcane	TCA Na Ta	10.01ha	Twice /2 years
	Actril D.S.	2.01 ha	Twice /2 years
	Diuron	2.0 kg/ha	Twice /2 years
	Lebaycid	1.51/ha	Twice /2 years
	Asulum	5.01/ha	Twice /2 years
	Dursban	1.01/ha	Twice /2 years
	Atrazine	8.01/ha	Twice /2 years
Rice	Benlate	30.4 kg/ha	ND
	Furadan	2.0 kg/nursery	ND
		1.8 kg/ha	-
	Lebaycid	1.5 kg/ha	ND
	Diazinon	1.5 kg/ha	ND

Adapted from Wandinga, 2000

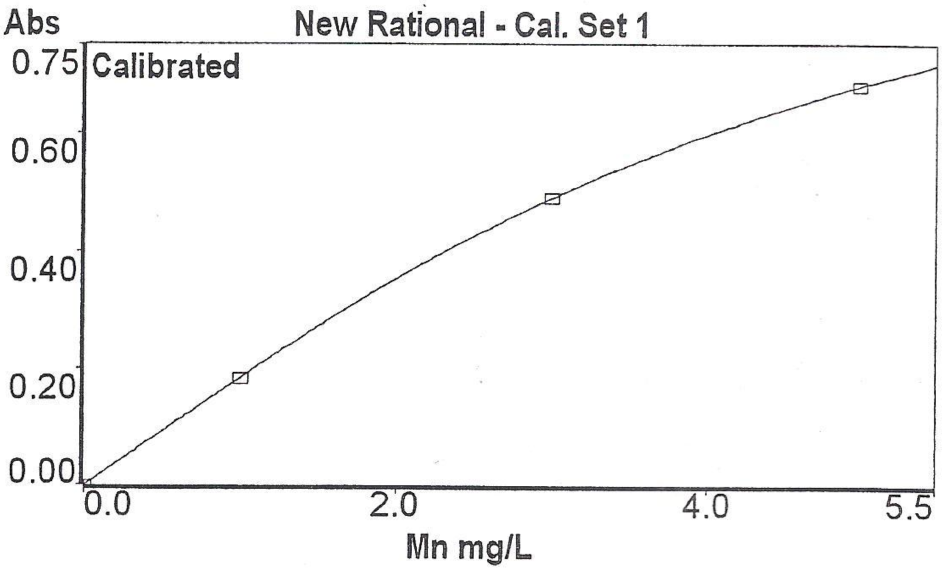
Appendix X: Calibration curve for Zinc



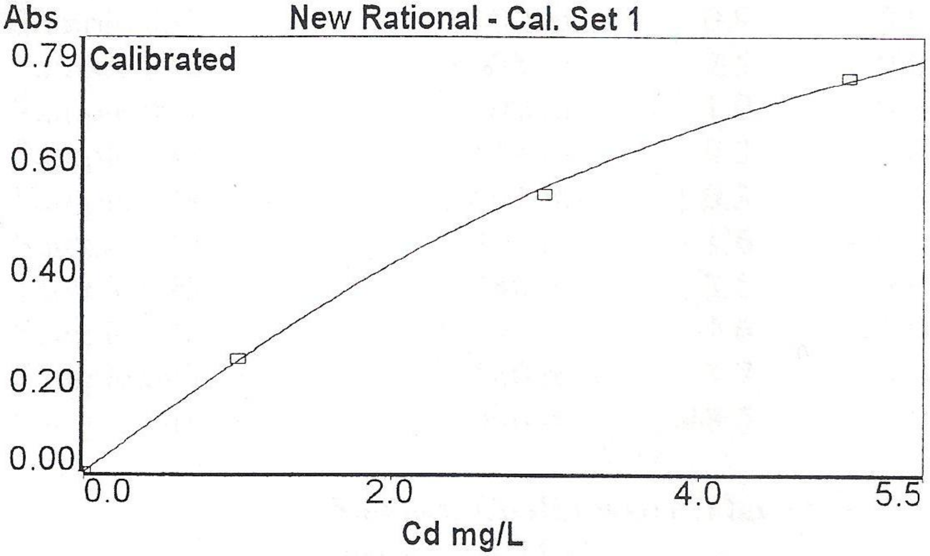
Appendix XI: Calibration curve for Cobalt



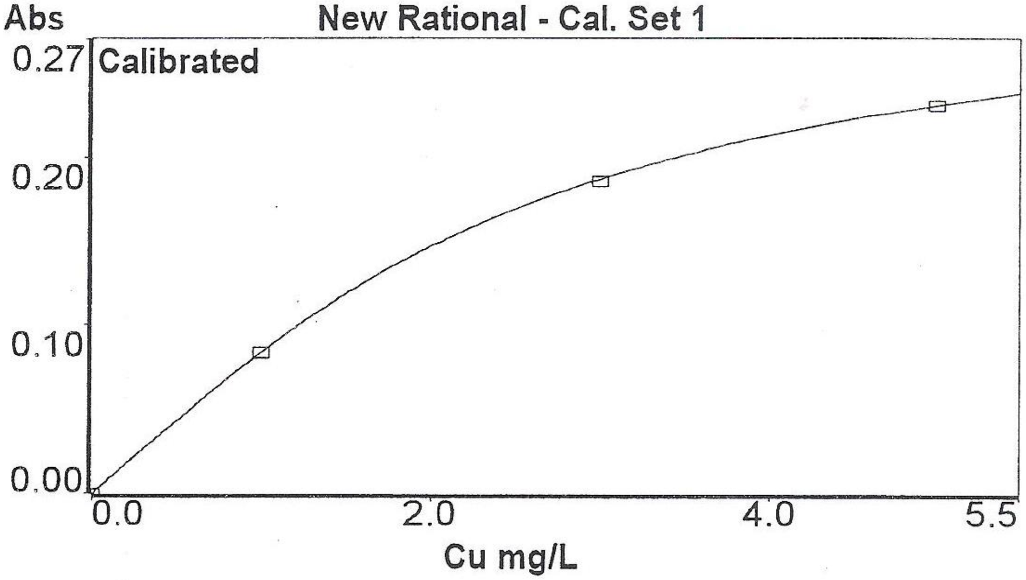
Appendix XII: Calibration curve for Manganese



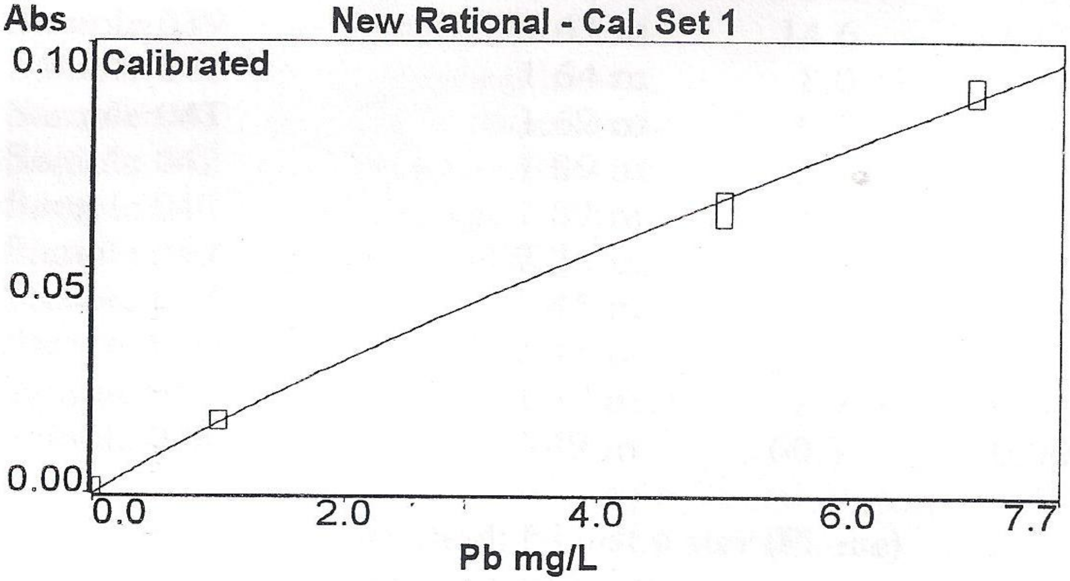
Appendix XIII: Calibration curve for Cadmium



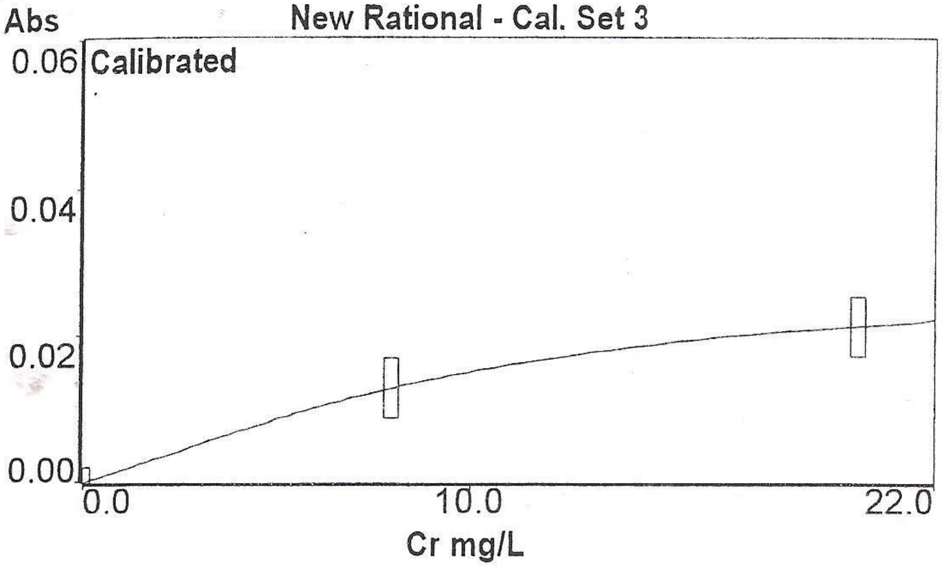
Appendix XIV: Calibration curve for Copper



Appendix XV: Calibration curve for Lead



Appendix XVI: Calibration curve for Chromium



Appendix XVII: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in water in field A

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P %
A1	0.195± 0.003	0.007± 0.000	1.759± 0.003	0.121± 0.007	0.026± 0.001	1.230± 0.088	4.495± 0.009	0.027	0.017
A2	0.204± 0.005	0.032± 0.000	1.217± 0.011	0.125± 0.027	0.049± 0.002	2.320± 0.087	5.335± 0.009	0.033	0.021
A3	0.181± 0.004	0.185± 0.109	1.282± 0.018	0.132± 0.018	0.017± 0.001	0.960± 0.033	4.367± 0.000	0.028	0.013
A4	0.189± 0.003	0.307± 0.280	2.730± 0.002	0.145± 0.011	0.013± 0.001	2.410± 0.022	2.976± 0.004	0.045	0.030

Appendix XVIII: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in water in field B

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P %
B1	0.190± 0.005	0.229± 0.003	0.437± 0.003	0.136± 0.016	0.025± 0.004	2.271± 0.055	3.985± 0.285	0.077	0.072
B2	0.827± 0.005	0.019± 0.000	1.421± 0.003	0.094± 0.020	0.281± 0.016	1.680± 0.076	3.418± 0.256	0.153	0.069
B3	0.333± 0.005	0.005± 0.000	0.861± 0.049	0.103± 0.009	0.057± 0.006	1.483± 0.016	4.789± 0.514	0.064	0.074
B4	0.757± 0.003	0.121± 0.003	1.231± 0.001	0.089± 0.018	0.231± 0.013	1.390± 0.071	4.396± 0.577	0.054	0.068
B5	0.796± 0.008	0.131± 0.005	1.030± 0.026	0.087± 0.011	0.265± 0.019	1.214± 0.097	4.104± 0.242	0.059	0.162
B6	0.895± 0.001	0.714± 0.182	1.834± 0.007	0.084± 0.015	0.114± 0.010	1.085± 0.014	2.554± 0.206	0.083	0.081
B7	1.311± 0.003	0.027± 0.000	2.538± 0.002	0.095± 0.015	0.183± 0.008	1.281± 0.079	5.715± 0.654	0.093	0.074

Appendix XIX: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in water in field C

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P %
C1	0.776± 0.004	0.085± 0.003	1.019± 0.003	0.090± 0.016	0.258± 0.003	1.250± 0.130	2.826± 0.853	0.052	0.130
C2	0.423± 0.003	0.047± 0.000	1.347± 0.034	0.112± 0.044	0.025± 0.069	1.534± 0.066	2.420± 0.000	0.119	0.109
C3	0.805± 0.009	0.058± 0.007	0.917± 0.057	0.121± 0.015	0.015± 0.098	1.782± 0.086	4.810± 0.621	0.271	0.013
C4	0.929± 0.003	0.069± 0.001	0.859± 0.013	0.107± 0.009	0.019± 0.051	1.637± 0.146	7.419± 0.249	0.201	0.103
C5	0.786± 0.010	0.062± 0.000	0.805± 0.006	0.095± 0.025	0.003± 0.001	1.641± 0.080	6.689± 0.081	0.193	0.234
C6	0.971± 0.009	0.008± 0.000	1.092± 0.044	0.109± 0.001	0.053± 0.002	1.626± 0.091	6.803± 0.190	0.107	0.094

Appendix XX: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in water in field D

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P%
D1	0.180± 0.011	0.849± 0.000	1.106± 0.037	0.418± 0.003	0.012± 0.005	1.894± 0.033	2.397± 0.138	0.090	0.002
D2	0.342± 0.022	0.736± 0.219	1.167± 0.017	0.691± 0.003	0.064± 0.051	1.890± 0.054	2.041± 0.579	0.071	0.013
D3	0.256± 0.010	0.477± 0.049	0.958± 0.049	0.408± 0.016	0.030± 0.027	2.263± 0.042	1.219± 0.214	0.032	0.001
D4	0.386± 0.011	0.612± 0.206	2.179± 0.021	0.380± 0.035	0.055± 0.031	1.451± 0.031	3.304± 0.252	0.142	0.006
D5	0.387± 0.002	0.585± 0.108	1.956± 0.014	0.433± 0.016	0.068± 0.022	2.417± 0.019	3.743± 0.237	0.101	0.007

Appendix XXI: Mean concentration of heavy metals (ppm), total nitrogen and total phosphorus in different fields (water)

	Mean concentration levels and sd in ppm Mean ± sd							**Total N and P**	
Field	**Zn**	**Co**	**Mn**	**Cd**	**Cu**	**Pb**	**Cr**	**N %**	**P %**
A	0.192± 0.004	0.133± 0.159	0.497± 0.009	0.131± 0.016	0.026± 0.187	2.213± 0.057	4.293± 0.508	0.033±	0.020±
B	0.729± 0.004	0.178± 0.228	1.336± 0.013	0.170± 0.015	0.165± 0.037	2.158± 0.087	4.137± 0.391	0.140±	0.100±
C	0.782± 0.006	0.055± 0.231	1.007± 0.026	0.106± 0.018	0.266± 0.038	1.578± 0.097	5.161± 0.332	0.207±	0.147±
D	0.310± 0.011	0.652± 0.116	1.473± 0.028	0.466± 0.015	0.446± 0.057	2.583± 0.036	2.541± 0.284	0.887±	0.312± ,

Appendix XXII: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in soil in field A

Plot	**Zn**	**Co**	**Mn**	**Cd**	**Cu**	**Pb**	**Cr**	**N %**	**P %**
A1	0.327± 0.003	0.023± 0.000	2.394± 0.006	0.091± 0.001	0.151± 0.004	1.070± 0.076	3.821± 0.415	0.094	0.073
A2	0.376± 0.006	0.296± 0.095	2.430± 0.002	0.090± 0.011	0.154± 0.021	1.152± 0.262	5.153± 0.103	0.102	0.083
A3	0.412± 0.003	0.372± 0.057	1.565± 0.002	0.088± 0.002	0.188± 0.016	1.118± 0.063	6.373± 0.194	0.087	0.061
A4	0.352± 0.006	0.335± 0.136	1.861± 0.006	0.092± 0.003	0.155± 0.003	1.326± 0.105	4.763± 0.271	0.110	0.090

Appendix XXIII: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in soil in field B

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P %
B1	0.368± 0.008	0.279± 0.018	3.375± 0.001	0.094± 0.008	0.120± 0.010	1.391± 0.043	5.721± 0.208	0.113	0.101
B2	0.585± 0.003	0.343± 0.066	2.423 ± 0.003	0.106± 0.008	0.356± 0.005	2.220± 0.046	4.320± 0.355	0.078	0.064
B3	0.276± 0.002	0.304± 0.000	1.668± 0.002	0.100± 0.001	0.216± 0.032	1.885± 0.072	3.219± 0.081	0.099	0.086
B4	0.313± 0.005	0.215± 0.000	2.103± 0.005	0.104± 0.002	0.161± 0.030	2.137± 0.059	5.113± 0.374	0.107	0.101
B5	0.403± 0.003	0.200± 0.023	3.987± 0.007	0.093± 0.010	0.193± 0.035	1.872± 0.030	4.588± 0.345	0.122	0.093
B6	0.282± 0.004	0.154± 0.000	2.731± 0.002	0.097± 0.009	0.149± 0.016	1.719± 0.011	5.307± 0.303	0.187	0.115
B7	0.592± 0.006	0.466± 0.128	4.144± 0.017	0.106± 0.008	0.220± 0.018	1.964± 0.054	6.093± 0.247	0.093	0.087

Appendix XXIV: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in soil in field C

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P %
C1	0.361± 0.009	0.256± 0.000	2.264± 0.007	0.104± 0.005	0.248± 0.013	1.896± 0.033	3.590± 0.097	0.161	0.083
C2	0.458± 0.006	0.139± 0.074	3.762± 0.004	0.108± 0.006	0.292± 0.016	1.964± 0.083	4.025 0.098	0.143	0.091
C3	0.325± 0.002	0.234± 0.000	1.791± 0.005	0.192± 0.006	0.217± 0.048	1.600± 0.070	4.991± 0.191	0.126	0.102
C4	0.261± 0.014	0.281± 0.059	3.276± 0.005	0.126± 0.019	0.327± 0.049	2.321± 0.064	5.948± 0.102	0.096	0.090
C5	0.528± 0.001	0.155± 0.000	2.624± 0.004	0.124± 0.011	0.194± 0.017	2.175± 0.085	6.050± 0.154	0.122	0.100
C6	0.605± 0.010	0.378± 0.031	3.730± 0.009	0.122± 0.016	0.317± 0.020	2.206± 0.046	5.276± 0.124	0.128	0.111

Appendix XXV: Concentration of heavy metals (ppm), total nitrogen and total phosphorus in soil in field D

Plot	Zn	Co	Mn	Cd	Cu	Pb	Cr	N %	P %
D1	0.378± 0.005	0.210± 0.020	3.318± 0.008	0.124± 0.003	0.260± 0.061	2.088± 0.103	3.453± 0.048	0.143	0.086
D2	0.357± 0.004	0.175± 0.012	2.273± 0.005	0.116± 0.007	0.319± 0.144	2.041± 0.095	5.718± 0.099	0.136	0.097
D3	0.493± 0.008	0.225± 0.000	2.224± 0.006	0.113± 0.026	0.328± 0.194	1.907± 0.119	5.271± 0.071	0.098	0.098
D4	0.543± 0.014	0.357± 0.000	3.418± 0.006	0.211± 0.012	0.227± 0.053	1.811± 0.168	4.898± 0.073	0.098	0.102
D5	0.541± 0.017	0.360± 0.063	4.120± 0.036	0.118± 0.023	0.312± 0.084	2.224± 0.098	6.415± 0.015	0.152	0.101

Appendix XXVI: Mean concentration of heavy metals (ppm), total nitrogen and total phosphorus in different fields in soil

	Mean concentration levels and sd in ppm Mean ± sd							Total N and P	
Field	**Zn**	**Co**	**Mn**	**Cd**	**Cu**	**Pb**	**Cr**	**N %**	**P %**
A	0.367± 0.005	0.257± 0.072	2.063± 0.004	0.090± 0.004	0.162± 0.011	1.167± 0.127	5.028± 0.246	0.098	0.077
B	0.403± 0.004	0.280± 0.076	2.919± 0.005	0.100± 0.009	0.202± 0.021	1.884± 0.045	4.909± 0.264	0.114	0.092
C	0.406± 0.007	0.241± 0.062	2.908± 0.006	0.129± 0.011	0.266± 0.027	2.027± 0.064	4.986± 0.128	0.129	0.096
D	0.462± 0.010	0.265± 0.019	3.071± 0.012	0.136± 0.014	0.289± 0.107	2.014± 0.117	5.151± 0.061	0.125	0.097

Appendix XXVII: Overall Mean concentration of the elements in water and soil

Mean values in ppm	**Water**	**Soil**
Zn (Mean ± sd)	0.505 ± 0.006	0.415 ± 0.006
Co (Mean ± sd)	0.219 ± 0.016	0.262 ± 0.036
Mn (Mean ± sd)	1.352 ± 0.017	1.491 ± 0.007
Cd (Mean ± sd)	0.176 ± 0.008	0.117 ± 0.013
Cu (Mean ± sd)	0.129 ± 0.049	0.237 ± 0.059
Pb (Mean ± sd)	1.668 ± 0.068	1.820 ± 0.086
Cr (Mean ± sd)	1.984 ± 0.372	5.005 ± 0.403
Total N %	0.095	0.088
Total P %	0.063	0.092

Appendix XXVIII: Temporal variation in concentration of heavy meals, total N and Total P in water

Element	**Dry season (ppm)**	**Rainy season (ppm)**
Zn	0.505 ± 0.006	0.593 ± 0.016
Co	0.219 ± 0.061	0.317 ± 0.064
Mn	1.352 ± 0.017	1.776 ± 0.032
Cd	0.176 ± 0.008	0.203 ± 0.007
Cu	0.129 ± 0.049	0.174 ± 0.050
Pb	1.668 ± 0.068	1.654 ± 0.006
Cr	1.984 ± 0.072	2.030 ± 0.034
Total N %	0.095	0.101
Total P %	0.063	0.144

Appendix XXIX: Temporal variations of heavy metals, total N and P in soil

Element	**Dry season**	**Rainy season**
Zn	0.415 ± 0.006	0.655 ± 0.007
Co	0.262 ± 0.036	0.281 ± 0.006
Mn	1.491 ± 0.007	1.704 ± 0.091
Cd	0.117 ± 0.013	0.219 ± 0.001
Cu	0.237 ± 0.059	0.323 ± 0.060
Pb	1.820 ± 0.086	1.876 ± 0.088
Cr	5.005 ± 0.003	5.000 ± 0.021
Total N %	0.118	0.214
Total P %	0.092	0.144