EXTENT OF EUTROPHICATION OF NAIROBI DAM, KENYA AND POSSIBLE IMPLICATIONS ON THE SURROUNDING ENVIRONMENT

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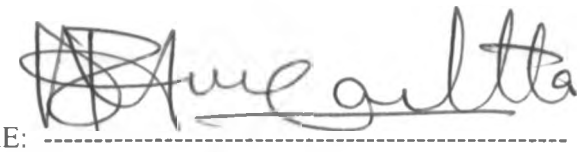
SIGNATURE:  ----------

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TABLE OF CONTENTS

TABLE OF CONTENTS *(contd...)*

PAGE

PAGE

PAGE

CHAPTER IV

PAGE

LIST OF TABLES

PAGE

PAGE

LIST OF FIGURES

PAGE

LIST OF ABBREVIATIONS

KEBS	Kenya Bureau of Standards
KS	Kenya Standard
U.S.A.	United States of America
mg/l	Milligrams per litre
mg/kg	Milligrams per Kilogram
ISO	International Organisation of Standardization
NEMA	National Environment Management Authority (of Kenya)
UNEP	United Nations Environmental Programme
TKN	Total Kjeldahl Nitrogen
N/A	Not Applicable / Not done
HZ	Water Hyacinth (growing) Zone
TDS	Total Dissolved Solids
N.T.U.	Nephelometric Turbidity Units
COD	Chemical Oxygen Demand
R^2	Square of Linear Correlation Coefficient
R	Linear Correlation Coefficient
C_w	Concentration of Nutrient in Water
C_s	Concentration of Nutrient in Sediment
C_p	Concentration of Nutrient in Plant
pH	The negative logarithm, in base 10 of the hydrogen ion concentration
MBAS	Methylene Blue Active Substances
NaDDBS	Sodium Do-decyl Benzene Sulphonate

NaDDS	Sodium Do-decyl sulphate ($C_{12}H_{25}SO_4Na$)
ISE	Ion-Selective Electrode
FES	Flame Emission Spectrometry
AAS	Atomic Absorption Spectrometry
LAS	Linear Alkyl Sulphonate
ABS	(Branched) Alkyl Benzene Sulphonate
w.e.f.	With effect from
TISAB	Total Ionic Strength Adjustment Buffer
HRM	House Reference Material
S.D. or s.d.	Standard Deviation
Std. Error	Standard error of the mean
HDPE	High Density Poly-ethylene
QC	Quality Control
PT	Proficiency Testing (sample)
RTD	Retained reference Laboratory sample
ATP	Adenosine Tri-phosphate
BOD	Biological Oxygen Demand

ABSTRACT

Since the year 1998, Nairobi Dam, Kenya, which used to be a scene of recreation before, has been infested with the water hyacinth and other aquatic weeds, probably due to Eutrophication. The current research aimed at investigating and understanding the Eutrophication state of Nairobi Dam. Possible recommendations have been made, aimed at assisting the relevant authorities to solve this problem and reverse the current condition of the dam.

In order to monitor the current Eutrophication state of the Dam, the levels of the following nutrients were determined in water, Sediments and Plants from Nairobi Dam and surrounding tributaries during various seasons of the year: Major nutrients ((Hydrolysable + PO_4^{3-}) - Phosphorous, Nitrate-Nitrogen, Total Kjeldahl-Nitrogen, Sulphate, Chloride, Sodium, Potassium, Calcium, Magnesium); Essential trace elements (Manganese, Iron, Zinc, Copper, Fluoride); Other parameters in water such as Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Conductivity, Dissolved Oxygen and pH.

The Water hyacinth (*Eichornia crassipes*) was found to be the major aquatic weed infesting Nairobi Dam, Kenya. It occupied an area of approximately 70%. It was also very persistent before, within and even immediately after the sampling period.

Results for the inorganic nutrients (except copper, sulphate and fluoride) showed that their overall mean concentrations in the dam water were much higher than in the inlet and outlet streams. This showed that the Dam has been

serving as a sink for excessive nutrients and hence assisted in the management of the surrounding aquatic environments.

Similar environmental relationships were observed for the physical and other parameters: Dissolved Oxygen, Anionic Surfactants, Turbidity, Electrical Conductivity, Total Dissolved Solids (TDS) and Chemical Oxygen Demand in water samples. The means for Dissolved Oxygen and Anionic Surfactants for the Dam water were lower while the means for the other parameters were higher than those for the Inlet and Outlet streams. This showed that the water hyacinth had lowered the clarity and Dissolved Oxygen for the Dam water, thus possibly contributing to the current disappearance of aquatic animals such as fish from Nairobi Dam.

Results for the available bulk inorganic nutrients showed that the overall mean concentrations in the dam sediments were much higher than in the inlet and outlet streams, while those for the trace element micronutrients, copper and zinc in the dam were intermediate between those for the inlet and outlet streams.

The mean concentration levels of the inorganic nutrients analyzed, on average were found to be the highest in the water hyacinth and other aquatic weeds analyzed as compared to the water and sediments from the same water hyacinth-growing zone. This showed that the water hyacinth could be used for concentrating these nutrients from the aquatic environment investigated and hence suitable for phytoremediation of the same nutrients.

Within the water hyacinth growing zone, the overall means of the major nutrients (Phosphorous and Nitrogen) exhibited corresponding levels as follows, in mg/l: (Hydrolysable + PO_4^{3-})-P: 4.489 ± 0.504, (NO_3^- - N): 1.032 ± 0.205, (Total Kjeldahl+NO_3^-)- N: 36.867 ± 4.371. These figures were much higher than the threshold values, namely: 0.1 mg/l for mean total Phosphorous and 0.8 mg/l for mean total Nitrogen, associated with eutrophication, as given in the literature. These figures confirm Eutrophication of Nairobi Dam and its extended water hyacinth-growing zone.

There was poor negative correlation ($R^2 = 0.1876$) between (Hydrolysable + PO_4^{3-}) – Phosphorous and (NO_3^-) – Nitrogen in water during the entire sampling period. Among the three major nutrients (Nitrogen, Phosphorous and Potassium), the best correlation was found between (Hydrolysable + PO_4^{3-}) – Phosphorous and (Total Kjeldahl + NO_3^-) - Nitrogen ($R^2 = 0.5244$). With respect to Nitrogen and Potassium, ***Phosphorous was found to be the limiting element, as it had negative intercept. It got exhausted first and was responsible for the proliferation of the water hyacinth in the aquatic environment studied. Any future eradication and control of this weed will have to deal with this nutrient.*** It was also found that using Linear Regression data, one could determine the limiting element between phosphorous and nitrogen in a water body and its extended water hyacinth growing zone under consideration if only one or a few samplings were done, provided all possible forms of the two nutrients were considered and enough sampling points in the water body in question were included in the sampling plan.

CHAPTER I

1.0 INTRODUCTION AND LITERATURE REVIEW

Eutrophication is the enrichment of a water body (usually of still or slow-flowing fresh water) with plant nutrients (e.g., by the input of organic material or by surface run-off containing NITRATES and PHOSPHATES). Eutrophication may happen naturally but it is often a form of pollution. It leads to an increase in the growth of aquatic plants and often to algal BLOOMS, which may smother higher plants; reduce light intensity; produce toxins which kill fish and through the aerobic decomposition of organic matter, deoxygenate the water, and thereby causing the death of many aquatic animals and higher plants. Eventually, the accumulation of organic matter may raise the bed of a lake until it becomes marsh, then dry land (Allaby, 1988).

1.1 Physical-chemical Factors associated with Eutrophication

The amounts of inorganic nitrogen and phosphorous needed for the growth of abundant algae and rooted aquatic weeds are relatively small. The generally accepted upper concentration limits for lakes free of algal nuisances are 0.3 mg/l of ammonia plus nitrate nitrogen and 0.02 mg/l of orthophosphate P at the time of spring overturn. Lakes with annual mean total nitrogen and phosphorous concentrations greater than 0.8 mg/l and 0.1 mg/l respectively, exhibit algal blooms and nuisance weed growths during most of the growing season (Hammer, 1977).

The nutrient balance (in aquatic systems) is a product of at least five phenomena: The carbonate cycle, the nitrogen cycle, the phosphate cycle, the level of photosynthesis, and the maintenance of aerobic processes (Chanlett, 1973). There are optimal ratios of NO_3^-/N and PO_4^{3-}/P for varied regimes. As the balance becomes tipped, some species become tipped, some species become predominant and the environment becomes unfavourable for many others. The rise in phosphates in lakes of low replacement as Wisconsin glacial lakes, of vast shallows as Lake Erie, or of very ancient origin as Lake Constance in Europe have produced a nutrient cycle highly favourable for great increases in algae growth. This is Eutrophication (Chanlett, 1973).

There is little doubt that as urbanization increases, particularly from industrial use of land and water, the quality of water decreases. However, quantitative data to support this observation are sparse. There are two principal effects of urbanization on water quality. First, the influx of waste materials tends to increase the dissolved-Solids content and decrease the Dissolved-Oxygen content. Second, as flood peaks as a result of the increased area of imperviousness and decreased lag time, less water is available for ground-water recharge. The stream becomes flashier in that flood peaks are higher and flows during non-storm periods are lower (Detwyler, 1971).

The activities of man upon the earth may affect the quality of ground water in two major ways: (i) by accelerating the rate of build-up of compounds or ions normally found in ground water and (ii) by adding or increasing the

concentration of dissolved solids during beneficial use of water (Detwyler, 1971).

In the practical case, municipal sewage contains both domestic and industrial waste products. From the domestic fraction come wastes from the human body, grease, ground garbage, and residues from commercial products such as soap and detergents (Detwyler, 1971). On the other hand, the industrial fraction may contain neutral, acidic or basic wastes, which may in turn contain organic compounds or inorganic wastes and sludge (Austin, 1986).

Organic solids in sewage are associated with man's activities and may reach the soil in varying degrees of degradation. Fundamentally, they are proteinaceous in nature and under aerobic conditions oxidize to nitrates, sulphates, carbonates and phosphates. Along the way, there may be ammonia, nitrites, and similar unoxidized compounds. Under anaerobic conditions, degradation products include amino acids and a considerable spectrum of intermediate compounds of notable fragrance and unpleasant taste, as well as ferric sulfide, which as a particulate matter, helps to clog the soil completely (Detwyler, 1971).

Of the decomposition products, ammonia is notably adsorbed on soil, where it displaces calcium, magnesium, sodium and potassium ions, which are then carried away by percolating water. Later, the ammonia is oxidized to nitrates by microbial activity and so becomes soluble and free to move with water. Phosphates too are adsorbed and taken out of the top horizons of soil. Numerous data show that when sewage is applied to a soil, the result is simply

an increase in the sulphates, bicarbonates, nitrates and other anions and cations normally found in ground water. Thus in summary, it may be said that contamination of ground water by degradable organics is largely confined to an increase in concentration of normal ground-water ions (Detwyler, 1971).

Chemicals from industrial and commercial sectors may reach new sites with municipal sewage, industrial wastes, agricultural fertilization, and the use of pesticides and herbicides for a number of purposes. Use of linear alkyl sulphonate (LAS), which is more degradable than branched alkyl benzene sulphonate (ABS), used previously in detergent formulations, reduced contamination problem. Hence, from a commercial formulation, the phosphate might be expected to be adsorbed on soil and the detergent biodegraded to an inorganic sulphate, which will travel with percolating water or with moving surface and ground water (Detwyler, 1971).

Nearly all lakes naturally change from a nutrient-poor ("oligotrophic") to a nutrient-rich ("eutrophic") condition gradually with time. But water pollution by man can greatly accelerate this aging process of Eutrophication. Lake Erie has become a classic example. Much of the nitrogen which is applied as inorganic nitrogen fertilizer on the 76,800 square Km of farmland in the Lake Erie basin washes into the lake. The lake also receives phosphates at a rate of 9,091 Kg daily, of which 3,036 Kg comes from the Detroit area alone. Household detergents and road salt additives are major sources of the phosphates. The nitrates and phosphates are important plant nutrients and their present quantities over-fertilize the lakes. 0.5 Kg of phosphates can grow 318

Kg of algae, provided other nutrients are available too. Huge masses of algae actually bloom in Lake Erie (U.S.A. / Canada) each year. When the algae die, they sink to the bottom, consuming oxygen in the water as they decay and releasing nutrients for another cycle of plant growth. In late summers, a 6,656 square-Km area of the lake has no oxygen available within 3 metres from the bottom for other aquatic life. This fertilization, decrease of oxygen, and increase in temperature have helped to bring about gross changes in the other aquatic life, including important commercial and sports fishes (Detwyler, 1971).

The present trophic nature of the Great Lakes is to a considerable degree the result of their gradual aging since formation. Evidence is accumulating, however, which indicates that human activity is greatly accelerating the eutrophication of all of the lakes except Lake Superior (U.S.A. / Canada). This evidence is most spectacular for Lake Erie (U.S.A. / Canada). A difficult problem is one of finding acceptable indices of change (Detwyler, 1971).

Various criteria have been used by different investigators to demonstrate Eutrophication. Hasler (1947) compiled information on 37 lakes affected by enrichment from domestic and agricultural drainage. Among the changes in many of these lakes were: the dramatic decline and disappearance of salmonid fishes and increases in populations of coarse fish; changes in the species composition of plankton; and blooms of plankton and blue-green algae. As the Untersee of Lake Zurich (Switzerland) changed from a salmonid to a coarse-fish lake, plankton abundance increased, different species became dominant in

the plankton, transparency decreased, and the dissolved oxygen content of the deep waters decreased. At the same time, the concentrations of chlorides and organic matter increased (Minder, 1943, 1938, 1918). Minder (1938) attributed the increase and changes in the plankton to the growing amount of phosphorous and nitrogen from domestic sources. Declines in the hypolimnetic oxygen, decrease in transparency, and increases in the abundance of plankton were cited by Edmondson *et al.* (1956) as evidence of Eutrophication of Lake Washington (U.S.A.). They attributed this increased productivity to the result of growing discharges of treated sewage into the lake. Similar changes were observed in Furesϕ Lake (Denmark) by Berg *et al.* (1958). Species composition of the phytoplankton changed, transparency decreased, dissolved oxygen concentrations became low in the hypolimnion layer, and conductivity rose. These changes have occurred during the last 40 to 50 years. Berg *et al.* (1958) stated "The cause is an increased introduction of material with the sewage" (Detwyler, 1971).

1.1.1 Phosphorous and Nitrogen as Indices of Eutrophication

Phosphorous concentrations of the sediments are of considerable importance from the standpoint of Lake Eutrophication (Brock, 1985). Much of the phosphorous is present in bound form and probably not available. Holdren *et al.* (1977) presented data for inorganic phosphorous concentrations of the interstitial water of Lake Mendota (U.S.A.) sediments and for cores taken at different times of the year. Although there was some variation throughout the year, at the deeper location, this variation was not great. The average value for

interstitial (soluble) phosphorous calculated from their data, 3.13 μg/ml, is considerably higher at all times than the lake water concentration, showing that the sediments are a source of soluble phosphorous. Phytoplankton and other phosphorous-rich particles settle out of the water column into the surficial sediments and undergo decomposition processes, which lead to the release of soluble phosphorous. This soluble phosphorous can then move back into the overlying water by molecular diffusion or advection (Brock, 1985). Although some phosphorous is adsorbed by Lake Mendota (U.S.A.) sediments (Shukla *et al.*, 1971; Williams *et al.*, 1970), a significant fraction of adsorbed phosphorous can be readily desorbed (Brock, 1985).

Nitrogen is one of the key nutrients in lake ecosystems. It is available to organisms in several forms: ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-). Although all of these forms of Nitrogen are available to various organisms, ammonium and nitrate are the most important for phytoplankton and bacteria (Brock, 1985).

Phosphorous is present in lakes only in the form PO_4^{3-} , so that the complications regarding oxidation and reduction discussed with Nitrogen do not arise. However, phosphorous is present in a number of different chemical forms such as orthophosphate, organic phosphates (including those present in organisms), metaphosphate, phosphorous adsorbed to mineral particles and calcium phosphate. (Brock, 1985).

Using the critical concentrations suggested by Sawyer (1947), the following critical values have been estimated in terms of annual loadings: P, 0.2-0.5 $g/m^2/yr$ and N, 5-10 $g/m^2/yr$. The loading functions are related to mean depths as follows:-

(a) Permissible loadings:

$$Log_{10}P_A = 0.6log_{10}H - 1.6, \quad \text{---------- (1)}$$

$$Log_{10}N_A = 0.6log_{10}H - 1.3. \quad \text{---------- (2)}$$

(b) Dangerous loadings:

$$Log_{10}P_D = 0.6log_{10}H - 0.43, \quad \text{---------- (3)}$$

$$Log_{10}N_D = 0.6log_{10}H - 0.13. \quad \text{---------- (4)}$$

Where:

P_A = Permissible threshold phosphorous loading for an oligotrophic lake,

P_D = Dangerous phosphorous loading (lowest limit) required for an Eutrophic lake,

N_A = Permissible threshold nitrogen loading for an oligotrophic lake, and

N_D = Dangerous nitrogen loading (lowest limit) required for an Eutrophic lake.

The phosphorous loadings, P_A and P_D and the nitrogen loadings, N_A and N_D, are in $g/m^2/yr$ and the mean depth, H, is in metres. Oligotrophic lakes are

supposed to occur at loadings below the permissible levels, while eutrophic lakes occur above the dangerous levels and mesotrophic lakes lie in between the permissible and dangerous levels (Krenkel and Novotny, 1980).

From analyzing algal growths, it was found that when the nitrogen/phosphorous ratios were greater than 15:1, phosphorous was the possible limiting nutrient, and when the ratios were less than 15:1, nitrogen was limiting. However, these ratios may vary from 5:1 to 20:1 (Krenkel and Novotny, 1980).

By plotting phosphorous versus nitrogen concentrations during various seasons, a straight-line relationship can usually be established. It is assumed that the limiting nutrient will be exhausted first, and will show as a negative intercept of the line on the axis of the limiting nutrient. The one which is not limiting will remain in solution, yielding a positive intercept of the line of best-fit (Krenkel and Novotny, 1980). Alternatively, the stoichiometric limiting nutrient uses the principles of conservation of mass and the stoichiometric composition of the algae biomass if that one nutrient is totally depleted. In order to calculate the stoichiometric limiting nutrient, one divides the concentration of each available nutrient in the water by the stoichiometric requirement of the algae (or other aquatic plants) for that nutrient, and states that the nutrient generating the lowest ratio is the "limiting nutrient" (Middlebrooks *et al.*, 1974).

With increasing development in Africa, the problems of Eutrophication of natural waters are beginning to emerge. Serious water pollution problems in South Africa (Toerien *et al.*, 1975), Kenya (Njuguna and Gaudet, 1979) and Zimbabwe (Thornton, 1979) have been described (Symoens *et al.*, 1981).

1.2 Role of some Inorganic Nutrient Ions in Biological Systems

About 25 elements are currently believed to be essential to plants and animals. These elements are classified as follows:-

(i) Trace metal ions: Fe, Cu, Mn, Zn, Co, Mo, Cr, Sn, V and Ni.

(ii) Bulk metal ions: Na, K, Mg and Ca.

(iii) Non-metallic elements: H, B, C, N, O, F, Si, P, S, Cl, Se and I. There is also some evidence that Sn, As and Br may possibly be essential trace elements (Hay, 1984).

1.2.1 Alkali Metal Cations (Sodium and Potassium)

Sodium is the principal extra-cellular cation and potassium is the principal intra-cellular cation. The cell is surrounded by a membrane which selectively allows out unwanted material or material produced for use elsewhere. It is in this barrier that the process of cation discrimination occurs. This transfer of material may be independent of an energy source (so-called facilitated diffusion) or may require energy (so-called active transport). This energy is believed to come from hydrolysis of Adenosine Tri-phosphate (ATP). The production of energy source for this process is generally known as the "Sodium pump". ATP is hydrolyzed by Na^+ - K^+ ATPase (Hay, 1984).

1.2.2 Calcium

The concentration of Ca^{2+} inside and outside of the cell are approximately 10^{-6} mol dm^{-3} and 10^{-3} mol dm^{-3} respectively. The range of biochemical and/or physiological processes are triggered off by entry of calcium ions into the cell or by release of the ions from internal organs. Calcium is implicated at some stage of the stimulus-secretion coupling, e.g. in secretion of histamine (from mast cells) and insulin (from pancreatic cells). These processes require energy and presence of calcium. Coagulation of blood (clotting) is dependent on calcium and involve a number of proteins. Deposition of calcium is an essential feature of the development of extra-cellular structures, e.g. shell, bones and teeth (for animals) (Hay, 1984) as well lignin in plants. Calcium-binding regulating proteins found in many calcium (II) dependent processes are identical. This type of protein, "Clamodulin" is the intracellular calcium receptor (Hay, 1984).

1.2.3 Magnesium

Magnesium is the centre of chlorophyll, the most important complex, which is the green plant pigment which can produce sugars and on which all life ultimately depends. It is also the fourth most abundant cation in the animal body, about half being present in the skeleton. It plays a major role in the regulation of vital biological processes, including enzymatic reactions, e.g. in the hydrolysis of many biologically important phosphate derivatives, with release of energy. Mg^{2+} can also substitute for Mn^{2+} in a number of enzymatic reactions (Hay, 1984).

1.2.4 Phosphorous

Phosphorous is necessary to all life. It functions in the storage and transfer of a cell's energy and in genetic systems. Universality of ATP (adenosine triphosphate) as an energy carrier and presence of phosphate groups in nucleotides and hence in nucleic acids, underscores living things need for phosphorous. It is found in meteorites, rocks, soils and even in the sun's atmosphere. It is not one of the rarest elements, but is more scarce than the other principal elements of living organisms (carbon, hydrogen, oxygen, nitrogen and sulphur) (Cole, 1975).

1.2.5 Nitrogen

Nitrogen is a constituent of numerous naturally occurring compounds such as amino acids, proteins and nucleic acids. These complex molecules are built up from smaller organic molecule, but the original source of the element lies in simple inorganic compounds. The 'nitrogen cycle' represents the transformation of inorganic nitrogen to organic nitrogen together with the reverse degradation process. In this cycle, soil ammonia is converted to nitrate by the action of microorganisms (nitrification). Nitrate is assimilated by plants and built into organic molecules. Higher species feeding on these plants convert such molecules into more complex compounds. On death, these compounds are broken down, leading to the reformation of ammonia. Denitrification is the process whereby nitrates are reduced by microorganisms, ultimately N_2 being produced. Atmospheric dinitrogen is fixed (i.e. converted to ammonia) by various bacteria (Hay, 1984).

1.2.6 Chloride

Chloride is the most recent addition to the list of essential elements. Although chloride (Cl) is classified as a micronutrient, plants may take up as much chloride as they do secondary elements such as sulfur. The primary roles of chloride include:

- Chloride is important in the opening and closing of stomata. The role of the chloride anion (Cl^-) is essential to chemically balance the potassium ion (K^+) concentration that increases in the guard cells during the opening and closing of stomata.

- Chloride also functions in photosynthesis, specifically in the water splitting system.

- Chloride functions in cation balance and transport within the plant.

- Chloride diminishes the effects of fungal infections in an as yet undefined way.

- Chloride competes with nitrate uptake, tending to promote the use of ammonium nitrogen. Lowering nitrate uptake may be a factor in chloride's role in disease suppression, since high plant nitrates have been associated with disease severity **(TETRA Technologies, Inc., 2005)**.

Most soil chloride is highly soluble and is found predominantly dissolved in the soil water. Chloride is found in the soil as the chloride ion. Being an anion,

it is fully mobile except where held by soil anion exchange sites. In areas where rainfall is relatively high and internal soil drainage is good, it may be leached from the soil profile. Also, where muriate of potash fertilizer is not regularly applied, chloride deficiencies can occur. Atmospheric chloride deposition tends to be rather high along coastal regions (due to particulate NaCl deposition in the air from the sea, after evaporation) and decreases as you progress inland. Chloride, nitrate, sulphate, borate, and molybdate are all anions in their available forms and in that form they are antagonistic to each other. Therefore, an excess of one can decrease the availability of another. Little information is available on other specific interactions that may occur.

Chloride deficiency symptoms include:

- Wilting due to a restricted and highly branched root system, often with stubby tips, and

- Leaf mottling and leaflet blade tip wilting with chlorosis has also been observed.

In particular, chloride deficiency in cabbage is marked by an absence of the cabbage odor from the plant **(TETRA Technologies, Inc., 2005)**.

1.2.7 ***Sulphur***

The organic sulphur of essential amino acids, cysteine and methionine originates biologically from various inorganic forms, such as SO_4^{2-}, $S_2O_3^{2-}$ H_2S and even elemental sulphur, which some bacteria can oxidize to sulphate. Various microorganisms and plants can bring about the enzymatic reduction of

sulphate and thiosulphate to yield H_2S, which may then be converted into thiol group of cysteine by the reactions:

L-Serine + acetyl-CoA = O-acetyl serine + CoA

O-Acetyl serine + H_2S = cysteine + acetate + H_2O

catalyzed by *serine acetyl transferase* and *cysteine synthase*, respectively. Yet another reaction for utilization of H_2S is:

Pyruvate + NH_3 + H_2S = Cysteine + H_2O

catalysed by the pyridoxal phosphate enzyme cystathionine γ- lyase, which can act on (or form) either cystathionine or cysteine (Lehninger. 1988).

Also, the iron-sulphur proteins contain iron and acid-labile sulphur in equi-molar amounts. The first to be discovered, *ferredoxin*, was found in an anaerobic bacterium, *Clostridium pasteurianum*, which is capable of fixing atmospheric nitrogen (Lehninger. 1988). ***(Also refer to the section under iron of this thesis).***

1.2.8 Manganese

Manganese (II) can act as an effective Lewis acid in such enzymes as oxalo-acetate decarboxylase and pyruvate carboxylase. Manganese-containing superoxide dismutases have been isolated from a variety of organisms. A diamine oxidase which contains manganese is also known. Like Fe (II), Mn

(II) is incorporated into ligands such as the porphyrins. This leads to the formation of haemoprotein and important components required for photosynthesis in the primitive blue-green algae. Some blue-green algae contain up 12 atoms of Mn per reaction centre. These various components, along with chlorophyll, contribute to the evolution of oxygen in the atmosphere during photosynthesis. In addition, manganese also appears to play an important role in several metabolic processes such as bone growth, glucose tolerance, reproduction, and development of the inner ear (Hay, 1984). It is a necessary nutrient for plants and animals. It stimulates plankton growth perhaps by activating enzyme systems and by having at least some effect on the vitamin thiamine (Cole, 1975).

1.2.9 Iron

Iron is by far the most widespread and important transition metal with a functional role in living systems. Iron-containing proteins participate in two main processes: oxygen-transport and electron-transfer. There are other molecules whose function is to store and transport iron itself. Iron also occurs in conjunction with molybdenum in enzymes that catalyze nitrogen fixation (Cotton and Wilkinson, 1988). Structurally, there are two types of iron-containing proteins. These are:

(i) **Heme Proteins**

Chief *heme* proteins are the *haemoglobins* (the red pigment in the blood of most animals, essential for absorbing and releasing molecular oxygen in

different parts of the body), *myoglobins*, *cytochromes* and some enzymes such as *catalase* and *peroxidase* (Cotton and Wilkinson, 1988).

(ii) **Iron-Sulphur Electron-transfer Proteins**

Examples of these include *Ferredoxins*, *Rubredoxin* and *High-potential Iron Proteins,* HiPIP's (Cotton and Wilkinson, 1988).

Iron is also necessary for photosynthesis in plants, where it is the metal part of at least two plant cytochromes that function in the transfer of electrons during photosynthesis. It is normally found in two states, the oxidized (Fe^{3+}) ferric and the reduced (Fe^{2+}) ferrous (Cole, 1975).

1.2.10 Zinc

Zinc (II) plays an important role as a Lewis acid in many metallo-enzymes, since ligand exchange processes on zinc (II) are rapid, with no ligand field effects (d^{10}) and is reasonably an effective Lewis acid as demonstrated in many model systems (Hay, 1984). An example is in the hydrolysis of the C-terminal amino-acid residue from a peptide or protein chain (Hay, 1984).

1.2.11 Copper

Copper is found in both plants and animals. A number of copper proteins, including enzymes, have been isolated. Examples are:

(i) **Ascorbic acid oxidase**

This catalyzes the oxidation of ascorbic acid (vitamin C) to dehydro-ascorbic acid with O_2 as the electron-acceptor (Cotton and Wilkinson, 1988).

(ii) **Cytochrome oxidase**

This is the terminal electron-acceptor of mitochondrial oxidative pathway. It contains heme and copper in a 1:1 ratio (Cotton and Wilkinson, 1988).

(iii) **Tyrosinases**

These catalyze the formation of melanin pigments in a host of plants and animals. These were the first enzymes showing essential copper activity (Cotton and Wilkinson, 1988).

(iv) **Haemocyanin**

Many lower animals, e.g. snails and crabs, contain a cupro-protein as oxygen-carrier, analogous to haemoglobin in mammals. This protein is called haemo-cyanin, though it contains no heme groups (Cotton and Wilkinson, 1988).

1.3 Significance of the Current Research Work

A combination of primary and secondary treatment of municipal waste water into one process utilizes a novel approach. The water hyacinth, long regarded as a weed, appears to thrive on sewage. It floats on the surface and its roots absorb the waste materials including toxic materials and heavy metals (Brooke and Reed, 1981a, b). The process is efficient and economical (Austin, 1986).

Tertiary sewage treatment involves further processing steps after secondary treatment, usually for the removal of pollutants, with no BOD. After

secondary treatment, water still contains phosphorous, nitrogen and carbon compounds in solution, which can serve as nutrients for the over-abundant growth of algae and other aquatic plants. The enrichment of waters with nutrients is referred to as Eutrophication (Austin, 1986).

Since phosphorous, a major ingredient required for growth of plants is used in detergents, excess growth of algae in natural waters receiving domestic waste discharges is generally blamed on the high phosphorous content of the water. Since complete removal of phosphorous from domestic waste cannot be accomplished by only limiting the use of phosphorous compounds in detergents, considerable work has been done in developing processes for removing phosphates from municipal waste water. The most common types of chemical treatment are precipitation with lime and/ or metallic hydroxides such as aluminium. It is about 90 to 95 % effective and the cost is less than $ 1.32 per 100 m^3 (Austin, 1986). Under some conditions, microorganisms can absorb quantities of phosphates greatly in excess of their usual needs, a so-called luxury uptake. This uptake is reversible, as decay of the cells can release the phosphate. A treatment plant such as the one used in the District of Columbia (U.S.A.), has a process that removes the sludge from the final clarifier rapidly and feeds it into a phosphorous stripper operated in the fashion of an anaerobic digester. About two-thirds of the phosphate in the sludge is released in the digester and can be removed by chemical means. About 90% removal of phosphorous can be accomplished (Austin, 1986).

In 1980, more than 500 plants in the U.S.A. and Canada used chemical treatment methods to remove phosphorous and nitrogen compounds. In 1972, only 10 such plants were operating (Austin, 1986).

1.4 Eutrophication: A World Phenomenon

Some of the lakes in the United States affected by accelerated Eutrophication are the Great Lakes, particularly Lake Erie. Other lakes affected include Lake Okeechobee, the Madison, Wisconsin lakes, Lake Champlain and Lake Washington. Some major rivers and estuaries respond to fertilization much as though they were lakes, for instance the Potomac River and estuary and San Francisco Bay and its tributaries (Hammer, 1977).

Numerous small lakes and reservoirs used for recreation exhibit symptoms of Eutrophication. The source of extra nutrients may be waste waters and, frequently, fertile land drainage. In clear water impoundments, fertilization leads to abundant plant growth and large populations of tolerant fish species; unfortunately, many of the desired game fish species find the environment unsuitable. Swimming and water skiing may be impaired by weed beds in shallow water. Small bodies of water that are light-limited by soil turbidity support neither heavy aquatic plant growth nor dense algal blooms. Photosynthesis is retarded by the lack of sunlight even though adequate plant nutrients are available. Although limiting productivity may have some aesthetic advantages, the high turbidity is detrimental to reproduction of game fishes (Hammer, 1977).

1.4.1 Possible Eutrophication of East African Waters

According to a recent survey of Naivasha area, Kenya, the levels of cadmium in water, soil and plant samples were found to be higher than the recommended and expected values given in the literature (Muigai, 1992). One of the sources of this elevation was postulated as possible use of phosphate rock fertilizers and sludge from both industrial and domestic sewage treatment-works (Piotrowski and Coleman, 1980). In the Naivasha area survey, the plants analyzed included both terrestrial and aquatic ones, among which was the floating aquatic fern, *Salvinia molesta*, which is environmentally troublesome to aquatic systems. This aquatic weed was infesting Lake Naivasha by then. It was found that Salvinia had the highest level of mercury, with considerably high levels of cadmium and lead and could therefore serve as a useful sink of heavy metals, especially mercury, cadmium and lead (Muigai, 1992). The proliferation of this weed in Lake Naivasha at that time, coupled with the high cadmium content in water, soil and plants were probable consequences of Eutrophication.

The presence of the water hyacinth in Lake Victoria, its environmental and ecological impact and its proposed control have well been reported in recent publications (LVEMP, 2003; U.S. Geological Survey, 2003). The weed is a major menace in the whole of East African region. During a regional harmonization workshop, available information and data suggested that nutrients enrichment, especially nitrogen and phosphorous from untreated wastes from municipalities and human settlements, Industrial effluents along

the shoreline, Agricultural practices (crop and livestock production) and Non-point sources (deposition of Nitrogen and Phosphorous from the atmosphere) were responsible for the persistence of water hyacinth in Lake Victoria (LVEMP, 2003).

1.5 Aquatic Weeds: A Physical Measure of Eutrophication

As Eutrophication of lakes, rivers, and estuaries proceeds, populations of aquatic plants growing there commonly "explode". Moderate numbers of these plants are beneficial, but in large quantities they may have numerous harmful effects. In recent years, aquatic plants have become overabundant in an increasing number of lakes and streams, paralleling trends in water enrichment (Detwyler, 1971).

As the expanding plants are usually introduced from foreign regions, they lack native predators to keep them in check. In many areas, these ruinous plants have been purposely introduced for their ornamental quality (Detwyler, 1971).

Aquatic weeds may foul water supplies by creating odours, tastes, or colours. Waterways used for supply such as irrigation canals, may become almost completely clogged. Esthetic values and recreational uses (boating, swimming, fishing, etc.) may be impaired. Water lost by evaporation from water hyacinth may be eight times as great as the loss from a normal water surface in arid areas. There are other commercial, economic, and other health effects as well (Detwyler, 1971).

Like terrestrial weeds, many aquatic weeds are adapted for persistence; vegetative reproduction may make removal by mowing hopeless, and many seeds are long-lived. Aquatic weeds have become a serious symptom and a result of our failure to manage our water resources (Detwyler, 1971).

1.5.1 The Water Hyacinth: A World Scourge

The scourge of some of the world's major rivers is water hyacinth, *Eichhornia crassipes* (Mart.) Solms in the family *Pontederiaceae*. The hyacinth is a native of South America, but it is now widely distributed over the warm regions of the earth. The plant is free-floating, has very fine roots and produces stolons and viable seeds. The leaves are 10 to 15 cm wide, bright green, shiny and because they are upright, serve as sails in front of the weed (Detwyler, 1971).

1.5.2 The Spread of Water Hyacinth in Africa

In Africa, water hyacinth is supposed to have been introduced first in Egypt, sometimes between 1879 and 1892 and in Natal in the early years of the 20th century. It was first reported in Southern Rhodesia (Zimbabwe) in 1937 and near Brazzaville in Congo (Zaire) in 1952. Soon, the weed had become a serious problem covering over 1,600-Km stretch of River Congo. In 1956-57, more than 150,000 Kg of water hyacinth / hour were being swept through Leopoldville by the Congo River. Several tributaries of Congo, namely Kasai, Ubangui, Sanga, Itimbiri, Mongala are involved in the spread of water hyacinth in the region (Gopal and Sharma, 1981).

The weed has been a serious problem in Egypt and Sudan and there are several detailed accounts of its spread along the Nile River system. The plant was first seen near Khartoum (Sudan) in 1958 when it was probably already present further south. It appears to have entered into Sudan from Congo through floodwaters of River Congo at the Nile-Congo divide. By 1981, the weed was widespread in Ethiopia, Egypt, Sudan, Zaire, Central African Republic, Madagascar, Mozambique, Natal, Eastern Cape, Rhodesia (Zimbabwe), Tanzania, Okovango basin in Botswana, Zambia (Kafue reservoir), Angola, Guinea, Senegal. By then, it did not appear to have reached Kenya, Nigeria, Uganda and Ghana as yet. The major river basins infested with water hyacinth were those of Rivers Kagera, Logone, Niger, Senegal, Zambezi, Sabi and their tributaries (Gopal and Sharma, 1981).

According to Gopal and Sharma (1981), distribution of water hyacinth in Africa showed no presence of the weed in Kenya by the year 1981. However, in recent years, Kenya has experienced its share of proliferation of this weed as cited in the literature section.

The methods of control, utilization and management of the water hyacinth have been discussed extensively in the literature (Detwyler, 1971; Gopal and Sharma, 1981; Thyagarajan, 1984).

1.6 Possible Eutrophication of Nairobi Dam

According to a recently published report on the Nairobi River basin (Okoth and Otieno, 2000), conductivity, TDS, BOD and Total Coliform counts increased eastwards (downstream). Although BOD levels were relatively low, total coliform counts at Nairobi Dam, Kibera Station (inlet to Nairobi Dam) were quite high. This was attributed to direct sewage inputs to the river from the large informal Kibera settlement due to lack of a municipal sewage disposal infrastructure. Low BOD, Total Coliform, Total Suspended Solids at the Nairobi Dam outlet station (relative to the inlet) indicated that Nairobi Dam could act as a sink for suspended sediment and organic matter and trapped the coliform (Okoth and Otieno, 2000).

In the same report, it was postulated that Nairobi Dam appeared to be an effective sink fo Pb and Zn, which tended to be removed from the aqueous phase by strong adsorption by organic matter. Phosphate (PO_4^{3-}) and Nitrate (NO_3^-) ions were generally low in the river (less than 2 mg/l) (Okoth and Otieno, 2000). It was also reported that highest concentrations of N occurred in Nairobi Dam, which was attributed to degradation of organic matter. A close, analytical scrutiny of the data showed that the levels of these critical nutrients in the dam were as follows: - NO_3^--N: 2 mg/l at inlet and ~ 1.5 mg/l at outlet; PO_4^{3-}-P: 0.15 mg/l at inlet and 0.15 mg/l at outlet. By intuition, the data tentatively shows that, according to Hammer (1977), the levels of NO_3^--N and PO_4^{3-}-P were well above the minimum annual mean total levels of 0.8 mg/l and 0.1 mg/l, respectively, required for eutrophication,

hence initially attributing eutrophic nature to Nairobi Dam. However, in the work compiled in that report, it was revealed that river samples were only collected once during the period, when runoff inputs were at a minimum and thus captured the effects of non-runoff related pollutants (Okoth and Otieno, 2000). It was recommended that a long term monitoring programme needed to be instituted in order to understand the full range of river behaviour, e.g. wet versus dry season and seasonal trends in order to define effective and sustainable river management policies (Okoth and Otieno, 2000). It was also pointed out that under changing environmental or physico-chemical conditions, sediment-bound trace elements can dissolve into the water column and several constituents can degrade or form more toxic forms. It was therefore recommended that it was important to carry out sediment-based studies of both the river-bottom sediments and catchment sediments to study the behaviour of sediment-bound trace elements in Nairobi Rivers (Okoth and Otieno, 2000).

Not much comprehensive work has been done on the Eutrophication of Nairobi Dam, especially with regard to seasonal variation. The water mass has in the recent years, since 1998, been largely covered with aquatic weeds, especially the water hyacinth (see Figures 1 A & B). However, the dam and its environs have attracted many NGOs and researchers in pursuit of information, data and solutions to inherent problems. Information and data on geological and chemical pollution assessment have been compiled in a report edited by Okoth and Otieno (2000). Related work on environmental impact of urbanisation on Nairobi Dam was conducted by Iole (2000). Potential

biological control of water hyacinth in Kenya, using micoherbicides has been reported (Mibey and Kariuki, *In Press*).

1.7 Statement of the Present Problem

Some decades ago, Nairobi Dam used to be a very attractive scene for recreation, as well as to offer certain services, such as domestic use and Church Baptism by immersion. As a result, tourists and local visitors would flock there frequently. The water was then clear and plant growth minimal. In the closing years of the 20th Century, the dam was infested with aquatic weeds especially the water hyacinth, leading to its imminent partial "death" and the recreational activities were no more.

The photographs shown in Figures 1A, B and C, taken during a visit to the dam on 24th May 2003, is a manifestation of the current problem, with Figure C showing some of the activities around Nairobi Dam. A clear infestation of the dam by the water hyacinth is evident, which is a probable consequence of Eutrophication.

The big question is: Can the present condition of Nairobi Dam be reversed? This can only be possible if the Eutrophication state of the dam is investigated and understood in order to take corrective measures. The water hyacinth has become a global menace and much work has been going on in its eradication and control (Detwyler, 1971; Thyagarajan, 1984). However, not much work has been comprehensively done in this country and its neighbours

A

B

Figures 1 A & B. Photographs of the Nairobi Dam, taken during a visit at the site on 24th May 2003, indicating the extent of infestation of the dam by the water hyacinth and with B also showing the principal investigator at the foreground.

C

Figure 1 C. Photograph of Nairobi Dam's entrance, showing farming activities around it, taken on 24th May 2003. One of its tributaries, Motoine River passes through the middle, while sugar cane and other subsistence crops feature in the background and foreground respectively.

on Eutrophication of rivers, lakes and dams. The current research was therefore intended to seal this loophole.

1.8 Justification for the Research Work

Previously, no detailed research work on Eutrophication of lakes, rivers and dams had been done in the East African region, especially in Kenya, and particularly in Nairobi Dam. Thus, a detailed data base needs to be accumulated, which would go a long way in assisting the relevant local authorities and ministries concerned with water, fisheries, recreation and environment in decision making. Based on the results of the parameters obtained, appropriate clean up models will be developed by the relevant authorities. Using Nairobi Dam as a model that has been developed in the current project, other areas inhabited by similar weeds could be managed. The research was therefore meant to provide a first detailed study on the Eutrophication of the above area. This will complement what has been reported on the pollution of Nairobi River basin, especially with regard to seasonal influence (Okoth and Otieno; 2000; Kithiia, 1992).

1.9 Objectives of the Research

1.9.1 General Objective

The main objective of the research was to determine the present Eutrophication state of Nairobi Dam, Kenya, in order to give suitable recommendations for corrective action measures.

1.9.2 Specific Objectives

The specific objectives of the research were to:

(a) Survey the different types of plant weeds infesting Nairobi Dam and provide plant density distribution by species.

(b) Determine the levels of major nutrients ((Orthophosphate plus hydrolysable) - phosphorous, Nitrate - N, Total Kjeldahl - Nitrogen (TKN), Sulphate, Chloride, Sodium, Potassium, Calcium, Magnesium); essential trace nutrient elements (Manganese, Iron, Zinc, Copper, Fluoride) and other parameters, such as Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Conductivity, Turbidity, Dissolved Oxygen, pH and Anionic Surfactants of water samples at point sources of Nairobi Dam in dry and wet seasons.

(c) Analyze levels of the above nutrients and parameters in the surrounding rivers and streams feeding into and out of the dam, during the same period.

(d) Establish the relationship between the parameters in (b) and (c) above.

(e) Study and deduce possible seasonal influences on the nutrient load.

(f) Determine levels of the above nutrients in Sediments and Plant samples in the above aquatic systems, in addition to water, during the same period in order to obtain their ratios to the water's loadings.

(g) Generate useful data base and information on wastewater management, using water hyacinth and other available weeds.

(h) Study possible correlation between various chemical species detected and draw deductions, e.g. between phosphorous and nitrogen levels in the above aquatic environment during various seasons to determine the limiting nutrient for the aquatic weed proliferation.

(i) Give recommendations to the relevant authorities with regard to Eutrophication of the above aquatic environment.

1.10 Hypothesis

The current apparent Eutrophication in Nairobi Dam is postulated to be mainly due to the abundance of phosphorous as a result of use and disposal of anionic surfactants in domestic sewage effluents. The element, which is most essential for the growth of the water-hyacinth in the shallow dam, is therefore expected to be the limiting element in the growth and proliferation of the water hyacinth in the dam and its environs.

CHAPTER II

2.0 THEORY OF THE PRINCIPAL ANALYTICAL TECHNIQUES

In order to monitor the current Eutrophication state of the Dam, the levels of the various parameters were determined in water from Nairobi Dam and surrounding tributaries and in Sediments and Plants from the same aquatic environments over a number of months. These parameters included: Nutrients (Phosphate, Nitrate, Total Kjeldahl Nitrogen, Sulphate, Chloride, Sodium, Potassium, Calcium, Magnesium); Essential trace elements (Manganese, Iron, Zinc, Copper, Fluoride) and other parameters, such as Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Conductivity, Dissolved Oxygen and pH. These were compared with other aquatic systems of the world which have exhibited Eutrophication in the past and relevant conclusions drawn. Possible correlation among the above parameters and seasonal influences on the nutrient loads in the area investigated were also determined.

In order to accomplish the above, the following analytical techniques were employed: Ultraviolet and Visible Absorption Spectrometry, Flame Emission and Atomic Absorption Spectrometry, Ion Selective Electrode, Titration and other routine physical and chemical laboratory procedures.

Below are the principles involved in some of the major selected techniques used above. The remaining physical and chemical techniques are simple

laboratory procedures, whose theories and principles can be found in most of the Analytical Chemistry textbooks.

2.1 Ultraviolet and Visible Absorption Spectrometry

The theory and instrumentation of this technique can be found in various text books such as Willard *et al.* (1986). In Absorption Spectrophotometry of the Visible and Ultraviolet regions of the spectrum, a source of radiation must be provided with each spectral region having its own requirements. All spectrophotometers include some way to discriminate between different radiation frequencies either through use of filters, prisms or gratings. The sample absorbs a portion of the incident radiation; the remainder is transmitted on to a detector where it is changed into an electrical signal and displayed, usually after amplification, on a meter, chart recorder, or some type of readout device. The instrument modules are depicted in schematic diagram shown in Figure 2.

The UV/Visible Spectrophotometer instruments used in the current project were:-

(a) DR LANGE Cadas 100 UV/Visible Spectrophotometer, Type-Nr. LPG 185 (made in W. Germany).

(b) ANTHELIE ADVANCED V2.5b - SECOMAM UV/Visible Spectrophotometer (made in France).

(c) Turner UV/Visible Spectrophotometer, Model Sp-850 (made in Dubuque, Iowa, U.S.A.).

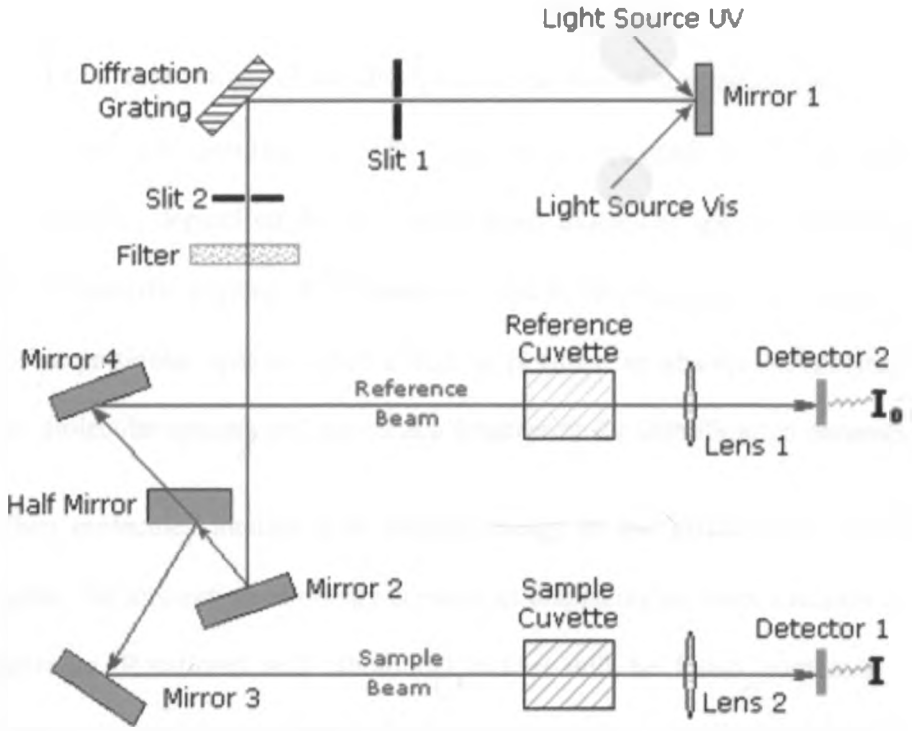

Figure 2. **Schematic diagram depicting Instrument modules for measuring UV/Visible Absorption of radiation.**

When an electromagnetic wave of a specific wavelength impinges upon a substance, the fraction of the radiation absorbed, ignoring losses due to reflections and scattering, will be a function of the concentration of the substance in the light path and the thickness of the sample. The transmittance, T, is defined as the ratio of the intensity (or radiant power) of unabsorbed radiation (relative to the blank), I, to the intensity of the incident radiation, I_o; thus $T = I/I_o$. Absorbance, A, is the base-ten logarithm of the reciprocal of the transmittance:

$$A = \log (1/T) = -\log (I/I_o) \quad \text{---------- (5)}$$

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Percent transmittance is 100T; percent absorption is 100(1-T).

Analytical applications of the absorptive behaviour of substances can be either qualitative or quantitative. The qualitative applications of absorption spectrometry depend on the fact that a given molecular species absorbs light only in specific regions of the spectrum and in varying degrees characteristic of that particular species. Such a display is called an absorption spectrum of that molecular species and serves as a fingerprint for identification purposes.

When molecules interact with radiant energy in the visible and ultraviolet region, the absorption of energy consists in displacing an outer electron in the molecule. Rotational and vibrational modes will be found combined with electronic transitions. Broadly, the spectrum is a function of the whole structure of a substance rather than of specific bonds. No unique electronic spectrum will be found; this is a poor region for the product identification by the "fingerprint" method. Information obtained from this region should be used in conjunction with other evidence to confirm the identity of a compound; for example, previous history of a compound, its synthesis, auxiliary chemical tests and other spectroscopic methods. On the other hand, electronic absorption often has a very large magnitude. Molar absorptivity values frequently exceed 10,000, whereas in the infrared they rarely exceed 1,000. Thus, dilute solutions are adequate in visible-ultraviolet spectrophotometry (Willard *et al.*, 1986).

2.1.1 Fundamental Laws of Photometry

As a beam of photons passes through a system of absorbing species, the rate of photon absorption with distance traversed is directly proportional to the

power of the photon beam, I, sometimes symbolized by P, since the intensity has units of energy per unit time or power. The reduction in intensity, -dI, can be stated mathematically as:

$$-(dI/dx) = kI \quad \text{----------} \quad (6)$$

In Equation (6), k is a proportional constant characteristic of the nature of the absorbing species and of the energy of the photons and I represents the radiant power at any distance x in the absorbing medium. Rearranging and separating variables in Equation (6) gives Equation (7):

$$(-dI/I) = -d(\ln I) = kdx \quad \text{----------} \quad (7)$$

This is a mathematical statement of the fact that the fraction of radiant power absorbed is proportional to the thickness traversed. Now, if it is stipulated that Io is the radiant power at b = 0, and that I represents the radiant power of the transmitted radiation emerging from the absorbing medium at x = b, then Equation (7) can be integrated along the entire radiation path:

$$-\int_{I_o}^{I} d\ln I = k\int_{0}^{b} dx \quad \text{----------} \quad (8)$$

Obtaining

$$\ln I_o - \ln I = \ln (I_o/I) = kb \quad \text{----------} \quad (9)$$

In simple terms, Lambert's Law (Equation (9)) states that, for a given concentration of absorber, the intensity of transmitted light, previously rendered plane parallel and entered the absorbing medium at right angles to the plane decreases logarithmically as the path length increases arithmetically.

Of much greater interest is the dependence of intensity on the concentration of absorbing species in solution. Beer found that increasing the concentration of absorber had the same effect as increase in the radiation-absorbing path length. Thus, the proportionality constant, k, in Equation (9) is in turn proportional to the concentration of absorbing solute, C, or

$$k = aC \quad \text{----------} \quad (10)$$

Use of base-ten logarithms instead of natural logarithms requires only that the value of k (or a) to be changed. Thus the combined law becomes

$$A = \log (I_o/I) = abC \quad \text{----------} \quad (11)$$

Where a incorporates the conversion factor to base-ten, namely, 2.303. This is the most familiar expression of the combined Lambert-Beer law, which is simply called Beer's law. If the sample path length is expressed in centimeters and the concentration in grams of absorber per liter of solution, the constant a, designated as absorptivity, has the units of liter g^{-1} cm^{-1}.

Frequently, it is desirable to specify C in terms of molar concentration, with b remaining in units of centimeters. Thus Equation (11) becomes

$$A = \log (I_o/I) = \varepsilon bC \quad \text{----------} \quad (12)$$

In Equation (12), ε, in units of liter mol^{-1} cm^{-1}, is called the molar absorptivity. In the older literature, molar absorptivity may have been called molar extinction coefficient or molar absorbancy index (Willard *et al.*, 1986).

A plot of absorbance versus concentration will be a straight line passing through the origin. Readout scales and meter scales on spectrophotometers are usually calibrated to read absorbance as well as transmittance.

Absorption of radiation by molecules at specific wavelengths is frequently used for quantitative analysis owing to the direct relationship between absorbance and concentration. Sensitivity of spectrometric analysis is dictated by the magnitude of the absorptivity and the minimum absorbance which can be measured with the required degree of certainty (Willard *et al.*, 1986).

2.2 ***Flame Emission and Atomic Absorption Spectrometry Analysis (FES and AAS)***

Combustion of flames provide a remarkably simple means for converting inorganic analytes in solution into free atoms. It is only necessary to introduce an aerosol of the sample solution into an appropriate flame and a fraction of all

of the metallic ions in the aerosol droplets are eventually converted into free atoms. Once the free atoms are formed, they may be detected and determined quantitatively at the trace level by atomic Flame Emission Spectrometry (FES), Atomic Absorption Spectrometry (AAS), or Atomic Fluorescence Spectrometry (AFS). Flame methods, properly applied, now provide results for a number of elements by which all other methods must be judged, especially at low levels. This is clearly the case of zinc, cadmium, the alkali metals, and the alkaline earths. In many situations, FES or AAS will be preferred over all others for elements such as Al, Cr, In, Mn, Pb and the heavier rare earths (Willard *et al.,* 1986).

In Flame Emission Spectrometry, a fine aerosol of the sample solution, following nebulization, is introduced into a flame where it is desolvated, vaporized and atomized. Subsequently, atoms are raised to an excited electronic state via thermal collisions with the constituents of the partially burned flame gases. Upon their return to a lower or ground electronic state, the excited atoms emit radiations that are characteristic for each element. The emitted radiation passes through a monochromator or suitable filters that isolate the desired spectral feature which is then registered by a photo detector whose output is amplified and read on a meter or recorder (Willard *et al.,* 1986).

Atomic absorption in flames is carried out by use of the principle originally discussed by Walsh (1955) and recently by Clesceri *et al.,* (1989). This entails the determination of the absorption at the line centre by using a narrow-line

source emitting the given resonance line of the element, whose emission line profile is less than the absorption line profile of the analyte in the flame. The flame gases are treated as a medium containing free unexcited atoms capable of absorbing radiation from an external source when the radiation corresponds exactly to the energy required for a transition of the test element from the ground electronic state to an upper excited electronic state. Unabsorbed radiation passes through a monochromator that isolates the exciting spectral line and into a photo detector. Absorption is measured by the difference in transmitted signal in the presence and absence of the test element (Willard *et al.*, 1986).

Atomic Absorption Spectrometry is ideally suited to the determination of the metal contents of water of all types such as rivers, lakes and wastewaters. The method is relatively free from spectral or radiation interferences as each metal has its own absorption wavelength and a source lamp composed of that element is used. The most troublesome type of interference is termed "chemical" and results from lack of absorption by atoms bound in molecular combination in the flame (Clesceri *et al.*, 1989).

Comparing the analytical performance of both AAS and FES, it can be seen that these methods supplement each other in many respects. The analytical performance of FES is better for alkali, alkaline-earth, and rare earth elements, as well as for Ga, In, and Tl. Absorption Flame Spectrometry permits Ag, Al, Au, Bi, Cd, Cu, Hg, Pb, Te, Sb, Se, and Sn to be detected with high sensitivity. The performance of both methods for other elements is very

similar. The choice of the method depends upon the matrix to be analyzed and the analysis-selectivity desired. In routine analysis it is reasonable to combine both methods. However, FES possesses one very important advantage in that it allows simultaneous quantitative multi-element analyses to be performed (Willard *et al.*, 1986).

Flame Emission Photometry is an atomic emission method for the routine detection of metal salts, principally Na, K, Li, Ca and Ba. Quantitative analysis of these species is performed by measuring the flame emission of solutions containing the metal salts. Solutions are aspirated into the flame. The hot flame evaporates the solvent, atomizes the metal and excites a valence electron to an upper state. Light is emitted at characteristic wavelengths for each metal as the electron returns to the ground state. Optical filters are used to select the emission wavelength monitored for the analyte species. Comparison of emission intensities of unknowns to either that of standard solutions or to those of an internal standard allows quantitative analysis of the analyte metal in the sample solution. However, use of low temperatures renders this method susceptible to certain disadvantages, most of them related to interference and the stability (or lack thereof) of the flame and aspiration conditions. Fuel and oxidant flow rates and purity, aspiration rates, solution viscosity and sample matrix affect these. It is therefore very important to measure the emission of the standard and unknown solutions under conditions that are as nearly identical as possible (Harris, 1995).

In the current work, Flame Emission Photometry (FEP) was used for the determination of levels of Na and K, while Flame AAS was used for the determination of levels of Ca, Mg, Mn, Fe, Cu and Zn in water samples directly and in the extracted sediment and plant samples, which were treated as described in the literature (ISO Standards Compendium, 1994 (a); Clesceri *et al.,* 1989; Thyagarajan, 1984).

2.2.1 Basic Principles of Atomic Spectroscopy

This has been discussed in details in the literature (Price, 1972). Atomic Absorption Spectrometry is based upon the absorption of radiation by free atoms. The basic reaction underlying AAS may be stated as follows:

$$R + h\upsilon \rightleftharpoons R^* \qquad \text{----------} \quad (13)$$

Where:

R is the ground state atom;

R* is the excited state atom;

h is the Planck's constant and

υ is the frequency.

An atom is said to be in the ground state when its electrons are in their lowest energy levels. When energy is transferred to such atoms by means of thermal or electrical excitation, a number of different excitation states result throughout the population. The ground state atom therefore absorbs energy to

yield the excited state, which in turn emits radiation following de-excitation process. Absorption or emission of light is therefore associated with the process of transition of atoms from one steady state to the other.

For the steady states m and n with energies E_m and E_n respectively, when $E_n > E_m$, then m to n transition results in the absorption of light and n to m transition results in emission of light with frequency υ_{mn}, given by:

$$\upsilon_{mn} = \frac{(E_n - E_m)}{h} \quad \text{---------- (14)}$$

According to Einstein's quantum theory of radiation (Price, 1972; Ewing, 1969), there may be three transitions between levels m and n:-

(a) Emission (n to m) from the excited state to a lower energy state taking place spontaneously.

(b) Absorption transitions (m to n) from a lower to a higher energy state taking place in response to the action of external radiation with a frequency, υ_{mn}. Subscript mn implies frequency of transition is from level m to n.

(c) Emission (n to m) transitions from an excited state to a lower energy state, stimulated by external radiation of the same frequency, υ_{mn}.

The n to m emission transitions thus include two types of transitions:-

(i) Spontaneous transitions taking place without any external source and

(ii) Transitions stimulated by external radiation.

The m to n absorption transitions are always stimulated by external radiation. This phenomenon forms the integral part of Atomic Absorption Spectrometry.

The proportion of excited to ground state atoms in a population at a given temperature can be considered with the aid of the Boltzmann relation (Ewing, 1969) as follows:

$$(N_n/N_m) = (G_n/G_m) \exp(-(E_n - E_m)/kT) \quad \text{---------- (15)}$$

where N is the number of atoms in a state n or m. G is the statistical weight of a particular state, k is the Boltzmann constant and T is the Kelvin temperature.

Since $E_n - E_m = \frac{h\,c}{\lambda}$,

where c is the speed of light and λ = wavelength, it follows that for a fixed T, N_n/N_m increases with wavelength. This latter ratio is very small over the temperature ranges of typical flames (3,000 – 4,000 °C), and has a value of around 10^{-10} – 10^{-4}, sodium at 3,000 K has a N_n/N_m value of 6×10^{-4}. This means there is a very low proportion of atoms in the first excited state, n, compared to that in the ground state, m. Absorption by atoms takes place within very narrow spectral regions of the order of hundredths of angstroms. In the laboratory, only those transitions involving the ground state are observed, yielding simple spectra. Absorptions involving the ground state are therefore known as resonance lines. This means that there is little possibility of coincidence of resonance lines, and therefore very little spectral interference, thus accounting for one of the main advantages of AAS (Welz, 1969).

For dilute solutions, the relation between intensity, absorbance and concentration of absorbing species involving monochromatic light is the same as that discussed under UV/Visible Spectrometry in section 2.1.1.

2.2.2 Instrumentation and Techniques

The schematic diagrams of the essential components of an Atomic Absorption Spectrophotometer and a Flame Photometer are shown in Figures 3 and 4, respectively.

The instruments used in the current project were:-

(i) (a) UNICAM 969 AA Atomic Absorption Spectrometer attached to DELL Optiplex attached to Pentium II Intel / DELL with Microsoft Windows 98 Data Systems

(b) PERKIN ELMER ANALYST 306 AAS attached to Pentium II Intel / DELL with Microsoft Windows 98 Data Systems

(ii) Corning 400 Flame Photometer

The functions, principles and techniques of spectral sources, flame atomization, monochromators, slits, detectors and read-out systems are well documented in the literature (Willard *et al.,* 1986; Welz, 1976; Price, 1972; Ewing, 1969).

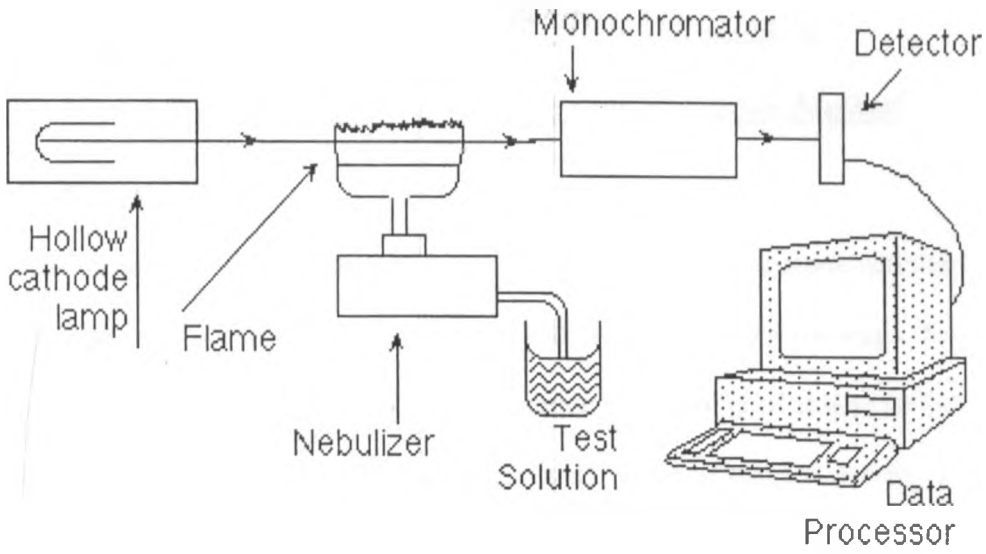


Figure 3. **Schematic diagram showing components of an Atomic Absorption Spectrophotometer.**

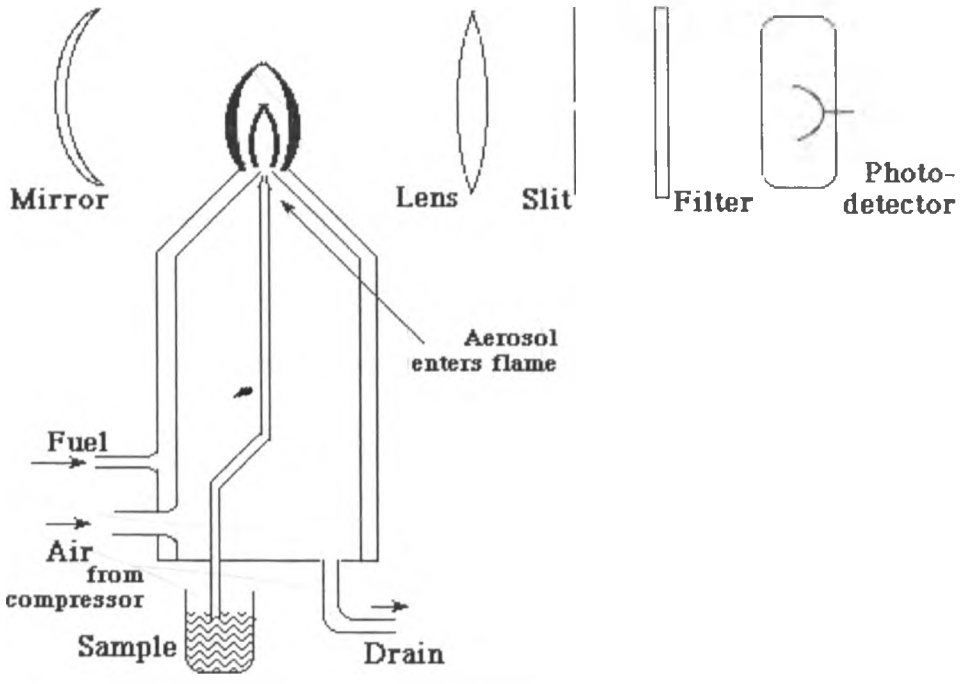


Figure 4. **Schematic diagram showing components of a Flame (Emission) Photometer.**

2.3 *Electrochemical Probe Methods – Determination of Fluoride and Chloride by Ion-Selective Electrode Method (ISE)*

When an ion-selective electrode comes in contact with an aqueous solution containing the specific ions, a potential difference develops between the measuring electrode and the reference electrode. The value of this potential difference is proportional to the logarithm of the value of that ion activity in accordance with the Nernst Equation at 25°C (ISO Standards Compendium, 1994 (a); Willard *et al.*, 1986):

$$E = E^{o} - (0.05915/n) \text{ Log } [red]/[ox] \quad \text{---------- (16)}$$

Where

E is the electrode potential;

E^{o} is the standard electrode potential;

n is the number of electrons transferred in the electrode reaction;

[red] is the concentration of the reduced form;

[ox] is the concentration of the oxidized form.

The above technique was used for the determination of fluoride and chloride ions. Temperature and ionic strength may influence the potential difference. Accordingly, these parameters should be the same during calibration and measurement and should be kept constant throughout the procedure.

The activity of the fluoride ions is also pH dependent. Values of pH between 5 and 7 have proved favourable for measurement. Special buffer solutions are used to fix the pH and the activity coefficient (ISO Standards Compendium,

1994 (a)). The following specific equipment was used in the analysis of fluoride and chloride in liquid samples and extracts:

(a) pH meter, DIGI 610 D6072 - Karl Kolb Scientific Technical Supplies, West Germany, with respective Ion Selective Electrodes.

(b) JENWAY ELECTRODES, Fluoride (F), (924-305 S/N 1209) and Chloride (Cl), (924-304 S/N 1191), with calomel reference electrode - for determination of Fluoride and Chloride ions respectively.

N.B. The ISE method for determination of chloride was only just for comparison and to supplement the data obtained with the principal titration method as described later.

2.4 Other Analytical Techniques / Tools Used

(a) Automated Distillation/Titration Unit – 2300 Kjeltec Analyzer Unit, Foss Tecator (Computerized), Made in Sweden – for determination of Total Kjeldahl Nitrogen.

(b) Turbidity Meter, TE/F – Trübungsphotometer LTP 5 DR. BRUNO LANGE Gmbh, Berlin, West Germany – for determination of Turbidity.

(c) Conductivity Meter – Karl Kolb Scientific Technical Supplies, West Germany; with Electrode WTW – LTA 100, K = 1.00 cm^{-1} – for determination of Conductivity.

(d) Dissolved Oxygen Meter, model OXI 42 - Karl Kolb Scientific Technical Supplies, West Germany – for determination of Dissolved Oxygen.

CHAPTER III

3.0 EXPERIMENTAL PROCEDURES AND ANALYTICAL TECHNIQUES *(METHODOLOGY)*

A map of part of the City of Nairobi showing Nairobi Dam, its tributaries and environs and the sampling points is shown in Figure 5. The area of the dam is approximately 0.274 Km^2. The samples collected and analyzed included water, sediments and plants from Nairobi Dam, and from its two main tributaries, Motoine and Ngong Rivers. Sampling was mainly done near the bridges, shores or where the dam and the rivers were easily accessible.

3.1 Sampling

3.1.1 Sampling and Sample Storage

Water samples were drawn in duplicate using clean High Density Poly-Ethylene (HDPE) plastic containers of 1L and 2L capacities, at the surface of various points of the dam and its two tributaries almost simultaneously. This was done by three well coordinated teams to avoid time variation effects. For every pair of samples, one was acidified by addition of 2ml of conc. H_2SO_4 (96-98% m/m) per litre of sample and stored at room temperature until the time of analysis. The untreated samples were stored in the fridge at 4^oC until the time of analysis. The addition of acid in one set of water samples greatly

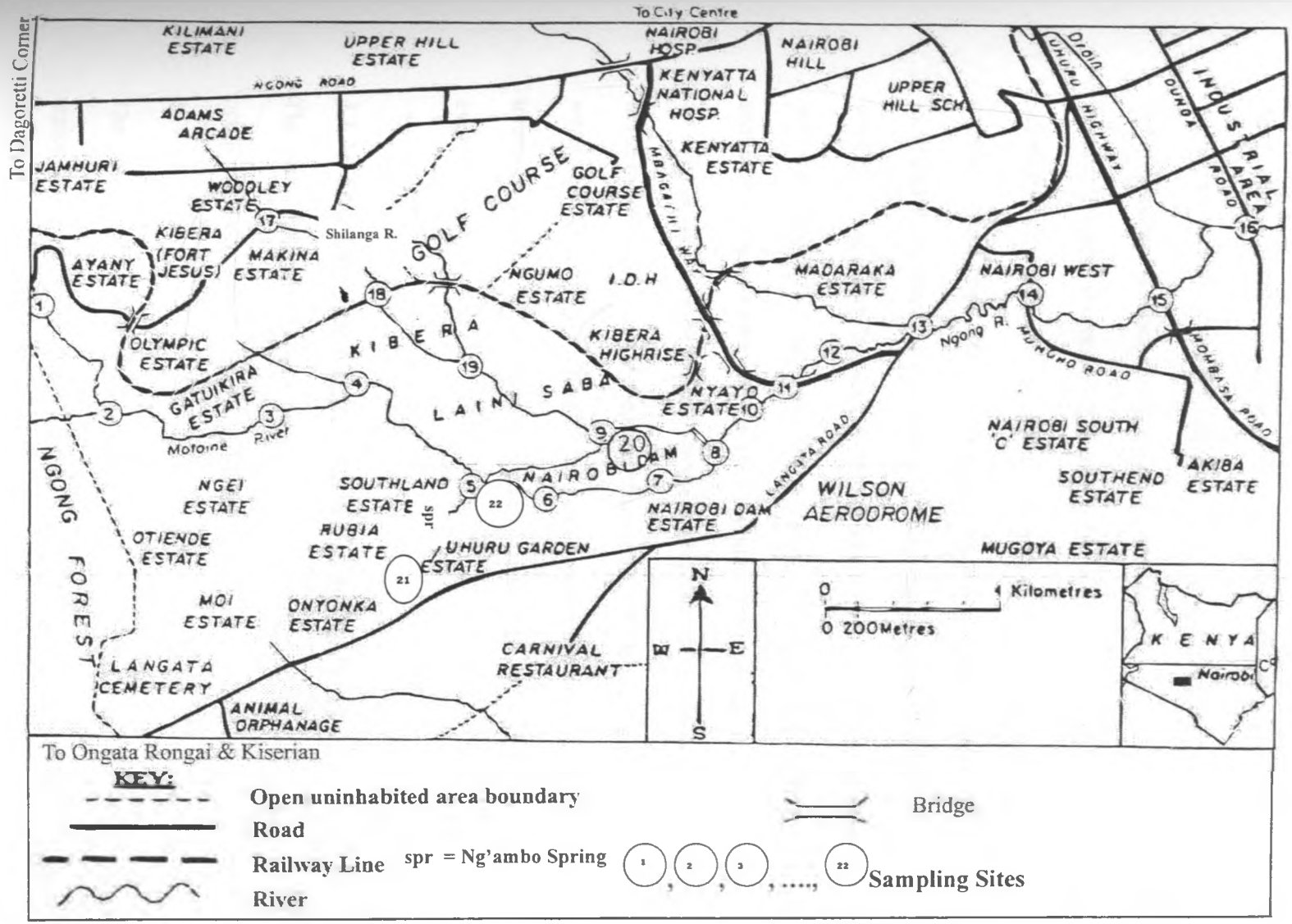


Figure 5. Map of Nairobi Dam, its major tributaries and environs, showing the sampling points

inhibited or prevented metabolic processes of micro-organisms which could cause changes in the sample (Report by the Working Party, 1980). Furthermore, it prevented flocculation and precipitation of, say, metal compounds and reduced adsorption on the surface of the container, thus keeping the inorganic nutrients in solution for a long duration of time. The wet sediments were also collected, where possible, at the respective points, using stainless steel scoops into 50 or 100 ml clean plastic bottles. Plant samples including the available water hyacinth or other aquatic weeds in Nairobi Dam were collected mainly by plucking the leafy part of the plant and / or stem, cut into small pieces and transferred into cellulose and polythene paper bags. The sediments were first analyzed for Total Kjeldahl Nitrogen and then dried in an air oven at 105°C for 3- 4 hours. On the other hand, plant samples were dried in the oven for 7-8 hours at the same temperature. Both were dried to constant weight, stored at room temperature and analyzed for the available/ extractable nutrients, as described in the appropriate sections. Analysis was done after every sampling.

3.1.2 Brief Environmental Description of Sampling Points

The environmental information of all the sampling points, including their neighbourhood vicinities is given in Table 1.

The sampling covered the various seasons / weathers experienced in the region, i.e. from 2nd October 2004 to 22nd April 2006, as shown later (Table 2).

TABLE 1. **ENVIRONMENTAL DESCRIPTION OF SAMPLING POINTS**

SP No.	Description & Location	Notes (Activities)
1	First Sampling Point of Motoine River (Inlet), bordering Nairobi International Show.	Clean water. No slums in the vicinity. Middle-class area.
2	Second Sampling Point of Motoine River.	Beginning of slum, no proper sewage disposal.
3	Third Sampling Point of Motoine River.	Midst of slum, raw sewage.
4	Fourth Sampling Point of Motoine River.	End of slum, slight farming activities.
5	Dam Entrance from Motoine River (Inlet).	No water hyacinth growing during most of the sampling seasons.
6	On Nairobi Dam Shore.	Covered by water hyacinth.
7	On Nairobi Dam Shore.	Covered by water hyacinth.
8	At Exit of Nairobi Dam.	Covered by water hyacinth.
9	Dam Entrance from Shilanga River (Inlet).	Covered by water hyacinth.
10	First Sampling Point on outlet. No slum in the vicinity. A new modern middle class residential area (Nyayo Estate) on one side.	Small-scale farming belonging to Langata Prison on the other side. Domestic waste water from estate pouring into the river.
11	Second Sampling Point along the Ngong River Outlet. Middle class estate on one side.	Flower farming on other side, but sewage effluents from higher areas pouring into the river.
12	No residential area in the vicinity.	Small-scale and flower farming activities on either side.

TABLE 1 *(contd...)*

SP No.	Description & Location	Notes (Activities)
13	Confluence with another stream passing through Kenyatta Hospital Estate.	Small-scale and flower farming and car-washing activities on either side.
14	Middle class residential areas on either side.	No slums, but slight agricultural activities.
15	Cemented river banks and bottom. No sediments available.	Flower farming, with a few middle-class residential areas and social amenities.
16	Final sampling point downstream at Mater Hospital bridge, after Uhuru Highway Drain confluence.	A few modern social and residential areas and the beginning of Industrial Area, with Lubrication and Metal Industries in place.
17	First Sampling Point upstream, along Shilanga River (Inlet), at Kibera DO's office.	Clean water, before slum, just after middle-class area.
18	Near the Railway Line.	Midst of slum, raw sewage.
19	At a confluence with river from Golf Course Estate.	End of slum, raw sewage.
20	Middle of Nairobi Dam.	Covered by water hyacinth.
21	First Sampling Point from Ng'ambo Spring (Inlet).	Clean (spring) water for domestic use, no slum. Middle-class area.
22	Dam Entrance from Ng'ambo Spring (Inlet).	No water hyacinth growing during most of the sampling seasons.

KEY USED IN TABLE 1: SP No. = Sampling Point Number

3.1.3 Climatic and Weather Conditions during the Sampling Seasons

The climatic and weather conditions during the sampling seasons are described in Table 2 below.

TABLE 2. **DESCRIPTION OF SAMPLING SEASONS AND WEATHER CONDITIONS**

SS No.	SAMPLING DATE	CLIMATIC / WEATHER CONDITION DESCRIPTIONS ON SAMPLING DAY & OTHER COMMENTS
1	**2/10/2004**	Dry weather, but a very light rain had fallen the previous month.
2	**12/2/2005**	Generally dry weather, not much different from the previous sampling of October 2004. However, there were quite appreciable rains on 25th & 29th January 2005.
3	**2/4/2005**	Fair weather. Moderate rainy Season. There were Heavy rains from 14th to 24th March 2005, before there was a pause.
4	**21/05/2005**	Moderate weather. It had just rained heavily the previous night till the beginning of sampling. Quite high water levels, with very fast speed were observed. Water hyacinth had been swept downstream by the long rains & absent from some sampling sites.
5	**9/7/2005**	Extremely cold weather. It had also not rained for nearly one month, except a few drizzles, just before sampling date.
6	**20/08/2005**	Extremely hot and sunny, with no rain. Last major rain recorded on the night of 29th July 2006. Cold season / weather had just ended.
7	**24/09/2005**	Extremely dry season and very warm temperatures. No rains during months of August and September. Normal water levels.

TABLE 2 *(contd...)*

SS No.	SAMPLING DATE	CLIMATIC / WEATHER CONDITION DESCRIPTIONS ON SAMPLING DAY & OTHER COMMENTS
8	**22/10/2005**	In the morning it was cold and cloudy, but during most of the day, it was extremely very hot, with no rain. There were light showers on the previous night and exactly one week before sampling day.
9	**19/11/2005**	During most of the week, including the sampling day, it was dry & hot. It had rained a bit only during the previous weekend.
10	**24/12/2005**	Extremely very hot dry season, with no rain. It had not rained for more than a month since the previous sampling.
11	**28/1/2006**	Extremely very hot dry season, with no rain. It had not rained for quite a long period, even since the previous sampling, except a few drizzles experienced once, one week before.
12	**10/3/2006**	Quite warm weather and at the beginning of the long rainy season. It had rained for previous 1½ weeks. This was after the long dry spell for over 3 months.
13	**22/4/2006**	Quite warm weather and during the long rainy season. It had rained during previous but one, and current week. Water hyacinth had been swept downstream by the rains and the plant was absent at various sites.

KEY USED IN TABLE 2: SS No. = SAMPLING SEASON NUMBER

3.2 *Chemicals and Materials Required*

3.2.1 Reagents

The stock chemicals used were of analytical grade. These, together with their sources, purities and other materials used are summarized below in Table 3, while others are given in the relevant sections under Methodology.

TABLE 3. **CHEMICALS AND OTHER MATERIALS USED**

SL No.	CHEMICAL / MATERIAL USED AND FORMULA	% PURITY	SUPPLIER / MANUFACTURER
1.	Sulphuric acid (H_2SO_4)	96 & 98	Panreac Quimica SA & S.d.fiNE-CHEM Ltd. Respectively
2.	Hydrochloric acid (HCl)	37	Riedel-de-Haen
3.	Sodium hydroxide (NaOH)	99	R.P. Normapur (AR)
4.	Potassium sulphate (K_2SO_4)	99.0	Panreac Quimica SA & BDH Chemicals Ltd.
5.	Copper Sulphate ($CuSO_4.5H_2O$)	99.0–100.5	Panreac Quimica SA
6.	Boric acid (H_3BO_3)	99	Aldrich Chemical Co. Ltd.
7.	Ammonium sulphate [$(NH_4)_2SO_4$]	99.5	BDH Chemicals Ltd.
8.	Barium chloride dihydrate ($BaCl_2.2H_2O$)	99.0	Panreac Quimica SA & Lab Tech Chemicals
9.	Ascorbic acid ($C_6H_8O_6$)	99.5-100	E.T. Monks & Co. Ltd.
10.	Ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$	99.0	Alpha-chemical Ltd. & May & Baker Ltd.

TABLE 3 *(contd...)*

SL No.	CHEMICAL / MATERIAL USED AND FORMULA	% PURITY	SUPPLIER / MANUFACTURER
11.	Antimony potassium tartrate hemihydrate [$K(SbO)C_4H_4O_6.½ H_2O$]	99	BDH Chemicals Ltd.
12.	Potassium dihydrogen phosphate (KH_2PO_4)	99.3	J.T. Baker Chemical Co. Ltd.
13.	Sodium salicylate ($C_6H_4OH.COONa$)	99.8	BDH Chemicals Ltd.
14.	Potassium sodium tartrate tetrahydrate (Rochelle salt)	99.5	Riedel-de-Haen
15.	Sodium nitrate ($NaNO_3$)	99.5	BDH Chemicals Ltd.
16.	Chloroform ($CHCl_3$)	99.0	Panreac Quimica SA
17.	Potassium chromate (K_2CrO_4)	99.5	Riedel-de-Haen
18.	Silver nitrate powder ($AgNO_3$)	99.5	R.P. Normapur (AR)
19.	Silver nitrate ampoule ($AgNO_3$)	0.1, 0.02 N	Normadose
20.	Sodium chloride (NaCl)	99.5	R.P. Normapur (AR)
21.	Potassium chloride (KCl)	99.5	BDH Chemicals Ltd.
22.	Sodium fluoride (NaF)	99.0	BDH Chemicals Ltd.
23.	Iron (II) sulphate heptahydrate ($FeSO_4.7H_2O$)	99.5	E.T. Monks & Co. Ltd.
24.	Potassium dichromate ($K_2Cr_2O_7$)	99.8	Riedel-de-Haen
25.	1,10-Phenanthroline monohydrate	N.I.	May & Baker Ltd.
26.	Methylene blue indicator	N.I.	May & Baker Ltd.
27.	Sodium dodecyl sulphate (NaDDS) ($C_{12}H_{25}SO_4Na$)	98.5	Sigma Chemicals Ltd.

TABLE 3 *(contd...)*

SL No.	CHEMICAL / MATERIAL USED AND FORMULA	% PURITY	SUPPLIER / MANUFACTURER
28.	Glacial acetic acid (CH_3COOH)	99.7	Panreac Quimica SA
29.	Ammonium acetate ($CH_3COO\ NH_4$)	97	Panreac Quimica SA
30.	Lanthanum oxide (La_2O_3)	99.8	Merck Chemicals (PTY) Ltd.
31.	Cesium chloride (CsCl)	99.9	Park Scientific Ltd.
32.	Bromocresol Cresol Green	N.I.	Kobian (K) Ltd.
33.	Methyl red indicator	N.I.	May & Baker Ltd.
34.	CDTA (Trans-1,2-diamino cyclohexane - N,N,N',N' - tetra acetic acid $((CH_2.COOH)_2N.CH(CH_2)_4.CH.N(CH_2.COOH).2H_2O$	97.5	BDH Chemicals Ltd.
35.	Ethanol, absolute (C_2H_5OH)	99.5	Panreac Quimica SA
36.	Methanol (CH_3OH)	99	Panreac Quimica SA
37.	Methyl orange indicator	N.I.	May & Baker Ltd.
38.	Phenolphthalein indicator	N.I.	Howse & McGeorge Ltd.
39.	Sodium sulphate (Na_2SO4)	99	R.P. Normapur (AR)
40.	Petroleum spirit (40-60°C)	N.I.	R.P. Normapur (AR)
	OTHER MATERIALS USED:		**SUPPLIER / MANUFACTURER**
1.	Teepol Detergent		Odex Chemicals Ltd.
2.	Distilled Water		Inorganic Lab (KEBS)
3.	Gooch crucibles, porosity 4 & 3		Sciencescope (K) Ltd.

TABLE 3 *(contd...)*

SL No.	OTHER MATERIALS USED:	SUPPLIER / MANUFACTURER
4.	Omo Washing Powder for std. (Sodium dodecyl benzene sulphonate)	Unilever (K) Ltd.
5.	Desiccant , Silica gel self-indicating, blue silica based	Sciencescope (K) Ltd.
6.	Filter papers, nos. 40, 540, 541	Whatman
7.	Ordinary Glass ware	Pyrex & Borosilicate
8.	pH buffer 4.0	Panreac Quimica SA
9.	pH buffer 7.0	Panreac Quimica SA

N.B. SL No. = Serial Number, N.I. = Not Indicated

3.2.2 Washing of Apparatus

All glassware, sample and other plastic containers used were rinsed with tap water, then soaked in washing detergent for at least 12 hours, thoroughly rinsed with running tap water, distilled water, 3-4 N HCl and finally with distilled water. Glass containers were dried in the oven at 105 $\pm$ 2°C and plastic ones at 70-80°C for about 30 minutes, before cooling and use. In addition, the HDPE sample plastic containers were rinsed several times with the water from the sampling site concerned, just before drawing the actual sample.

3.2.3 Preparation of Reagents

In the preparation of reagents, water that had been distilled in glass was used throughout the analysis. For the preparation of individual stock, working and

calibration standards and other reagents, reference is made to the appropriate section under sample preparation.

3.3 Sample Preparation and Pretreatment

3.3.1 Water Samples

Since interstitial (soluble) nutrient ions and other parameters were to be determined, water samples did not undergo any preliminary sample preparation / extraction apart from the usual analytical treatment as described in the respective procedures. For the determination of the physical parameters (Dissolved Oxygen, Turbidity, Electrical Conductivity and Total Dissolved Solids) and sulphate, the untreated (un-acidified) samples (B) were used. For the determination of other nutrients, the acidified samples (A) were used, after filtering through Filter Paper No. 40 or 540. For all these determinations, dilutions were done where necessary. Distilled water blank was included as well for Quality control and blank correction.

3.3.2 Sediments, Soils and Plants – Extraction

About 1 gram of sample was accurately weighed on an analytical balance and extracted with 35ml of buffered extracting solvent (2% Acetic acid (v/v) in 1M Ammonium acetate in water) by shaking on a mechanical shaker at 200 oscillations per minute for 30 minutes as recommended in the literature (Perkin Elmer, 1996; Rehm and Caldwell, 1968). This was filtered through filter paper No. 40 or 540. The residue was rinsed several times and the filtrate diluted to 250 ml with distilled water in a volumetric flask. Determination of

the available nutrients was performed on the filtrate. A reagent blank, containing all reagents, without the sample was treated in the same way as the samples and its readings subtracted from the samples.

3.4 Sample Analysis

The nutrient ions and physical parameters were determined in the water samples as described in the literature (ISO Standards Compendium, 1994 (a); Fresenius *et al.*, 1988), while sediment and plant samples were pre-treated as described above before analysis. Five (n = 5) representative soil samples were also included in the final sampling for comparison with the sediments.

The anionic parameters (Hydrolysable + Orthophosphate)-Phosphorous, Nitrate-Nitrogen and Anionic Surfactants were analyzed by use of UV/Visible Spectrometry, Sulphate by Gravimetric (precipitation) method, Fluoride and Chloride by Ion-Selective Electrode technique and Chloride mainly by Titration. The essential trace and bulk metals (Mn, Fe, Zn, Cu, Ca, Mg, K & Na) were analyzed by calibration with respective appropriate standard solutions, using Flame Atomic Absorption Spectrophotometer (with their respective hollow cathode lamps) and Flame (Emission) Photometer. Sediment and plant sample extracts were analyzed for the nutrient parameters using the same techniques as for water. The water samples were filtered but not digested. Chemical Oxygen Demand (COD) for water was obtained by employing standard analytical methods, using titration with Potassium dichromate.

The other physical parameters (Dissolved Oxygen, Total Dissolved Solids (TDS), Electrical Conductivity, Turbidity and pH) were analyzed according to the following literature methods (ISO Standards Compendium, 1994 (b); Kenya Bureau of Standards, 1985):

3.4.1 Quantitative Method for Determination of Anionic Species using Ultraviolet and Visible Absorption Spectrophotometer

An Ultraviolet / Visible absorption spectrum of each species to be determined was obtained either from the literature or experimentally by means of a scanning spectrophotometer. From an inspection of the absorption spectra, a suitable absorption band was selected for each species as explained in the literature (Willard *et al.*, 1986).

Sample extracts were complexed with suitable reagents, which converted the ion of interest into a species or molecule, that absorbed in the Visible region of the spectrum at a suitable wavelength. Since Absorbance was proportional to the Concentration of the species (as demonstrated under Results and Discussions), this technique was used to determine the concentration of Orthophosphate, Nitrate and Anionic Surfactants (ISO Standards Compendium, 1994 (a); Fresenius *et al.*, 1988; Dr. Lange Manual, 1986), as described below:-

3.4.1.1 Determination of (Hydrolysable plus Orthophosphate) - Phosphorous

Principle:

Reaction of orthophosphate ions with an acid solution containing molybdate and antimony ions forms an antimony phosphomolybdate complex. Reduction of the complex with ascorbic acid forms a strongly coloured molybdenum blue which absorbs in the visible and near infra-red regions of the spectrum at 880 nm or 700 nm (ISO Standards Compendium, 1994 (a)).

Interferences:

It is reported that silica (> 5 mg Si/L), H_2S (> 2 mg S/L), fluoride (> 200 mg/L), iron (> 10 mg/L), vanadate (10 mg V/L), chromium (50 mg/L) and arsenate cause an increase in absorbance. On the other hand, nitrite concentrations greater than 1 mg N/L may bleach the colour formed.

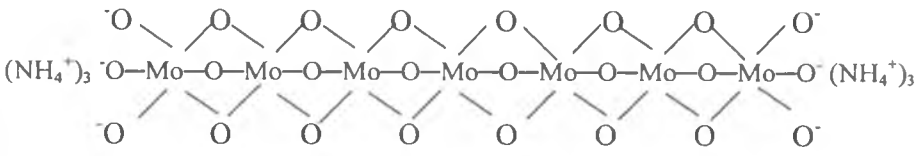
Reactions (Lee, 1983):

$$PO_4^{3-}+(NH_4)_6Mo_7O_{24}+[SbOC_4H_4O_6]^-+10H^+ \rightarrow PO_4Mo_7O_{21}SbO_4+6NH_4^++C_4H_8O_6+3H_2O$$

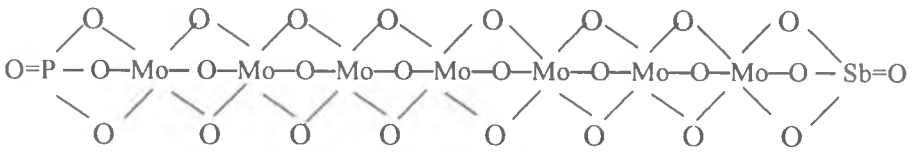
$$PO_4Mo_7O_{21}SbO_4 +20e^- +20H^+ \xrightarrow[\text{Ascorbic acid}]{\text{(Reduction with}} H_2PO_4Mo_7O_{12}SbO_4 +9H_2O$$

(Light yellow complex) (Molybdenum blue, a hetero polyacid)

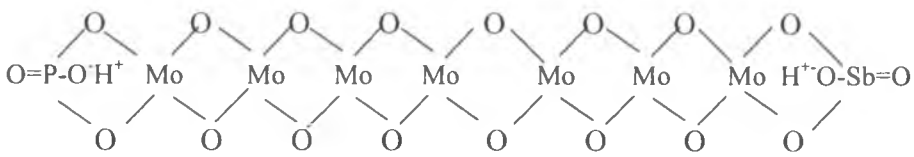
The structural formula for anhydrated ammonium heptamolybdate, $[(NH_4)_6Mo_7O_{24}]$ is:



while that for the antimony phosphomolybdate complex initially formed ($PO_4Mo_7O_{21}SbO_4$), where molybdenum has coordination number and oxidation number of 6, is:



On the other hand, the structure of the final reduced molybdenum blue ($H_2PO_4Mo_7O_{12}SbO_4$), where molybdenum has coordination number and oxidation number of 4, may be illustrated as follows:



Preparation of Reagents:

9M Sulphuric acid solution

500 ± 5 ml of distilled water was added to a 2 L beaker. To this, 500 ± 5 ml of sulphuric acid (ρ = 1.84 g/ml) was cautiously added, with continuous stirring and mixed thoroughly.

2M Sulphuric acid solution

300 ± 3 ml of distilled water was added to a 1 L beaker. To this, 110 ± 2 ml of 9 mol/L of sulphuric acid solution was cautiously added, with continuous

stirring and cooling. This was diluted to 500 ± 2 ml with water and mixed thoroughly.

2M Sodium hydroxide solution

80 g of sodium hydroxide pellets were dissolved in distilled water, cooled and diluted to 1 L with the same distilled water.

Ascorbic acid solution, 100 g/L

10 g of ascorbic acid ($C_6H_8O_6$) was dissolved in water and diluted to 100 ml with distilled water, thoroughly mixed and stored in an amber glass bottle in a refrigerator at 4°C. It could be used as long as it remained colourless.

Acidified molybdate solution

13 g of ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] was added to 0.35 g antimony potassium tartrate hemihydrate [$K(SbO)C_4H_4O_6.½ H_2O$] in a clean glass container. To this was added 200 ml of water followed by 300 ml of 9 mol/L sulphuric acid with continuous stirring and mixed well.

Orthophosphate, stock standard solution (50 mg of P/L)

0.2197 g of dry KH_2PO_4 was dissolved in about 800 ml of water in a 1 000 ml volumetric flask. 5 ml of 9 mol/L sulphuric acid was added and made up to the mark with water, mixed well and refrigerated at 4°C.

Orthophosphate, standard solution (2 mg of P/L)

20 ml of orthophosphate stock standard solution above was pipetted into a 500 ml volumetric flask. This was made up to the mark with water, mixed well and refrigerated at 4°C.

1ml of this standard contained 2 µg of P.

Procedure:

The acidified water samples were filtered through No. 40 or 540 filter papers. 40 ml of the water fitrate had its pH adjusted to 3-10, using 2 M sulphuric acid or sodium hydroxide. To 40 ml of the sediment extract and 5 ml of the plant extract was added 1 ml of the ascorbic acid solution followed by 2 ml of acidified molybdate solution. The solution was brought to 50 ml mark with distilled water, mixed thoroughly and left to stand for at least 30 minutes and diluted if necessary for analysis. For calibration process, 0.0; 1.0; 3.0; 5.0; 8.0; 10.0 and 15.0 ml of the orthophosphate standard solution (2 mg P/L) were transferred by means of pipette to a series of 50 ml volumetric flasks, diluted to about 40 ml with distilled water. To this solution was added 1 ml of the ascorbic acid solution followed by 2 ml of acidified molybdate solution. The solution was brought to 50 ml mark with distilled water, mixed thoroughly and left to stand for at least 30 minutes. The absorbance for the standards and sample solutions were read at 880 nm with a UV / Visible Spectrophotometer. A calibration graph of absorbance against the phosphorous content, in mg/l, of the calibration solutions was plotted and linear correlation coefficient ascertained to be $\geq$ 0.99. From the graph, the sample phosphorous contents

were calculated. Spiked water and acid-washed sand were treated in the same way as the samples, for Quality Control validation.

3.4.1.2 Determination of Nitrate – Nitrogen

Principle:

Nitrate ions and sodium salicylate react in an alkaline medium to form a yellow sodium p-nitro salicylate, which can be determined spectrophotometrically at 420 nm (Fresenius *et al.*, 1988).

Interferences:

If the concentrations of nitrate are less than 0.5 mg/L, then the method is inaccurate. Also, presence of other species absorbing at 420 nm will also give false positive results.

Reaction Equations: (Morrison and Boyd, 1983)

$$NO_3^- + 2H_2SO_4 \leftrightarrow H_2O + 2HSO_4^- + NO_2^+$$

(Nitrate ion) (Nitronium ion)

$$C_6H_4OH.COONa + NO_2^+ \rightarrow [C_6H_3^+.H.OH.NO_2.COONa]$$

(Sodium salicylate)

$$[C_6H_3^+.H.OH.NO_2.COONa] + HSO_4^- \rightarrow C_6H_3.OH.NO_2.COONa + H_2SO_4$$

$$2C_6H_3.OH.NO_2.COONa + H_2SO_4 \rightarrow 2C_6H_3.OH.NO_2.COOH + Na_2SO_4$$

$$2C_6H_3.OH.NO_2.COOH + NaOH \rightarrow C_6H_3.OH.NO_2.COONa + H_2O$$

(Sodium (p-nitro) salicylate)

Preparation of Reagents:

Sodium salicylate solution

0.5 g of sodium salicylate was dissolved in distilled water, diluted to 100 ml in a volumetric flask and mixed well. This solution was prepared afresh daily.

Sodium hydroxide and potassium sodium tartrate mixed solution

400 g of sodium hydroxide pellets and 16 g of potassium sodium tartrate (Rochelle salt) were dissolved in a plastic beaker with distilled water. The mixture was cooled in ice, made up to 1 L and stored in a plastic container.

Nitrate stock standard solution (1000 mg of NO_3^-/L)

1.37 g of sodium nitrate was dissolved in distilled water. 1 ml of chloroform was added and made up to 1 L with distilled water. This was stored at $\leq 15^oC$.

Nitrate standard solution (100 mg of NO_3^-/L)

The nitrate stock standard solution was diluted with distilled water in the ratio 1:10, by diluting 10 ml to 100 ml with distilled water. From this, the calibration standard solutions were made.

Nitrate calibration standard solutions

From the 100 mg/l nitrate standard solution, calibration solutions were prepared in the range (0.0, 1.0, 3.0, 6.0, 9.0 and 12.0) mg/l by pipetting respectively (0.0, 1.0, 3.0, 6.0, 9.0 and 12.0) ml into 100 ml volumetric flasks and diluting to mark with distilled water. The 0.0 mg/l served as blank for zero correction of the instrument.

Procedure:

50 ml of the calibration standard solutions, acidified water samples, sediment and plant extracts, including their respective blanks and spiked Quality Control sample solutions were transferred into 100 ml plastic beakers. 2 ml of sodium salicylate solution was added and evaporated to near dryness in the air oven at 105 $\pm$ 2°C. The residue was cooled at room temperature. 2 ml of conc. Sulphuric acid was added and the solution allowed to stand for 10 minutes. 15 ml of distilled water was added followed by 15 ml of Sodium hydroxide / potassium sodium tartrate mixed solution. This was cooled to room temperature and transferred to 100 ml volumetric flask and made to the mark with distilled water. These were stirred and mixed well. The absorbance of the calibration standard and sample solutions, their respective blanks and recovery spikes were measured, using a calibrated UV / Visible Spectrophotometer at 420 nm after taking the zero reading using a blank test solution and operated as per manufacturers' instructions. A calibration graph of absorbance against the concentration was plotted and its linear correlation coefficient, i.e. r ascertained to range from 0.99 to 1.00. Using the linear regression equation, the sample nitrate was calculated. This value was multiplied by the factor 0.226, which is the stoichiometric ratio of the relative atomic mass of nitrogen to the relative formula mass of the NO_3^- species, i.e. (N/ NO_3^-), or (14/(14+(16*3)), to obtain the corresponding NO_3^--N concentration.

3.4.1.3 ***Determination of Anionic Surfactants***

This was done by using a combination of methods from ISO (ISO Standards Compendium, 1994 (a)) and those from other literature as well (Koga *et al.*, 1999).

Principle:

Determination of anionic surfactants is done by extraction of the water sample with acidic methylene blue solution. Measurement of the absorbance of the separated organic phase is done at the maximum absorption wavelength of 650 nm. Evaluation is by means of a calibration curve. For reasons of purity and stability, the preferred standard is dodecyl benzene sulfonic acid methyl ester (tetra propylene type, relative molecular mass 340), although other surfactants may be used as standards. The calibration standard is prepared from the standard dodecyl benzene sulfonic acid ester after saponification to the sodium salt. Calculation of the MBAS (methylene blue active substances) is usually expressed as sodium dodecyl benzene sulphonate (Koga *et al.*, 1999; ISO Standards Compendium, 1994 (a)).

Interferences:

Cationic substances (such as quaternary ammonium compounds) and proteins which form compounds with anionic surfactants may lower the MBAS level. On the other hand, organic sulphates, sulphonates, carboxylates, phenols and inorganic anions such as cyanate, nitrate, thiocyanate and sulphide can also be methylene blue active.

Expected Reactions:

$2C_{12}H_{25}C_6H_4SO_3Na + H_2SO_4 \longrightarrow 2C_{12}H_{25}C_6H_4SO_3H + Na_2SO_4$ (A)

(Sodium dodecyl benzene Sulphonate (NaDDBS))

(Dodecyl benzene sulphonic acid)

$2C_{12}H_{25}SO_4Na + H_2SO_4 \longrightarrow 2C_{12}H_{25}SO_4H + Na_2SO_4$ (B)

(Sodium dodecyl Sulphate (NaDDS))

(Dodecyl sulphuric acid)

Preparation of Reagents:

Acid methylene blue solution

0.350 g of methylene blue was dissolved in about 500 ml water and 6.50 ml sulphuric acid (ρ = 1.84 g/ml) added and stirred. This was diluted to 1 000 ml and mixed well.

Ethanol (C_2H_5OH), 95% (v/v)

Into a 100ml volumetric flask was transferred 95 ml of absolute ethanol. This was diluted to mark with distilled water.

Phenolphthalein indicator solution

1.0 g phenolphthalein was dissolved in 50 ml ethanol and 50 ml of distilled water added, while stirring.

Sodium dodecyl benzene sulfonic acid salt (NaDDBS) standard ($C_{12}H_{25}$ $C_6H_4SO_3Na$) (A)

This was prepared by extraction of the commercially available Omo powdered detergent, from Unilever (Kenya) Limited, the most commonly used household detergent that contains the sodium salt.

To obtain the active detergent matter of almost absolute purity, 15 gm of Omo detergent powder was weighed. 600 ml of 95% ethanol (neutralized by addition of 0.1 N alcoholic NaOH, using phenolphthalein indicator solution) was added. This was placed on a water bath at 65-68°C for about 15 minutes. This was cooled to room temperature and filtered on suction pump, using sintered glass crucible of porosity 3. The filtrate was evaporated to dryness (constant weight) for about 3 hours at 105°C. The difference in weight represented the Active Detergent matter (Kenya Bureau of Standards, 2003 (b)).

Sodium dodecyl sulphate (NaDDS) Standard, purity 98.5% ($C_{12}H_{25}SO_4Na$) (B)

This was purchased from the manufacturer in its Analytical grade form (Table 3). It was solely used for analytical sensitivity comparison with the NaDDBS standard above during the extraction process.

From each of the solid standards (A and B), stock and calibration standard solutions were made as follows:

Stock standard solutions (A and B)

400 to 450 mg of each of the standards was weighed and transferred to a 1 000 ml one-mark volumetric flask, diluted to mark with distilled water and mixed well. This was stored in the fridge at about 4°C.

Working standard solutions (A and B)

10 ml of the stock standard (A and B) was diluted to mark with distilled water in a 50 ml one-mark volumetric flask and mixed well.

Calibration standard solutions (A and B)

From the working standard solution (A and B) was pipetted (0.0, 1.0, 2.0, 4.0, 6.0 and 8.0) ml into 100 ml volumetric flasks. These were diluted to the mark with distilled water. The 0.0 ml (no standard dilution) served as a standard blank for instrumental zero correction.

Procedure:

100 ml of the calibration standard solutions were transferred into 250 ml separating funnels. 5 ml of acidified methylene blue solution was added and mixed well. This was extracted twice with 15 ml of chloroform each. The (lower) chloroform layers were combined together and diluted to 100 ml with chloroform. The absorbance readings were taken on a UV / Visible Spectrophotometer at 650 nm for plotting calibration graphs. The linear

correlation coefficient was determined and ascertained to be in the range 0.99 to 1.00.

The un-acidified water samples (B) were filtered through a filter paper no. 40 or 540. 50 ml of the filtrate was diluted to 100 ml with distilled water and extracted the same way as the calibration standard solutions above. The combined chloroform extracts were diluted to 50 ml with chloroform and the absorbance readings taken on the same spectrophotometer under the same conditions as the standards. A sample blank containing 50 ml of distilled water was extracted and treated the same way as the samples. Its value was subtracted from that of the samples.

3.4.1.4 Determination of Total Kjeldahl (Proteinaceous and Ammoniacal) Nitrogen – (TKN): Automated Distillation & Titration

Principle:

The sum of ammoniacal and organic (proteinaceous) nitrogen (Total Kjeldahl Nitrogen) may be determined by titrating with HCl, using mixed indicator, the ammonia evolved by digesting the sample with sulphuric acid in the presence of a catalyst and reacting the digest with NaOH, steam distilling off and condensing the ammonia into a titration vessel containing (boric acid) receiver solution, with the colour changing from green to light red at the end point.

Interferences:

Nitrate and/ or nitrite may cause positive errors through reduction to ammonium ions and negative errors by forming ammonium salts with

ammonium ions in the sample and subsequently releasing gaseous N_2 instead of ammonia (ISO Standards Compendium, 1994 (a)).

Reaction Equations:

$$\underset{\text{(Protein / Organic nitrogenous material in water, sediment or plant)}}{R(CO.NH)_{5.25}(COO^-)(NH_3)^+} \xrightarrow[\text{with } H_2SO_4)]{\text{(Hydrolysis / Digestion}} 3.125(NH_4)_2SO_{4\,(aq)} + CO_{2\,(g)}$$

$$(NH_4)_2SO_{4\,(aq)} + 2NaOH_{\,(aq)} \longrightarrow Na_2SO_{4\,(aq)} + NH_{3\,(g)} + H_2O_{\,(l)}$$

$$\underset{\text{(Ammonia gas)}}{NH_{3\,(g)}} + \underset{\text{(Boric acid)}}{B(OH)_{3\,(aq)}} + H_2O_{\,(l)} \longrightarrow (NH_4)^+(B(OH)_4)^-_{\,(aq)}$$

$$(NH_4)^+(B(OH)_4)^-_{(aq)} + HCl_{\,(aq)} \longrightarrow NH_4Cl_{\,(aq)} + H^+(B(OH)_4)^-_{\,(aq)},$$

which is the final titration reaction, with respective end points.

Reagents used (Tecator Manual, 1997):

Sodium hydroxide solution (40%, m/m)

Sodium hydroxide solution, 4%, m/v (1 M)

Concentrated sulphuric acid (96%)

Potassium sulphate salt / Copper (II) sulphate as catalyst

Standard hydrochloric acid (0.5 N)

Bromo Cresol Green

Methyl red

Boric acid (H_3BO_3)

Methanol (CH_3OH)

Indicator solution A

0.1 ± 0.01 g of methyl red was dissolved with 100 ml of methanol.

Indicator solution B

0.1 ± 0.01 g of bromocresol green was dissolved with 100 ml of methanol.

Boric acid (1%, m/v with mixed indicator) as receiver solution

100 ± 1 g of boric acid (H_3BO_3) was dissolved in 10 litres of distilled water and cooled to room temperature. 70 ml of indicator solution A and 100 ml of indicator solution B followed by 5 ml of 1 M NaOH were added to this solution and mixed thoroughly. The alkali was necessary to achieve a positive blank value (Tecator Manual, 1997).

Ammonium sulphate $(NH_4)_2SO_4$, dried (for making liquid spiked reference materials).

Procedure:

30 ml of liquid (water, liquid blank and recovery) samples or 0.3-1 g of solid (sediment, dried plant and solid recovery) samples were weighed into clean dry digestion tubes. 0.8 g of $CuSO_4.5H_2O$ and 7 g of K_2SO_4 were added to each of the digestion tubes. 10 ml of (96%) conc. Sulphuric acid was added from a dispenser and mixed carefully by swirling the tube by hand. The rack with digestion tubes containing the samples was placed besides the automated digester and fitted with the exhaust manifold on top. The vacuum source (scrubber) was turned on to maximum air flow. The tubes and exhaust

manifold were placed in the pre-heated digester at 420°C and the heat shields hooked on the stand. The tube contents were digested for 3-5 minutes with maximum air flow through the manifold. The flow was then adjusted until the fumes were just contained. The digestion was continued until all samples were clear with a blue green solution. This was normally about 30 minutes, depending on sample type. The stand with the tubes and exhaust manifold were removed and the entire assembly cooled sufficiently at room temperature, but avoiding solidification. However, if formed, any solid was dissolved by placing the digestion tube in the pre-heated digester for a short time.

The Automated Distillation / Titration – 2300 Kjeltec Analyzer Unit, Foss Tecator (Computerized) was started up (according to the instrument's operating manual). The suitable Kjeldahl programme was selected for reading the nitrogen content in %, m/m. One or two blanks were run, their display noted and their value recorded. The prepared digestion tube was placed in position and the safety door closed. When the cycle was over, the results were noted and the safety door opened to remove the digestion tube ready to insert the next sample digestion tube and the cycle repeated. These included the liquid and solid spiked and House Reference Materials (HRM) (Kenya Bureau of Standards, 1990; ISO, 1983).

Calculation of results:

$$\text{Total Kjeldahl Nitrogen (TKN), \%, m/m} = \frac{1.401 \times (V_2 - V_1) \times N}{B}$$

Where V_2 = Volume of hydrochloric acid required for the sample;

V_1 = Volume of standard hydrochloric acid required for the blank;

N = Normality of hydrochloric acid used in titration;

B = Mass in grams of the sample taken for determination.

3.4.1.5 Determination of Chloride by Titration

Principle:

Reaction of chloride with silver ions forms insoluble silver chloride, which precipitates quantitatively. Addition of a small excess of silver ions from silver nitrate, using potassium chromate as indicator will turn the colour from orange to red brown, to form silver chromate (Mohrs method). This reaction is used for indicating the end-point. The pH is maintained in the range of 5 to 9.5 throughout the titration in order to allow precipitation (ISO Standards Compendium, 1994 (a)).

Interferences:

Substances forming insoluble silver compounds (such as Br^-, I^-, S^{2-}, CN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$), compounds forming complexes with silver ions (such as NH_4^+ and $(S_2O_3^{2-})$), substances which reduce chromate ions (such as Fe^{2+} and SO_3^{2-}) and others such as SCN^-, CrO_4^{2-} and PO_4^{3-} give erroneously higher chloride values. On the other hand, highly coloured or turbid solutions such as hydrated iron oxide may obscure the end point.

Reaction Equations:

$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} \downarrow$

$2Ag^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow Ag_2CrO_{4\,(aq)}$
(Orange) (Red brown)

Reagents:

Silver nitrate, standard volumetric solution, 0.02 M $AgNO_3$

3.3974 of silver nitrate ($AgNO_3$), previously dried at 105°C, was dissolved in water and diluted to 1 000 ml in a volumetric flask and stored in an all-glass amber bottle. Alternatively, this was made from a 0.02 N $AgNO_3$ ampoule as directed by the manufacturer.

Silver nitrate, standard volumetric solution, 0.1 M $AgNO_3$

This was made from a 0.1 N $AgNO_3$ ampoule as directed by the manufacturer.

Potassium chromate, indicator, 100 g/L solution

10 g of potassium chromate (K_2CrO_4) was dissolved in distilled water and diluted to 100 ml.

Chloride stock standard solution, 1000 mg/l and QC recovery standard solutions

1.6501 g of NaCl (99.9% purity) was dissolved in distilled water and diluted to 1 000 ml in a volumetric flask to form the stock solution. From this, using appropriate dilutions, lower chloride standard solutions were made for QC recovery and spikes.

Nitric acid solution, 0.1 M (made from a 0.1 N HNO_3 ampoule as directed by the manufacturer)

Sodium hydroxide solution, 0.1 M (made from a 0.1 N NaOH ampoule as directed by the manufacturer)

Procedure:

100 ml or a smaller volume (V_a) of un-acidified filtered water sample, blank, spike / recovery, sediment or plant sample extract was transferred into a 250 ml conical flask. The pH was checked and adjusted to 5 to 9.5, using nitric acid or sodium hydroxide solutions as appropriate. This pH range was to allow for complete precipitation to take place, as recommended in the literature (ISO Standards Compendium, 1994 (a)). To this, 1 ml of potassium chromate indicator solution was added. This solution was titrated by dropwise addition of silver nitrate solution from a burette until the colour of the solution just changed to a reddish brown and the volume noted (V_s). Where the titrant volume exceeded 25 ml, the determination was repeated using a smaller test portion volume.

Calculation of results:

The chloride content, ρ_{cl}, in milligrams per litre, is given by the formula:

$$\rho_{cl} = \frac{(V_s - V_b)cf}{V_a}$$

Where

ρ_{Cl} is the concentration of chloride, in milligrams per litre;

V_a is the volume, in millilitres, of the test sample (maximum 100 ml);

V_b is the volume, in millilitres, of the silver nitrate solution used for the titration of the blank;

V_s is the volume, in millilitres, of the silver nitrate used for the titration of the sample;

c is the actual concentration, expressed in moles per litre of the silver nitrate solution;

f is the conversion factor,

f = 35 453 mg/mol.

3.4.1.6 Determination of Sulphate - Gravimetric Method Using Barium Chloride

Principle:

Acidification of the liquid sample with hydrochloric acid followed by boiling with barium chloride solution for at least 20 min to promote coagulation results in precipitation of barium sulphate. This is followed by filtration through a tared sintered-glass crucible, washing the precipitate free from chloride, drying at 105°C and reweighing when cool. The increase in mass of the crucible is due to the barium sulphate precipitate formed by reaction of barium with sulphate ions in the sample (ISO Standards Compendium, 1994 (a); Kenya Bureau of Standards, 1985 (b)).

Interferences:

Sulphides and sulphites could interfere if samples are unduly exposed to air, causing oxidation to sulphate to occur before analysis. Organic compounds present in substantial amounts may also interfere by absorption or co-precipitation.

Reaction Equation:

$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}\downarrow$

Reagents:

Hydrochloric acid (6 M)

500ml ± 10 ml of concentrated hydrochloric acid [ρ(HCl) = 1.18 g/ml] was carefully mixed with water and diluted to 1 litre in a measuring cylinder. This was stored in a glass or polyethylene bottle.

Barium chloride, dihydrate solution (100 g/L)

100 g ± 1 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in about 800 ml of distilled water, warming the mixture to aid dissolution. The solution was cooled, diluted to 1 litre with distilled water in a measuring cylinder and stored in a polyethylene bottle.

Methyl orange indicator solution, about 1 g/L

100 mg of methyl orange was dissolved in about 50 ml of water, warming the mixture to aid dissolution. The solution was cooled, diluted to 100 ml with distilled water in a measuring cylinder and stored in a glass bottle.

Silver nitrate solution, about 0.1 M

17g ± 1g of silver nitrate, $AgNO_3$, was dissolved in about 800 ml of distilled water, diluted to 1 litre in a measuring cylinder and stored in an amber glass bottle.

Procedure:

200 ml of un-acidified filtered water samples, their blank and spikes; 50 ml of sediment and plant sample extracts, their blank and spikes were transferred into 500 ml conical flasks and 2 drops of methyl orange indicator added. This was acidified with 2 ml ± 0.2 ml of hydrochloric acid. The contents were boiled for at least 5 minutes on a hot plate. To the boiling solution was added slowly about 12 ml of hot (about 80°C) barium chloride solution and this was heated further for at least one hour. The solution was covered, allowed to cool and stand for at least 12 hours at room temperature to allow for precipitation to form. The precipitate was filtered on an accurately weighed sintered-glass crucible (m_1) (of porosity value of 4) fitted to a Buchner flask, equipped with safety guard for vacuum filtration. The precipitate formed was filtered and rinsed with cold water through the crucible using gentle suction. The precipitate was washed with chloride-free cold water. To ascertain whether washings and hence the barium sulphate were free from chloride, about 5 ml of the filtrate was collected and checked for any turbidity formation with 5 ml of silver nitrate solution. The washing continued until this test was negative. The crucible was removed, dried at 105°C ± 2°C in an air-oven for about 1 hr, cooled in a desiccator and weighed. The process of heating, cooling and

weighing continued until a constant weight was obtained. For any batch of samples, a blank containing 200 ml of distilled water was treated the same way as the samples and its value, m_0 obtained by subtraction.

Calculation of results:

The mass of barium sulphate in the test sample, m, in grams, was calculated as follows:

$$m = m_2 - m_1 - m_0$$

Where

m_0 is the mass in grams of the blank calculated, with no sample;

m_1 is the mass of the empty crucible, in grams;

m_2 is the mass of the crucible with the precipitate formed from the sample.

The concentration of sulphate (mg/l) in the liquid sample (water or solid sample extract) was calculated from the following equation:

$$[SO_4^{2-}]\ (mg/l) = \frac{(m \times 0.4116 \times 10^6)}{V}$$

Where

m is the mass of barium sulphate precipitate, in grams;

V is the test portion volume, in milliliters;

0.4116 is the gravimetric factor.

3.4.1.7 Determination of Fluoride and Chloride Using Ion-Selective Electrode Method (ISE)

Principle:

Using a fluoride or chloride ion-selective electrode, with a suitable reference electrode, the voltage potential reading is proportional to the logarithm of the fluoride or chloride ion concentration.

Interferences for Fluoride Analysis:

Cations such as calcium, magnesium, iron and aluminium form complexes with fluoride or precipitates to which the electrode does not respond. Hence addition of buffer, TISAB as a de-complexing agent is necessary to free bound fluoride. However, BF_4^- anion is not de-complexed by addition of the buffer.

Preparation of Reagents for Fluoride Analysis:

Sodium hydroxide solution, NaOH 5 M

100 g $\pm$ 0.5 g of sodium hydroxide pellets were dissolved cautiously in distilled water, cooled and diluted to 500 ml.

Total Ionic Strength Adjustment Buffer (TISAB)

58 g of sodium chloride (NaCl) and 57 ml of glacial acetic acid [ρ (CH_3COOH) = 1.05 g/ml] were added to 500 ml of water in a 1 litre beaker. The mixture was stirred until dissolution of NaCl was realized. 150 ml of the 5M NaOH solution and 4 g of CDTA (trans-1,2-diaminocyclohexane-

N,N,N',N'-tetraacetic acid) were added. Further stirring was done until all the solids had dissolved. The solution was adjusted to pH 5.2 with sodium hydroxide solution using a pH meter. The solution was transferred to a 1 000 ml volumetric flask, made up to the mark with distilled water and mixed well.

Fluoride standard stock solution (1 000 mg/l)

2.2328 g of NaF (99%) was dissolved in distilled water in a 1 000 ml volumetric flask then diluted to the mark and mixed thoroughly. The solution was stored in a HDPE plastic container at ambient temperature.

Fluoride calibration standard solutions:

From the fluoride standard stock solution were made the following working (calibration standards) solutions, by appropriate dilutions: 0.01, 0.02, 0.05, 0.1, 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, and 5.0 mg/l.

Reagents (for Chloride Analysis) – Chloride calibration standard solutions:

Using the 1000 mg/l Chloride stock standard solution (ref. section 3.4.1.5), the following working (calibration standards) solutions were made: 0.5, 0.8, 1.0, 5.0, 10.0, 20.0, 40.0, 70.0 and 100.0 mg/l.

Procedure for determination of Fluoride and Chloride:

For the determination of fluoride, 25 ml of the buffer solution (TISAB) was mixed with 25 ml each of the calibration standard solutions, un-acidified filtered water samples, sediment and plant sample extracts and their

corresponding spikes into a plastic beaker. For the determination of chloride, the buffer solution was not added. In this latter case, the sample solution volume was doubled (i.e. about 50 ml).

The suitable ion selective electrode (fluoride or chloride) was immersed successively into calibration and sample solutions after appropriate instrumental conditioning. Their potential readings, in mV were taken. A calibration graph of voltage potential versus logarithm of (fluoride or chloride) ion concentration was plotted, its linear correlation coefficient, r, determined and ascertained to be in the range 0.99-1.00. From the graph, the sample fluoride and chloride contents were determined. The ISE method for determination of chloride was used for support of and comparison with the data obtained from titration method as described earlier.

3.4.2 Flame Emission and Atomic Absorption Spectrometry Analysis (FES and AAS)

The theory and applicability of these techniques are well documented in the literature (Willard *et al.*, 1986; Walsh, 1955; Greenberg *et al.*, 1985) as discussed in Chapter 2. In the current work, Flame Emission Spectrometry (FES), i.e. Flame Photometer, was used for the determination of the levels of Na and K, while Atomic Absorption Spectrometry (AAS) was used for determination of Ca, Mg, Mn, Fe, Zn and Cu in water samples as well as in sediments and plants. The latter two sample types were treated as described in Section 3.3.2.

Aspiration of the water samples into a flame of sufficient thermal energy caused any sodium and potassium present to emit their characteristic radiation. Measurement of the intensity was done at a wavelength of 589.0 nm for sodium and 766.5 nm for potassium. Samples were aspirated directly into the AAS, with appropriate dilutions, for the determination of available Ca, Mg, Mn, Fe and Cu, without need for digestion or extraction, using standard procedures, as cited in the literature above. For the determination of calcium and magnesium, when using air/ acetylene flame, caesium chloride solution (as an ionization buffer) was added (so that one litre of the final solution contained 2.5 gram of CsCl and 0.8 ml of conc. (37%) hydrochloric acid) and when using nitrous oxide/ acetylene flame, lanthanum oxide (La_2O_3) was added, so that one litre of the final solution contained 1000 mg of lanthanum and 20 ml of conc. (37%) hydrochloric acid (Perkin Elmer, 1996; ISO Standards Compendium, 1994 (a)). In the current work, the oxidant/ fuel mixtures indicated below were mostly used for the following techniques:

(a) AAS for Ca and Mg - Nitrous oxide/ acetylene flame was used

(b) AAS for other metals – Air/ acetylene flame was employed

(c) Flame Photometer for Na and K – Air/ n-butane flame was used

In determining the amounts of available/ extractable major and trace metal nutrients (K, Na, Ca, Mg, Mn, Fe, Zn, Cu) in sediment and plant samples, they were treated with 1M Ammonium acetate buffer in 2% Acetic acid solution in water, thus bringing the minerals into solution, as described in Section 3.3.2. These were then analyzed as water samples and diluted where necessary.

Spiked recovery samples were also included for reference and analytical Quality Control.

Metals were analyzed using the recommended standard wavelengths and conditions in AAS as listed in Table 4 (Hinga *et al.*, 1980).

TABLE 4. **AAS INSTRUMENTAL CONDITIONS EMPLOYED**

METAL ANALYTE AND SYMBOL	**WAVELENGTH, λ, in nm**	**BAND PASS, nm**	**CALIBRATION Standard Solution Concentrations, mg/l**	**SOURCE OF STD. STOCK SOLUTION, 1000 mg/l**
CALCIUM, Ca	422.7	0.5	0.0, 0.2, 0.4, 0.6, 0.8, 1.0	Panreac Quimica SA
MAGNESIUM, Mg	285.2	0.5	0.0, 0.2, 0.4, 0.6, 0.8, 1.0	Panreac Quimica SA
MANGANESE, Mn	279.5	0.2	0.0, 0.5, 1.0, 1.5, 2.0, 2.5	Panreac Quimica SA
IRON, Fe	248.3	0.2	0.0, 0.5, 1.0, 1.5, 2.0, 2.5	Panreac Quimica SA
ZINC, Zn	213.9	0.5	0.0, 0.2, 0.4, 0.6, 0.8, 1.0	Panreac Quimica SA
COPPER, Cu	324.8	0.5	0.0, 0.2, 0.4, 0.6, 0.8, 1.0	Panreac Quimica SA

N.B. Appropriate dilutions were made from the Standard stock solution to obtain the calibration standard solutions required.

3.4.3 *Estimation of Organic Matter in Water/ Effluent – Determination of Chemical Oxygen Demand (COD)*

The estimation of the oxygen requirements of organic matter by determination of oxygen consumed from boiling acid potassium dichromate solution has advantages over the measurement of permanganate value. A much higher degree of oxidation of organic matter is achieved, which means that the scope for serious errors is reduced. It should be noted that the Chemical Oxygen Demand (COD) is not a measure of organic carbon, though the same chemical reactions are involved. The COD test is simpler and in many cases may suffice, but sometimes both may be required and their ratio may be informative (Hanson, 1973).

Principle:

The sample is boiled under reflux with potassium dichromate in strong sulphuric acid. Part of the dichromate is reduced by organic matter and the excess is determined by titration with iron (II) sulphate using 1,10-phenanthroline indicator. The COD is expressed in mg of oxygen absorbed from standard dichromate per litre of sample.

Interferences:

High levels of oxidizable inorganic materials interfere. Due to its high concentrations, chloride is often the most serious source of interference. Others include nitrite (NO_2^-), ferrous iron (Fe^{2+}) and sulphides (S^{2-}).

Reaction Equation:

$C_nH_aO_bN_c + (n+(a/4) - (b/2)-(3/4)c)O_2 \rightarrow nCO_2 + ((a/2) - (3/2)c)H_2O + cNH_3$

(Organic cpd.)

Reagents used:

Distilled water

Antibumping granules

Diluted Sulphuric acid, about 9 N

250 ml of conc. Sulphuric acid was added to 500 ml of water in a 1 L volumetric flask and diluted to the mark with water.

Iron (II) sulphate, 0.125 N

34.75 g of iron (II) sulphate heptahydrate, $FeSO_4.7H_2O$ was dissolved in 100 ml of diluted sulphuric acid and diluted to 1 litre.

Potassium dichromate, 0.125 N

6.129 g of potassium dichromate was dissolved in water and diluted to 1 litre.

Iron (II) – 1,10 – phenanthroline indicator solution

3.475 g of iron (II) sulphate heptahydrate, $FeSO_4.7H_2O$ was dissolved in 500 ml of water. 7.427 g of 1,10 – phenanthroline was added. The mixture was shaken until dissolved.

Procedure:

5 ml of 0.125 N potassium dichromate and 10 ml of concentrated sulphuric acid were transferred to a 150-ml flat-bottomed flask and mixed well. This was cooled in a tray containing cold running water. 5 ml of the sample was added and mixed well. A few anti-bumping granules were added and the mixture boiled under reflux for about 1 ½ hours. The solution was allowed to cool, 45 ml of water added and cooled in running water until quite cold. One drop of Iron (II) – 1,10 – phenanthroline indicator solution was added and the residual dichromate titrated with 0.125 N Iron (II) sulphate added from a 5-ml microburette. A blank determination was carried out in a similar manner using 5 ml of distilled water instead of the sample.

Calculation of results:

Since 1.0 ml of 0.125 N potassium dichromate ≡ 1.0 mg of oxygen,

$$\text{COD, mg/l} = \frac{(\text{Blank titre (ml)} - \text{Sample titre (ml)}) \times 1000}{\text{Volume of Sample taken (ml)}}$$

3.4.4 Determination of Total Dissolved Solids (TDS)

The total dissolved solids content (TDS) of the water samples was determined using the recommended standard (gravimetric) method (Kenya Bureau of Standards, 1985).

Principle:

A representative filtered water sample is evaporated to dryness at 105°C. The residue remaining is weighed as total dissolved solids.

Procedure:

The un-acidified water samples (B) were filtered through no. 40 or 540 filter paper. 100 ml of the filtrate was transferred into pre-weighed 100 ml plastic beakers and evaporated for about 12 hours in an air oven at 105 $\pm$ 2°C. The beaker with TDS was cooled in a desiccator and weighed and the TDS content calculated from the formula shown below.

Calculation of results:

$$\text{TDS content, mg/l} = \frac{(\text{Wt. of beaker with TDS (g)} - \text{Wt. of empty beaker (g)}) \times 10^6}{\text{Sample Volume, in ml}}$$

3.4.5 Determination of Other Physical) Parameters: General Methods

The dissolved oxygen, electrical conductivity, Turbidity, Temperature and pH were determined using standard procedures (ISO Standards Compendium, 1994 (b)). These methods were direct, simple and done as per conventional procedures or as recommended in respective manuals, charts and literature. The following were used in determining the above parameters:

pH – pH indicator paper, range 1 – 14, from Labline Products, for Kanha Laboratory, Nairobi

Temperature – thermometer, (range 0 to 200 degree C)

Turbidity - Turbidity Meter, TE/F – Trübungsphotometer LTP 5 DR. BRUNO LANGE Gmbh, Berlin, West Germany (the un-acidified samples, B were diluted 20 times before reading)

Electrical Conductivity - Conductivity Meter – Karl Kolb Scientific Technical Supplies, West Germany

Dissolved Oxygen - Dissolved Oxygen Meter, model OXI 42 - Karl Kolb Scientific Technical Supplies, West Germany

CHAPTER IV

4.0 RESULTS AND DISCUSSIONS

4.1 Preliminary Taxonomic Survey Results

Table 5 below shows different types of plant weeds infesting Nairobi Dam. This survey was by physical estimation. The results show that the Water hyacinth was by far the major aquatic weed currently infesting Nairobi Dam.

TABLE 5. **AQUATIC PLANT DENSITY DISTRIBUTION BY SPECIES IN NAIROBI DAM – MACROPHYTES**

SL No.	BOTANICAL NAME OF THE SPECIES	COMMON LOCAL NAME OF THE SPECIES	DESCRIPTION OF GROWING CONDITION/ MODE	APPROX. % AREA OF DAM OCCUPI-ED
1.	*Eichornia crassipes*	Water hyacinth	Floating	70.00
2.	*Typha domingensis* Pers.	Typha (Ndothua)	Water logged	6.00
3.	*Leersia hexandra* Sw.	"A Water grass form"	Floating mud (mat)	6.00
4.	*Pennisetum purpureum*	Napier grass	Dry mud	5.00

TABLE 5 *(contd…)*

SL No.	BOTANICAL NAME OF THE SPECIES	COMMON LOCAL NAME OF THE SPECIES	DESCRIPTION OF GROWING CONDITION/ MODE	APPROX. % AREA OF DAM OCCUPI-ED
5.	*Cyperus dives*	Sledge "big" (Ithanji)	Mud	4.00
6.	*Hydrocotyle ranunculoides* L.f.		Floating mud	3.00
7.	*Hydrocotyle manii* Hook F.		Floating mud	3.00
8.	*Cyperus rotundus*	Sledge "small"		0.15
9.	*Commelina bengalensis* L.	Wandering jew (Mukengeria)	Mud/ Dry – wet	0.15
10.	*Calcasia esculenta* Engl.	Arrow root	Mud	0.15
11.	*Crassocephalum picridifolium* (DC.) S. Moore		Floating mud (mat)	0.15
12.	*Polygonum Pulchrum* Blume		Floating mud	0.15
13.	*Rumex steudelii* A. Rich.	(Mugagatio)	Mud	0.15
14.	*Pavonia patens*	Edge	Riverine	0.15

TABLE 5 *(contd...)*

SL No.	BOTANICAL NAME OF THE SPECIES	COMMON LOCAL NAME OF THE SPECIES	DESCRIPTION OF GROWING CONDITION/ MODE	APPROX. % AREA OF DAM OCCUPI-ED
15.	*Polygonum senegalense*		Macrophytes/ mud	0.15
16.	*Datura stramonium* L.		Dry-wet	0.15
17.	*Tithomia diversifolium* (Hemsl.) A. Gray		Dry-wet	0.15
18.	*Saccharum officinalis* L.	Sugar cane	Dry-wet	0.15
19.	*Sphaeranthus suaveolens*		Water logged	0.15
20.	*Ipomoea hildebrandtii*		Dry-wet	0.15
21.	*Sorghum arundinaceum* (Desv.) Stapf.	Sudanese grass	Water logged	0.15
22.	*Xanthium pungens* Wallr.		Water-side	0.15
23.	*Verbena bonariensis*		Water logged/ wet	0.15
24.	*Achyranthus aspera*	(Magwata ng'ondu)	Dry-forest / Water logged	0.15
25.	*Ipomoea cairica*		Dry / Wet	0.15
26.	*Polygonum setosulum* A. Rich		Water logged	0.15

TABLE 5 *(contd...)*

SL No.	BOTANICAL NAME OF THE SPECIES	COMMON LOCAL NAME OF THE SPECIES	DESCRIPTION OF GROWING CONDITION/ MODE	APPROX. % AREA OF DAM OCCUPI-ED
27.	*Pennisetum clandestinum*	Kikuyu grass	Wet place– Upland	0.15

4.2 Preliminary Water Analytical Results – 1st Sampling

The results for the first preliminary (trial) - sampling analysis for the inorganic nutrients are presented in Table 6 and depicted in Figures 6 to 10. It is worth noting that during the first two samplings, the main aim was to explore salient profiles and possible inter-nutrient correlations. It was therefore not found necessary to analyse for the physical parameters except water temperature and pH. Therefore, for the first and second samplings, only chemical nutrient parameters are reported.

TABLE 6. **1ST WATER SAMPLING (2ND OCTOBER 2004): MEAN NUTRIENTS ANALYSIS RESULTS (± s.d.) (PRELIMINARY / TRIAL)**

VARIABLE →	(X)	(Y)	(X)	(Y)	(X)	(Y)
Sampling Site No. ↓	**PO_4^{3-}-P (mg/l)**	**NO_3^--N (mg/l)**	**K (mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
1	0.121 ± 0.002	1.313 ± 0.021	24.00 ± 0.48	130.0 ± 2.6	38.55 ± 0.077	12.20 ± 0.073
2	2.643 ± 0.048	0.215 ± 0.004	32.00 ± 0.64	120.0 ± 2.4	40.65 ± 0.122	8.800 ± 0.035
3	2.825 ± 0.052	9.593 ± 0.156	44.00 ± 0.88	170.0 ± 3.4	43.75 ± 0.219	10.75 ± 0.022
4	3.957 ± 0.073	0.192 ± 0.003	40.00 ± 0.80	160.0 ± 3.2	37.55 ± 0.338	9.450 ± 0.057
MEAN, IN 1	**2.387 ± 0.044**	**2.828 ± 0.046**	**35.00 ± 0.70**	**145.0 ± 2.9**	**40.13 ± 0.191**	**10.30 ± 0.046**
MEAN, into	**2.959 ± 0.054**	**1.735 ± 0.028**	**131.7 ± 2.63**	**357.1 ± 7.14**	**88.79 ± 0.406**	**20.41 ± 0.090**
5	2.368 ± 0.043	0.180 ± 0.003	85.00 ± 1.70	320.0 ± 6.4	214.4 ± 0.429	44.95 ± 0.090
6	3.299 ± 0.060	0.122 ± 0.002	40.00 ± 0.80	165.0 ± 3.3	42.70 ± 0.384	11.00 ± 0.033
7	0.610 ± 0.011	0.426 ± 0.007	57.00 ± 1.14	240.0 ± 4.8	64.15 ± 0.193	17.20 ± 0.103
8	2.667 ± 0.049	0.045 ± 0.001	35.00 ± 0.70	130.0 ± 2.60	34.55± 0.138	9.500 ± 0.000
9	4.295 ± 0.079	1.208 ± 0.020	94.00 ± 1.880	320.0 ± 6.40	184.3 ± 1.291	27.10 ± 0.108
MEAN, Dam	**2.811 ± 0.052**	**3.749 ± 0.061**	**57.833 ± 1.157**	**217.5 ± 4.35**	**96.11 ± 0.481**	**19.86 ± 0.056**

TABLE 6 *(contd…)*

VARIABLE	(X)	(Y)	(X)	(Y)	(X)	(Y)
Sampling Site No. ↓	**PO_4^{3-} - P (mg/l)**	**NO_3^- - N (mg/l)**	**K (mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
10	2.574 ± 0.047	0.062 ± 0.001	34.00 ± 0.68	130.0 ± 2.60	34.35 ± 0.103	9.050 ± 0.054
11	2.289 ± 0.042	9.608 ± 0.157	35.00 ± 0.70	130.0 ± 2.6	31.75 ± 0.095	8.650 ± 0.052
12	2.166 ± 0.040	0.147 ± 0.002	34.00 ± 0.68	130.0 ± 2.6	30.75 ± 0.184	8.350 ± 0.033
13	1.962 ± 0.036	0.255 ± 0.004	34.00 ± 0.68	130.0 ± 2.6	31.10 ± 0.218	8.400 ± 0.042
14	1.819 ± 0.033	1.548 ± 0.025	33.00 ± 0.66	130.0 ± 2.6	31.80 ± 0.413	8.500 ± 0.043
15	1.821 ± 0.033	0.129 ± 0.002	30.00 ± 0.60	120.0 ± 2.4	31.65 ± 0.19	8.000 ± 0.040
16	3.813 ± 0.070	0.240 ± 0.004	25.00 ± 0.50	115.0 ± 2.3	23.05 ± 0.069	5.350 ± 0.021
MEAN, out	**2.349 ± 0.043**	**1.713 ± 0.028**	**32.14 ± 0.643**	**126.4 ± 2.53**	**30.64 ± 0.179**	**8.043 ± 0.040**
17	2.078 ± 0.038	0.225 ± 0.004	12.00 ± 0.24	120.0 ± 2.4	17.30 ± 0.173	2.750 ± 0.017
18	5.029 ± 0.092	0.341 ± 0.006	600.0 ± 12.0	1250 ± 25.0	359.2 ± 0.00	68.65 ± 0.275
19	4.059 ± 0.074	0.264 ± 0.004	170.0 ± 3.4	550.0 ± 11.0	84.50 ± 0.254	30.30 ± 0.091
MEAN, IN 2	**3.722 ± 0.068**	**0.277 ± 0.005**	**260.7 ± 5.21**	**640.0 ± 12.80**	**153.7 ± 0.140**	**33.90 ± 0.127**
20	3.628 ± 0.067	20.51 ± 0.334	36.00 ± 0.720	130.0 ± 2.60	36.55 ± 0.183	9.400 ± 0.019

TABLE 6 *(contd...)*

Linear Regression Analysis of Nutrient Pairs (x, y)						
VARIABLE	(X)	(Y)	(X)	(Y)	(X)	(Y)
NUTRIENT/ STATISTIC	**$PO_4^{3-}P$ (mg/l)**	**NO_3^-N (mg/l)**	**K (mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
Regressi-on Equations	y = 2.1495x - 2.3073		y = 2.0133x + 84.106		y = 0.1673x + 3.5355	
Square of R	0.1085		0.9762		0.9302	
correlation coefficient, R	R(a) =	0.3294	R(b) =	0.9880	R(c) =	0.9645
MEANS (HZ)	2.516 ± 0.046	3.101 ± 0.051	47.00 ± 0.94	177.7 ± 3.55	66.95 ± 0.33	14.74 ± 0.052

N.B.

n = 4 replicates, unless otherwise if indicated; HZ = Water Hyacinth Growing Zone.

X and Y represent the first and second named nutrients respectively, whose linear regression correlation data parameters have been worked out, for the pairs shown.

MEAN, IN 1; MEAN, IN 2, MEAN, into; MEAN, Dam; and MEAN, out are the means of the waters from: Motoine River inlet (sites 1-4); Shilanga River inlet (sites 17-19); (Combined mean of) all inlet waters; Nairobi Dam (sites 5-9,20) and Ngong River outlet (sites 10-16) respectively.

MEANS (HZ) = Means from the WATER HYACINTH GROWING ZONE, i.e. sites 5-14,20

Concentrations reported up to 4 significant figures (max.).

For statistical calculations, see foot of Table 7.

TABLE 6 *(contd...)*

VARIABLE	(X)	(Y)	(X)	(Y)	
Sampling Site No. ↓	**Mn (mg/l)**	**Fe (mg/l)**	**Zn (mg/l)**	**Cu (mg/l)**	**Cl (mg/l)**
1	4.570 ± 0.041	6.830 ± 0.362	< 0.0125	0.110 ± 0.019	96.40 ± 0.227
2	4.400 ± 0.004	25.80 ± 0.052	0.480 ± 0.020	0.150 ± 0.134	124.8 ± 0.29
3	4.520 ± 0.037	15.09 ± 0.709	0.350 ± 0.037	0.130 ± 0.038	110.6 ± 0.26
4	4.030 ± 0.021	15.31 ± 0.138	0.610 ± 0.082	0.110 ± 0.036	42.50 ± 0.10
MEAN, IN 1	**4.380 ± 0.026**	**15.76 ± 0.437**	**0.360 ± 0.039**	**0.125 ± 0.053**	**93.58 ± 0.22**
MEAN, into	**6.433 ± 0.061**	**11.51 ± 1.24**	**0.364 ± 0.034**	**0.071 ± 0.048**	**183.5 ± 0.43**
5	60.79 ± 0.244	619.0 ± 0.62	0.130 ± 0.012	0.090 ± 0.048	198.5 ± 0.47
6	6.300 ± 0.006	18.83 ± 0.169	0.130 ± 0.008	0.020 ± 0.020	85.10 ± 0.20
7	4.240 ± 0.009	10.38 ± 0.00	0.130 ± 0.007	0.080 ± 0.066	178.7 ± 0.42
8	4.220 ± 0.060	3.580 ± 0.093	0.410 ± 0.023	0.140 ± 0.140	65.20 ± 0.154
9	55.06 ± 0.11	83.95 ± 0.420	7.830 ± 0.031	0.360 ± 0.081	167.3 ± 0.39
MEAN, Dam	**22.85 ± 0.114**	**124.6 ± 2.201**	**1.535 ± 0.102**	**0.132 ± 0.090**	**128.1 ± 0.30**
10	4.360 ± 0.030	2.730 ± 0.606	0.530 ± 0.049	0.180 ± 0.153	62.40 ± 0.147

TABLE 6 *(contd...)*

VARIABLE	(X)	(Y)	(X)	(Y)	
Sampling Site No. ↓	**Mn (mg/l)**	**Fe (mg/l)**	**Zn (mg/l)**	**Cu (mg/l)**	**Cl (mg/l)**
11	4.360 ± 0.070	2.520 ± 0.501	0.220 ± 0.006	0.170 ± 0.038	68.10 ± 0.16
12	4.460 ± 0.017	2.390 ± 0.315	0.140 ± 0.009	< 0.0083	73.70 ± 0.174
13	4.510 ± 0.045	2.390 ± 0.449	0.330 ± 0.035	0.070 ± 0.039	82.30 ± 0.194
14	4.540 ± 0.045	1.870 ± 0.017	0.180 ± 0.049	0.150 ± 0.018	70.90 ± 0.167
15	4.860 ± 0.049	3.110 ± 0.056	0.040 ± 0.001	0.050 ± 0.038	59.60 ± 0.14
16	3.000 ± 0.021	3.210 ± 0.424	0.330 ± 0.028	0.050 ± 0.004	51.10 ± 0.12
MEAN, out	**4.299 ± 0.039**	**2.603 ± 0.335**	**0.254 ± 0.025**	**0.096 ± 0.049**	**66.87 ± 0.158**
17	2.760 ± 0.064	5.770 ± 0.531	0.340 ± 0.045	< 0.0083	53.90 ± 0.127
18	11.57 ± 0.197	1.670 ± 0.867	0.370 ± 0.016	< 0.0083	507.7 ± 1.2
19	13.18 ± 0.039	10.13 ± 0.324	0.400 ± 0.023	< 0.0083	348.9 ± 0.82
MEAN, IN 2	**9.170 ± 0.100**	**5.857 ± 0.574**	**0.370 ± 0.028**	**< 0.0249**	**303.5 ± 0.72**
20	6.480 ± 0.046	11.83 ± 0.769	0.580 ± 0.073	0.100 ± 0.053	73.70 ± 0.174

TABLE 6 *(contd...)*

Linear Regression Analysis				
VARIABLE	(X)	(Y)	(X)	(Y)
NUTRIENT/ STATISTIC	**Mn (mg/l)**	**Fe (mg/l)**	**Zn (mg/l)**	**Cu (mg/l)**
Regression Equations	y = 6.8076x - 29.555		y = 0.0351x + 0.0898	
Square of R	0.6348		0.6788	
Correlation coefficient, R	R(d) =	0.7973	R(e)=	0.8239
MEANS (HZ)	14.48 ± 0.062	69.04 ± 0.36	0.965 ± 0.028	0.124 ± 0.060
Detection Limits (mg/l)	**0.0305**	**0.0545**	**0.0125**	**0.0083**

N.B.

HZ = WATER HYACINTH (GROWING) ZONE

X and Y represent the first and second named nutrients respectively, whose linear regression correlation data parameters have been worked out, for the pairs shown.

Concentrations reported up to 4 significant figures (max.).

4.2.1 Major Nutrient Profiles In Water (1st Sampling)

Figures 6A and 6B depict the profiles of the major nutrients: Potassium, Sodium, Calcium, Magnesium, Chloride, manganese and iron. The profiles for the major bulk nutrients (Potassium, Sodium, Calcium, Magnesium and Chloride) were very similar at the different sampling sites, i.e. those sites which registered the highest level of a given nutrient also indicated the highest levels of the other bulk nutrients. This shows that the source of these bulk nutrients was almost the same - most likely the raw sewage from the informal settlements in Kibera and the surrounding areas.

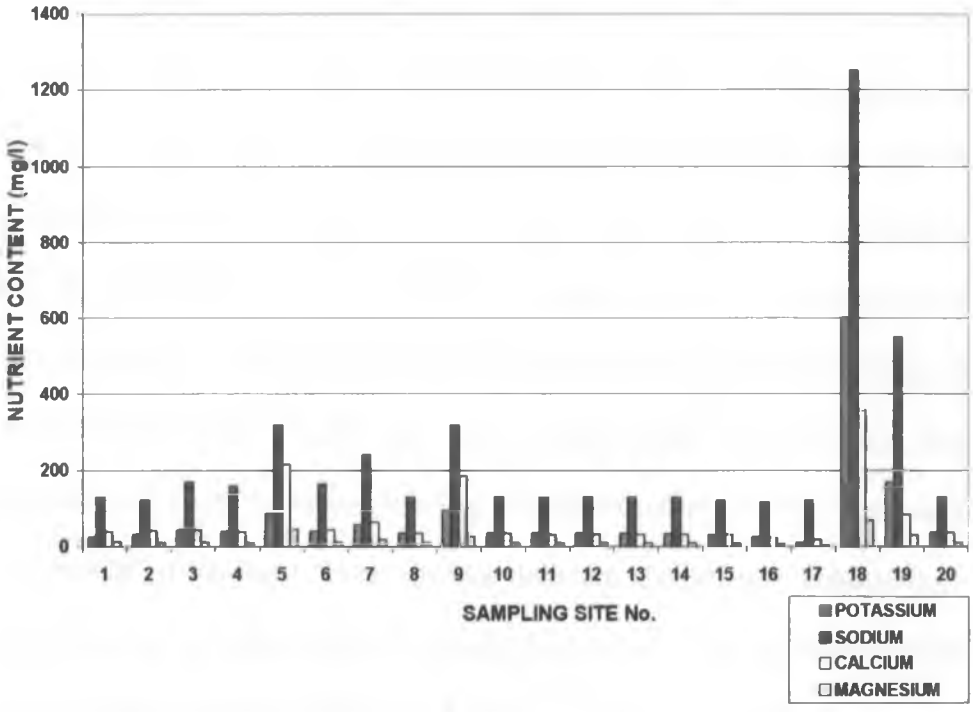


Figure 6a. **Major Bulk Cationic Nutrient Profiles in Water (1st Sampling).**

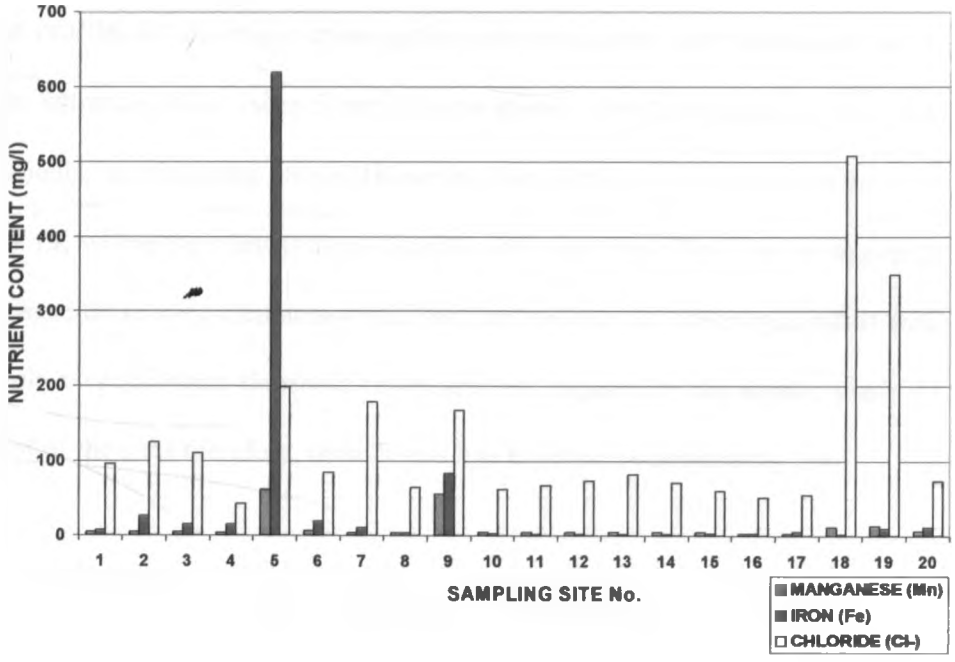


Figure 6b. **Manganese, Iron and Chloride Profiles in Water (1st Sampling).**

The profiles for the bulk nutrients (potassium, sodium, calcium, magnesium and chloride) showed that the levels of these nutrients generally increased gradually from site no. 1 (lower point upstream) to site 4 and then sharply to site no. 5 (dam entrance), before dropping back at site 6. This rise and fall continued alternately through sites 7, 8 (dam exit), 9 and 10. It was notable that these nutrients were high at both dam entrances (sites 5 & 9) but low at the exit (site 8). After this, these levels remained almost constantly low up to sites 16 (final point downstream) and 17 (upper point upstream) and then steadily rose to site 18 before levelling downwards sharply to site 19 through 20 (middle of the dam). These profiles therefore also initially indicate their accumulation in Nairobi Dam or assimilation by the water hyacinth or other aquatic plants and that the dam was acting as a sink for the nutrients.

The profiles for the major trace nutrient elements (iron and manganese) at the dam entrance points (sites 5 and 9) were closely similar to those for the bulk nutrients, as discussed above. However, they differed immensely at sites 18 and 19, where their levels were considerably very low. This was as expected because these trace elements would become toxic to the water hyacinth if their levels exceeded their threshold values that are required by the aquatic plant. At most of the sites therefore, these levels had to remain considerably low.

4.2.2 Profiles For Other Nutrients In Water (1st Sampling)

The profiles for other nutrients are shown in Figure 7. The profiles for NO_3^--N and PO_4^{3-} - P differed from those already described for other major nutrients

as well as from each other (Figure 7). The former nutrient (NO_3^- - N) gave sharp maxima peaks at sites 3, 11 & 20, with the middle of the dam (site 20) indicating the highest level. On the other hand, the latter nutrient (PO_4^{3-} - P), whose trend was closer to other bulk nutrients, showed peaks at sampling sites 4, 6, 9, 16 & 18 (shown also more clearly in Figure 8).

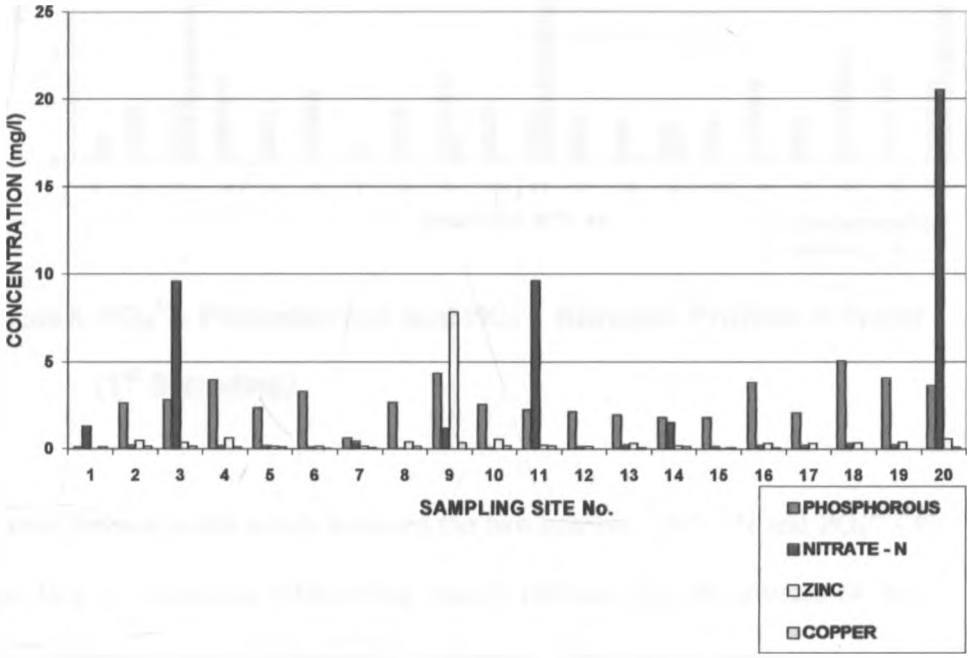


Figure 7. **PO_4^{3-} - Phosphorous, NO_3^- - Nitrogen, Zinc and Copper Profiles in Water – 1st Sampling.**

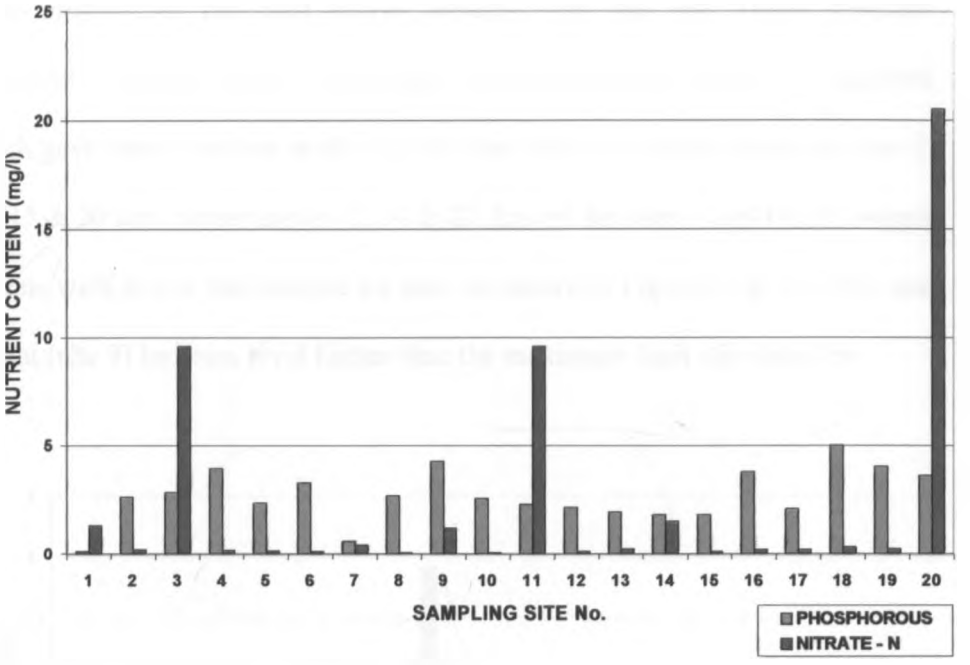


Figure 8. **PO_4^{3-} - Phosphorous and NO_3^- - Nitrogen Profiles in Water (1st Sampling).**

The difference in the trends between the two nutrients (NO_3^--N and PO_4^{3-} - P) and lack of consistent relationship clearly indicate that the sources of these two nutrients were completely different. The latter nutrient is more anthropogenic than the former. It was possible that the middle of the dam could have been harbouring the nitrifying bacteria, which were able to convert atmospheric nitrogen to nitrates, that could in turn be assimilated by the water hyacinth and other aquatic plants and ultimately to nitrogenous organic matter, such as protein, that was useful to the plant. Alternatively, the source of high nitrate levels could also have been from run-offs from fertilized soil around the dam.

4.2.3 Selected Trace Micronutrient Element Profiles in Water

The profiles for zinc and copper differed from the rest. These indicated relatively very low levels, with copper showing the least. These two nutrients both gave sharp maxima at site 9, with zinc showing smaller peaks at sites 2, 4, 13 & 20 and copper at sites 2, 14 & 20. Except for sites 1 and 15, the copper levels were below the baseline for zinc, as shown in Figures 9 & 10. Only one point (site 9) had zinc level higher than the maximum limit stipulated by

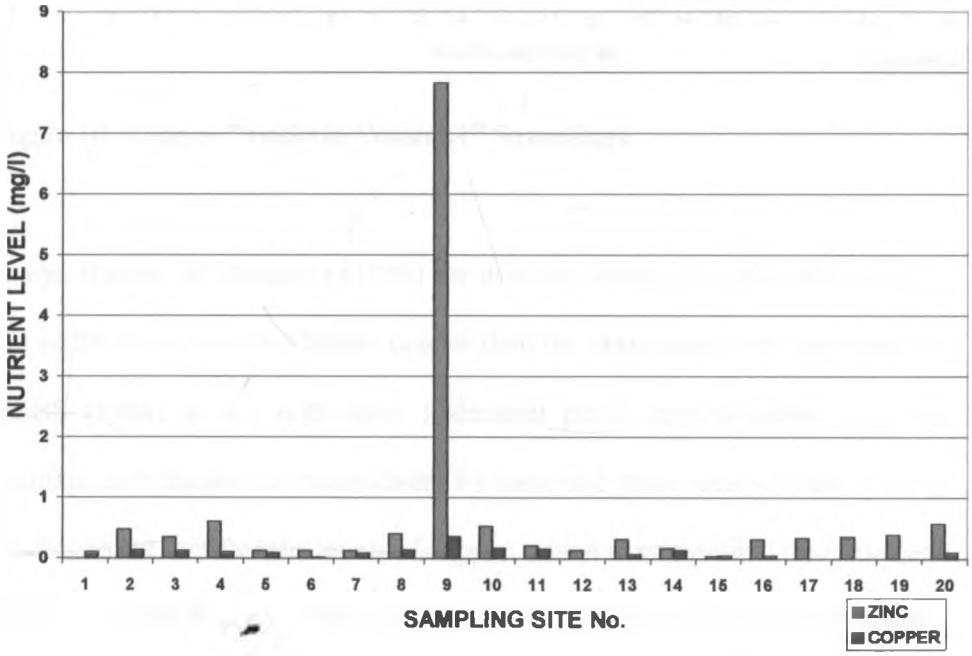


Figure 9. **Trace Element Nutrients (Zinc and Copper) Profiles in Water (1st Sampling).**

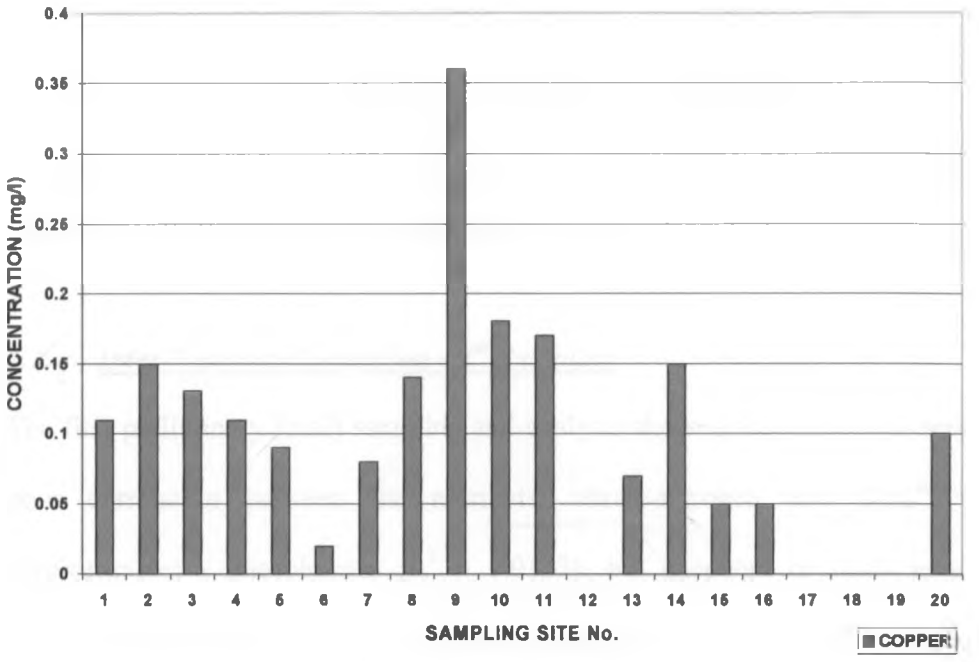


Figure 10. **Copper Profile in Water (1st Sampling).**

Kenya Bureau of Standards (1996) for drinking water (5 mg/l), while only 5 out of 20 sites registered higher copper than the maximum level stipulated by KEBS (1996) of 0.1 mg/l after 1 decimal place approximation, showing minimal contribution of enhancement by these two trace metals. It also clearly vindicates the fact that the levels of copper, which is an essential trace element (Cotton and Wilkinson, 1988) and supports the growth of the aquatic plants, were not high enough to cause any toxicity or death to the water hyacinth and hence encouraged its proliferation in the aquatic environment studied. Furthermore, among the dam's entry points, only site 9 showed the (highest) peak maxima for copper. This shows that on average, the water influents to the dam did not contribute any appreciable pollution, detrimental to the growth of the aquatic plants and the general aquatic environment. This was mainly because, since there were no major chemical industries encountered in the

region under consideration, any copper detected could only be due to the untreated domestic sewage or other geological factors. Since this is just a trace nutrient element, one would expect minimal contribution from the combined domestic sewage influents from human wastes and other sources.

4.2.4 Inter-Nutrient Correlation – 1st Sampling

The first preliminary (trial) sampling and analysis showed that there was very poor correlation between the nutrients: nitrate-nitrogen and (PO_4^{3-} + Hydrolysable) - Phosphorous (R^2 = 0.0133), but excellent or fairly good correlation between other pairs of bulk inorganic nutrients in the same Periodic Table Groups, or blocks or having the same physiological or environmental roles as follows, in descending order:- between K & Na (R^2 = 0.9782), between Ca & Mg (R^2 = 0.9468), between Mn & Fe (R^2 = 0.6357) and between Zn & Cu (R^2 = 0.5373).

4.3 Water Analytical Results for 2nd Sampling

The analytical results for the second sampling are recorded in Table 7.

TABLE 7. ***2ND WATER SAMPLING NUTRIENTS ANALYSIS RESULTS (± s.d.): (12TH FEBRUARY 2005)***

VARIABLE	(X)	(Y)	(X)	(Y)	(X)	(Y)
Sampling Site No. ↓	**PO_4^{3-} - P (mg/l)**	**(TK+NO_3^-)-N (mg/l)**	**K (Mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
1	0.051 ± 0.001	0.123 ± 0.022	13.81 ± 0.276	45.79 ± 0.916	18.05 ± 0.00	4.900 ± 0.015
2	11.55 ± 0.212	72.80 ± 13.12	38.05 ± 0.761	149.2 ± 2.984	28.90 ± 0.145	7.250 ± 0.051
3	8.331 ± 0.153	53.91 ± 9.713	39.06 ± 0.781	138.8 ± 2.777	31.25 ± 0.344	7.900 ± 0.016
4	6.441 ± 0.118	55.83 ± 10.059	39.06 ± 0.781	128.5 ± 2.57	33.65 ± 0.067	8.950 ± 0.018
MEAN, IN 1	**6.594 ± 0.121**	**45.67 ± 8.228**	**32.49 ± 0.650**	**115.6 ± 2.312**	**27.96 ± 0.126**	**7.250 ± 0.025**
MEAN, into	**6.334 ± 0.116**	**58.98 ± 10.63**	**79.94 ± 1.599**	**232.2 ± 4.644**	**39.31 ± 0.213**	**12.44 ± 0.043**
5	4.895 ± 0.090	33.72 ± 6.075	34.01 ± 0.680	107.8 ± 2.157	28.85 ± 0.173	7.850 ± 0.024
6	10.99 ± 0.202	101.4 ± 18.26	50.17 ± 1.003	159.5 ± 3.191	80.25 ± 0.00	15.05 ± 0.045
7	3.616 ± 0.066	45.83 ± 8.257	44.11 ± 0.882	138.8 ± 2.777	51.30 ± 0.154	10.90 ± 0.011
8	2.405 ± 0.044	95.03 ± 17.12	76.00 ± 1.520	220.0 ± 4.40	123.0 ± 0.492	24.80 ± 0.099
9	1.743 ± 0.032	22.36 ± 4.029	86.53 ± 1.731	237.1 ± 4.742	49.15 ± 0.197	13.20 ± 0.04
MEAN, Dam	**4.011 ± 0.090**	**60.59 ± 10.92**	**54.81 ± 1.096**	**165.3 ± 3.306**	**72.68 ± 0.23**	**13.91 ± 0.035**
10	3.453 ± 0.063	17.20 ± 3.100	44.11 ± 0.882	138.8 ± 2.777	33.80 ± 0.135	9.10 ± 0.027
11	3.392 ± 0.062	16.30 ± 2.937	42.09 ± 0.842	133.7 ± 2.674	34.00 ± 0.442	9.30 ± 0.037

TABLE 7 *(contd..)*

VARIABLE	(X)	(Y)	(X)	(Y)	(X)	(Y)
Sampling Site No. ↓	**PO_4^{3-} - P (mg/l)**	**$(TK+NO_3^-)$-N (mg/l)**	**K (mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
12	3.264 ± 0.060	16.32 ± 2.941	42.09 ± 0.842	128.5 ± 2.57	34.20 ± 0.239	9.50 ± 0.086
13	3.006 ± 0.055	16.42 ± 2.959	41.08 ± 0.822	118.2 ± 2.363	33.00 ± 0.429	9.15 ± 0.037
14	3.289 ± 0.060	25.32 ± 4.562	39.06 ± 0.781	107.8 ± 2.157	30.95 ± 0.186	8.600 ± 0.034
15	2.199 ± 0.040	8.158 ± 1.470	38.05 ± 0.761	107.8 ± 2.157	32.95 ± 0.198	8.800 ± 0.026
16	4.938 ± 0.091	11.38 ± 2.050	34.01 ± 0.680	118.2 ± 2.363	28.95 ± 0.29	7.550 ± 0.008
MEAN, out	**3.363 ± 0.062**	**15.87 ± 2.86**	**40.07 ± 0.801**	**121.9 ± 2.437**	**32.55 ± 0.274**	**8.857 ± 0.035**
17	2.276 ± 0.042	0.132 ± 0.024	13.81 ± 0.276	92.32 ± 1.846	16.40 ± 0.246	3.350 ± 0.017
18	4.140 ± 0.076	179.0 ± 32.25	220.5 ± 4.411	590.8 ± 11.82	59.15 ± 0.177	22.10 ± 0.044
19	11.55 ± 0.212	51.11 ± 9.208	195.3 ± 3.906	480.1 ± 9.601	87.75 ± 0.176	32.65 ± 0.098
20	5.969 ± 0.109	65.26 ± 11.76	38.05 ± 0.761	128.5 ± 2.57	103.5 ± 0.207	11.65 ± 0.012
MEAN, IN 2	**5.989 ± 0.110**	**76.74 ± 13.83**	**143.2 ± 2.864**	**387.7 ± 7.755**	**54.43 ± 0.200**	**19.37 ± 0.053**

TABLE 7 ***(contd...)***

VARIABLE:	(X)	(Y)	(X)	(Y)	(X)	(Y)
Sampling Site No. ↓	**PO_4^{3-} - P (mg/l)**	**$(TK+NO_3^-)$-N (mg/l)**	**K (mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
Linear Regression Analysis Parameters of the above Data						
Regression Equations, R^2 and R:	Y = 7.8249x + 8.6349		y = 2.5368x + 23.26		y = 0.1258x + 4.8516	
	R^2 =	0.3820	R^2 =	0.9704	R^2 =	0.7257
	R(a) =	0.6181	R(b) =	0.9851	R(c) =	0.8519
MEANS (HZ) (n = 11)	4.184 ± 0.077	41.375 ± 7.455	48.844 ± 0.977	147.166 ± 2.943	54.727 ± 0.241	11.736 ± 0.041

N.B.:

X and Y represent the first and second named nutrients respectively, whose linear regression correlation data parameters have been worked out, for the pairs shown. Sample replicates, n = 4 unless otherwise if indicated.

MEAN, IN 1; MEAN, IN 2; MEAN, into; MEAN, Dam; and MEAN, out are the means of the nutrients for (waters from): Motoine River inlet (sites 1-4); Shilanga River inlet (sites 17-19); (Combined mean of) all inlets; Nairobi Dam (sites 5-9 & 20); and Ngong River outlet (sites 10-16) respectively.

MEANS (HZ) = Means from the WATER HYACINTH GROWING ZONE, i.e. sites 5-14 & 20 in Figure 5.

Concentrations reported up to 4 significant figures (max.).

For calculation of Standard Deviation, refer to end of Table 18.

For a given environment with n_1 sampling points, the mean nutrient, $\bar{u}$ is calculated as: $\bar{u} = (\sum u_i)/n_1$; for the two inlet rivers with respective mean nutrients, $\bar{u}_1$ and $\bar{u}_2$, with respective n_1 and n_2 number of sampling points and standard deviations s_1 and s_2, the pooled mean ($\bar{u}_{pooled}$) and Std. Deviation, (S_{pooled}) are calculated by the following formulae: $\bar{u}_{pooled} = (n_1\bar{u}_1 + n_2\bar{u}_2)/(n_1 + n_2)$; $S_{pooled} = \sqrt{((n_1-1)s_1^2 + (n_2-1)s_2^2)/(n_1+n_2-2)}$

For Standard Deviation calculation, refer to end of Table 18.

TABLE 7 *(contd...)*

VARIABLE	X	Y	X	Y	
Sampling Site No. ↓	**Mn (mg/l)**	**Fe (mg/l)**	**Zn (mg/l)**	**Cu (mg/l)**	**Cl (mg/l)**
1	3.130 ± 0.044	7.500 ± 2.918	0.390 ± 0.087	0.022 ± 0.002	201.4 ± 0.477
2	1.450 ± 0.012	13.40 ± 4.261	1.090 ± 0.062	0.101 ± 0.004	48.20 ± 0.114
3	2.780 ± 0.025	17.45 ± 3.612	1.060 ± 0.014	0.106 ± 0.004	119.1 ± 0.281
4	3.380 ± 0.000	18.75 ± 1.163	1.010 ± 0.047	0.088 ± 0.002	76.60 ± 0.180
MEAN, IN 1	2.685 ± 0.021	14.28 ± 3.483	0.888 ± 0.076	0.079 ± 0.004	111.3 ± 0.262
MEAN, into	5.250 ± 0.033	22.06 ± 3.378	1.081 ± 0.061	0.092 ± 0.006	158.0 ± 0.372
5	2.660 ± 0.011	16.55 ± 2.267	0.840 ± 0.024	0.099 ± 0.009	90.80 ± 0.214
6	19.24 ± 0.000	66.50 ± 2.261	1.130 ± 0.006	0.104 ± 0.004	96.40 ± 0.227
7	7.320 ± 0.044	51.05 ± 3.420	1.340 ± 0.058	0.085 ± 0.004	99.30 ± 0.234
8	17.97 ± 0.054	177.7 ± 0.355	2.240 ± 0.213	0.125 ± 0.003	113.4 ± 0.267
9	16.69 ± 0.083	40.75 ± 2.038	1.360 ± 0.038	0.071 ± 0.007	130.5 ± 0.307
MEAN, Dam	11.78 ± 0.051	67.64 ± 3.495	1.415 ± 0.051	0.104 ± 0.006	98.80 ± 0.233
10	3.810 ± 0.034	17.85 ± 1.499	0.750 ± 0.049	0.05 ± 0.005	79.40 ± 0.187
11	3.790 ± 0.011	19.60 ± 1.372	0.810 ± 0.077	0.047 ± 0.004	85.10 ± 0.200
12	3.760 ± 0.041	21.00 ± 1.323	0.840 ± 0.0378	0.052 ± 0.003	76.60 ± 0.180
13	3.620 ± 0.022	19.60 ± 0.039	0.960 ± 0.029	0.063 ± 0.002	39.70 ± 0.094
14	3.310 ± 0.017	21.50 ± 1.333	1.050 ± 0.058	0.064 ± 0.006	59.60 ± 0.140
15	3.220 ± 0.023	20.80 ± 3.058	1.160 ± 0.017	0.060 ± 0.007	76.60 ± 0.180
16	1.650 ± 0.003	21.55 ± 0.711	1.290 ± 0.027	0.106 ± 0.013	79.40 ± 0.187
MEAN, out	3.309 ± 0.020	20.27 ± 1.335	0.980 ± 0.046	0.063 ± 0.006	70.91 ± 0.167
17	2.690 ± 0.019	27.65 ± 0.774	1.150 ± 0.026	0.071 ± 0.011	39.70 ± 0.094
18	11.73 ± 0.012	34.25 ± 1.576	1.400 ± 0.025	0.111 ± 0.008	360.2 ± 0.849
19	11.59 ± 0.058	35.40 ± 0.779	1.470 ± 0.021	0.145 ± 0.003	260.9 ± 0.615
MEAN, IN 2	**8.670 ± 0.030**	**32.43 ± 1.043**	**1.340 ± 0.024**	**0.109 ± 0.007**	**220.3 ± 0.519**

TABLE 7 *(contd...)*

VARIABLE	X	Y	X	Y	
Sampling Site No. ↓	**Mn (mg/l)**	**Fe (mg/l)**	**Zn (mg/l)**	**Cu (mg/l)**	**Cl (mg/l)**
20	6.770 ± 0.054	53.35 ± 1.067	1.580 ± 0.025	0.140 ± 0.003	62.40 ± 0.147
Linear	**Regression**	**Analysis**	**Parameters**	**of the**	**Data**
Regression Equations, R^2 and R	y = 5.1814x + 4.0514 R^2 = 0.5167 R(d) = 0.7188		y=0.0529x+0.0198 R^2 = 0.5522 R(e) = 0.7431		
MEANS (HZ) n = 11	8.085 ± 0.034	45.95 ± 1.543	1.173 ± 0.056	0.082 ± 0.005	84.84 ± 0.200

N.B.

n = Number of samples (as indicated) or sample replicates (usually 4 unless otherwise if indicated); Concentrations reported up to 4 significant figures (max.); For calculation of Standard Deviation, refer to end of Table 18.
HZ = WATER HYACNTH GROWING ZONE

X and Y represent the first and second named nutrients respectively, whose linear regression correlation data parameters have been worked out, for the pairs shown.

4.3.1 Inter-Nutrient Correlation – 2nd Sampling and Comparison between the First Two Samplings

During the second and other subsequent samplings, Total Kjeldahl nitrogen was analyzed along with nitrate – nitrogen and the two added together. This was necessitated by the poor linear correlation between the soluble phosphorous and nitrate-nitrogen registered in the first sampling, as discussed earlier. The second sampling results showed that the linear correlation between phosphorous and 'Total' Nitrogen ((Total Kjeldahl + nitrate) - nitrogen) was far much better, i.e. (R^2 = 0.8587) than that involving

phosphorous and nitrate-nitrogen for the first sampling, while correlation between the other nutrient pairs remained fairly satisfactory as follows:-

Between K & Na (R^2 = 0.9875), between Ca & Mg (R^2 = 0.6047), between Mn & Fe (R^2 = 0.5147) and between Zn & Cu (R^2 = 0.554). This is tentatively expected for elements in the same group or those close to one another like copper and zinc. Comparison between correlation data from all sampling points for these nutrient pairs during the first two samplings of 2nd October 2004 and 12th February 2005 (i.e. nos. 1 & 2) are as shown in Figures 11 – 15. The notably fair positive linear correlation between phosphorous and 'Total' Nitrogen ((Total Kjeldahl + nitrate) - nitrogen), i.e. (R^2 = 0.8587), which was found to be significantly higher than 0.5000, can be explained by the fact that the nutrient balance (in aquatic systems) is a product of at least five phenomena: The carbonate cycle, the nitrogen cycle, the phosphate cycle, the level of photosynthesis, and the maintenance of aerobic processes (Chanlett, 1973). There are optimal ratios of NO_3^-/N and PO_4^{3-}/P for varied regimes. As the balance becomes tipped, some species become tipped, some species become predominant and the environment becomes unfavourable for many others. (Chanlett, 1973). In the current, for existence of suitable correlation between these two nutrients (nitrogen and phosphorous), all possible environmental forms of nitrogen had to be considered When these parameters were thus determined, Nitrogen (from nitrates, NH_3 and Proteins) and Phosphorous (mainly from PO_4^{3-} species), both of which are in the same Periodic Table group, correlated very well.

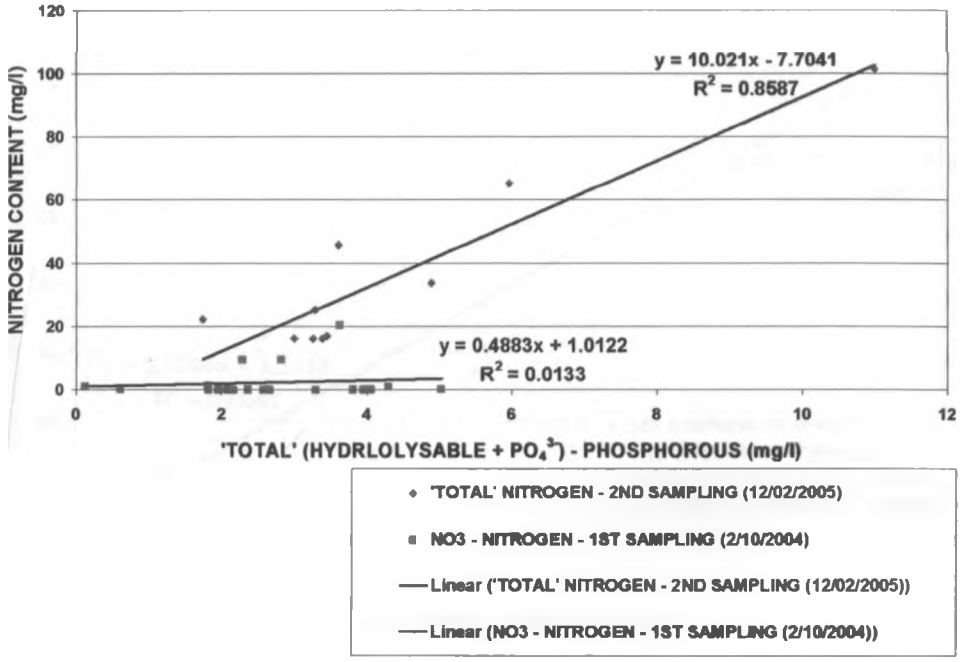


Figure 11. **Graphs of Nitrogen versus Phosphorous Concentrations in Nairobi Dam Basin Water (1st & 2nd Samplings).**

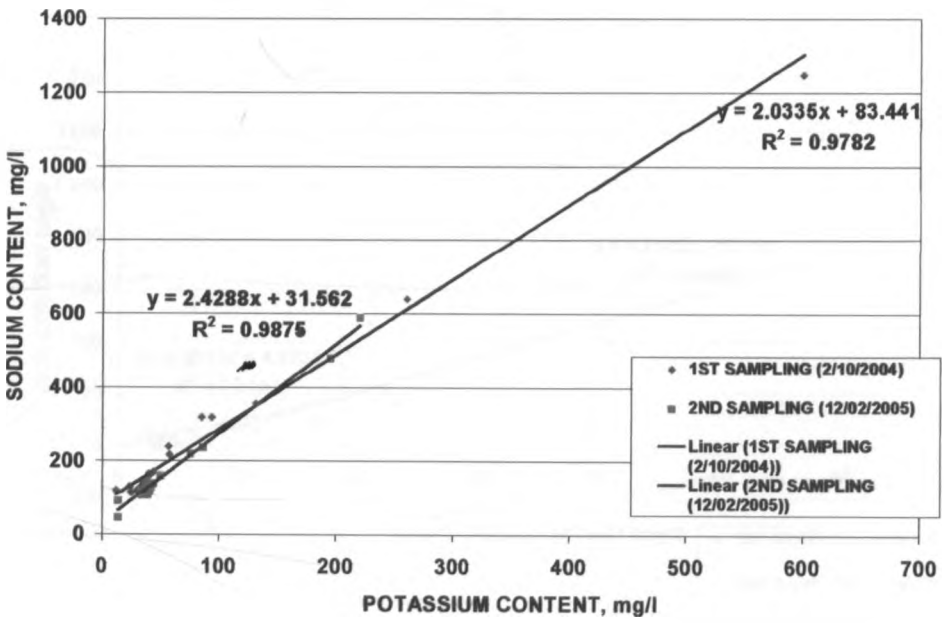


Figure 12. **Correlation Graphs of Sodium vs. Potassium Concentrations in Nairobi Dam Basin Water (1st & 2nd Samplings).**

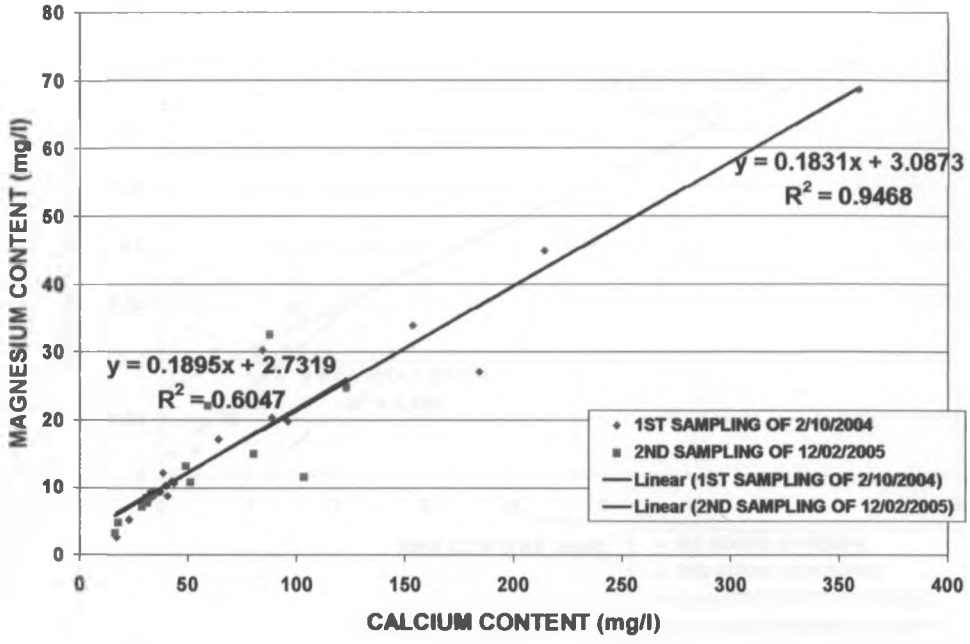


Figure 13. **Graphs of Magnesium versus Calcium Concentrations in Water (1st & 2nd Samplings).**

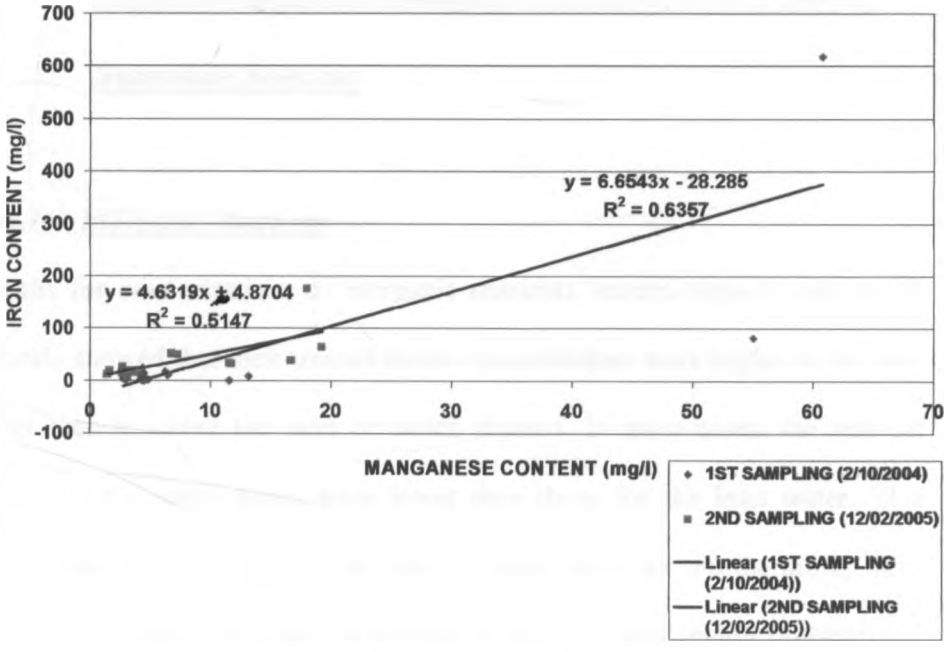


Figure 14. **Correlation Graphs of Iron vs. Manganese Concentrations in Nairobi Dam Basin Water - All Points (1st & 2nd Samplings).**

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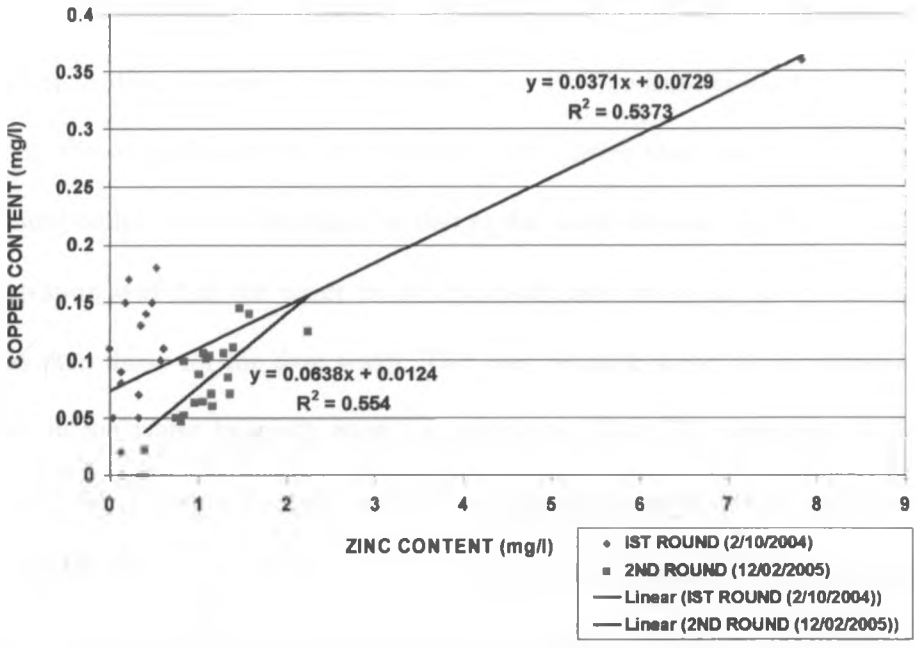

Figure 15. **Correlation Graphs of Copper vs. Zinc Concentrations in Nairobi Dam Basin Water (1st & 2nd Samplings).**

4.4 Summary of Mean Analytical Results of Water for All Sampling Seasons

4.4.1 Inorganic Nutrients

Results for concentrations of inorganic nutrients, except copper, sulphate & fluoride showed that their overall mean concentrations were higher in the dam water than in either the inlet or outlet streams. In most cases, the nutrient levels for the outlet water were lower than those for the inlet water. This shows that the dam acted as a filter for these nutrients. Furthermore, there weren't noticeable informal settlements in the sampling region downstream. For the majority of the nutrients, the accumulation in the dam could have been contributed mainly by the presence of the dying, rotting aquatic weeds, which

accumulated these nutrients as discussed later. Currently, there has been no major harvesting of these weeds from the dam. For the trace essential element copper, the overall mean level in the dam was lower than those in both the inlet and outlet streams but closer to that in the outlet stream. Another notable observation was that the water in the hyacinth zone recorded lower nutrient levels than those for the dam water. This was because some of the sampling points in the water hyacinth zone, i.e. sites nos. 10 to 14, were part of the outlet stream. Since the outlet stream recorded the lowest nutrient content as explained above, these sites (nos. 10 to 14) lowered the overall water-hyacinth mean relative to the dam. These results for soluble inorganic nutrients are summarized in Table 8.

TABLE 8. **SUMMARY OF MEAN CONCENTRATIONS (in mg/l) OF INORGANIC NUTRIENTS IN WATER FROM DIFFERENT AQUATIC ENVIRONMENTS OF NAIROBI DAM BASIN**

Nutrient: → / ZONE ↓	P (n=13) ± Std. Error	N (n=12) ± Std. Error	K (n=13) ± Std. Error	Na (n=12) ± Std. Error	Ca (n=13) ± Std. Error	Mg (n=13) ± Std. Error
INLETS:	3.150 ± 0.508	33.06 ± 4.686	42.11 ±8.67	175.4 ± 22.33	40.69 ± 4.73	9.916 ± 1.098
DAM:	5.700 ± 0.707	45.88 ± 6.263	47.14 ± 4.697	192.7 ± 20.37	66.46 ± 6.194	12.77 ± 0.96
OUTLETS:	3.080 ± 0.285	27.83 ± 3.328	32.62 ± 2.216	144.9 ± 12.46	34.41 ± 3.144	8.345 ± 0.416
Hyacinth Zone:*	4.489 ± 0.504	36.87 ± 4.371	42.58 ± 3.781	176.4 ± 16.76	50.28 ± 3.951	11.05 ± 0.685

TABLE 8. *(contd...)*

Nutrient: → / ZONE ↓	Mn (n=13) ± Std. Error	Fe (n=13) ± Std. Error	Zn (n=13) ± Std. Error	Cu (n=13) ± Std. Error	Cl⁻ (n=13) ± Std. Error	SO_4^{2-} (n=11) ± Std. Error	F⁻ (n=9) ± Std. Error
INLETS:	3.204 ± 0.435	7.927 ± 1.877	0.378 ± 0.090	0.215 ± 0.130	80.95 ± 13.98	31.61 ± 5.313	1.143 ± 0.151
DAM:	11.18 ± 1.603	43.57 ± 8.153	0.953 ± 0.152	0.209 ± 0.125	97.93 ± 12.32	31.52 ± 3.87	0.957 ± 0.122
OUTLETS:	3.358 ± 0.314	3.872 ± 1.476	0.231 ± 0.092	0.262 ± 0.181	60.33 ± 5.343	12.84 ± 1.136	1.004 ± 0.142
Hyacinth Zone:*	7.136 ± 0.962	25.37 ± 4.656	0.631 ± 0.131	0.088 ± 0.041	82.98 ± 9.31	24.83 ± 3.469	0.949 ± 0.126

N.B.

* This refers to areas where water hyacinth was consistently found or expected in many sampling seasons, i.e. Sampling Sites, numbers 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 20 & 22;

Concentrations reported up to 4 significant figures (max.).

n = Sample size, i.e. the number of seasons involved

Std. Error (Standard Error of the mean) = $\frac{\text{Standard Deviation of the mean}}{\sqrt{n}}$

The above results show that the mean concentration levels of sulphate and fluoride in the dam were lower than those for the inlet streams. For sulphate, the difference could be due to its assimilation by the water hyacinth and other aquatic plants. Any excess of nutrient was adsorbed by the sediments (as will be discussed later) and desorbed into the aqueous phase when conditions were favourable, to be used by the plant. This explains why the outlet water registered the lowest mean sulphate level. On the other hand, all the mean

values for fluoride in water from the various environments studied were lower than the maximum safe level of 1.5 mg/l for drinking water, set by KEBS (1996). Its mean level in the dam water was also lower than those for the inlet and outlet streams. This indicates that fluoride pollution in the aquatic environment was not prevalent in the area studied and that the sewage influents on average did not contribute high alarming fluoride levels. Any fluoride present in the entire area was purely of geological origin.

It is worth noting that although fluoride is a trace essential element in the formation of teeth in animals, it acts as an inhibitor of glycolysis, such as in the fermenting yeast (Lehninger, 1988). It therefore shows that fluoride is biologically more deleterious than essential, particularly to the plants such as the (green) water hyacinth, which can photosynthesize their own sugars with the help of chlorophyll. This is in agreement with the current findings, that there were no such fluoride levels as to pose any antagonism to the growth of the water hyacinth and other aquatic plants.

4.4.2 Seasonal Influences on the Inorganic Nutrient Load

The comparative trends for the inorganic nutrients determined in all the sampling seasons in the three classes of aquatic environments are depicted in Figures 16 to 28. These show that during the rainy, cold or wet seasons, the levels of most inorganic nutrients were predictably low while in the dry or hot seasons, these were fairly high. This was because, since the environment studied was more urban than agricultural, the main source of these nutrients was the untreated sewage from the two major streams feeding the dam, at all times throughout the year. During the rainy season, these were purely diluted,

without any significant contribution from the surrounding soils and light agriculture practised in the area. On the other hand, during the cold dry seasons, the nutrient levels remained almost unchanged. Furthermore, during drought or dry seasons, as expected, these levels increased due to evaporation of the water, which led to the concentration of the various nutrients under consideration (refer to Table 2 for seasonal and weather variations). These results indicate that any subsistence farming practised in the vicinity and the geology of the area studied had very little influence on the eutrophication parameters.

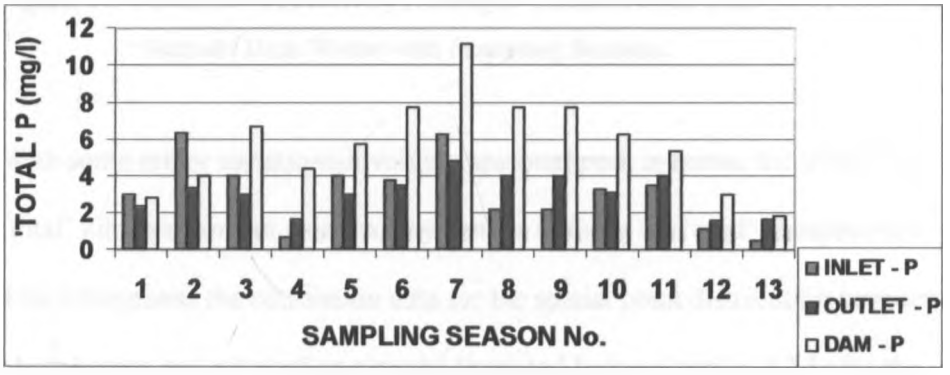

Figure 16. **Variation of 'Total' Hydrolysable Phosphorous Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

Figure 16 shows that the mean 'total' hydrolysable phosphorous content in the water from all the three environments (inlets, outlet and dam) rose consistently from sampling season 1 to 3, then dropped during (the rainy) season 4 (refer to Table 2) increasing during the dry spell until season number 7. The phosphorous load then decreased henceforth, with fluctuations, before consistently falling during the rainy period (seasons 12 and 13). This shows that the levels of nutrients in the aquatic systems of the three environments were almost directly affected by the climatic and seasonal variations and not

by the agricultural practices and geological factors. These only depended on the untreated sewage effluents from the surrounding residential areas.

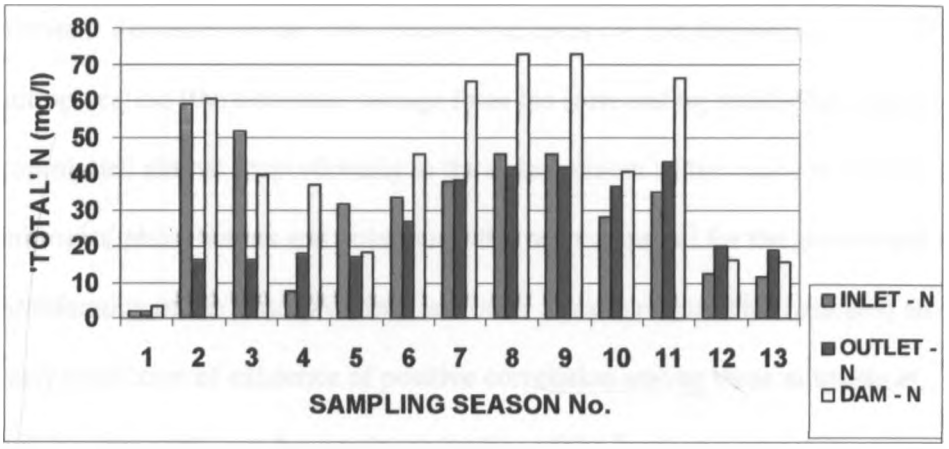

Figure. 17. **Variation of ($TK+NO_3^-$) Nitrogen Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

With some minor variations involving seasonal peak maxima, the trends for 'total' nitrogen content were closely similar to those for 'total' phosphorous. This strengthens the correlation data for the spatial point distribution between phosphorous and nitrogen as already discussed before (section 4.3.1) for the first two seasons since nitrogen and phosphorous are in the same Periodic Table group.

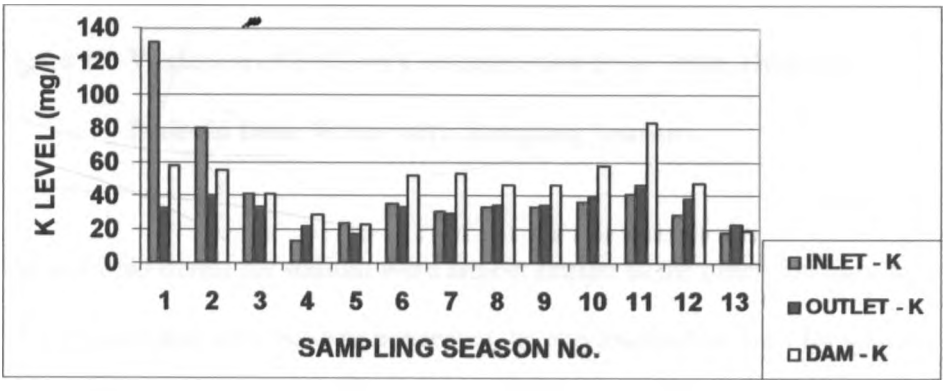

Figure 18. **Variation of Potassium Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The trends for potassium depicted in Figure 18 were similar to the major nutrients discussed so far. This clearly vindicates the fact the major source of eutrophication (the untreated sewage from the surrounding residential areas) contributed almost proportionally to the enhancement of the major nutrients (nitrogen, phosphorous and potassium) that were required for the growth and proliferation of the water hyacinth and other aquatic plants. This indicated an early prediction of existence of positive correlation among these nutrients as will be discussed later for the determination of the limiting element in section 4.5.2.

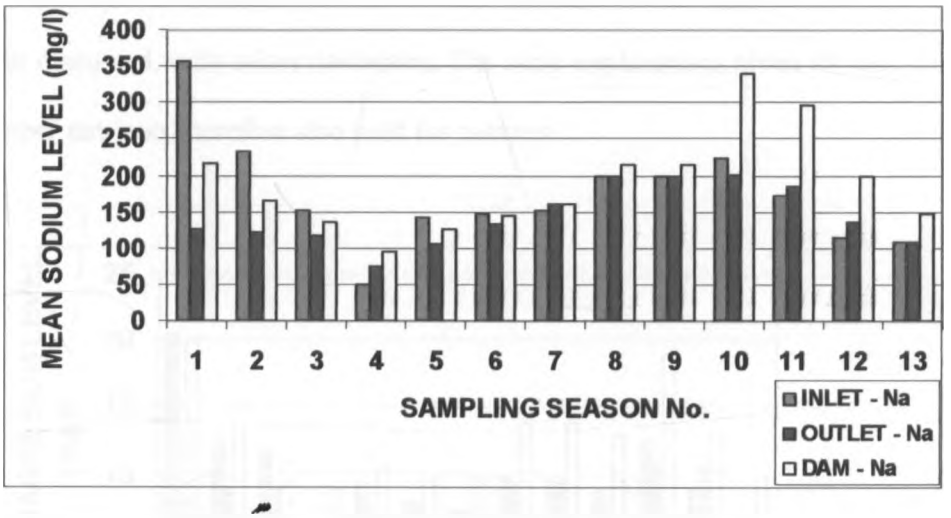

Figure 19. **Variation of Sodium Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The seasonal trends for sodium were almost similar to the other nutrients so far discussed and very close to potassium, as previously discussed for spatial point distribution involving the two group 1 elements during the first two sampling seasons.

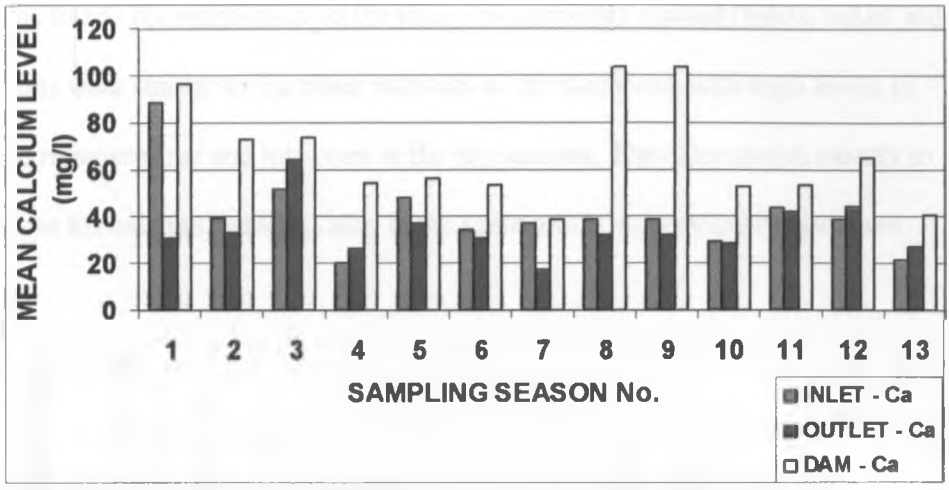

Figure 20. **Variation of Calcium Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The trends for calcium were almost similar to the other inorganic nutrients so far discussed, with minor deviations. The same explanations given for the other nutrients therefore also hold for calcium.

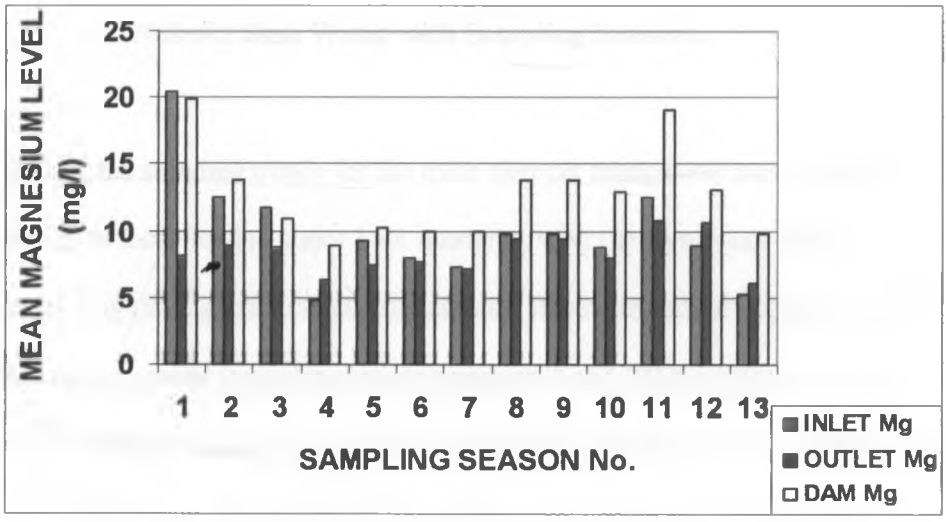

Figure 21. **Variation of Magnesium Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The trends for magnesium in the three environments studied (inlets, outlet and dam) were similar to the other nutrients so far discussed, with high levels in the rainy seasons and low ones in the dry seasons. They also match closely to those for calcium, which is also in the same group, as previously discussed.

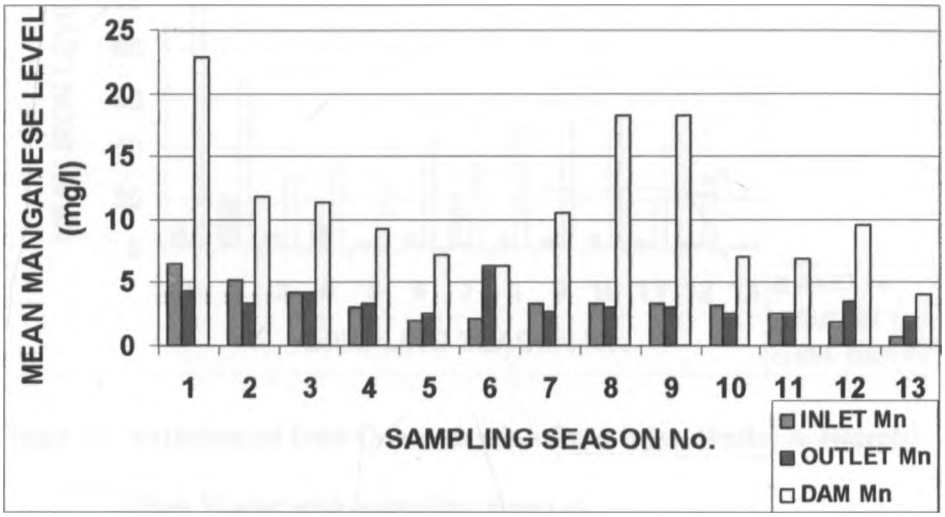

Figure 22. **Variation of Manganese Concentration from Inlet, Outlet and Nairobi Dam Water with Sampling Seasons.**

Though the seasonal trends for the trace element manganese were somewhat similar to those for the major bulk nutrients, with the dam water always registering the highest manganese contents, there were some slight deviations. The rainy seasons (sampling season numbers 4 and 12) were not associated with the lowest manganese contents, especially in the dam water, though there was a slight drop from season 3 to 4. This clearly points to the fact that though rainfall generally lowered the nutrient levels, there was also the possibility of existence of an equilibrium between the aqueous phase and the sediments, thus

creating compensation of any dilution from the sediment reserves, which are known to be a source of manganese (Cole, 1975).

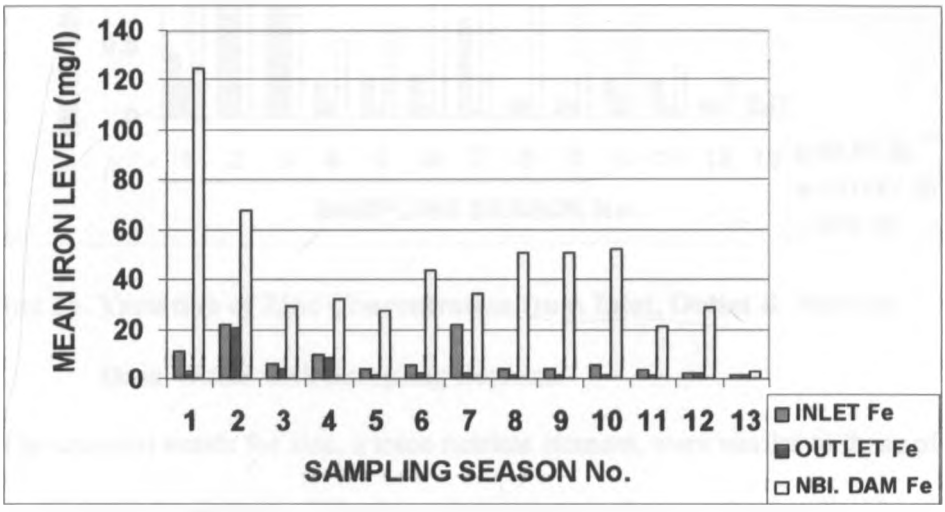

Figure 23. **Variation of Iron Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The seasonal trends for iron were closely similar to those for manganese, both elements being found in the d block of the Periodic Table. Both elements are also environmentally similar (Cole, 1975) and so the same discussion under manganese also applied to iron. For iron an additional source on the onset of long rains could be the extensive use of iron sheets (through acid rain dissolution) in the sprawling settlements of the area studied as seen in Figures 1 A to C.

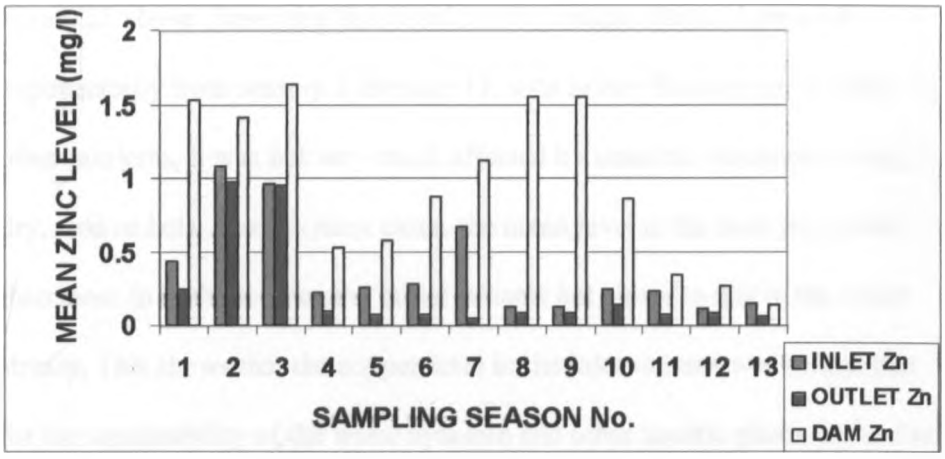

Figure 24. **Variation of Zinc Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The seasonal trends for zinc, a trace nutrient element, were similar to those of the major bulk nutrients. This shows that although the use of galvanized iron sheets (containing zinc) could contribute to the enhancement of zinc, especially during the rainy seasons, the major source of this nutrient, just like for the major bulk ones, was the incoming untreated sewage from the informal settlements of the area studied.

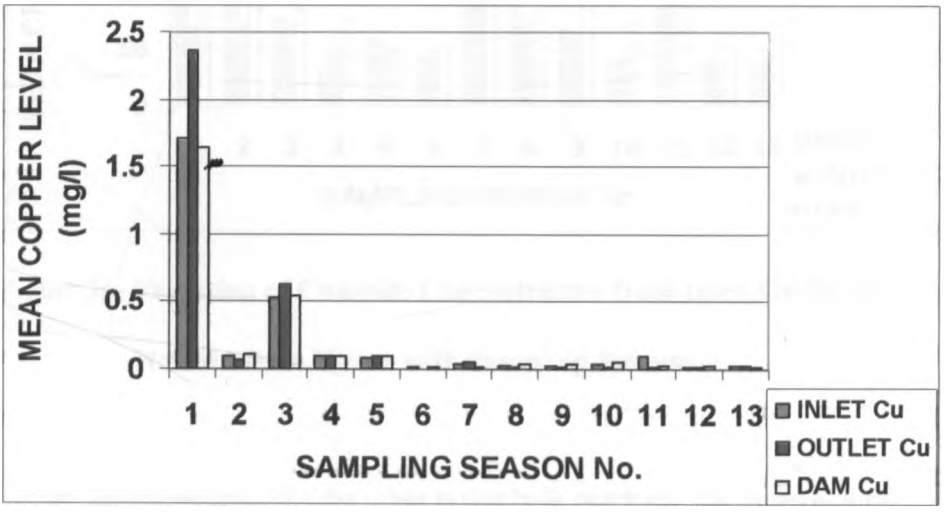

Figure 25. **Variation of Copper Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

Figure 25 above shows that the mean copper content almost decreased exponentially from seasons 1 through 13, with minor fluctuations. Unlike other nutrients, it was not very much affected by seasonal variations (rainy, dry, cold or hot). Also, in most cases, the mean level in the dam was lower than those in both the inlet and outlet streams but closer to that in the outlet stream. This shows that the copper level in the inlet streams was so low that for the sustainability of the water hyacinth and other aquatic plants in the dam, copper had to undergo bioaccumulation in these weeds, but once the threshold safe level was attained, then any toxic excess contents were removed by the main outlet stream, to ward off any interference and destruction of the aquatic plants.

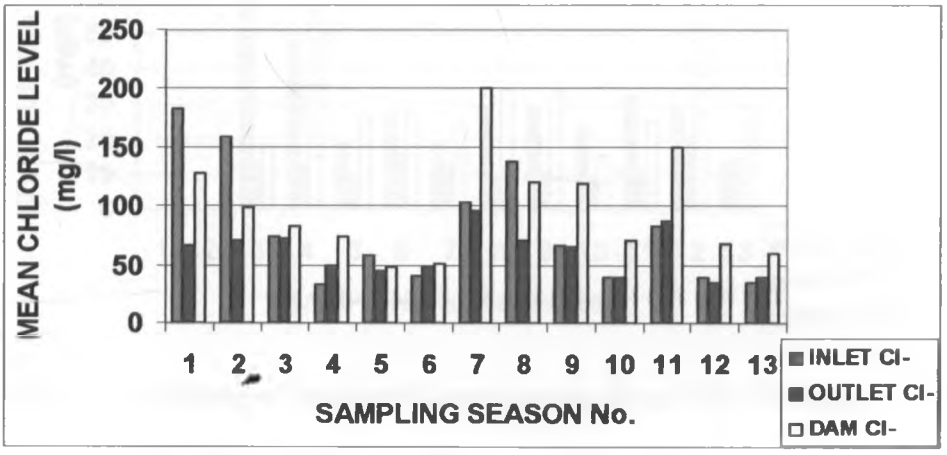

Figure 26. **Variation of Chloride Concentration from Inlet, Outlet and Nairobi Dam Water with Sampling Seasons.**

Figure 26 shows that, like the other major bulk nutrients, the mean chloride content in the three environments was directly influenced by the seasonal variations. Thus, the lowest levels were registered during the rainy and cold

sampling season numbers 4, 5, 12 and 13. The chloride profiles were closely similar to those of potassium and sodium. With a few exceptions, the chloride levels were higher in the dam water than those in either inlet or outlet streams. This was expected because chloride is an essential nutrient element, as discussed in the literature section. It is principally present in common salt (sodium chloride), a very major ingredient in human food. After the body has consumed the amount needed, the excess sodium, potassium and chloride ions are excreted out of the body through urine and faeces. Possible sources were therefore the untreated sewage containing human body and domestic wastes.

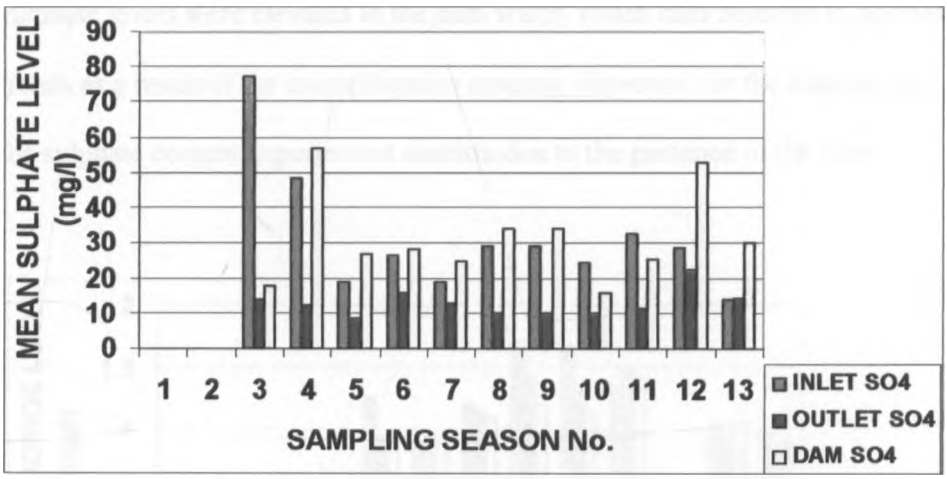

Figure 27. **Variation of Sulphate Concentration from Inlet, Outlet & Nairobi Dam Water with Sampling Seasons.**

The available data in Figure 27 shows that the sulphate trends in the three environments (inlets, outlet and dam) were very similar to those for other major nutrients. However, a major deviation was that although the onset of the rainy seasons (numbers 4 and 12) registered lower mean sulphate levels in the inlet waters than those in the preceding seasons, the dam water registered

higher levels during the rainy seasons. This could be explained by the fact that the dam was far much nearer the busy Langata Road than the inlets (refer to Figure 5), where the traffic density was high, with possible use of gasoline and diesel. When burned, sulphur was converted to the oxides of sulphur (sulphur dioxide and sulphur trioxide through oxidation mechanisms). During the rainy seasons, the oxides were dissolved by the rain water to form acid rain, as represented by the following equations:

$2SO_2 + O_2 \rightarrow 2SO_3$ and

$SO_3 + H_2O \rightarrow H_2SO_4$

It was therefore possible that during the onset of the rainy seasons, the sulphate levels were elevated in the dam water, which later reverted to normal trends as a result of the eutrophication process. However, for the inlet streams, the sulphate content experienced dilution due to the presence of the rains.

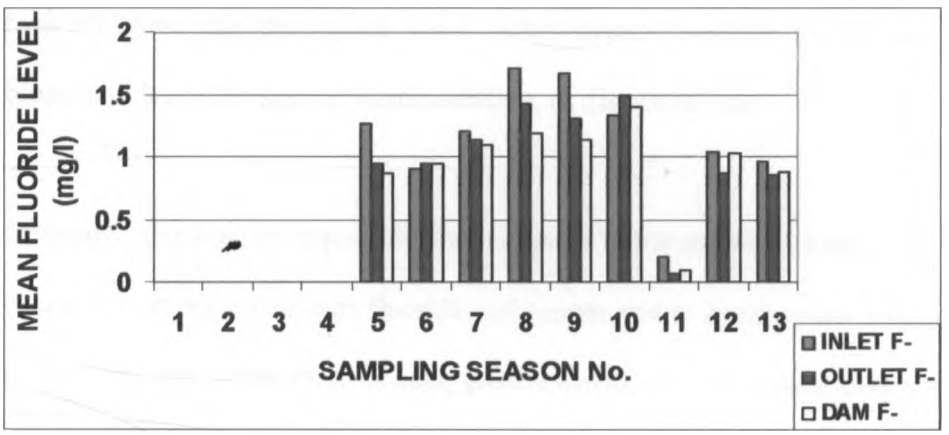

Figure 28. **Variation of Fluoride Concentration from Inlet, Outlet and Nairobi Dam Water with Sampling Seasons.**

The available data depicted in Figure 28 shows that fluoride did not seem to follow the environmental relationship exhibited by the major bulk nutrients. In most sampling seasons, the mean level of fluoride content in the dam water was not the highest among the three different environments studied. It was either lower than in either inlet or outlet streams or intermediate between these two. Also, cold and rainy sampling seasons (numbers 5, 12 and 13) did not necessarily register the lowest fluoride content. This indicates that the source of fluoride in the whole region studied could be more geological than anthropogenic. This suggests little or no use of fluoride in the residential areas of interest. Furthermore, as compared to the other nutrients, fluoride is relatively not a major essential nutrient and plants' growth does not depend very much on it. The levels of fluoride were generally below the maximum limit of 1.5 mg/l for drinking water, set by KEBS (1996). This indicated minimal pollution with regard to this trace element, especially within the water hyacinth zone and the Ngong River outlet stream, possibly as a result of bioaccumulation through phytoremediation, as discussed later.

Generally, the seasonal trends for the inorganic nutrients were closely similar except for the trace elements fluoride and copper and to some extent, sulphate in the water from the three aquatic environments studied (inlets, outlet and dam). It is evident that in most cases, the dam water registered higher values than either the inlet or outlet water. This shows that most of the nutrients, which are essential for the proliferation of the water hyacinth, were accumulated in the dam.

The similarity of the seasonal influences for most inorganic nutrients could principally be explained by the seasonal trends. During the rainy seasons (refer to Table 2), the nutrient levels were generally very low compared to the dry seasons, as expected due to dilution. This indicates that activities other than sewage disposal, such as farming, had very little influence on the overall nutrient level. The magnitude of these levels in the dam depended wholly on the incoming nutrient loads, which were in turn determined by the degree of sewage disposal into the rivers, as opposed to farming, light industries and other daily activities, as suggested previously in other reports (Okoth and Otieno, 2000).

4.4.3 Summary of Distribution of Physical and Other Parameters in Water

The results for the means of the physical and other parameters, which included Dissolved Oxygen, Turbidity, Electrical Conductivity, Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Anionic Surfactants, Temperature and pH in water, over the whole sampling period, are summarized in Table 9. The environmental relationships for these parameters, except Dissolved Oxygen, Anionic Surfactants, Temperature and pH were closely similar to those observed for the inorganic nutrients. The mean Dissolved Oxygen and Anionic Surfactants for the dam water were lower than for inlet and outlet streams while Turbidity, Electrical Conductivity, TDS and COD were higher than for either inlet or outlet water. This strengthens the fact that the Dam has been serving as a sink and hence for management of excessive nutrients in the surrounding aquatic environments, as earlier discussed.

TABLE 9. **SUMMARY OF OVERALL MEANS OF LEVELS OF PHYSICAL AND OTHER PARAMETERS IN WATER FROM DIFFERENT AQUATIC ENVIRONMENTS OF NAIROBI DAM BASIN** *(UNITS AS SHOWN)*

Zone → / Parameter ↓	Dam Inlet Mean: (n_1 = 8) ± Std. Error	Dam Mean: (n_1 = 7) ± Std. Error	Dam Outlet Mean: (n_1 = 7) ± Std. Error	Hyacinth Zone Mean: (n_1 = 12) ± Std. Error
Dissolved Oxygen (mg/l) (n_2 = 11)	11.12 ± 1.741	7.875 ± 1.085	14.09 ± 3.031	10.46 ± 1.823
Turbidity (N.T.U.) (n_2 =11)	133.4 ± 51.51	232.7 ± 96.93	34.45 ± 5.259	145.8 ± 56.99
Electrical Conductivity, 25°C (µs/cm) (n_2 = 11)	647.9 ± 82.35	856.9 ± 108.3	718.6 ± 79.72	807.0 ± 95.99
Total Dissolved Solids (TDS) (mg/l) (n_2 = 11)	387.5 ± 50.28	494.5 ± 53.22	340.5 ± 36.81	439.1 ± 46.28
Chemical Oxygen Demand (COD) (mg/l) (n_2 = 8)	65.50 ± 11.47	90.04 ± 11.60	57.88 ± 22.94	79.03 ± 16.21
(MBAS) Anionic Surfactants (mg/l) (n_2 = 10)	1.169 ± 0.306	0.854 ± 0.190	0.893 ± 0.166	0.633 ± 0.124
Temperature (°C) (n_2 = 13)	25.98 ± 0.75	25.57 ± 0.84	25.72 ± 0.79	25.71 ± 0.79
pH (n_2 = 13)	5.88 ± 0.16	5.98 ± 0.11	5.90 ± 0.13	5.96 ± 0.12

NOTES FOR TABLE 9:

n_1 represents the number of sampling points per season in a particular environment, n_2 = Number of sampling seasons involved, with Standard Error, Std. Error = s.d./$\sqrt{n_2}$, where s.d. is the Standard deviation, over n_2 seasons; MBAS = Methylene Blue Active Substances; Each entry is the overall mean of means of a given parameter in that aquatic environment for all the sampling seasons involved, n_2; Concentration values and other results above reported up to 4 significant figures (max.).

The reduced dissolved oxygen could probably explain the current disappearance of fish from Nairobi Dam. In addition, the lower value of the anionic surfactants in the dam also suggests that the dam was assisting in the biodegradation of the anionic surfactants (soaps and detergents). It should be noted also that most detergents used in Kenya, such as 'Omo' contain sulphur, which is essential for the growth of plants, such as the water hyacinth. These aquatic plants could therefore be useful in accelerating this degradation.

When significance tests were done, using the formulae given at the end of Table 16, there was found neither significant difference (at $\alpha = 0.05$), i.e. at 95% confidence, between the anionic surfactant levels in the dam and outlet water, nor for temperature and pH in the three environments (inlet, dam and outlet water) at the same significance level. The water pH was slightly acidic (mean pH range from 5.2 to 6.8).

However, the above results show that the mean anionic surfactant level was higher in the outlet stream compared to the dam. Though most of the residential areas downstream were middle-class in nature, some of them (such as near sampling sites nos. 10 and 11) were found to be emitting domestic

waste water, possibly containing anionic surfactants. Since the plant density decreased tremendously downstream, the anionic surfactant content remained relatively high due to minimal or complete absence of biodegradation, as a result of scarcity of the water hyacinth along the outlet stream.

Scrutiny of the above physical parameter results at a glance (Dissolved Oxygen and pH) also suggests eutrophic activity of Nairobi Dam. This is further strengthened by the high Total Dissolved Solid content in the dam water, which was far higher than that reported for Eutrophic Lake Itasca waters (U.S.A) of about 185 mg/l (Cole, 1975). The same author reported that for a eutrophic lake, carbon dioxide collects, oxygen becomes scarce or absent and the pH falls. This will be discussed later for the inorganic nutrients in the relevant sections.

4.4.4 Seasonal Influences On The Other Parameters

The comparative trends for the physical and other parameters in all the sampling seasons in the three classes of aquatic environments are depicted in Figures 29 to 34. As was pointed earlier, these parameters were not determined during the first two preliminary samplings (Season nos. 1 and 2).

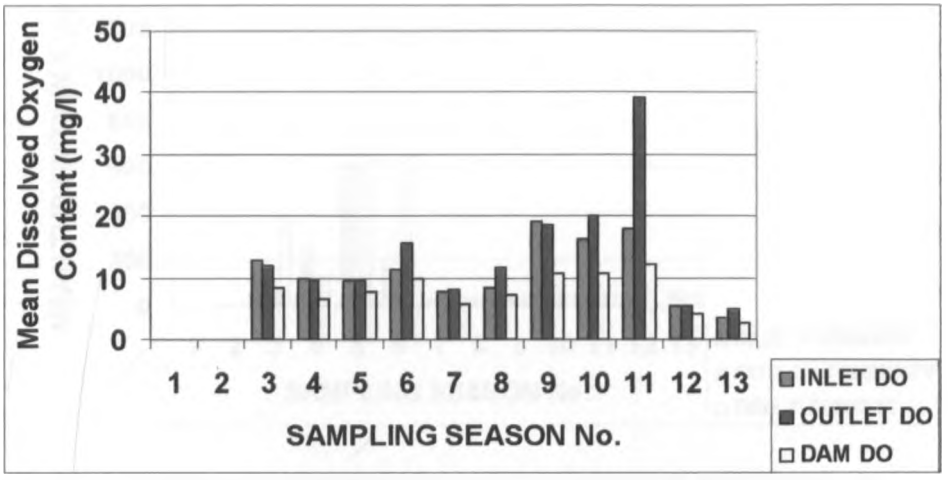

Figure 29. **Variation of Dissolved Oxygen (DO) Content from Inlet, Outlet & Dam Water of Nairobi Dam Basin with Sampling Seasons.**

The available data in Figure 29 shows that although the seasonal trends were similar to those of the major inorganic parameters, during all the sampling seasons involved, the lowest mean of Dissolved Oxygen levels were recorded for the dam water, while the highest values were found in the outlet streams. Currently, there have been no measures to remove the water hyacinth and other aquatic weeds from Nairobi Dam. Since the proliferation of these aquatic plants affects aquatic animals such as fish negatively by reducing the amount of dissolved oxygen in the water body through aerobic decomposition of these plants and respiration (Allaby, 1988), the current findings could probably explain why there is no longer existence of fish in Nairobi Dam and hence no more fishing and other related activities that used to be carried out before.

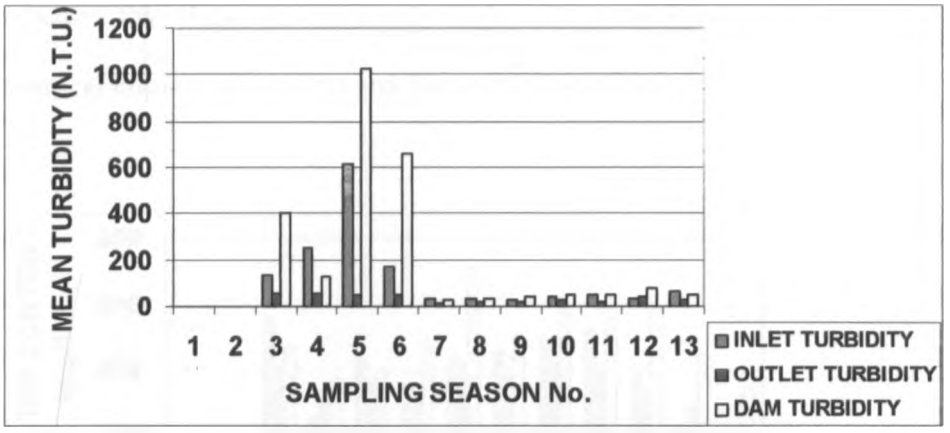

Figure 30. **Variation of Turbidity from Inlet, Outlet & Dam Water of Nairobi Dam Basin with Sampling Seasons.**

As expected, the seasonal trends for Turbidity (Figure 30) were generally similar to those for most inorganic nutrients. This indicates that there was generally high correlation between the inorganic chemical nutrient parameters and Turbidity.

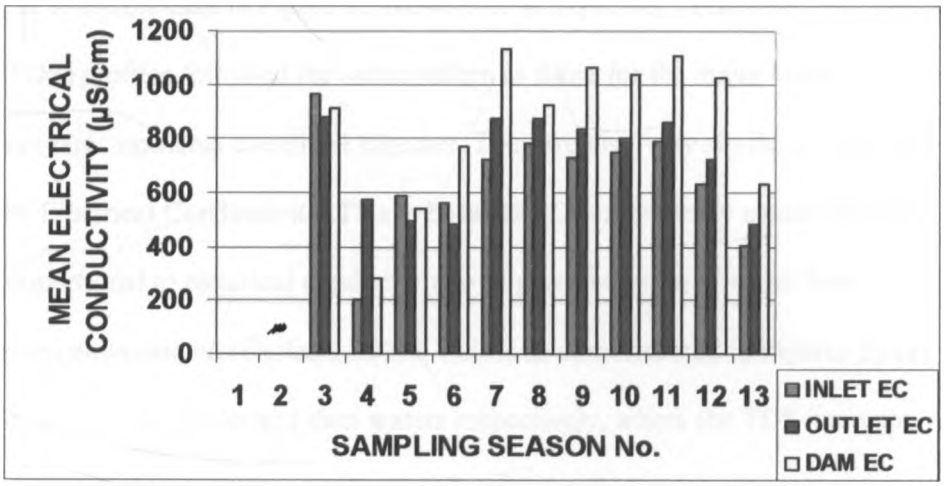

Figure 31. **Variation of Electrical Conductivity (EC) from Inlet, Outlet and Dam Water of Nairobi Dam Basin with Sampling Seasons.**

Like for turbidity, the seasonal trends for Electrical conductivity in Figure 31 were generally also similar to those for most inorganic nutrients. This

indicates that there was generally high correlation between the inorganic chemical nutrient parameters and Electrical Conductivity.

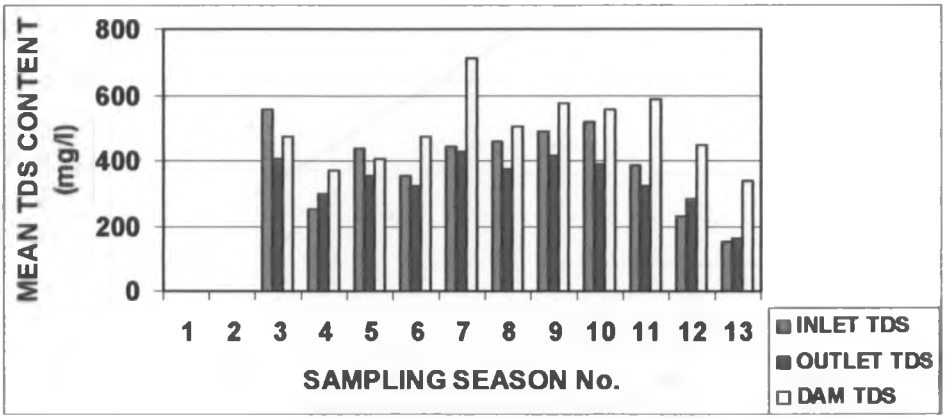

Figure 32. **Variation of Total Dissolved Solid (TDS) Content from Inlet, Outlet & Dam Water of Nairobi Dam Basin with Sampling Seasons.**

The available data in Figure 32 shows that as expected, Total Dissolved Solids (TDS) profiles followed the same pattern as those for the major chemical inorganic nutrients combined together. They are also very similar to those for the Electrical Conductivity. This is because TDS is generally closely directly proportional to electrical conductivity of a given solution or water from a given environment (Carlson, 2005). This is as demonstrated in Figures 33 (a) to (c) for inlet, outlet and dam waters respectively, where the TDS intercept represents the mean non-conducting dissolved solid level in the water over the whole sampling period. From the three graphs, the dam water had the highest TDS intercept (218.5 mg/l), followed by the outlet stream (129.2 mg/l), while the inlet streams had the lowest (72.92 mg/l).

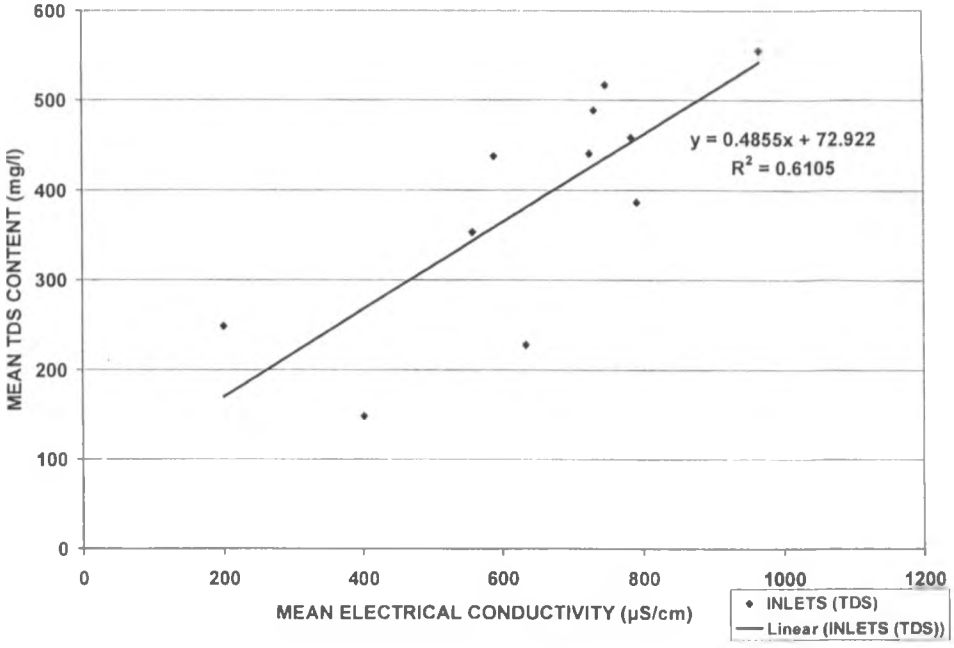

Figure 33 (a). **Mean of Total Dissolved Solids (TDS) Content vs. Mean of Electrical Conductivity (EC) from Inlet Streams of Nairobi Dam Basin for different Sampling Seasons.**

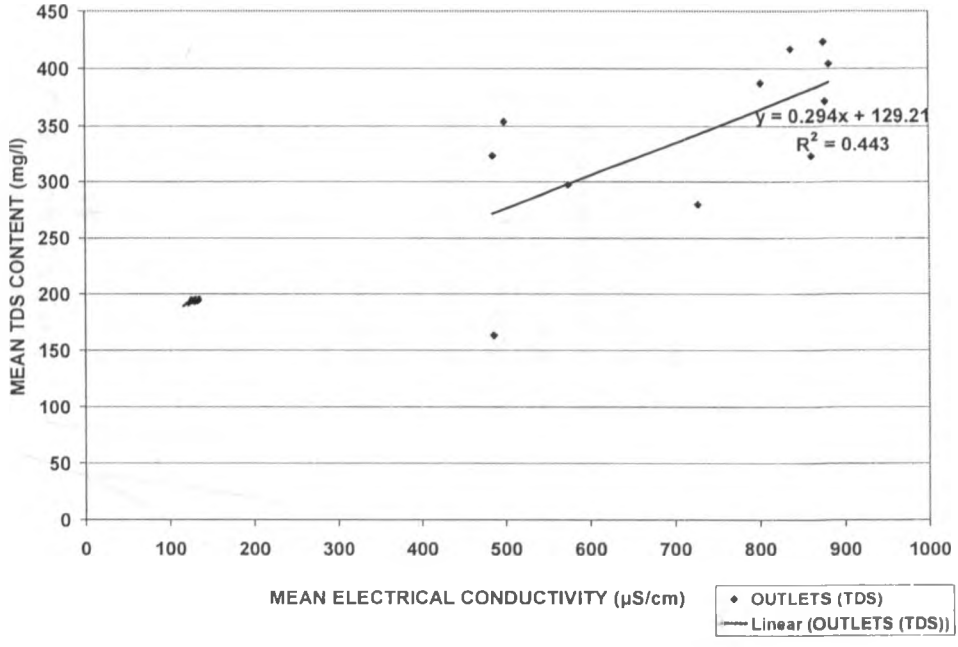

Figure 33 (b). **Mean of Total Dissolved Solids (TDS) Content vs. Mean of Electrical Conductivity (EC) at Outlet Stream Water of Nairobi Dam Basin for different Sampling Seasons.**

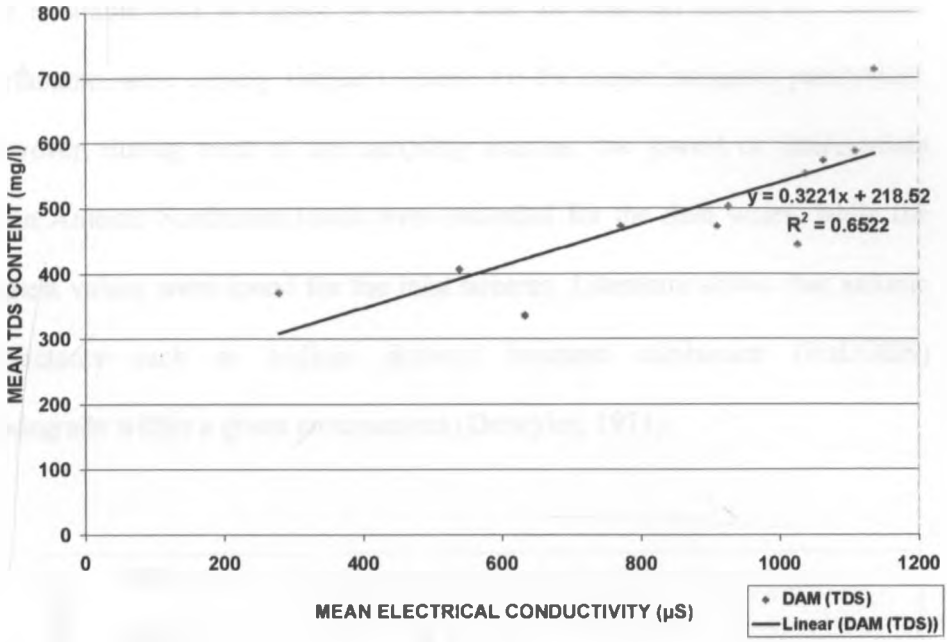

Figure 33 (c). **Mean of Total Dissolved Solids (TDS) Content vs. Mean of Electrical Conductivity (EC) from Nairobi Dam Water for different Sampling Seasons.**

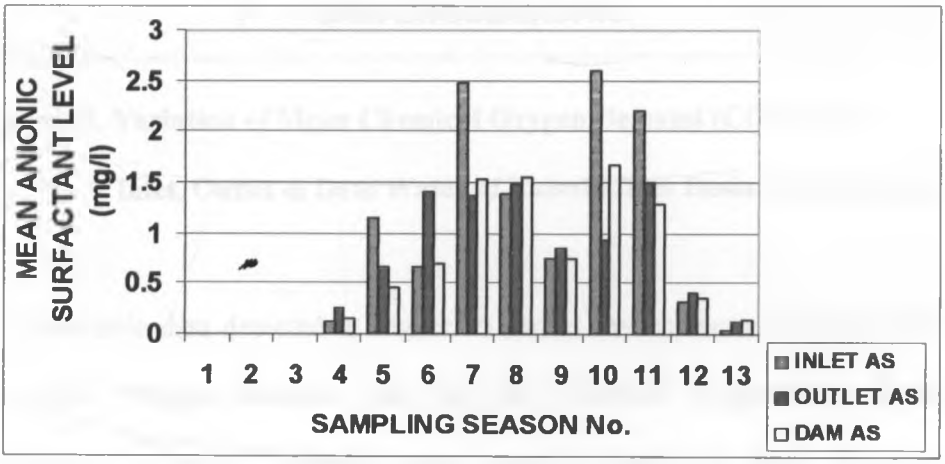

Figure 34. **Mean of Anionic Surfactants (AS) Level for Inlet, Outlet & Dam Water of Nairobi Dam Basin for different Sampling Seasons.**

The available data in Figure 34 shows that the seasonal trends for Anionic Surfactants were closely similar to those for the major inorganic parameters. However, during most of the sampling seasons, the lowest or intermediate mean Anionic Surfactant levels were recorded for the dam water, while the highest values were found for the inlet streams. Literature shows that anionic surfactants such as sodium dodecyl benzene sulphonate (NaDDBS) biodegrade within a given environment (Detwyler, 1971).

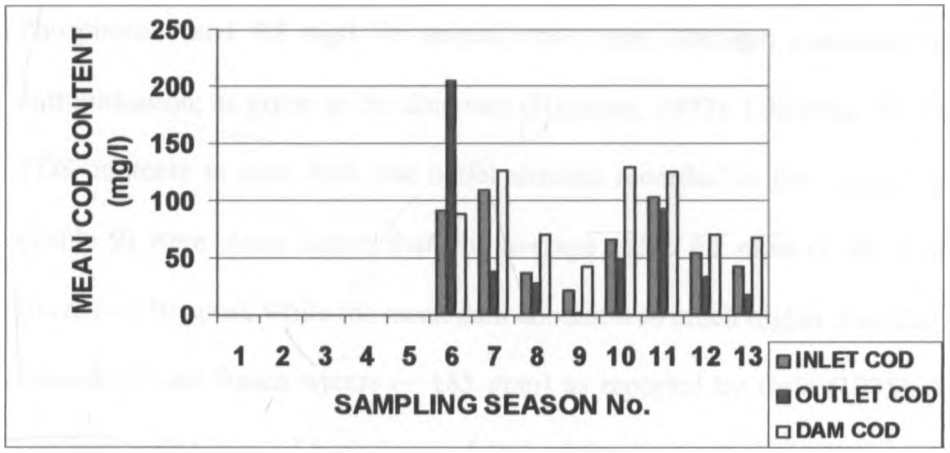

Figure 35. **Variation of Mean Chemical Oxygen Demand (COD) at the Inlet, Outlet & Dam Water of Nairobi Dam Basin with Seasons.**

The available data depicted in Figure 35 shows that the seasonal trends for Chemical Oxygen Demand, just like for Electrical conductivity, Total Dissolved Solids and Turbidity were generally similar to those for most inorganic nutrients. These profiles indicate that there was generally high correlation between the inorganic chemical nutrient parameters and these physical parameters.

4.4.5 *Evaluation of Possible Existence of Eutrophication in Nairobi Dam*

The summarized data shows that within the water hyacinth zone, the overall means of the 3 major nutrients (Phosphorous, Nitrogen and Potassium) were respectively as follows, in mg/l: (Hydrolysable + PO_4^{3-}) - P: 4.489 ± 0.504, (NO_3^- -N): 1.032 ± 0.205, (Total Kjeldahl + NO_3^-) - N: 36.867 ± 4.371, (Soluble Potassium), K: 42.580 ± 3.781. These figures showed much higher levels than the threshold values, namely: 0.1 mg/l for annual mean total Phosphorous and 0.8 mg/l for annual mean total Nitrogen associated with eutrophication, as given in the literature (Hammer, 1977). Likewise, the mean TDS contents in both inlet and outlet streams recorded in the current work (Table 9) were much higher than the average value for most of the world's rivers (~ 120 ppm), while the mean dam content was much higher than that for eutrophic Lake Itasca waters (~ 185 ppm) as reported by Cole (1975). This confirms exhibition of high level of Eutrophication in Nairobi Dam and its extended water hyacinth-growing zone.

4.5 *Determination of Limiting Nutrient Element: Two Alternative Approaches*

4.5.1 *Method A: Water-to-Plant Stoichiometric Ratio Method*

It was found that using the 'water to plant' ratio approach, as proposed by Middlebrook *et al.* (1974) in determining the limiting element, the three major, bulk elements Nitrogen, Potassium and Phosphorous had the least ratios. Among these three, the least was nitrogen. However, there was no significant

difference (at $\alpha = 0.05$, i.e. at 95% confidence level) among the three (refer to footnote of Table 16 for significant test calculations). These are shown in Table 10.

TABLE 10. **SUMMARY OF OVERALL MEANS OF CONCENTRATION RATIOS FOR ESSENTIAL NUTRIENTS IN NAIROBI DAM BASIN BETWEEN WATER AND PLANTS**

Nutrient / Element	Mean Ratio, C_w/C_p	Std. Error of Mean	Sample Size, n	%R.S. Error of Ratio	Rank (Position) of Ratio	Role of Nutrient
Phosphorous, P	**0.00151**	0.000423	13	28.0	3	Bulk
Nitrogen, N	**0.000969**	0.000107	12	11.1	1	Bulk
Potassium, K	**0.000983**	0.000123	13	12.5	2	Bulk
Sodium, Na	**0.00279**	0.000263	12	9.4	4	Bulk
Calcium, Ca	**0.00775**	0.000861	13	11.1	8	Bulk
Magnesium, Mg	**0.00406**	0.000436	13	10.8	6	Bulk
Manganese, Mn	**0.0184**	0.0138	13	74.6	9	Trace
Iron, Fe	**0.187**	0.0472	13	25.2	12	Trace
Zinc, Zn	**0.0215**	0.00731	13	34.1	10	Trace
Copper, Cu	**0.0233**	0.0178	13	76.2	11	Trace
Chloride, Cl^-	**0.00369**	0.000769	10	20.9	5	Bulk
Sulphate, SO_4^{2-}	**0.00447**	0.00140	9	31.3	7	Bulk
Fluoride, F^-	**2.76**	1.42	6	51.3	13	Trace

NOTES FOR TABLE 10:

C_w = Nutrient concentration in water, in mg/l; C_p = Nutrient concentration in water hyacinth or other plants (in mg/kg); %R.S. Error = % Relative Standard Error, i.e. 100*(S.D.)/(Mean*√n), where S.D. = Standard

deviation of mean ratio; Calculation figures reported up to 4 significant figures (max.)

When significance tests were performed between the three lowest mean ratios, i.e. among Phosphorous, Nitrogen & Potassium and also between Phosphorous and other close bulk nutrients, the following observations were made:

(i) There was no significant difference (at 95% confidence level, i.e. at $\alpha = 0.05$) among the mean ratios of levels in water to plants of the major nutrients (N, P, K) during the whole sampling period, i.e. from 2nd October 2004 to 22nd April 2006 – using the ratio approach. However,

(ii) There was significant difference (at $\alpha = 0.05$) between the ratios for phosphorous and three other closer bulk nutrients, i.e. Na, Cl^- and Ca using the same approach.

The above findings therefore suggest that according to the water-to-plant stoichiometric ratio method, any of the three major nutrients (nitrogen, phosphorous and potassium) could have been limiting. However, this method did not statistically give the specific limiting nutrient element among these three.

4.5.2 Method B: Linear Regression Correlation Method

Poor negative correlation was found between (Hydrolysable + PO_4^{3-}) - Phosphorous and (NO_3^-) - Nitrogen ($y = -0.2176x + 2.1471$, $R^2 = 0.1876$) on average in water sampled during the entire period (between 2nd October 2004 and 22nd April 2006). On the other hand, there was also poor positive

correlation between (Hydrolysable + PO_4^{3-}) - Phosphorous and Potassium (y = 2.142x + 32.964, R^2 = 0.0815) during the same sampling period. The positive potassium-intercept however shows that phosphorous was more limiting than potassium. These two correlations are graphically shown in Figures 36 and 37 respectively.

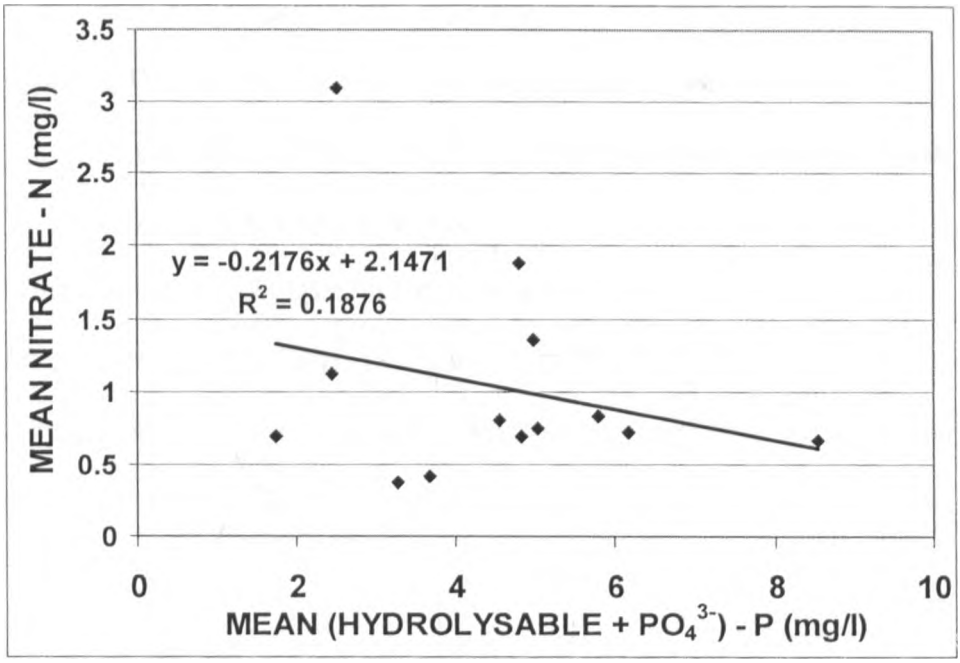

Figure 36. **Mean Nitrate – Nitrogen Concentration vs. Mean 'Total' Phosphorous Concentration in Water from Nairobi Dam Basin.***

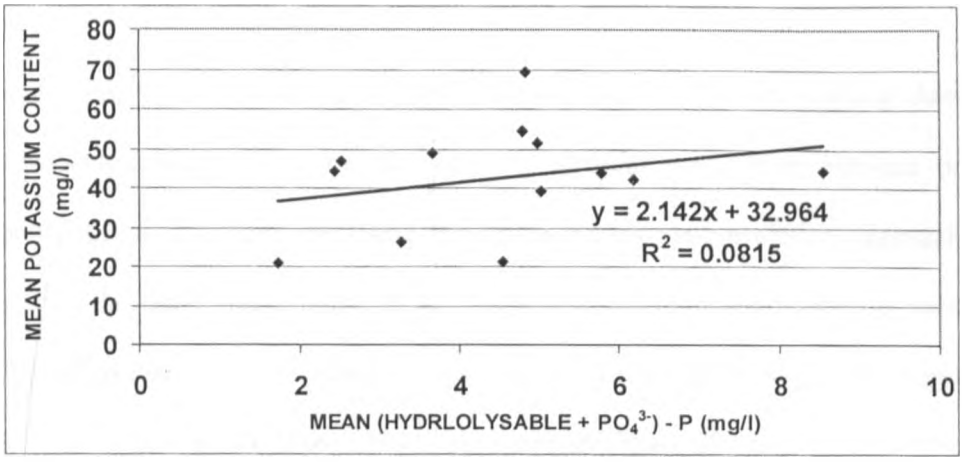

Figure 37. **Overall Mean Concentration of Potassium vs. Mean Concentration of 'Total' Phosphorous in Water from Hyacinth Zone of Nairobi Dam Basin.***

* This refers to Nairobi Dam, its two tributary inlets and one tributary outlet

Better (positive) correlation was found between (Total Kjeldahl + NO_3^-) - Nitrogen and Potassium contents in water sampled from the water hyacinth zone ($y = 0.6484x + 18.309$, $R^2 = 0.4801$), as shown graphically in Figure 38.

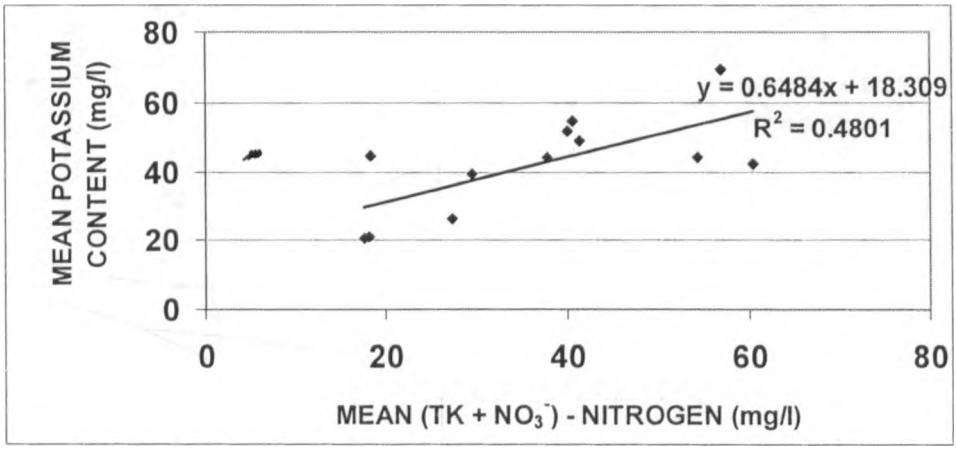

Figure 38. **Overall Mean Concentration of Potassium vs. Mean Concentration of 'Total' Nitrogen in Water from Hyacinth Zone of Nairobi Dam Basin.**

The regression equation also shows that nitrogen was more limiting than potassium. At this juncture, the limiting element was either nitrogen or phosphorous. Furthermore, using the linear regression-correlation approach among the three nutrients (N, P, K), the best correlation was found between (Hydrolysable + PO_4^{3-}) - Phosphorous and (Total Kjeldahl + NO_3^-) - Nitrogen ($y = 6.1118x + 8.424$, $R^2 = 0.5244$), as shown in Figure 39. This final positive correlation and the corresponding regression equation both suggest that with respect to Nitrogen and Potassium, ***Phosphorous was the limiting element (i.e. had negative intercept). It got exhausted first and was responsible for the proliferation of the water hyacinth in the aquatic environment studied. Any future eradication and control of this weed will have to deal with this nutrient element.***

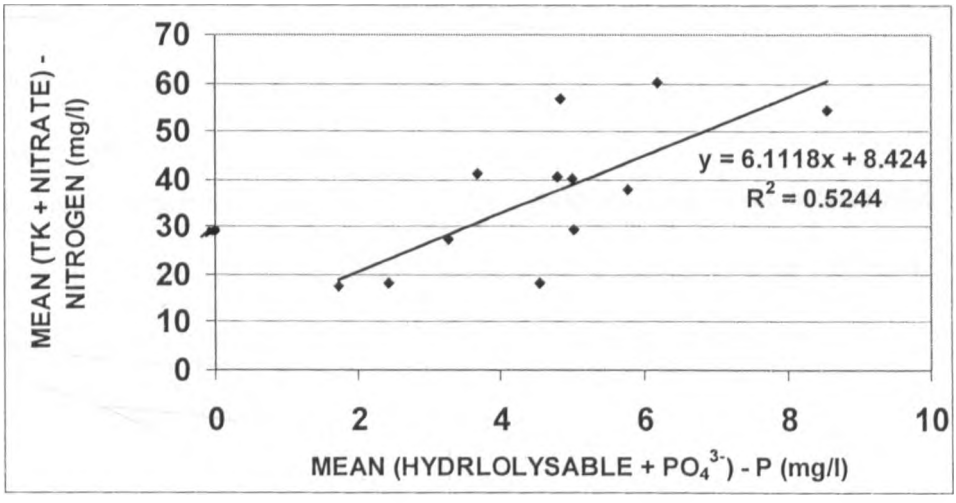

Figure 39. **Overall Mean Concentration of 'Total' Nitrogen vs. Mean Concentration of 'Total' Phosphorous in Water from Hyacinth Zone of Nairobi Dam Basin.**

4.5.3 *Proposed Faster Refined Linear Regression Correlation Method for Nutrient Pairs and for Limiting Element Determination*

The conventional linear regression correlation method, which is recommended in the literature (Krenkel and Novotny, 1980) and was used as described above in the current work, is tedious. It takes a lot of time because the different seasons and weather conditions experienced in a given region have to be covered. These will vary from very cold to extremely hot conditions and from very wet (heavy rainfall) to extremely dry weather conditions. In Kenya, where the current research was carried out, this normally takes a minimum of one year. This would therefore be the shortest period required to generate any useful data giving variation in the nutrient loads in the aquatic environment studied, in order to gauge the level of eutrophication experienced therein by plotting the relevant graphs. It was therefore necessary to devise a faster, less tedious method for future researchers, using the same linear regression correlation approach (Method B above).

In order to meet the above objective, individual correlation data between the same parameters described before (sections 4.2.4 and 4.3.1) were compiled and compared with the overall and mean data. This has been statistically summarized in Table 11.

TABLE 11. **SUMMARY OF LINEAR REGRESSION ANALYSIS PARAMETERS FOR MEANS OF ESSENTIAL NUTRIENTS CONTENT PAIRS IN WATER FROM WATER-HYACINTH ZONE OF NAIROBI DAM BASIN BY SAMPLING SEASONS** (Conc. in mg/l)

VARIABLE→	(X)	(Y_1)	(Y_2)	(X)	(Y)	(X)	(Y)
PARAMETER → / SAMPLING SEASON No. & DATE ↓	PO_4^{3-}-P (mg/l)	NO_3^- - N (mg/l)	($TK+NO_3^-$)- N (mg/l)	K (mg/l)	Na (mg/l)	Ca (mg/l)	Mg (mg/l)
1. OCT. 2004	y = 2.1495x - 2.3073			y = 3.4605x+15.083		y = 0.1673x+3.5355	
	R^2 = 0.1085			R^2 = 0.9732		R^2 = 0.9302	
	R(a)=	0.3294		R(b) =	0.9865	R(c) =	0.9716
2. FEB. 2005	y=7.8249x+8.6349			y = 2.5368x + 23.26		y = 0.1258x+4.8516	
	R^2 = 0.382			R^2 = 0.9704		R^2 = 0.7257	
	R(a) =		0.6181	R(b) =	0.9851	R(c) =	0.8519
3. APR. 2005	y = 5.4235x+2.188			y = 1.6523x+64.771		y = 0 148x - 0.1946	
	R^2 = 0.9358			R^2 = 0.9017		R^2 = 0.7986	
	R(a)=		0.9674	R(b) =	0.9496	R(c) =	0.8936
4. MAY 2005	y = -0.3207x + 28.375			y = 2.0577x + 33.7		y = 0.108x + 3.244	
	R^2 = 0.0008			R^2 = 0.5759		R^2 = 0.9246	
	R(a)=		0.0283	R(b) =	0.7589	R(c) =	0.9616
5. JUL. 2005	y = 1.7716x + 10.038			y = 1.9282x+78.738		y = 0.0963x+4.4228	
	R^2 = 0.1501			R^2 = 0.6704		R^2 = 0.7613	
	R(a)=		0.3874	R(b) =	0.8188	R(c) =	0.8725
6. AUG. 2005	y = 4.2401x + 13.439			Na NOT DONE, R		y = 0.082x + 5.5629	
	R^2 = 0.6869			ALSO NOT DONE		R^2 = 0.8897	
	R(a)=		0.8288		**********	R(c) =	0.9432
7. SEP. 2005	y = 4.1933x + 18.512			y = 2.6522x+70.031		y = 0.113x + 5.5446	
	R^2 = 0.8084			R^2 = 0.6266		R^2 = 0.9245	
	R(a)=		0.8991	R(b) =	0.7916	R(c) =	0.9615

TABLE 11 *(contd...)*

VARIABLE→	(X)	(Y_1)	(Y_2)	(X)		(Y)	
PARAMETER → / SAMPLING SEASON No. & DATE ↓	PO_4^{3-}-P (mg/l)	NO_3^- - N (mg/l)	(TK+NO_3^-)- N (mg/l)	K (mg/l)	Na (mg/l)	Ca (mg/l)	Mg (mg/l)
8. OCT. 2005	y = 4.231x+34.216			y = 2.2994x+111.57		y = 0.0548x+8.6806	
	R^2 =		0.2169	R^2 =	0.6357	R^2 =	0.8578
	R(a)=		0.4657	R(b) =	0.7973	R(c) =	0.9262
9. NOV. 2005	y=6.6144x+8.8643			y = 4.4358x-8.8241		y = 0.3276x+0.2121	
	R^2 =		0.6587	R^2 =	0.986	R^2 =	0.8112
	R(a)=		0.8116	R(b) =	0.9930	R(c) =	0.9007
10. DEC 2005	y=2.5442x+27.439			y = 6.2894x-39.557		y = 0.214x + 1.7195	
	R^2 =		0.2647	R^2 =	0.964	R^2 =	0.9506
	R(a)=		0.5145	R(b) =	0.9818	R(c) =	0.9750
11. JAN 2006	y=7.6522x+19.809			y = 2.793x + 55.712		y = 0.3245x-0.2791	
	R^2 =		0.2059	R^2 =	0.9029	R^2 =	0.433
	R(a)=		0.4538	R(b) =	0.9502	R(c) =	0.6580
12. MAR. 2006	y=0.1683x+17.926			y = 4.3375x-15.425		y = 0.2054x+0.7177	
	R^2 =		0.003	R^2 =	0.9483	R^2 =	0.8054
	R(a)=		0.0548	R(b) =	0.9738	R(c) =	0.8974
13. APR. 2006	y = 5.1526x+8.526			y = -3.1034x+202.7		y = 0.2553x-0.7396	
	R^2 =		0.5863	R^2 =	0.086	R^2 =	0.9865
	R(a)=		0.7657	R(b) =	0.2933	R(c) =	0.9932

TABLE 11 *(contd...)*

Analysis of above regression analysis parameters:

Variable →	(X)	(Y_1)	(Y_2)	(X)	(Y)	(X)	(Y)
Parameter→	**PO_4^{3-}P (mg/l)**	**NO_3^--N (mg/l)**	**(TK+NO_3^-)-N (mg/l)**	**K (mg/l)**	**Na (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**
Means of Regression Parameters	Y = 4.124617X + 16.49727			y = 2.6547x+48.728		y = 0.1651x+2.8675	
	R^2 =		0.4083	R^2 =	0.7701	R^2 =	0.8307
	R =		0.5663	R =	0.8567	R =	0.9082
Overall Regression Equation Parameters	y = 6.1118x+8.424			y = 3.1719x+41.705		y=0.09x+6.5228	
	R^2 =		0.5244	R^2 =	0.6046	R^2 =	0.2693
	R(a)=		0.7242	R(b) =	0.7776	R(c) =	0.5189
	y = -0.2176x + 2.1471						
	R^2 =	0.1876					
	R =	0.4331	(for NO_3^-)				

TABLE 11 *(contd...)*

VARIABLE→	(X)	(Y)	(X)	(Y)	(X)	(Y)
PARAMETER → / SAMPLING SEASON No. & DATE ↓	Mn (mg/l)	Fe (mg/l)	Zn (mg/l)	Cu (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)
1. OCT 2004	y = 6.8076x-29.555		y = 0.0351x+0.0898		y = 1.5071x-98.073	
	R^2 = 0.6348		R^2 = 0.6788		R^2 = 0.6427	
	R(d) = 0.797308		R(e) = 0.823893		R(f) = 0.801686	
2. FEB 2005	y = 5.1814x+4.0514		y = 0.0529x+0.0198		y=-0.2139x+83.023	
	R^2 = 0.5167		R^2 = 0.5522		R_2(n=2)= 1	
	R(d) = 0.718818		R(e) = 0.743102		R(f) = 1	
3. APR 2005	y = 2.7741x-4.8763		y =-0.0245x+0.5919		y=-0.0441x+18.022	
	R^2 = 0.8138		R^2 = 0.0094		R^2 = 0.0135	
	R(d) = 0.902109		R(e) = 0.096954		R(f) = 0.11619	
4. MAY 2005	y=0.1791x-5.6722		y=0.0098x+0.0924		Y=-0.2532x+53.821	
	R^2 = 0.148		R^2 = 0.1911		R^2 = 0.0751	
	R(d) = 0.384708		R(e) = 0.43715		R(f) = 0.274044	
5. JUL 2005	y = 3.7271x-3.2586		y = 0.0053x+0.0888		y = 1.4683x - 50.75	
	R^2 = 0.724		R^2 = 0.0344		R^2 = 0.2692	
	R(d) = 0.850882		R(e) = 0.185472		R(f) = 0.518845	
6. AUG 2005	y = 8.7783x-17.768		y = 0.0231x-0.0004		y = -0.1221x+27.775	
	R^2 = 0.7151		R^2 = 0.8829		R^2 = 0.009	
	R(d) = 0.845636		R(e) = 0.939628		R(f) = 0.094868	
7. SEP 2005	y = 3.8958x - 7.914		y = 0.0062x+0.0576		y = 0.0057x+18.478	
	R^2 = 0.6351		R^2 = 0.0134		R^2 = 0.0135	
	R(d) = 0.796932		R(e) = 0.115758		R(f) = 0.11619	
8. OCT 2005	y = 2.2985x+2.6506		y=-0.0042x+ 0.0596		y = 0.2061x+2.0331	
	R^2 = 0.8213		R^2 = 0.3444		R^2 = 0.1665	
	R(d) = 0.906256		R(e) = 0.586856		R(f) = 0.408044	
9. NOV 2005	y = 10.786x-24.996		y = 0.0186x + 0.002		y = 0.3311x+15.376	
	R^2 = 0.5835		R^2 = 0.1789		R^2 = 0.8063	
	R(d) = 0.763872		R(e) = 0.422966		R(f) = 0.897942	

TABLE 11 ***(contd...)***

VARIABLE→	(X)	(Y)	(X)	(Y)	(X)	(Y)
PARAMETER → / SAMPLING SEASON No. & DATE ↓	Mn (mg/l)	Fe (mg/l)	Zn (mg/l)	Cu (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l
10. DEC 2005	y = 4.4205x+7.5221		y = 0.0483x+0.0048		y = 0.0083x+11.315	
	R^2 =	0.1593	R^2 =	0.872	R^2 =	0.0025
	R(d) =	0.399124	R(e) =	0.933809	R(f) =	0.0500
11. JAN 2006	y = 1.9945x + 2.3628		y = 0.0195x+0.0114		y = 0.1536x - 1.6746	
	R^2 =	0.4623	R^2 =	0.0822	R^2 =	0.7174
	R(d) =	0.679926	R(e) =	0.286705	R(f) =	0.846995
12. MAR 2006	y = 3.0407x - 3.6914		y = 0.0169x + 0.015		y = 0.6031x + 6.4529	
	R^2 =	0.9588	R^2 =	0.0697	R^2 =	0.7405
	R(d) =	0.979183	R(e) =	0.264008	R(f) =	0.860523
13. APR 2006	y = 0.3584x + 1.1154		y = 0.036x - 0.0002		y = 0.0009x + 22.101	
	R^2 =	0.586	R^2 =	0.0667	R^2 =	5.00E-06
	R(d) =	0.765506	R(e) =	0.258263	R(f) =	0.002236
Means of Regression Parameters	y = 4.1725x - 6.1561		y = 0.0187x+0.0794		y = 0.2808x + 8.3000	
	R^2 =	0.596823	R^2 =	0.305854	R^2 =	0.342785
	R =	0.753097	R =	0.468813	R =	0.460582
Overall Regression Parameters	y = 4.3435x - 5.3402		y = 0.1517x-0.0048		y=-0.0219x+26.608	
	R^2 =	0.6649	R^2 =	0.2412	R^2(Poor)!=	0.0047
	R(d) =	0.815414	R(e) =	0.491121	R(f) =	0.068557

N.B. / KEY:

R^2 = Square of Linear correlation coefficient, R = Linear correlation coefficient, x & y are the first (x) and second (y) nutrient variables of the above data respectively. The above regression analysis data was computed from the Water Hyacinth growing zone (Sampling points nos. 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 20 & 22), i.e. n = 12 for every nutrient and sampling season.

The overall above data shows that the correlations between the nutrient elements in each pair were positive, except between (orthophosphate-phosphorous and nitrate-nitrogen) and between (chloride and sulphate). These exceptional pairs, together with (zinc and copper) also had the lowest linear correlation coefficients (< 0.500). On the other hand, the highest (positive) correlation (> 0.500) was found between (manganese and iron), (potassium and sodium), ('total' PO_4^{3-} - phosphorous and 'total' nitrogen) and (calcium and magnesium) in that order. This evidently shows that species of similar charges (mostly in the same periodic table groups or blocks) exhibited much higher correlation than the differently charged ones. This was expected because the bonding and hence chemical characteristics between species of the same charge or group, say potassium and sodium are relatively identical, compared to those pertaining to different charges or groups. Charges of a particular sign, such as group one or two cations will have comparably higher interaction with the oppositely charged ions, such as chloride or sulphate respectively, than dissimilar ones.

The above concept, which was apparent in the current study, was demonstrated by the poor correlation between orthophosphate-phosphorous and nitrate-nitrogen. On the other hand, the fairly high correlation between 'total' orthophosphate-phosphorous and 'total' nitrogen (Organic + Inorganic – N) can be explained by recalling from the literature review that Phosphorous is present in lakes (including dams) only in the form PO_4^{3-}, with phosphorous exhibiting an oxidation number of 5, so that the complications regarding oxidation and reduction discussed with Nitrogen do not arise (Brock, 1985).

Therefore, for existence of suitable correlation between these two nutrients (nitrogen and phosphorous), all possible environmental forms of nitrogen had to be considered but for phosphorous, it was sufficient to consider the (hydrolysable and orthophosphate) - phosphorous by simple preservation with 2 ml of concentrated H_2SO_4 for every litre of water sample and then determine the orthophosphate – phosphorous amount in the resulting supernatant liquid. When these parameters were thus determined, Nitrogen (from nitrates, NH_3 and Proteins) and Phosphorous (mainly from PO_4^{3-} species), both of which are in the same Periodic Table group, correlated very well.

The best overall correlation encountered between manganese and iron can be explained by the fact highlighted by Cole (1975): manganese is very close to iron in the redox transformations of lakes and behaves in much the same manner, both being soluble in the bivalent oxidation state. Manganese has four valence states, alternating between reduced soluble and oxidized (less soluble) conditions. Being soluble in the bivalent state, manganese is reduced and mobilized at a higher redox voltage than iron. Under strong oxidizing conditions, manganese is part of the colloidal micro zone seal and it serves with iron as a barrier between deeper sediment and supernatant water probably in the tetravalent or trivalent condition (Cole, 1975).

Among the nutrient pairs with overall low linear correlation coefficients (< 0.500), zinc and copper had the highest R (0.4911). This can be explained by the fact that both these two are d-block elements. However, zinc exists exclusively as Zn^{2+}, which is usually very stable, with filled d orbitals (d^{10}).

However, copper can exist as Cu^{2+} (d^9) as well as Cu^{+} (d^{10}), of which the cupric (+II oxidation) state is relatively much more stable. Also, these two nutrients are trace elements and any excessive levels beyond the threshold safe limit become toxic to the aquatic plants, leading to their imminent death. The overall correlation between these two nutrients was found, as expected, to lie between the two extremes. Zinc was generally found to be higher than copper in the water samples from the water hyacinth zone. This shows that the water hyacinth and other aquatic plants in the environment studied could tolerate higher levels of zinc than copper. This is also supported by the fact that the major sources of zinc in the area were rain (containing levels from 2.5 to 12 mg/m^3) (Cole, 1975) and its use in the manufacture of galvanized iron sheets (Kenya Bureau of Standards, 2003 (a)) which are rampant in the sprawling settlements, as reflected in Figures 1A and C of this thesis.

The data also shows that for the determination of the most probable limiting elements, phosphorous and nitrogen, when 'total' phosphorous and 'total' nitrogen were determined as described in the text above, 11 out of 12 linear regression relationships indicated positive correlation, with nitrogen having a positive intercept. It can therefore be concluded from the current work, that one could determine the limiting element between these two nutrients in a water body, whose eutrophication status was to be determined, with a confidence of about 92% just in one single sampling period or at most twice, as long as this was done carefully, as currently demonstrated. In order to achieve this, a major precaution would be to explore all the major nutritive forms of these elements, such as (Ortho phosphate and hydrolysable) –

Phosphorous and (Total Kjeldahl and nitrate) – Nitrogen determined in the current project. In addition to this, one should map out enough sampling points of the water body under consideration, where the eutrophication was suspected. In the current research work, this was the Water-Hyacinth growing zone, where the aquatic weed was consistently present. Once this is done, the correlation and linear regression data should be able to assist in predicting the limiting nutrient, which can then easily be tackled environmentally. This would save time and the resources required for a long-time repeated sampling and assist in solving the problem in good time.

4.6 Correlation between Phosphorous and Other Parameters in Water and Their Interpretation

In order to explore possible dependency of phosphorous, which has already been confirmed to be the limiting nutrient element, on other related parameters, the following correlations were investigated from the results involving the water hyacinth-growing zone, already tabulated.

4.6.1 Correlation Between Phosphorous And Chemical Oxygen Demand (COD)

Figure 40 shows the variation of the mean chemical oxygen demand (COD) with the mean phosphorous content in the water samples within the Water Hyacinth-growing Zone (Sampling points 5-14, 20 & 22 in Figure 5), including the linear regression equation and correlation coefficient over the various sampling seasons investigated.

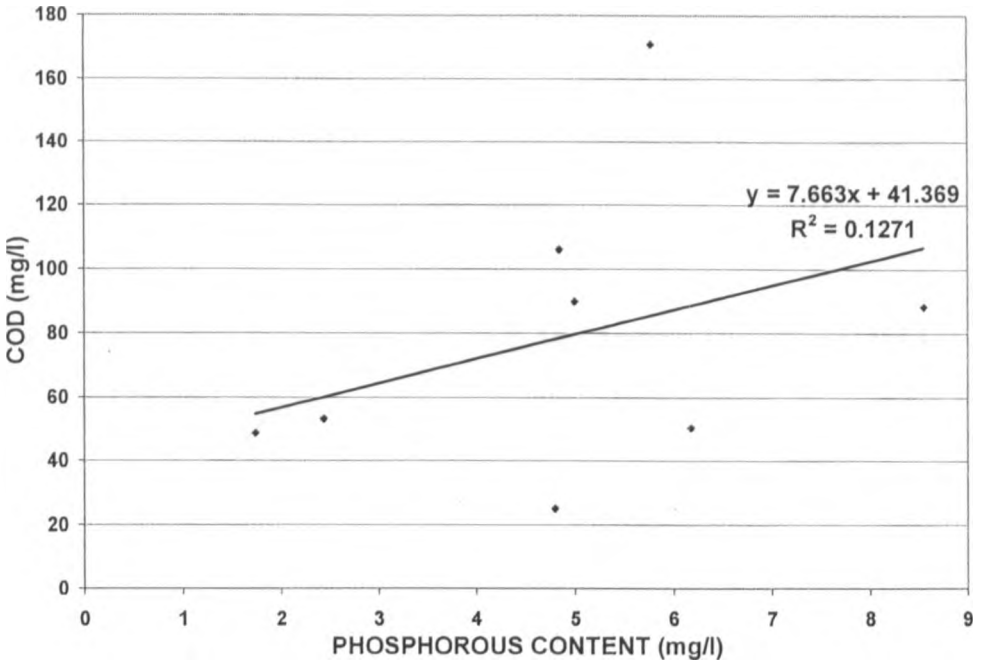

Figure 40. **Mean Chemical Oxygen Demand (COD) vs. Mean Phosphorous Concentration in Water Hyacinth Zone during 6^{th}–13^{th} Sampling Seasons.**

The correlation obtained above suggests that though not the exact measure but a representation of the rough estimate of the total organic carbon, chemical oxygen demand (COD), which has a positive intercept in the regression equation above and by extension, the organic carbon could not have been the limiting nutrient/ parameter, with respect to phosphorous. This therefore confirms further that phosphorous is the overall limiting nutrient element for the proliferation of the water-hyacinth in the aquatic environment studied, as discussed earlier. This is due to the fact that carbon is already abundant in the atmosphere, augmented by the organic carbon-rich sewage, emanating from the informal settlements (slums) of Kibera and the neighbourhood. Furthermore, the water hyacinth, which is green, can photosynthesize its own organic carbon, using atmospheric carbon dioxide and water, with the help of

sunlight and chlorophyll. On the other hand, phosphorous was more limited, since the dam was initially a shallow, fresh-water body and so phosphorous had to be supplemented from external sources for the growth and proliferation of the water hyacinth and other aquatic plants.

4.6.2 Correlation Between Phosphorous And Anionic Surfactants (MBAS)

The graph for the variation of anionic surfactant content (as sodium dodecyl benzene sulphonate (NaDDBS) or as Methylene blue active substances (MBAS)) with phosphorous level in water samples from the water hyacinth-growing zone is illustrated in Figure 41.

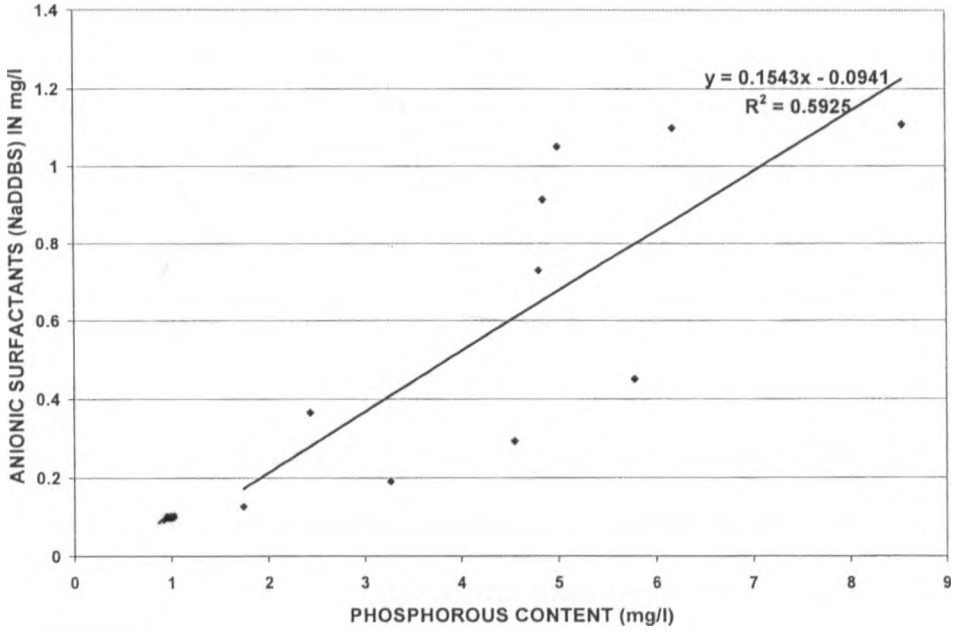

Figure 41. **Mean Concentration of Anionic Surfactants (NaDDBS) vs. Mean Concentration of Phosphorous in Water from Nairobi Dam Basin* Water-Hyacinth Zone during 4th – 13th Samplings** (R = 0.7697).

* This refers to Nairobi Dam, its two tributary inlets and one tributary outlet.

Figure 41 reveals that there was fairly high positive correlation between the anionic surfactant content and that of phosphorous, within the water hyacinth-growing zone. This strongly confirms that use of phosphorous-containing surfactants (soaps and detergents) for domestic use in the region studied is the major source of phosphorous. The COD data suggests that the other contributing source of enhanced phosphorous, to some extent, was untreated raw domestic sewage, due to lack of an elaborate sewage treatment and disposal system in the area.

4.7 Nutrients Distribution In The Sediments

It was found that the entire results of the available bulk inorganic nutrients showed that their overall mean concentrations in the dam sediments were much higher than the corresponding ones in either the inlet or the outlet streams, while those for the trace elements, copper and zinc in the dam were intermediate between the inlet and outlet streams. Among the nutrients analyzed, calcium and sulphate had exceptionally high concentrations, even higher than sodium and chloride respectively. It is worth recalling however, from results presented before (Table 8), that these two nutrients (calcium and sulphate) did not record the highest concentration levels in water. This shows that these two were present and more available in the sediments than other nutrients analyzed, thus revealing that in addition to the inlet streams' contribution of the two nutrients, the geology of the entire area studied (represented by the sediments) could have been a major source of calcium and

sulphate. The overall results are summarized in Table 12 for soluble nutrients in mg/kg.

TABLE 12. **OVERALL MEAN CONCENTRATIONS OF AVAILABLE NUTRIENTS IN SEDIMENTS FROM VARIOUS ENVIRONMENTS OF NAIROBI DAM BASIN***

PARAMETER → / AQUATIC ENVIRONMENT ↓	PO_4^{3-} - P (mg/kg) ± Std. Error	$(TK+NO_3^-)$-N (mg/kg) ± Std. Error	K (mg/kg) ± Std. Error	Na (mg/kg) ± Std. Error	Ca (mg/kg) ± Std. Error	Mg (mg/kg) ± Std. Error	Mn (mg/kg) ± Std. Error
DAM INLET MEAN, n = 10	62.26 ± 9.915	995.1 ± 198.8	535.0 ± 48.28	1988 ± 381.4	3927 ± 284.7	422.5 ± 92.61	1230 ± 138.6
DAM MEAN, n = 10	228.5 ± 63.24	2933 ± 460.7	1899 ± 252.3	5295 ± 942.8	6621 ± 671.1	935.0 ± 134.4	1963 ± 276.3
DAM OUTLET MEAN, n = 10	174.0 ± 47.16	1574 ± 253.1	705.1 ± 40.20	2219 ± 577.8	5126 ± 403.2	579.9 ± 73.27	1320 ± 99.87
HYACINTH ZONE MEAN, n = 10	216.0 ± 41.72	2376 ± 322.9	1430.4 ± 153.1	4063 ± 770.87	6008 ± 464.2	804.1 ± 107.7	1729 ± 172.2

N.B.:

* This refers to Nairobi Dam, its two tributary inlets and one tributary outlet;

Concentrations reported up to 4 significant figures (max.).

TABLE 12. *(contd...)*

PARAMETER → / AQUATIC ENVIRONMENT ↓	Fe (mg/kg) ± Std. Error	Zn (mg/kg) ± Std. Error	Cu (mg/kg) ± Std. Error	Cl^- (mg/kg) ± Std. Error	SO_4^{2-} (mg/kg) ± Std. Error	F^- (mg/kg) ± Std. Error
DAM INLET MEAN, n = 10	142.1 ± 36.52	155.7 ± 26.53	4.135 ± 1.743	1416 ± 295.2	4241 ± 565.7	136.5 ± 77.38
DAM MEAN, n = 10	192.4 ± 44.73	110.5 ± 19.15	4.864 ± 1.934	2622 ± 462.0	5209 ± 914.9	202.2 ± 113.1
DAM OUTLET MEAN, n = 10	138.2 ± 28.56	64.57 ± 27.26	6.725 ± 3.073	2109 ± 617.9	4000 ± 814.8	159.5 ± 89.28
HYACINTH ZONE MEAN, n = 10	166.3 ± 32.69	89.43 ± 23.76	5.210 ± 2.156	2407 ± 436.9	4793 ± 822.2	187.1 ± 104.3

The above results show that relative to the sediments from the inlet and outlet aquatic environments, the dam sediments appeared to concentrate most of the inorganic nutrients at higher levels. The dam could thus be more useful as a sink for these nutrients from its surrounding aquatic environments. The dam sediments also act as a reservoir for these nutrients, to be released to the aqueous phase by dissolution whenever needed.

4.8 Nutrient Concentration Ratios By Sediments And Plants From The Aquatic Environment

In an uncontaminated aquatic environment, the sediments, just like the soil in the terrestrial environment, act as a source for storage of the nutrient ions for any possible growth of aquatic plant. These nutrients are transferred from the sediments to the water and consequently into the plant. On the other hand, in a contaminated environment, in addition to the water reservoir (lake, lagoon or dam), the source of contamination (mainly the feeding stream) contributes immensely to the augmentation of these nutrients in the aquatic plants. It was therefore crucial in the current study to determine the concentration ratios of these nutrients in the sediments and plants, with respect to the respective aquatic environments.

4.8.1 Accumulation Of Nutrients In Sediments Relative To The Water

The mean concentration ratio factors of the inorganic nutrients in the sediments from the water hyacinth zone, relative to the respective aquatic environments are shown in Table 13. The results indicate a minimum of fourteen fold concentration ratio factor for these nutrients in the sediments, relative to the respective aquatic (water) environments. The trace nutrients manganese, zinc and fluoride registered the highest concentration ratios, in that order, while most bulk nutrients registered the lowest. This was expected because the trace nutrients are held in reserve in the sediments, while the bulk

ones are dissolved in the aqueous phase, ready for assimilation by the aquatic plants.

TABLE 13. **OVERALL SEASONAL MEAN CONCENTATIONS OF NUTRIENTS FOR SEDIMENTS RELATIVE TO WATER FROM WATER-HYACINTH ZONE (C_s/C_w) IN DESCENDING ORDER**

NUTRIENT / ELEMENT	SAMPLE SIZE, n	Mean Ratio, C_s/C_w (Conc. in Sediment/ Conc. in Water) ± Std. Error
MANGANESE, Mn	13	435.206 ± 73.859
ZINC, Zn	13	434.666 ± 203.045
FLUORIDE, F^-	6	301.537 ± 131.026
SULPHATE, SO_4^{2-}	9	300.459 ± 78.871
COPPER, Cu	13	194.100 ± 72.997
MAGNESIUM, Mg	13	145.095 ± 62.232
CALCIUM, Ca	13	144.532 ± 13.558
'TOTAL' PHOSPHOROUS, P	13	118.137 ± 35.784
'TOTAL' NITROGEN, N	12	90.107 ± 18.427
POTASSIUM, K	13	44.463 ± 7.197
CHLORIDE, Cl^-	10	34.835 ± 9.032
SODIUM, Na	12	27.542 ± 5.033
IRON, Fe	13	14.622 ± 6.122

N.B. C_s = Nutrient concentration in the sediments in mg/kg and C_w = Nutrient concentration in the water in mg/l

'Total' Phosphorous ratio refers to ratio of Available or Extractable (PO_4^{3-}) – Phosphorous in sediments to (Hydrolysable + PO_4^{3-}) – P in water, while 'Total' Nitrogen refers to (Total Kjeldahl + Nitrate) – Nitrogen for both sediments and water

A notably apparent anomaly in the above data is evident for the "trace" nutrient element, iron. This recorded the least concentration factor, in contrast to the closely associated element, manganese. Iron is found in two states, the oxidized ferric (Fe^{3+}) and the reduced ferrous (Fe^{2+}). Low pH and reducing conditions promote the solubility of iron. Most ferrous compounds are soluble. In aqueous environments, the common ferric compounds are insoluble; as a result, iron precipitates in alkaline and oxidized conditions (Cole, 1975).

At pH values from 7.5 to 7.7, a threshold is reached where iron in the form of $Fe(OH)_3$ is precipitated automatically. This means that iron would not be found except in acidic and neutral water that is very low in oxygen and with redox potentials of 0.3 to 0.2 volt – such as in hypolimnion of a stratified eutrophic lake. With the introduction of oxygen at circulation, the iron would be oxidized and precipitated. Thus, in well-oxygenated waters, ferric iron occurs but is rare because of its insolubility (Cole, 1975).

According to the foregoing results and literature, it is evident that the iron present in the aqueous phases of the water hyacinth zones was in the reduced ferrous state (Fe^{2+}). This is further supported by the fact that the dam water recorded acidic pH and low dissolved oxygen as was discussed earlier in section 4.4.2. Since in the current study, the sediment to water ratio for iron was much lower than that for manganese, it could therefore be concluded that between these two essential transition metal ions, iron was relatively more favourable to eutrophication than manganese in Nairobi Dam and its extended water-hyacinth growing zone. Thus iron encouraged the proliferation of the

water hyacinth in the aquatic environment studied, compared to manganese, which was relatively more bound to the sediments.

4.8.2 *Accumulation of Nutrients in Plants Relative to the Water – Phytoremediation*

The mean concentration ratio factors of the inorganic nutrients in the aquatic plants, mainly the water hyacinth, relative to the respective aquatic environments are shown in Table 14 below. The results indicate a minimum of two fold concentration ratio for these nutrients in the plants, relative to the aquatic (water) environment. The major bulk nutrient elements (Potassium, Nitrogen and Phosphorous) registered the highest ratios.

TABLE 14. **OVERALL SEASONAL MEANS OF NUTRIENT CONCENTRATIONS FOR PLANTS RELATIVE TO THE AMBIENT WATER (C_p/C_w) IN DESCENDING ORDER**

NUTRIENT / ELEMENT	SAMPLE SIZE, n	Mean Ratio, Cp/C_w (Conc. in Plant/ Conc. in Water) ± Std. Error
POTASSIUM, K	12	1233.881 ± 155.775
'TOTAL' NITROGEN, N	13	1210.220 ± 166.619
'TOTAL' PHOSPHOROUS, P	13	1024.959 ± 158.216
SULPHATE, SO_4^{2-}	9	922.874 ± 455.703
IRON, Fe	13	605.422 ± 477.804
COPPER, Cu	13	580.565 ± 152.860

TABLE 14 *(contd...)*

NUTRIENT / ELEMENT	SAMPLE SIZE, n	Mean Ratio, Cp/C_w (Conc. in Plant/ Conc. in Water) ± Std. Error
SODIUM, Na	12	401.064 ± 42.736
CHLORIDE, Cl^-	10	391.354 ± 75.335
MAGNESIUM, Mg	13	282.111 ± 29.242
MANGANESE, Mn	13	230.205 ± 30.055
CALCIUM, Ca	13	160.668 ± 26.692
ZINC, Zn	13	114.694 ± 28.745
FLUORIDE, F^-	6	2.603 ± 1.440

N.B.:

C_p = Nutrient concentration for the plant in mg/kg and C_w = Nutrient concentration for the water in mg/l (from the same environment).

'Total' Phosphorous ratio refers to ratio of Available or Extractable (PO_4^{3-}) – P in plants to (Hydrolysable + PO_4^{3-}) – P in water, while

'Total' Nitrogen refers to (Total Kjeldahl + Nitrate) – Nitrogen for both plants and water

The above data clearly indicates that the water hyacinth and the other accompanying aquatic plants were efficient accumulators for the inorganic nutrients studied, with concentration factors of 2.6 for fluoride and at least 100 for the other nutrients. The available aquatic weeds, particularly the water hyacinth could therefore be used for the phytoremediation and hence for the wastewater management of the aquatic environment studied and possibly other water bodies experiencing similar eutrophication problems.

4.8.3 Comparison of Nutrient Concentration Ratios between Aquatic Plants and Sediments

The following are mean concentration ratios for the seasonal mean inorganic nutrient levels in the aquatic plants, mainly the water hyacinth, relative to the respective sediments in the same environment, as presented in Table 15.

TABLE 15. **OVERALL MEANS OF RELATIVE NUTRIENT CONCENTRATION RATIOS BY WATER HYACINTH AND OTHER AQUATIC PLANTS OVER THE SEDIMENTS IN DESCENDING ORDER**

NUTRIENT / ELEMENT	Mean Ratio, (Conc. in Plant/ Conc. in Sediment) ± Std. Error	SAMPLE SIZE, n	ROLE OF NUTRIENT
COPPER, Cu	23761.16 ± 14215.65	13	TRACE
POTASSIUM, K	31.298 ± 3.827	13	BULK
PHOSPHOROUS, P	26.512 ± 4.389	10	BULK
CHLORIDE, Cl^-	18.595 ± 5.340	10	BULK
NITROGEN, N	17.425 ± 1.314	10	BULK
SODIUM, Na	17.272 ± 2.070	12	BULK
MAGNESIUM, Mg	3.145 ± 0.319	13	BULK
SULPHATE, SO_4^{2-}	2.176 ± 0.534	9	BULK
FLUORIDE, F^-	1.295 ± 0.511	6	TRACE
IRON, Fe	1.108 ± 0.445	10	TRACE
CALCIUM, Ca	1.095 ± 0.109	13	BULK

TABLE 15 *(contd...)*

NUTRIENT / ELEMENT	Mean Ratio, (Conc. in Plant/ Conc. in Sediment) ± Std. Error	SAMPLE SIZE, n	ROLE OF NUTRIENT
MANGANESE, Mn	0.616 ± 0.061	13	TRACE
ZINC, Zn	0.417 ± 0.075	13	TRACE

The results show that except for fluoride, iron, calcium, manganese and zinc, the concentration of the nutrients in the plants were at least twice, higher than with respect to the sediments. It is also evident that copper, though a trace nutrient element was relatively more highly concentrated in the plants than in the sediments. The aquatic plants, especially the water hyacinth could therefore be used to detoxify excessive levels of this element from polluted waters, as long as it does not exceed levels toxic to the water hyacinth plant itself.

4.9 Background Values Of Nutrient Levels In Dry Soils From Various Sampling Points For Comparison With Sediments

The statistical analysis of the nutrients for representative samples (n = 5) from the area of study in the last sampling season are shown in Table 16. The statistical formulae and interpretation are as described in various statistical text books such as Bailey (1981).

TABLE 16. **STATISTICAL TESTS OF SIGNIFICANT DIFFERENCES IN NUTRIENT LEVELS BETWEEN ANALYTICAL DATA OF SELECTED SOIL AND SEDIMENT SAMPLES**

Sample type, Nutrient & Statistic	Sample size, n_1 or n_2	Sample mean, $\bar{u}_1$ or $\bar{u}_2$	Sample s.d., s_1 or s_2	Pooled s.d., i.e. s^*	Calculated t value**	Tabulated t ($\alpha = 0.05$)	Is difference significant at 95% Confidence?
Phosphorous (P)							
Soils	5	69.254	30.658				
Sediments	5	79.466	54.247				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Phosphorous between Soils and Sediments:				**44.061**	**0.366**	**2.306**	**No**
Nitrogen (N)							
Soils	5	1864.759	509.234				
Sediments	5	791.453	650.561				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Nitrogen between Soils & Sediments:				**584.19**	**2.905**	**2.306**	**Yes**
Potassium (K)							
Soils	5	733.2222	218.501				
Sediments	5	518.416	54.606				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Potassium between Soils & Sediments:				**159.26**	**2.133**	**2.306**	**No**
Sodium (Na)							
Soils	5	7942.653	3497.060				
Sediments	5	5855.938	1179.079				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Sodium between Soils & Sediments:				**2609.6**	**1.264**	**2.306**	**No**

TABLE 16 *(contd...)*

Sample type, Nutrient & Statistic	Sample size, n_1 or n_2	Sample mean, $\bar{u}_1$ or $\bar{u}_2$	Sample s.d., s_1 or s_2	Pooled s.d., i.e. s*	Calculated t value**	Tabulated t (α = 0.05)	Is difference significant at 95% Confidence?
Calcium (Ca)							
Soils	5	3409.878	1791.410				
Sediments	5	3123.681	1043.491				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Calcium between Soils & Sediments:				**1466**	**0.309**	**2.306**	**No**
Magnesium (Mg)							
Soils	5	480.644	198.344				
Sediments	5	368.741	147.600				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Magnesium between Soils & Sediments:				**174.82**	**1.012**	**2.306**	**No**
Manganese (Mn)							
Soils	5	221.890	118.496				
Sediments	5	1419.698	680.163				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Manganese (Mn) between Soils & Sediments:				**488.19**	**3.879**	**2.306**	**Yes**
Iron (Fe)							
Soils	5	10.836	2.792				
Sediments	5	65.049	45.956				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Iron (Fe) between Soils & Sediments:				**32.556**	**2.633**	**2.306**	**Yes**

TABLE 16 *(contd...)*

Sample type, Nutrient & Statistic	Sample size, n_1 or n_2	Sample mean, $\bar{u}_1$ or $\bar{u}_2$	Sample s.d., s_1 or s_2	Pooled s.d., i.e. s^*	Calculated t value**	Tabulated t (α = 0.05)	Is difference significant at 95% Confidence?
Zinc (Zn)							
Soils	5	42.616	20.018				
Sediments	5	153.258	194.626				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Zinc (Zn) between Soils & Sediments:				**138.35**	**1.265**	**2.306**	**No**
Copper (Cu)							
Soils	5	Not detected	Not detected				
Sediments	5	0.000129	0.000177				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Copper (Cu) between Soils & Sediments:				**0.0001**	**1.621**	**2.306**	**No**
Chloride (Cl^-)							
Soils	5	6987.916	1453.723				
Sediments	5	2449.311	994.069				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Chloride (Cl^-) between Soils & Sediments:				**1245.3**	**5.763**	**2.306**	**Yes**
Sulphate (SO_4^{2-})							
Soils	5	5056.395	4563.874				
Sediments	5	4699.208	3338.299				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Sulphate (SO_4^{2-}) between Soils & Sediments:				**3998.3**	**0.141**	**2.306**	**No**

TABLE 16 *(contd...)*

Sample type, Nutrient & Statistic	Sample size, n_1 or n_2	Sample mean, $\bar{u}_1$ or $\bar{u}_2$	Sample s.d., s_1 or s_2	Pooled s.d., i.e. s^*	Calculated t value**	Tabulated t (α = 0.05)	Is difference significant at 95% Confidence?
Fluoride (F)							
Soils	5	453.629	69.150				
Sediments	5	473.240	39.418				
D.f. (n_1+n_2-2)	8						
Significant difference parameters for Fluoride (F) between Soils & Sediments:				**56.283**	**0.551**	**2.306**	**No**

KEY USED IN TABLE 16:

$n_{1 \text{ or } 2}$ = Soil or sediment sample size; $\bar{u}_{1 \text{ or } 2}$ = Mean of the nutrient content in soil or sediment respectively, i.e. $(\sum u)/n$; S.d., $s_{1 \text{ or } 2}$ = Sample Standard deviation for soils and sediments respectively (refer to end of Table 18 for the formula). * Square of Pooled s.d., $s^2 = ((n_1-1)s_1^2 + (n_2-1)s_2^2)/(n_1+n_2-2))$; ** t, i.e. Calculated Student's t test value = $(|\bar{u}_1 - \bar{u}_2|)/(s^*(\sqrt{(1/n_1)+(1/n_2)})$; α = Level of significance, D.f. = Combined degrees of freedom for soils and sediments = $n_1 + n_2 - 2$ (Bailey, 1981).

Table 16 indicates that there seemed to be no significant differences (at 95% confidence, level $\alpha = 0.05$) between the mean concentration of nutrients in soil and sediments for 'total' Phosphorous, Potassium, Sodium, Calcium, Magnesium, Zinc, Copper and Sulphate in the last sampling period, i.e. on 22nd Apr. 2006 - using the Standard analytical methods. However, there was significant difference between the mean concentration of nutrients in soil and sediments for 'total' Nitrogen, Manganese, Iron and Chloride (at 95% confidence level), using the described analytical methods.

It can therefore be deduced with 95% confidence, from the data in Table 16, that the distribution of the nutrients phosphorous, potassium, sodium, calcium, magnesium, zinc, copper and sulphate between the soil and sediments from representative sites of the region studied was the same. This shows that these nutrients were confined in the aqueous phase and their adsorption on the sediments was minimal. There was therefore no significant deviation from the background levels represented by the sediments. A notable observation was that for the trace nutrient elements zinc and copper, since their levels were not significantly higher in the sediments compared to the soil at ($\alpha = 0.05$), any appreciably detectable levels of these two nutrient elements in the aquatic environment could only have been contributed by the untreated sewage.

On the other hand, at the same significant level ($\alpha = 0.05$), the mean concentration levels of ($TK+NO_3^-$) – Nitrogen and chloride in soil were higher than in sediments. This shows that due to their high solubility in water, these nutrients had been leached from the sediments into the water. It could also be deduced that the soil in the area had high nitrogen, indicating high possibility of the presence of the nitrifying bacteria, capable of transforming atmospheric nitrogen to ammonia, part of which is converted to nitrates by nitrification (Hay, 1984). This is even supported by the fact that these bacteria are generally known to thrive in the root nodules of legumes such as beans, which are some of the subsistence crops generally grown in the area of study as clearly depicted in Figure 1C. The statistical data also indicated that the dry

soil analyzed was rich in chloride and could possibly act as an alternative source of this nutrient in addition to the sewage.

At the same significant level ($\alpha = 0.05$), manganese and iron levels were higher in the sediments than in the soils. This shows that the sediments could adsorb these 'trace' nutrients and release them to the aqueous phase when needed and under favourable pH conditions.

4.10 Analytical Quality Control: Data for Calibration and Nutrient Recovery

In order to evaluate the sensitivity, reliability and accuracy of the analytical methods, linear calibration graphs of the various parameters with known standards were obtained by plotting the respective instrumental response against concentration or logarithm $_{10}$ of concentration and regression equations and correlation coefficient, R or its square (R^2) obtained. An R value ≥ 0.99 was generally obtained, showing highly acceptable calibration.

On the other hand, recoveries of known concentrations of spiked and proficiency testing samples were also done, along with the field samples. These (sample, standard and spike) were subjected to the same analytical procedures. For the water samples, distilled water spiked with the relevant nutrient solutions was used to determine the available (soluble) nutrients, whereas for sediments and plants, acid washed sand spiked with the stock solutions containing ions of interest was treated like the samples and the

corresponding parameters determined. The ratio of the experimental value to the expected (spiked) one was then converted to percentage recovery.

4.10.1 Calibration Data

The calibration data for the various parameters is summarized in Table 17 and depicted in Figures 41 to 53.

TABLE 17. **CALIBRATION DATA: INSTRUMENTAL READINGS* FOR DIFFERENT CONCENTRATIONS OF VARIOUS PARAMETERS** (concentrations in mg/l, ranging from 0.04 to 100 mg/l, for the different techniques used)

Conc. → / Nutrient ↓	0.0	0.04	0.05	0.10	0.12	0.20	0.32	0.40
PO_4^{3-} - P	0.0000	0.027			0.086	0.14	0.225	0.281
Nitrate,NO_3^-	0.0000							
Ca	0.0000					0.0070		0.0134
Mg	(-ve) 0.0008					0.0519		0.1083
Mn	(-ve) 0.0006							
Fe	(-ve) 0.0008							
Zn	0.0010					0.0228		0.0456
Cu	(-ve) 0.0008					0.0045		0.0100

TABLE 17 (*contd...*)

Conc. → / Nutrient ↓	0.0	0.04	0.05	0.10	0.12	0.20	0.32	0.40
F^-			297	315		333		

* For AAS and UV/Visible methods, this represents Absorbance reading; for Flame Photometer method (Na, K) this represents the emitted intensity reading while for ISE method (F^-, Cl^-), this represents the cell potential in mV.

TABLE 17 (*contd...*)

Conc. → / Nutrient ↓	0.5	0.6	0.8	1.0	1.4	1.5	1.8	2.0	2.2
PO_4^{3-} - P		0.407							
Nitrate, NO_3^-	0.116					0.284			
K	2.5			5				10	
Na	2.5			5				10	
Ca		0.0206	0.0274	0.0337					
Mg		0.1554	0.2065	0.2501					
Mn	0.0181			0.0355		0.0537		0.0699	
Fe	0.0083			0.0168		0.0244		0.0321	
Zn		0.0667	0.0853	0.1040					
Cu		0.0153	0.0207	0.0254					
F		369		388	396		402		406
Cl				40					

TABLE 17 (*contd...*)

Conc. → / Nutrient ↓	2.5	3.0	4.0	4.5	5	6	8	10	20	40	70	100
Nitrate, NO_3^-		0.513		0.8		0.962						
K			20			30	40	50				
Na			20			30	40	50				
Mn	0.0865											
Fe	0.0407											
Cl					76			95	114	133	146	154

Anionic Surfactant as (NaDDBS) (mg/l)	0.000	0.881	1.762	3.524	5.286	7.048
Absorbance	0.000	0.198	0.428	0.8405	1.254	1.5425

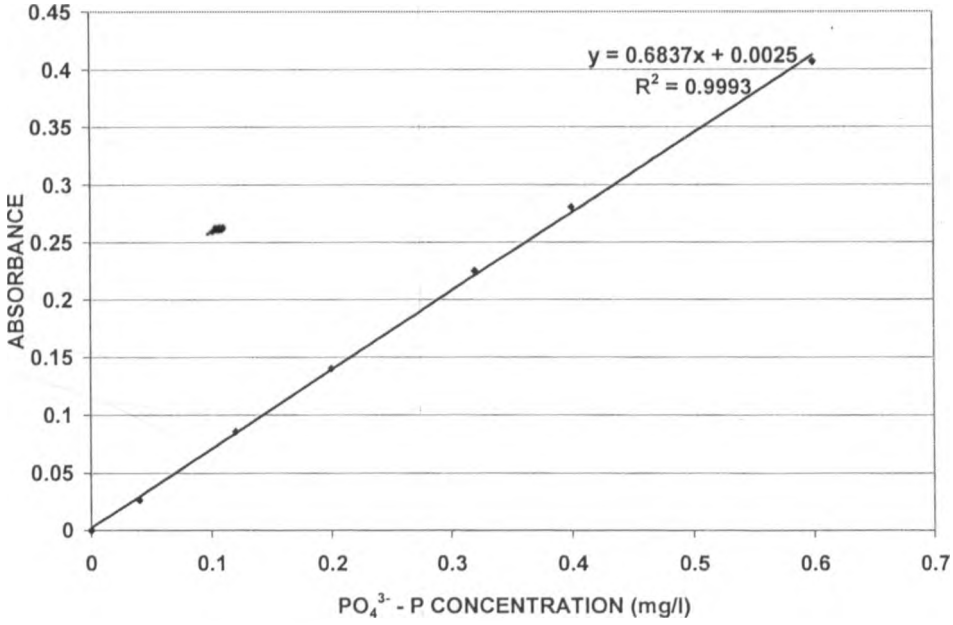

Figure 42. **Calibration Graph for PO_4^{3-} - P (UV/Visible at 880 nm)**

(R = 0.9997).

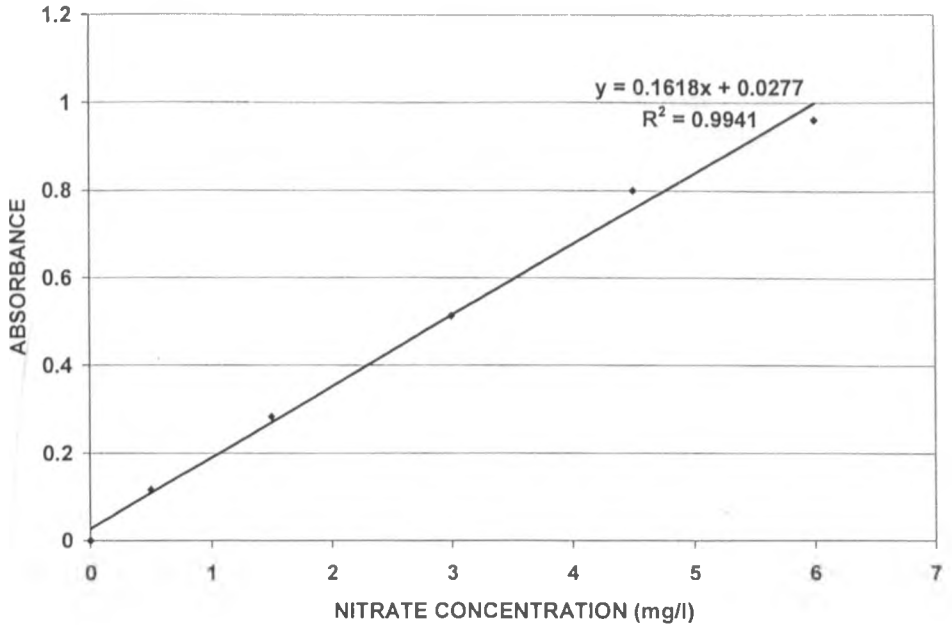

Figure 43. **Calibration Graph for Nitrate at 420 nm (UV/Visible)**

(R = 0.9970).

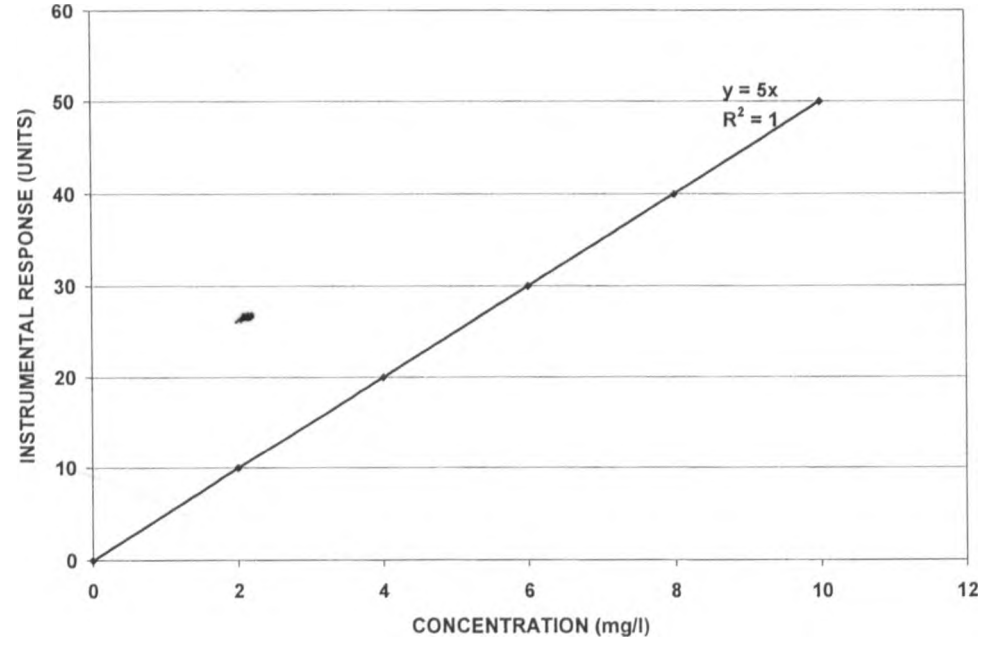

Figure 44. **Calibration Graph of K & Na by Flame Photometer (Typical Hypothetical Case)** (R = 1.0000 (100 % Linearity)).

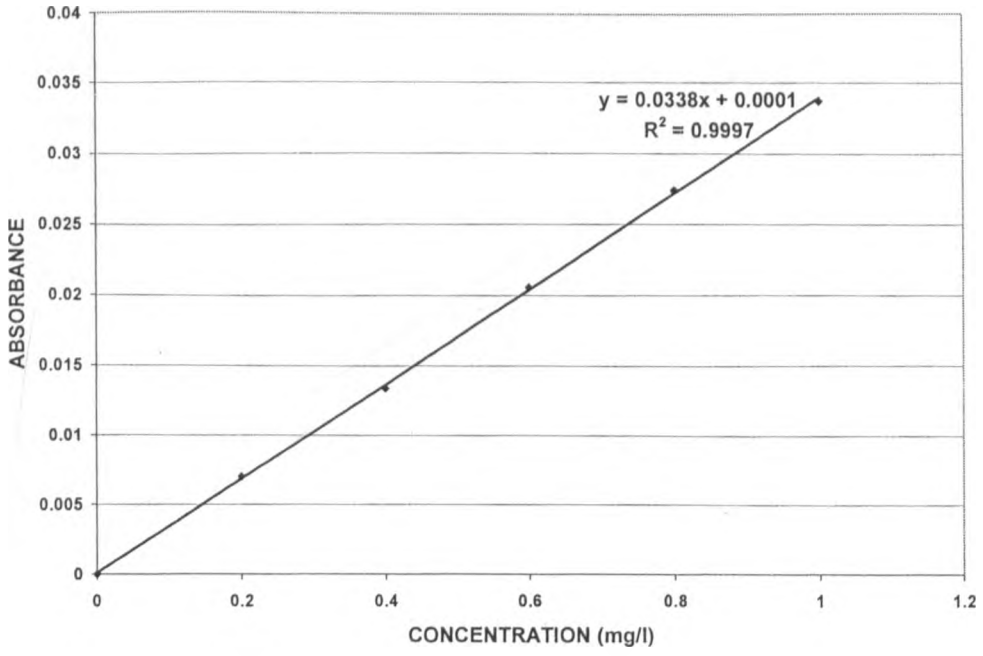

Figure 45. **Calibration Graph for Calcium with AAS** (R_{Ca} = 0.9999).

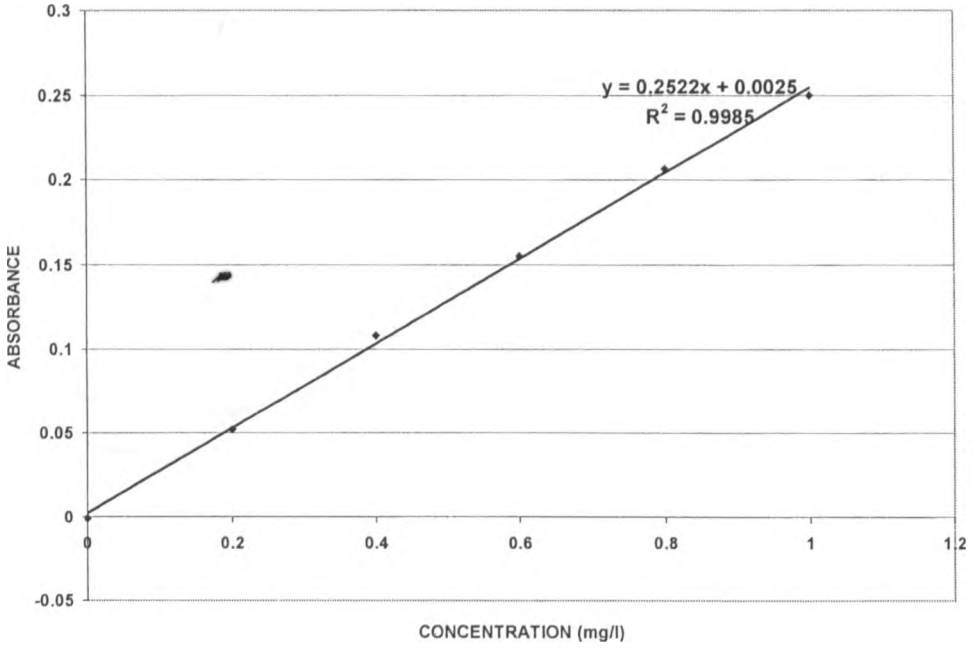

Figure 46. **Calibration Graph for Magnesium (AAS)** (R_{Mg} = 0.9993).

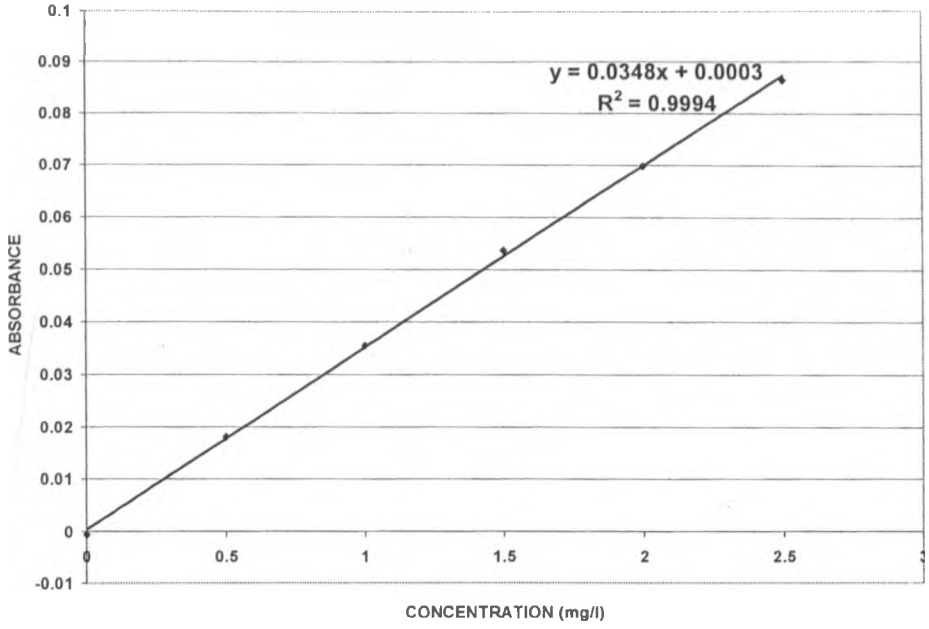

Figure 47. **Calibration Graph for Manganese (AAS)** (R_{Mn} = 0.9997).

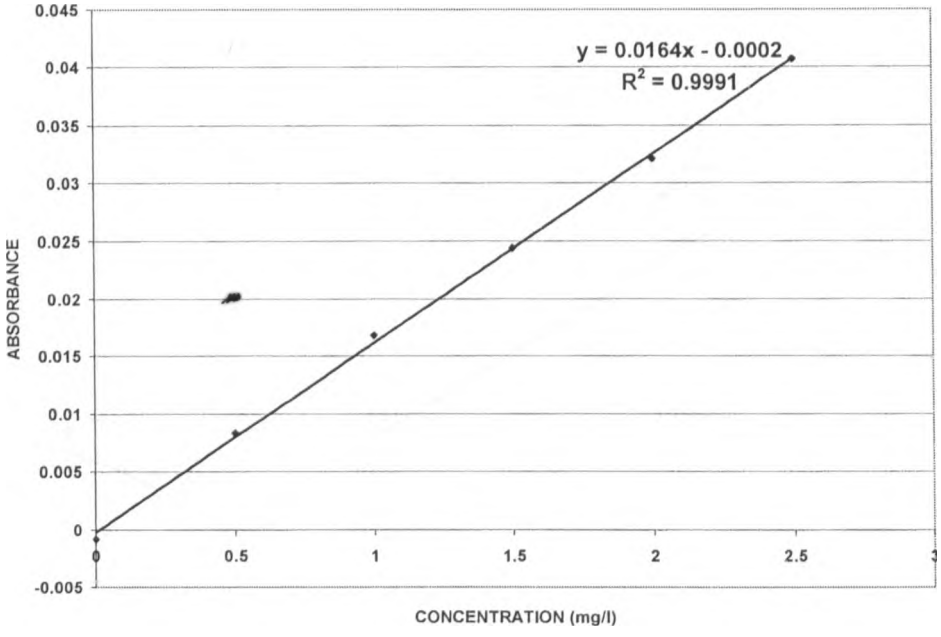

Figure 48. **Calibration Graph for Iron (AAS)** (R_{Fe} = 0.9996 .

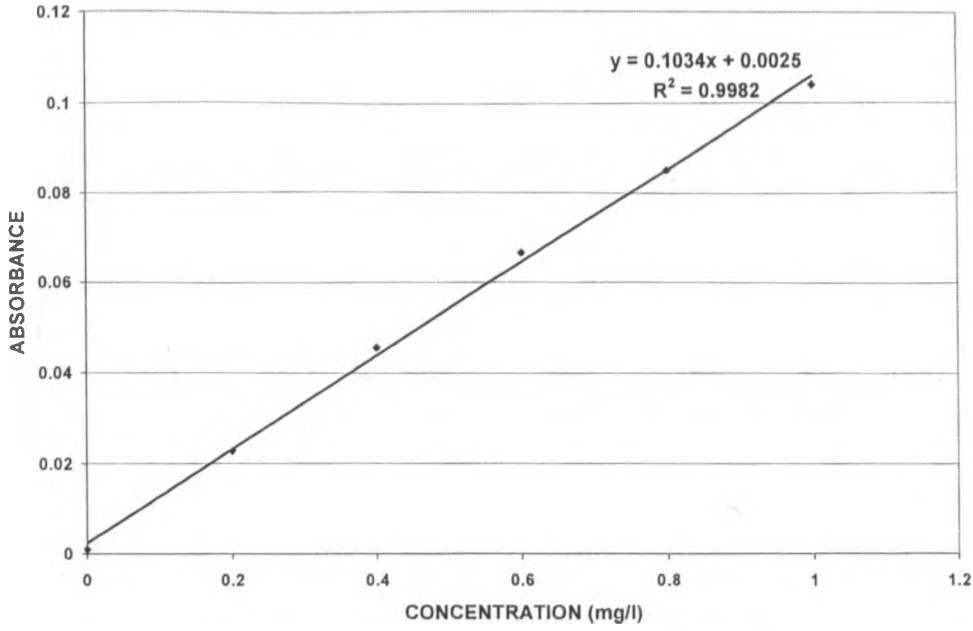

Figure 49. **Calibration Graph for Zinc (AAS)** (R_{Zn} = 0.9991).

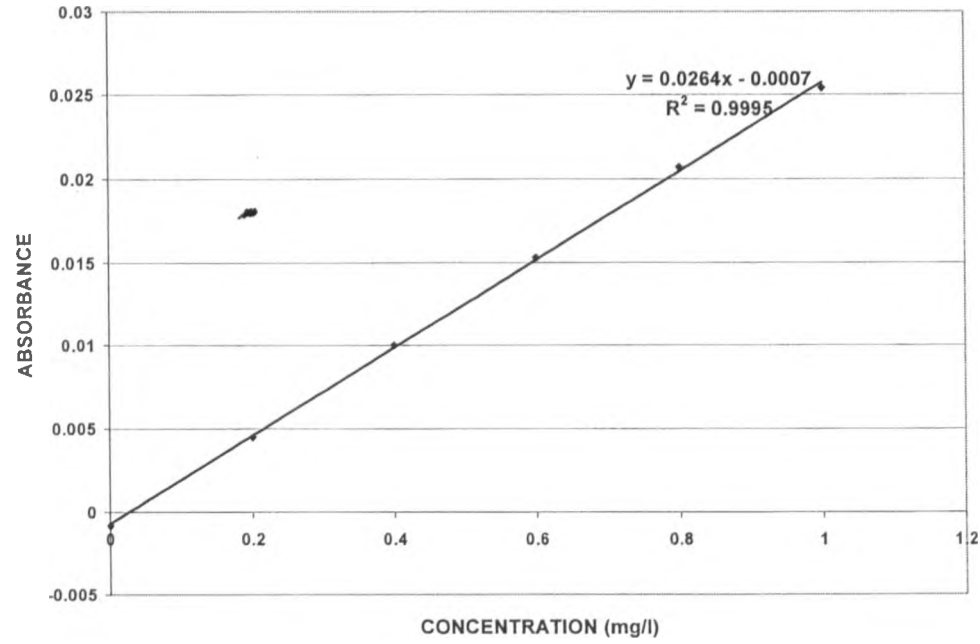

Figure 50. **Calibration Graph for Copper (AAS)** (R_{Cu} = 0.9998).

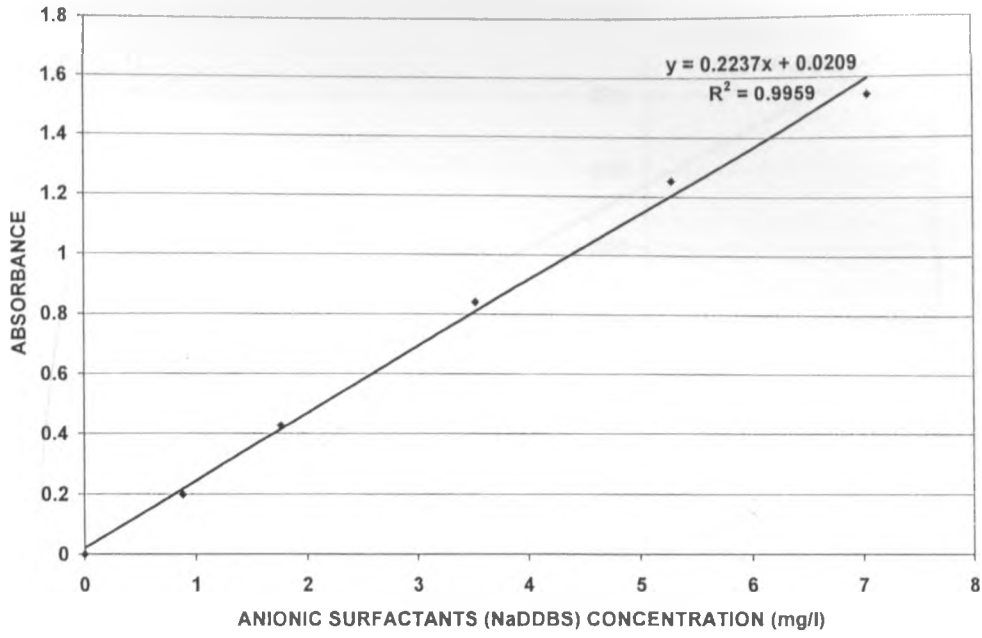

Figure 51. **Calibration Graph for Anionic Surfactants (MBAS), as NaDDBS by UV/ Visible at 650 nm** ($R_{(NaDDBS)}$ = 0.9979).

The proportionality between concentration and absorbance in the above graphs were excellent, as evidenced by the high correlation coefficients, R, which were between 0.99 and 1.00, inclusive and hence use of the linear regression equations in calculating the unknown sample concentrations was justified. Similar correlation was observed for fluoride and chloride calibration when cell potential was plotted against Log_{10}(Concentration), as depicted in Figures 52 and 53, where R values were also between 0.99 and 1.00 inclusive.

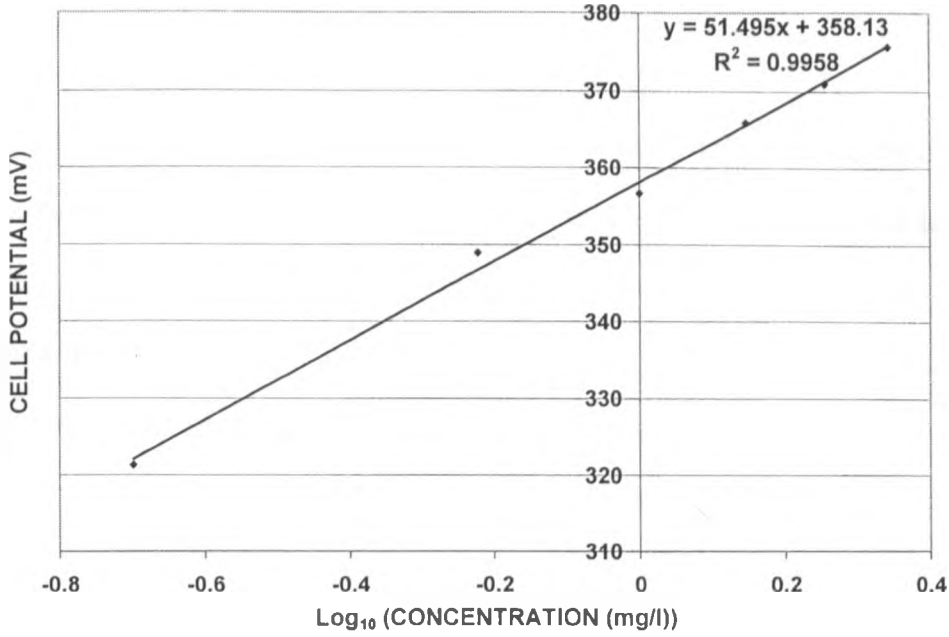

Figure 52. **Calibration of Fluoride in Aqueous Solutions by Ion Selective Electrode Method** (R_F = 0.9979).

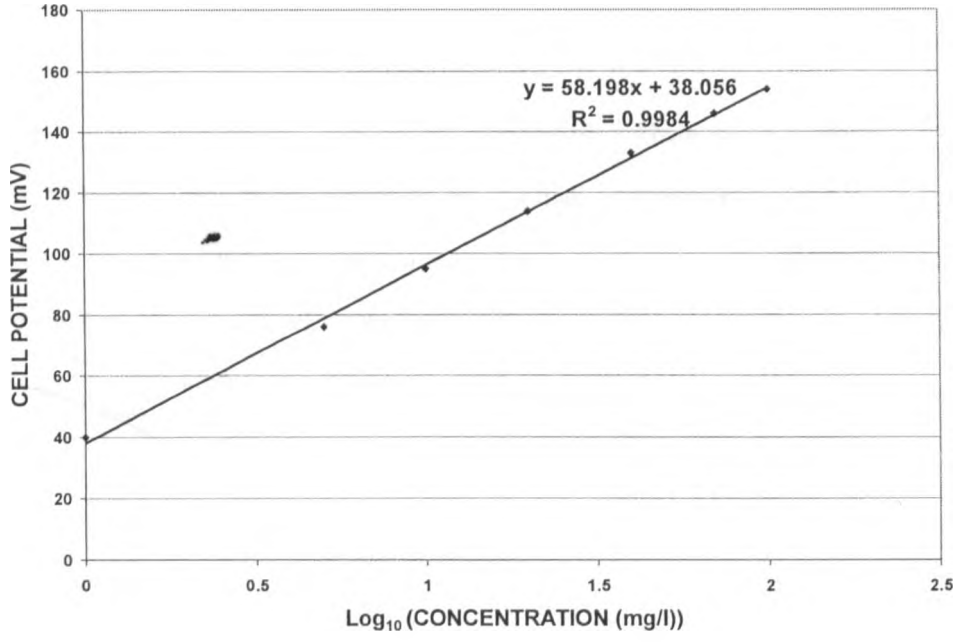

Figure 53. **Calibration Graph of Chloride in Aqueous Solutions by Ion Selective Electrode Method** (R_{Cl^-} = 0.9992).

4.10.2 Recovery Data with Reference Materials

Recovery data for liquid and solid samples are shown in Tables 18 and 19, respectively. At every time of analysis, recovery samples were used to validate the unknown sample data. Recovery samples consisted of spikes containing the parameters of interest, in matrixes very similar to the sample in question, different from the actual calibration standards; in-house reference materials with statistically ascertained values and proficiency testing samples, with statistically certified values. After analyzing such a reference sample on a given day, its experimental value was divided by the expected (ascertained or spiked) one and the quotient multiplied by 100 to give % recovery. The data obtained on different calibration days for sample analysis (over a period of about 14 months) has been compiled and statistically analyzed (mean, s.d. and confidence interval range computations) as summarized in Tables 18 and 19.

TABLE 18. **NUTRIENT RECOVERY DATA FOR WATER**

Sample Identification Code & Parameter analyzed	**Expected (spiked or assigned) Conc. level, mg/l**	**Mean of experimen-tal Conc. Obtained, mg/l**	**Sampl-e Size, n**	**Mean % Recovery**	**% RSD of Recover-y**	**95% C.L. of % Recov-ery**
TKN-1: Nitrogen	10,598.144	10,649.585	1	100.5	N/A	N/A
TKN-2: Nitrogen	5,299.072	5,458.533	1	103.0	N/A	N/A

TABLE 18 ***(contd...)***

Sample Identification Code & Parameter analyzed	**Expected (spiked or assigned) Conc. level, mg/l**	**Mean of experimen-tal Conc. Obtained, mg/l**	**Sampl-e Size, n**	**Mean % Recovery**	**% RSD of Recover-y**	**95% C.L. of % Recov-ery**
TKN-3: Nitrogen	2,119.629	2,210.907	1	104.3	N/A	N/A
TKN-4: Nitrogen	105.981	105.916	8	99.94	2.601	94.7 - 105.1
TKN-5: Nitrogen	42.393	43.071	1	101.6	N/A	N/A
TKN-6: Nitrogen	21.196	20.736	7	97.80	7.359	83.1 - 112.5
TKN-7: Nitrogen	8.479	8.460	4	99.78	15.469	68.8 - 130.7
INHOUSE 1A: NO_3^-	15.5	14.952	1	96.46	N/A	N/A
PT2: K	5.367 $\pm$ 0.884	5.686	19	106.0	5.625	94.7 - 117.2
PT2 (C.F.2): Na	51.894 $\pm$ 10.868	49.266	10	94.94	8.040	78.9 - 111.0
SPIKES: 0.1ppm Ca	0.100	0.110	4	110.3	7.079	96.1 - 124.4

TABLE 18 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, mg/l	Mean of experimen-tal Conc. Obtained, mg/l	Sampl-e Size, n	Mean % Recovery	% RSD of Recover-y	95% C.L. of % Recov-ery
0.5ppm Ca	0.5	0.504	11	100.8	11.009	78.7 - 122.8
0.13ppm Ca	0.130	0.124	1	95.40	N/A	N/A
0.2ppm Ca	0.20	0.222	1	111.0	N/A	N/A
RTD. 04: 0.86ppm	0.86	0.912	2	106.0	7.018	92.0 - 120.1
0.1ppm Mg	0.1	0.1089	11	108.9	8.041	92.8 - 125.0
0.5ppm Mg	0.5	0.535	17	106.9	5.120	86.5 - 117.2
0.1ppm Mn	0.1	0.105	13	105.4	5.674	94.0 - 116.7
0.5ppm Mn	0.5	0.534	21	106.8	5.872	95.1 - 118.5
PT4/05: Mn	0.37 $\pm$ 0.15	0.385	4	104.0	9.693	84.6 - 123.4
0.1ppm Fe	0.1	0.102	5	102.0	9.656	82.7 - 121.3

TABLE 18 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, mg/l	Mean of experimental Conc. Obtained, mg/l	Sample Size, n	Mean % Recovery	% RSD of Recovery	95% C.L. of % Recovery
0.5ppm Fe	0.5	0.513	15	102.7	5.509	91.7 - 113.7
0.6ppm Fe	0.6	0.647	1	107.8	N/A	N/A
1.0ppm Fe	1.0	1.079	4	107.9	4.057	99.8 - 116.0
6.0ppm Fe	6.0	6.419	1	107.0	N/A	N/A
PT2/04: Fe	1.23 ± 0.15	1.059	1	86.90	N/A	N/A
PT4/05: Fe	0.51 ± 0.20	0.486	3	95.36	13.562	67.9 - 122.5
0.1ppm Zn	0.1	0.106	12	105.5	6.971	91.6 - 119.4
0.2ppm Zn	0.2	0.215	2	107.5	9.767	88.0 - 127.0
0.5ppm Zn	0.5	0.520	17	103.9	4.821	94.3 - 113.5
0.6ppm Zn	0.6	0.65	1	108.3	N/A	N/A
0.8ppm Zn	0.8	0.818	1	102.3	N/A	N/A

TABLE 18 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, mg/l	Mean of experimental Conc. Obtained, mg/l	Sample Size, n	Mean % Recovery	% RSD of Recovery	95% C.L. of % Recovery
1.0ppm Zn	1.0	0.990	2	98.95	0.051	98.8 - 99.1
RTD.03: Zn	0.7735 ± 0.1965	0.895	1	115.7	N/A	N/A
PT4/05: Zn	1.38 ± 0.28	1.372	3	99.40	2.050	95.3 - 103.5
0.1ppm Cu	0.1	0.111	7	110.6	4.040	102.5 - 118.7
0.4ppm Cu	0.4	0.445	1	111.3	N/A	N/A
0.5ppm Cu	0.5	0.536	16	107.1	6.867	100.3 - 114.0
0.6ppm Cu	0.6	0.581	1	96.83	N/A	N/A
0.8ppm Cu	0.8	0.794	2	99.19	5.792	87.6 - 110.8
PT4/05: Cu	1.00 ± 0.37	1.106	3	110.6	0.957	108.7 - 112.5
Check 5ppm: Cl^- (ISE)	5	4.502	3	90.04	7.197	75.6 - 104.4

TABLE 18 *(contd...)*

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, mg/l	Mean of experimental Conc. Obtained, mg/l	Sample Size, n	Mean % Recovery	% RSD of Recovery	95% C.L. of % Recovery
Check 10ppm: Cl^- (ISE)	10	11.783	1	117.8	N/A	N/A
Check 20ppm: Cl^- (ISE)	20	18.985	1	94.93	N/A	N/A
Check 50ppm: Cl^- (Titration)	50	52.116	1	104.2	N/A	N/A
Check 100ppm: Cl^- (Titration)	100	104.941	1	104.9	N/A	N/A
RTD.05: Cl^- (Titration)	65 ± 5	60.270	1	92.72	N/A	N/A
Check 0.1ppm: F^-*	0.1	0.0963	3	96.30	3.696	88.9 - 103.7
Check 0.2ppm: F^-*	0.2	0.182	5	91.05	10.447	70.2- 111.9

TABLE 18 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, mg/l	Mean of experimental Conc. Obtained, mg/l	Sample Size, n	Mean % Recovery	% RSD of Recovery	95% C.L. of % Recovery
Check 1.0ppm: F^-*	1.0	0.972	2	97.16	0.691	95.8 - 98.8
Check 1.4ppm: F^-*	1.4	1.500	5	107.1	5.357	96.4 - 117.9
Check 1.8ppm: F^-*	1.8	1.864	3	103.6	5.572	92.4 - 114.7
Check 2.2ppm: F^-*	2.2	2.340	1	106.4	N/A	N/A
Check 6ppm: SO_4^{2-}**	6	6.226	4	103.8	7.205	89.3 - 118.2
Check 8ppm: SO_4^{2-}**	8	8.129	2	101.6	1.149	98.3 - 102.9
Check 9ppm: SO_4^{2-}**	9	8.952	2	99.47	1.150	97.2 - 101.8
Check 10ppm: SO_4^{2-}**	10	9.741	3	97.41	4.398	88.6 - 106.2

TABLE 18 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, mg/l	Mean of experimen-tal Conc. Obtained, mg/l	Sampl-e Size, n	Mean % Recovery	% RSD of Recover-y	95% C.L. of % Recov-ery
Check 20ppm: SO_4^{2-**}	20	20.271	2	101.4	1.523	98.3 - 104.4
Check 30ppm: SO_4^{2-**}	30	30.719	2	102.4	1.832	98.7 - 106.1

KEY USED FOR TABLE 18:

TKN = Total Kjeldahl Nitrogen; %RSD = %Relative Standard Deviation, i.e. 100*SD/Mean; 95%C.L. of % Recovery = 95% Confidence Limits, i.e. Mean % Recovery ± 2* SD of % Recovery; N/A = Not Applicable; * Fluoride by ISE method, ** Sulphate by gravimetric method; ISE = Ion Selective Electrode method; PT = Proficiency testing Sample; RTD / INHOUSE = Retained reference Laboratory sample, which has been analyzed for many times with an assigned value, $\bar{u}$; Check Std = A standard solution or spike used for analytical QC verification, treated and read in same manner as the samples;

$$\text{Sample SD, Standard Deviation} = \sqrt{\left(\left(\sum_{i=1}^{n}(x_i - (\sum_{i=1}^{n}x_i/n))^2\right)/(n-1)\right)}.$$

An ideal hypothetical quantitative analysis should give high accuracy, i.e. recovery of 100%. However, due to systematic and random experimental errors, it is usually not practically possible to obtain such an ideal accuracy. The actual experimental value usually deviates ***positively*** or ***negatively*** from

the mean of the 'true' result. In the former case, possible sources of large deviations could include contamination, chemical interferences due to matrix effects (Willard *et al.*, 1986; Welz, 1976; Price, 1972; Ewing, 1969) and lack of proper calibration. On the other hand, large negative deviations could be due to sample loss during analysis, equipment malfunction and chemical interference as well. The 95% confidence interval, i.e. Mean (or assigned value) ± 2σ is the most preferred statistical allowance for recovery. The 'true' practical deviation for any type of analytical work has to be set depending on the prevailing technical limitations. In the current work, a % recovery of 100% ± 30% was adopted, giving an 'acceptable' range of 70%-130%.

It is evident from the results presented in Table 18 that most of the recovery data for liquid (water) samples obtained during the period of analysis for the current project was within the above specified 'acceptable' range. However, values with high (especially positive) deviations from the central value (100%) were probably due to systematic and random errors, statistical variations from the assigned means, contamination or even the inherent and matrix interferences of the analytical techniques employed, as discussed in the appropriate sections.

TABLE 19. **NUTRIENT RECOVERY DATA FOR SEDIMENTS AND PLANTS**

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, %, m/m	Mean of experimen-tal Conc. Obtained, %, m/m	Sampl-e Size, n	Mean % Recovery	% RSD of Recover-y	95% C.L. of % Recov-ery
HRM: TKN	3.246 ± 0.052	3.240	19	99.82	0.719	98.4 – 101.3
HRM2: TKN	10.453 ± 0.384	10.620	1	101.6	N/A	N/A
QC-(S/P)C: NO_3^-	0.050	0.051	1	102.0	N/A	N/A
QC-(S/P)B: NO_3^-	0.100	0.098	1	98.30	N/A	N/A
QC-(S/P)B: PO_4^{3-} - P	0.0050 ± 0.00004	0.0046	2	92.03	5.492	81.0 – 103.0
QC-(S/P)A_1: K	0.100	0.092	9	92.65	7.512	77.6 – 107.7
QC-(S/P)A_2: K	0.098	0.098	1	99.49	N/A	N/A
QC-(S/P)A_3: K	0.097	0.093	1	96.69	N/A	N/A
QC-(S/P)A_1: Na	0.100	0.107	1	107.0	N/A	N/A

TABLE 19 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, %, m/m	Mean of experimental Conc. Obtained, %, m/m	Sample Size, n	Mean % Recovery	% RSD of Recovery	95% C.L. of % Recovery
QC-(S/P)A_1: Ca	0.098 ± 0.0016	0.097	7	99.07	13.509	72.1 – 126.1
QC-(S/P)A_1: Mg	0.098 ± 0.0016	0.099	6	100.5	14.993	70.5 – 130.5
QC-(S/P)A_1: Mn	0.100	0.097	5	97.83	5.633	86.6 – 109.1
QC-(S/P)A_2: Mn	0.097	0.092	3	95.44	7.803	79.8 – 111.0
QC-(S/P)C: Mn	0.050	0.045	1	90.75	N/A	N/A
QC-(S/P)A: Fe	0.100	0.086	2	86.43	18	68.4 – 104.4
QC-(S/P)A_1: Zn	0.100	0.082	5	82.52	4.053	74.4 – 90.6
QC-(S/P)A_2: Zn	0.097	0.076	3	79.19	2.327	74.5 – 83.8
QC-(S/P)C: Zn	0.050	0.039	1	79.40	N/A	N/A

TABLE 19 ***(contd...)***

Sample Identification Code & Parameter analyzed	Expected (spiked or assigned) Conc. level, %, m/m	Mean of experimen-tal Conc. Obtained, %, m/m	Sampl-e Size, n	Mean % Recovery	% RSD of Recover-y	95% C.L. of % Recov-ery
QC-(S/P)A_1: Cu	0.100	0.093	5	93.79	7.854	78.1 – 109.5
QC-(S/P)A_2: Cu	0.097	0.093	3	96.17	3.115	89.9 – 102.4

N.B. TKN = Total Kjeldahl Nitrogen; C.L. = Confidence Limits; N/A = Not Applicable; QC-(S/P)A: Fe, QC-(S/P)A, B or C refers to Analytical Quality Control (QC) sub-samples A, B and C (Acid-washed sand spiked with parameter of interest as shown above) for evaluation of nutrient analysis in sediments and plants (S/P); HRM = House Reference Material; Other terms and meanings are the same as explained in Table 18.

As is evident from the above results, nearly all the percentage recoveries for solid samples (plants and sediments) were statistically well within the range of 70 to 130 %, i.e. 100 ± 30 %. This therefore demonstrated fairly accurate, precise data within the 95 % confidence interval and the results were therefore reliable. Values with high deviations from the central value (100%) were probably due to the same reasons given before for liquid samples (Table 18).

CHAPTER V

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In the current research work, investigation of extent of Eutrophication of Nairobi Dam, Kenya has revealed the following:

- The Water hyacinth (*Eichornia crassipes*) was found to be the major aquatic weed infesting the dam. It occupied an area of approximately 70%.

- All inorganic nutrient contents (except copper, sulphate and fluoride) in the dam were higher than the other surrounding aquatic environments (inlet and outlet rivers). The dam therefore served as a sink for various nutrients which were needed for the proliferation of the water hyacinth and other aquatic weeds. These weeds after decaying were dissolved in the dam water, thereby elevating the levels of the inorganic nutrients in the dam water.

- The dam could serve for suitable environmental management of the nutrient ions investigated, i.e. Phosphorous, Nitrogen, Potassium, Sodium, Calcium, Magnesium, Manganese, Iron, Zinc and Chloride.

- Similar environmental relationships were observed for the physical parameters: Dissolved Oxygen, Turbidity, Electrical Conductivity and Total Dissolved Solids (TDS) in water samples. The mean dissolved oxygen for the dam water was lower while the other parameters were higher than for either inlet or outlet streams. This showed that the water hyacinth had lowered the clarity and dissolved oxygen of the dam water, thus contributing to the current disappearance of fish and other aquatic animals from Nairobi Dam.

- Within the water hyacinth zone, the overall mean of the major nutrients (Phosphorous and Nitrogen) exhibited corresponding levels as follows, in mg/l: (Hydrolysable + PO_4^{3-})-P: 4.48938, (NO_3^- - N): 1.03636, (Total Kjeldahl + NO_3^-)- N: 36.8671. These figures were much higher than the threshold annual mean values, namely: 0.1 mg/l for "Total" Phosphorous and 0.8 mg/l for "Total" Nitrogen, associated with eutrophication, as given in the literature. This currently confirms exhibition of Eutrophication in Nairobi Dam and its extended water hyacinth-growing zone.

- There was poor negative correlation ($R^2 = 0.1876$) between (Hydrolysable + PO_4^{3-}) – Phosphorous and (NO_3^-) – Nitrogen in water during the entire sampling period. Among the three major nutrients (Nitrogen, Phosphorous and Potassium), the best correlation was found between (Hydrolysable + PO_4^{3-}) – Phosphorous and (Total Kjeldahl + NO_3^-) - Nitrogen ($R^2 = 0.5244$).

- With respect to Nitrogen and Potassium, phosphorous was found to be the most limiting nutrient element (i.e. it had negative intercept). It got exhausted first and was responsible for the proliferation of the water hyacinth in the aquatic environment studied. Therefore, any future eradication and control of this weed will have to deal with this nutrient element.

- The limiting nutrient, Phosphorous must have originated from anthropogenic activities. These are postulated to be mainly the untreated (raw) sewage from the surrounding informal, low-income settlements and use of phosphorous-containing soaps and detergents.

- Using Linear Regression data, one could determine the limiting element between phosphorous and nitrogen in a water body and its extended water hyacinth growing zone under consideration if only one or a few samplings were done, provided all possible forms of the two nutrients were considered and enough sampling points in the water body in question were included in the sampling plan.

- The available aquatic weeds, particularly the water hyacinth could therefore be used for the phytoremediation and hence for the wastewater management of the aquatic environment studied and possibly other water bodies experiencing similar eutrophication problems.

- The levels of most major inorganic nutrients and zinc in the three aquatic environmental systems (inlet, dam and outlet water) were almost directly affected by the climatic and seasonal variations and not by the agricultural practices, geological factors and even type of roofing material used. These decreased appreciably during the rainy seasons as a result of dilution.

- On the onset of the long rainy seasons, the mean sulphate levels in the inlet waters were lower than those in the preceding seasons but the dam water registered higher levels during the rainy seasons. This could be explained by the proximity of the dam to the busy Langata Road, where traffic density was high. Possible use of gasoline and diesel could have led to emission of sulphur dioxide and sulphur trioxide through oxidation mechanisms. These sulphur oxides could have been dissolved by the rain water to form acid rain. It was therefore possible that during the rainy seasons, the sulphate contents were elevated in the dam water, which later reverted to normal levels as a result of the eutrophication process. However, for the inlet streams, the sulphate content experienced dilution as a result of the rains, also taking into account that the inlet streams were about a kilometre from the main road.

- On the other hand, the trace inorganic elements (manganese, iron, copper and fluoride) were not similarly lowered on the onset of the rainy season through dilution. Their possible enhancement sources during the rainy seasons could have been de-sorption from the sediments (for Mn and Fe), existence of outlet control mechanism for the sustainability of the water

hyacinth and other plants (for copper) and the nature of the geology of the area studied (for fluoride).

5.2 Recommendations

Based on the results and conclusions indicated above, the following have been recommended for further research or suitable action by the relevant national and international bodies and authorities:

- Suitable measures are needed to reduce Phosphorous in order to eradicate the water hyacinth and other aquatic weeds in the environment studied.

- Eutrophication of aquatic systems could and should be managed once its extent has been understood.

- In the Nairobi Dam case study, possible methods of eliminating or dealing with the magnitude of eutrophication and hence proliferation of aquatic weeds, especially the water hyacinth would be:

  → Precipitation of iron (III) phosphate from the water using iron (III) chloride solution, represented by the following equation:

$$FeCl_{3(aq)} + PO_4^{3-}{}_{(aq)} = FePO_{4(s)}\downarrow + 3Cl^-_{(aq)}$$

→ By-passing of the inlet streams (rerouting) away from the dam, by creating alternative outflow escapes downstream.

→ Harvesting of the water hyacinth and other aquatic plants generated in the dam and utilizing them for various economic, gainful purposes, such as animal feeds. However, this would offer only short term solution, as the eutrophication would continue unchecked.

→ Upgrading of the surrounding informal settlements, equipping them with necessary amenities such as toilets, modern sewerage systems, and decent houses, in order to improve and maintain high quality aesthetic standards of the surrounding aquatic environment (streams, rivers and the dam). With this regard, stringent measures should be taken by the relevant environmental authorities to curb any dumping of raw sewage directly into the aquatic systems (rivers and dam) as this would enhance the gravity of eutrophication.

→ Use of herbicides to control water hyacinth is common. Westerdahl and Getsinger (1988) report excellent control of water hyacinth by the use of the aquatic herbicides 2,4-D, diquat, and a combination of diquat and complexed copper. Fair control of water hyacinth is obtained with endothall dipotassium salt, endothall dipotassium salt and complexed copper, endothall dimethylalkylamine salts, and glyphosate.

- Once the eutrophication problem has been solved by applying one of the above methods, the same and other nutrients should regularly be checked to evaluate the effectiveness of elimination of this problem.

- Further studies on effective utilization of the water hyacinth weed after removal from the dam need to be done in order to maximize the usefulness and profitability of Nairobi Dam as an alternative measure to tackling the eutrophication problem of the dam and its environs.

- Further research needs to be done in Kenya, East Africa and the entire African continent in order to understand and manage the eutrophication phenomenon in this particular part of the world, with respect to the activities of man.

- In order to avoid and control the emergence of obnoxious weeds, such as the water hyacinth, the relevant national statutory bodies, mainly KEBS (Kenya Bureau of Standards) and NEMA (National Environment Management Authority) and other international bodies, such as UNEP should consider banning the use of phosphorous and its compounds in surfactants. Alternative binders for soap and detergent manufacture such as silicates or nitrogen-containing salts are recommended for use in areas or regions with fresh natural water sources (such as rivers, lakes and dams). This would protect their natural state.

- More comprehensive studies on phytoremediation need to be done in order to determine the most suitable and available aquatic weeds necessary for the wastewater management of the aquatic systems in this region and other parts of the world.

- Further similar research needs to be conducted, in order to determine the dependence of the level of nutrients and other Eutrophication parameters on the depth of the aquatic environment studied, particularly the dam and to draw suitable conclusions with regard to the annual nutrient load functions.

- In the light of possible analytical interferences, further confirmatory research needs to be conducted using more versatile alternative methods in order to ascertain high nutrient levels encountered in the current work. Such methods may include Energy-Dispersive X-Ray Fluorescence Analysis (ED-XRFA), for the metallic nutrients and Ion Chromatography, for the anionic nutrients determination.

- With reference to nitrogen, the formal definition of Eutrophication should officially be modified to 'Total' Nitrogen, i.e. (Total Kjeldahl + Nitrate) – Nitrogen instead of just Nitrate - Nitrogen, in order to obtain suitable positive correlation with (Hydrolysable + PO_4^{3-}) - Phosphorous. This was particularly exemplified in the current case study involving Nairobi Dam, Kenya.

- Air pollution studies need to be conducted regularly along the Nairobi Dam basin in order to monitor the levels of the oxides of sulphur and their contribution to acidity of the surrounding aquatic systems and their high sulphate contents.

- Bio-degradation studies for anionic surfactants such as sodium dodecyl benzene sulphonate (NaDDBS) in various environments need to be done in order to ascertain the respective organic and inorganic byproducts, such as sulphates.

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