Determination of Levels of Nutrients, Organic Matter and Trace Heavy Metals in River Migori

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April 1999
DECLARATION

This Thesis is my original work and has not been presented for a degree in any other University

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Dedicated To My Wife Gladys Nyamvula,
My sons, Brian J. Mbovu and George L. Gajue.
ACKNOWLEDGEMENT

I wish to express my sincere thanks to my University Supervisors, Dr. Joseph Chacha and Dr. Jane Murungi for guiding me through this work.

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Migori is situated in a rich agricultural heartland and strategically placed on the Makuyu-Isebania-Musoma highway. In recent times, and with the renewed East African Cooperation, the town has attracted rapid population and commercial growth, with the mushrooming of many small-scale industrial enterprises – the *Jua-Kali* industries.

The town is not served by clean piped water and the majority of the population depends almost entirely on the raw untreated water for their domestic use. This makes the general population vulnerable to any contaminants, either from natural or artificial sources.

This study was undertaken to establish the concentration levels of nutrients (as Nitrite-N, Nitrate-N and Phosphate-P), organic matter (as dissolved oxygen DO, biological oxygen demand BOD, and chemical oxygen demand COD) and the trace metals (cadmium, chromium, copper, lead and zinc). The study also attempted to relate the levels of these parameters in the river water with the agricultural and town’s activities.

The Nitrate-N levels were determined by the Brucine method, and those of Nitrite-N, by the Griess method. Phosphate-P levels were determined by the Molybdenum complexation method.
DO and BOD levels were determined by the Winkler’s titration method and the COD levels by the titration of the remaining potassium dichromate with ferrous ammonium sulphate after the oxidation of the organic matter.

The levels of the trace metals were determined by Atomic Absorption Spectrophotometry.

The averages of the mean levels of the parameters from the four stations on the section of the river, and within the period of study were as follows:

1) The organic matter: DO, 7.03 mgO₂/l; BOD, 5.98 mgO₂/l and COD, 81.84 mgO₂/l.
2) The nutrients: NO₃-N, 0.213 mg/l; NO₂-N 0.044 mg/l and PO₄-P 0.170 mg/l.
3) The trace metals (µg/l): Cd (0.311), Cr (6.04), Cu (4.288), Pb (46.77) and Zn (32.52).

This study established that:

I. The levels of organic matter were low but still significant, with mean levels increasing in the wet season.

II. The PO₄-P levels were above the maximum allowed concentration (MAC) recommended by the World Health Organisation (WHO). NO₃-N and NO₂-N levels were low. The changes in the mean levels of the nutrients (PO₄-P and NO₃-N), and especially during the wet season decreased downstream from the potential agricultural region.

III. The levels of the trace metals, except for lead were generally low. Lead and cadmium were comparatively higher in the dry season, whereas chromium and zinc levels seemed to increase during the wet season. The mean copper levels did not vary significantly between the dry and wet seasons.
From the findings of this study, it was concluded that:

1) The agricultural activities may have an influence on the quality of River Migori.

2) The activities in the town could also have an influence on the water quality of the river, in view of the fact that higher levels of lead and chromium were detected after the town.

3) The river water may not be safe for express domestic use.
CHAPTER 1

1.0 INTRODUCTION

The quality of water is a major concern for humankind since it is directly linked with human welfare. The water quality criterion is based on the objectives of the water use, such as drinking, agricultural use, recreation, for food products such as fish, for aesthetics and industry. The aqueous environment i.e. rivers, lakes, estuaries, and oceans is influenced by natural (biogenic) factors such as types of soils, climatic factors and population densities, but more so by human activities (anthropogenic factors) namely agriculture and industry.

Rapid population increase in Kenya (from 10 million in 1963 to about 30 million at present) have resulted in increased expansion of the urban, agricultural and industrial activities. This has resulted in vast wastewaters being generated and discharged directly into rivers and lakes with little or no treatment at all. This has resulted to their pollution. Water pollution is a state of deviation from the pure condition whereby its normal properties and uses are affected.

Municipal wastewaters containing mostly domestic wastes and effluents from industry, and institutions such as schools and hospitals are responsible for water pollution with suspended and dissolved organic and inorganic solids. Among the organic substances present in domestic wastewaters are carbohydrates, lignins, proteins, fats, soaps, synthetic detergents, oil, grease and ammonia from domestic sewage. The inorganic...
substances include potentially toxic elements such as arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), mercury (Hg), and zinc (Zn). These toxic elements may sometimes be in low concentration to present any adverse effects to human life but might well be at phytotoxic levels, which would cause an impact on the ecological system of a receiving water body.

Run-offs from agricultural fields applied with fertilizers may contain nutrients such as nitrates (NO$_3^-$) and phosphates (PO$_4^{3-}$) and trace metals such as Zn, Cd, and Cu that appear as impurities in the fertilizers. Industries also produce gaseous emissions and particulate matter that eventually reach water bodies by direct fall-out or by precipitation as rain. These gaseous emissions include mainly oxides of carbon, oxides of nitrogen (NO$_x$), oxides of sulphur (SO$_x$), chlorofluorohydrocarbons (CFHC). Nitrogen dioxide (NO$_2$) gas, which is responsible for the formation of nitric acid rains, is formed through natural chemical processes from nitrous oxide (N$_2$O). However the bulk part of NO$_x$ is released into the atmosphere from anthropogenic activities. The annual global input of NO$_x$ is estimated to be 86 million tons. Acid rains that end up in lakes and rivers may contain these pollutants. Particulate matter in the atmosphere (aerosols) includes dust and soot from both manufacturing and the automobile industry. Inorganic particulate matter (IPM) may contain toxic trace metals such as Pb, Cd and Hg, adsorbed on to the soot. Organic particulate matter (OPM) may contain toxic compounds such as polycyclic aromatic hydrocarbons (PAH) and other volatile organic compounds from fuels. The particles that have a diameter of greater than 2 $\mu$m but less than 10 $\mu$m remain airborne for long periods, and are transported by air currents in the atmosphere. Lead and PAH aerosols
are among these particles. They fall out on land and are eventually washed off into receiving water bodies during storms. This probably explains the ubiquitous nature of lead and PAH aerosols.  

Organic substances derived from natural sources that have been detected in unpolluted rivers include the breakdown of life substance such as proteins, ammonium ions, carbon dioxide, phenols, methane, hydrogen sulphide, urea, amino acids and phosphates. Complex substances such as humic acids, fulvic acids and tannins, play a significant role in regulating the toxicity of trace metals and trace toxic organic substances. These substances are formed by the combination of the intermediates of the life substances. The yellow to brown colour in natural water has been shown to be caused by complex molecules such as vanillin, vanillic acid and 3,5-dihydroxybenzoic acid. 

Microorganisms present in natural water for example algae, fungi and bacteria control the chemical and biological processes occurring in the water. Carbon-fixation is controlled by algae, nitrogen-fixation by bacteria, and the decomposition of organic matter present in the water by bacteria and fungi during the process of respiration. Microorganisms are particularly sensitive to contaminants, be they in macro or trace amounts. Pollution effects to the algae for instance may be followed by changes in density and composition of algal species which may have an adverse effect on the higher life forms up the food chain in that ecosystem.

Trace metals may be present in natural unpolluted waters through the process of erosion of running water on rocks and soils. Elemental composition of river water is
thought to approach that of the soils in its drainage basin. The average abundance of some heavy metals in the earth’s crust is given in Table 1 below:

<table>
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<th>Igneous rocks</th>
<th>Sedimentary rocks</th>
<th>Earth soil</th>
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</thead>
<tbody>
<tr>
<td>Cr</td>
<td>100</td>
<td>160</td>
<td>200</td>
</tr>
<tr>
<td>Fe</td>
<td>$5.63 \times 10^4$</td>
<td>$3.3 \times 10^4$</td>
<td>$3.8 \times 10^4$</td>
</tr>
<tr>
<td>Ni</td>
<td>75</td>
<td>95</td>
<td>40</td>
</tr>
<tr>
<td>Cu</td>
<td>55</td>
<td>57</td>
<td>20</td>
</tr>
<tr>
<td>Zn</td>
<td>7.0</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb</td>
<td>12.5</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Thus, as illustrated above the sources of water pollution are quite varied, and are either of biogenic or anthropogenic origin. Contaminants from biogenic sources may be present though in very low concentration.

To manage our water resources effectively, it is important to continuously monitor the natural water systems and where possible, establish the causes and effects of the water pollution in the water systems.

Developed countries have the financial resources and effective legislation against pollution problems. Unfortunately the same cannot be said of many developing
countries, Kenya included. Although Kenya has put in place legislation (The water Act chapter 372) to preserve her water resources, some factories have continued to discharge raw or partially treated wastes in the rivers and lakes. Consequently pollution impacts have been felt in Nairobi-Athi river systems, Ngong River, some major rivers flowing into lake Victoria and L. Victoria itself.

The excessive growth of algal blooms, the emergence, rapid growth and spreading of the water hyacinth has negatively affected the ecology of L. Victoria, in terms of production and transport. As a result, the livelihood of more than 11.2 million dependent on the lake is at stake. The situation in L. Victoria has aptly been described as “the once clear, life-filled lake is murky, smelly and choking with algae”

Pollution effects of aquatic ecosystems have been attributed to enhanced levels of nutrients (nitrogen and phosphorus being the major nutrients implicated in excessive biomass production and eutrophication), toxic trace metals such as Cd, Cu, Pb and Zn, and organic matter. Pollution monitoring and assessment has therefore involved:

a) Measurement of physical and chemical attributes as temperature, pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), turbidity, total suspended solids (TSS), conductivity, total dissolved solids (TDS) and toxins including trace metals and trace organic matter, as pesticides, PAH, and polychlorobiphenyls (PCBs).

b) Biological monitoring by use of organisms as indicators, either as individual species or biological communities of an ecosystem. Certain qualities (for example behaviour, growth rate, reproductivity, abundance, biomass, species community, biodiversity, rate of photosynthesis and rate of nutrient cycling) are chosen as a
measure, and quantified to determine the response of the organisms towards toxins and other ecological changes of the aquatic ecosystem.

A summary on physical and chemical properties, sources, distribution and uses, and general effects of the parameters that have been assessed in this project, namely nitrogen and phosphorous, organic matter and the trace metals Cd, Cr, Cu, Pb and Zn. is presented in the following sections.

1.1 Nutrients: Sources and Distribution

1.1.1 Nitrogen

Nitrogen, with a chemical symbol N, is an element with atomic number 7 and relative atomic mass, RAM of 14.0067. At room temperature, it is a gas (m.p = -210°C, b.p = -195.8°C) and its density is approximately equal to that of the air (1.25 kgm⁻³).

Nitrogen occurs abundantly in nature and it is an essential constituent of proteins, and is therefore a major component of all living organisms. It forms part of other essential constituents of cells: the chlorophyll that is essential for photosynthesis, the nucleic acids (DNA and RNA) in which the pattern for the organism's growth and development are encoded, the proteins, and the walls that hold cells together.¹⁴

In nature, nitrogen is found in combined form as potassium nitrate (saltpetre) KNO₃, sodium nitrate (chile saltpetre) NaNO₃, and to a lesser extent calcium nitrate Ca (NO₃)₂. In both natural and polluted waters, nitrogen may be present in many forms including
ammonia, organic nitrogen, nitrites and nitrates. Nitrates are the end products of the aerobic stabilisation of organic nitrogen and may enter water via fertilizers and agricultural runoff. Organic nitrogen is hydrolysed to ammonium, $\text{NH}_4^+$ which is then oxidised to the nitrate ($\text{NO}_3^-$), by natural processes in the water (fig 1.1, the Nitrogen cycle). Nitrites ($\text{NO}_2^-$) are the immediate products of conversion of ammonia to nitrates. Nitrites are known to be toxic to fish. Free nitrogen is also converted to nitrates by bacteria.

![Nitrogen cycle diagram](image)

*Fig. 1.1: Nitrogen cycle*
1.1.2. Phosphorus

Phosphorus, P has atomic number 15 and RAM of 30.9738.

The metabolism of all known forms of life is believed to involve phosphorus and hence this element is widely distributed in plant and animal tissue. Phosphorus has a major role in the structure of nucleic acids (for example DNA) and in molecules (for example ATP); involved in the storage and use of energy in cells.\(^\text{14}\) It occurs most commonly in dissolved form as the inorganic phosphate ion \(\text{PO}_4^{3-}\).

Phosphorus as an element has probably been known as early as the 12th century. Phosphorus occurs in different allotropic forms, from crystalline forms to liquid phosphorus \(\text{P}_4\).

Established oxides of phosphorus include \(\text{P}_4\text{O}_{10}\), those with general formula \((\text{PO}_2)_x\) and \((\text{P}_2\text{O}_5)_x\) where \(x\) is an integer. In both organic and inorganic matter, phosphorus is always present in nature as the orthophosphate, the most stable oxidation state.

Over one billion kilograms of elemental phosphorus are produced annually by furnaces in the USA and about 9/10ths is commercially utilised in the production of fertilizers, primarily the superphosphate.\(^\text{16}\) The major part of the remaining phosphorus is converted to phosphoric acid, a large part of which is used in the manufacture of sodium and calcium salts. Sodium tripolyphosphate, \(\text{NaH}_2\text{P}_3\text{O}_{10}\) and tetrasodium pyrophosphate, \(\text{Na}_4\text{P}_2\text{O}_7\) are the main detergent builders. Also, phosphoric acid and its sodium and calcium salts are widely used in foodstuff industry. Phosphorus is also used in metal technology.\(^\text{16}\)

In water, phosphorus occurs most commonly as the orthophosphate \(\text{PO}_4^{3-}\). Phosphorus concentration in natural unpolluted waters is normally less than 0.01 mg/l\(^{-1}\) as it is utilised
by plants and converted into cell structures. Much of the phosphorus may also be unavailable because it is adsorbed or suspended on inorganic particles such as iron, aluminium or organic polyphenols.¹⁴

Fig. 1.2: Phosphorus cycle¹⁵
In the presence of calcium, phosphorus may be precipitated as the hydroxyapatite.

\[
6\text{HPO}_4^{2-} + 10\text{CaCO}_3(s) + 4\text{H}_2\text{O}(l) \rightarrow \text{Ca}_3(\text{PO}_4)_2 \cdot (\text{OH})_2(s) + 10\text{HCO}_3^{-} + 2\text{OH}^-.
\]

1.1

High concentration of phosphorus is likely to occur in waters that receive sewage and leaching or runoff from cultivated land. Figure 1.2 represents the phosphorus cycle in an aquatic ecosystem.

1.1.3 Pollution Effects of Nutrients to the Aquatic Environment

In a natural non-perturbed ecosystem, a steady state in the symbiotic functions of the aquatic biota, with respect to the processes of photosynthesis and respiration prevails, which leads to natural adaptation of specific ecological communities (eqn. 1.2). \(^{17}\)

\[
106\text{CO}_2 + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 122\text{H}_2\text{O} + 18\text{H}^+ (\text{+ Trace Elements: Energy}) \rightarrow \text{Algal protoplasm}
\]

\[
\begin{array}{c}
\text{R} \\
\text{P}
\end{array}
\]

\[
\begin{array}{c}
(C_{106}H_{263}O_{110}N_{16}P_{1}) + 138\text{O}_2
\end{array}
\]

\[\text{P}=\text{Photosynthesis} \quad \text{R}=\text{Respiration}\]

Addition to the receiving water body of excess of inorganic algal nutrients (N & P) from external sources leads to the problem of eutrophication. The immediate result is the dramatic change in the density and composition of phytoplankton and other aquatic plants, and a corresponding change in the zooplankton, resulting in changes in species distribution at all trophic levels. \(^{18}\) Another effect of the accumulation of organic matter through
increased photosynthesis is the increased rate in decomposition processes that puts a lot of demand on the dissolved oxygen.

The changes brought about by eutrophication have substantial ecological and economic consequences. Certain algae species are poisonous to some fish species and have been linked with serious diseases as liver failure and cholera, and incidents of gastric and non-gastric ailments.\textsuperscript{19,20}

In Kenya, cases of typhoid, dysentery and cholera caused by unclean water, reported in the Lake Victoria basin and on occasions even in the city of Nairobi have been in the news. In fact with the dramatic climatic changes caused by the \textit{El Nino} weather phenomenon, water-borne diseases, have claimed hundreds of lives.

The colonisation of L. Victoria by the water hyacinth, \textit{Eichhornia crassipes} is an ecological tragedy of international magnitude. Currently, foreign governments, non-governmental organisations (NGOs) and international organisations through the United Nations Development Programme (UNDP), in conjunction with the Kenya government have set aside manpower and millions of shillings to salvage the lake from this ecological disaster. In 1986, L. Naivasha was closed down due to excessive growth of the waterweed, \textit{Salvania molesta}.

Nitrite, an intermediate ion in the oxidation of ammonium compounds to nitrates, has been shown to be toxic on fish, (Sec 2.1.2). Nitrites can also be converted to nitrosamines, which are carcinogens.

Cleaning operations that use phosphate detergents may also enhance the levels of phosphates in streams and rivers. The detergents builders added as triphosphate, $P_3O_{10}^-$ are
responsible for aquatic pollution with phosphates. The polyphosphate builders undergo fast biodegradation by hydrolysis to produce the orthophosphate.

\[
P_{2}O_{10}^{5-} + 2H_{2}O \rightarrow 2HPO_{4}^{2-} + H_{2}PO_{4}^{-}
\]

The phosphate has no direct threat to aquatic animal life but may cause the problem of eutrophication.

Phosphorus has been shown to be a limiting nutrient in determining productivity in inland waters. In estuaries and marine coastal waters, nitrogen has been shown to be more limiting.\textsuperscript{21}

1.2. Organic Matter in Natural Waters

Organic matter in natural waters may be enhanced from domestic and municipal sewage inputs, agro-based industrial effluents, runoff from agricultural lands and from the synthetic organic chemical industry. Synthetic organic chemicals include organic chemicals used as intermediates in synthesis, pesticides, fuels, detergents, food and feed additives, solvents, paints, lacquers, rubber chemicals, household products, plastics, fibres, and pharmaceuticals. These may enter the aquatic environment through their various uses or as waste products. Most of the organic pollutants are present in parts per million (ppm) to parts per billion (ppb). These, however, have the properties of bioconcentration through organisms of trophic webs or directly from the water and have been shown to be toxic, carcinogenic and mutagenic.\textsuperscript{22}
The alarming aspect about aquatic contamination with organic pollutants is the exponential growth of the chemical industry. It was estimated by 1974, that the number of synthesized chemicals totalled 1.8 million and was growing at an annual rate of 250,000 new formulations. 300 to 500 reached the stage of commercial production, with global production of 100 to 200 million tons. It is estimated that up to one third of the total production of these synthetic organic chemicals finds its way into the environment.

The United States Environmental Protection Agency (USEPA) has worked out a ranking system for the 20 most hazardous water soluble chemicals that include phenol, benzene, ammonia, chlorine, DDT, nitrophenol, among others.

Some toxic trace organic compounds of concern in the aquatic environment are pesticides, polycyclic aromatic hydrocarbons (PAH), detergents, polychlorinated biphenyls (PCBs) and chlorinated hydrocarbons (CHC). The toxicity of these trace organics has been identified singly or in combination with other environmental chemicals. These trace toxic organics may reach man directly from the water or through the food chain. Fish, for example have been known to bioconcentrate trace organics as DDT, and PCBs to unacceptable high levels.

Even though an organic discharge may not be directly toxic to the aquatic life, it may result in a number of physical, chemical and biological changes.

A serious consequence of an organic discharge is the biodegradation of the organic matter that leads to exhaustion of the dissolved oxygen of the water. In anaerobic conditions, sulphate $\text{SO}_4^{2-}$ ions and nitrate $\text{NO}_3^-$ ions, present in the water act as electron acceptors to form hydrogen sulphide, $\text{H}_2\text{S}$ and ammonia, $\text{NH}_3$ respectively which are responsible for the
foul ordour and taste that renders the water unsuitable for domestic, industrial and aesthetic uses.

1.2.1 Pollution Effects of Organic Matter

Some effects of increasing the amount of organic in a water body are briefly outlined below:

I. Increased turbidity

Increased turbidity from dissolved and particulate organic matter in a water body leads to a decrease in light penetration and primary production, which in turn reduces the availability of food higher up the food chain.

II. Biological changes in receiving waters

Biological changes relate to the changes in dissolved oxygen caused by photosynthesis and respiration. The concentration of DO will depend on the rates of these two processes. The concentration of dissolved oxygen (in mgO₂/l) is the absolute amount of oxygen required by aerobic organisms for their survival. The concentration of DO, apart from being influenced by photosynthesis and respiration, also depends on temperature, salinity, air pressure, the rate of flow or turbulence and chemical processes taking place in the waters. Supersaturation (>20 mgO₂/l) may occur in sluggish or stagnant waters due to a slow rate of escape of the DO from the water.
Increase of organic matter (oxygen demanding wastes) increases the rate of consumption or decomposition of the organic wastes by microorganisms as fungi, bacteria and protozoan. This process of decomposition use up DO of the water, and the rate at which the process occurs is measured as the biological oxygen demand, BOD.

III. The Effect of Organic Matter on the Chemoreception of Aquatic Organisms

Other than the effect of low dissolved oxygen, organic matter may affect the chemoreception membranes of aquatic and marine animals. Organic pollutants may mask the chemoreceptors to relevant biological and chemical information and even damage the chemoreceptor causing death to the animals. Some of the organic matter that have been proven injurious to chemoreception membranes include some fractions of water soluble crude oil, pesticides, and detergents.

IV. Toxic Effects of Trace Organic Chemicals

The presence of trace organic chemicals has been positively found to cause behavioral changes, physiological damage and even death to aquatic organisms. Toxicity of these chemicals has been attributed to single molecules and/or in combination with other environmental chemicals. For example, the water soluble fraction of crude oil containing numerous isomers of aromatic polynuclear hydrocarbons (PAH) was found to be more toxic than any two constituent compounds when exposed to *G. morhua*. The toxicity of the organic chemicals may, also be influenced by their metabolites as a result of degradation of the parent molecule in aqueous solution. Gomaa and Faust,
identified the more persistent intermediates of parathion and paraoxon on oxidation with potassium permanganate as nitrophenol, 2,2'-dihydroxy-5, 5'-dinitrodiphenyl and 2-hydroxy-5-nitrobenzoic acid. The metabolites of DDT, DDD and DDE were found to be equally toxic.

1.3 The Trace Metals

1.3.1 Introduction

Trace metals are defined as those occurring at 1000 ppm or less in the earth's crust. Trace heavy metals are those metallic elements whose specific gravity is greater than 5.

Trace metals can be divided into two groups. Those which occur naturally in trace amounts in most waters and are plant nutrients, and those which do not occur in measurable amounts in natural waters, are potentially toxic in low concentrations, and have been widely distributed as a result of human activity. Plant nutrients include cobalt (Co), copper (Cu), manganese (Mn), molybdenum (Mo), and Zn. Examples of the toxic metals include Cd, Pb, and Hg.

Trace metals usually exert their biological effects as essential micronutrients or as toxins by forming stable co-ordinate bonds in proteins where they function as catalysts in redox reactions (for example Fe, Cu, and Mo) or form part of active centres of enzymes (for example Co, Zn). The trace metals known to be essential in one or more biological systems are Mn (in enzymes), iron Fe (most importantly in haeme-containing respiratory pigments), Co (in vitamin B12), Cu (in enzymes involved in redox reactions), Zn (in
enzymes) and Mo (proteins involved in electron transfer and photosynthesis). Man is exposed to heavy trace metals mainly through drinking water, the air we breathe, and habits as cigarette smoking and industrial exposure.

The toxicity of trace metals is attributed to their accumulation in body tissues and their competitive interference with essential elements of Zn-, Cu- and Fe-dependent enzymes. The action of metalloenzymes is inhibited when one metal ion of the metalloenzyme is replaced by another metal ion of similar size and charge.

1.3.2 Cadmium

1.3.2.1 Occurrence, Distribution and Uses

Cd has atomic number 48 and RAM 112.42. Its specific gravity at 20°C is 8.65; melting point, 320.9°C and boiling point 767°C. The predominant oxidation state in nature is Cd\(^{2+}\).

In fresh water, Cd is extensively associated with colloidal and particulate matter, and the soluble speciation is confined to the free Cd\(^{2+}\) ions, together with small amounts of CdCl\(_2\), CdSO\(_4\) and CdOH\(^+\). Cd occurs in small concentrations in igneous rocks, sedimentary rocks, in shales, marine clays and in marine phosphorites. Agricultural soils from unpolluted areas usually contain less than 1 ppm Cd. Kenyan soils have been found to contain Cd levels of the range 0.25-2.5 ppm.
Areas in which enhanced levels of Cd are found are usually linked with the occurrence of zinc-related manufacturing processes and metal plating operations. Smaller but important sources of Cd are as by-product of Cu-refining, and to a lesser extent, Pb-processing.  

Natural emission of Cd to the environment is associated with volcanic eruptions, power generation facilities, by burning agricultural and municipal wastes, including dried sewage sludge. Other sources of Cd-contamination of the environment include non-ferrous metal production, production of Cd-containing materials, iron and steel production and from phosphatic fertilizers.

The world production of Cd metal was estimated at 18,900 tonnes by 1979, with the USA, the USSR, Japan and Canada being the main producers.

Cadmium is a fairly expensive metal of low mechanical strength. It is used in electroplating for protection against corrosion, in special alloys and solders. It is also used as a pigment in yellow or brown paints. Cadmium is used in alkaline Ni-Cd rechargeable batteries. Discarded used Ni-Cd batteries pose environmental hazards since interaction of nickel and cadmium on toxicity have been found to be more harmful.

The world consumption of cadmium from its main uses, viz. batteries, pigments, stabilisers, plating, and alloys, was estimated at 9692 tons by 1965, 10917 tons by 1970 and 7903 tons by 1975.
Organo-cadmium is increasingly used in the plastic industry. Alkyl-cadmiums are used as polymerising catalysts in polyvinyl chloride (PVC) manufacture. Cadmium laurate, stearate, and palmitate are used as stabilisers on plastics.

Cadmium is not an essential element in living organisms and is highly toxic even at low concentrations. USEPA considers Cd as one of the most potentially hazardous chemicals.  

1.3.2.2 Effects of Cadmium on Human Life

Cadmium is not an essential element but it is found to occur in many body tissues. Cadmium absorbed from food is transported to the body tissues via the blood, in the red blood cells where it is bound to the low molecular weight protein, metallothionein. Most cadmium is stored in the liver and kidney which together contain about 50% of the cadmium body burden. Cadmium in the kidneys have a long biological half-life of about 20 years, which explains its accumulation. Only a small amount of accumulated cadmium, about 0.005 to 0.1% per day is excreted through urine and faeces. Cadmium in the blood has a half-life from 2-3 months; hence cadmium levels in blood can be a useful indicator of recent exposure to cadmium. 

Chronic cadmium intoxication may be as a result of long term exposure via inhalation of cadmium fumes or dust, or peroral exposure to contaminated food and beverages. The critical organ in which the first signs of adverse effects of cadmium may be seen is the kidney. One major sign of this effect is the decrease in the renal tubular reabsorption of low molecular weight proteins, such as beta-2-microglobulin and retinal-binding proteins. A continuous catabolism of the cadmium metallothionein
takes place after reabsorption, and cadmium is split from the metallothionein and bound to newly formed metallothionein in the tubular cells. It is supposed that kidney damage is prevented until such a stage is reached that the kidneys no longer produce enough metallothionein, and free cadmium ions become very toxic in enzymatic processes. In more advanced cases, more extensive damage of the kidney occurs. Later stage manifestations of cadmium intoxication include anaemia, liver disorders, effects on bone in the form osteoporosis and/or osteomalacia. In Japan, the manifestation of severe renal tubular damage and osteomalacia has been called the itai-itai disease, which was caused by consumption of contaminated rice grown under irrigation from mine waters contaminated with cadmium.

Other studies have indicated that inhaled cadmium may contribute to development of lung cancer and occupational exposure to cadmium, probably from cadmium oxide may be responsible for prostrate cancer. The immediate clinical effects of cadmium intoxication from contaminated food or drink may give rise to gastrointestinal symptoms including vomiting and diarrhea, and in severe cases shock. Contamination of food may arise from cadmium-containing solders in water pipes, cooling or heating devices or from dissolution of cadmium pottery painted with cadmium containing pigments.
1.3.3 Chromium

1.3.3.1 Occurrence, Distribution and Uses

Cr has atomic number 24 and RAM 51.996. Its specific gravity at 20°C is 7.14; the melting point and boiling point are 1890°C and 2482°C, respectively.

The predominant states of oxidation in nature are Cr$^{3+}$ and Cr$^{6+}$. The probable main soluble species in freshwater are confined to Cr(OH)$\text{3}^{-}$ and CrO$_4^{2-}$.

Essentially Cr is obtained from chromite, the mineral iron and magnesium chromoaluminate, (Fe, Cr, Al)$_2$O$_3$.(Mg, Fe)O. The mineral is arbitrarily classified according to the richness of Cr metal in the ore:

a) Metallic chromites containing about 48% Cr$_2$O$_3$ used in metallurgical industry.
b) Chemical chromites having Cr$_2$O$_3$ content of about 45% and
c) Chromites used in refractory processes containing about 36% Cr$_2$O$_3$.

Chromium has a number of important industrial applications:

a) The main application of Cr being in the metallurgical industry in the production of ferrochromes, silicochromes, and is added to other elements to form stainless steels, refractory steels and in tool making processes.
b) Another very important use of Cr is in the chemical industry. The most important chemical is the sodium dichromate salt, Na$_2$Cr$_2$O$_7$·2H$_2$O, which is used in the production of:
   (i) Chromic acid, mainly used in chromium plating processes
   (ii) Chromium sulphate, used in leather tanning
(iii) The anhydride Cr₂O₃, a base for pigments.

The consumption of chromites in the chemical industry is given as 25% used in Cr-plating, 30% in pigments, 15% in leather tanning and 30% other uses.⁴⁴

(c) The refractory industries use Cr in the production of ovens in the metallurgical and glass making industry as well as linings in blast furnaces.

An examination of the qualitative and quantitative wastes arising from industrial use of Cr reveals losses of Cr into the environment of varied magnitude depending on the type of industry, with the highest in the chemical industry and in production of ferrochromes.⁴⁴

Other sources of Cr contamination may be encountered in cleaning operations, in the production of special Cr-steels, stainless and refractory steels. Waste products from phosphate industry, from certain pyrites used in production of sulphuric acid, products from burning of certain fossil fuels (coal, petrol), and those produced by oxidation of organic compounds by chromic compounds may also contain Cr.

Water pollution by hexavalent chromium Cr⁶⁺ (in the form CrO₄²⁻, or Cr₂O₇²⁻) may arise from industrial wastes containing chromic acid, deposition and electroplating mainly practised by the automobile industry and from industrial water cooling (refrigeration) circuits to which are added certain Cr compounds that act as corrosion inhibitors. Leather tanning, aluminium anodising (galvanising), polishing and surface treatments are the other sources of water pollution with Cr.

Pollution by trivalent chromium, Cr³⁺ may arise in industrial wastes from industries using directly Cr³⁺ such as glass manufacturing, production of ceramics, photographic industries, and textile colouring manufacturing.

Cr is one of the least toxic of the trace metals at low concentrations and it is essential to plant and animal life when its oxidation state is (+3).
1.3.3.2 Effects of Chromium on Human Life

Chromium is one of the least toxic metals at low concentration and is in fact essential for fat and carbohydrate metabolism in mammals, forming part of the glucose tolerance factor. The main source of chromium and other essential trace metals that are micronutrients is dietary intake. Deficiencies may be as a result of inadequate dietary intake and bioavailability as in overly refined junk foods, increased body loses and intravenous feeding.

Deficiency of chromium may lead to glucose intolerance in the body. Man is exposed to chromium mainly from industry. The toxic effluents from a leather-tanning factory in Athi River, believed to contain chromium wastewaters killed thousands of fish and affected many other farming activities downstream River Athi. Heavy industrial exposure (glass and cement manufacturing, leather tanning and textile industries) may lead to teratogenesis (causing foetal abnormalities) genotoxicosis (causing chromosomal aberrations) mutagenesis and carcinogenesis. Exposure of chromium from industry has also been associated with lung cancer.
1.3.4 Copper

1.3.4.1 Occurrence, Distribution and Uses

Cu has atomic number 29 and AM 63.546. It has a specific gravity of 8.92 (at 20°C), and the melting and boiling points are 1083°C and 2582°C respectively. Copper consists of two natural isotopes: Cu-63 and Cu-65, which constitute 69.09% and 30.91% respectively.

Copper is found in nature as the fine metal and in combined form. It occurs in three oxidation states, Cu°, Cu+ and Cu2+. The more probable main species in water are CuCO3 and CuOH+.

Cu constitutes 70 mg/kg of the earth's crust, occurring as constituent of several ores, principally sulphide, oxide and carbonate, less commonly as antimonides, arsenites, phosphates, silicates and sulphates. Among the more common minerals is chalcopyrite, CuFeS that is thought to account for 50% of the World's copper deposits, chalcocite CuS, bornite, Cu5FeS4, tetrahedrite Cu8S4S13, cuprite Cu2O.

Copper is widely distributed in the environment, in soils, rocks, seawater, plants and animal organisms. The atmosphere contains about 2.6 x 10^3 tons Cu, the hydrosphere, 5.0 x 10^9 tons in the aqueous environment and 7.5 x 10^12 tons in the sediments, the biosphere about 2.9 x 10^7 tons and the lithosphere contain 1.4 x 10^15 tons. Fossil fuels together with dead biota contain a Cu content of 1.034 x 10^11 tons. The world production of copper for the period 1971 - 1980 is estimated at 82.5 x 10^6 tons.

Copper is used in electrical, construction, plumbing and automotive industry. The largest single user of copper is the electrical industry accounting for over 50% of the total
consumption. Of the $2158.9 \times 10^6$ tons of copper consumed worldwide, 69.5% is used in the wire mills, $1.85 \times 10^{-4}$ % in the secondary smelters, 5.51% in foundries and miscellaneous uses account for $1.4 \times 10^{-2}$ %.  

Anthropogenic sources account for about 75% of global Cu emissions into the environment. Total annual emissions of copper for the period 1971-1980 is estimated at $5.6 \times 10^4$ tons from the following contributing sectors: metallurgical industries 48.2 %, phosphate fertilizer production 1.07%, wood combustion 1.32%, mining operations 1.42%, coal combustion 8.39%, industrial applications 8.74%, waste incineration 9.46% and combustion of oil (gasoline) 21.4%. Emissions from natural sources release about $1.85 \times 10^4$ tons to the environment with wind blown dusts contributing 64.9% and volcanic particles 19.5% of the total. Other sources of Cu contamination of the environment include municipal and industrial sewage.

In water, copper is mobile and soluble at low pH. It precipitates in alkaline conditions and is thus not toxic. In humic waters, it may occur at fairly high concentration but since it is bound to organic molecules it is not available to act as a toxin.

1.4.3.2 Effects of Copper on Human Life

Copper is a micronutrient, forming an essential part of cytochrome oxidase and various other enzymes involved in redox reactions in the cells. At least 30 proteins and enzymes containing copper have been reported. The average man ingests 3-5 mg of copper per day from food and water. The actual need is 2 mg and this may lead to copper accumulation in the body. The average man has a body copper content of
Dietary copper toxicosis is rare in humans. Large amounts of orally ingested copper are toxic. For example, acidic foods or beverages that have been in prolonged contact with the metal or consumption of contaminated water (containing 9.7 ppm of the metal) may cause acute gastrointestinal disturbances and even death. \(^{31}\) Abnormally high copper levels are characteristic of a number of diseases. These may include anaemia, haemochromatosis, cirrhosis and yellow atrophy of the liver, tuberculosis and Wilson's disease. Wilson's disease is caused by hereditary copper in the liver that leads to accumulation of copper to abnormally high levels. This may lead to necrosis in the hepatocytes that may be accompanied by acute hepatitis.\(^{48}\) Excess copper in the brain cause neurologic disorder and all sorts of psychiatric disturbances. Patients with Wilson's disease and excess copper deposits are treated by chelation therapy.\(^{49}\)

1.3.5 Lead

1.3.5.1 Occurrence, Distribution and Uses

Lead is the heaviest element in subgroup (IV) B of the Periodic Table. Its atomic number is 82 and RAM is 207.19, depending on the source. Its specific gravity at 20°C is 11.35 and the melting point and boiling points are 327.4°C and 1620°C respectively.
Lead has two main oxidation states, Pb$^{2+}$ and Pb$^{4+}$; and Pb$^{2+}$ greatly predominates in the aquatic environment. The percentage of a particular inorganic species in fresh water is influenced by the pH, sec 2.1.2. Generally, PbCO$_3$ predominates with other species being Pb(OH)$_2$, Pb(CO$_3$)$_2$$^{2-}$, PbSO$_4$ and PbCl$_2$.$^{33}$

The occurrence of lead in uncombined form is rare and in comparatively small amounts. Rocks containing small amounts of lead are igneous and metamorphic rocks, carbonaceous shales and some phosphate rocks. Lead is recovered commercially from a range of ores of which galena, PbS and to a lesser extent, cerrusite, PbCO$_3$, anglesite, PbSO$_4$, and others are important. Often, deposits are also rich in zinc, and zinc-copper ores. These mixed ores give significant amounts of silver, gold, bismuth, antimony, arsenic, cadmium, tin, etc.

Sources of lead are found in many countries of the world. Global lead in 1975 was 3.6 x 10$^6$ tons.$^{50}$ This production, together with recycled and recovered sources meets a world usage of 4.1 x 10$^6$ tons which remains constant.$^{50}$

The main industrial uses of lead are in the manufacture of lead acid batteries, pigments and chemicals, tetraethyl lead, alloys, pipe and sheet and cable sheathing.

Lead consumption by use in Japan, USA and Europe in 1980 is estimated at 1700 x 10$^3$ tons, of which about 50% went into the manufacture of lead acid batteries.$^{51}$ In addition to these uses of lead metal, there are many applications of its organic forms. Compounds from lead acetate to zirconate, some of which are often highly toxic, are used as biocides. Alkyl-lead antiknock derivatives are produced on a large scale (301000 tons in 1975) and are a cause of environmental concern. The production is however slowly declining (357000 tones in 1974).$^{52}$ Other organolead compounds are used in detonators, plastics and catalysts. These, apart from biocides have less access to the environment.
Nriagu,\textsuperscript{39} estimates that the global atmospheric emissions from man-made sources were $438 \times 10^3$ tons per year for the period 1974-1975 in contrast to only $18.55 \times 10^3$ tons per year from natural mobilization and inputs. Atmospheric discharges from the combustion of lead in petrol (61%), from steel and base metal production (23%), and from the mining and smelting of lead (8%) are the major contributors, with coal combustion and numerous minor activities comprising the remainder. Lead in the soil is usually immobile and barely soluble. Hydrous metal oxides, clay minerals, and organic suspended particles readily adsorb lead in drainage waters. The dumping of sewage sludge may create local hot spots for environmental pollution with lead, where up to 10,000 $\mu$gg$^{-1}$ Pb dry weight have been quoted.\textsuperscript{54} Of current concern is the use of lead in drinking-water distribution and domestic plumbing.

Lead, although a highly available element is not essential to human life, and is potentially toxic.

1.3.5.2 Effects of Lead on Human Life

The absorption of lead in the gastrointestinal tract will depend on the presence of food in the tract, minerals such as calcium and phosphate in doses equivalent to those in ordinary meals. It was observed that more lead was absorbed in fasting subjects, and the uptake of lead was reduced by the presence of these minerals.\textsuperscript{55} Age and sex have also been shown to affect lead uptake.\textsuperscript{56}

There are three main routes of lead exposure to human life; through food, water and air, food being the major contributor.\textsuperscript{56} Lead in food can be derived naturally or as a
result of human activity. For example directly from dust falls on crops, or indirectly from dust fall on soil, contaminated water for irrigation and sewage sludge used as fertilizer. Lead-solder cans constitute a major source of lead in food. Acidic foods, particularly, can dissolve lead from the lead solder in the side seam of the can. It is approximated that 55 - 85% of a persons daily exposure to lead originates from food, and hence 15 - 45% from both water and air. Lead pipes in the domestic water supply system have been implicated with elevated lead levels in drinking water. Concentration of lead in air varies, and is found to be higher in urban areas (from automobile exhaust burning leaded gasoline) as compared to rural and remote areas.

About 90% of the total body burden of lead is bound to bone, with a retention time of 5 years, while the remainder is loosely bound to blood and soft tissues. Lead in the blood can be related to the intake of lead, the concentration in diet, water or air and to different health effects due lead exposure.

An early sign of the biochemical effect of lead is the inhibition of amino-levulinic acid dehydrase (ALA-D) in the biosynthesis of haem. This has been observed at lead in blood concentration of 10µg / 100ml. A decreased activity of ALA-D results in the increased urinary excretion of the protein amino levulinic acid (ALA) which has been observed at lead in blood concentration of 40µg / 100ml. These changes in haem biosynthesis may not have adverse health effects but may be used as indicators of biological response to elevated lead absorption.

Anaemia has been reported at lead in blood levels of 40µg / 100ml in children and 60 -80µg / 100ml in lead-exposed workers. Lead exposures may have serious effects on the central nervous system (mostly in children) and peripheral nervous system (PNS) after long exposure to lead. The effects on PNS range from paresis to slight
functional impairment. The major neurophysiological disturbances consist of slowing of motor conduction velocity, slowing of the sensory conduction velocity and electromyographic disturbances.\textsuperscript{37}

These symptoms begin to occur at lead in blood concentration of 40-50\(\mu\)g/100ml and become more prominent in the range 50-70\(\mu\)g/100ml.\textsuperscript{61}

Lead in high doses cause encephalopathy whose symptoms are ataxia, coma and convulsions, observed at lead in blood levels of 60\(\mu\)g/100ml (in children) and 80\(\mu\)g/100ml in adults.\textsuperscript{47}

Neurological sequelae can follow in severe or repeated episodes of lead encephalopathy, characterised by impaired ability to learning, motor incoordination, disturbed sensory perception and inability to concentrate.\textsuperscript{61} From data on experimental animals it is suspected that lead acetate, lead subacetate and lead phosphate could be considered as carcinogens to humans.\textsuperscript{62}

1.3.6 Zinc

1.3.6.1 Occurrence, Distribution and Uses

Zinc is one of the most useful of the metals only ranking fourth in consumption after steel, aluminium and copper. The world total zinc reserves are estimated at 290 million tons, and the largest reserves are in Canada, Australia the former USSR and US.\textsuperscript{63}

Zinc is an element with atomic number 30 and RAM 65.38. Its specific gravity is 7.14 (at 20\(^\circ\)C), melting point and boiling point being 419.5\(^\circ\)C and 907\(^\circ\)C respectively. The predominant oxidation state is Zn\(^{2+}\). Zinc is an abundant element in rocks and ores but it is
present in natural waters as minor constituents because of lack of solubility of the free metal and its oxides. It is present only in trace quantities in most alkaline surface and ground waters, but more may be present in acidic waters. Other than complexation by organic material, main probable dissolved zinc inorganic species are $\text{ZnO}^+$, $\text{Zn}^{2+}$ and $\text{ZnCO}_3^\circ$.  

Zinc occurs in nature mainly as the sulphide complexes (blends) or silicate complexes (calamine) and also as carbonates. The earth’s crust contains 65-80 mg/kg Zn.  

The blend often contains iron (up to 26%), some manganese, cadmium (up to 5% as in the case of libramite), silver and more rarely tin and mercury, this last element being often found in treated effluents. Calamine is a silicate complex of zinc (SiO$_2$, 2ZnO, H$_2$O). Smithsonite or zinc carbonate (ZnCO$_3$) may also contain other elements as Fe, Mn, Ca, and more rarely Cd and In.  

The world production of zinc has continued to grow albeit gradually from $4,442 \times 10^3$ tons in 1966 to $5,486 \times 10^3$ tons in 1972 to $5,693 \times 10^3$ tons in 1977.  

The principal industrial uses of zinc are identified as in the protection of surfaces against corrosion (galvanising), in alloys of zinc, in alloys of copper and light metals, and in various forms of thin zinc sheets (plates, leaves, bands). Other industrial uses include the manufacture of paints of zinc oxide, glass and ceramics, and in chemical and pharmaceutical industries.  

The sources of industrial effluent containing zinc concentration (mg/l) have been found to be in the range: metallurgy and polishing (0.2-1,500), galvanising (2-350), silverplating (0-200), production of rayon (20 - 1000). Other sources of environmental contamination with zinc include mine waters, paper manufacture (bleaching with zinc dithionite), paint
production (zinc tetrahydroxochromate) and pigments (lithopone-ZnS, BaSO₄) and zinc in dry batteries.

1.3.6.2 Effects of Zinc on Human Life

Zinc is an essential element to animal and human life. Over 20 different zinc metalloenzymes are known including carbonate anhydrase, alkaline phoshatase, alcohol dehydrogenase and other zinc activated enzymes. Humans' main intake of zinc is dietary.

Zinc content in the adult human body is about 2.5 g with the highest concentrations, 100-200 mg/kg occurring in the eye, hair, bone, and male reproductive organs, 40-50 mg/kg in the liver, kidney and muscles.

The World Health Organization (WHO) recommends a daily intake ranging from 6 mg (infants) to 27 mg in lactating mothers. The clinical symptoms of zinc deficiency include impaired taste, menstrual lethargy and other disturbances as rough skin, delayed wound healing and susceptibility to infection. Chronic deficiency in paediatric and adolescent age groups cause growth retardation and delayance of sexual maturity.

With regard to zinc intoxication, "metal fever" demonstrated by pulmonary manifestations, fever, chills and gastroenteritis has been reported among industrial workers exposed to the fumes, while acute zinc toxicity has been observed in renal failure patients following hemodealysis, characterised by nausea, vomiting and severe anaemia.
From the above discussion, it is apparent that elevated levels of nutrients, organic matter and the heavy metals in our rivers and lakes, particularly where these levels are enhanced from anthropogenic sources can cause serious problems to water users. This may be so especially to the poorer regions of the country where raw and untreated water is the only available resource.

1.4 Background Information on Migori River Basin

River Migori drains the administrative districts of Transmara, Migori, Kuria and Suba and enters Lake Victoria at Kadem point. It extends for about 150 km.

The drainage basin is mainly in the Nyanza Province. The drainage basin is located between $0^\circ 45'S$ and $1^\circ 15'S$; and $34.2^\circ E$ and $35^\circ E$. It rises 1216 to 2134 m above sea level.

This region normally receives long and reliable rains, extending from March to May and short rains in August and September, with an annual total of about 800mm around the lake shores and increasing inland to about 2000 mm.

The River Migori drainage basin is a rich agricultural area that supports a high population density (at an average of 270 persons/km$^2$ as at 1986). This region lacks adequate physical facilities such as clean piped water and waste treatment facilities. Migori town is situated on the River Migori and strategically placed on the Mukuyu-Isebania-Musoma highway. The rapid population and commercial growth has attracted both formal and informal industries. Since the only waste treatment facility near the river at Migori town only serves the district hospital and the district administration headquarters; any
wastewater generated from the town and its surroundings could have an effect on the quality of the water of the River Migori. The people along the river depend entirely on the untreated river water that may be affected for all their domestic needs, cleaning activities, washing of clothes and utensils and bathing. Further unhygienic practices such as defecating along the river may cause faecal contamination of the water and possibly introduce pathogens as virus and protozoa. This could be a likely cause to diseases such as typhoid and cholera that are endemic in this region.

The Dutch-funded Intensive Urban Development Programme stationed at Migori town in conjunction with the Netherlands Development Agency (SNV) have embarked on programmes designed to alleviate poverty and help in urban planning of the town. One immediate area of concern has been the sinking of boreholes to provide clean water.

The major industry in the region is the Sony Sugar Industry that discharges into Kuja. There is a fish processing plant at Midas in Migori town that is estimated to process about 20 ton/day of fish. This processing plant does not discharge its effluents into the river.

Other smaller industries with pollution potential are the Jua-Kali industries that have mushroomed in the town and other trading centres, and have received a lot of attention from the government and donor agencies. The main activities of these industries include repair of vehicles, panel beating, spraying of motor vehicle and car washing. These activities have the potential to pollute the river with oils and heavy metals.

This region has great contrasts in elevation and geology, which in turn give rise to a wide range of climate, soils and land use. The long rainy season associated with temperate
equatorial climate enables sustenance of a range of subsistence crops, cash crops and livestock production. Sugarcane and tobacco are the major cash crops in the region.

For the year 1996/97 (ending June 30th), tobacco farmers received gross proceeds of Ksh. 635 million. A BAT (K) limited and Mastermind Tobacco companies have invested into this economy by provision of expertise, seedlings, fertilizers, and pesticides. Over 15,250 ha is under sugarcane and 3,500 ha is under tobacco growing. Other crops grown include maize, sorghum, finger millet, sweet potatoes, beans, cassava and bananas, covering an estimated total of 132,466 ha; with maize alone under 56,285 ha, comprising 42.5%. Maize earned farmers Ksh 860 million in 1995.

Fertilizer application with recommended rate for the growth of maize, tobacco and sugarcane are given as:

Maize: Diammonium phosphate, DAP (100 kg P$_{2}$O$_{5}$/ha), calcium ammonium nitrate, CAN (200 kg N/ha), Ammonium sulphate nitrate, ASN (200 kg N/ha)

Tobacco: CAN (100 kg/ha), Nitrogen, Phosphorus, Potassium, NPK (400 kg N/ha).

Sugarcane: Single superphosphate, SSP (50 kg P$_{2}$O$_{5}$/ha), triple superphosphate, TSP (50 kg P$_{2}$O$_{5}$/ha), CAN (80-130 kg N/ha), urea (80-120 kg N/ha).

A survey conducted and published by 1977, indicated that subsistence crops as maize received more frequent and bigger quantities of fertilizers and pesticides. The survey further indicated that about 100% of the farmers used P$_{2}$O$_{5}$ on food crops and 96% used N-fertilizer, but only about 36% of the farmers used K$_{2}$O on the food crops. With the rising costs of fertilizers and pesticides, cash crops are currently prioritised for fertilizer application over food crops.
Livestock production has continued to grow, and the 1988 statistics revealed 895,683 heads of cattle, about 29% increase in the 1987 count. The number of sheep and goats for the same period was 309,500; pigs 3,733; poultry 5,361,000 and donkeys 28,802.\footnote{11}

Pollution index from nitrogen and phosphorus artificial fertilizers in the waterways based on the recommended maximum and minimum values per hectare of the fertilizers has been calculated. Nutrient loading from animal waste has also been calculated. The results indicate that there is considerable contribution of nutrient enrichment from animal waste as much as from artificial fertilisers.\footnote{72}

Against this background, this study was undertaken to investigate some water quality characteristics of River Migori on a section traversing Migori town and attempted to establish its suitability for domestic use.

1.5 Objectives of the study

The purpose of this study was to assess the quality of the River Migori waters at Migori town, as the river enters the town, in the town (upstream) and where it leaves the town (downstream). Specifically, the objectives were to establish the levels of the following parameters during the dry and wet seasons:

1. a) Nutrients as nitrate-nitrogen, nitrite-nitrogen, and phosphate-phosphorus.

   b) Organic matter as the collective parameters, the Biological Oxygen Demand BOD, and the Chemical Oxygen Demand, COD.
c) The trace heavy metals (Cd, Cr, Cu, Pb and Zn).

2. To determine the impact of agricultural activities upstream, industrial and settlement activities in the town on the suitability of the Migori River waters for domestic use by the community.
CHAPTER 2

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

A lot of research work has been done in establishing the levels of certain physico-chemical parameters in various water bodies - rivers, streams, lakes, oceans etc., their effects to aquatic and marine life, the limiting concentrations at which adverse effects become apparent or are tolerated. Toxicity testing has included procedures in the determination of these levels and the organisms' response (behavioral or physiological) towards the toxins, and the ecological changes caused by the toxin or pollutant in the aquatic environment. Standard procedures as the median effective concentration (EC$_{50}$) i.e. the concentration at which a specified effect is observed in half the population, median lethal concentration (LC$_{50}$), the concentration at which half the population dies, have been used valuably in assessing water quality.

The effects of some of the physical and chemical parameters on water quality assessment and the effects to aquatic/marine biota are briefly reviewed below.
2.1.1 pH

The pH of an aqueous solution may be defined as the decadic logarithm of the reciprocal of the hydrogen ion activity \( \log \text{pH} = - \log a_{H^+} \). Changes in pH may directly affect aquatic biota such as causing stress and depression, or influence the chemical properties of water on toxicological behaviour of a substance. pH changes in natural waters may be affected by the presence of humic substances, changes in carbonate equilibrium due to bioactivity of plants, in some cases by hydrolysable salts, and discharge of waste water of industrial or domestic origin.

Stress and depression have been shown to occur due to Adenylate Energy Change (AEC), in the body tissues of the affected organisms. AEC is the measure of the metabolite energy of an organism that controls physiological development of an organism. AEC in the organism is available from nucleotide pool mainly in the form of adenosine triphosphate ATP. AEC varies on a scale from 0 to 1, and has been correlated with the viability of microorganisms. Values between 0.8 and 0.95 were found in cells that were actively growing and dividing, between 0.5 and 0.75 are indicative of cells in stationary growth, and those below 0.5 are usually moribund with no recovery even if the cells are placed on optimum environmental conditions. For example exposure to gulf killifish *Fundulus grandis* to low pH resulted in decreased AEC in the brain, gills and muscle. The amount of change in adenine nucleotides and AEC was related to the degree of the acidity and duration of exposure. The greatest changes were found in killifish after 96 - hr exposure to
pH 4. For example, total adenylates decreased from controls (20μg/mg protein) by 18%, 30% and 44% in brains of killifish exposed to pH 6.5, 5 and 4 respectively, for 96 hours. Brain AEC of controls was 0.835, and after 96 hrs at pH 6.5, AEC was 0.75; at pH 5, 0.62; and at pH 4, 0.574. Other tissues tested showed a similar correlation for the same duration of testing apart from the muscles, which altered only slightly.

Many studies have demonstrated that pH influences the toxicity of heavy metals to microbiota, mainly by affecting the chemical speciation of the metals and the extent of complexation of metals to organic constituents in the aqueous medium.  

Fig 2.1: Effect of the composition of the test medium on toxicity of Cd as a function of pH on the growth rate of Saprolegnia sp.  

- Medium 1 (2.0% glucose + 1.0 % neopeptone).
- Medium 2 (1.0% glucose, 0.25% peptone. 0.1% NH₄NO₃, 0.05 % MgSO₄·7H₂O, 0.02 %CaCl₂. H₂O, 0.02% yeast extract)
Studies on pH-Cd interactions have shown that toxicity of Cd to bacteria *Alcaligenes faecalis* and *Bacillus careus* and to the fungi, *Trichoderma viride* and *Aspergillers niger* was potentiated when the pH of the medium was increased from 7 to 8 and 9.

Similarly, the toxicity of Cd was increased when natural acidic soil (pH 5.0) was adjusted to 7.2. The potentiation of Cd toxicity in alkaline media was attributed to the formation of CdOH⁺, which as a monovalent cation would presumably penetrate biological membranes more readily than divalent Cd²⁺, or to the reduced competition between protons H⁺ and Cd²⁺ or Cd OH⁻ for sites on the cell, due to low H⁺ concentration at higher pH. Cd has also been shown to be more toxic to algae, *Chlorella pyrenoidosa* at pH 8.3 than at pH 7.3 or 6.6 with enhanced toxicity at pH 8.3 being correlated with increased uptake of Cd.

![Graph](image)

**Fig. 2.2: Effect of pH on the toxicity of Cd, Pb and Zn to mycelial growth rates of a Saprolegnia sp. on medium 1**

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The toxicity of Cd as a function of pH also depends on the media, see Fig. 2.1 above. The toxicity effect of Zn, Pb and Cd as a function of pH is summarized on Fig. 2.2 above.

The toxicity of Cu to spores of *Fusarium lycopersici* increased as the pH was increased. Increasing the pH from 5 to 8 increased the toxicity of Cu to growth and photosynthesis of *Chlorella pyrenoidosa*. Increasing the pH from 3.5 to 4.7 increased the toxicity of Cu to the fungus, *Aureobasidium pullalans* with increased toxicity paralleling increased uptake of Cu. Acid-tolerant strains of *Scytalidium* sp. and *Pericilium nigricans* tolerated better in very acidic media, that is, pH 2.6 and 2.0 respectively than in media at pH 4.6 and 6.8 respectively.

There is evidence that pH affects the kinetics of chemical oxidation of organic substances in aqueous solution and hence influence the toxicological behaviour of these substances. It has been shown that these reactions are faster in alkaline medium. For example, the rate of reaction of the pesticide disquat with potassium permanganate at pH 9.13 is about 77 times faster than at pH 5.12, whereas paraquat-KMnO₄ reaction is about 62 times faster at pH 9.23 than at pH 5.12. Similar observations were made with ClO₂ and Cl₂ as the oxidants. In some systems the effect of increasing hydroxonium ions H₃O⁺, that is lowering the pH, lead to no reaction between the oxidant and pesticide. For example, ClO₂ had no effect on disquat and paraquat at pH values 5.06, 6.17 and 7.12. This could be a serious threat to aquatic life in case of polluted waters since it allows more contact time of the organism with the pesticides.
2.1.2 Temperature

Temperature affects the kinetics of the oxidation reaction of organic matter in natural waters to their simplest and non-toxic forms.

Using model reactions, Gomaa and Faust, 76 demonstrated that rate constants of oxidation of the herbicides disquat and paraquat with KMnO₄ are dependent on temperature, the reaction rates increasing at higher temperatures. Temperature also affects the physiological processes in microbes (such as growth and photosynthesis) and their sensitivity towards trace metals. Metal-temperature studies showed growth rates of Scenedesmus sp. and Chlorella sp. decreased less in the presence of Cu when exposed at 23°C than at 18°, 29° or 35°C. 27

The toxicity of Zn²⁺ to growth of Aspergillus niger was unaffected by increasing the temperature from 25°C to 37°C, but ZnCl⁺ / ZnCl₂ / ZnCl₃⁻ was more toxic at 25 than at 37°C. Euglena gracilis was more tolerant to Cr⁶⁺ when exposed at 20°C than at the sublethal temperature of 31.5 °C. 27 The toxicity of Cu to Paramecium tetraurelia, and Zn to Chilomonas paramecium decrease as the temperature was increased, and there was no definitive temperature - toxicity relationships for Cu and Cr⁶⁺. 27

Other studies have shown that extreme temperature changes have an effect on the AEC in fish and mollusks. Brook Trout, Salvelinus fontinalis, acclimated for 10 weeks at 4°C had a lower AEC (0.89) in white muscle compared to those at 24°C (AEC of 0.93). 27 The AEC was approximately 20% less in mollusks, P. ebeninus, kept at 29°C than at 20°C. 27 For the bivalve, Trichomya hirsuta, collected from the inlet and outlet sides of a water power
cooling plant, the AEC of the bivalves was 0.78 on the inlet side and was 0.68 on the outlet side where the temperature was 8\(^{0}\) higher.  

2.1.3 Algal Nutrients

The major nutrients that contribute to eutrophication are phosphorus as phosphate \(\text{PO}_4^{3-}\), and nitrogen as nitrate \(\text{NO}_3^-\). \(\text{NO}_3^-\) and \(\text{PO}_4^{3-}\), the end products of aerobic stabilization of organic nitrogen and organic phosphate respectively are not toxic to aquatic organisms. In natural unpolluted waters \(\text{NO}_3^-\) concentration is less than 0.1 mgNl\(^{-1}\) and that of \(\text{PO}_4^{3-}\), is less than 0.1 mgPl\(^{-1}\), since these nutrients are constantly being taken up and converted into cell structures.  

The biomass production in natural waters is determined by nutrient intake, other factors such as rate of photosynthesis considered, in a stoichiometric sense (Eqn. 1.2). The stoichiometry demonstrates in a very simplistic way the adaptability of algae communities to obtaining ecological situations. Nutrient fluxes have been shown to cause shifts in algae species. For example, low N/P ratios appear to favour N-fixing blue-green algae whereas high N/P ratios achieved by controlling P input favoured a “water bloom” that was less objectionable. From evidence on whole-lake experiments, Schindler, 77 showed P as a limiting nutrient in maximum biomass production in inland waters. The same experiments also demonstrated the biological mechanism for correction of nitrogen and carbon deficiencies. These experiments concluded that primary production, that is C-fixation, has
a strong correlation \((r = 0.78)\) to phosphorus loading in fresh waters.\(^{77}\) The problem of eutrophication, as manifested by increased biomass production from increased nutrient intake has a direct bearing on the demand for the dissolved oxygen \((140 \text{g of oxygen per } 1 \text{ g of phosphorus, cf. Eqn. 1.2})\), and an alteration of the phytoplankton community. Eutrophication therefore affects the health, distribution and abundance of many heterotrophic communities higher in the food chain as a result of altering the algae communities and the changes caused to the dissolved oxygen content of the water (see Section 1.1.3).

Other studies have shown that the organic material introduced into fresh water bodies from domestic sources \((20 \text{ to } 100 \text{ mg organic matter per liter})\) is small in comparison to the organic material that can be biosynthesized from introducing fertilizing constituents \((3 \text{ to } 8 \text{ mgP l}^{-1}\), which can yield 300-800 mg organic matter per liter).\(^{78}\) Vollenweiders,\(^{79}\) has related external sources of nutrients such as natural and agricultural runoff, industrial and municipal contributions to lake eutrophication. He was able to show on the basis of data for twenty lakes that valid correlation can be established between areal limiting nutrient (phosphorus in this case) loading \((\text{gm}^{-2} \text{ year}^{-1})\) and mean lake depth on the one hand and the degree of eutrophication on the other hand.

Figure 2.3 is Vollenweiders phosphorus model for lake eutrophication.
Nitrites (NO$_2^-$) which may be introduced into receiving water bodies by sewage effluent or industrial effluent, and are intermediates in the formation of nitrate (see the Nitrogen-cycle) are toxic to aquatic organisms at certain concentrations. The toxicity of nitrites has been reviewed by Lewis and Morris. Nitrite enters the fish through the chloride cells. From blood plasma, nitrite diffuses into red blood cells where it oxidizes the iron to +3 oxidative state, resulting in the formation of methaeglobin, which lacks the capacity to bind with oxygen. During activity (high oxygen demand), the fish may die of anoxia. The toxicity of nitrite is modified by chloride concentration and to a lesser extent by carbonate and nitrate anions.
For example, toxicity tests carried out on channel catfish, *Ictalurus puctatus* and freshwater prawns, *Macrobrachium rosenbergii* have shown reduced growth at 3.71 mg/l $\text{NO}_2^-$ for the catfish, and 35% growth reduction at 1.8 mg/l $\text{NO}_2^-$ for the prawns.

The lethal $\text{NO}_2^-$ concentration ($LC_{50}$ values in mg/l) required to kill half the test population within a 96-hr exposure for fathead *Pimephales promelas*, rainbow trout, *Salmo gairdneri* and the blue tilapia, *Tilapia aurea* were 2.99 (at low Cl$^-$ concentration), 0.24 (low Cl$^-$) and 16 (at high Cl$^-$ concentration) respectively.

### 2.1.4 Organic Matter

Organic enrichment in receiving water bodies results in various chemical and physical changes that in turn drives the biological changes within the receiving waters. Organic matter contains nutrients (of special interest, P and N) that are mineralized by decomposers resulting in increased concentration of dissolved and particulate nutrients, but also with a loss of dissolved oxygen. As with nutrient enrichment, an organic discharge that may not be directly toxic to aquatic life may cause significant changes in community structure and biological processes. (Synthetic organic matter as pesticides, and PCBs are toxic). Partial biodegradation of proteins and N-containing organic material can lead to elevated ammonia and nitrite concentrations which are toxic to many aquatic organisms.
Dissolved oxygen deficiency results from BOD and COD associated with pollution by industrial and domestic wastes. BOD is normally assessed by measuring the rate at which oxygen disappear from a solution in a sealed bottle kept for 5 days at 20°C. BOD is a useful measure of organic enrichment. The expected BOD values for natural unpolluted rivers range between 0.5 - 5.00 mgO₂/l.11

The main source of water contamination in the lake Victoria basin is the agro-chemical and food processing industrial effluent. Many factories do not treat their effluents and BOD values of 5,000 mgO₂/l has been recorded for effluents discharging in to River Nyando.11 Treated effluents contain lower BOD values. Effluents discharged into River Nzoia from Nzoia Sugar factory have reported BOD values of about 150 mg O₂/l.11 Both dilution and aerobic biodegradation are expected to occur downstream but this certainly leads to higher values at point sources and within the vicinity than the recommended levels. The Kenya government recommends a BOD value of 80mgO₂/l.11

The organic matter in water also undergoes non-biological degradation. All organic contaminants are supposed to be thermodynamically unstable in natural aquatic environments. The atoms (e.g. N, P, C) in these compounds are found in their reduced valence states. As a result, oxidation to higher valence occurs in aerobic conditions to yield, under favourable conditions stable products, CO₂, NO₃⁻ and PO₄³⁻. The amount of oxygen required is measured in terms of chemical oxygen demand, COD. The conversion of organic compounds into their simple and stable products have been shown by simple thermodynamics models to be feasible.25
Low levels of oxygen are harmful to aquatic organisms, particularly those that entirely depend on their oxygen from the water medium.

The fish response to low oxygen levels is avoidance reaction and swim away to better aerated areas. Supersaturation levels of DO have been found to cause mortality in fish and particularly the less mobile lower stages of life as eggs and fry. Studies on *P. premelas* have reported reduced growth at O$_2$ concentrations (mgO$_2$/l) below 7.9, reduced production below 3.0 and no spawning at 1.0. Other studies on invertebrates have indicated LC$_{50}$ values, in mgO$_2$/l of 3.6 (14.0°C) for *A. lycorias*, at 5.0 (18.5°C) for *B. laurentina* at 2.2 (18.5°C) for *L. nebulosa* and at 4.8 (18.5°C) for *P. dorsata*.

Studies done in the USA have identified about 100 synthetic trace organic chemicals. The maximum concentration of these chemicals ranged from 0.06 ppb for the pesticide toxaphene, to 113 ppb for chloroform. These levels appear to be low but aquatic organisms have the ability to bioconcentrate these chemicals directly from the water, or the food web to lethal values.

Food and water are the principal pathways for the uptake of toxic substances by an organism. It has been established that the uptake of the substances largely depend on their concentrations. From food, the residual concentration of the substances, in the range

\[
\text{CH}_2\text{O} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})
\]
μg kg⁻¹ to mg kg⁻¹ is normally the preferred pathway other than from water where the concentration may be in ng l⁻¹. As the concentration of the substance in the water increases to within μg l⁻¹ levels, uptake from water becomes an important pathway.\(^7\)

The toxicity of a substance therefore depends on the rate at which it can be bioconcentrated, (which further depends on its biological half-life, \(T_{1/2}\)) in the organism. Experiments have shown that \(T_{1/2}\) values vary from 2 hours for compounds as carbon tetrachloride to no apparent elimination for PCBs in fishes.\(^7\)

2.1.5 The Dynamics of Trace Heavy Metals in Aquatic Organisms

On entering an aquatic ecosystem a trace metal may remain in solution, or it may become adsorbed onto a particle thus forming a complex, which may then become immobilized in the sediments; or it may be accumulated in aquatic organisms where it may or may not cause its harmful effects. The susceptibility of aquatic organisms to trace metals is influenced by various physical, chemical and biological factors, which either alter the toxic potential of the metal or change the organism’s vulnerability to it.

Some of the physical and chemical factors include:

a) **pH**: This has an effect on the chemical speciation of the metal, Sec 2.1.0.

b) **Temperature**: This controls the rate of metabolic processes in the organism and will determine the uptake and hence toxicity of a particular type of metal, Sec 2.1.1.
c) **Redox potential** $E_h$: Anaerobic conditions ($E_h$ value is negative) in aquatic environments leads to microbial conversion of e.g. $SO_4^{2-}$ to $S^{2-}$, thus precipitating most metals as their sulphides (e.g. CdS, HgS) and hence reducing their bioavailability.

$E_h$ values also determine the valence of some metals. For example in oxygenated conditions Cr occurs as Cr (VI), while in anoxic condition, as Cr (III).\(^{81}\) These two have different toxicities to microbiota.\(^{76}\)

d) **Presence of inorganic cations**: Other cations may reduce the toxicity of heavy metals by competing for sites on cells surfaces between the cations present in the aquatic environment and the cationic speciation of the heavy metals. Fe has been shown to reduce the uptake of Cd by some microbiota.\(^{76}\) Mg influences toxicity of Cu in photosynthesis, and Zn to growth of *P. triconutum* and of Cd to the growth of *E. Coli*.\(^{76}\)

e) **Inorganic anions**: These exert an influence on the speciation of metals.

Metals form coordinate complexes with, for example OH\(^{-}\), or Cl\(^{-}\) present in the aquatic environment. Cd may occur as a mixture of Cd\(^{2+}\)/CdOH\(^{+}\) (in freshwater) or CdCl\(^{+}\)/CdCl\(_2\)/CdCl\(_3\)\(^{-}\) (in seawater). These speciation forms exert different toxicities to microbiota. S\(^{2-}\), CO\(_3^{2-}\) and PO\(_4^{3-}\) reduce the toxicity of heavy metals probably by precipitation.\(^{76}\)

f) **Organic matter**: Soluble and insoluble organic matter influences the bioavailability of metals by forming metal complexes with the organic matter.
g) **Metal - Metal Interaction:** Pollutant emissions usually contain multiple metals. The microbial response to multiple metals has been shown from different studies to be potential antagonistic, synergistic or additive. For example the interactions of Cu and Zn on toxicity to the algae *S. costatum, T. pseudonana* is synergistic, Cu and Cd on the bacterium *K. pneumoniae* was synergistic, Cu and Pb to algae *S. capricornutum* was antagonistic and Cu and Cr (VI) to the bacterium *K. pneumoniae* was additive.76

A number of studies, under natural or simulated conditions have been carried out to investigate the effects of trace metals into functioning aquatic ecosystems. These studies have focused species richness, diversity and composition, functional changes for example in respiration and metabolism and toxicity tests on lethal and sublethal effect of trace metals on aquatic organisms.

Trace metal concentration in rivers in moderately unpolluted regions is generally low. In the absence of anthropogenic sources, Cd levels in surface water are less than 1 µg/l. However as much as 3.2 mg/l was detected in ground water resulting from the seepage of Cd from electroplating plants. Maximum concentration of Cd found in surface waters of the USA is about 130 µg/l. 87 A survey conducted in the USA found that surface waters contain Cr in the concentration range of 1 to 112 µg/l with a mean concentration of 14 µg/l. 87 Kopp and Kroner, reported a concentration range of 1 to 280 µg/Cul for surface
waters in the USA with a mean of 15 $\mu$gl$^{-1}$, while Bowen, reported a concentration range of 0.6-400 $\mu$gCu$\text{l}^{-1}$ with a mean concentration of 10 $\mu$gl$^{-1}$ in river water.  

Lead concentrations established, ranged from 1 to 50 $\mu$gl$^{-1}$. For Zn, Bowen, established the concentration range of 0.2 $\mu$g to 1mg$l^{-1}$, while Durum et al, established a range of 10-50 $\mu$gl$^{-1}$ with some samples exceeding 5 mg$l^{-1}$. 

Analyses of heavy metals in Kenyan waters have established moderate to high levels, and at times exceeding the maximum USEPA recommended values as in Ngong river. Other studies have been done on Nairobi river, Ruaraka river, Lake Victoria, and some major rivers flowing into Lake Victoria. The ability of organisms to bioconcentrate metal to high levels poses a real threat of metal pollution higher up in the food chain.

Tables 2.1a and 2.1b below summarize the concentration factor of some metals by some plankton flora in fresh water lakes. Concentration factor is the ratio of the concentration of the substance in the organism to the concentration in the water).

Table 2.1a: Concentration factors in planktons and Brown algae

<table>
<thead>
<tr>
<th>Element</th>
<th>Plankton</th>
<th>Brown algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$8.7 \times 10^4$</td>
<td>$1.7 \times 10^4$</td>
</tr>
<tr>
<td>Cu</td>
<td>$1.7 \times 10^4$</td>
<td>$9.2 \times 10^2$</td>
</tr>
<tr>
<td>Zn</td>
<td>$6. \times 10^4$</td>
<td>$3.4 \times 10^3$</td>
</tr>
<tr>
<td>Pb</td>
<td>$4.1 \times 10^4$</td>
<td>$7.0 \times 10^4$</td>
</tr>
</tbody>
</table>

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Table 2.1 b: concentration factors in macrophytes

<table>
<thead>
<tr>
<th>Macrophyte</th>
<th>Elements</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Fe</td>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>Elodea</td>
<td>1950</td>
<td>8770</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>Myriophyllum</td>
<td>1600</td>
<td>6280</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>Potomogeton</td>
<td>740</td>
<td>4064</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Najas</td>
<td>560</td>
<td>3513</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

Some mollusks and arthropods have been found with a concentration factor of up to hundreds of thousands on certain tissues that are rarely used as food by man. In case of polluted waters, commercial fish were found to contain unacceptable high levels of trace metals, and fish sales from such waters were prohibited. Cd and Hg are among the trace metals that accumulate in some fish species.

Zn, Cu, Pb and Cd have shown a negative correlation to benthic macroinvertebrate species diversity with metal concentration. It has also been demonstrated that dominant species of a periphyton community were eliminated in a eutrophic stream by continuous addition of dosages of 120 µgCuL⁻¹. It has further been established that copper levels of up to 6 µgL⁻¹ make some certain macroinvertebrates more vulnerable to predation, probably by a change in behaviour from the stress caused by metal contamination.

Early life stages of an organism have been found to be more sensitive to pollutants than are adults. The duration and type of exposure have a strong effect on fauna.
Some effects of the trace metals have been summarized in Table 2.2.

Table 2.2: Summary data of some trace metals and their effects on various organisms (concentration in mg/l$^{-1}$)\textsuperscript{30}

<table>
<thead>
<tr>
<th>Metal</th>
<th>Organism</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td><em>Pimephales promelas</em></td>
<td>96-h LC$_{50}$ at 0.63</td>
</tr>
<tr>
<td></td>
<td><em>Salmo salar</em></td>
<td>28-d growth effect at 0.00013</td>
</tr>
<tr>
<td></td>
<td><em>Daphnia magna</em></td>
<td>21-d LC$_{50}$ at 0.005</td>
</tr>
<tr>
<td></td>
<td><em>Tubifex tubifex</em></td>
<td>48-h LC$_{50}$ at 0.03-0.72</td>
</tr>
<tr>
<td></td>
<td><em>Morone saxatilis</em></td>
<td>96-h LC$_{50}$ at 0.0037</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td><em>Morone saxatilis</em></td>
<td>96-h LC$_{50}$ at 30.4</td>
</tr>
<tr>
<td></td>
<td><em>Pimephales promelas</em></td>
<td>96-h LC$_{50}$ at 17.6</td>
</tr>
<tr>
<td></td>
<td><em>Salmo gaidneri</em></td>
<td>96-h LC$_{50}$ at 20.2</td>
</tr>
<tr>
<td></td>
<td><em>Daphnia magna</em></td>
<td>24-h EC$_{50}$ at 1.79</td>
</tr>
<tr>
<td></td>
<td><em>Tubifex tubifex</em></td>
<td>48-h LC$_{50}$ at 0.06 to 4.57</td>
</tr>
<tr>
<td>Cu</td>
<td><em>Salmo salar</em></td>
<td>avoidance at 0.0024</td>
</tr>
<tr>
<td></td>
<td><em>Salmo salar</em></td>
<td>96-h LC$_{50}$ at 0.0048</td>
</tr>
<tr>
<td></td>
<td><em>Daphnia magna</em></td>
<td>21-d LC$_{50}$ at 0.044</td>
</tr>
<tr>
<td></td>
<td><em>Tubifex tubifex</em></td>
<td>48-h LC$_{50}$ at 0.006 to 0.89</td>
</tr>
<tr>
<td></td>
<td><em>Periphyton</em></td>
<td>Population effect 0.06</td>
</tr>
<tr>
<td>Metal</td>
<td>Organism</td>
<td>Effect</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Pb</td>
<td><em>Pimephales promelas</em></td>
<td>96-h LC₅₀ at 5.58</td>
</tr>
<tr>
<td></td>
<td><em>Salmo gaidneri</em></td>
<td>96-h LC₅₀ at 1.2</td>
</tr>
<tr>
<td></td>
<td><em>Daphnia magna</em></td>
<td>96-h LC₅₀ at 0.612</td>
</tr>
<tr>
<td></td>
<td>Invertebrates (general)</td>
<td>Metabolic effect at 0.0001</td>
</tr>
<tr>
<td></td>
<td><em>Tubifex tubifex</em></td>
<td>72-h LC₅₀ at 27.5</td>
</tr>
<tr>
<td>Zn</td>
<td><em>Pimephales promelas</em></td>
<td>96-h LC₅₀ at 2.54</td>
</tr>
<tr>
<td></td>
<td><em>Salmo salar</em></td>
<td>avoidance by young at 0.054</td>
</tr>
<tr>
<td></td>
<td><em>Tubifex tubifex</em></td>
<td>72-h LC₅₀ at 46.0</td>
</tr>
<tr>
<td></td>
<td><em>Algae</em></td>
<td>Population effect 0.05</td>
</tr>
<tr>
<td></td>
<td><em>Lepomis macrochirus</em></td>
<td>96-h LC₅₀ at 1.9</td>
</tr>
</tbody>
</table>

h: hours    d: days

LC₅₀: Lethal effective concentration   EC₅₀: Median effective concentration

From the research findings by various authors extracted from Dallas & Jay, ³⁰ and from the few examples cited above it is evident that Cd is the most toxic element, and Cr (VI) the least toxic. The toxicity of these metals in the aquatic environment is attributed to their active ions. The threshold limiting values are given in the Appendix I.
3.0 EXPERIMENTAL WORK

3.1 Cleaning Procedures and Analysis

3.1.1 Cleaning of Apparatus

Cleaning procedures were adopted from Gems/water Operational Guide, Basset et al. and Golterman et al. All the plastic and glassware apparatus were initially soaked in 2M nitric acid for 48 hours then washed with soap.

500 ml plastic samplers for trace metals and nutrients and glassware apparatus used were then rinsed with aqua regia, followed by tap water and then rinsed several times with distilled water in that order. Drying of glassware was carried out in a hot temperature oven at 120°C.

150 ml plastic containers for COD water samples and related glassware apparatus were rinsed with aqua regia followed by tap water and distilled water in that order and finally rinsed with (1+2) sulphuric acid (i.e. 1 volume of water to 2 volumes of acid). 250 ml
BOD bottles were rinsed with 5M HCl and thoroughly rinsed with tap water followed by distilled water.

The cleaning procedure was repeated after each test. For BOD test, the bottles were kept clean with acidic iodine after each test, and only rinsing with distilled water was done.

3.2 Sampling Stations

The stations were established along the course of River Migori to determine the quality of the water upstream, before the Migori town, within the town and as the river leaves the town. Four stations were selected and marked S₁, S₂, S₃, & S₄ (Fig. 3.1).

Station S₁ was set on River Hibwa, a tributary of the Migori River, approximately 6km upstream from the town. S₁ was designed to establish the water quality characteristics from the agricultural activities, mainly tobacco growing and other subsistence crops. S₂ was located approximately 5km downstream from S₁ just before the River Migori enters the town. S₂ was designed to establish the water quality characteristics from all the agricultural activities upstream as the river enters the Migori town. S₃ was located about 4km downstream from S₂ in the town, and S₄ located at approximately 5km from S₃ as the river leaves the town. S₃ and S₄ were designed to establish the town’s impact on the water quality of the River Migori. Sampling stations were located to determine the effects of agricultural activities (particularly tobacco growing in Kuria district and sugarcane...
Fig. 3.1: Map showing the R. Migori drainage basin land use and the areas under investigation marked by sampling stations S1, S2, S3, & S4.

Source: Survey of Kenya Atlas 1988

Inset Below:
Position of the R. Migori Drainage Basin In Kenya.

Scale 1:1,000,000

Reference:
- Boundary, International
- Boundary, Provincial
- Boundary, District
- Main Roads
- Rivers
- Main Towns
- Other Towns
- Domestic Animals
- Main Food Crops
- Main Cash Crops
growing in Migori district), the various industrial and settlement activities in Migori town on the levels the parameters investigated in the river water.

3.3 Sampling, Preservation and Storage

Sampling methods, preservation and storage were adopted from the Operational Water Guide.\(^7\)

Sampling was carried out in the months of July, August and September 1996. After this sampling was discontinued because of the prevailing drought at the time. The expected long rains from March to May failed, and since we were interested in investigating, particularly the variation of nutrient concentration from the agricultural fields with the weather pattern, we had to wait for the rains. The rains finally came around June 1997 and within a very short time the river swelled dangerously. The rains stopped almost immediately. And when sampling was resumed by July, the volume of the river had subsided to levels just before the rains. Then the \textit{El-Nino} rains came from November and December 1997, swelling the river again. Since the water level did not subside for a long period of time, sampling was not done until January 1998.

A 2.5-liter plastic container, mounted on an iron sampler, painted with rust inhibitor was used. Grab samples were taken mid-stream.
3.3.1 Trace Metals

500 ml of the unfiltered water sample was added to the 500 ml plastic containers from the 2.5-liter plastic sampler at each station, and preserved with 1 ml of concentrated nitric acid. Distilled water blanks were treated similarly. The samples were analysed within the first month of collection.

3.3.2 Nutrients

From the 2.5-liter sampler, about 500-ml of water sample was filtered (Whatman filter paper diameter, \(d = 5.5\) cm, pore size 0.7 \(\mu\)m, Whatman Ltd., England) into 500 ml plastic containers at each station, tightly stoppered and cooled on crushed ice and analysed within 24 hrs. Distilled water blanks were treated similarly.

3.3.3 Chemical Oxygen Demand

150 ml of the unfiltered samples were taken from the 2.5-liter sampler, preserved with 3 ml of (1+2) sulphuric acid, and cooled on crushed ice and analysed within 24 hours. Distilled water blanks were treated similarly.
3.3.4 Biological Oxygen Demand

50 ml of the untreated sample from the 2.5-liter sampler was transferred into two 250-ml containers, each containing about 50 ml dilution water. The mixture was thoroughly shaken, and more dilution water was added to make 250 ml of the mixture. DO was determined for one sample at each station and the duplicate samples were cooled on crushed ice. DO of the dilution water blanks was also determined and duplicate samples were also cooled on crushed ice.

3.3.5 Dissolved Oxygen

Samples for dissolved oxygen, DO were collected using a 500-ml sampling container. The water sample was added into separate 250-ml glass bottles and analysed for dissolved oxygen in the field.

3.4 Analyses of the parameters

3.4.1 Weighing

All weighing was done using an analytical balance (Gebr. Bosch W. Germany) model S-2000.
3.4.2 pH

The pH of the untreated water samples was measured by a portable pH meter, model Hanna Checker 1, Z35,109-1 (Sigma Chemical Co. USA). The pH of the water was determined in the field. About 40 ml of water was added into an 80-ml beaker and the pH determined by the use of a portable battery-operated pH meter. The pH meter was calibrated using commercially obtained buffer tablets (S.d Fine Chemicals, Boisar) as per manufacturer’s instructions.

3.4.3 Temperature

Temperature was determined with a thermometer having the temperature range 0-100°C and an accuracy of 1°C divisions. About 200 ml of the water was transferred into a beaker and the temperature measured immediately after sampling in the field.

3.4.4 Nutrients Analyses

In the analysis of nutrients, the natural colour of the water sample was removed with aluminium hydroxide suspension prepared from ammonium aluminium sulphate (May &
Baker Ltd., Dagenham, England) and concentrated ammonia (Aldrich Chemical Co. Inc. USA) and neutralized with dilute sulphuric acid using bromothymol blue indicator.

3.4.4.1 Nitrite - Nitrogen

Nitrite-nitrogen was determined by the Griess test. A stock solution of AnalaR grade sodium nitrite (BDH, Chemicals Ltd., Poole England) containing 0.4926g/l was prepared, from which a working solution containing 1µg/ml of nitrite-nitrogen, NO₂⁻-N was used to obtain the calibration graph of the standards of the following concentrations (mg/l NO₂⁻-N): 0.5, 0.1, 0.15 and 0.2.

AnalaR grade sulphanilic acid and N (1-naphthyl)-ethylenediamine dihydrochloride, (both from BDH Chemicals Ltd., Poole England) were prepared in strongly hydrochloric acid solutions.

To the clear neutralized samples, standards and blanks, sulphanilic acid was added followed by N (1-naphthyl)-ethylenediamine dihydrochloride and sodium arsenite buffer. The reddish pink colour was allowed to develop for about 15 minutes. The absorbance was then read at 500 nm on the Spectronic-20 spectrophotometer (Milton and Roy Co. USA).
N (1-naphthyl)-ethylenediamine dihydrochloride and sodium arsenite buffer. The reddish pink colour was allowed to develop for about 15 minutes. The absorbance was then read at 500 nm on the Spectronic-20 spectrophotometer (Milton and Roy Co. USA).

3.4.4.2 Nitrate - Nitrogen

Nitrate-N was determined using the Brucine-Sulphanilic acid reagent method.\(^87, 95\)

The working solution, containing 0.01 mg/ml of the nitrate-nitrogen, NO\(_3\)-N was prepared from a stock solution of 0.721 g/l of AnalalR grade potassium nitrate (May & Baker, Dagenham, England). The calibration graph was prepared using solutions of the standards having the following concentrations (mg/l NO\(_3\)-N): 0.4, 0.8, 1.2, 2.0.

50 ml of the neutralized samples, standards and blanks were evaporated to dryness in separate beakers. The residue was taken up with 10 ml of distilled water and transferred to 50-ml volumetric flasks.

To each flask brucine-sulphanilic acid reagent (BDH Chemical Ltd., Poole England) was added followed with 14M sulphuric acid. The flasks were allowed to stand for sometime for the yellow colour to develop, then distilled water was added to the mark. Immediately the flasks were transferred to a water bath at room temperature for the temperatures to equilibrate. Distilled water was then added to the 50-ml mark, and the absorbance of each test solution was read on the Spectronic-20 at 410 nm.
3.4.4 Phosphate - Phosphorus

Phosphate-P levels were determined as the orthophosphate using ammonium molybdate reagent.\(^{87,94}\)

The stock solution of phosphate-phosphorus was prepared from AnalaR grade potassium dihydrogen phosphate (BDH Ltd., Poole England) containing 4.39g/l of the salt. A working phosphate solution, containing 1μg/ml phosphate-phosphorus, PO\(_4\)-P was prepared from the stock solution. The following standards in μg/l PO\(_4\)-P: 50, 100, 200, 300, were used in the preparation of the calibration graph.

50 ml of each sample, blanks and standards were transferred into a series of separating funnels. Dilute sulphuric acid, followed with the ammonium reagent were added to form the phosphomolybdic acid which was concentrated into 10 ml of redistilled hexan-1-ol (both from BDH Chemicals Ltd., Poole, England). Tin (II) chloride (May & Baker, Dagenham, England) reagent was then added to form the blue coloured molybdenum complex. The blue complex in the organic layer was transferred into cells and absorbance obtained at 690 nm.
3.4.5 Dissolved Oxygen Test

The dissolved oxygen, DO was determined using the Winkler’s titration method. The dissolved oxygen in 250 ml of the untreated samples was determined in the field at each sampling station. The DO was fixed with manganese (II) sulphate followed with alkaline iodide azide reagent (prepared from sodium hydroxide, sodium azide (all from BDH Chemicals Ltd., Poole, England) and sodium iodide (Aldrich Chemical Co., Inc., USA)).

The iodine was released on addition of phosphoric acid (88 - 93%). 100 ml of solution containing iodine was immediately transferred to conical flasks and titrated with sodium thiosulphate solution to starch indicator end point. The indicator was prepared from sodium starch glycollate (BDH Chemicals, Poole, England).

3.4.6 Biological Oxygen Demand Test

The dissolved oxygen, DO for the biological oxygen demand, BOD test was obtained by the Winkler’s titration method. Fresh dilution water was prepared at each station from solutions containing 1 ml each of iron (III) chloride (May & Baker Ltd., Dagenham, England); phosphate buffer (prepared from sodium hydroxide, potassium dihydrogen phosphate, calcium chloride (all from BDH
Ltd., Poole, England) and magnesium sulphate (Aldrich Chemicals Co. Inc. USA) in 1 liter of solution.

The BOD was obtained from the difference in DO values of the test samples obtained in the field and the DO values after incubation for 5 days. The differences in the DO values of the dilution water, both in the field and after incubation were obtained. The BOD was worked out from the formula given in Appendix A8.

3.4.7 Chemical Oxygen Demand Test

The chemical oxygen demand, COD values were determined using potassium dichromate as the oxidising agent. 87

20 ml of the treated samples and blanks were added into a series of 250-ml Erlenmeyer distillation flasks. The samples and blanks were corrected for nitrite with sulphamic acid (BDH Chemicals Ltd., Poole, England). Potassium dichromate (Aldrich Chemicals Co. Inc., USA) solution was added followed with sulphuric acid (specific gravity =1.84) containing silver sulphate (May & Baker Ltd., Dagenham, England). The set-up was refluxed for 2 hours, and the experiment was allowed to cool. The mixture in the flask was then titrated with ferrous ammonium (BDH Chemicals Ltd., Poole, England) to ferroin indicator end point.
3.4.8 Heavy Metals Analyses

The procedure for the analysis of the heavy metals was adopted from Golterman et al. 94

Stock solutions of cadmium, chromium, copper and zinc were prepared each containing 1g/l of the metal. Cadmium and zinc solutions were prepared from their respective metals, but chromium was prepared from 2.4239 g/l of the Analar grade ammonium dichromate salt (metals and salt from BDH Chemicals Ltd., England), and copper from 3.8020 g/l of the Analar grade copper nitrate (Farmilalia Carloerba, S.p.A Milano).

Working solutions containing 10 mg/l of each metal solution were used to prepare standards of the following concentration in mg/l:

\[
\begin{align*}
\text{Cd/Zn} & : 0.1, 0.2, 0.3, 0.4 \\
\text{Cr/Cu/Pb} & : 0.4, 0.8, 1.2, 1.6
\end{align*}
\]

The samples and blanks were digested with concentrated nitric acid and 30% hydrogen peroxide, followed with concentrated sulphuric acid. Preconcentration was achieved by evaporation from 250ml to 50ml of treated samples. Filtration was done through sintered glass filters, and volumes corrected with distilled water to 50 ml.
The absorbances were read on an Atomic Absorption spectrophotometer model SpectrAA-10, at the analytical conditions shown in the table below. The recovery rate for the method of preconcentration by evaporation was found to be in the range 53 - 73%.

Table 3.1: Analytical Conditions for Atomic Absorption Spectrophotometer

<table>
<thead>
<tr>
<th>Metal</th>
<th>Slit width (mm)</th>
<th>Wave length (nm)</th>
<th>Flame</th>
<th>L/Range (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.5</td>
<td>228.8</td>
<td>Air-acetylene</td>
<td>0.02 - 2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.2</td>
<td>359.9</td>
<td>Air-acetylene</td>
<td>0.2 - 10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>324.8</td>
<td>Air-acetylene</td>
<td>0.05 - 6</td>
</tr>
<tr>
<td>Pb</td>
<td>1.0</td>
<td>217</td>
<td>Air-acetylene</td>
<td>0.2 - 10</td>
</tr>
<tr>
<td>Zn</td>
<td>1.0</td>
<td>213.9</td>
<td>Air-acetylene</td>
<td>0.05 - 2</td>
</tr>
</tbody>
</table>
4.0 RESULTS AND DISCUSSION

4.1 SUMMARY OF RESULTS

The results of the analyses of the different water samples that were collected over a period of five months are presented in this chapter.

The water samples were analysed for thirteen (13) parameters namely temperature, pH, DO, BOD, COD, NO₂⁻N, NO₃⁻N, PO₄-P, cadmium, chromium, copper, lead and zinc, covering four stations. Five (5) samples were collected from each station and analysed for each parameter. The analytical data for the four stations and for the five sampling months over the study period is summarised in tables 4.1.1 to 4.1.6. Graphical representation of mean levels at the four stations and the mean levels in the five months is shown in figures 4.2.1 to 4.2.13.
Table 4.1.1: Mean Monthly Parameter values and their corresponding Standard Deviations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Jul '96</th>
<th>Aug '96</th>
<th>Sep '96</th>
<th>Jul '97</th>
<th>Jan '98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °C</td>
<td>22.5 ± 2.12</td>
<td>23.2 ± 2.75</td>
<td>23.5 ± 2.60</td>
<td>23.0 ± 2.60</td>
<td>22.0 ± 0.82</td>
</tr>
<tr>
<td>pH</td>
<td>7.56 ± 0.085</td>
<td>7.31 ± 0.296</td>
<td>7.22 ± 0.420</td>
<td>8.06 ± 0.348</td>
<td>7.65 ± 0.137</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>5.58 ± 2.940</td>
<td>3.15 ± 3.018</td>
<td>5.28 ± 3.091</td>
<td>6.52 ± 3.237</td>
<td>7.82 ± 2.238</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>80.55 ± 14.623</td>
<td>46.93 ± 13.442</td>
<td>66.67 ± 4.122</td>
<td>83.34 ± 11.102</td>
<td>135.98 ± 104.66</td>
</tr>
<tr>
<td>NO₂-N (mg/l)</td>
<td>0.056 ± 0.003</td>
<td>0.077 ± 0.032</td>
<td>0.012 ± 0.004</td>
<td>0.028 ± 0.020</td>
<td>0.064 ± 0.054</td>
</tr>
<tr>
<td>NO₃-N (mg/l)</td>
<td>0.196 ± 0.023</td>
<td>0.202 ± 0.059</td>
<td>0.146 ± 0.044</td>
<td>0.078 ± 0.005</td>
<td>0.364 ± 0.015</td>
</tr>
<tr>
<td>PO₄-P (mg/l)</td>
<td>0.203 ± 0.018</td>
<td>0.251 ± 0.009</td>
<td>0.128 ± 0.036</td>
<td>0.052 ± 0.030</td>
<td>0.260 ± 0.143</td>
</tr>
<tr>
<td>Cd (μg/l)</td>
<td>nd</td>
<td>1.79 ± 1.337</td>
<td>nd</td>
<td>0.23 ± 0.392</td>
<td>nd</td>
</tr>
<tr>
<td>Cr (μg/l)</td>
<td>6.67 ± 2.357</td>
<td>3.34 ± 1.668</td>
<td>2.17 ± 3.753</td>
<td>nd</td>
<td>14.08 ± 3.805</td>
</tr>
<tr>
<td>Cu (μg/l)</td>
<td>7.62 ± 10.783</td>
<td>3.63 ± 1.374</td>
<td>nd</td>
<td>4.31 ± 1.857</td>
<td>5.18 ± 3.219</td>
</tr>
<tr>
<td>Pb (μg/l)</td>
<td>nd</td>
<td>80.57 ± 9.939</td>
<td>9.03 ± 6.455</td>
<td>113.63 ± 47.380</td>
<td>3.85 ± 2.842</td>
</tr>
<tr>
<td>Zn (μg/l)</td>
<td>nd</td>
<td>50.23 ± 87.007</td>
<td>nd</td>
<td>66.22 ± 41.361</td>
<td>58.73 ± 86.412</td>
</tr>
</tbody>
</table>

nd = not detected
Table 4.1.2: Mean Parameter values and corresponding Standard Deviations between the dry and wet seasons

[Mean ± S.D]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dry</th>
<th>Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. °C</td>
<td>23.0 ± 2.52</td>
<td>22.0 ± 0.82</td>
</tr>
<tr>
<td>pH</td>
<td>7.54 ± 0.287</td>
<td>7.65 ± 0.137</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>5.13 ± 3.072</td>
<td>7.82 ± 2.238</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>69.37 ± 8.117</td>
<td>135.98 ± 104.664</td>
</tr>
<tr>
<td>NO₂-N (mg/l)</td>
<td>0.043 ± 0.015</td>
<td>0.064 ± 0.054</td>
</tr>
<tr>
<td>NO₃-N (mg/l)</td>
<td>0.155 ± 0.033</td>
<td>0.364 ± 0.015</td>
</tr>
<tr>
<td>PO₄-P (mg/l)</td>
<td>0.158 ± 0.023</td>
<td>0.260 ± 0.143</td>
</tr>
<tr>
<td>Cd (µg/l)</td>
<td>0.50 ± 0.432</td>
<td>0.02 ± 0.000</td>
</tr>
<tr>
<td>Cr (µg/l)</td>
<td>3.04 ± 1.944</td>
<td>14.08 ± 3.805</td>
</tr>
<tr>
<td>Cu (µg/l)</td>
<td>3.89 ± 3.503</td>
<td>5.18 ± 3.219</td>
</tr>
<tr>
<td>Pb (µg/l)</td>
<td>50.81 ± 15.943</td>
<td>3.85 ± 2.842</td>
</tr>
<tr>
<td>Zn (µg/l)</td>
<td>29.11 ± 32.092</td>
<td>58.73 ± 86.412</td>
</tr>
</tbody>
</table>
Table 4.1.3: Significant t-test values and degrees of freedom (d.f) for the number of samples of each parameter between the dry and wet season.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>t</th>
<th>d.f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>0.827</td>
<td>18</td>
</tr>
<tr>
<td>pH</td>
<td>0.784</td>
<td>18</td>
</tr>
<tr>
<td>BOD</td>
<td>1.712</td>
<td>18</td>
</tr>
<tr>
<td>COD</td>
<td>2.318</td>
<td>18</td>
</tr>
<tr>
<td>NO$_2$-N</td>
<td>1.288</td>
<td>18</td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>7.995</td>
<td>18</td>
</tr>
<tr>
<td>PO$_4$-P</td>
<td>2.525</td>
<td>18</td>
</tr>
<tr>
<td>Cd</td>
<td>2.455</td>
<td>18</td>
</tr>
<tr>
<td>Cr</td>
<td>7.984</td>
<td>18</td>
</tr>
<tr>
<td>Cu</td>
<td>0.690</td>
<td>18</td>
</tr>
<tr>
<td>Pb</td>
<td>6.215</td>
<td>18</td>
</tr>
<tr>
<td>Zn</td>
<td>1.059</td>
<td>18</td>
</tr>
</tbody>
</table>
Table 4.1.4: Mean values and corresponding standard deviation at the Four stations over the study period.

[Mean ± S. D]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>S_1</th>
<th>S_2</th>
<th>S_3</th>
<th>S_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. °C</td>
<td>20.9 ± 1.24</td>
<td>23.8 ± 1.60</td>
<td>24.0 ± 1.73</td>
<td>23.25 ± 1.77</td>
</tr>
<tr>
<td>pH</td>
<td>7.60 ± 0.08</td>
<td>7.51 ± 0.50</td>
<td>7.31 ± 0.42</td>
<td>8.00 ± 0.41</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>7.69 ± 1.12</td>
<td>6.85 ± 0.61</td>
<td>6.56 ± 1.22</td>
<td>-</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>3.48 ± 2.06</td>
<td>7.67 ± 1.72</td>
<td>5.68 ± 3.82</td>
<td>7.25 ± 3.89</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>78.13 ± 22.84</td>
<td>115.13 ± 100.23</td>
<td>61.34 ± 15.09</td>
<td>72.77 ± 5.89</td>
</tr>
<tr>
<td>NO_3-N (mg/l)</td>
<td>0.053 ± 0.046</td>
<td>0.057 ± 0.045</td>
<td>0.040 ± 0.022</td>
<td>0.025 ± 0.035</td>
</tr>
<tr>
<td>NO_2-N (mg/l)</td>
<td>0.178 ± 0.140</td>
<td>0.213 ± 0.127</td>
<td>0.249 ± 0.095</td>
<td>0.211 ± 0.193</td>
</tr>
<tr>
<td>PO_4-P (mg/l)</td>
<td>0.217 ± 0.142</td>
<td>0.190 ± 0.113</td>
<td>0.159 ± 0.084</td>
<td>0.111 ± 0.036</td>
</tr>
<tr>
<td>Cd (μg/L)</td>
<td>0.66 ± 1.137</td>
<td>0.50 ± 1.118</td>
<td>0.08 ± 0.148</td>
<td>nd</td>
</tr>
<tr>
<td>Cr (μg/L)</td>
<td>5.04 ± 6.646</td>
<td>5.13 ± 3.326</td>
<td>4.87 ± 6.214</td>
<td>9.13 ± 12.916</td>
</tr>
<tr>
<td>Cu (μg/L)</td>
<td>2.78 ± 3.486</td>
<td>4.65 ± 6.133</td>
<td>3.21 ± 2.777</td>
<td>6.52 ± 0.96</td>
</tr>
<tr>
<td>Pb (μg/L)</td>
<td>33.36 ± 41.577</td>
<td>40.60 ± 53.208</td>
<td>29.04 ± 36.420</td>
<td>84.09 ± 117.246</td>
</tr>
<tr>
<td>Zn (μg/L)</td>
<td>57.02 ± 83.843</td>
<td>46.50 ± 67.488</td>
<td>13.53 ± 23.429</td>
<td>13.05 ± 9.631</td>
</tr>
</tbody>
</table>

- = not done
Table 4.1.5.1: Significance t-test values with corresponding degrees of freedom between Stations over the sampling period

\[ t \ (d.f.) \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( S_1 S_2 )</th>
<th>( S_1 S_3 )</th>
<th>( S_1 S_4 )</th>
<th>( S_2 S_3 )</th>
<th>( S_2 S_4 )</th>
<th>( S_3 S_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp</td>
<td>3.203(8)</td>
<td>3.257(8)</td>
<td>2.431(8)</td>
<td>0.190(8)</td>
<td>0.515(8)</td>
<td>0.678(8)</td>
</tr>
<tr>
<td>pH</td>
<td>0.397(8)</td>
<td>1.517(8)</td>
<td>2.141(8)</td>
<td>0.685(8)</td>
<td>1.694(8)</td>
<td>2.629(8)</td>
</tr>
<tr>
<td>BOD</td>
<td>3.491(8)</td>
<td>1.185(8)</td>
<td>1.915(8)</td>
<td>1.062(8)</td>
<td>0.221(8)</td>
<td>0.644(8)</td>
</tr>
<tr>
<td>COD</td>
<td>0.805(8)</td>
<td>1.371(8)</td>
<td>0.508(8)</td>
<td>1.187(8)</td>
<td>0.943(8)</td>
<td>1.578(8)</td>
</tr>
<tr>
<td>NO(_2)-N</td>
<td>0.139(8)</td>
<td>0.175(8)</td>
<td>1.083(8)</td>
<td>0.759(8)</td>
<td>1.255(8)</td>
<td>0.811(8)</td>
</tr>
<tr>
<td>NO(_3)-N</td>
<td>0.414(8)</td>
<td>0.938(8)</td>
<td>0.309(8)</td>
<td>0.508(8)</td>
<td>0.019(8)</td>
<td>0.395(8)</td>
</tr>
<tr>
<td>PO(_4)-P</td>
<td>0.333(8)</td>
<td>0.786(8)</td>
<td>1.618(8)</td>
<td>0.492(8)</td>
<td>1.490(8)</td>
<td>1.174(8)</td>
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<tr>
<td>Cd</td>
<td>0.226(8)</td>
<td>1.125(8)</td>
<td>1.300(8)</td>
<td>0.825(8)</td>
<td>1.000(8)</td>
<td>1.270(8)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.025(8)</td>
<td>0.042(8)</td>
<td>0.629(8)</td>
<td>0.081(8)</td>
<td>0.671(8)</td>
<td>0.665(8)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.592(8)</td>
<td>0.213(8)</td>
<td>2.397(8)</td>
<td>0.479(8)</td>
<td>0.682(8)</td>
<td>2.666(8)</td>
</tr>
<tr>
<td>Pb</td>
<td>0.239(8)</td>
<td>0.175(8)</td>
<td>0.192(8)</td>
<td>0.401(8)</td>
<td>0.755(8)</td>
<td>1.003(8)</td>
</tr>
<tr>
<td>Zn</td>
<td>0.219(8)</td>
<td>1.117(8)</td>
<td>1.165(8)</td>
<td>1.032(8)</td>
<td>1.097(8)</td>
<td>0.042(8)</td>
</tr>
</tbody>
</table>
Table 4.1.5.2: Tabulated critical t-values with corresponding degrees of freedom (d.f) at 95% Confidence Limit.

<table>
<thead>
<tr>
<th>d.f</th>
<th>( t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2.306</td>
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<tr>
<td>12</td>
<td>2.180</td>
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<td>14</td>
<td>2.140</td>
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<tr>
<td>15</td>
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<td>16</td>
<td>2.190</td>
</tr>
<tr>
<td>18</td>
<td>2.090</td>
</tr>
</tbody>
</table>
Table 4.1.6: The range of values of the parameters at the Four Stations during the study period.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>S₁</th>
<th>S₂</th>
<th>S₃</th>
<th>S₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. °C</td>
<td>20.0 - 23.0</td>
<td>21.0 - 25.0</td>
<td>22.0 - 25.0</td>
<td>22.0 - 24.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.46 - 7.67</td>
<td>6.84 - 8.23</td>
<td>7.00 - 7.78</td>
<td>7.71 - 8.29</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>7.41 - 8.50</td>
<td>6.15 - 7.21</td>
<td>5.70 - 7.78</td>
<td>-</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>1.00 - 6.10</td>
<td>5.70 - 10.25</td>
<td>5.51 - 3.14</td>
<td>4.50 - 10.00</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>61.60 - 117.60</td>
<td>35.20 - 289.10</td>
<td>44.00 - 71.43</td>
<td>68.60 - 76.93</td>
</tr>
<tr>
<td>NO₃-N (mg/l)</td>
<td>0.008 - 0.114</td>
<td>0.012 - 0.128</td>
<td>0.015 - 0.057</td>
<td>0.00 - 0.50</td>
</tr>
<tr>
<td>NO₂-N (mg/l)</td>
<td>0.083 - 0.384</td>
<td>0.076 - 0.365</td>
<td>0.188 - 0.358</td>
<td>0.074 - 0.347</td>
</tr>
<tr>
<td>PO₄-P (mg/l)</td>
<td>0.037 - 0.422</td>
<td>0.032 - 0.338</td>
<td>0.085 - 0.251</td>
<td>0.086 - 0.137</td>
</tr>
<tr>
<td>Cd (μg/l)</td>
<td>0.020 - 6.626</td>
<td>0.020 - 2.501</td>
<td>0.020 - 0.251</td>
<td>0.020</td>
</tr>
<tr>
<td>Cr (μg/l)</td>
<td>0.060 - 15.220</td>
<td>0.060 - 9.134</td>
<td>0.060 - 13.700</td>
<td>0.060 - 18.266</td>
</tr>
<tr>
<td>Cu (μg/l)</td>
<td>0.020 - 8.487</td>
<td>0.020 - 15.250</td>
<td>0.020 - 4.902</td>
<td>6.450 - 6.586</td>
</tr>
<tr>
<td>Pb (μg/l)</td>
<td>0.500 - 81.060</td>
<td>0.500 - 100.260</td>
<td>14.940 - 101.000</td>
<td>10.120 - 166.995</td>
</tr>
<tr>
<td>Zn (μg/l)</td>
<td>0.020 - 185.760</td>
<td>0.020 - 150.700</td>
<td>0.020 - 40.580</td>
<td>6.240 - 19.860</td>
</tr>
</tbody>
</table>
4.2. DISCUSSION OF RESULTS

4.2.1. Temperature

The mean water temperatures rose from 20.9°C at station S1 and reached a maximum at 24.0°C at S3, then slightly dropped to 23.2°C at station S4, Fig. 4.2.1.1. The mean temperature at S2 was comparable to that at S3, which averaged 23.8°C. This observed trend in the changes of levels of temperature between stations could not be linked to any activities that could cause thermal pollution. This trend was explained by the warming effect with the progress of the sunny day. The correlation coefficient, r between the water temperature and ambient temperature was 0.88.

Mean temperature levels between the stations S1, and S2, and S1 and S3 were quite statistical significant (cf. significant index values (S.I.V), Table 4.1.5.1. with the critical S.I.V. Table 4.1.5.2). Samples at station S1 were collected in the morning hours when the temperatures were moderately cool, while at the stations S2 and S3, samples were collected in the afternoon hours, the hottest time of the day. At S4, samples were collected in the evening hour when temperatures were moderately cool but the water temperatures were still warmer.

The mean monthly temperatures were highest during September, at 23.5°C and lowest in January '98, at 22°C, Fig 4.2.1.2. The temperature range over the study period was 20°C - 25°C, with a mean temperature of 23.0°C during the dry season, and 22.0°C during, the wet season. There was no statistical significant difference in the mean levels of temperature between the two seasons, (t = 0.827 d.f = 18).
Fig. 4.2.1.1: Mean Temperature levels at the Four Stations

Fig. 4.2.1.2: Mean Monthly Temperature levels
Temperature values cited from studies of some rivers include; the Nairobi-Athi-Sabaki (Kenya) 15 - 32°C, 8 Nzoia (Kenya) 25 - 30°C, 98 Great Ruaha (Tanzania) 19 - 27°C, 99 the Zambezi (Southern Africa) 19 - 26°C, 100 and Mudi river (Malawi) 20 - 29°C. 101 The temperature values compare well with those obtained for River Migori. These are ambient temperature ranges experienced within the tropics; and even though some rivers like the Nairobi-Athi-Sabaki and Mudi flow through industrial centres within their respective countries, these temperature ranges do not give any indication of thermal pollution.

4.2.2 pH

The pH values over the four stations during the study period ranged from 6.84 to 8.29. The mean pH values were above 7.0 units, and ranged from 7.30 to 8.00 units. The pH values decreased gradually from station S1 to S3 and sharply increased to the highest recorded value at station S4 (Fig 4.2.2.1). The pH values compare favourably well with those obtained from other studies, for example some pH values reported were in the following range:

Nairobi-Athi river systems, 6.9 - 7.6, 8 River Nzoia, 7.3 - 7.8; 98 the Nile (North Africa), 8.0 - 8.9, 102 and the Mudi river (Malawi), 6.0 - 8.7. 101 The pH values fall within the limits recommended by the USEPA, (6.0-8.5). 96 The pH values at each station remained fairly constant as indicated by the small standard deviations, indicating that the river water is well buffered. The changes in pH from one station to another were only significant between stations S3 and S4. S3 is at the town centre and the discharge
Fig. 4.2.2.1: Mean pH levels at the Four Stations

Fig. 4.2.2.2: Mean Monthly pH levels
from the slaughterhouse immediately before the station could probably be a cause for
the slight lowering of the pH at S3.

The mean pH levels during the dry and wet seasons were 7.54 and 7.65 respectively
($t = 0.784$). The highest mean monthly pH level of 8.06 was recorded in July '97. It is
interesting to note that the nitrate and phosphate concentrations were lowest during this
month. The lower concentration of these anions in water could probably have an effect
on the ionization of the water that could possibly have led to fewer hydrogen ions in
solution ($H^+_{(aq)}$) and hence, the higher pH.

4.2.3 Dissolved Oxygen

The mean DO levels were within the range of 6.56 to 7.69 mg/l, which remained fairly
constant throughout the sampling period. The highest mean level was recorded at
station S1 and decreased gradually to 6.85 mg/l at station S2, and was lowest at station
S3. The river at station S1 was more turbulent than at the other stations, which explains
the higher levels of DO due to better reaeration. The DO test was not done for station
S4, because at this point the river is very wide and rocky, making sampling at mid-
stream extremely dangerous. An overall mean of 7.03 mgO2/l was recorded for the
three stations, which represents 96.3% saturation.

The WHO recommends dissolved oxygen saturation of about 80%. 96 The Sondu-Miriu
river in the L. Victoria drainage basin had a DO concentration range of 8.45 to 12.4
mgO2/l; 103 Mukuvusi river, Harare (Zimbabwe) had a mean DO concentration of
5.0mg/l.104 Generally, flowing systems have higher levels of DO due to better
reaeration.
Fig. 4.2.3: Mean DO levels at the Three Stations
4.2.4 Biological Oxygen Demand

The mean BOD$_3$ levels during the sampling period ranged from 3.48 mgO$_2$/l at station S$_1$ and sharply increased to the maximum recorded value of 7.67 mgO$_2$/l at station S$_2$, then fell to 5.68 mgO$_2$/l at station S$_3$ and again rose to 7.25 mgO$_2$/l at station S$_4$.

The changes in BOD levels between stations were only significant between S$_1$ and S$_2$. S$_2$ is on the River Hibwa, the main tributary of River Migori after their confluence. The organic load in the main River Migori before station S2 could have caused the changes in the levels of BOD between S$_1$ and S$_2$. The stations on the main Migori river, S$_2$, S$_3$, and S$_4$ did not show any statistical significant variation (Table 4.1.1). This could also confirm the absence of biodegradable organic matter from any point source within the area of study.

The mean recorded BOD levels at each station throughout the sampling period was above the USEPA recommended limits (of less than 3 mgO$_2$/l). The mean BOD levels are also greater than those expected of unpolluted rivers (2.0-5.0 mgO$_2$/l). This was therefore indicative of some biodegradable organic matter in the river.

It is worth to note that despite the increased water volume of the river, and therefore the expected dilution during the period after the rainy season, BOD levels were generally higher at each station during the period after the rains (mean = 7.8 mgO$_2$/l) than during the dry season (mean = 5.13 mgO$_2$/l). This increase in biodegradable organic matter although not statistically significant was explained by increased nutrient in the river resulting from the run-off containing fertilisers from the cultivated land as well as animal wastes.
Fig. 4.2.4.1: Mean BOD levels at the Four Stations

Fig. 4.2.4.2: Mean Monthly BOD levels
The higher nutrient levels could have supported larger populations of micro-organisms in the river that could have led to higher levels of biosynthesised organic matter. Alternatively, some biodegradable organic matter could have been washed into the river from the catchment areas.

The BOD levels obtained in this study were very low compared to BOD levels (mgO₂/l) reported in other studies are for example the Nairobi-Athi systems (Kenya) 0.1-72, Ngong river 4-230; the Mudi river (Malawi) 2-162; and the River Mukuvusi, mean = 2.8. All these rivers traverse some industrial centres in their respective major towns. BOD levels in rivers in the developed countries such as the Cedar (USA) 2-12, are comparably low even though some of these rivers drain some of the most densely populated and industrialised centres in the world.

4.2.5 Chemical Oxygen Demand

The COD analysed gave mean levels that ranged from 61.34 mgO₂/l at station S₃ to the highest mean value of 115.13 mgO₂/l at station S₂, while the mean values at S₁ and S₄ were 78.13 and 72.77 mgO₂/l respectively (Fig 4.2.5.1). No significant changes in the COD levels were recorded between the stations over the sampling period.

The mean COD level during the dry season was 69.37 mgO₂/l and the mean during the wet season was 135.98 mgO₂/l. There was a significant change in COD levels between the two seasons (t = 2.314, d. f. = 18). Stations S₃ and S₄ recorded the lowest mean COD levels throughout the sampling period as indicated by the small standard
Fig. 4.2.5.1: Mean COD levels at the Four Stations

Fig. 4.2.5.2: Mean Monthly COD levels
deviations at these stations compared to the other two. The higher COD levels at S1 and S2, especially after the rains could be as a result of the wash-off containing non-biodegradable organic matter from the agricultural lands around these two stations. This could also suggest very little input of non-biodegradable organic matter from the town into the river. The absence of major industries with the potential to pollute the river with organic matter could explain these comparatively low levels at S3 and S4. In the analysis of the organic matter carried out, the monthly changes in BOD and COD showed a similar trend (Figs. 4.2.4.2 and 4.2.5.2) and registered a correlation, r of +0.93. Overall, however, the mean COD values throughout the sampling period remained low (WHO limit = 250mg O2/l) suggesting little contamination of the river with organic matter. Comparing the results from other studies such as Ngong river, with COD levels ranging from 23 - 538 mgO2/l, the Migori river is less polluted with organic matter. COD levels in rivers in developed countries are much lower, for example in Po (Italy) the COD levels ranged from 3.0 - 7.2 mgO2/l.

4.2.6 Nitrite - Nitrogen

The nitrite levels in the river water were measured as the nitrite-nitrogen (NO2-N). The mean nitrite levels ranged from 0.025 mgN/l at station S4 to 0.057 mgN/l at station S2. Station S1 recorded a mean NO2-N level of 0.053 mg/l and S2 recorded a mean level of 0.040 mg/l. There wasn't any statistically significant variation in the NO2-N levels between the stations throughout the sampling period, and the levels generally remained low. The almost uniform decrease in the NO2-N concentration downstream from
Fig. 4.2.6.1: Mean Nitrite-N levels at the Four Stations

Fig. 4.2.6.2: Mean Monthly Nitrite-N levels
station S₂ suggested no nitrite input from the town. Nitrite is an intermediate in the
conversion of organic nitrogen to nitrite, and there being little organic matter (and in
the absence of anthropogenic sources) the low levels are understandable. But the
detection of nitrite at all should be of concern because the effects of nitrite to aquatic
dwelling life have been demonstrated at concentrations as low as 0.06 mg/l⁻¹. The maximum
recorded levels at stations S₁ and S₂ on particular sampling days were 0.114 and 0.128
mgN/l respectively.

The mean monthly changes in nitrite-N levels did not show a definite trend. The mean
during the dry season was 0.043 mgN/l and the mean level during the wet season was
0.064 mgN/l. There was no statistical significant variation between the seasons.

Despite these low levels, slightly higher levels were recorded at station S₁ and S₂. The
lowest mean levels at station S₄ suggested very little contamination with nitrite-N, if
any from the town. Figures 4.2.6.1. and 4.2.6.2. show the mean levels at the four
stations and the mean monthly levels over the study period.

There is scarce literature on levels of nitrite-N on Kenyan rivers that has been
published. The Sondu-Miriu river in the Lake Victoria drainage basin recorded a nitrite-N range of
between 0.06-0.08 mgN/l. The Po river in Italy reported nitrite-N levels in the range
0.06-0.2 mgN/l. These levels compare favourably with the findings of this study.
4.2.7 Nitrate-Nitrogen

The mean nitrate-nitrogen concentration levels increased from station S1 (0.178 mgN/l) through to station S2 (0.213 mgN/l) and reached a maximum at S3 (0.249 mgN/l) when it dropped to 0.211 mgN/l at station S4 (Fig 4.2.7.1). The mean levels of nitrate-N between the stations did not show any statistically significant difference. However the slight increase in the levels of nitrate-N from station S1 to S2 was attributed to the contribution from the River Migori before the station S2.

S3 is at the centre of the town. The various domestic washings that are almost entirely carried out in the river could probably have caused higher nitrate-N levels at this station. The mean monthly nitrate-N levels over the sampling period generally decreased from July '96 to the lowest recorded level in July '97. The highest levels were recorded after the rains in January '98 (fig. 4.2.7.2). The mean nitrate-N level during the dry season was 0.155 mgN/l and the mean level recorded during the wet season was 0.364 mg/l. The mean levels between the two seasons registered a significant variation, \( t = 12.995, \text{ d.f.} = 18 \). This variation was explained from the wash-off into the river during the rainy season that contained nitrates from the cultivated lands applied with nitrogenous fertilizers and also from animal wastes. The changes in nitrate levels during the rainy season further confirms the suggested explanation since the nitrate levels gradually decreased from S1 downstream to S4, (Fig 4.2.7.3).
Fig. 4.2.7.1: Mean Nitrate-N levels at the Four Stations

Fig. 4.2.7.2: Mean Monthly Nitrate-N levels
Fig. 4.2.7.3: Nitrate-N levels in the rainy Season
Compared to nitrate-N levels from studies on other rivers, the levels found in the Migori were low. The Sondu-Miriu for instance registered nitrate-N levels in the range of 2.83 to 55.08 mg N/l. The Po (Italy) had nitrate-N levels in the range 0.59 - 2.35 mg N/l. The nitrate-N levels in the Ngong river were in the range 0.12 - 0.91 mg N/l, which was comparable to the River Migori.

The levels of nitrate-N throughout the sampling period remained below the WHO maximum permissible level of 10 mg/l.

4.2.8. Phosphate - Phosphorus

The phosphate-P levels in the river were determined as the orthophosphate, $\text{PO}_4^{3-}$. The observed $\text{PO}_4^{3-}$-P levels ranged from 0.032 - 0.422 mg P/l. The mean levels at the four stations over the study period ranged from 0.111 mg P/l at $S_4$ to 0.217 mg P/l at $S_1$ (Fig. 4.2.8.1.). No significant changes in the levels between the stations were established.

The mean monthly changes in the levels of mean phosphorus followed a similar pattern to that of nitrate-N, (c.f. Figs. 4.2.7.2. and 4.2.8.2). The monthly changes in Phosphate-P and Nitrate-N registered a correlation, $r$ of +0.85.

The mean Phosphate-P level during the dry season was 0.158 mg P/l and the level during the wet season was 0.260 mg P/l. There was a significant difference between the two seasons ($t = 2.575, df = 18$). The same reasons advanced for the elevated nitrate-N levels during the rainy season (viz. wash-off into the river containing phosphate fertilisers from the cultivated fields) could be extended to elevated Phosphate-P levels.

Phosphate-P levels decreased downstream, with higher levels recorded for samples in...
Fig. 4.2.8.1: Mean Phosphate-P levels at the Four Stations

Fig. 4.2.8.2: Mean Monthly Phosphate-P levels
Fig. 4.2.8.3: Phosphate-P values in the rainy Season
the agricultural region, Fig.4.2.8.3.

Phosphate levels (mgP/l) reported in other studies include the Nairobi-Athi river systems, 0.06-0.89, 8 Nzoia, 0.05-0.12, 98 the Rhine (W. Europe) 0.15-0.440 102 and the Amazon (S. America), 0.0-0.03.107

The mean Phosphate-P levels at all the stations exceeded the WHO maximum permissible levels of 0.01-0.05 mg/l.96

4.2.9 Cadmium

The concentration of Cd, within the study period was generally low. A mean concentration value of about 0.661 μg/l was recorded at station S1, and the mean values were decreased gradually to station S2 (0.500 μg/L) and at station S3 was 0.084 μg/L. No Cd was detected at station S4 (Fig.4.2.9.1).

The mean monthly changes in the levels of cadmium did not demonstrate any definite trend, and no Cd was detected in three out of the five months when sampling was done (Fig. 4.2.9.2).

The mean level of Cd obtained in the dry season was 0.50 μg/l and no cadmium was detected at all in all the four stations during the wet season. A significant difference in the levels of Cd (t = 2.455, d. f. = 18) existed between the two seasons, meaning that there was a higher likelihood of detecting some Cd in the dry season.

Cd levels in Kenyan soils have been established to be in the range of 0.25-2.5 μg/g. 37

Earlier studies had established that the composition of elements (in particular heavy metals) in river water approached that of the elemental composition of the soil in the
Fig. 4.2.9.1: Mean Cadmium levels at the Four Stations

Fig. 4.2.9.2: Mean Monthly Cadmium levels
drainage basin. The trace amounts detected in the river water could therefore be attributed to erosional effect of the river in its drainage basin.

4.2.10 Chromium

The mean chromium (VI) concentration values slightly increased from $5.044 \, \mu g/l$ at station $S_1$ to $5.127 \, \mu g/l$ at station $S_2$, then decreased to $4.871 \, \mu g/l$ at station $S_3$, and finally increased to $9.133 \, \mu g/l$ at $S_4$ (Fig. 4.2.10.1.). There was no significant variation in Cr levels in all the stations. The mean monthly Cr levels gradually decreased from $6.67 \, \mu g/l$ in July '96 to its all time low in July '97 before it sharply rose to $14.08 \, \mu g/l$ soon after the rains (Fig. 4.2.10.2). The mean Cr level during the dry season was $3.04 \, \mu g/L$ and during the wet season, $14.08 \, \mu g/L$. There was a significant variation ($t = 7.984$, d.f = 18) between the two seasons. Relatively higher concentrations were recorded in all the four stations after the rains. From Table 1, Cr is on average more abundant in the soil than most other heavy metals. The higher Cr levels in the wet season could have originated from the erosional effect in the drainage basin. Other sources that could have contributed to some Cr contamination could be the various cleaning operations, wash-off from cultivated fields applied with Cr-contaminated phosphatic fertilizers and wash-off containing waste products from burning of petrol (Sec. 1.3.3). The mean Cr levels obtained during the study period were however lower than the WHO limits of $50 \, \mu g/l$. 
Fig. 4.2.10.1: Mean Chromium levels at the Four Stations

Fig. 4.2.10.2: Mean Monthly Chromium levels
4.2.11. Copper

The mean copper concentrations levels recorded over the study period at the four stations were generally low. The mean levels increased from 2.780 µg/l at station S₁ to 4.648 µg/l at station S₂, then dropped to 3.205 µg/l at station S₃ and finally increased sharply to 6.518 µg/l at station S₄ (fig. 4.2.11.1). There was no statistical significant variation of copper levels between the four stations (Table 4.1. 5.1).

The mean monthly copper levels decreased from 7.62 µg/l in July ‘96 and was lowest in September ‘96, then rose gradually to 5.18 µg/l (Fig. 4.2.11.2).

The seasonal changes in the copper mean levels were not statistically significant (t = 0.690, d.f = 18). Under practical considerations, the copper levels were independent of the weather pattern, and the smaller t-values between stations suggested almost uniform distribution in all the four stations. The most likely source for the copper in the river was therefore attributed to natural sources.

The WHO recommends 1000 µg/l as the maximum permissible level of copper content in the water.

Compared with studies on other rivers, the Migori contains very low copper levels. Levels in the range 10-115 µg/l have for example been recorded for the Ngong river. The Mudi river (Malawi) had copper levels ranging from 10 - 90 µg/l and Po (Italy) had copper levels ranging from 0 - 15 µg/l. The mean copper levels recorded in Mukuvusi (Zimbabwe) ranged from 9 - 38 µg/l.
Fig. 4.2.11.1: Mean Copper levels at the Four Stations

Fig. 4.2.11.2: Mean Monthly Copper levels
4.2.12. Lead

The mean lead concentration values increased gradually from stations $S_1$ to $S_4$. The mean concentrations (in $\mu$g/l) were recorded were as follows: 33.365 at station $S_1$, 40.595 at $S_2$, 29.039 at $S_3$ and 84.09 at $S_4$ (Fig. 4.2.12.1). There was no significant variation in the levels of lead between the stations (Table 4.1.5.1). The mean concentration of lead at station $S_4$ was above the WHO maximum allowed limit of 50$\mu$g/l. At one instance or the other, lead levels at each station, as given by the range of values (Table 4.1.6) exceeded the internationally recommended maximum limits.

The seasonal changes in the levels of lead were quite significant ($t = 5.215$, d.f = 18), with higher levels detected during the drier season. This analysis showed uncomfortably higher levels of lead in Migori river during the study period. These higher levels are indicative of lead-contamination of the river. Lead contamination of the environment is ubiquitous and has always been associated with burning of leaded gasoline, the chief contributor of anthropogenic pollution of the environment with lead. In rivers, lead is localised in the sediments and the equilibrium ensuing between the river water and the sediments release the lead into the water. During the dry weather, when the volume of the river is small, lead concentration in the river water become significant as compared to the period soon after the rains when the lead levels decrease due to increased dilution.

Lead levels in Kenyan soils have also been found to be quite high, in the range of 13-341 $\mu$g/g. The higher levels of lead in the river could therefore be as a result of the atmospheric fallout of lead aerosols that are eventually washed into the river, and also
Fig. 4.2.12.1: Mean Lead levels at the Four Stations

Fig. 4.2.12.2: Mean Monthly Lead levels
to the erosional effect of the river on its drainage basin. The relatively higher lead levels at S4 were also attributed to the wash-off of the lead aerosols from the busy Migori-Isebania highway.

Other studies have equally found higher levels of lead in the river water; Ngong river, 41 - 195 μg/l; Mudi river, 10 - 510 μg/l, and Mukuvusi river 270 - 400 μg/l.104

4.2.13 Zinc

The general trend in the changes in the mean levels of Zn from one station to another was very similar to that of Cd (c.f. Fig. 4.2.9.1. with Fig. 4.2.13.1). A correlation, r of + 0.988 between the zinc and cadmium mean levels were established during the study period for the four stations. The mean zinc levels were found to decrease downstream from station S1 (Fig. 4.2.13.1). However no significant changes in the levels of Zn was observed between the stations.

The mean monthly changes in levels of zinc did not follow any definite pattern, (Fig. 4.2.13.2). The seasonal changes in mean levels of zinc, also did not show any statistical significant variation (t = 1.059, d.f = 18).

The mean Zn levels were far less than the maximum allowed levels of 1500μg/l.96 Zn levels in Kenyan soils have been found to vary from 36-290 μg/g.35 The zinc detected in the river could therefore have originated from natural sources. Studies on other rivers have established moderate to high zinc levels compared to the levels established in the River Migori (which ranged from 0-185μg/l): the Ngong river, 13 - 891μg/l; Po river (Italy), a mean of 41 μg/l.106 Mukuvusi river, 9-12μg/l;104 Po river (Italy), a mean of 41 μg/l.106
Fig. 4.2.13.1: Mean Zinc levels at the Four Stations

Fig. 4.2.13.2: Mean Monthly Zinc levels
From these results, the levels of the trace metals except for lead were found to be very low. In the absence of any obvious source of contamination, (such as from industrial sources) the presence of trace amounts were considered as natural. Most of the heavy metals appear as impurities in phosphatic fertilizers. Cd and Zn are examples of the trace metals whose levels have shown to decrease downstream (Fig. 4.2.9.1 and 4.2.13.1). Hence there either was some contribution from the agricultural activities, or the soils in the agricultural lands could have higher levels of Cd and Zn, or both.

Mean lead levels were particularly high at station S4. Depending on the physicochemical form of lead present in the river, this could cause serious health problems to the water users. On average, the parameter levels during the dry and wet seasons were different even though in some cases no significant statistical difference existed.
CHAPTER 5

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

The relative increase in the water temperature from one station to another was attributed to the progressive warming effect of the sun’s heat during the day as illustrated by the strong correlation between ambient temperature and the water temperature.

The pH of the Migori river at the section that was studied was slightly alkaline, the average of the mean being 7.60 units. The small standard deviations per station indicated that the river water is well buffered. This could also be indicative of the absence of any pollution from external sources.

The dissolved oxygen levels were high, an average of the mean being 7.03 mgO$_2$/l. This is expected of a flowing system. Indeed, higher amounts of oxygen were recorded at the stations that were more turbulent.

The biological oxygen demand levels were generally low the average of the mean being 5.98 mgO$_2$/l. The highest level of BOD was recorded at the station where the speed of river was at its lowest. This fact could possibly have allowed more resident time for the
organisms/nutrients leading to comparatively larger amounts of biosynthesised organic matter.

The COD levels were also generally low, with an average of mean being 81.84 mgO₂/l. The trend in the change of the mean COD levels was similar to those of the BOD. These results showed that there was a little but significant amount of organic matter introduced into the river from external sources, especially during the wet season.

The nitrite-N and nitrate-N concentrations were quite low, the average of the mean being 0.044 and 0.213 mg N/l respectively. Given the inconsistencies of the weather, no timely sampling could be planned. Any wash-off from the drainage basin immediately it started raining was probably not accounted for, and this could have led to the low levels, especially of nitrate-N that were obtained. The average phosphate-P concentration was 0.170 mg/l. The changes in the mean levels of phosphate-P decreased downstream from the agricultural potential areas. This fact, together with the changes in the levels of nitrate-N and phosphate-P decreasing downstream from the rich agricultural areas during the rains confirmed the contribution from the agricultural activities in the region towards elevated nutrient levels in the river water.

The levels of heavy metals (in µg/l) were quite low, the mean average being; Cd (0.311), Cr (6.04), Cu (4.288), Pb (46.77) and Zn (32.52). Mean levels of Cd and Zn decreased downstream from the agricultural potential areas. On the other hand the mean levels of Cr and Pb generally increased downstream, ($r = 0.99$) and the mean
levels were highest at S₄. The presence of the trace metals in the river water could therefore be attributed to geochemical factors, some agricultural and town’s activities.

5.2 CONCLUSION

From the results and discussion presented in chapter 4, it was concluded that:

a) The R. Migori, at the section covered in this study, contained significant levels of nutrients (phosphate), organic matter and the trace metals especially lead. The average levels of lead were quite high and on some instances exceeded the maximum allowed concentration. These levels could be dangerous in view of the toxicity of lead. Further, the detection of organic matter, which is associated with water-diseases, makes the river water unsuitable for express domestic use.

b) There was some evidence of elevated nutrient concentration during the wet season. The trend in the levels of the nutrients (nitrates and phosphates) suggested some input from the agricultural activities. The agricultural activities could also have some effects on the distribution of Cd and Zn. Thus, agricultural activities around the region may have an effect on the water quality of River Migori around the Migori town. On the other hand it was not obvious to relate the activities of the town with the changes in the levels of Cd, Cu and Zn. There could however be some contribution of Cr and Pb levels from the town’s activities since the levels of these elements were comparatively high at station S₄, immediately after the town.

The raw river water around Migori town and its surroundings may not be entirely safe for domestic consumption because of the high levels of lead, phosphate, BOD and COD, which were obtained. Lead is toxic. The increase in organic matter with the rains
could be linked to the increase in microorganism population as bacteria and other
disease causing agents. This could probably be one of the reasons for the recurrent
outbreaks of water-borne disease such as cholera and typhoid fever with the advent of
the rains.

5.3 RECOMMENDATIONS

Further research work on the Migori river could include: -

a) Expanding the research work to include the characterisation of organic matter. This
   is necessary because of the presence of faecal matter along the river that could
   introduce dangerous microorganisms as bacteria and protozoan.

b) Speciation studies could be conducted to investigate and establish the chemical
   forms of these trace metals in the river water, especially of lead.

c) An intensive research work to be conducted to cover the whole river up to Lake
   Victoria, and where possible estimate the contribution of the R. Migori to the
   pollution of the lake.

d) Determination of the levels of trace metals in the River Migori sediments.
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In: Regional Seas Reports and Studies No. 45, UNEP.


APPENDIX

I. Threshold Limiting Values (T.L.V.) of the Toxic Heavy Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.L.V. (μg/l)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

II. Statistical Treatment of Data

1. Mean

\[ \text{Mean} \bar{X} = \frac{\sum_{i=1}^{n} X_i}{n} \]

Where \( X_i \) is the \( i \)th term of the determination and \( n \) is the total number of determinations.

2. Standard Deviation

\[ \text{Standard deviation, } S = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1}} \]
The standard deviation was used as a measure of dispersion of the readings obtained.

3. Coefficient of correlation

Coefficient of correlation was used to find out if there was any correlation in the levels of some of the parameters.

\[
\begin{align*}
\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y}) \quad \sum_{i=1}^{n}(x_i - \bar{x})^2 (y_i - \bar{y})^2
\end{align*}
\]

4. t-significance test

\[
t = \frac{X_1 - X_2}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}
\]

where \( S_p \) is the pooled standard deviation.

\[
S_p^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}
\]
The calculated t value was compared with the tabulated values at 95% Confidence Limit. If the calculated t value is greater than the tabulated critical value, one concludes that there was a significant statistical variation.

III. Expression of Results

1. Trace Metals

The relationship below was used to find the concentration of the metals in the different water samples.

\[ C_a (\mu g/l) = (C_t - C_b) \times \frac{50}{250} \]

where \( C_t \) = concentration of test sample in \( \mu g/l \).

\( C_b \) = concentration of blank in \( \mu g/l \).

2. Dissolved Oxygen

The following relationship was used to calculate the dissolved oxygen in the water samples.

\[ DO (mg/l) = \frac{\text{Vol. of 0.0125M of thiosulphate (ml)} \times 101.6}{\text{Vol. titrated (ml)}} \]
3. Biochemical Oxygen Demand

\[
BOD \text{ (mg/l)} = \frac{1000}{250} [S_m - S_t - (D_m - D_t)]
\]

Where

- \( S_m \) = DO conc. of the mixture before incubation.
- \( S_t \) = DO conc. of the mixture after incubation.
- \( D_m \) = DO conc. of dilution water before incubation
- \( D_t \) = DO conc. of dilution water after incubation

4. Chemical Oxygen Demand

\[
COD \text{ (mg/l)} = \frac{(a - b)c \times 8000}{20}
\]

Where

- \( a \) = Vol. of ferrous ammonium sulphate (ml) used for blank
- \( b \) = Vol. of ferrous ammonium sulphate (ml) used for sample
- \( c \) = conc. in (mol/litre) of ferrous ammonium sulphate