DETERMINATION OF SOME CHEMICALLY AND BIOLOGICALLY TOXIC
SUBSTANCES IN UNDERGROUND WATERS IN AREAS SURROUNDING
NAIROBI

A Thesis submitted in partial fulfilment for the degree of
Master of Science at Kenyatta University.
DECLARATION

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

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This work is dedicated to my dear parents, Dixon and Alice, and my brothers Jeremy Musyimi and Victor Musyoka, and my dear sister Rhodah Syombua.
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ABSTRACT

30 samples were collected from areas around Nairobi during the wet and dry seasons of the year 1994. The samples were analysed for heavy metals—cadmium, copper, zinc, lead and manganese, nitrates/nitrites and dissolved organic carbon (DOC) by spectroscopic methods and for the presence of pathogenic bacteria using microbiological techniques.

The overall range for copper, zinc, lead, manganese, nitrates/nitrites and dissolved organic carbon (DOC) during the two seasons in the three divisions were: 0.01-1.30, 0.01-15.50, 0.01-1.00, 0.01-3.30, 0.02-15.00 and 2.00-30.80 respectively. The mean levels of copper, zinc, lead, manganese, nitrates/nitrites and DOC in Kangundo division during the two seasons were: 0.30, 1.90, 0.19, 0.57, 5.60 and 12.26 respectively. In Ngong division, the mean levels for copper, zinc, manganese lead, nitrates/nitrites and DOC during the wet and dry seasons were: 0.13, 0.91, 0.38, 0.21, 2.20 and 5.32 respectively. During the wet and dry seasons, the mean levels for copper, zinc, manganese, lead, nitrates/nitrites in Kikuyu division were: 0.22, 4.81, 0.68, 0.36, 7.93, and 2.20 respectively. All the levels are in pmm.

The highest levels of copper, nitrates/nitrites and DOC were found in Kangundo division. Kikuyu division had
the highest levels of lead, Manganese and zinc. Kangundo division had five wells with pathogenic bacteria, Ngong division had four while Kikuyu had two of all the eleven wells that contained pathogenic bacteria during the wet season. Only two wells in Kangundo contained pathogenic bacteria during the dry season.

Wells and boreholes in Kangundo contained more copper, dissolved organic carbon, nitrates/nitrites than those in the other two divisions. Zinc, lead and manganese were prevalent in water samples from Kikuyu division.

Pathogenic bacteria were more prevalent in water samples during the wet season. There were more bacteriologically contaminated water sites in Kangundo—5 of the 11 contaminated sites during the wet season and all the 2 contaminated sites during the dry season.

Generally the levels of the heavy metals and nitrates/nitrites were high during the dry season while those of dissolved organic carbon were high during the wet season.

The results obtained show that the levels of the heavy metals and nitrates/nitrites are mostly below the maximum permissible levels set by the World Health Organisation (W.H.O.). The highest level of nitrates/nitrites was 15ppm which is below the W.H.O. maximum acceptable limit of 45-50ppm. Highest levels of zinc, lead, manganese and copper were 15.5ppm, 1.0ppm, 3.3ppm and 1.3ppm, respectively. The levels of zinc,
lead and manganese were above the W.H.O. maximum permissible levels of 15ppm, 0.1ppm and 0.5ppm respectively. The highest copper level of 1.3ppm was below the W.H.O. maximum permissible level of 1.5ppm.

The presence of some of these substances at toxic levels revealed that these waters are occasionally contaminated and as such are not as safe as is usually assumed.
CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

About 60% of all the persons in the developing countries live without an adequate supply of drinking water; 75% live without any kind of sanitation facility [1]. Many communities in these countries depend on underground waters for their domestic consumption. In Kenya about 75% of the population lives in the rural areas and the 25% lives in the urban centres and cities. In most cases the rural folks use untreated waters which may contain some chemically and biologically toxic substances.

The cost of consuming polluted water in terms of human suffering is enormous. Diarrhoea, amoebiasis, polio, typhoid and round worm are but a few of the infections introduced by insufficient and polluted water supplies. Unsafe water brings high infant and child mortality and those who survive to adulthood, suffer poor health loss of productivity and shortened life.

The urban minority use water provided by municipal councils and is usually treated to remove pathogenic microbes and suspended matter by chlorination and coagulation methods.
Most manufacturing industries and factories are situated in Nairobi and some of their effluents find their way into Nairobi and Athi rivers while others get into underground waters. This explains why underground water sites in areas surrounding Nairobi were selected for sampling.

Man needs an average of 40-50 litres of water per day for domestic use and personal hygiene. In industrialized nations 400-500 litres per day are common requirements; and since water is scarce tens of millions of women and children in developing countries spend about 8 hours a day fetching polluted water. To meet this drastic demand for water, existing water sources have to be exploited; and especially ground water.

Ground water refers to water from wells and bore holes. Their depths lie approximately between 5-80 metres below the earth's surface [2]. The sources of ground water are underground streams and aquifers.

Ground water is generally a very good source of drinking water because of the purification properties of the soil [3]. It is also used for irrigation and spraying, and where surface water is scarce, it is used for industrial purposes. In many arid and semi-arid zones, it is the main source of water. But although it is more protected than surface waters, ground water appears to be subject to pollution [4]; a phenomenon that can be defined as follows:
Pollution is a modification of the physical, chemical and biological properties of water; restricting or preventing its use in the various applications where it plays a part [5].

Ground waters generally have higher dissolved mineral concentrations than surface waters [6]. This is because of the intimate contact between the carbon dioxide bearing water and the rocks and the length of time of dissolution [6]. Additionally, carbon dioxide may be added to the water in the soil by activities of micro-organisms [7].

Approximately 75% [8] of Kenya's population lives in the rural areas and the water they use is mainly from bore holes, wells, rivers and dams. This water is usually untreated and may contain some chemically and biologically toxic substances [9].

1.1.1 ORIGINS OF GROUND WATER POLLUTION

Ground water pollution is usually traced back to four main origins [7]: industrial, domestic, agricultural and bacteriological pollution, each family being divided up into continuous and accidental types.

(1) Industrial pollution is carried to the aquifer by
(a) Used waters which contain chemical compounds and trace elements such as metals.
(b) Rain infiltrating through waste disposals.
(c) Accidents like the breaking of a pipe line.

(2) Domestic pollution is carried to the aquifer by
(a) Rain infiltrating through sanitary landfills.
(b) Accidents like breaking up of septic tanks.

(3) Agricultural pollution is due to irrigation water or rain water carrying away fertilizers, mineral salts, and pesticides.

(4) Bacteriological pollution mainly originates in domestic wastes such as faecal excretion.

The parameters that are normally studied in ground pollution (or qualification) are presented in Table 1. The presence of these elements and compounds in water does not necessarily mean that it is polluted; and, actually the pollution criteria will depend on the type of use made of the water; for example, the toxic levels of these substances in water used for drinking are different from those of water used for personal hygiene, recreation (swimming pools for instance) or irrigation. In these last cases, the hazards are less well known. There are no norms or international standards or regulations for controlling the levels of toxic substances in water that is not used for drinking. International norms have been recommended by the World Health Organization (1972) for drinking
water quality only and these are presented in Table 2 for Zn, Mn, Pb, Cu, Cd and NO$_3^-$/NO$_2^-$ [10].

<table>
<thead>
<tr>
<th>Metal/Compound/Ion</th>
<th>Cd</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>NO$_3^-$/NO$_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum conc. admissible in ppm</td>
<td>0.01</td>
<td>0.50</td>
<td>15.00</td>
<td>1.5</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td>Maximum conc. proposed in ppm</td>
<td>0.005</td>
<td>0.05</td>
<td>5.00</td>
<td>0.05</td>
<td>0.05</td>
<td>45-50</td>
</tr>
</tbody>
</table>

1.1.2 **TOXIC METALS**

Toxic metals are widely spread in two spheres - the biosphere and the atmosphere [11]. Their natural concentration is rarely such as to raise anxiety. These elements can interfere detrimentally with metabolic
processes of many organisms including man, in a variety of environments, if they are taken in excessive quantities [12].

All chemical elements circulate in the biosphere in characteristic paths between the organism and the environment called biogeochemical cycles [11]. Some of these metals are essential for man in trace amounts [12]; for example, Copper, Zinc and Manganese. However, at high concentrations, these metals become toxic [13]. The other metals, such as lead are regarded as non-essential. Toxic metals when taken in excess may damage cells and inhibit enzyme activities. Specific toxicity of these metals vary widely in man and animals [14]. For example, while copper is an essential element for man in trace amounts, it is lethal to fish and other aquatic invertebrates in levels as low as 0.005-0.025 ppb.

A further special feature of these metals is that they are non-biodegradable [15] and undergo biogeochemical cycle with substantially different residence times in various spheres of the environment. Within this cycle; they will be taken up by man, mainly from food and drinking water [16]. In this respect, toxic metals constitute a health risk; because although some are excreted most have a tendency of accumulating in vital organs [17].

Although it is not possible to quantify the hazards and deleterious effects associated with the
contamination of the environment with trace metals in common use, some elements present greater health problems than others [14].

1.2 ENVIRONMENTAL EFFECTS OF TOXIC METALS

1.2.1 CADMIUM

Cadmium is mostly found associated with zinc in carbonate and sulphide rocks [18]. It is also a by-product in the refining of copper, lead and zinc. Cadmium is applied in a variety of industrial processes like electroplating of iron and steel. It increases the tensile strength and anti-corrosive properties of copper with which it may be alloyed. Cadmium provides many pigments and is a principle component of nickel-cadmium batteries. It is also used in the manufacture of plastics.

1.2.1.1 HUMAN AND ENVIRONMENTAL EFFECTS OF CADMIUM

Cadmium has no known biological function for man and is toxic to all living organisms [19]. Studies of dietary cadmium exposures from several countries indicate that average daily intakes in populations in Europe and U.S.A are 20-40μg/day [20] which is below the maximum level of 70μg/day set by the World Health Organization (W.H.O.). The cadmium content of most fresh
There are a few recorded instances of cadmium poisoning in man due to consumption of water or fish. The most significant example of intoxication is in the Jinstu area of Japan in 1940-1960's - the Itai-Itai disease [21]. Untreated metal mine water had been discharged into local rivers. Portable water was heavily contaminated and was used to irrigate rice fields which in turn became heavily contaminated with cadmium. Some of the prominent effects of cadmium were experienced in lungs, kidneys and bones.

Presently, this element is of great concern because not only is it highly toxic, but its toxicity is cumulative. Experiments in animals have shown that some of the effects of cadmium may be prevented by administration of other metals during or prior to cadmium exposure. For example, cadmium induced anaemia can be treated with excess iron and cadmium induced acute testicular necrosis can be prevented by administration of zinc, cobalt or selenium. These results suggest that the interaction of cadmium with other essential metals like zinc and iron is an important factor in cadmium toxicity. The concentration of cadmium in water that is lethal to fish ranges from 0.01 - 10mg/l [22] depending on test animal, time of exposure, water hardness, pH and water salinity. Because of its high availability and intrinsic toxicity, cadmium ranks among the most toxic metals to man.
COPPER

Copper has been utilized for its ductility, malleability and conductivity properties since ancient times. Copper plays a vital role in all branches of engineering and science. It is used in jewellery, in copper plating or as a base metal for silver and other precious metals such as gold and diamond. Copper compounds are used as insecticides, fungicides and molluscicides [23].

The total global mine production of copper has been estimated to be $3.07 \times 10^6$ metric tonnes annually. The total flux of copper released into the atmosphere is approximately 75,000 metric tonnes a year of which 5,000-13,000 tonnes are deposited into the oceans through wet and dry depositions [24].

HUMAN AND ENVIRONMENTAL EFFECTS OF COPPER

Copper has been identified in all living organisms. It is an essential [12] trace element to healthy life of many plants and animals; usually occurring as part of the prosthetic group of oxidising enzymes. Copper is also essential in a number of important proteins including hemocuprein and hepatocuprein.
For many invertebrates, copper is the key component of the respiratory pigments. Copper is also believed to act as a catalyst in some stages of haemoglobin synthesis, although it does not enter into the structure of haemoglobin itself. Copper improves the utilization of ammonia sources of nitrogen, resulting in improved growth in plants.

The dietary content of most western diets is 2-5mg of Cu/day. The total amount of copper in a normal adult is about 72mg [25]. Soluble copper levels in uncontaminated fresh water range from 0.5-10µg/l. Copper is not acutely toxic to man. Only inordinately large amounts of orally ingested copper are toxic. Abnormally high liver copper levels are characteristic of a number of diseases in man [26]. These include anaemia, herechromatosis, cirrhosis and yellow atrophy of the liver, tuberculosis and Wilson's disease.

Copper in water is exceedingly toxic to aquatic biota, in contrast to low toxicity to mammalian consumers of water [27]. Concentrations as low as 0.005-0.025µg/l are lethal to some invertebrates and fish specimens within four days. Toxicity of copper in plants is generally manifested as general chlorosis and stunting of growth.

1.2.3 LEAD

Lead is a metal which is extensively used, the
world production in the early 1970's being about 4 million tonnes [11]. This metal has been used by man for many thousands of years [19] and can be regarded as a long standing environmental contaminant. Lead is used for piping, building materials, solders paint, ammunition and castings. In the recent times, lead has been used mainly in storage batteries, chemicals, pigments and as an additive to gasoline.

Mining, smelting and refining of lead as well as the production and use of these lead-based products give rise to release of lead into the environment [28]. Automobile exhausts account for about 50% of the total inorganic lead taken by man; other major anthropogenic inputs include non-ferrous metal production.

1.2.3.1 HUMAN AND ENVIRONMENTAL EFFECTS OF LEAD

Human exposure to lead occurs through air, water and food [29]. The amount of lead naturally present in uncontaminated waters is about 3µg/l. Typical dietary lead intake lie in the range 100-500µg/day for adults. Surface as well as drinking water levels are usually below 1µg/l. However, higher concentrations in tap water are encountered in soft water areas where the plumbing system is based on lead pipes and may occasionally rise to over 1µg/l. Lead is taken and retained by living organisms and hence the lead content of the human body reflects the extent to which lead is present as a
contaminant in the environment [16]. The major human effects of lead are manifested in three organ systems—the haematological system, the central nervous system and the renal system [17]. The toxicity of lead is based on the fact that it is a potent enzyme inhibitor because it binds sulphydryl groups.

The toxicity of lead to aquatic biota indicates a marked difference between the chemical forms of lead [30]. Both inorganic and organic forms of lead are relatively non-toxic at levels up to 5ppm. There is often little accumulation of lead in marine and fresh water species and consequently lead is not a threat to fisheries except in cases of extreme pollution.

1.2.4 MANGANESE

Manganese is one of the elements that occur in fairly large quantities in the earth's crust and was first isolated in 1774 [18]. World production of manganese was about 18 million tonnes in 1969 and rose to 27 million tonnes in 1975.

About 95% of the world's production of manganese is used in metallurgy of ordinary steel [18]. It is also used in dry batteries, manufacture of driers for paints and varnishes, as a decolourizer in glass industry and for manufacture of manganese salts such as permanganates and manganates. Organo-metallic fuel additives are a minor source at present, but could significantly
increase exposure if they gain widespread use.

1.2.4.1 HUMAN AND ENVIRONMENTAL EFFECTS OF MANGANESE

Manganese is essential for normal growth, skeletal formation, and for normal reproductive function in mammals and poultry. It has been shown to be necessary for the synthesis of chondroitin sulphate in chicks [31]. Deficiency states have been induced in animals by feeding them with manganese deficient diets.

An estimated 3-7mg of manganese are ingested daily with a well balanced diet. Nuts and cereals are richest in manganese, followed in order by dried fruits, roots, fresh fruits, non-leafy vegetables, animal tissue, poultry and poultry products, fish and sea foods [32].

Although possible manganese deficiencies in man had not been demonstrated until fairly recently, Schroeder and his co-workers [33] had been of the opinion for a long time, that certain disease states, for example, diabetes, pregnancies involving nervous instability and convulsions, disorders of bony and cartilaginous growth in infants and children, rheumatoid arthritis, certain types of sterility in males and females should be investigated for possible manganese deficiencies.

One case of apparent manganese deficiency occurring in a human volunteer in a vitamin K deficiency study was
reported by Doisy [34]. Changes in hair and beard colour, low hair growth and weight loss were noted. This clinical picture was duplicated in chicks fed on a similar diet. The experiment was not repeated in other humans however.

Chronic manganese poisoning is a hazard mainly associated with mining activities, dry-cell battery industries and in welding. The disorder is characterised by psychological and neurological [35] manifestations. In chronic manganese poisoning (manganism), victims exhibit a psychiatric disorder characterised by irritability, difficulty in walking, speech disturbances and compulsive behaviours that may include running and fighting. Additional to these central nervous system effects, liver cirrhosis is frequently observed. Victims of chronic manganese poisoning show a tendency of recovering slowly once removed from excessive exposure [34].

1.2.5 ZINC

The world zinc reserves are estimated to be 290 million metric tonnes and the largest reserves are in Canada, U.S.A., Australia and the former Soviet Union. It ranks fourth [18] among the metals next to steel, aluminium and copper in annual global consumption. In 1977, the world consumption was estimated at 5693 thousand metric tonnes.
Zinc finds industrial applications in galvanic protection of structural steel, as a reinforcing agent for rubber, in viscose rayon manufacturers, in the manufacture of brass and other alloys and fungicides that contain zinc.

1.2.5.1. HUMAN AND ENVIRONMENTAL EFFECTS OF ZINC

Zinc has been considered an essential element for mammals since Raulin [36] in 1869 demonstrated that it was necessary in the nutrition of the mould *Aspergillus niger*. Its role as an essential nutrient for man became established following investigations by Prasad et al. in Iran and Egypt [37].

More than twenty different zinc metallo-enzymes have been identified. These include carbonic anhydrase and alcohol dehydrogenase. Zinc plays a vital role in the biosynthesis of nucleic acids, RNA polymerases and DNA polymerases. Thus zinc is involved in the healing process of tissues in the body. A number of other physiological processes, including hormone metabolism, immune responses and stabilization of ribosomes and membranes require zinc [38].

Human intake of zinc is via foodstuff and water [16]. The most reported daily intakes of zinc range from 8-14mg. The W.H.O. has recommended daily, dietary zinc intakes ranging from 6mg (infants) to 27mg (lactating mothers) With regard to zinc intoxication
acute zinc toxicity has been observed in renal failure following haemodialysis, characterised by nausea, vomiting, fever and severe anaemia [40].

The presence of zinc in fresh water in other than trace amounts is known to have toxic effects of varying intensities to aquatic organisms. Acute toxic conditions often kills fish [41]. The actual course of death is due to direct damage of gill membrane by ionic zinc which leads to collapse of weakened pillar system and consequently restricts blood flow through the gill capillaries. Plants are badly affected by high levels of zinc, unless they happen to be the species that are zinc tolerant.

1.2.6 TOXIC METALS IN WATER

Water is essential for both the sustenance of life and most manufacturing processes, and is particularly susceptible to contamination by heavy metals [29]. Natural processes such as weathering of rocks, soil and volcanic activities and windblown dust continuously add heavy metals to natural waters. In addition there are now increasing large quantities being added by man's activities. Anthropogenic sources of pollution include those associated with fossil and coal combustion, industrial effluent, solid waste, sewage effluent disposal, sludge disposal, fertilizers, mining and metal processing [42].
17

Industrial effluent, solid waste, sewage effluent disposal, sludge disposal, fertilizers, mining and metal processing [42].

Heavy metals are present in trace amounts in most natural waters, with concentrations generally being less than 1μg/l. The low concentration of trace elements in natural waters is due to adsorption [43] of ionic or dissolved forms of the trace elements on particular matter such as clay minerals, hydrous iron and manganese oxides and organic particulates. Sedimenting of particulate organic matter leads to the accumulation of heavy metals in the sediments of surface water. The amounts of trace elements adsorbed increases gradually with pH. Other process capable of limiting soluble trace elements concentrations in natural waters include co-precipitation and uptake by biota.

1.3 NITRATES AND NITRITES IN DRINKING WATER

The presence of nitrites in water originates from nitrates. The chief source of nitrates is from farmlands where they are used as fertilizers [44]. Nitrates are easily converted to nitrites by heat and intestinal bacteria [45]. The W.H.O. acceptable levels for nitrates in drinking water are 50-100ppm, but levels above 100ppm are not recommended [45]. A slightly lower W.H.O. international standard of less than 45ppm makes allowance for higher fluid intake in hotter climate
In 1977, a W.H.O. European working group on health hazards from drinking water proposed an adoption of 50ppm as the maximum acceptable levels for infants and 100ppm as the maximum for the population as a whole. Nitrates are not significantly removed by conventional water treatment and techniques for reducing nitrate levels in drinking water and sewage effluent is the subject of considerable research worldwide.

1.3.1 HEALTH EFFECTS OF NITRATES AND NITRITES

Nitrates themselves are not highly toxic but they are easily converted into the more toxic nitrites by intestinal bacteria and heat in the stomach. This correlation emphasizes the fact that the determination of nitrites in drinking water cannot be divorced from nitrates.

That excessive quantities of nitrates in drinking water present a health risk to young artificially fed babies was recognised since the first cases of cyanosis due to methaemoglobinaemia [47] were discovered by Comly in 1945. Low gastric acidity in infants permits the growth of nitrate-reducing bacteria in the upper gastric-intestinal tract; allowing ingested nitrates to be reduced to nitrite [48]. The effect is enhanced in the presence of infection causing diarrhoea. On absorption the nitrite combines with haemoglobin to form methaemoglobin, which cannot transport oxygen. The
infant suffers from cellular anoxia, manifested as clinical cyanosis; when approximately 10% of the total haemoglobin has been converted to methaemoglobin [49]. Intravenous injection of methylene blue and ascorbic acid have proved useful in treating methaemoglobinaemia, though survival is rare when more than half of the total haemoglobin has been destroyed. There are other factors that render infants under three months of age particularly susceptible to the development of methaemoglobinaemia from nitrates/nitrites in drinking water. In addition to their low gastric acidity which allows coliform organisms to flourish, infants have a higher fluid intake in relation to their body weight than adults. Foetal haemoglobin, which predominates in new-borns, is more readily oxidized by nitrites than haemoglobin and the enzyme systems responsible for the reduction of methaemoglobin are not fully developed at birth. Nitrates may be concentrated by repeated boiling of water for feeds and bacterial contamination of water itself or dried milk powder may increase the potential for nitrate reduction.

Early weaning onto nitrate-rich vegetables such as spinach and medication with drugs such as bismuth nitrates prescribed for infantile diarrhoea, may provide additional sources of nitrates.

Since 1945, some 2000 cases of methaemoglobinaemia have been reported in world literature [50] with a case fatality of 8%. The results of surveys by Walton in
U.S.A. in 1951 [51], by Sattelmacher in 1962 covering 14 countries [52] and by Simon et al. in Germany in 1964 [53] suggest that the majority of the cases of methaemoglobinemia have occurred where nitrate/nitrite levels have exceeded 100 ppm. There are rare cases where the nitrate levels were less than 50 ppm.

Most of the methaemoglobinemia cases reported in literature have been associated with private and bacterially contaminated wells [49]. At present doubts remain about the correlation between the concentration of water-borne nitrates and the frequency of cases of methaemoglobinemia. By reviewing the situation in 1974, the international standing committee on water quality and treatment concluded that there was insufficient evidence to allow raising the permitted level of 45-50 ppm and the maintenance of this standard provided the margin of safety [45].

Shuval and Gruener [54] concluded from their studies that nitrates and nitrites are more toxic than is generally recognised. Laboratory experiments with rats showed that transplacental passage of nitrites can occur causing raised methaemoglobin levels in the foetus and impaired growth. Exposure of mice to nitrites in drinking water caused behavioural effects such as lowered motor activity and increased aggression, and rats chronically exposed to nitrite showed thinning and ballooning of cardiac blood vessels.
Some evidence that nitrates may affect the central nervous system in human beings was produced by Petukhov and Ivanov [55] when they studied 39 Russian children whose drinking water contained 105ppm, as compared to another group of children whose drinking water contained 8ppm.

Current concern on rising nitrate levels in drinking water stems from the fact that nitrites, derived from bacterial reduction of ingested nitrates may react in vivo with secondary nitrogen compounds occurring naturally in certain foods to form N-nitroso compounds [56]. These compounds are potent carcinogens when administered to laboratory animals but as yet they have not been shown to be the cause of any human cancer.

1.4 PATHOGENIC MICROBES

Our world is populated by invisible creatures too small to be seen by the naked eye. These life forms, the microbes [57] may be seen with the aid of a microscope. Despite their small size, the effects of microbes on human beings and the world in general are critical for maintaining life on earth. Microbes are grouped into six categories:

(i) Protozoa (ii) fungi (iii) cyanobacteria (iv) bacteria (v) virus and (vi) microscopic algae. In this project, only pathogenic bacteria have been studied.
1.4.1 MICROBES IN THE ENVIRONMENT

Microbes exist virtually everywhere [58-59]. They are found in food, air, water and soil. The air we breathe carries a wide variety of microbes. Their varied nature allows them to survive in very unlikely environments. Microbes have been found in the air miles above the earth, in natural hot springs at 90°C and at least one type grows well at 250°C. In the present study only coliforms (bacterial) which exist in water have been screened.

1.4.2 MAN AND WATER RELATED DISEASES

Waterborne diseases are those transmitted through the ingestion of contaminated water, and acts as the passive carrier of the infectious or chemical agent. The classic waterborne diseases, cholera and typhoid fever, so frequently observed in the past in densely populated areas of the world, have been effectively controlled by the protection of water sources and treatment of contaminated water supplies. These classic diseases gave water supply its reputation as an important factor in the reduction of infectious diseases [60]. Diseases
caused by viruses, protozoa and helminths may also be transmitted by contaminated drinking water. However, it is important to note that these diseases are transmitted through faecal-oral route from man to man or animal to man with water being one of the several possible routes of infection.

Some of the diseases associated with coliform bacteria are: cholera, diarrhoea, dysentery and typhoid [61].

1.5 DISSOLVED ORGANIC CARBON

According to Thurman 1985 [9] total organic matter comprises Dissolved Organic Carbon (DOC) that can pass through a 0.45μm silver or glass fibre filter and is the most important term used in the study of organic carbon.

Sometimes the presence of organic matter in water may be noticed by its colour. Colour is not a clearly defined term but in New Zealand, colour is listed as an aesthetic parameter [62], with the highest desirable level of 5 T.C.U. (True colour units).

Colour is an aesthetic parameter in potable waters and is as such not thought to lead to adverse health effects. It is listed because it is a quality of water that is likely to affect the consumers appreciation of the water. The removal of colour is one reason why water is treated. Therefore, colour is an indication of the
effectiveness of water treatment. Apart from visual displeasure, the presence of organics giving rise to colour can cause problems during disinfection. Consumers are not concerned with the visual displeasure of water but about the possible health significant organics that may be in water. It is generally assumed that most colour in potable waters is due to naturally occurring organic matter such as fulvic and humic acids and tannins. Fulvic and humic acids are heterogenous mixtures of organic acids, alcohols, aromatics and alipatics.

One good feature of these organics is that they are biodegradable and their fate in water is governed [63] by physical, chemical, biological and environmental factors. These organics are leached into drinking water from the soil and dead plant and animal [64-66] remains. Some of these organics are toxic, mutagenic and carcinogenic [64]. Organic substances occur in the environment either as a result of natural processes or their introduction by human activity. Natural sources contribute the majority of organic materials in natural waters via decay of vegetation and animal tissues, animal excretion, photosynthetic by-products and extracelluar release of organic matter by plankton and aquatic macrophytes. Humic substances are by far the most frequently occurring natural material in drinking water supplies.

Much of the mutagenic activity associated with
organic by-products of disinfection results from the reaction of the disinfectant with precursor organic matter in the water source which is of unknown chemical structure.

All disinfectants produce organic by-products. The structures of some by-products are known. The extend and rate of reaction are dependent upon water characteristics. There may be a wide variety of possible reaction pathways and products. Identification of specific by-products is difficult and costly [65]. The total environmental impact of the reaction by-products is not yet established and is under active investigation.

1.6 OBJECTIVES

1. To determine the consumable levels of
(a) toxic metals- cadmium, copper, lead, manganese and zinc.
(b) nitrites/nitrates, and
(c) dissolved organic carbon in underground waters in areas surrounding Nairobi.

2. To screen the water for the presence of pathogenic coliforms.

3. To compare the levels of these toxic metals and nitrates/nitrites with those set by World Health Organisation as the acceptable standards.
LITERATURE REVIEW

1.7 DETERMINATION OF TOXIC METALS IN WATER

1.7.1 Several methods have been used to determine heavy metal concentrations in water. These can be classified into major groups as:

1.7.1.1 CLASSICAL METHODS

These involve measurements of mass (gravimetric analysis) and volume (volumetric analysis). Both methods are used to determine heavy metals in water. However, for gravimetric analysis, pretreatment by separation is necessary [67]. One of the major limitations of classical methods is their low sensitivity and are not recommended for trace analysis.

1.7.1.2 ELECTROCHEMICAL METHODS

In this group, polarography [68-69] and ion selective electrodes [70] have been applied for the determination of heavy metals in water and other materials. Each analytical method has its own advantages and disadvantages, for example polarography is very sensitive to solution composition, dissolved oxygen and
capillary characteristics. Also impurities in the background electrolyte limit sensitivity; but the impurities can be removed by constant potential electrolysis[71].

Although the inorganic tradition is particularly strong in electroanalytical determination of metal ions, many organic compounds can also be determined directly. The electroanalytic controllable parameter of potential is similar to the spectroscopic controllable parameter of wavelength in that it permits adjustable selectivity in analysis; but the selectivity of electroanalytical is normally inferior to that of spectroscopic methods [72].

1.7.1.3 SPECTROSCOPIC METHODS

Several techniques developed in this category are based on the interaction of atoms with radiation permitting quantitative determination of elements. Some of these are colorimetry [70], fluorometry and mass spectroscopy [73], x-ray spectroscopy [74], fluorescence absorption spectrophotometry [75], arc emission spectroscopy and inductively coupled plasma [76] and Atomic Absorption Spectrophotometry (AAS) [77].
1.7.2 ATOMIC ABSORPTION SPECTROPHOTOMETRY

Atomic absorption spectrophotometry (AAS) is an analytical technique for determination of elements, based upon the absorption of optical radiation by free atoms in the gaseous state. Interaction of free atoms with various forms of energy results in three very closely related spectroscopic phenomena which can be used for analysis: emission, absorption and fluorescence. AAS has very high specificity, sensitivity and rapidity.

The use of atomic absorption in analytical chemistry began in the forties, when it was applied in the determination of mercury in laboratory air. It was Walsh who recommended that AAS can be extended to less easily vaporised elements, for example, transition metal elements [77]. Hollow cathode lamps or gas discharge tubes served as background sources of radiation. This led to improved instrumentation, more reliable sources of radiation, hotter flames and non-flame atomizers which enabled the technique to be extended to every metallic element in the periodic table. From that time, interest in the method has risen steadily and since 1957, commercial instruments for AAS have appeared in increasing numbers.
1.7.2.1 THEORY OF ATOMIC ABSORPTION SPECTROPHOTOMETRY

Atomic absorption is a physical process involving the absorption, by free atoms of an element, of light at a wavelength specific to that element. Absorption of light is associated with the transition of one steady state to another. For example, for the steady state 1 and 2, with energies $E_1$ and $E_2$, respectively, where $E_2 > E_1$, the transition $1 \rightarrow 2$, results in absorption of light radiation and the transition $2 \rightarrow 1$ results in emission of radiation with frequency;

$$\nu_{1 \rightarrow 2} = \frac{E_2 - E_1}{h} \quad \text{(i)}$$

where $h$ is Planck's constant.

The $1 \rightarrow 2$ transitions are always stimulated by absorption of external radiation. This phenomenon forms the basis of atomic absorption spectrophotometry (AAS).

For an unexcited atom, each electron is in the ground state otherwise it is excited. The proportion of the excited to ground state atoms in a population at a given temperature is given by the general statement of
Maxwell-Boltzman law:

\[ \frac{N_1}{N_0} = \frac{g_1}{g_0} \exp \left( \frac{E_0 - E_1}{kT} \right) \quad \ldots \ldots (ii) \]

Where,

- \( N \) is the number of atoms in states 0 or 1,
- \( g \) is the statistical weight for the state 0 or 1,
- \( T \) is absolute temperature, and
- \( k \) is the Boltzman constant.

0 and 1 represent ground and excited states respectively.

At most temperatures likely to be encountered in flames and electrothermal atomizers, all the atoms with electrons in higher states than the first excited state can be neglected. Unless \( T \) is very large, the exponential term is very small.

The specific wavelengths at which an atom with their valency electrons in the ground state can absorb radiation are called resonance wavelengths.

To determine how much light is absorbed by a cloud of atoms, consider a parallel beam of light, at a resonance wavelength for all the atoms concerned striking a cell with \( N \) atoms. Let the cell be of unit cross-sectional area and the intensity of incident light be \( I_0 \) watts per unit area enter the cell. The intensity remaining after absorption is given by,
The expression $I_o/I_1$ is defined as absorbance. \( kL \) is the product of the absorption coefficient \( k \) and the cell length \( L \), which is proportional to the number of atoms in the cell. For this reason, absorbance is the preferred read-out mode of modern atomic absorption spectrophotometers, giving a direct relationship between absorbance and concentration. This relationship [equation (iv)] is known as Beer-Lambert's law.

Hence an establishment of a calibration curve by plotting absorbance against concentration forms the basis of quantitative analytical technique for AAS.

1.7.2.2 INSTRUMENTAL PRINCIPLES OF AAS

The most important components of AAS are:

(a) Light source
This emits narrow resonance line profile with little background noise and should have a stable and reproducible output of sufficient intensity to ensure high signal-to-noise ratios. The source should be easy to start, have a short warm-up time and a long shelf life.

(b) Atom cells

They produce atomic vapour of the metal to be determined. Commonly used atom cell atomizer for AAS is flame, although significant amount of analytical work is performed by electrically heated graphite atomizers. The flame is required to produce ground state atoms and air-acetylene or nitrous-acetylene flames are frequently used. For elements that can form refractory compounds, nitrous-acetylene flame is used since it produces high temperatures.

(c) Monochromators

This is a wavelength selector that isolates the resonance line from the non-absorbing lines situated close to it in the spectrum. Such lines may originate from the metallic cathode or the lamp fill gas and molecular emission and background radiation that
originate from the flame. Optical gratings are more often used as monochromators than prisms because the performance of the former is constant throughout the spectrum. However, the latter have high performance in ultraviolet region.

(d) Detector, amplifier and read-out systems

Detectors in modern instruments are made of photomultipliers having cathodes coated with photosensitive materials that amplify optical signals received from the monochromators. The photons received strike the photosensitive material and eject electrons. Each electron produced repeats the process until an amplification factor of $10^6$ or greater is achieved. After amplification, the signal is read out on an analogue or digital display. In modern instruments, read-out facilities may be handled by an inbuilt microprocessor.

1.7.3 DETERMINATION OF DISSOLVED ORGANIC CARBON

Most conventional methods for measuring dissolved organic carbon (DOC) concentrations in fresh water either require specialized equipment or involve time consuming chemical oxidation procedures [78]. An alternative technique is to measure the absorbance of
water at a specific wavelength and equate this to established DOC/absorbance relationships [79-82].

Lewis and Tyburczy (1974) investigated the validity of these relationships at a number of wavelengths and concluded that absorbance at 360nm provided maximum sensitivity and minimum variability [83]. The present study evaluates the relationship between DOC concentrations and absorbance at 360nm in water samples.

The regression equation

\[ \text{DOC (gM}^{-3}) = 59.6 \times \text{Ab} + 1.9 \]

where gM\(^{-3}\) are grammes per cubic meter, and Ab is absorbance; reliably predicted DOC concentrations within the range 1.6 - 43.2 gM\(^{-3}\) [66,84-86]. This relationship is similar to that observed for Venezuelan and South eastern United States waters indicating that it may have widespread utility for estimating DOC concentrations in soft waters where DOC is dominated by humic substances.

1.7.3.1 DISSOLVED ORGANIC CARBON (DOC) IN UNDERGROUND WATER SOURCES

It is generally assumed that DOC in potable waters is due to naturally occurring organic matter such as
fulvic and humic acids, and tannins. Smaller organics are less likely to give rise to visible colour, because they do not contain chromophores that absorb in the visible region. The UV-visible spectrum of natural organic matter often shows little more than a featureless curve that increases in intensity with decreasing wavelength.

There are many types of chromophores that can give rise to absorption bands in the UV region. Absorption arises from $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electron transitions involved in multiple bonded units such as $\text{NO}_2^-$, $\text{C}=$-$\text{C}$, $\text{C}=$-$\text{O}$ and lone pair(s) of electrons (-OH, -OR, -NH$_2$). Carboxylic acids, aromatic acids and phenolics have absorption maximum in the 190-280nm region.

Humic and fulvic acids are heterogeneous mixtures of organic acids, alcohols, amines, aromatics and aliphatics. They are large molecules that contain many of these functional groups, in close proximity and sometimes distant enough for them to behave as discrete entities. When behaving as discrete entities, they are likely to have absorption maximum in the UV region 180-280nm.

When in close proximity, they may be highly conjugated and give rise to visible colour. Chromophores are defined as structural units which absorb at selective wavelengths. Even small structural changes to
these units can bring about significant changes in the wavelength of the radiation absorbed. Structural changes may arise from processes such as pH change leading to protonation/deprotonation reactions, ionic strength variations (unwinding or coiling of large organics), or chemical reactions such as isomerism, complexation or oxidation.

1.7.3.1.1 Effect of pH

pH affects the acid-base properties of many naturally-occurring organics. Protonation and deprotonation reactions affect the electron transfer bands, for example

\[
\text{Phenol} \rightleftharpoons \text{Ph-OH} \rightleftharpoons \text{Ph-O}^- \]

\[
\lambda_{\text{max}} = 210\text{nm} \quad \lambda_{\text{max}} = 235\text{nm} \quad \varepsilon = 6200 \quad \varepsilon = 9400
\]

1.7.3.1.2 Effect of oxidation

Under slightly alkaline conditions, phenolic entities can be oxidized to quinones. This often leads to increased conjugation and a corresponding shift in absorption maximum to longer wavelengths. This type of
atmospheric oxidation occurs in unpreserved water samples. Even under acidic conditions such as acid preserved water samples oxidation may still occur. An example of this is:

\[
\text{Catechol Quinone} \quad \lambda_{\text{max}} = 274\text{nm} \quad \lambda_{\text{max}} = 390\text{nm} \\
\varepsilon = 2400 \quad \varepsilon = 1400
\]

The quinone is more highly conjugated than catechol and a corresponding shift in absorption maximum towards the visible region is observed.

Therefore from the foregoing, it can be said that measuring colour or DOC at a fixed wavelength, whether colour be visual or a measure of toxic potential by-products, is most likely to be misleading. Absorbance at a fixed wavelength for natural organic matter may not be quantitative, because the organic matter is a heterogeneous mixture of organics.

DOC concentrations in this study were obtained at 360nm because it provided maximum sensitivity and minimum variability.

It is generally recognised that much of the DOC and colour in waters comes from humic substances (mostly polymeric organic acids) which make up up to 75% of the total dissolved organic carbon [9, 85], and are health
significant and this explains why a fixed wavelength was used in the determination of DOC.

Table 3 below shows acronyms of commonly used terms for organic matter in water [85].

Table 3. Acronyms of Common Organic Matter Found in Water.

<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>SOC</td>
<td>Suspended organic carbon</td>
</tr>
<tr>
<td>POC</td>
<td>Particulate organic carbon</td>
</tr>
<tr>
<td>FPOC</td>
<td>Fine particulate organic carbon</td>
</tr>
<tr>
<td>CPOC</td>
<td>Course particulate organic carbon</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>POM</td>
<td>Particulate organic matter</td>
</tr>
<tr>
<td>TOM</td>
<td>Total organic matter</td>
</tr>
<tr>
<td>COM</td>
<td>Colloidal organic matter</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
</tbody>
</table>

Total organic carbon (TOC) is the sum of DOC and Suspended Organic Carbon (SOC). Although it may be measured directly on a carbon analyzer in itself, it is not a useful term. Instead separate measurements for dissolved organic carbon are made because of the following reasons.

1. DOC is chemically more reactive because it is a measure of individual organic compounds in the dissolved state, while Particulate Organic Carbon (POC) and SOC are both discrete plant and animal
organic matter and organic coatings on silt and clay. Total organic carbon measured on the entire sample does not distinguish between these two important fractions.

2. SOC and POC increase dramatically with increasing discharge, while DOC varies less. Thus, TOC will reflect the increase of SOC and POC rather than DOC. If DOC is not measured separately, TOC will have little imperative meaning.

Table 4 shows the "average" concentrations of dissolved and particulate organic carbon with surface and ground water. Dissolved organic carbon varies with the type of water from approximately 0.5mg/l sea water to over 30mg/l for coloured water from swamps.

Table 4. Levels of Humic Substances in Natural Water.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>DOC of Humic Substances in g/M³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground water</td>
<td>0.20-15.00</td>
</tr>
<tr>
<td>Sea water</td>
<td>0.50-2.00</td>
</tr>
<tr>
<td>Stream</td>
<td>0.20-2.50</td>
</tr>
<tr>
<td>Lake</td>
<td>0.50-2.00</td>
</tr>
<tr>
<td>River</td>
<td>1.00-4.00</td>
</tr>
<tr>
<td>Wetlands</td>
<td>10.00-30.00</td>
</tr>
<tr>
<td>Marsh</td>
<td>15.00-17.00</td>
</tr>
<tr>
<td>Bog</td>
<td>30.00-35.00</td>
</tr>
</tbody>
</table>
Coloured water may contain DOC concentrations above the limits indicated in the table 4 above.

Dissolved organic carbon in ground water ranges from 0.2 to 15mg/l within a median concentration of 0.7mg/l. The majority of all ground waters have concentrations of DOC below 2mg/l [86-89]. However there are exceptions; for example, in the South eastern United States, organic rich surface waters recharge ground water that contribute DOC in the form of humic substances. In these waters DOC range from 6-15mg/l [85,90]. Ground waters associated with coal deposits may also have larger than average concentrations of DOC from 5 to over 30mg/l.

Stewart and Wetzel in 1981 [91] expressed concern that relationships between water colour and DOC may be affected by specific processes which alter molecular weight distribution of organic matter such as adsorption and precipitation of DOC with calcium inputs of 'new' leachate during periods of rainfall. Consequently, they proposed that DOC/absorbance relationships were likely to be valid only when applied to soft waters in which system-to-system differences in the age and origin of dissolved organic matter were minimised.
1.7.3.2 ABSORPTION OF ELECTROMAGNETIC RADIATION BY ORGANIC MOLECULES

If light from an ultra-violet radiation is passed through a sample of an organic molecule such as an amino acid or benzene, some of the light is absorbed. In particular, some of the wavelengths (frequencies) are absorbed and others are virtually unaffected. When a molecule absorbs its resonance wavelength, electrons are promoted to higher energy orbitals. The energy $E_1 - E_2$ corresponds to the absorption of energy exactly equivalent to the energy of the wavelength absorbed; for example, benzene absorbs at 225 nm and this corresponds to an energy absorption of 470 KJ mol$^{-1}$. While this example refers specifically to ultra-violet light, the same principle holds for the absorption of energy from any part of the electromagnetic spectrum by any substance [92]. A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude

$$\Delta E = h\nu \quad \text{(vi)}$$

where

$\Delta E$ is the change in energy

$h$ is the Planck's constant
1.7.3.3 INSTRUMENTAL PRINCIPLES OF UV SPECTROPHOTOMETRY.

With the introduction of the Beckman DV spectrophotometer with its quartz optics and ultraviolet accessory unit; the chemist was for the first time able to obtain reliable ultra-violet absorption spectra conveniently and within reasonable time. With the advent of automatic recording and many improvements in instrumentation, there are now a number of excellent commercially available ultraviolet spectrophotometers which are capable of meeting all of the requirements of the analytical chemist. Certain characteristic design and operational features of ultraviolet spectrophotometers are as follows:

(a) Light Source

Hydrogen discharge lamps with quartz windows provide a continuous spectrum of radiant energy in the 185-375 watts region. In one type of the discharge lamp, the hydrogen in the tube is bombarded by electrons being emitted by a heated cathode filaments; the excited electrons of the gas then emit the continuum when they
return to their ground state. A deuterium lamp produces a ultraviolet continuum spectrum having a very high radiant power; several times that of the hydrogen lamp. The d.c. voltage of the electric supply to these lamps is vigorously controlled by electronic voltage regulators to ensure a controlled discharge. Most ultraviolet sources are surrounded by a jacket through which cooling water flows. A collimating mirror or lens is mounted opposite the exit window of the source lamp in order to condense the energy and provide rectilinear radiant energy to monochromators. Several source units also incorporate a mercury discharge lamp which can be used to periodically check the accuracy of the wavelength scale. Most commercial spectrophotometers are designed so that the deuterium and tungsten lamps for visible spectrophotometry, can be rapidly interchanged.

(b) Monochromators

Monochromators for radiant energy of the UV region cannot have glass optics and thus prisms of quartz, fused silica or echlette gratings are used as the dispersive device. Littrow prisms are quite extensively used in prism monochromators because they provide the maximum dispersion with a minimum expenditure of optical material. The back surface of the prism is aluminized.
normal to the optic axis. Synthetic quartz is usually used for optics when measurements are to be made below 200 watts.

Double Littrow prism, Littrow prism-echlette grating, single grating, and double grating monochromators have been used in commercial spectrophotometers.

Two important considerations in evaluating the performance of spectrophotometers which are related to the design of the monochromators are:

(1) the amount of stray radiant energy, and

(2) the resolution.

The radiant energy which reaches the detector at wavelengths which do not correspond to the spectral position selected is termed "stray radiation". Double monochromator instruments usually have less than 0.001 percent stray radiant energy. Well designed single monochromator instruments have less than 0.1 percent stray radiant energy except in extreme lower wavelength region; this value may then approach 1 percent.

Resolution is considered to be the difference in wavelengths of two absorbance maxima which can be detected as being two discrete absorption bands. Double monochromators have resolutions of the order of 0.1nm in the near UV regions; while the resolving power of single monochromators will be about 0.2-0.5nm. The resolution
of a spectrophotometer depends on the use of narrow slit width and is, therefore, dependent on the radiant power of the source; the sensitivity of the detectors, and the gain of the amplifier. Front-surfaced, aluminized mirrors are used for collimating and condensing optical beams in order to minimize selective absorption and reflection losses.

(c) Absorption cells

Absorption cells for UV spectrometry are fabricated with silica optical windows. The sample and reference absorption cells should be matched with respect to optical path length and transmittance at specific wavelengths. It is especially important to remember that even though two cells have identical lengths, transmittance characteristics may be quite different in the uv region, unless they are purchased as matched cells. Several of the commercial spectrophotometers have electrical compensation systems coupled to the wavelength scanning mechanism so that by the adjustment of a number of "multipots" each corresponding to a specific wavelength; it is possible to compensate electrically to zero absorbance and thus eliminate variations in the spectral transmittance of the two absorption cells. This compensation method also
corrects for differences in the spectral response characteristics of the two phototubes used to monitor the reference and sample beams and for differences in the optical efficiency of two optical paths in certain instruments. Therefore, it is especially important in UV spectrophotometer measurements to mark each cell and consistently use one as the reference cell and the other as sample cell.

(d) Detectors

UV spectrophotometers use either vacuum photoemission phototubes or electron multiplier phototubes as detectors. The photocathode surfaces are coated with antimony-caesium or other elements having high sensitivity to uv-radiant energy. The photocurrent output of these detectors is amplified. In the case of many single beam instruments, a d.c. amplifier is employed with either the output read on a deflection type meter or the resulting voltage drop across a resistor balanced by a potentiometer calibrated in transmittance/or absorbance. In double beam operation, the chopping of the optical beam gives a signal which favours the utilization of a.c. amplification. The ratio of the two signals may give a direct readout on a meter or the difference in signal can cause the motor of a
recorder to adjust the slide wire position in order to attenuate the reference signal. The magnitude of the potentiometer slide wire of adjustment is proportional to difference in the output from the two signals. Several instruments attenuate the reference optical beam in order to obtain null balance recording. In general, the use of photomultipliers; a.c. amplification and double beam operation can give a photometric accuracy of about 0.005 absorbance in the middle of 0-1 absorbance range. Better resolution is also obtainable in examining solutions exhibiting ultraviolet absorptivities with these highly sensitive photometers. Several instruments incorporate a scale expansion device which permits one to expand the readout by definite factors. Hence, weak absorbance spectra can be expanded in order to improve the delineation of the absorbance maxima or transmittance minima.

1.8 MICROBIAL EXAMINATION OF DOMESTIC WATER

To determine the potability of water, quantitative bacteriological examination should be undertaken. However, there is no single test or even a combination of tests that is wholly satisfactory [93] because, it only gives a fraction of the total count. Theoretically it would be better to examine water for the presence of
specific pathogenic micro-organisms. This is impractical because of the following reasons:

(1) The methods are expensive, tedious and slow and by that time water has already been consumed.

(2) The number of pathogenic organisms may be quite small compared to the non-pathogenic organisms and would be overlooked.

(3) Non-pathogenic organisms may interfere with the examination of pathogens.

The direct examination for pathogens is therefore not used in routine water analysis. Methods commonly used for bacteriological examination of water are based on:

(1) The examination of the presence or absence of the more common organisms of intestinal or sewage origin called coliforms.

(2) The approximate determination of the total number of bacteria present in water.

1.8.1 TESTS FOR COLIFORMS

To detect the presence of coliform organisms in water, a number of selective and differential media are used [94]. The tests are performed in three successive
steps.

1. presumptive test,

2. confirmed test, and

3. completed test.

1.8.1.1 PRESUMPTIVE TEST

A series of lactose broth or lauryl sulphate tryptose broth fermentation tubes are inoculated with measured amounts of water and incubated at 35°C for 24-48 hours. The formation of gas in the inverted vial in the fermentation tube within 48 hours indicates positive presumptive test. Absence of gas at the end of 48 hours indicates negative presumptive test. This means that the water does not contain coliforms and is considered safe.

1.8.1.2 CONFIRMED TEST

Sometimes a false positive presumptive test is obtained. This may be due to presence of yeasts or certain Clostridium species and some other organisms. In order to be certain that the gas produced is due to coliforms, a confirmed test must be performed. Two procedures are normally employed. In one method a drop of culture from a positive lactose broth is transferred to brilliant green lactose-bile fermentation broth tube
and is incubated for 24-48 hours at 35°C. The appearance of gas within 48 hours constitutes a positive confirmed test. The dye inhibits gram-positive organisms and eliminates false presumptive test.

In the other method, a drop of culture from positive lactose broth is streaked on a petri-dish containing Endos or Eosin-methylene blue agar. The appearance of colonies with or without metallic sheen within 24 hours indicates a positive confirmed test. This method has been employed in the present study.

1.8.1.3 COMPLETED TEST

Isolated colonies from petri-dishes are transferred into lactose fermentation broth and the presence of gram-negative and non-sporing Bacilli on the slant give evidence that coliform bacteria are present in the water sample.

1.9 DETERMINATION OF NITRATES/NITRITES IN POTABLE WATERS

1.9.1 Determination of Nitrates

There are many methods of determination of nitrates in potable waters such as colorimetry [95], gravimetry
and spectroscopy.

(a) Colorimetry

This method involves the reaction of the substance being determined with a standard reagent to form a coloured product. The concentration of which is proportional to colour intensity. Nitrates react with many reagents to form coloured products. One such reagent is phenol-2-4-disulphonic acid. In acetic acid medium it reacts with nitrates to form a 6-nitro derivative which has an intense yellow colour.

(b) Gravimetry

Nitrates react with nitron in acetic acid medium to form a sparingly soluble salt which precipitates, allowing the determination of nitrates. The disadvantages of these methods are interferences from other ions such as nitrites, perchlorate and chromium (III).

1.9.2 Determination of Nitrites

Nitrites can also be determined by colorimetry.
COLORIMETRIC DETERMINATION OF NITRITES

In acetic acid solutions nitrites react with a primary aromatic amine to produce a diazonium salt. This diazonium salt couples with an aromatic phenol to form a coloured azo-dye. The reaction is highly selective and is sufficiently sensitive to detect 1μg/l [95]. A re-examination of the diazotization and coupling reactions conducted by Rider and Mellon with modern instruments, disclosed that four requirements govern the success of nitrite determination [99].

1. Diazotization should be carried out in a strongly acidic medium.
2. Diazotization should be conducted in as cool solution as possible.
3. Coupling should be attempted only after diazotization is complete, and
4. Coupling should be carried out in as a low acidity as is consistent with colorimetric stability.

In colorimetric determination of nitrites there may be interferences from amines, oxidizing agents, coloured substances, complex formers and agents that disturb the acid-base balance.
(b) Gravimetric Determination of Nitrites

Nitrites can be determined gravimetrically by oxidation to nitrates, with excess warm acidified potassium permanganate. The nitrates thus formed are reacted with nitron in acetic acid medium to form a sparingly soluble salt which precipitates.

From the foregoing it is evident that colorimetric as well as gravimetric methods for determining both nitrates and nitrites are cumbersome, tedious, time-consuming and expensive.

1.9.3 SPECTROSCOPIC DETERMINATION OF NITRATES AND NITRITES

Both nitrates and nitrites absorb ultra-violet radiation at 302nm and this allows simultaneous determination of both nitrates and nitrites [100]. This method is highly selective and is sufficiently sensitive to detect 0.02 ppm. There are very few interferences such as amines and arsenic(III). Nitrates absorb at 210nm and 302nm [98, 101], but at 210nm there many interferences from chlorides, carboxylic acids and copper (II) complexes which absorb in the range 208-255nm [102].
2.1 CLEANING OF GLASSWARE AND PLASTIC CONTAINERS

All plastic containers used in sample collection were cleaned with concentrated chromic acid, washed with detergent and rinsed with distilled de-ionised water and dried at room temperature. Glassware containers were similarly cleaned and dried in an oven at 100-120°C.

2.2 Preparation of Standard Solutions

The standard solutions were prepared from the pure metal or analytical grade metal oxide for toxic metal analysis. Analar sodium nitrate and sodium nitrite were used for the determination of nitrates/nitrites.
Table 5 [77] shows the masses of analytically reagents used in making the standard solutions and the diluents used in each case.

Table 6 shows the operating parameters of the spectrophotometers used in the determination of the metals, DOC and nitrates/nitrites.
<table>
<thead>
<tr>
<th>Metal/metal oxide</th>
<th>Diluent</th>
<th>Conc. ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000 g of Cd</td>
<td>HCl</td>
<td>1000</td>
</tr>
<tr>
<td>metal</td>
<td>1% V/V</td>
<td></td>
</tr>
<tr>
<td>1.000 g of Cu</td>
<td>HNO₃</td>
<td>1000</td>
</tr>
<tr>
<td>metal</td>
<td>1% V/V</td>
<td></td>
</tr>
<tr>
<td>1.0772 g of PbO</td>
<td>HNO₃</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>1% V/V</td>
<td></td>
</tr>
<tr>
<td>1.5825 g of MnO₂</td>
<td>HCl</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>1% V/V</td>
<td></td>
</tr>
<tr>
<td>1.000 g of Zn</td>
<td>HCl</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>1% V/V</td>
<td></td>
</tr>
<tr>
<td>1.371 g of NaNO₃</td>
<td>de-ionized water</td>
<td>1000</td>
</tr>
<tr>
<td>1.500 g of NaNO₂</td>
<td>de-ionized water</td>
<td>1000</td>
</tr>
<tr>
<td>Operating Parameters</td>
<td>Cd</td>
<td>Cu</td>
</tr>
<tr>
<td>----------------------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Wave length (nm)</td>
<td>228.8</td>
<td>324.7</td>
</tr>
<tr>
<td>Slit width (nm)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Lamp current (mA)</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Flame</td>
<td>Air/acetylene</td>
<td></td>
</tr>
<tr>
<td>Sensitivity (ppm)</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Detection limit (ppm)</td>
<td>0.015</td>
<td>0.005</td>
</tr>
</tbody>
</table>
2.3 INSTRUMENTATION

Determination of dissolved trace metal element concentrations were done using computerised Varian Atomic Absorption Spectrophotometer model SpectrAA-10 (Varian Manufacturing Co. Ltd Australia).

Dissolved Organic carbon (DOC) was determined using Pye Unicam UV-vis Spectrophotometer model Sp8-150 (Pye Unicam Instruments Ltd, England). The total nitrates/nitrite levels were determined using Spectronic UV-vis Spectrophotometer model Sp-20 (Milton Roy Co. Ltd England).

The instrumental setting for the analysis of the substances determined were as shown in Table 6.

2.4 SAMPLING SITES

Samples from the three divisions of Kangundo in Machakos district, Ngong in Kajiado district and Kikuyu in Kiambu district were collected during the wet and dry
seasons. The wet season was between the months of April and June 1994 and the dry season was between the months of September and November 1994.

Samples were collected from 15 sites in Kangundo division. The sites from which samples were collected are: Kithimani, Nguluni, Kwa Musembi, Isooni, Sengani, Tala market, Vangala, Kalandini, Katine, Kyaume, Kitunduni, Kisukioni, Ngonda, Kyamulendu and Silanga. In Ngong division 13 sites were selected for sampling. Two of these sites lie on the border between Nairobi and Ngong. They are Karen and Kikeni. Seven of these sites were in Kiserian location, two in Ongata Rongai and two in Ngong township. Samples were taken from 12 sites in Kikuyu division at Kikuyu town, Sigona, Muguga, Zambezi, Wangige, Kiguni, Lower Kabete, Upper Kabete, Kirangari, Ondiri, Thogoto and at Alliance. Five samples each from Kabete water works and Kenyatta University were collected for comparison purposes since water at these two sites is treated. Figure 1 shows the locations from where samples were collected.
FIGURE 1
Map showing Sites from Where Sample were collected

and 1 to 5 SITES FROM WHICH SAMPLES WERE COLLECTED
Water samples for trace metal analysis were collected during the wet and dry months of 1994. Recovery tests were carried out to determine if the sampler contaminated the water samples. Solutions of known concentrations for each metal were placed in the sampler for 24 hours. Analysis was then carried out in triplicate at two concentration levels of 5ppm and 10ppm.

Recovery was then calculated from the difference between the results obtained for water stored in the sampler for a day and freshly prepared samples. Recovery efficiently averaged between 100%, 102%, 98%, 104% and 98% for Zn, Cu, Cd, Mn and Pb respectively. These results indicated that the sampler did not significantly contaminate or alter the concentrations of the metals under study.
Five samples were collected from each site with polyethylene bottles which had previously been rinsed thoroughly with Analar HNO₃ (10%) and distilled de-ionized water. In wells/boreholes, water was drawn manually with a plastic container and the sampler was submerged and opened beneath the water surface [103] to avoid contamination. The water samples were neither filtered at the sampling site nor in the laboratory because one of the objectives of the study was to determine consumable levels of these metals in domestic water supplies since water is not filtered before use in contemporary Kenyan rural homes. The samples were transported overnight to the laboratory and acidified with Analar HNO₃ to a pH of 2 or less to prevent the loss of the trace elements through adsorption on the surface of the container and inhibit metabolic processes of microorganisms which might cause changes in trace metal levels in the sample [104]. Furthermore, it also prevents flocculation and precipitation of the trace metal compounds. Evaporation by the use of a hot plate was used
as a concentration technique prior to analysis. This was done only when the levels of the metal being determined in the unconcentrated sample was below the detection limit of the instrument (Table 6). A graphite furnace was also used in cases where the levels could not be detected even after concentration. With the graphite furnace levels of the trace metals were determined in ppb after which they converted to ppm. The determination of trace metal concentrations was done using atomic absorption spectrophotometry. Working standards and blanks were acidified as the samples. They were prepared on the same day analysis was performed. Volumetric flasks were soaked in 10% HNO₃ when not in use to avoid contamination. The mean concentrations and standard deviations for the pentaplicate determinations were calculated using equation C-1 and C-2. They are shown in appendix A and are given in Tables 11-16.
2.5.2 DISSOLVED ORGANIC CARBON (DOC)

Five samples were collected from each site. Samples were collected and transported overnight and kept in a refrigerator until analysis. This was to inhibit the metabolic processes of micro-organisms and biodegradation reactions which could significantly alter the concentrations of DOC.

Distilled deionized water was put in sample bottles and stored under the same conditions as the samples. It was used as a control sample. Samples were filtered using a 0.45μm glass fibre filter prior to analysis. DOC was determined by recording the absorbance of the sample at 360nm in the visible - UV region using a UV-vis spectrophotometry and substituted in the equation for DOC/absorbance relationship [82]. Analysis was done for DOC in each of the five samples and the mean taken as representative. The mean and standard deviations for
samples within a site were calculated using equations C-1, and C-2 and are shown in appendix A and are given in tables

2.5.3 NITRATES/NITRITES

Samples were filtered and preserved in a buffer [105] solution and transported overnight in plastic containers and kept in a refrigerator for two days until analysis. The buffer was 0.01M aluminium sulphate, 0.01M silver sulphate, 0.02M boric acid and adjusted to pH 3.0 with 0.1M sulphuric acid. Constituents of the buffer solution complex, precipitate, decompose or otherwise remove interfering ions [106]. The buffer suppresses the activity of microorganisms because of its low pH and high concentrations of silver ions and boric acid. The silver ions also precipitated most anions. The aluminium sulphate precipitated most organic matter by coagulation. The samples were filtered before analysis.
Analar grade NaNO₃ and NaNO₂ were used to prepare the standard solutions for the determination of NO₃⁻/NO₂⁻ respectively. They were buffered as the samples in equal volumes. Distilled deionized water was used as a control. A calibration curve from 0.1mg/l, 10mg/l and 100mg/l solutions of the standards was determined. The standards were 50% NO₃⁻ and 50% NO₂⁻. Absorbance was recorded at 302nm and fitted in the calibration curve. Analysis was done using UV-vis spectrophotometer for the five samples and the mean and the standard deviation were taken as representative of each site and are given in tables. They were calculated using equations c-1 and c-2.

2.5.4 SCREENING WATER FOR THE PRESENCE OF PATHOGENIC COLIFORMS.

The analysis of water for the presence of pathogenic coliform bacteria was carried out in three steps; the presumptive, the confirmed and the completed tests. Three
samples were taken from each site in polyethylene bottles which were thoroughly cleaned with detergent and rinsed with distilled deionized water. The bottles were then sterilized when closed in an autoclave at 120°C and a pressure of 2355N/M². The bottles were carried to the collection site and submerged in water before opening to avoid contamination by aerial bacteria. The samples were transported overnight and kept in a refrigerator to prevent or inhibit microbial activities such as multiplication and the die off rate.

2.5.4.1 PRESumptive TEST

In the presumptive test 10ml, 1ml and 0.1ml portions of each sample were inoculated in three different tubes with double strength lactose broth for the 10ml portion, and single strength lactose broth for the 1ml and 0.1ml portions. Three sets for each of the 10ml, 1ml and 0.1ml portions were inoculated.
Preparation of lactose fermentation broth

Lactose fermentation broth was prepared by weighing:

- Beef extract: 3.0g
- Peptone: 5.0g
- Lactose: 5.0g

These masses were dissolved in one litre of distilled deionized water. For double strength lactose broth, twice the concentrations of the ingredients were used; they were then sterilized in an autoclave at 120°C and a pressure of 2355 N/M² and incubated at 37°C for 48 hours and observed for the presence of gas. Gas formation within 48 hours constituted a positive presumptive test.

In the presumptive test, pure lactose fermentation broth and distilled deionized water were sterilized in an autoclave at 120°C and a pressure of 2355 N/M² and used as control samples; to find out if pathogenic coliforms were from the deionized sterilized water, or from the sterile lactose fermentation broth or from the water samples. The control samples gave a negative presumptive test within 48
69

hours indicating that pathogenic coliforms were from the water samples.

2.5.4.2 CONFIRMED TEST

The confirmed test was applied to all the samples that gave a positive presumptive test (i.e. formation of gas within 24 hours) or a doubtful presumptive test (i.e. formation of gas within 48 hours) using Eosin Methylene Blue (EMB) agar.

The positive and doubtful samples were streaked on a sterilized petri-dish of EMB agar to give well isolated colonies [58], using a loop sterilized over a Bunsen-flame.
Preparation of Eosin Methylene Blue (EMB) agar

The EMB agar was prepared by weighing:

- Peptone: 10.0g
- Lactose: 5.0g
- Sucrose: 5.0g
- Dipotassium phosphate: 2.0g
- Agar: 13.0g
- Eosin Y: 0.40g
- Methylene Blue: 0.065g

and dissolving in one litre of distilled water and then sterilizing in an autoclave at 120°C and a pressure of 2355N/M².

The plates were then incubated at 37°C for 48 hours and examined for the formation of typical coliform colonies. Pure EMB was also incubated at 37°C for 48 hours to act as a control sample. Two well isolated colonies were picked and transferred to an agar slope and incubated at
37°C for 48 hours. Formation of darkish colonies on the agar slope indicated a positive confirmed test.

2.5.4.3 THE COMPLETED TEST

From the EMB plates two colonies were picked and each transferred to an agar slope and lactose broth fermentation tube and incubated at 37°C for 48 hours. The latter was to show that the darkish colonies were pathogenic bacteria if they formed gas within 48 hours.

From the agar slope a gram stain and a spore-stain were made. Gram-stain was made by smearing with a wire-loop, sterilised over a flame and mounted onto a microscope slide, and washed with crystal violet for one minute and rinsed with sterilised water. The slide was again washed with Grams iodine solution for one minute followed by acetone-ethanol mixture (50ml of acetone to 30ml of ethanol) and safranine solution for one minute and blot
dried. Oil emulsion was applied to the slide, mounted on a microscope and viewed.

The formation of gas in the lactose broth and demonstration of gram-negative, non-spore forming rods in the agar culture constituted a satisfactory completed test. A plate with pure sterile EMB agar was used as control sample in which EMB was transferred to a lactose broth and an agar slope and treated as the sample. Failure of gas formation in the lactose fermentation broth and gram-negative non-spore forming rods in the agar culture constituted a satisfactory proof that the samples in the completed test were not contaminated and that coliforms did not come from the EMB plate but from the water samples streaked onto the EMB plates.
CHAPTER THREE

RESULTS AND DISCUSSION

3.1 INTRODUCTION

The samples for analysis were collected during the wet months of April-June and the dry months of September-November of the year 1994 from 40 sites located in three divisions around Nairobi.

These sites are distributed in the three divisions; Kangundo, Ngong and Kikuyu as 15, 13 and 12 respectively figure 1.

The samples for analysis were collected during the wet months April-June and the dry months September-November of the year 1994 from 40 sites located in the three divisions around Nairobi.

The sites were chosen on demographic factor of population; more sites were selected in areas with high populations within a distance of at least three kilometres and at most five kilometres with the hope that sites that are far apart were expected to have significant differences in the heavy metal concentrations. Sites which are very near each other may not have significant differences in their heavy metal concentrations since the origin of the metals may be the same such as underground rocks whose chemical composition does not change appreciably over a
short distance.

The range, median and mean of the substances quantified in the water samples are shown in tables AB1-AB3 below.

Table AB1. Range, Median and Mean for Toxic Substances in Wells and Boreholes in Kangundo in ppm.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Range</th>
<th>Median</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.01-1.20</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.01-7.10</td>
<td>0.28</td>
<td>1.90</td>
</tr>
<tr>
<td>Lead</td>
<td>0.001-0.30</td>
<td>0.06</td>
<td>0.19</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.01-3.30</td>
<td>0.10</td>
<td>0.57</td>
</tr>
<tr>
<td>Nitrates</td>
<td>0.02-12.00</td>
<td>2.15</td>
<td>0.56</td>
</tr>
<tr>
<td>Nitrates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC (mg/l)</td>
<td>2.00-30.80</td>
<td>3.40</td>
<td>12.26</td>
</tr>
</tbody>
</table>

Table AB2. Range, Median and Mean for Toxic Substances in Wells and Boreholes in Ngong in ppm.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Range</th>
<th>Median</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.01-0.40</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.01-2.80</td>
<td>0.10</td>
<td>0.91</td>
</tr>
<tr>
<td>Lead</td>
<td>0.01-1.00</td>
<td>0.10</td>
<td>0.21</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.01-0.75</td>
<td>0.10</td>
<td>0.38</td>
</tr>
<tr>
<td>Nitrates</td>
<td>0.02-5.25</td>
<td>0.50</td>
<td>2.2</td>
</tr>
<tr>
<td>Nitrites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC(Mg/l)</td>
<td>2.00-13.8</td>
<td>2.50</td>
<td>5.32</td>
</tr>
</tbody>
</table>
Table AB. Range, Median and Mean for Toxic Substances in Wells and Boreholes in Kiku in ppm.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Range (ppm)</th>
<th>Median</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.01-1.30</td>
<td>0.10</td>
<td>0.22</td>
</tr>
<tr>
<td>Lead</td>
<td>0.01-0.90</td>
<td>0.10</td>
<td>0.38</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.01-2.30</td>
<td>0.23</td>
<td>0.68</td>
</tr>
<tr>
<td>Nitrates/nitrites</td>
<td>0.02-15.00</td>
<td>4.60</td>
<td>7.93</td>
</tr>
<tr>
<td>DOC (mg/l)</td>
<td>2.10-16.80</td>
<td>2.80</td>
<td>12.20</td>
</tr>
</tbody>
</table>

Several researchers have investigated the levels of heavy metals in Kenyan with a view of determining whether such levels have reached toxic concentrations.

Kiilu[107] determined the levels of five heavy metals (Mn, Zn, Pb, Cu and Cd) in lake Victoria and lake Nakuru using atomic absorption spectrophotometry. The levels of the heavy metals determined were found to be present in concentrations below the maximum acceptable limits set by W.H.O. The mean concentrations in ppm of the results obtained by Kiilu are as shown in Tables 7 and 8 below[107].
Table 7 Dissolved Heavy Metal Concentration in ppm in Lake Victoria.

<table>
<thead>
<tr>
<th>LAKE SITE</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Mn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Car Wash</td>
<td>0.194</td>
<td>0.012</td>
<td>0.012</td>
<td>0.054</td>
<td>0.018</td>
</tr>
<tr>
<td>Hippo Point</td>
<td>0.192</td>
<td>0.011</td>
<td>-</td>
<td>0.048</td>
<td>0.020</td>
</tr>
<tr>
<td>Usenge Bay</td>
<td>0.174</td>
<td>0.020</td>
<td>0.012</td>
<td>0.041</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 8 Dissolved Heavy Metal Concentrations in ppm in Lake NAKURU

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Mn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old Bridge</td>
<td>0.192</td>
<td>0.160</td>
<td>0.108</td>
<td>0.093</td>
<td>0.218</td>
</tr>
<tr>
<td>Presidents</td>
<td>0.196</td>
<td>0.148</td>
<td>0.114</td>
<td>0.086</td>
<td>0.204</td>
</tr>
<tr>
<td>Pavillion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Park Entrance</td>
<td>0.184</td>
<td>0.158</td>
<td>0.112</td>
<td>0.082</td>
<td>0.208</td>
</tr>
</tbody>
</table>

The relatively high concentrations of heavy metals in lake Naukru was attributed to the discharge of sewage effluent from Nakuru town into the lake. This effluent is rich in both organic and inorganic nutrients for the growth of algae and other aquatic organisms on which the flamingos feed.
The levels of the heavy metals obtained in the two Kenyan lakes are generally lower than the levels of the metals obtained in this study. This is because ground waters have generally high dissolved mineral contents than surface waters because of the intimate contact between the carbon dioxide bearing water and the underground rocks [6].

Williams et. al determined five metals (Zn, Cu, Ni, Cd and Pb) in a river in the Manuherika catchment area in New Zealand using an atomic absorption spectrophotometer with a graphite furnace. The mean concentrations in ppm are shown in Table 9 below.

Table 9: Average Concentrations (ppm) of Dissolved Trace Metals in the Manuherika Catchment Area in New Zealand [103].

<table>
<thead>
<tr>
<th>Date</th>
<th>Concentration in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>March 1983</td>
<td>0.21</td>
</tr>
<tr>
<td>May 1983</td>
<td>0.43</td>
</tr>
<tr>
<td>July 1983</td>
<td>0.41</td>
</tr>
<tr>
<td>October 1983</td>
<td>0.26</td>
</tr>
<tr>
<td>December 1983</td>
<td>0.21</td>
</tr>
<tr>
<td>June 1985</td>
<td>0.27</td>
</tr>
<tr>
<td>Sept. 1985</td>
<td>0.17</td>
</tr>
<tr>
<td>Dec. 1985</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Manganese was detected in 34 and 35 sites during the wet and dry the seasons respectively. Zinc was found in 36 sites during the wet season and in 35 sites during the dry season. Copper was present in 23 sites during the wet
season and 25 sites during the dry season. Lead occurred in 29 sites in wet season and in 32 sites during the dry season.

Table A1 in appendix A shows the correlation coefficients (r-values) and the regression equations found when correlating the values obtained during the dry (y-axis) and the wet (x-axis) seasons. The correlation coefficients were calculated using equations C-3 in appendix A1. Equation C-4 was used to determine t-values in the 95%, 99% and 99% confidence limits.

The bar charts in figures B1, B2, B3, B4, B7, B8, B9, B10, B13, B14, B15, B16 in appendix B show the comparisons of the levels of these metals in various sites during the wet and dry seasons in the three divisions. Zinc and manganese were the most prevalent metals in all the sites. This is because these are the more abundant of the five metals in the earth's crust [18].

There were sites that did not contain some of the metals in both seasons, for example in Kangundo there were five, two, one, and two sites that did not contain copper, lead, zinc and manganese, respectively during the two seasons. Two sites in Ngong did not contain either copper or lead. Only one site in Kikuyu contained no copper.

The concentrations of most metals were below both the World Health Organization (W.H.O.) [108,109] and the Kenyan [110] maximum permissible limits. The W.H.O maximum
permissible limits are given in Table 2. The limits for toxic substances in drinking water in Kenya are given in Table 10. The highest levels of manganese, zinc, copper and lead were 3.30ppm, 15.50ppm, 1.30ppm and 1.00ppm, respectively. The levels of Manganese, zinc and lead of 3.30ppm, 15.50ppm and 1.00ppm, respectively were above the highest permissible limits set by the World Health Organization. Except for manganese, the highest levels were obtained during the dry season.

Dissolved organic carbon was detected in 37 sites during the wet season and 31 sites during the dry season. Generally there were high DOC concentrations during the rain season than during the dry season.

The correlation coefficient (r-value) and the regression equation found when correlating values obtained during the dry (y-axis) and the wet (x-axis) seasons are shown in table A1 in appendix A.

The bar charts in figures B6, B12 and B18 in appendix B show the comparisons of the levels of DOC during the wet and dry seasons in the three divisions of Kangundo, Ngong and Kikuyu respectively.

The highest and lowest levels of DOC were 30.80mg/l and 2.50mg/l during the wet season and 7.20mg/l and 2.00mg/l during the dry season.

The highest levels of nitrates/nitrites during both the dry and wet seasons were 15.0ppm and 8.10ppm,
respectively. The W.H.O. maximum acceptable and proposed limits for nitrates/nitrites in drinking water are 45-100 ppm [108]. A total of 32 and 30 sites had nitrates/nitrites during the dry and wet seasons, respectively.

Table A1 in appendix A shows the correlation coefficient (r-value) and the regression equation obtained when correlating values obtained during the dry (y-axis) and the wet (x-axis) seasons.

The bar charts in figures B5, B11 and B17 in appendix B show the comparisons of the levels of nitrates/nitrites during the wet and dry seasons in the three divisions of Kangundo, Ngong and Kikuyu respectively.

Pathogenic coliforms were detected in more sites during the wet season than during the dry season. There were a total of 11 sites with pathogenic coliforms during the wet season and only 2 sites during the dry season. In Kangundo division pathogenic bacteria were detected in 4 and 2 sites during the wet and dry seasons, respectively. 4 sites in Ngong division and 2 sites in Kikuyu division had pathogenic bacteria during the wet season. No pathogens were detected during the dry season in sites in these two divisions. Pathogenic bacteria were detected more in shallow wells than in deep wells. No pathogens were detected in boreholes.
Table 10. Limits for Toxic Substances in Drinking Water.[110]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Upper Limit in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>0.005</td>
</tr>
<tr>
<td>Lead</td>
<td>0.050</td>
</tr>
<tr>
<td>Copper</td>
<td>1.000</td>
</tr>
<tr>
<td>Zinc</td>
<td>5.000</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.100</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.001</td>
</tr>
<tr>
<td>Nitrate</td>
<td>10.000</td>
</tr>
<tr>
<td>Fluoride</td>
<td>1.500</td>
</tr>
<tr>
<td>Chloride</td>
<td>250.000</td>
</tr>
<tr>
<td>Sulphate</td>
<td>400.000</td>
</tr>
<tr>
<td>Iron</td>
<td>0.300</td>
</tr>
</tbody>
</table>
The levels of toxic substances obtained are tabulated in tables 11 to 16.

Table 11: Levels of toxic metals in ppm in wells and bore holes in Kangundo 1.

<table>
<thead>
<tr>
<th>Site</th>
<th>Metal</th>
<th>Copper Conc. in ppm</th>
<th>Zinc Conc. in ppm</th>
<th>Lead Conc. in ppm</th>
<th>Manganese Conc. in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
</tr>
<tr>
<td>Kithimani</td>
<td>ND</td>
<td>ND</td>
<td>0.2 ± 0.05</td>
<td>2.70 ± 0.10</td>
<td>0.05 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>ND</td>
<td>0.05 ± 0.001</td>
<td>0.10 ± 0.03</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>Kwa Musembi</td>
<td>0.01 ± 0.003</td>
<td>0.03 ± 0.008</td>
<td>2.20 ± 0.02</td>
<td>7.10 ± 0.10</td>
<td>0.02 ± 0.003</td>
</tr>
<tr>
<td>Kwa Musembi</td>
<td>ND</td>
<td>ND</td>
<td>1.50 ± 0.10</td>
<td>0.80 ± 0.02</td>
<td>ND</td>
</tr>
<tr>
<td>Sengeni</td>
<td>0.20 ± 0.08</td>
<td>0.04 ± 0.005</td>
<td>0.20 ± 0.05</td>
<td>0.40 ± 0.03</td>
<td>0.04 ± 0.001</td>
</tr>
<tr>
<td>Sengeni</td>
<td>ND</td>
<td>ND</td>
<td>0.10 ± 0.08</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Tala</td>
<td>0.10 ± 0.003</td>
<td>ND</td>
<td>1.00 ± 0.10</td>
<td>2.00 ± 0.20</td>
<td>ND</td>
</tr>
<tr>
<td>Tala</td>
<td>ND</td>
<td>ND</td>
<td>0.10 ± 0.02</td>
<td>0.15 ± 0.01</td>
<td>0.50 ± 0.04</td>
</tr>
<tr>
<td>Vangala</td>
<td>0.40 ± 0.02</td>
<td>0.10 ± 0.02</td>
<td>0.15 ± 0.01</td>
<td>0.20 ± 0.03</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Kalandini</td>
<td>0.35 ± 0.04</td>
<td>1.20 ± 0.03</td>
<td>ND</td>
<td>ND</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Kalandini</td>
<td>ND</td>
<td>ND</td>
<td>0.35 ± 0.09</td>
<td>0.02 ± 0.001</td>
<td>ND</td>
</tr>
<tr>
<td>Kyaume</td>
<td>0.90 ± 0.07</td>
<td>0.60 ± 0.01</td>
<td>0.35 ± 0.09</td>
<td>0.02 ± 0.001</td>
<td>ND</td>
</tr>
<tr>
<td>Kitunduni</td>
<td>ND</td>
<td>ND</td>
<td>0.03 ± 0.008</td>
<td>0.01 ± 0.002</td>
<td>ND</td>
</tr>
<tr>
<td>Kisukeni</td>
<td>0.20 ± 0.07</td>
<td>0.30 ± 0.04</td>
<td>ND</td>
<td>ND</td>
<td>0.10 ± 0.08</td>
</tr>
<tr>
<td>Ngonda</td>
<td>ND</td>
<td>ND</td>
<td>0.45 ± 0.06</td>
<td>6.00 ± 0.70</td>
<td>ND</td>
</tr>
<tr>
<td>Kyaumulendo</td>
<td>0.01 ± 0.003</td>
<td>0.30 ± 0.005</td>
<td>0.20 ± 0.02</td>
<td>ND</td>
<td>0.06 ± 0.004</td>
</tr>
<tr>
<td>Kyaumulendo</td>
<td>ND</td>
<td>ND</td>
<td>0.01 ± 0.003</td>
<td>3.00 ± 0.80</td>
<td>0.01 ± 0.007</td>
</tr>
<tr>
<td>Silanga</td>
<td>0.01 ± 0.003</td>
<td>ND</td>
<td>0.01 ± 0.003</td>
<td>3.00 ± 0.80</td>
<td>0.01 ± 0.007</td>
</tr>
</tbody>
</table>

ND stands for Not Detected
Table 12 Levels of toxic metals in wells and bore holes in Ngong environs.

<table>
<thead>
<tr>
<th>SITE</th>
<th>COPPER Conc. in ppm</th>
<th>ZINC Conc. in ppm</th>
<th>LEAD Conc. in ppm</th>
<th>MANGANESE Conc. in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
<td>DRY</td>
</tr>
<tr>
<td>001</td>
<td>ND</td>
<td>0.10 ± 0.07</td>
<td>0.10 ± 0.06</td>
<td>1.10 ± 0.020</td>
</tr>
<tr>
<td>002</td>
<td>0.23 ± 0.03</td>
<td>0.10 ± 0.04</td>
<td>ND</td>
<td>2.60 ± 0.20</td>
</tr>
<tr>
<td>003</td>
<td>ND</td>
<td>0.01 ± 0.002</td>
<td>0.02 ± 0.002</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>004</td>
<td>0.10 ± 0.04</td>
<td>0.30 ± 0.01</td>
<td>0.06 ± 0.002</td>
<td>0.10 ± 0.07</td>
</tr>
<tr>
<td>Kiserian Govt</td>
<td>ND</td>
<td>0.08 ± 0.002</td>
<td>0.04 ± 0.003</td>
<td>ND</td>
</tr>
<tr>
<td>Lolua</td>
<td>ND</td>
<td>ND</td>
<td>0.10 ± 0.04</td>
<td>ND</td>
</tr>
<tr>
<td>Quarry</td>
<td>ND</td>
<td>0.05 ± 0.002</td>
<td>0.01 ± 0.003</td>
<td>2.30 ± 0.02</td>
</tr>
<tr>
<td>Ngong town</td>
<td>ND</td>
<td>0.40 ± 0.03</td>
<td>0.01 ± 0.001</td>
<td>0.10 ± 0.04</td>
</tr>
<tr>
<td>Ongata Rongai</td>
<td>ND</td>
<td>0.10 ± 0.04</td>
<td>0.50 ± 0.02</td>
<td>2.80 ± 0.020</td>
</tr>
<tr>
<td>Kiserian town</td>
<td>ND</td>
<td>0.10 ± 0.04</td>
<td>0.02 ± 0.002</td>
<td>ND</td>
</tr>
<tr>
<td>Karen</td>
<td>0.08 ± 0.002</td>
<td>0.06 ± 0.003</td>
<td>0.08 ± 0.002</td>
<td>0.10 ± 0.08</td>
</tr>
<tr>
<td>005</td>
<td>0.02 ± 0.001</td>
<td>0.06 ± 0.005</td>
<td>0.10 ± 0.04</td>
<td>0.50 ± 0.02</td>
</tr>
<tr>
<td>Kikeni</td>
<td>0.13 ± 0.03</td>
<td>0.06 ± 0.005</td>
<td>0.17 ± 0.05</td>
<td>0.83 ± 0.01</td>
</tr>
</tbody>
</table>

ND stands for Not Detected.
<table>
<thead>
<tr>
<th>SITE\SUBSTANCE</th>
<th>COPPER Conc. in ppm</th>
<th>ZINC Conc. in ppm</th>
<th>LEAD Conc. in ppm</th>
<th>MANGANESE Conc. in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
<td>DRY</td>
</tr>
<tr>
<td>Kikuyu</td>
<td>0.22 ± 0.02</td>
<td>ND</td>
<td>0.02 ± 0.001</td>
<td>0.13 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.60 ± 0.01</td>
<td>0.90 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.09 ± 0.008</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>Sigona</td>
<td>ND</td>
<td>ND</td>
<td>0.10 ± 0.03</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.063 ± 0.001</td>
<td>0.10 ± 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03 ± 0.007</td>
<td>0.24 ± 0.029</td>
</tr>
<tr>
<td>Muguga</td>
<td>0.09 ± 0.002</td>
<td>0.10 ± 0.04</td>
<td>2.90 ± 0.10</td>
<td>0.07 ± 0.003</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.10 ± 0.04</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.53 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Zambezi</td>
<td>0.03 ± 0.003</td>
<td>0.10 ± 0.04</td>
<td>9.30 ± 0.65</td>
<td>0.03 ± 0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.15 ± 0.02</td>
<td>0.10 ± 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.31 ± 0.025</td>
<td></td>
</tr>
<tr>
<td>Wangige</td>
<td>0.08 ± 0.001</td>
<td>0.21 ± 0.03</td>
<td>0.08 ± 0.002</td>
<td>0.60 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.18 ± 0.01</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.30 ± 0.20</td>
<td>0.60 ± 0.02</td>
</tr>
<tr>
<td>Kiguni</td>
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<td>ND</td>
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<td>0.20 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.38 ± 0.04</td>
<td>0.80 ± 0.01</td>
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<tr>
<td></td>
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<td>0.10 ± 0.04</td>
<td>0.23 ± 0.028</td>
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<tr>
<td>Lower Kabete</td>
<td>0.02 ± 0.008</td>
<td>ND</td>
<td>0.14 ± 0.01</td>
<td>0.60 ± 0.002</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>0.10 ± 0.03</td>
<td>0.90 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.31 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Upper Kabete</td>
<td>ND</td>
<td>0.10 ± 0.03</td>
<td>0.01 ± 0.008</td>
<td>0.08 ± 0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.06 ± 0.003</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
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<td>0.30 ± 0.10</td>
<td>0.51 ± 0.017</td>
</tr>
<tr>
<td>Kirangari</td>
<td>0.01 ± 0.008</td>
<td>ND</td>
<td>0.10 ± 0.04</td>
<td>0.05 ± 0.001</td>
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<td></td>
<td></td>
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<td>0.95 ± 0.01</td>
<td>0.30 ± 0.002</td>
</tr>
<tr>
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<td>0.43 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Ondiri</td>
<td>ND</td>
<td>1.10 ± 0.10</td>
<td>0.10 ± 0.04</td>
<td>0.80 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03 ± 0.008</td>
<td>0.06 ± 0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01 ± 0.008</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>Thogoto</td>
<td>0.01 ± 0.008</td>
<td>0.10 ± 0.04</td>
<td>4.50 ± 0.30</td>
<td>10.40 ± 0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.10 ± 0.04</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01 ± 0.009</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>Alliance B.</td>
<td>ND</td>
<td>ND</td>
<td>1.40 ± 0.15</td>
<td>8.13 ± 0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01 ± 0.008</td>
<td>0.05 ± 0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ND</td>
<td>0.10 ± 0.04</td>
</tr>
</tbody>
</table>

ND stands for Not detected
<table>
<thead>
<tr>
<th>SITE</th>
<th>NITRATES: NITRITES in ppm</th>
<th>DOC in g/l</th>
<th>Pathogenic bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
</tr>
<tr>
<td>Kithimani</td>
<td>6.00 ± 0.50</td>
<td>ND</td>
<td>20.40 ± 0.20</td>
</tr>
<tr>
<td>Nquluni</td>
<td>7.30 ± 0.5</td>
<td>1.50 ± 0.3</td>
<td>9.30 ± 0.75</td>
</tr>
<tr>
<td>Kwa Mvunbi</td>
<td>7.50 ± 0.1</td>
<td>1.80 ± 0.3</td>
<td>10.80 ± 0.40</td>
</tr>
<tr>
<td>Isooni</td>
<td>8.10 ± 0.2</td>
<td>ND</td>
<td>4.90 ± 0.20</td>
</tr>
<tr>
<td>Sengani</td>
<td>5.20 ± 0.1</td>
<td>ND</td>
<td>5.50 ± 0.15</td>
</tr>
<tr>
<td>Tala</td>
<td>6.40 ± 0.4</td>
<td>0.80 ± 0.01</td>
<td>3.10 ± 0.20</td>
</tr>
<tr>
<td>Vangala</td>
<td>0.02 ± 0.004</td>
<td>4.50 ± 0.20</td>
<td>2.50 ± 0.20</td>
</tr>
<tr>
<td>Kalandini</td>
<td>0.20 ± 0.06</td>
<td>ND</td>
<td>11.70 ± 0.50</td>
</tr>
<tr>
<td>Katine</td>
<td>0.20 ± 0.007</td>
<td>5.30 ± 0.1</td>
<td>ND</td>
</tr>
<tr>
<td>Kyaume</td>
<td>1.50 ± 0.1</td>
<td>3.00 ± 0.2</td>
<td>16.80 ± 0.70</td>
</tr>
<tr>
<td>Kitunduni</td>
<td>1.30 ± 0.10</td>
<td>2.00 ± 0.1</td>
<td>3.00 ± 0.25</td>
</tr>
<tr>
<td>Kisukioni</td>
<td>ND</td>
<td>ND</td>
<td>2.80 ± 0.40</td>
</tr>
<tr>
<td>Ngonda</td>
<td>2.30 ± 0.2</td>
<td>1.50 ± 0.1</td>
<td>22.80 ± 0.80</td>
</tr>
<tr>
<td>Kvaume</td>
<td>ND</td>
<td>0.20 ± 0.01</td>
<td>4.40 ± 0.10</td>
</tr>
<tr>
<td>Silanga</td>
<td>5.40 ± 0.7</td>
<td>12.00 ± 0.8</td>
<td>30.80 ± 1.20</td>
</tr>
</tbody>
</table>

ND stands for Not Detected.
Table 15. Levels of Nitrates, Nitrites, Dissolved Organic Carbon, and the presence of pathogenic bacteria in wells and bore holes in Ngong

<table>
<thead>
<tr>
<th>SITE, SUBSTANCE</th>
<th>NITRATES, NITRITES in ppm</th>
<th>DOC in g/l</th>
<th>Pathogenic bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
</tr>
<tr>
<td>001</td>
<td>0.20 ± 0.01</td>
<td>4.00 ± 0.01</td>
<td>2.50 ± 0.50</td>
</tr>
<tr>
<td>002</td>
<td>0.04 ± 0.002</td>
<td>5.25 ± 0.01</td>
<td>2.70 ± 0.60</td>
</tr>
<tr>
<td>003</td>
<td>0.02 ± 0.001</td>
<td>0.20 ± 0.01</td>
<td>3.0 ± 0.20</td>
</tr>
<tr>
<td>004</td>
<td>0.02 ± 0.001</td>
<td>0.50 ± 0.02</td>
<td>3.10 ± 0.30</td>
</tr>
<tr>
<td>Kiseraian Govt</td>
<td>0.04 ± 0.003</td>
<td>ND</td>
<td>2.40 ± 0.50</td>
</tr>
<tr>
<td>Lolua</td>
<td>0.02 ± 0.002</td>
<td>0.20 ± 0.01</td>
<td>1.80 ± 0.40</td>
</tr>
<tr>
<td>Quarry</td>
<td>ND</td>
<td>3.50 ± 0.20</td>
<td>3.00 ± 0.30</td>
</tr>
<tr>
<td>Ngong Town</td>
<td>ND</td>
<td>2.00 ± 0.10</td>
<td>2.40 ± 0.50</td>
</tr>
<tr>
<td>Ongata Rongai</td>
<td>0.04 ± 0.002</td>
<td>0.80 ± 0.21</td>
<td>4.00 ± 0.20</td>
</tr>
<tr>
<td>Kiseraian Town</td>
<td>ND</td>
<td>2.10 ± 0.10</td>
<td>2.40 ± 0.50</td>
</tr>
<tr>
<td>Karen</td>
<td>ND</td>
<td>2.50 ± 0.25</td>
<td>2.70 ± 0.40</td>
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<tr>
<td>005</td>
<td>0.04 ± 0.002</td>
<td>1.10 ± 0.07</td>
<td>ND</td>
</tr>
<tr>
<td>Kikeni</td>
<td>ND</td>
<td>4.80 ± 0.40</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND stands for Not Detected.
<table>
<thead>
<tr>
<th>SITE SUBSTANCE</th>
<th>NITRATES/NITRITES in ppm</th>
<th>DOC in g M⁻¹</th>
<th>Pathogenic bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WET</td>
<td>DRY</td>
<td>WET</td>
</tr>
<tr>
<td>Kikuyu</td>
<td>4.80 ± 0.35</td>
<td>12.50 ± 0.30</td>
<td>2.20 ± 0.40</td>
</tr>
<tr>
<td>Sigona</td>
<td>6.00 ± 0.20</td>
<td>9.70 ± 0.30</td>
<td>2.700 ± 0.20</td>
</tr>
<tr>
<td>Muguga</td>
<td>6.20 ± 0.25</td>
<td>10.20 ± 0.40</td>
<td>2.50 ± 0.50</td>
</tr>
<tr>
<td>Zambezi</td>
<td>7.40 ± 0.20</td>
<td>15.00 ± 0.30</td>
<td>3.00 ± 0.80</td>
</tr>
<tr>
<td>Wangige</td>
<td>ND</td>
<td>ND</td>
<td>3.70 ± 0.10</td>
</tr>
<tr>
<td>Kiguni</td>
<td>0.04 ± 0.001</td>
<td>0.50 ± 0.01</td>
<td>4.20 ± 0.20</td>
</tr>
<tr>
<td>Lower Kabete</td>
<td>0.04 ± 0.0014</td>
<td>10.60 ± 0.50</td>
<td>5.20 ± 0.10</td>
</tr>
<tr>
<td>Upper Kabete</td>
<td>0.02 ± 0.001</td>
<td>ND</td>
<td>2.45 ± 0.40</td>
</tr>
<tr>
<td>Kirangari</td>
<td>ND</td>
<td>2.10 ± 0.10</td>
<td>2.40 ± 0.40</td>
</tr>
<tr>
<td>Ondiri</td>
<td>ND</td>
<td>3.00 ± 0.10</td>
<td>4.20 ± 0.20</td>
</tr>
<tr>
<td>Thogoto</td>
<td>0.10 ± 0.04</td>
<td>2.20 ± 0.18</td>
<td>3.00 ± 0.10</td>
</tr>
<tr>
<td>Alliance B</td>
<td>0.10 ± 0.40</td>
<td>4.60 ± 0.60</td>
<td>16.80 ± 0.45</td>
</tr>
</tbody>
</table>

ND stands for Not Detected.
3.3 DISCUSSION

3.3.1 HEAVY METALS IN UNDERGROUND WATER AQUIFERS

Sources of Trace Metals in Natural Waters

Sources of trace metals are basically two - either natural (chemical weathering of rocks, volcanic activity) or man influenced (burning of fossil fuels, mining operations, industrial use of trace metals). Man's influence is essentially a kinetic one in that the rate or flux of trace metals in the general biogeochemical cycle is accelerated at specific points in the cycle. Specifically, activities in industrialized cities have accelerated the flux of trace metals in both the atmosphere and the biosphere.

Natural Sources

On a geologic time scale chemical weathering and volcanic or tectonic activities have been the major release mechanisms operating to introduce trace metals into waters. In the case of mercury, for example, volcanic activity can be responsible for major natural inputs in a localized sense. On the other hand, chemical weathering of igneous and metamorphic rocks is responsible for the major natural
flux of trace metals into aquatic environments. The role of chemical weathering reactions in producing the chemical composition of natural waters has been extensively studied [111]. The significance of biochemical weathering is understood to a lesser extent. However, the role of natural organic chelating agents in the weathering process is significant even if unquantified [112].

**Industrial, Mining and Fossil Fuels**

In many urbanized regions and in areas where there has been considerable disruption of natural materials through excavations, mining and road building, the exposed and loose materials undoubtedly weather at accelerated rates. The exposure of fresh rock to the atmosphere by mining is known to be one process that accelerates the mobilization of trace metals into aquatic systems.

Airborne particulates and gaseous species can be significant sources of trace metals in natural waters when deposited as dry fallout or rainout. Evidence indicates that the general order of volatility of some trace metals as oxides is as follows: As > Hg > Cd > Pb > Zn > Cu [113]. For example, these metals are released into the atmosphere by forest fires, smelting operations, the burning of fossil fuels and, for lead, the burning of leaded gasoline. Few reliable estimates are available on the quantities of trace
metals entering natural waters through industrial and
domestic waste effluents. With increasingly strict state
effluent standards being imposed to protect receiving
waters, more reliable data may be generated through
effluent monitoring programs.

The results of this study are discussed in light of
the above introduction and the location of the sites in
relation to Nairobi.

Cadmium was not detected in any of the 40 sites in the
two seasons during which analyses were done. This is
probably due to the fact that cadmium concentrations were
below the detection limit of the instrument (Table 6) even
after preconcentration and that the amount of cadmium in
the earth's crust is the lowest of the five metals [18].
There is also the possibility of cadmium co-precipitating
with other metals such as manganese and suspended matter.
There is also the possibility of up-take by biota.

The absence of some these metals in some of the sites
is due to differences in the chemical composition of the
soils. Kikuyu division with rich volcanic soil has the
highest percentage number of sites with the metals during
either of the seasons. This is because during volcanic
eruption, most elements in the lava and others in basement
rocks deep in the earth's crust were brought to the
surface. They usually get into underground waters as
nitrates during the rain season.
Kangundo and Ngong divisions have semi-arid tropical climate with sandy and alluvial soils respectively which are not as rich as volcanic soils in mineral content and thus they have more sites lacking a majority of the metals.

There were some sites in which trace metals were present during the wet season only and vice versa. The former is due to the fact that there are many seasonal underground streams which pass through underground rocks and dissolve the trace metals and transport them to underground waters; during the dry season, these streams dry up. The latter observation can be attributed to the fact that the metals were originally present in micro-quantities which were not detectable during the wet season but during the dry season, the rate of evaporation is higher than the rate of trace metal adsorption, precipitation and uptake by aquatic biota.

The presence of these metals in underground waters can be explained by the fact that they occur as insoluble ores in rocks [114]. Water contains dissolved carbon dioxide in form of weak carbonic acid and dilute nitrous and nitric acids formed by atmospheric oxidation of nitrogen by lightning. When underground water streams containing these weak acids pass over or through rocks, they dissolve the heavy metals in trace amounts and carry them into the wells and bore-holes. During the wet season, large amounts of surface water drain into underground water aquifers and the
trace amounts of these metals are diluted to levels below the detection limit of the analytical instrument. However during the dry season, the levels of these metals increase. This explains why heavy metals were in more sites during the dry season than in the wet season.

Except for manganese, the highest levels for all metals were obtained during the dry season. This is because during the dry season water salinity and pH increase due to the hydrolysis of carbonates, sulphates and phosphates to hydrogen carbonates, hydrogen sulphates and hydrogen phosphate respectively, with the subsequent production of hydroxide ions. Manganese would then precipitate out as insoluble hydroxides [107]. The lowering of the levels of manganese during the dry season may be due to the fact that manganese has the ability to remain fixed to suspended matter [115]. As a result, manganese has a shorter residence time and settles rapidly onto sediments, leading to low concentrations of the dissolved metal in the water column. This situation of increased metal concentration in sediments than in water samples has been reported by Pande [116] in lake Naini Tal in India.

Lead was more prevalent in sites found in Kikuyu. This may be attributed to anthropogenic activities. Kikuyu division has a high population density [8] and the local people practise intensive farming. Pesticides and fertilizers used by the farmers within the water catchment
areas probably end-up draining into the underground waters. Fertilizers may contain upto 400ppm lead which constitute a major source of soil pollution and eventually the water system. Kikuyu division is one of the most densely populated areas in Kenya and people own vehicles and there are many jua kali garages in most rural centres. Emissions of lead with exhaust gases from gasoline combustion may result into significant inputs of lead into the environment. Long term leaching of battery acids, diesel and other oils from these jua kali garages may find their way into underground waters giving rise to lead levels. It also has a developed road network and there is extensive excavation for building stones. This exposes underground rocks to rapid weathering, especially the rapidly-weathered sulphide mineral [117].

Copper levels were high in Kangundo and Kikuyu divisions with mean concentration of 0.30 and 0.22ppm respectively as compared to Ngong with a mean of 0.13ppm. This may be due to the fact that both Kangundo and Kikuyu divisions have high population densities [8] and practise intensive farming. The high levels of copper may then be a reflection of the extent to which it is used as fungicides and insecticides in the coffee and small scale horticultural farms. However, the levels of copper were high during the wet season. This is mainly due to differences in well
construction. Majority of the wells in Kangundo are open surface water run-off drains directly into the wells during the rain season. During the dry season the levels decrease due to lowering of the water table. On the other hand, majority of the wells in Kikuyu division have in built quarry walls from the bottom of the well to about half a metre above the surface. This prevents surface water containing toxic pollutants from draining directly into the wells. The water containing the dissolved copper then drains into wells via the soil where it is filtered and retained by the soil for long periods of time.

Most of the local people in Ngong from where samples were collected are rich migrant communities majority of whom practise small scale and urban farming in their home yards and do not use fertilizers.

The mean levels of zinc in Ngong, Kangundo and Kikuyu divisions were 0.91, 1.90 and 4.81ppm respectively. This is attributed to differences in soil characteristics. The entire Kikuyu division has red volcanic soil which is rich in mineral content. Some parts of Kangundo division have rich volcanic soil especially areas around Tala, while the area around Nguluni (Figure 1) has loam and sandy soils which are poor in mineral content. The areas in Ngong from where samples were collected have loam soil. Loam and sandy soil are easily leached leading and have low mineral contents.

From the low levels of the toxic metals, most of which
were below both the maximum acceptable limits set by the W.H.O. and the Kenyan government, it was concluded that there was no evidence of industrial pollution in sites from which samples were obtained. This might be due to the industrialists adhering to environmental safety regulations set by the Kenya National Environmental Secretariat (K.N.E.S) and United Nations Environmental Programme (UNEP) regarding treatment and discharge of industrial effluent or that the toxicants are accumulating and have not percolated deep enough to reach the water table since Kenya is a relatively young country in terms of industrialization.

There are many reported cases in literature [118] where toxic wastes were dumped in one locality and pollute water in far away places due to migration of the toxins through water; for example in 1947 the Michigan Department of Health was notified that water from wells tapping the glacial drift in the western part of the village of Douglas in Allegan county had turned yellow. The wells were removed from service pending analysis of water samples. The analysis revealed a chromate content of 10.80ppm [118].

The source of contamination was quickly located. About 3 years before the contamination occurred, a metal plating company was discharging its waste into an infiltration pit. Discharge of the industrial wastes had resulted in contamination of the glacial-drift aquifer for at least 1000 feet in one direction from the pit and to a depth of
37 feet. The rate of migration of the waste was about 1 foot/day.

Although the 1947 analysis of water from other wells far away from the village of Douglas showed no chromate content, water from the wells was analysed periodically as a safeguard.

3.3.2 DISSOLVED ORGANIC CARBON

Dissolved Organic carbon (DOC) was obtained at high concentrations during the wet season. It was also observed that DOC was in more sites during the wet season. This is because rain dissolves previously bound DOC on soil particles and accelerates decay of animal and plant remains. Since DOC is also biodegradable it is broken down into carbon dioxide and smaller units such as methane, hydrogen sulphide, amines, carbon dioxide etc. DOC biodegradation is accelerated by rise in temperature especially during the dry season and this explains why fewer sites contained DOC in the season.

DOC was more prevalent in open shallow wells as compared to boreholes. This because open wells allow direct drainage of surface water while in the case of bore holes and covered wells, the DOC in water gets into the underground aquifers through the soil. Some of the DOC is filtered and retained by the soil where it is biodegraded into gaseous
products by soil microbes.

3.3.3 NITRATES/NITRITES IN UNDERGROUND WATER AQUIFERS

Nitrate and nitrite get into underground waters from three sources: from nitrous and nitric acids formed via atmospheric oxidation of nitrogen by lightning, nitrogen fixation by soil bacteria and nitrogenous fertilizers applied in farms to increase crop yield.

The amounts of nitrates/nitrites in ground water samples were higher in Ngong and in Kikuyu divisions during the dry season. In Tala, the NO$_3^-$/NO$_2^-$ levels were higher during the rainy season. The increase in the levels of NO$_3^-$/NO$_2^-$ in underground water sources in Ngong and Kikuyu division was probably due to decrease in the water-table owing to a high rate of evaporation and uptake by boita during the dry season, and nitrification by soil bacteria.

The fact that the levels of NO$_3^-$/NO$_2^-$ decreased during the dry season in Kangundo division points to a possibility that the chief source of the NO$_3^-$/NO$_2^-$ during the rain season is the nitrogenous fertilizers used in farming which drain into the open wells during surface run-off of rain water. Tala in Kangundo division is a highly populated area with 10,000 persons/square Km. The communities have settled in this area for more than 150 years and the soil requires
commercial fertilizers to produce food crops.

Nitrate in solution reaches the water table through cracks and fissures and by percolation through intergranular spaces on a rate depending on the type of stratum. Studies have suggested that most of the downward movement through chalk takes place by percolation at a rate of roughly one meter per year [119].

Since water table lies at depths of 5-80 metres, many years may elapse before nitrates applied at the land surface reach the chalk aquifers and go into supply. Bearing in mind that the movement of nitrates is slow, and that there is also a time interval between exposure and death, it may be too soon for the full impact of increasing fertilizer usage, via water-borne nitrate to be apparent. Even though the available data on nitrate levels may be misleading when water samples for analysis were obtained weeks after acute illness, during which time the nitrate levels have changed considerably, information about possible contributory factors to certain disease conditions may also be lacking.

Methods for treatment of small sources of waters should be devised. It is acknowledged that this is a difficult area in which to exercise control but available study evidence suggests generally that no adverse overt health effects on local populations have occurred. It is important to realize that inspite of the extended knowledge
on purification systems it is better to rely on well-protected, raw water sources for which "relatively simple" purification methods are sufficient to produce safe drinking water.

3.3.4. PATHOGENIC BACTERIA IN UNDERGROUND WATERS.

Introduction

The fate of pathogenic bacteria and other microbes in the subsurface is determined by their survival time and retention by soil particles. Both survival time and retention are largely determined by three factors: climate, soil properties, and soil pH and organic matter. Climate controls two important factors that determine bacterial survival: temperature and rainfall. The survival of micro-organisms is greatly prolonged at low temperatures, typically below 4°C, they can survive for months and even years. Table 17 shows some of the factors that affect bacterial survival times.

At higher temperatures, inactivation or die-off is fairly rapid due to dehydration. In case of bacteria, the die-off rate is approximately doubled with each 10°C rise in temperature between 5 - 30°C (121). Above 30°C, temperature is the dominant factor.
Table 17. Factors that Determine the Survival of Pathogenic Bacteria. [120]

<table>
<thead>
<tr>
<th>Factor</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>Greater survival time in moist soils and during times of high rainfall.</td>
</tr>
<tr>
<td>Moisture holding capacity</td>
<td>Survival time is less in sandy soils with lower water holding capacity.</td>
</tr>
<tr>
<td>Temperature</td>
<td>Longer survival at low temperatures.</td>
</tr>
<tr>
<td>pH</td>
<td>Shorter survival time in acid soils (pH 3.5) than in alkaline soils.</td>
</tr>
<tr>
<td>Organic matter</td>
<td>Increased survival time and regrowth when sufficient amounts are present.</td>
</tr>
<tr>
<td>Antagonism from soil microflora</td>
<td>Increased survival time in sterile soil.</td>
</tr>
</tbody>
</table>
A major factor in determining the survival of bacteria in the soil is moisture. Young and Greenfield [121] showed that moisture was a major factor in the viability of Escherichia coli in soils. Beard [122] stated that moisture was the most important determining factor in the survival of Salmonella typhosa. Bacterial survival was determined in various types of soil exposed outdoors in day flower pots, survival was greatest during the rain season. Table 17 below shows some of the most important factors that influence the survival times of pathogenic microbes in the soil or ground waters.

It was observed that pathogenic bacteria were more prevalent during the rainy season. Pathogens bacteria were detected in five water samples from Kangundo as compared to four in Ngong and two in Kikuyu during the wet season. During the dry season there were only two sites in Kangundo in which pathogenic bacteria were present.

The observations regarding the presence of pathogenic bacteria in underground waters will be discussed in light of the above introduction.

Rainfall mobilizes previously retained bacteria and greatly promotes their transport to ground waters [124 126]. The nature of the soil also plays a major role in determining survival and retention of bacteria. Soil properties influence moisture holding capacity, pH and organic matter all of which control the survival of
bacteria in the soil. Other soil properties such as particle size, cation-exchange capacity and clay content influence bacterial retention. Microbial resistance to environmental factors varies among different species as well as strains. Bacteria are largely removed by filtration processes.

From the wide geographic area of study from which samples were collected the soil texture varied from place to place. Kangundo and parts of Ngong divisions experience semi-arid climatic conditions with loam soil while Wangige in Kikuyu Division experience tropical climate with heavy rainfall and volcanic clay soils. The former areas become extremely hot during the dry season with temperatures above 30°C and this explains why during the wet season water in these areas is contaminated with bacteria from pit latrines which are of the same depth as the wells especially in Kangundo where the water table is very near the surface. These bacteria are immobilised during the dry season due to decrease in underground water.

From the data collected in this study, it is evident that ground water in Kenya is not as safe as is generally assumed. From oral interviews with villagers of Vangala in Tala of Kangundo Division, there were reported case fatalities due to bacterially contaminated water; but this information could not be independently verified.

Chemical toxicity from heavy metals, dissolved
organic matter and nitrates largely go unnoticed in all the areas from which samples were collected. Most people associated water toxicity with pathogenic microbes which were assumed to be removed by simple boiling.

Majority of the people asked about their understanding of toxic substances in drinking water responded that the water toxicity was indicated by-

(i) Short term toxic chemical effects.
(ii) Colour of the water, though assumed to be harmless.
(iii) Odour
(iv) saltiness (salinity) and taste.

From the foregoing it is clear that the Kenyan rural folk is largely ignorant of the dangers inherent in consuming untreated water. This is mainly due to illiteracy and poverty in which some people are faced with a no alternative source of water. The existing regulations regarding standards of safe water should be enforced. Other laws should also be enacted in which it is made mandatory that people who do not use treated water should take samples of the water they use to government laboratories for analysis at a fee at least twice a year — during the wet and dry seasons.

Treated water samples were collected from Kenyatta University and Kabete water works during the wet and dry seasons. They were quantified for the toxic substances and
screened for the pathogenic bacteria. The aim was to find out if treated water consumed in Nairobi conformed to W.H.O. specifications. Water from both sites was found not to contain toxic metals even after pre-concentration. This is probably due to adsorption of the metal ions (Cd, Cu, Zn Mn and Pb) onto the surfaces of the storage tanks and the pipes such that levels were below the detection limit of the analytical instrument. Precipitation of the trace metals could also have reduced their concentrations below detectable levels since water consumed in Nairobi is transported from Sasumua and Ndakaini dams which are over 100 kilometres away. Pathogenic bacteria were also not detected due to chlorination during treatment. Kenyatta University water was found to have both dissolved organic carbon and suspended organic matter. Suspended organic matter was observed as the residue left on a 0.45μm filter. No dissolved organic carbon was detected during the dry season. Two samples (out of 5) contained dissolved organic carbon (DOC) of 2.05mg/l and 3.10mg/l.
CHAPTER 4

CONCLUSION AND RECOMMENDATIONS FOR FURTHER RESEARCH

4.1 CONCLUSION

From the results obtained in this study it was deduced that toxic metals are present in water mostly in trace amounts below the W.H.O. maximum admissible levels. Some potable underground waters contain toxic metals in levels higher than those set by the W.H.O. for example zinc, lead and manganese were detected at levels of 15.50ppm, 1.00ppm and 3.30ppm, respectively. These levels are above the W.H.O. maximum admissible limits (Table 2). These high concentrations were detected at the following sites; Zambezi in Kikuyu, Ongata Rongai and Sengani for zinc, lead and manganese, respectively. The levels of toxic metals were generally higher during the dry season. Manganese occurred in higher concentrations during the wet season than during the dry season, the levels of cadmium in underground waters were extremely low; below the detection limit of the instrument.

It was also noticed that the levels of nitrates/nitrites in underground waters sometimes reflect the use of nitrogenous fertilizers in farmlands although in the areas studied there were no levels detected which were
above the W.H.O. maximum acceptable and the W.H.O. maximum admissible limits of 45ppm and 100ppm respectively. The highest detected concentration was 15ppm. It was found that underground waters are occasionally contaminated with pathogenic bacteria.

4.2 AREAS OF FURTHER RESEARCH

There are many toxic substances in potable waters which were not quantified in this study; such as isolation and characterisation of dissolved organic carbon, anions such as sulphates, halides and phosphates and screening for the presence of other pathogenic microbes such as fungi and virus.

Chlorination of water has been shown to be one of the active precursors for the production of carcinogens due to the inherent oxidation of dissolved organic carbon to very reactive compounds [127].

In Kenyan urban towns and centres where water is treated by chlorination, a study needs to be conducted to find out if chlorination produces any of the known carcinogens such as aromatic chloramines since it is well known that the type of dissolved organic carbon (or total organic carbon) depends on the source of the water; underground, river or dam, the additives added during disinfection and the type of piping used in transportation.
Further research work need to be conducted on the heavy metal speciation in natural underground water aquifers.

4.3 HEAVY METAL SPECIATION IN NATURAL WATERS

The speciation of an element is the determination of the individual physico-chemical forms of that element which together make up its total concentration. It is now a well known fact that speciation measurements are necessary for the study of toxicity of metals to aquatic organisms and an understanding of trace metal transportation in natural water systems. Measurement of the total concentration of a trace element provides no information about its bioavailability or its interaction with sediments and suspended particles.

Three different basic approaches have been used to investigate the speciation of trace metals:

(i) study of the behaviour and reactions of an element in a model water system,
(ii) prediction of the species distribution using thermodynamic modelling, and
(iii) the determination of species or group of species in real water samples.

The toxicity of trace elements to man depends on the form ingested. The alkyl compounds of mercury and lead are
highly toxic because they are lipid soluble and materials such as the lead halide aerosols emitted by automobiles can enter the lungs and be absorbed directly into the bloodstream. Mercury and tin form organo-metallic compounds which are more toxic than the inorganic ions. Change in oxidation state of an element can have profound effect on its bio-availability and toxicity. Chromium(III) is an essential element while chromium(IV) is highly toxic. Arsenic(III) is more toxic than arsenic(V). Most studies of the toxicity of heavy metals for fish have shown that the free hydrated metal ion is the most toxic form.

Inorganic aluminium species are apparently more toxic than aluminium bound to organic ligands. Toxicity of heavy metals is governed by such processes as complexation with organic and inorganic metal ligands, and adsorption to clays, organic particulates and hydrous metal oxides. Complexes formed by coordination with weak field monodentate ligands are usually of low stability and are suspected of being more potent toxicants. Strong field monodentate complexes are relatively more stable and are considered to less potent toxicants than weak field complexes. Species associated with colloidal particles are considered or assumed to be non-toxic.

It is difficult to either detect individual species in the complex aquatic media by only direct method or by isolating them from water. Trace metals may be associated
with forms ranging from simple molecules and ions via hydrolysis products to form colloids and pseudo-colloids or be adsorbed on and incorporated in suspended inorganic and organic particles. It is necessary to consider kinetics and thermodynamics data together with analytical data in order to infer the physical and chemical forms present; distinguish between oxidized and reduced, complexed and non-complexed, dissolved and colloidal and monomeric and polymeric species.

Using voltametric methods, metal speciation studies have revealed that most trace elements occur as complexes of the following ligands: hydroxo, carbonato, bicarbonato, chloro, flouro, bromo, sulphato and organic acids like amino acids in the natural waters [30].

Speciation studies on Kenyan lake waters have been carried out by some researchers [107,128]; and this work needs to be extended to underground waters.
REFERENCES


Health Effects of Trace Metal Concentrations of Zinc. 
Amer. J. Physiol. 107, 146.

Part II: Health Effects, 3rd Ed. John Wiley and 

4, 313-333.

41. Skidmone, J.F. (1964) Toxicity of Zinc Compounds to 
Aquatic Animals with Special Reference to Fish. 

42. United Nations Environmental Programme (1980) Waste 
Discharge into the Marine Environment. Principles and 

43. Wright, R.F. and Henriksen, A. (1973) Trace Metal 
Concentrations in Natural waters. Water Research. 


Statistical Treatment of Data
1. Mean

The mean levels of each substance for each area was carried out for pentaplicate determinations. This was done to ensure accuracy into the actual value of the levels. The mean was calculated using equation C-1 below.

\[ \bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \]  

\[ \text{where} \]

\[ x \] is the mean

\[ x_i \] is the \( i \)th term of the eight determinations

\[ n \] is the total number of determinations (8).

2. Standard deviations and relative standard deviation (rsd)

This was used to measure dispersion of the obtained readings about the mean. The following equation was (c-2) used to calculate the standard deviation.

\[ s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \]  

\[ \text{............}(c-2) \]
3. Correlation coefficient (r)

Results of wet and dry seasons were correlated by the Pearson (or product-moment) correlation coefficient (r) to test whether the corresponding readings got for each region for each substance during the two seasons were comparable. The following equation (C-3) was used to correlate dry and wet season levels treated as x and y variables respectively.

\[
 r = \frac{\sum_{i=1}^{n} (x_i - \bar{x}) (y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 (y_i - \bar{y})^2}} \quad \ldots \ldots \quad (C-3)
\]

The degree of correlation between the two methods was treated as fair for \(0.90 < r < 0.95\), good for \(0.95 < r < 0.99\) and excellent for \(r > 0.99\).
4. **t-test on the r-value**

The statistical test used to test whether the correlation (r) obtained for all substances for each area were significant was t-test given by the equation below:

\[ t = \sqrt{\frac{(n-2)}{(1-r^2)}} \]  \hspace{5mm} (C-4)

Where \( n \) is the number of data points.

The t-values calculated were compared with tabulated t-values at 95%, 98% and 99% confidence level using a two tailed test and \((n-2)\) degrees of freedom. The null hypothesis in these cases was that there was no correlation between the mean levels obtained during the wet and dry seasons.

If the \( t_{\text{calculated}} > t_{\text{tabulated}} \), the null hypothesis is rejected; that is, we conclude in such a case that a significant correlation does exist. Conversely, when \( t_{\text{calculated}} < t_{\text{tabulated}} \), the null hypothesis is accepted; that is, we conclude that in such a case there is no significant relationship.
APPENDIX B

FIGURES (BAR CHARTS)

Figures showing the comparisons of the concentrations of toxic substances during the wet and the dry seasons with the site names abbreviated as serial numbers.

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Name of Sites in Kangundo</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>Kithimani</td>
</tr>
<tr>
<td>002</td>
<td>Nguluni</td>
</tr>
<tr>
<td>003</td>
<td>Kwa Musembi</td>
</tr>
<tr>
<td>004</td>
<td>Isooni</td>
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<tr>
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<td>Tala</td>
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<td>Vangala</td>
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<td>Kyamulendu</td>
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<tr>
<td>015</td>
<td>Silanga</td>
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<td>Serial Number</td>
<td>Name of Sites in Ngong</td>
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<td>006</td>
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<td>Ongata Rongai</td>
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<td>Kiserian Town</td>
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<tr>
<td>012</td>
<td>Karen</td>
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<td>Kikení</td>
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<table>
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<th>Serial Number</th>
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</thead>
<tbody>
<tr>
<td>001</td>
<td>Kikuyu Town</td>
</tr>
<tr>
<td>002</td>
<td>Sigona</td>
</tr>
<tr>
<td>003</td>
<td>Muguga</td>
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<td>012</td>
<td>Alliance B.</td>
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</table>
LEVELS OF Copper DURING Wet and Dry Seasons

Figure B1

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Series 1 wet  Series 2 dry
LEVELS OF Zinc DURING Wet and Dry Seasons

![Graph showing levels of zinc during wet and dry seasons.](image)

- Series 1 wet
- Series 2 dry

Figure B2
LEVELS OF Lead DURING Wet and Dry Seasons

Levels of Lead in ppm

Series 1 wet - Series 2 dry

Language Division Figure B3
LEVELS OF Manganese DURING Wet and Dry Seasons

Levels of Manganese in ppm

<table>
<thead>
<tr>
<th>Site</th>
<th>Series 1 wet</th>
<th>Series 2 dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td></td>
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<td>2</td>
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<td>15</td>
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</tbody>
</table>

Kagundo Division Figure B4
LEVELS OF Nitrates/Nitrites DURING Wet and Dry Seasons

Levels of Nitrates/Nitrites in ppm

<table>
<thead>
<tr>
<th>Site</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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</tr>
</tbody>
</table>

- Series 1 wet
- Series 2 dry

Languado Division Figure B5
LEVELS OF DOC DURING Wet and Dry Seasons

Levels of DOC in mg/l

site

Series 1 wet  Series 2 dry

Kenagundo Division Figure B6
LEVELS OF Copper DURING Wet and Dry Seasons

Figure B7
LEVELS OF Zinc DURING Wet and Dry Seasons

![Graph showing levels of zinc during wet and dry seasons.](image)

**Legend:**
- ■ Series 1 wet
- □ Series 2 dry

**Figure B8**
Levels of Lead during Wet and Dry Seasons

Figure B9
LEVELS OF Manganese DURING Wet and Dry Seasons

![Bar chart showing levels of manganese in ppm for 13 sites, with different patterns for series 1 (wet) and series 2 (dry).]

Myong Division Figure B10
LEVELS OF Nitrates/Nitrites DURING Wet and Dry Seasons

Figure B11
LEVELS OF DOC DURING Wet and Dry Seasons.

The graph shows the levels of DOC (Dissolved Organic Carbon) in mg/l for different sites during the wet and dry seasons. The bars represent the levels of DOC for each site, with the wet season data indicated by solid bars and the dry season data by striped bars. The graph illustrates higher DOC levels during the wet season compared to the dry season for most sites.
LEVELS OF Copper DURING Wet and Dry Seasons

Kikuyu Division Figure B13
LEVELS OF Zinc DURING Wet and Dry Seasons

Figure B14
LEVELS OF Lead DURING Wet and Dry Seasons

Levels of Lead in ppm

Levels of Lead in ppm

site

1 2 3 4 5 6 7 8 9 10 11 12

Series 1 wet  Series 2 dry

Figure B15
LEVELS OF Manganese DURING Wet and DRY Seasons

![Graph showing levels of Manganese during wet and dry seasons.](image)

**Levels of Manganese in ppm**

**Site**

---

Series 1 wet: [Bars]
Series 2 dry: [Bars]

**Figure B16**
LEVELS OF Nitrates/Nitrites DURING Wet and Dry Seasons

![Bar chart showing levels of nitrates/nitrites during wet and dry seasons for different sites.]

Kikuyu Division Figure B17
LEVELS OF DOC DURING Wet and Dry Seasons

![Bar chart showing levels of DOC during wet and dry seasons for different sites.](chart.png)

Kikuyu Division Figure B18