

ANALYSIS OF CONSTITUENT CHEMICALS AND THEIR EFFECTS ON
THE PHYSICO-CHEMICAL PROPERTIES OF SPRING WATER IN
GICHUGU DIVISION KIRINYAGA DISTRICT

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for the Award of the Master of Science Degree in Chemistry of Egerton University

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DEDICATION

I dedicate this work to my late mother Mary Nyambura, my husband Wanjau and Daughter Njeri.

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ABSTRACT

Gichugu division has numerous springs, which are a manifestation of potentially high volumes of groundwater whose character is determined by the interplay between itself and precipitation, rivers, soils and vegetation. This study was aimed at determining groundwater chemistry in the area by use of such analytical methods as Atomic Absorption Spectroscopy (AAS), Flame photometry, titration and UV spectrophotometry. Some parameters like pH, temperature, dissolved oxygen and conductivity were analysed using appropriate meters. Ion selective electrode was used for fluoride analysis. Groundwater in Gichugu- division is characteristically different from river water in terms of fizzling, characteristic taste and clarity. These physical properties could be explained in terms of chemical composition of the water which is different from the river water, the later being fresh and not tasty or fizzy. The water consists mainly of the bicarbonates and chlorides of sodium, calcium and magnesium. Sodium bicarbonate dominates the groundwater. Chloride is the second dominant anion, the water can therefore be said to contain high concentration of sodium bicarbonate and sodium chloride. These two sodium salts explain the salty taste of the water. Dissolved gases in the water can be used to explain fizzling e.g. free carbon dioxide released by inorganic decomposition in the soil. This gas being under pressure, causes fizzling as it try to escape. Due to inter-relationship between free carbon dioxide, carbonate and bicarbonates, the water is slightly acidic (pH 6.2). This is because the free CO_2 combines with water partly to form carbonic acid (H_2CO_3). The pH is outside the normal range (6.5-8.5) and might also have contributed towards the taste of this water. This water is also moderately hard (119.3 mg/1 CaCO_3). It was established that a common groundwater aquifer underlies the area. Clarity of this water is due to its filtration through soil and rock, its long residence time in the underground and also downward movement in recharge areas (percolation) and lateral movement through aquifers (underflow) that results in significant purification. Iron (0.583 mg/1) and manganese (0.306 mg/1) were found in excess of WHO recommended limits (0.3 mg/1 and 0.1 mg/1 respectively) for potable water quality while fluoride was in relatively low amounts (0.497 mg/1). However, their levels in this water do not make this water unsuitable for drinking since they are still within the acceptable tolerance levels.

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DEFINITION; ABBREVIATIONS AND TERMS

APHA	American Public Health Association
AWWA	American Water Works Association
CDN	Catholic Diocese of Nakuru
EEC	European Economic Commission
GEMS	Global Environmental Monitoring System
ICCA	International Council of Chemicals Association
IWA	International Water Association
NPR	National Research Programme
SDWA	Safe Drinking Water Act
TCU	True Colour Units
TISAB	Total Ionic Strength Adjustment Buffer
TON	Threshold Odour Number
UNEP	United Nations Environmental Programme
UNESCO	United Nations Educational, Scientific and Cultural Organisation
USEPA	United Nations Environmental Protection Agency
WEF	Water Environmental Federation
WHO	World Health Organization
WMO	World Meteorological Organisation
Potable	Drinkable
River	A natural flow of large amount of water that continues in a long line across land
Spring	Natural outcrops of groundwater that appear as small waterholes
Stream	A small narrow river
Well	A deep manmade hole which act as a source of groundwater discharge

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Water is an excellent solvent and as a result, contains substances in solution that makes it usable for one purpose or another. It is therefore important to know the quality of water in any community and the 'quality requirements' for various water users. The chemical quality of water is a valuable tool in water investigations. Apart from its importance in the use of water, differences in the chemical quality of water from one place to another in an area may either reflect differences in the mineral composition of the aquifers or the existence of geological structures such as faults, which affect the movement of the water (Ralph and Frank, 1968).

Both surface water and groundwater originate from rainfall. After reaching the ground surface, rainwater forms surface run off or groundwater flow. It leaches out constituents from the ground strata, in particular carbonates, sulphates, chlorides, calcium, magnesium and sodium salts and as such waters from two neighbouring sources whether springs, wells, rivers or streams very rarely have precisely the same chemical composition or taste. This has resulted to progressive degradation of water quality in many rivers, lakes and aquifers hence impairing water usability (Hofkes, 1981).

In nature, all water contains some impurities. As water flows in streams, sits in lakes and filters through layers of soil and rock in the ground, it dissolves or absorbs the substances that it comes into contact with. Some of these substances are harmless. In fact, some people prefer mineral water precisely because minerals give it an appealing taste although at certain levels, minerals, just like man-made chemicals, are considered contaminants that can make water unpalatable or even unsafe (National Environmental Board, 2000).

The basic requirements for drinking water are that it should be free from pathogenic (disease causing) organisms, containing no compounds that have an adverse effect in the short or long term, on human health, fairly clear i.e. low turbidity, little colour, not saline. It should contain no compounds that cause an offensive taste or smell and not causing corrosion or encrustation of the water supply system or staining of clothes washed in it. In recent times, groundwater chemistry has become important since it is the most common source of potable water supply in the world (Freeze and Cherry, 1979).

Gichugu division of Kirinyaga district has numerous streams/rivers and protected springs,

which serve as the sources of water for domestic use to the surrounding communities. The springs such as Kindiri, Kongu, Ngungu, Kabuga, Kainamui etc and streams such as River Kiringa, River Kabuyu, River Nyamindi, River Kathogondo etc are a manifestation of the potentially high volume of ground and surface water in the area. These springs are either from within the stream or near a river/stream. The strangest aspect of spring water is that it is very different from the water in the river/ stream in terms of taste, clarity and also the way it fizzes. People of Gichugu call it *Munyu* (salt), which suggests that the water is salty. This taste makes Gichugu people to drink this water and not the stream water, which they use for any other domestic use like washing and cooking. Their animals drink from the springs also.

According to District Agriculture Office, Kerugoya (1996), in the upper parts of Gichugu, bordering the Mt. Kenya forest, is found rich red clay soils where tea and dairy farming are the major occupations. The zone is also the major coffee-growing zone in Kirinyaga district. Undergroundwater in this area has a characteristic taste.

In general terms, groundwater consists of a number of major ions, which form compounds. These are mainly calcium, magnesium, sodium, potassium and to a lesser extent iron and manganese. These are all cations, which are found combined with anions to form compounds that are referred to as salts. The major anions are carbonate, hydrogen carbonate, sulphate and chloride. Despite the fact that Gichugu division has a large number of such springs with interesting characteristics, no information concerning the chemical composition has been documented.

1.2 Physical Description of the Study Area

1.2.1 Location and Size

Kirinyaga District is one of the six districts of Central Province. It borders Nyeri to the west, Murang'a to the Southwest, Machakos and Mbeere to the south and Embu to the east. It is located between latitudes 10 and 1' South and longitude 37° and 38' East and occupies 1,437 sq.km. This area is about 0.3% of Kenya's total land area and about 10.9% of Central Province. To the north of the district, Mt. Kenya forest occupies about 21 % of the district's total land area. The district has four (4) divisions, namely; Gichugu, Ndia, Mwea and Kerugoya Kutus municipality (Kirinyaga District Development Plan, 1997).

1.2.2 Topography and Geology

Mt. Kenya lies to the north of the district. The area, rising from 2,000 m to about 4,800 m is interspersed with open U-shaped valleys and ridges. In this part, many streams have merged. The area flanking the mountain is permanently covered by natural forests, and lower down in the settlements, tea and coffee together with subsistence crops e.g. maize, potatoes, beans and bananas are cultivated. The geological structure of Kirinyaga District comprises two major rock types; the volcanic and basement systems. The soils are formed on volcanic rocks from Mt. Kenya; Pliocene to Pleistocene basalts, phenolites and pyroclastics. The predominant rock type is the quaternary. The rock structure has influenced river patterns in the district. This is due to differences in resistance to erosion that has resulted in steep-sided banks and waterfalls and also forms interesting features such as the natural bridge over River Nyamindi (*Ndaraca ya Ngai*). Most of these rocks have no economic value as far as mining is concerned because they are entirely volcanic in origin; hence there is virtually no possibility of discovering valuable minerals.

1.3 Statement of the Problem

There are a number of springs in Gichugu division, Kirinyaga district which serve as a source of drinking water to the community. These springs are found near Streams/ Rivers and some are found within a flowing river. The springs (whether in or out of the river) have water that is different (in terms of physical characteristics) from the fresh water found in the rivers. The water in these springs is tasty and it fizzes like carbonated water. This difference in physical properties is thought to be due to some chemical properties that are different from those of river water. It should be of interest therefore to find out the chemical constituents that have contributed to the altered physical characteristics of the spring water. Such constituents will include cations as well as anions such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , etc. In addition, parameters like dissolved oxygen; water hardness, pH and electrical conductivity will be determined in order to find out the impact of the altered chemical properties to the overall physical properties of the unique spring waters.

1.4 Objectives

The main objective of this study is: -

To attempt to explain the strange properties of Gichugu spring water such as fizzling, taste etc. in

terms of chemical composition of the water.

The specific objectives are: -

1. To collect water samples from several springs of Gichugu division in Kirinyaga district and to subject them to analysis of-
 - Cations (Fe^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc.), Using AAS and flame photometer.
 - Anions (NO_2^- , NO_3^- , HCO_3^- , Cl^- , F^-) and NH_3 , using UV-Vis, titration and ion selective electrode
 - Conductivity, pH, temperature and dissolved oxygen using appropriate meters
 - Total hardness
3. To assess the potability of this water by comparing the physical- chemical properties with the set standards (WHO and other international standards).
4. To make appropriate recommendations.

1.5 Justification / Significance of the Study

Over the past five to ten years, increased public awareness of environmental issues has caused consumers to be conscious about the quality of drinking water. This is reflected by the large increase of the sales of bottled water and home treatment systems. In Gichugu division, springs are used as the major sources of drinking water. Though spring water has been considered to be pure because of its filtration through layers of soil, it has its own health and acceptability problems based on concentration level of certain chemical parameters. It is therefore important to understand the level of toxicity of the chemical elements and compounds in water used for domestic purposes. Gichugu spring water has some strange physical properties like fizzling and taste but its chemical compositions, which could explain these physical properties; have not been investigated. The knowledge of the chemical compositions will therefore go along way in trying to understand the relationship between chemical composition and these physical-chemical properties of the water. It will also be useful to all those concerned with issues relating to water quality and health, including environmental and public health scientists, water scientists, policy-makers and those responsible for developing standards and regulations.

CHAPTER TWO

LITERATURE REVIEW

2.1 Groundwater Resources and their Composition

Global concerns about water scarcity include not only surface water sources but groundwater sources as well. Some 1.5 billion people rely on groundwater sources, withdrawing about 20 percent of global water (Shiklomanov, 1997). Water present underground and often in large reservoirs called aquifers is accessed by wells or springs. Springs are a natural source of groundwater discharge at a rate high enough to form a channel on the earth's surface. They are merely outcrops of groundwater that appear as small waterholes or wet spots at the foot of hills or riverbanks (Hofkes, 1981). Although over drafting from and polluting groundwater aquifers are known to be widespread and growing problems, comprehensive data on groundwater resources and pollution trends are not available on a global level (UNEP, 1996).

The physical and chemical composition of groundwater reflects not only the mineral composition of the various rock strata with which the water has been in contact, but also the various chemicals that percolate into groundwater. Along with their associated seeps and outflow brooks, springs provide a unique habitat for endemic species (organisms restricted to a localized area) of animals and plants because they usually provide a nearly constant physical and chemical environment (Wetzel, 1990).

Groundwater, the preferred source of drinking water for most people in the world is polluted particularly through industrial activities, poor sanitation practices, mining, soil erosion, animal feedlots and agricultural chemicals and fertilizers (IWA 2002). The rainfall that passes through the soil picks up a variety of minerals from the earth itself. Where considerable amount of organic matter are present either in the subsoil or in the infiltrating water, the oxygen content of the groundwater may be exhausted through microbial processes. Consequently, certain chemical reactions may be taking place through which NH_3 and H_2S are formed from the nitrates and the sulphates present in the groundwater. Similarly, iron and manganese would be dissolved in the water (Hofkes 1981).

2.2 Water Resources of Kirinyaga District

Kirinyaga District has the advantage of being on the windward side of Mt. Kenya, which is the source of its rivers. The district has several alternative sources of water namely rivers, canals, undergroundwater and roof catchment. These streams merge in the lower areas to form bigger streams and rivers with increased water volumes. Among the main rivers are, Rupingazi, Nyamindi, Thiba, Rwamuthabi, Ragati and Thagana. All these rivers ultimately empty themselves into the Tana River, which leaves the district in the southern part towards its final destination, the Indian Ocean. As they flow down the slope, they form a radial type of drainage pattern. Rupingazi River forms the boundary between Kirinyaga and Embu Districts.

Nyamindi River provides the main source of water for rice irrigation in Mwea. Rice irrigation is supplemented by water from River Thiba. Rwamuthambi and Ragati drain into the Thagana River to form a boundary between Murang'a and Kirinyaga Districts to the southwest. Water is partly diverted from the main Thagana River to provide water for fishponds by the fisheries department. There are many more minor tributaries which join these major rivers and which become the principal domestic water supply as well. There is also great potential for undergroundwater in the district. However, undergroundwater is not suitable for domestic use (washing and cooking) as it is either contaminated or salty. The district has adequate surface water resources and also undergroundwater and from this, it can be concluded that the district at present has adequate water for industrialisation. There is also potential for hydro-electric power stations given that the district has U-shaped valleys which would provide good sites for dam construction and also the permanent nature of major rivers (District Agriculture office, Kerugoya, 1996).

Among the four divisions of Kirinyaga District, Gichugu division has the most surface water supplies; these are Kianyaga, Ngariama, Kabare, Nyagithuci, Kaguma, Kiang'ombe, Kiangwenyi, Teithia, Karuti and Nyaru (District Water Engineers office, Kerugoya, 1996). However, the supply systems at some points are not adequate serving a larger population than planned for. The perennial snow and ice at the peak of Mt. Kenya maintains constant flow of these rivers all the year around and this makes the district self reliant and well endowed with reliable water sources in rural and urban areas. Rapid population growth continues to outstrip the natural supply of water. This has made it difficult in some areas to get clean water because rivers have been contaminated and made unsafe by effluence mainly from coffee factories, especially

in the lower Mwea and Ndia Divisions (District Agriculture office, Kerugoya, 1996).

The district intends to rehabilitate all the existing water supply works; Kerugoya, Wanguru, Thagana, Kabare and Ngariama with an objective of improving and conserving the environment as an important source of water as well as to supply potable and adequate water to all people in the district. There are on going projects by Kabare Rural Water Supply, Kenera Women Group Water project. South Ngiroche Women Group and Kariru Water Project all with an aim of providing sufficient and safe water to the rural communities (District Planning Unit, Kerugoya, 1996).

2.3 Water Quality

Chemicals have contaminated surface and groundwater for many decades. However, it is known to contain much less natural organic matter and fewer disease causing microorganisms than does water in the lakes and rivers (Colin, 1995). Water quality is degraded directly through chemical and nutrient pollution and indirectly when the capacity of ecosystems to filter water is degraded and when land-use changes, leads to increase in soil erosion. Although developed countries have improved water quality to some extent in the past 20 years, water quality in developing countries has been degraded substantially. Decreasing water quality poses a particular threat to the poor who often lack ready access to potable water and are most susceptible to diseases associated with polluted water (Revenga et al, 2000).

Groundwater comes into close contact with various minerals, which are soluble in water to varying degrees. The dissolved minerals determine the usefulness of the water for various purposes and the presence of some minerals beyond certain limits may make it unsuitable for irrigation, drinking, or industrial purposes, and may result in corrosion (Garg, 1982). While most chemical elements in groundwater such as Zinc, Copper, Manganese, and Lead etc. are potentially toxic; other essential elements like fluoride and Iron (at required levels) may give rise to health problems due to their deficiency in water. The toxicological and deficiency problems of the chemical constituents in water continue to become more apparent as people progressively switch from traditional supplies of surface water to biologically safer groundwater. It is consequently important to understand groundwater characteristics in terms of its chemical constituents (Ogenge, *et al.*, 2002).

Today, an examination of water quality is an assessment of chemicals, organisms, minerals and organic compounds, which the water contains (Caircross, 1980). Although water

quality measurements that focus on levels of contaminants are useful, they do not directly tell us how water pollution affects fresh water ecosystems (Karr & Chu, 1999). Variation in water quality from place to place is due to different rock formations from which the waters are derived, to the depth from which they come, to the nature of the underground circulation and most of all to the climatic conditions of the localities considered. The quality of groundwater therefore depends on a number of factors: -

- The nature of the rainwater, which can vary considerably, especially in terms of acidity due to pollution.
- The nature of existing groundwater, which may be tens of thousands years old.
- The nature of the soil through which water must percolate.
- The nature of the rock comprising the aquifer.

Fresh water systems especially wetlands play an essential role in maintaining water quality by removing contaminants and helping to break down and disperse organic wastes. But the filtering capacity of wetlands and other habitats is limited and can be overwhelmed by an excess of human waste, agricultural run off or industrial contaminants (World Resources, 2000). However, information about water quality on a global level is poor and difficult to obtain for a number of reasons. Water quality problems are often local. In addition, monitoring for water quality is by no means universal and water quality standards often vary significantly from country to country. Nonetheless, existing information makes it clear that there are many consistent trends in the contamination of water supplies worldwide. One hundred years ago, the main contamination problems were faecal and organic pollution from untreated human waste and the by-products of early industries. These pollution sources have been greatly reduced in most industrialised countries with consequent improvements in water quality (Shiklomanov, 1997 & UNEP/GEMS, 1995).

2.4 Factors Influencing Water Quality

Both natural and human factors influence the quality of water. Management of quality of water from whichever source must begin with identification of those factors involved that individually or jointly affect the water source. The degree of the impact of operative factors varies depending on the type and characteristic of source involved. For example, a volatile chemical may remain in groundwater supply but that same chemical may volatilise out of a

surface supply (APHA, 1992; AWWA, 1992 and WEF, 1992).

Factors influencing water quality are classified as either natural or human. Natural factors include climate, watershed characteristics, geology, microbial growth, fire, and saltwater intrusion and density (thermal) stratification. Human factors on the other hand are categorized as two distinct types- point or non -point. Point sources are those sources of contamination characterized by a single or discrete conveyance such as terminus of a pipe or collection of pipes. Examples include - wastewater discharges, industrial discharges, hazardous waste facilities, mine drainage, spills and releases. Non-point sources in contrast involve large and diffuse sources of contamination such as agricultural runoff, livestock, urban runoff, land development, landfills, erosion, atmospheric deposition and recreational activities.

The primary effect of climate on water quality is the precipitation. Wet climate or periods of heavy precipitation result in high rates of runoff or flood conditions that cause resuspension of sediment and increased turbidity, colour, metals or other contaminants. Under dry conditions, prolonged drought conditions, lower rates of run off can cause stagnation thereby increasing the likelihood of microbiological activity and algae growth (AWWA, 1991).

Topography affects flow rates. Steep slopes may result in erosion of topsoils or stream banks thereby introducing debris, sediments and nutrients that can increase algae, colour and turbidity. Local geology directly impacts the quality of both surface and groundwater. Groundwater with high hardness for example derives its calcium and magnesium contents from the sub surface geologic formation through which it travels. The presence of radionuclides in groundwater as another example results from the local geology. Soils play a significant role in water quality often acting as buffering agents for acidic precipitates (APHA, 1992, AWWA, 1992, WEF, 1992).

Application of pesticides, herbicides and fertilizers are the key agricultural activities that affect the quality of groundwater. The application of fertilizers to enhance crop production is of major concern to water suppliers because dissolved nutrients in the runoff accelerate eutrophication of the receiving water body. Nitrogen in the form of nitrates is a contaminant found in the groundwater underlying agricultural areas. Erosion caused by improper tilling technique is yet another agricultural activity that can adversely affect water quality through increased sediment load, colour and turbidity (AWWA, 1991).

2.5 Significance of Some Major Water constituents and properties

For the purposes of this discussion, major constituents are defined as those commonly present in concentrations exceeding 1.0 mg/l. The dissolved cations that constitute a major part of the dissolved-solids content generally are calcium, magnesium, sodium, and potassium; the major anions are chloride and bicarbonate. Some other dissolved constituents have been included in this chemical analysis because they may be particularly significant in considering suitability of water for certain purposes. Sometimes these constituents attain concentrations comparable to those of major components. They include hydrogen ion or acidity, iron, manganese, forms of nitrogen (other than nitrate) and fluoride. Minor constituents in addition to the ones listed above, whose occurrence in fresh natural water has been investigated to a significant extent, include the alkaline-earth metals (Cobalt, Copper, Zinc, Cadmium and Lead).

Certain properties of water solutions besides the contents of specific ions have commonly been included in water analyses. Hardness in water is commonly expressed in terms of an equivalent quantity of calcium carbonate. Other properties included in this water analysis were conductance, temperature and dissolved oxygen. These constituents and properties are discussed in more detail as appropriate in the following sections.

Besides being chemically safe for human consumption, water to be used in the home should be free of undesirable physical properties such as colour or turbidity and should have no unpleasant taste or odour. Harmful micro organisms should be virtually absent; however, they are not usually considered in ordinary chemical analyses. The presence of harmful micro organisms is considerably more difficult to ascertain than most other properties of water, but it is a highly important consideration (Hem, 1985).

Temperature

Impinging solar radiation and the atmospheric temperature bring about interesting spatial and temporal thermal changes in natural waters which manifest in setting up of conventional currents and thermal stratification. Discharge of heated effluents also brings about thermal changes in natural waters. Excessively high temperatures deplete dissolved oxygen and interfere with normal stream ecology (thermal pollution). Temperature is basically an important factor for its effects on chemical and biological reactions in water. A rise in temperature of water accelerates chemical reactions, reduces solubility of gases, amplifies taste and odour, and

elevates metabolic activity of organisms. Groundwater temperature is uniform and is below air temperatures (Hem, 1985).

2.5.1 Taste and Odour

Odour and taste are useful indicators of water quality even though odour-free water is not necessarily safe to drink. Odour is also an indicator of the effectiveness of different kinds of treatment. In its purest state, water is both odourless and tasteless. However, as organic and inorganic substances dissolve in water, it begins to take on characteristic taste and sometimes odour. Generally, the inorganic salts at concentrations found naturally in drinking water do not adversely affect the taste (Twort *et al.*, 1994).

Both tastes and odour are caused by the interactions of many substances present. These may include soil particles, decaying vegetation, organisms (plankton, bacteria, fungi), various inorganic salts (Chlorides and Sulphides of Sodium, Calcium, Iron and Manganese), organic compounds and gases. However, present methods of measuring taste and odour are still fairly subjective and the task of identifying an unacceptable level for each chemical in different waters requires more study. As mentioned above, some contaminant odours are noticeable even when present in extremely small amounts. Standards related to odour and taste are Chloride, Copper, foaming agents, Iron, Manganese pH, Sulphate, threshold Odour Number (TON), total dissolved solids, and Zinc (USEPA, 2000). Of the ions that may be present in water, Iron can be tasted at a concentration of about 0.05 mg/l, Copper at about 2.5 mg/l, Manganese at about 3.5 mg/l, and Zinc at about 5 mg/l (Water Research Centre, 1981).

While the detection of solutes in water by taste is, of course, a function of individual sensitivity, offensive odours and tastes account for most consumers' complaints about water quality (Twort *et al.*, 1994). The salt concentration in water should be approximately the same as in saliva for the water to taste neutral (Bartoshuk, 1974).

2.5.2 Calcium, Magnesium and Hardness

Calcium and Magnesium are found in great abundance in all natural waters and their source lies in the rocks from which they are leached. Calcium concentration varies greatly in natural waters depending upon nature of the basin. The two ions are the principle causes of water hardness. The term hardness comes from the fact that typical hard water reacts with ordinary soap to form a scum. Boiling also precipitates some hardness and forms the scale found inside kettles. The precipitate formed by heating is the temporary hardness consisting of bicarbonates of

calcium and magnesium. Hardness of water was therefore understood to be a measure of capacity of water for precipitating soap. It is not caused by a single substance but by a variety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations, although other cations, e.g. Barium, Iron, Manganese, Strontium and Zinc, also contribute (AWWA, 1991).

Hardness is most commonly expressed as milligrams of calcium carbonate equivalent per litre, water containing less than 50 mg of calcium carbonate per litre generally being considered as soft. Although hardness is caused by cations, it may also be discussed in terms of carbonate (temporary) and non- carbonate (permanent) hardness (WHO, 2003). Calcium and Magnesium, the two principal ions, are present in many sedimentary rocks, the most common being limestone and chalk. They are also present in a wide variety of industrial products and are common constituents of food. The taste threshold for the calcium ion is in the range 100–300 mg/l, depending on the associated anion, but higher concentrations are acceptable to consumers. Hardness levels above 500 mg/l are generally considered to be aesthetically unacceptable, although this level is tolerated in some communities (Zoeteman, 1980).

In drinking water, hardness is in the range 10–500 mg of calcium carbonate per litre. Estimated daily intakes of 2.3 and 52.1 mg of magnesium in soft- and hard-water areas, respectively, have been reported, based on adults drinking 2 litres of water per day. In most large-scale studies, an inverse relationship between the hardness of drinking water and cardiovascular disease has been reported (Dzik, 1989). The results of several studies have suggested that a variety of other diseases are inversely correlated with the hardness of water, including anencephaly and various types of cancer. However, the significance of these results is unclear, and it has been suggested that the associations may reflect disease patterns that can be explained by social, climatological, and environmental factors, rather than by the hardness of the water (Nerbrand, 1992).

Some data still, suggest that very soft waters with a hardness of less than 75 mg/l may have an adverse effect on mineral balance, but detailed studies are not available. However, there does not appear to be any convincing evidence that water hardness causes adverse health effects in humans. In contrast, the results of a number of epidemiological studies have suggested that water hardness may protect against disease and therefore the available data are inadequate to prove any causal association (WHO, 2003).

Depending on the interaction of other factors, such as pH and alkalinity, water with hardness above approximately 200 mg/l may cause scale deposition in the distribution system, as well as increased soap consumption. In contrast, soft water, with a hardness less than about 100 mg/l, has a greater tendency to cause corrosion of pipes, resulting in the presence of certain heavy metals, such as Cadmium, Copper, Lead, and Zinc, in drinking-water (National Research Council, 1977). Twort *et al.* (1994) gave the following descriptive terms commonly applied for hardness.

Table 1: Water hardness description

Hardness description	Hardness as (mg/l of CaCO ₃)
Soft	0-50
Moderately soft	50-100
Slightly hard	100-150
Moderately hard	150-200
Hard	Over 200
Very hard	Over 300

Source: (Twort et al, 1994)

Determination of total hardness in this study was done using EDTA titrimetric method. It is based on formation of a soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.5 , the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium have been complexed the solution turns from wine red to blue, marking the end point of the titration. Magnesium ion must be present to yield a satisfactory end point. To ensure this, a small amount of neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction (APHA, 1992, AWWA, 1992, WEF, 1992).

2.5.3 Fluoride and Tooth discolouration (Dental fluorosis)

Fluorine is a common element that does not occur in the elemental state in nature because of its high reactivity. It accounts for about 0.3 g/kg of the Earth's crust and exists in the form of

fluorides in a number of minerals, of which fluorspar; cryolite and fluorapatite are the most common. Fluorides are more common in groundwaters than in surface waters. The main sources of fluoride in water are different fluoride bearing rocks. In areas rich in fluoride-containing minerals, well waters may contain up to about 10 mg of fluoride per litre. The highest natural level reported is 2800 mg/l (Office of Drinking Water, 1985). Although sodium fluoride is soluble in water, Aluminium, Calcium and Magnesium fluorides are only sparingly soluble (USEPA, 1985).

Fluoride concentrations in the groundwater of some villages in China were greater than 8 mg/l (Anonymous, 1990). In Canada, fluoride levels in drinking-water of <0.05–0.2 mg/l (non-fluoridated) and 0.6–1.1 mg/l (fluoridated) have been reported in municipal waters; in drinking-water prepared from well water, levels up to 3.3 mg/l have been reported. In the USA, 0.2% of the population is exposed to more than 2.0 mg/l. In the Netherlands, year-round averages for all drinking-water plants are below 0.2 mg/l (Slooff, 1988). In some African countries where the soil is rich in fluoride-containing minerals, levels in drinking water can be very high (e.g., 8 mg/l in the United Republic of Tanzania (Fitzgerald et al., 2000). In a large survey of groundwater boreholes in Kenya, the majority of the samples (61.4%) had fluoride ion concentration above 1.0 mg/l while 19.5 % had above 5 mg/l. Excess levels of fluoride were found to occur in most parts of the country, especially in the Nairobi, Rift Valley, Eastern and Central Provinces. The supplies contained fluoride at levels exceeding 1.5 mg/l, with several in the range 3–9 mg/l (Nair, *et al.*, 1984).

Fluoride may be an essential element for animals and humans. Many epidemiological studies of possible adverse effects of the long-term ingestion of fluoride via drinking water have been carried out. These studies clearly establish that fluoride primarily produces effects on skeletal tissues (bones and teeth). It has an adverse effect on tooth enamel and may give rise to mild dental fluorosis (prevalence: 12–33%) at drinking-water concentrations between 0.9 and 1.2 mg/l. This has been confirmed in numerous subsequent studies, including a recent large-scale survey carried out in China, which showed that, with drinking-water containing 1 mg of fluoride per litre, dental fluorosis was detectable in 46% of the population examined. In general, dental fluorosis does not occur in temperate areas at concentrations below 1.5–2 mg of fluoride per litre of drinking water (Chen et al., 1988). Low concentrations provide protection against dental caries, especially in children. The pre- and post-eruptive protective effects of fluoride increase

with concentration up to about 2 mg of fluoride per litre of drinking water; the minimum concentration of fluoride in drinking water required is approximately 0.5 mg/l (WHO, 2003).

Elevated fluoride intakes can also have more serious effects on skeletal tissues. Skeletal fluorosis (with adverse changes in bone structure) may be observed when drinking water contains 3–6 mg of fluoride per litre. Crippling skeletal fluorosis usually develops only where drinking water contains over 10 mg of fluoride per litre. The USEPA (1985) considers a concentration of 4 mg/l to be protective against crippling skeletal fluorosis. There is no evidence to suggest that the guideline value of 1.5 mg/l set in 1984 and reaffirmed in 1993 needs to be revised (Murray, 1986).

Fluoride is usually determined by means of an ion-selective electrode, which makes it possible to measure the total amount of free and complex-bound fluoride dissolved in water. The method can be used for water containing at least 20 µg/l (Slooff, 1988). In this study, fluoride ion determination was done using ion selective electrode (fluoride/fluoride combination electrode) model 96-09. Fluoride standard (NaF) obtained from Thermo Orion Beverly; MA USA with TISAB was used as the standard solution.

2.5.4 Corrosivity and Staining

Corrosivity, and staining not only affect the aesthetic quality of water, but may also have significant economic implications. Other effects of corrosive water, such as the corrosion of iron and copper, may stain household fixtures, and impart objectionable metallic taste and red or blue-green colour to the water supply as well. Corrosion of distribution system pipes can reduce water flow. Staining of laundry and household fixtures can occur from water with iron, manganese or copper in solution. Manganese is always present with iron in groundwater and causes staining yielding a dark- brown to black precipitate. Standards related to corrosion and staining are Chloride, Copper, Corrosivity, Iron, Manganese, pH, Total Dissolved Solids, Zinc (WHO, 2001).

2.5.5 Conductivity

Conductivity is a measure of the ability of a solution to carry electrical current. As this ability is dependent upon the presence of ions in solution, a conductivity measurement is an indicator of the total dissolved ions in water. Pure water is a poor conductor of electricity. Acids, bases and salts in water make it relatively good conductor of electricity. Thus, the higher the

concentration of electrolytes in water, the more is its electrical conductance. Because conductivity varies with temperature, it is conveniently reported at 25°C (Twort *et al*, 1994).

2.5.6 Dissolved Oxygen

Oxygen dissolved in water, often referred to as DO, is a very important parameter of water quality and is an index of physical and biological processes going on in water. There are two main sources of dissolved oxygen in water; diffusion from air, and photosynthetic activity within water. Diffusion from air is a physical phenomenon and depends upon solubility of oxygen, which in turn, is influenced by factors like temperature, water movements and salinity. Photosynthetic activity is a biological phenomenon carried out by autotrophs and depends upon autotrophy population, light conditions, and available gases (Barnard and Nordstrom, 1982).

2.5.7 Chloride

Chloride is widely distributed in nature as salts of Sodium (NaCl), Potassium (KCl), Magnesium Chloride (MgCl₂) and Calcium (CaCl₂). Chlorides are leached from various rocks into soil and water by weathering. The chloride ion is highly mobile and is transported to closed basins or oceans. Its presence in surface and groundwater is mainly from both natural and anthropogenic sources, such as run-off containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas. Treatment processes in which chlorine or chloride is used may also considerably increase it (Ottawa, 1990).

Chloride in water increases the electrical conductivity of water and thus increases its corrosivity. It reacts with metal ions to form soluble salts thus increasing levels of metals in drinking water. The toxicity of chloride salts depends on the cation present; that of chloride itself is unknown. Although excessive intake of drinking-water containing sodium chloride at concentrations above 2.5 g/l has been reported to produce hypertension this effect is believed to be related to the sodium ion (WHO, 2003).

Chloride concentrations in excess of about 250 mg/l can give rise to detectable taste in water, but the threshold depends upon the associated cations. Taste thresholds for sodium chloride and calcium chloride in water are in the range 200–300 mg/l. The taste of coffee is affected if it is made with water containing a chloride concentration of 400 mg/l as sodium chloride or 530 mg/l as calcium chloride. (Zoeteman, 1980).

The mean chloride concentration in several rivers in the United Kingdom was in the range 11–42 mg/l. In the USA, aquifers prone to seawater intrusion have been found to contain chloride at concentrations ranging from 5 to 460 mg/l whereas contaminated wells have been reported to have an average chloride concentration of 141 mg/l. Chloride levels in unpolluted waters are often below 10 mg/l and sometimes below 1 mg/l (Phelan, 1987).

A number of suitable analytical techniques are available for chloride in water, including silver nitrate titration with chromate indicator, mercury (II) nitrate titration with diphenylcarbazone indicator, potentiometric titration with silver nitrate, iron (III) mercury (II) thiocyanate colorimetry, chloride ion-selective electrode, silver colorimetry, and ion chromatography. Limits of detection range from 50 µg/l for colorimetry to 5 mg/l for titration. In this study, chloride determination was done using iron (III) mercury (II) thiocyanate colorimetry. The method was based on formation of iron (III) thiocyanate when chloride ion reacts with mercury (II) thiocyanate in the presence of iron (III) ions (AWWA, 1992, APHA 1992, WEF, 1992).

2.5.8 Total Iron and Manganese

Iron is among the most abundant metals in the earth's crust, of which it accounts for about 5%. Elemental iron is rarely found in nature, as the iron ions Fe^{2+} and Fe^{3+} readily combine with oxygen- and sulphur-containing compounds to form oxides, hydroxides, carbonates, and sulphides. It is most commonly found in nature in the form of its oxides (Elinder, 1986). From Dahi personal communication (1991) Iron (as Fe^{2+}) concentrations of 40 µg/l can be detected by taste in distilled water. In mineralised spring water with total dissolved solids content of 500 mg/l, the taste threshold value was 0.12 mg/l. In well water, iron concentrations below 0.3 mg/l were characterized as unnoticeable, whereas levels of 0.3–3 mg/l were found acceptable.

The median iron concentration in rivers has been reported to be 0.7 mg/l. In anaerobic groundwater where iron is in the form of iron (II), concentrations will usually be 0.5–10 mg/l, but concentrations up to 50 mg/l can sometimes be found. Concentrations of iron in drinking-water are normally less than 0.3 mg/l but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution (Baltimore, 1979). Although no health-based guideline value for iron is proposed, staining of laundry and plumbing may occur at concentrations above 0.3 mg/l. Iron also promotes undesirable bacterial growth ("iron bacteria") within a waterworks

and distribution system, resulting in the deposition of a slimy coating on the piping (Ottawa, 1990).

Manganese is also one of the most abundant metals in the Earth's crust, usually occurring with iron. It is a component of over 100 minerals but is not found naturally in its pure (elemental) form (ATSDR, 2000). Manganese is an element essential to the proper functioning of both humans and other animal, as it is required for the functioning of many cellular enzymes. It can exist in 11 oxidative states; the most environmentally and biologically important manganese compounds are those that contain Mn^{2+} , Mn^{4+} or Mn^{7+} (USEPA, 1994).

A health-based guideline value of 0.4 mg/l should be adequate to protect public health. It should be noted that the presence of manganese in drinking water would be objectionable to consumers if the manganese is deposited in water mains and causes water discoloration. Concentrations below 0.05 mg/l are usually acceptable to consumers, although this may vary with local circumstances (WHO , 2003)

2.5.9 Nitrate, Nitrite and Nitrogen

Nitrogen is one of the most abundant elements in the atmosphere. About 80 percent of the air we breathe is nitrogen. It is found in the cells of all living things and is a major component of proteins. Inorganic nitrogen may exist in the free state as a gas, N_2 , as nitrate, NO_3^- , nitrite, NO_2^- or ammonia, NH_3 . Organic nitrogen is found in proteins and is continually recycled by plants and animals. Nitrogen-containing compounds act as nutrients in streams and rivers. Nitrate reactions in fresh water can cause oxygen depletion as shown by the conversion scheme below.



Aquatic organisms depending on the supply of oxygen in the stream will die if high concentration of NO_3^- is present. The major routes of entry of nitrogen into bodies of water are municipal and industrial wastewater, septic tanks, feedlot discharges, animal wastes (including birds and fish) and discharges from car exhausts. Bacteria in water quickly convert nitrites to nitrates (Garg, 1987 & Twort et al., 1994).

The spectrophotometer was used to determine the concentration of nitrite and nitrate in the water samples. For nitrite, the method is based on conversion of sulphanilic acid to diazonium salt by nitrite. The resulting compound is coupled with N- (1-naphthyl) - ethylene

diaminedihydrochloride as shown below. The intensity of the purple red azo dye (N-naphthylamine-p-azobenzene sulphuric acid) that is formed is directly proportional to the concentration of nitrite in the sample. Sulphanilic acid was used to detect nitrous acid (AWWA, 1992, APHA, 1992, WEF, 1992).

2.5.10 Ammonia

Ammonia in water is released as an end product of decomposition of organic matter and also as an excretory product of some aquatic animals. It dissolves in water to form ammonium hydroxide, which further dissociates into ammonium (NH_4^+) and hydroxyl (OH^-) ions. The degree of ionization depends on the temperature, the pH, and the concentration of dissolved salts in the water (Environmental Protection Agency, 1989).



Domestic wastes being often rich in nitrogenous organic matter and many industrial effluents add to the ammonia load in water leading to toxic levels at certain times. Natural levels in groundwaters are usually below 0.2 mg of ammonia per litre. Higher natural contents (up to 3 mg/l) are found in strata rich in humic substances (Dieter, 1991). Surface waters may contain up to 12 mg/l Ammonia which can however, indicate faecal contamination, compromise disinfections efficiency, cause taste and odour problems, result in nitrite formation in distribution systems, and cause the failure of filters for the removal of manganese (International Organization for Standardization, 1986).

The threshold odour concentration of ammonia in water is approximately 1.5mg/l. A taste threshold of 35 mg/l has been proposed for the ammonium cation. Ammonia is not of direct importance for health in the concentrations to be expected in drinking water. A health-based guideline has therefore not been derived (WHO, 2003).

There are several methods that are used for determination of ammonia viz Nesslerization method, phenate method, titration method, ammonia selective electrode method and automated phenate method. The two major factors that influence selection of method are concentration and presence of interferences. The manual phenate method was used in this analysis, because of the concentration suspected to be present in the water samples. It has a sensitivity of $10\mu\text{g NH}_3\text{-N/l}$

and is useful for up to 500 μ g NH₃-N/l. Preliminary distillation is required if colour or turbidity is present, as was the case in our analysis. Distillation into sulphuric acid absorber is mandatory for this method. It operates on the principle that an intensely blue compound, indophenols is formed by the reaction of ammonia, hypochlorite and phenol catalysed by manganous salt (AWWA, 1992, APHA 1992, WEF, 1992).

2.5.11 The pH

The pH of water is a measure of the acid–base equilibrium and, in most natural waters, is controlled by the carbon dioxide–bicarbonate–carbonate equilibrium system. An increased carbon dioxide concentration will therefore lower pH, whereas a decrease will cause it to rise. Hydrogen ion concentration in water, denoted by its pH value, affords a measure of acidity or alkalinity of water (WHO, 2003). Although pH usually has no direct impact on water consumers, it is one of the most important operational water-quality parameters. The pH value thus represents the balance of a series of equilibria existing in the water. It is sometimes taken as a measure of the solvent power of water for various rock minerals. However, such reactions proceed only so far as new equilibria are reached (Garg, 1987). Temperature will also affect the equilibria and the pH. In pure water, a decrease in pH of about 0.45 occurs as the temperature is raised by 25 °C. In water with a buffering capacity imparted by bicarbonate, carbonate, and hydroxyl ions, this temperature effect is modified. The pH of most raw water lies within the range 6.5–8.5 (APHA, 1989).

2.5.12 Lead and copper

Lead is the commonest of the heavy elements, accounting for 13 mg/kg of the earth's crust. Several stable isotopes of Lead exist in nature, including, in order of abundance, ²⁰⁸Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁴Pb. It is present in tap water to some extent as a result of its dissolution from natural sources but primarily from household plumbing systems in which the pipes, solder, fittings, or service connections to homes contain Lead. PVC pipes also contain Lead compounds that can be leached from them and result in high Lead concentrations in drinking water. Lead is exceptional in that most Lead in drinking water arises from plumbing in buildings and the remedy consists principally of removing plumbing and fittings containing it. This requires time and money, and it is recognized that not all water will meet the guideline immediately (WHO, 1989).

The level of Lead in drinking water may be reduced by corrosion-control measures such as the addition of lime and the adjustment of the pH in the distribution system from <7 to 8–9. Lead is a cumulative general poison, infants, children up to 6 years of age, the foetus, and pregnant women being the most susceptible to adverse health effects. Its effects on the central nervous system can be particularly serious. On the assumption of a 50% allocation to drinking water for a 5-kg bottle-fed infant consuming 0.75 litres of drinking water per day, the guideline value is 0.01 mg/l. Infants are considered to be the most sensitive subgroup of the population. However, this guideline value is also for other age groups (WHO, 2003).

2.5.13 Sodium and Potassium

Sodium and Potassium compounds are very soluble so that the element is present in most natural waters. Besides geological influence, potassium and sodium salts are highly soluble and are thus widely used as agricultural fertilizers. The threshold taste for sodium in drinking water depends on several factors such as the predominant anion present and the temperature. At room temperature, the threshold values are about 20 mg/l for sodium carbonate, 150 mg/l for sodium chloride, 190 mg/l for sodium nitrate, 220 mg/l for sodium sulphate, and 420 mg/l for sodium bicarbonate. WHO recommends 200 mg/l Na (maximum) on taste basis, salinity and scaling. In a survey of 2100 water samples in the USA in 1963–1966, the sodium ion concentrations found were in the range 0.4–1900 mg/l; in 42% of the samples, the concentrations were in excess of 20 mg/l, but in 5% they were greater than 250 mg/l. In a later survey of 630 water-supply systems in the same country, the sodium ion concentrations found ranged from less than 1 to 402 mg/l with similar distribution of values (WHO, 2003).

Although it is generally agreed that sodium is essential to human life, there is no agreement on the minimum daily requirement. However, it has been estimated that a total daily intake of 120–400 mg will meet the daily needs of growing infants and young children, and 500 mg those of adults. In general, sodium salts are not acutely toxic because of the efficiency with which mature kidneys excrete sodium. However, acute effects and death have been reported following accidental overdoses of sodium chloride. Excessive salt intake seriously aggravates chronic congestive heart failure, and ill effects due to high levels of sodium in drinking-water have been documented (WHO, Regional Office for Europe, 1979).

Sodium and potassium concentrations can be determined by direct aspiration atomic

absorption spectroscopy. Detection limits of 2 and 40 µg/l can be achieved with flame atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry, respectively. In this experiment, a flame photometer, model Corning M410, Ciba Corning Diagnostic Scientific instruments, was used for Sodium and Potassium because the two are readily ionized. Calibration curves of flame emission versus Sodium/Potassium ion concentration were prepared and the Sodium/Potassium concentrations of the samples were determined.

2.6 WHO Guidelines for drinking water

The quality of water, whether it is used for drinking, irrigation or recreational purposes is significant for health in both developing and developed countries worldwide. An immediate purpose of the usual quality-of-water study is to determine if the water is satisfactory for a proposed use. Accordingly, the subject of water-analysis interpretation must often include some consideration of standards and tolerances that have been established for water that is to be used for various purposes. Standards for water to be used for drinking and other domestic purposes have been established in many countries. Published literature contains tolerance levels and related data for constituents of water to be used in drinking, agriculture, in industry, for propagation of fish, and for a number of other specific purposes. For instance, water from mineral and hot springs is used medicinally in many places, and the mystic qualities of natural warm springs have been of great interest to man since prehistoric time (Hem, 1985).

In responding to the challenge of improving water quality, countries develop standards intended to protect public health. Recognising this, the World Health Organization has developed a series of normative "guidelines" that present an authoritative assessment of the health risks associated with exposure to health hazards through water and of the effectiveness of approaches to their control (WHO, 2001).

The first WHO document dealing specifically with public drinking-water quality was published in 1958 as International Standards for Drinking water. It was subsequently revised in 1963 and in 1971 under the same title. In 1984–1985, the first edition of the WHO Guidelines for Drinking-water Quality (GDWQ) was published in three volumes: Volume 1, Recommendations; Volume 2, Health criteria and other supporting information; and Volume 3, Surveillance and control of community supplies. Second editions of these volumes were published in 1993, 1996 and 1997, respectively. Additions to Volumes 1 and 2 of the second

edition were published in 1998, addressing selected chemicals. An addition on microbiological aspects reviewing selected micro organisms was published in 2002.

The GDWQ are subject to a rolling revision process. Through this process, microbial, chemical and radiological aspects of drinking water are subject to periodic review, and documentation related to aspects of protection and control of public drinking water quality is accordingly prepared/updated. During preparation of the third edition of the GDWQ, it was decided to include a public review via the World Wide Web in the process of development of the health criteria documents. To date, the various WHO guidelines (Guidelines for drinking-water quality, Guidelines for the safe use of wastewater and excreta in agriculture and aquaculture and Guidelines for safe recreational water environments) have been developed in isolation from one another (WHO, 2003).

The physical and chemical standards given in third edition under WHO guidelines for drinking water quality were used in this analysis and are listed in table 2 below.). The reason for choosing the WHO guidelines is because they are perhaps the most important standards relating to water quality. They are used universally and are basis for EEC and USEPA legislation. The primary aim of the WHO guidelines for drinking water quality is the protection of public health and thus the elimination or reduction to a minimum of constituents in water that are known to be hazardous to health and well being of the community). The former WHO international standards for drinking may still apply in many countries who adopted them as their national standards with modifications to allow for local in-country conditions (AWWA, 1991).

Table 2: WHO drinking water values for substances and parameters that may give rise to complaints from consumers and the reasons for the complaints

Contaminant	WHO guidelines	Noticeable Effects
Aluminium	0.05 -0.2 mg/l	Deposition, discolouration
Ammonia	1.5 mg/l	Odour and taste
Cadmium	0.003 mg/l	
Calcium	-	Hardness
Chloride	250 mg/l	Salty taste, corrosion
Chromium	0.05 mg/l	-
Colour	15 colour units	Appearance
Copper	1.0 mg/l	Metallic taste; blue-green staining of laundry and sanitary ware
Corrosivity	Non-corrosive	Metallic taste; corroded pipes/ fixtures staining
Dissolved oxygen	-	Indirect effect
Fluoride	1.5 mg/l	Tooth discoloration
Foaming agents	0.5 mg/l	Frothy, cloudy; bitter taste; odour
Hardness	-	High hardness: Scale deposition, scum formation Low hardness: Possible corrosion
Iron	0.3 mg/l	Rusty colour; sediment; metallic taste; reddish or orange staining of laundry and sanitary ware
Magnesium	-	Hardness
Manganese	0.10 mg/l	Black to brown colour; black staining of laundry and sanitary ware; bitter metallic taste
Nickel	0.02 mg/l	
Nitrate	50 mg/l	Odour and taste
Nitrite	3 mg/l	Odour and taste
Odour	3 TON	"Rotten-egg", musty or chemical smell
pH	6.5 - 8.5	Low pH: bitter metallic taste; corrosion high pH: slippery feel; soda taste; deposits
Potassium	-	Indirect effect
Silver	0.1 mg/l	Skin discoloration; graying of the white part of the eye
Sodium	200 mg/l	Taste
Sulfate	250 mg/l	Salty Taste, corrosion
Taste and odour	-	Should be acceptable
Temperatures	-	Should be acceptable
Total Dissolved Solids	500 mg/l	Hardness; deposits; coloured water; staining; salty taste
Turbidity	5 NTU	Appearance
Zinc	3 mg/l	Appearance, Metallic taste

Source: (WHO, 2003)

CHAPTER THREE
MATERIALS AND METHODS

3.1 Collection of the Water Samples

Using clearly labelled 1-litre polythene bottles, water samples were collected in replicate from eight springs and seven streams (plates 1-8) of three locations of Gichugu division i.e. Baragwi, Ngariama and Kabare (figure 1). They were refrigerated pending laboratory analysis. The refrigeration was to avoid any chemical reactions likely to occur before laboratory analysis. Certain properties of water, especially its pH, temperature, conductance and dissolved oxygen are so closely related to the environment of the water, that they are likely to be altered by sampling and storage, and a meaningful value can be obtained only in the field. They were therefore measured at the collection site by use of Jenway model 3405-electrochemical analyser.



Plate 1: Kabuga spring & Kabuga stream



Plate 2: Ngungu spring & Mukengeria stream

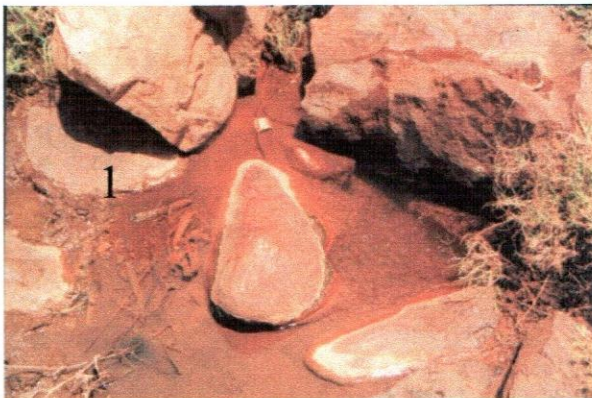


Plate 3: Kindiri spring



Plate 4: Kabaruru spring & Kabuyu stream



Plate 5: Kongu spring & Nyamindi River

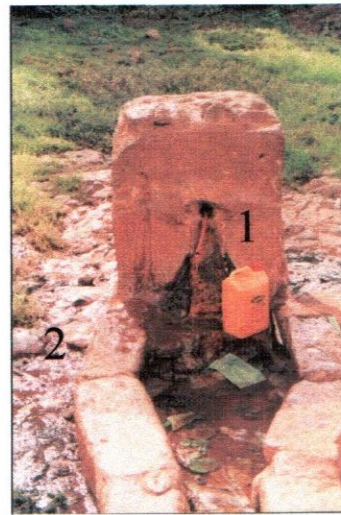


Plate 6: Matiru spring & Nyamindi River

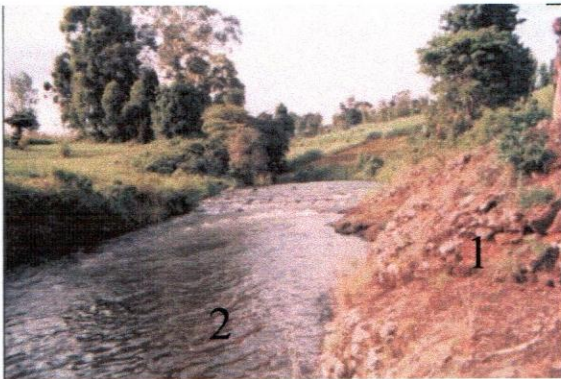


Plate 7: Kainamui spring & Nyamindi River



Plate 8: Wanjiku spring & Kathogondo stream

Key

1: Spring

2: Stream/River

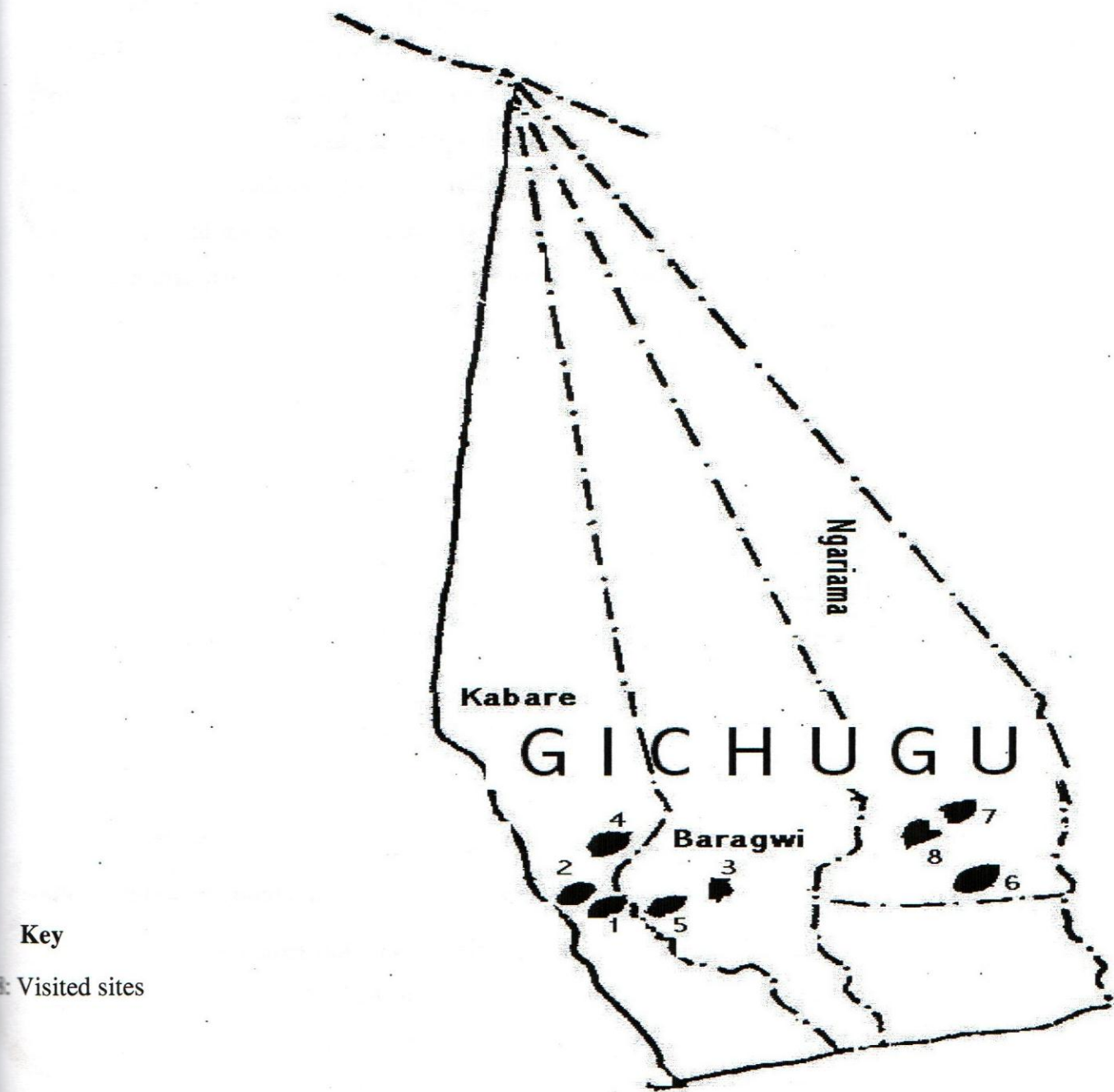


Figure 1: Sampling sites in the study area (District Water Engineers' Office, Kerugoya, 1996)

3.2 Determination of Cations

Metals were analysed by spectrophotometry using standard addition method in which a ChemTech Analytical CTA-2000 Atomic Absorption Spectrophotometer was used. The method of standard addition was used due to its usefulness in avoiding the effects of interferences when the composition of the sample matrix is unknown. The principle behind the working of the instrument is that radiation from the Hollow Cathode Lamp is made from the element of interest. It is modulated and passed through a flame into which is sprayed the solution for analysis. The radiation then passes to a monochromator where the particular resonance line due to the atomic vapour in the flame is measured by means of a photo multiplier tube (PMT). The photocurrent is amplified, demodulated and fed to a logarithmic converter and then to the display. With this system, any emission from the flame is not detected, and when a log converter is used the display indicates directly in absorbance on a linear scale (Chemical Analytical Ltd, 2000).

To release more of the metals that could be held in suspended particles, the samples were pre-treated with concentrated nitric acid (5 ml in every 1000 ml of the sample). For magnesium and calcium, the samples were diluted 200 times. To 1ml of the sample, 1ml Lanthanide chloride was added to release more of the Mg^{2+} and Ca^{2+} from the water samples. This was then topped up to 200 ml. A calibration curve for each analysed cation was constructed and the samples were then aspirated. The concentrations of elements of interest in the unknown samples were obtained from the calibration curves (Appendix A).

3.2.1 Sodium and potassium

Preparation of standard stock solution of sodium and potassium

A standard stock solution of sodium ions was prepared by dissolving 3.088g of analar grade sodium sulphate (Na_2SO_4) in 1 litre distilled water (1000 mg/l). By suitable dilutions of the stock solution prepared, a series of working standards containing 10, 15, 20, 25 and 30 mg/l were prepared. A calibration curve (appendix A) was prepared and was used to determine the concentration of sodium in water samples.

A standard stock solution of potassium ions was prepared by dissolving 1.912g of potassium chloride (KCl) in 1 litre distilled water (1000 mg/l). By suitable dilutions of the stock solution prepared, a series of working standards containing 2, 4, 6, 8 and 10 mg/l were prepared. Following the same procedure as indicated above for sodium, the water samples were analysed

for potassium.

3.3 Non-Metal Determination

3.3.1 Ammonia

Reagents to be used in the preliminary distillation step were first prepared as follows: -

a) Ammonia free water

This was prepared by distillation. To eliminate traces of ammonia in distilled water, 0.1 ml concentrated sulphuric acid was added to 1 litre of distilled water followed by redistillation. The first 100 ml distillate was discarded and the rest was stored in amber coloured glass container to which 10g ion exchange resin was added. This was covered using parafilm to keep it airtight. The ammonia-free water was used to clean the glassware and to prepare the other reagents.

b) Sodium tetra borate solution

Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) solution was prepared by placing 9.5 g of the solute into 1000 ml volumetric flask and making up to the mark using the ammonia free water.

c) Borate buffer solution

This was prepared by adding 88 ml of 0.1M NaOH solution to approximately 500 ml of 0.025M $\text{Na}_2\text{B}_4\text{O}_7$ solution followed by dilution to 1 litre in 1000 ml volumetric flask.

d) Sodium hydroxide 6M

A little ammonia free water was used to dissolve 12g of NaOH pellets in a 250-ml beaker. The solution was then transferred to a 50-ml volumetric flask and made up to the mark.

e) Neutralisation agent: Sodium hydroxide 1M

A little ammonia free water was used to dissolve 10g of NaOH pellets in a small 250-ml beaker. The solution was transferred to 250-ml volumetric flask and made up to the mark using the ammonia free water.

f) 0.5M sulphuric acid

An aliquot of concentrated sulphuric acid (6.25 ml) was measured and transferred to a 250 ml volumetric flask. This was diluted up to the mark using ammonia free water.

g) 0.02M sulphuric acid

Using ammonia free water, 1.0 ml concentrated sulphuric acid was measured into a 1 litre volumetric flask and diluted to the mark.

Procedure for sample preparation

A Markham distillation unit was used. In to the distillation flask, 500ml ammonia free water and 20ml borate buffer solution were put and the pH was adjusted to 9.5 using 6M NaOH solution drop wise. A few glass beads were added and the mixture was used to steam out the distillation apparatus until there were no more traces of ammonia in the distillate. Ammonia free water was used to dilute 25ml of the sample to 500ml. This was neutralized to approximately pH 7 with dilute acid or base using a pH meter. 25ml borate buffer was added and the pH was adjusted to 9.5 with 6M NaOH using a pH meter.

Distillation

The tip of the delivery tube was immersed below the receiving acid solution. The distillate was collected in a 250 ml Erlenmeyer flask containing 50 ml 0.02M sulphuric acid. At least 200 ml of the distillate was collected. The distillate receiver was lowered so that the end of the delivery tube will not come into contact with the liquid while distillation was continuing during the last two minutes. The distillate was neutralized using 1M NaOH and then diluted to 500 ml using ammonia free water. Ammonia was then determined via the phenate method.

Phenate method

Ammonia free water was used to prepare all the reagents used in this method.

a) 6% NaOCl solution

An aliquot of NaOCl (6 ml) was measured into a 100-ml volumetric flask and was diluted to the mark using ammonia free water.

b) Hypochlorous acid reagent

This reagent was prepared by adding 10ml of 6% NaOCl to 40 ml of ammonia free water and the pH was adjusted to 7 with dilute HCl. The reagent was prepared weekly because of its instability.

c) Manganese sulphate solution

MnSO₄.H₂O, 36.4g was weighed on an electronic balance and dissolved in a 100ml beaker. The solution was transferred into a 100ml volumetric flask and made up to the mark using distilled water.

d) Phenate reagent

NaOH, 2.5g and 10g phenol were dissolved in about 50 ml ammonia free water in a 100ml beaker. The solution was transferred into a 100-ml volumetric flask and was made up to the mark using the ammonia free water. The solution was prepared weekly because it darkens on standing.

e) Stock ammonium Chloride solution

A small amount of NH₄Cl was dried at 100°C for five hours. It was then cooled in a desiccator for ten minutes. 0.3819g of the dried anhydrous NH₄Cl was dissolved in ammonia free water and was transferred into a 1000 ml volumetric flask and made up to the mark.

f) Standard ammonium solution

Into a 1000 ml volumetric flask, 5ml of stock ammonium solution, was pipetted and was diluted to the mark using the ammonia free water.

Procedure for determination of ammonia

One-drop of MnSO₄ solution was added to 100 ml sample in 100 ml beaker. This was placed on a magnetic stirrer and 0.5 ml. Hypochlorous acid solution was added. Immediately, 0.6 ml phenate reagent was added a drop at a time using a pipette. The mixture was stirred vigorously during the addition-of the reagent for 10 minutes. A blank and the standard were carried through the procedure. Absorbance was measured at 630nm using the blank to zero the spectrometer.

Preparation of calibration curve

Ammonia calibration curve was prepared in the range of 0.1 to 5 mg/l by measuring five portions of 1 ml, 3 ml, 7 ml and 10 ml of the standard ammonia solution that was treated exactly as the sample. Samples' concentrations were read from the calibration curve (appendix A).

3.3.2 Nitrite

Reagents were prepared as follows

a) Potassium permanganate solution

Potassium permanganate, 100 mg was weighed and dissolved in 100 ml distilled water in a beaker. The solution was transferred into 250-ml volumetric flask and made up to the mark using distilled water.

b) Nitrite free water

Nitrite free water was prepared by adding 1ml conc. sulphuric acid and 0.2ml MnSO_4 to 1000 ml distilled water. The solution was made pink with 2ml KMnO_4 solution and this was redistilled in borosilicate apparatus. The initial 50 ml of the distillate was discarded. This water was used to rinse the glassware and to prepare the reagents.

c) Sulphanilic acid solution

Potassium hydrogen sulphate, 6.8g and 0.865g of sulphanilic acid were weighed and dissolved in about 50 ml nitrite free water. This was topped up to the mark in a 250 ml volumetric flask.

d) N- (1-naphthyl)-ethylene diamine dihydrochloride solution

Nitrite free water was used to dissolve 0.04g N- (1-naphthyl) -ethylene diaminedihydrochloride. The solution was transferred to a 100 ml volumetric flask and made up to the mark. This solution was stored in a black bottle and was kept in the dark to avoid photochemical reactions.

Preparation of stock solution

Solid sodium nitrite was dried for five hours in an oven at 100°C and was cooled in a desiccator for ten minutes. A stock solution was prepared by dissolving 1.283g followed by dilution in a 1000 ml volumetric flask with nitrite free water.

Preparation of standard solution

About 10 ml of 250 mg/l nitrite solution was pipetted into a 250 ml volumetric flask and was made up to the mark. From this, the following concentrations were prepared 0.5 mg/l, 1

mg/l, 2 mg/l, 2.5 mg/l, 3 mg/l, 3.5 mg/l and 4mg/l.

Treatment of the working standards

Into a 50 ml volumetric flask was added 10 ml of 0.5 mg/l solution and was made up to 30 ml with nitrite free water. Sulphanilic acid solution, 25 ml was added and the solution was allowed to stand for ten minutes. This was followed by addition of 2.5 ml N- (1-naphthyl)-ethylene diamine dihydrochloride solution and the solution was allowed to stand for twenty minutes after which it was made to the mark with distilled water. Absorbance was measured at 540 nm. The sample and other standards were treated as above.

3.3.3 Nitrate

The sample was first treated with a strong reducing agent (zinc powder). This was to reduce nitrate to nitrite.



Nitrite free water was used to rinse the glassware and to the reagents prepared above were used.

Preparation of the stock solution

Solid sodium nitrate was dried for five hours in an oven for about 100°C and was cooled in a desiccator for ten minutes. 1.518g were weighed and were diluted in a 1000 ml volumetric flask with nitrite free water.

Preparation of standard solutions

About 10 ml of 250mg/l nitrate solution was pipetted into a 250ml volumetric flask and was made up to the mark with the nitrite free water. From this solution the following concentrations were made 0.5mg/l, 1mg/l, 1.5mg/l, 2mg/l, 2.5mg/l, 3mg/l, 3.5mg/l and 4mg/l using appropriate dilutions.

Treatment of working standard solutions

About 10ml of 0.5mg/l working standard solution was put in 250ml sample bottles. 50 ml of calcium acetate solution was added followed by 1ml manganese (II) sulphate solution. 0.05g of zinc powder was added followed by vigorous shaking for about 30 minutes in an electric shaker. The solution was filtered and transferred to a 250 ml volumetric flask. 2.5 ml of sulphanilic acid was added and the solution was left to stand for ten minutes. Absorbance values

were recorded at 540nm. This was repeated for the other standards. A calibration curve was prepared. Nitrate free water was used as the blank. The above procedure was repeated for the sample.

3.3.4 Chloride

Preparation of reagents

a) Alcoholic mercury (II) thiocyanate:

Mercury (II) thiocyanate, 0.03g was dissolved in 100 ml of industrial methylated spirit in a 250 ml conical flask. The resulting solution was stored in a glass stoppered reagent bottle.

b) Ferric alum solution

Ferric alum, 6.0g were dissolved in 100 ml of 6M nitric acid. The solution was stored in a 250 ml glass reagent bottle.

c) Standard stock solution of chloride ion

Using analar grade sodium chloride as a source of Cl ion, 100 ml of solution containing 1000 mg/l Cl was made in deionized water.

d) Working solutions of chloride ion

250 ml of 100 g/l Cl solution was prepared. From this solution, standard-working solutions containing 15, 20, 40, 60, and 80 mg/l of Cl were prepared using appropriate dilutions.

e) Preparation of reagent blank

Using a pipette, 10 ml of deionized water was put into a clean 100 ml beaker. 2.0 ml of ferric alum solution and 1.0 ml of alcoholic mercuric thiocyanate solution were added. After 10 minutes the reagent was ready for use in the reference beam of the spectrophotometer.

Preparation of calibration curve

10 ml of each of the working standard solutions was pipetted into separate 100ml beakers. To each solution, 2.0 ml of ferric alum solution followed by 1 ml of mercury (II) thiocyanate were added. After 10 minutes absorbance of each solution was taken at 470 nm using a 1 cm cell, against a reagent blank in the reference beam. A curve of absorbance versus concentration of Cl⁻ was plotted (Appendix A).

3.3.5 Fluoride

Sample preparation

Into a beaker, 50 ml of the sample and 50 ml of TISAB were put. Electrodes were rinsed with distilled water then placed in sample solution followed by thorough stirring. When a stable reading was displayed, the meter was calibrated by recording the mV value. An appropriate amount of the standard solution was pipetted into a beaker followed by thorough stirring. When a stable reading was displayed, the mV value was recorded. The first reading was subtracted from the second reading to find ΔE . To determine the original sample concentration, a certain variable Q was multiplied by the concentration of added standard as given in the instruction manual.

3.3.6 Bicarbonate

Bicarbonate (HCO_3^-) ions were determined by titrating the water samples with a standard sulphuric acid solution of 0.0 IN using methyl orange indicator. 5 ml of the sample were pipetted and was diluted to 25 ml. 2 drops of methyl orange were added. This was titrated with 0.0 IN H_2SO_4 until the first orange colour appeared. The titre was recorded (APHA, 1992, AWWA, 1992, WEF, 1992).

3.3.7 Total Hardness

Reagents

a) Buffer solution

A buffer solution was prepared by dissolving 16.9 g ammonium chloride (NH_4Cl) in 143 ml concentrated ammonium hydroxide (NH_4OH) followed by 1.25 g magnesium salt of EDTA. This was diluted to 250 ml with distilled water.

b) Calmagite

This indicator is stable in aqueous solution and has a sharper end point. 0.10 g of the indicator was dissolved in 100 ml distilled water.

c) Standard EDTA titrant

The titrant was prepared by dissolving 3.723g of analytical reagent-grade disodium ethylenediaminetetraacetate dihydrate in distilled water followed by dilution to 1000 ml.

Procedure for determination of hardness

Using a porcelain container, 25ml of the sample was diluted to 50 ml with distilled water followed by 2 ml of buffer solution. To the resulting solution, 1 to 2 drops of indicator solution were added. Standard EDTA titrant was then added slowly, with continuous stirring until the last reddish tinge disappeared. The last few drops were added 3 to 5 intervals. At the end point, the solution turned blue (APHA, 1992, AWWA, 1992, WEF, 1992).

$$\text{Hardness (EDTA) as mg CaCO}_3/\text{l} = \frac{A \times B \times 1000}{C}$$

Where: A = volume of titration for sample

B = mg CaCO₃ equivalent to EDTA titrant

C = volume (ml) sample

The data obtained was analysed using Statistical Analysis System (SAS) and Excel computer packages, which gave the mean concentrations of investigated parameters and their differences (significant/insignificant at $\alpha = 0.05$) between the springs and the streams/rivers (Appendix B).

CHAPTER FOUR

RESULTS AND DISCUSSION

Chemical analyses carried out in this study area were on groundwater and surface water from 15 sources; 8 springs and 7 streams that were used as representatives of domestic water sources of Gichugu Division. In every site visited, a spring and a stream were sampled except for site 3 where only a spring was sampled because there was no stream next to it. Tables 3 and 4 depict concentration of each investigated physical and chemical parameters.

Table 3: Cations contributing to the groundwater and surface water quality in the study area

Cation Source	K mg/l	Na mg/l	Fe mg/l	Pb mg/l	Cu mg/l	Zn mg/l	Ca mg/l	Mg mg/l	Cd mg/l	Mn mg/l	Co mg/l
MwK1	43.600	359.250	0.822	0.100	0.007	0.020	10.000	117.400	0.001	0.036	0.010
KS1	0.018	1.866	0.162	0.010	0.006	0.003	6.800	4.000	0.001	0.017	0.010
MwN2	28.570	255.240	1.068	0.054	0.115	0.014	42.800	73.600	0.001	0.713	0.010
MS2	0.351	4.201	0.304	0.000	0.011	0.001	5.400	2.400	0.001	0.074	0.010
MwK3	49.610	350.580	0.278	0.012	0.011	0.005	88.000	141.600	0.001	0.136	0.010
MwK4	29.570	362.260	1.080	0.080	0.012	0.012	62.000	165.000	0.001	0.216	0.010
KS4	0.652	6.244	0.144	0.016	0.006	0.002	11.200	5.200	0.001	0.161	0.010
MwK5	20.550	72.170	0.133	0.080	0.008	0.003	166.000	149.600	0.001	0.385	0.030
KR5	0.953	2.645	0.178	0.020	0.003	0.005	5.600	1.000	0.004	0.053	0.010
MwM6	40.590	506.24	0.232	0.055	0.014	0.022	128.000	128.200	0.001	0.134	0.010
NR6	1.053	4.104	0.074	0.023	0.001	0.002	9.000	1.000	0.001	0.024	0.010
MwK7	41.590	455.660	0.777	0.106	0.014	0.011	70.000	82.400	0.001	0.596	0.010
NR7	0.652	2.158	0.075	0.002	0.004	0.004	4.000	0.200	0.001	0.054	0.010
MwK8	33.580	510.140	0.270	0.058	0.008	0.017	74.800	50.200	0.001	0.237	0.020
KS8	0.351	1.866	0.080	0.013	0.007	0.001	7.000	0.400	0.001	0.041	0.010

1,2,3,4,5,6,7,8 are the numbers of sites in order of sampling

MwK1 –Munyu wa Kabuga	KS1 –Kabuga stream
MwN2 –Munyu wa Ngungu	MS2 –Mukengeria stream
MwK3 –Munyu wa Kindiri	KS4 –Kabuyu stream
MwK4 –Munyu wa Kabaruru	KR5 –Kiringa River
MwK5 –Munyu wa Kongu	NR6 –Nyamindi River
MwM6 –Munyu wa Matiru	NR7 –Nyamindi River
MwK7 –Munyu wa Kainamui	KS8 –Wanjiku stream
MwK8 –Munyu wa Wanjiku	

Table 4: Anions and physical parameters contributing to the groundwater and surface water quality in the study area

Parameter Source	NO ₃ ⁻ mg/l	NO ₂ ⁻ mg/l	Cl ⁻ mg/l	NH ₃ mg/l	F ⁻ mg/l	TH mg/l	pH	DO mg/l	Ec μS/cm	HCO ₃ ⁻ mg/l	T °C
MwK1	0.064	0.031	4.270	0.040	0.758	129.86	6.050	0.500	2.770	181.500	25
KS1	0.163	0.020	3.477	2.110	0.197	8.060	6.830	1.200	0.070	86.000	25
MwN2	0.071	0.039	4.395	0.160	0.456	131.000	6.070	0.600	2.250	104.060	25
MS2	0.107	0.039	3.811	1.620	0.215	3.210	7.640	2.200	0.050	93.000	25
MwK3	0.068	0.035	6.860	0.210	0.235	128.260	6.40	0.800	3.470	171.210	25
MwK4	0.086	0.022	4.060	0.090	0.262	91.380	6.210	0.700	2.870	119.000	25
KS4	0.161	0.017	3.890	1.500	0.256	9.620	7.080	1.700	0.090	81.000	25
MwK5	0.080	0.037	3.770	0.230	0.342	205.000	6.340	0.600	3.080	164.600	25
KR5	0.086	0.017	4.190	0.730	0.127	8.060	7.370	1.700	0.050	99.000	25
MwM6	0.085	0.033	7.860	0.350	0.875	131.000	6.490	0.700	5.730	106.370	25
NR6	0.093	0.022	3.850	2.000	0.133	1.600	7.680	1.700	0.040	76.000	25
MwK7	0.080	0.033	5.610	0.110	0.391	83.370	6.400	0.400	4.340	152.620	25
NR7	0.100	0.022	3.440	0.680	0.155	1.600	7.570	2.100	0.050	79.000	25
MwK8	0.088	0.039	6.270	0.070	0.659	54.510	6.340	0.700	4.030	178.540	25
KS8	0.109	0.024	5.520	2.230	0.133	3.210	7.430	2.100	0.040	95.000	25

TH –Total hardness

Ec –Electrical conductivity

DO –Dissolved oxygen

From the tables one can tell the physico-chemical parameters contributing to quality of each particular source (spring or stream) e.g. of all the investigated chemical parameters in Kabuga spring (source 1) and Kabuga stream (source 2), sodium is the most abundant (359.25 mg/l) among the cations and bicarbonate (181.5 mg/l) among the anions. The spring water is slightly acidic with a pH of 6.5 and also slightly hard (129.860 mg/l of CaCO₃) while the stream water is almost neutral with a pH of 6.83 and soft (8.06 mg/l).

This study however looks at the general contribution of each parameter to the quality of groundwater and surface water of Gichugu area hence the mean values. Tables 5, 6 and 7 give the mean values of each parameter in the springs (Source 1) and in the streams (source 2). They

also show the extent of variation (whether significant or insignificant at $\alpha=0.05$) for each parameter (Appendix B).

Table 5: Mean values of cationic constituents of the groundwater and surface water of Gichugu area

	K mg/l	Na mg/l	Fe mg/l	Pb mg/l	Zn mg/l	Cd* mg/l	Mn mg/l	Co* mg/l	Cu* mg/l	Ca mg/l	Mg mg/l
Source 1	35.960	358.943	0.583	0.081	0.013	0.001	0.306	0.014	0.024	80.200	113.500
<i>Stdev</i>	9.535	144.906	0.395	0.030	0.007	0.000	0.239	0.007	0.037	48.548	40.607
Source 2	0.576	3.298	0.145	0.012	0.003	0.001	0.068	0.010	0.005	7.000	2.030
<i>Stdev</i>	0.364	1.632	0.082	0.009	0.002	0.001	0.048	0.000	0.003	2.422	1.923

* Mean concentrations for these elements are not significantly different between the two sources

Table 6: Mean values of anionic constituents in the groundwater and surface water of Gichugu area

	NO ₃ ⁻ mg/l	NO ₂ ⁻ mg/l	HCO ₃ ⁻ mg/l	Cl ⁻ mg/l	F ⁻ mg/l	NH ₃ mg/l
Source 1	0.077	0.034	147.240	5.387	0.497	0.158
<i>Stdev</i>	0.009	0.006	32.493	1.499	0.238	0.102
Source 2	0.117	0.023	87.000	4.025	0.173	1.553
<i>Stdev</i>	0.032	0.008	8.813	0.707	0.050	0.634

Table 7: Mean values of physical parameters in groundwater and surface water of Gichugu area

	TH mg/l	pH	DO mg/l	Ec μ S/cm	T °C
Source 1	119.300	6.200	0.625	3.568	25
<i>Stdev</i>	44.846	0.161	0.128	1.108	0.000
Source 2	5.050	7.400	1.814	0.056	26
<i>Stdev</i>	3.405	0.313	0.348	0.018	0.000

The most abundant constituents in groundwater are two alkali metals sodium (with a mean of 358.943 mg/l) and potassium (with a mean of 35.96 mg/l) and two alkaline earth metals calcium (with a mean of 80.20 mg/l) and magnesium (with a mean of 113.5 mg/l). For the anions, bicarbonate (with a mean of 147.24 mg/l) is the most abundant while nitrate (0.077

mg/l), chloride (5.387 mg/l), fluoride (0.497 mg/l), ammonia (0.158 mg/l) and nitrite (0.034 mg/l) all occur in small but rather appreciable amounts.

Electrical conductivity levels range from 0.05 u,S/cm to 5.73 u,S/cm with a mean value of 3.567 u,S/cm and 0.056 }iS/cm in the groundwater and surface water respectively. The pH values range of 6.3 in the groundwater and 7.3 in the surface water. Dissolved oxygen had a mean value of 0.625 mg/l in the groundwater and 1.814 mg/l in the surface water. Total hardness measured in the groundwater ranged between 54 -205 mg/l in the groundwater and 1.6 -9.6 mg/l in the surface water. Similarly, calcium (7.0 mg/l), magnesium (2,03 mg/l), potassium (0.576 mg/l) and sodium (3.298 mg/l), are still the most abundant cationic constituents in surface water although their mean values are much less compared to those of the groundwater. For anions, bicarbonate (87.0 mg/l) is the most abundant followed by chloride (4.025 mg/l), ammonia (1.553 mg/l) fluoride (0.173 mg/l), nitrate (0.117 mg/l), and nitrite (0.023 mg/l) respectively.

Correlation analysis carried out on the data from the eight different sites and two different sources (springs and streams) of the study area yielded significant variations between the sources but showed no significant differences between the sites. This insignificant variation between the sites suggests that one groundwater aquifer generally underlies Gichugu area. Between the sources however, most elements and physical parameters had higher concentrations in groundwater than in surface water but the trend is similar (Figures 2, 3 and 4).

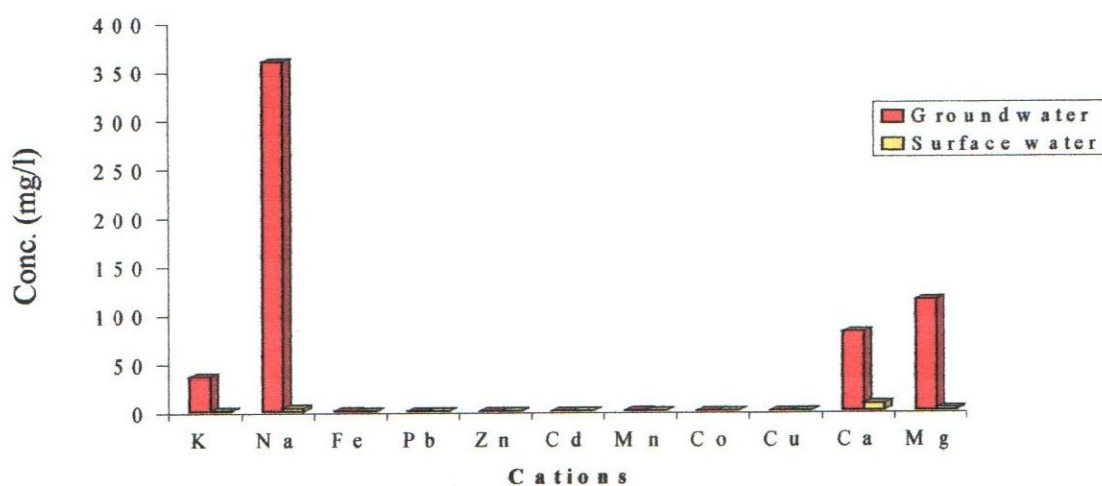


Figure 2: Mean values of cationic constituents of the groundwater and surface water of Gichugu area

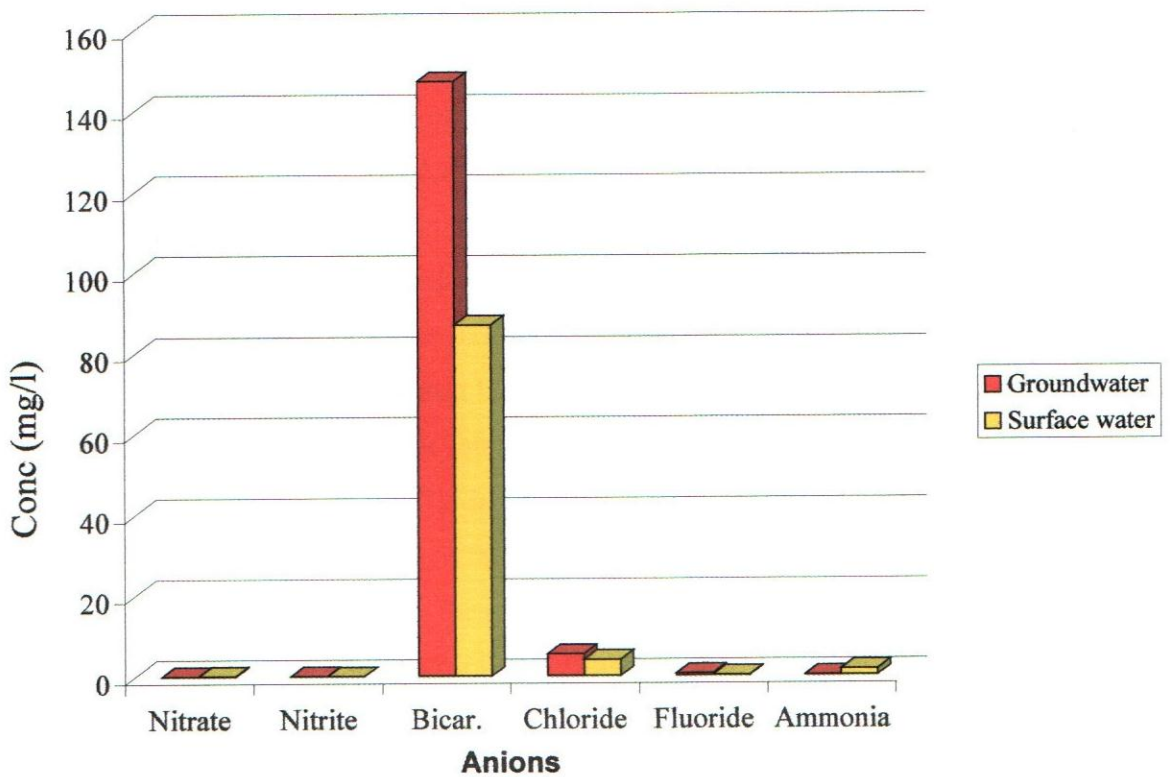


Figure 3: Mean values of anionic constituents of groundwater and surface water of Gichugu area

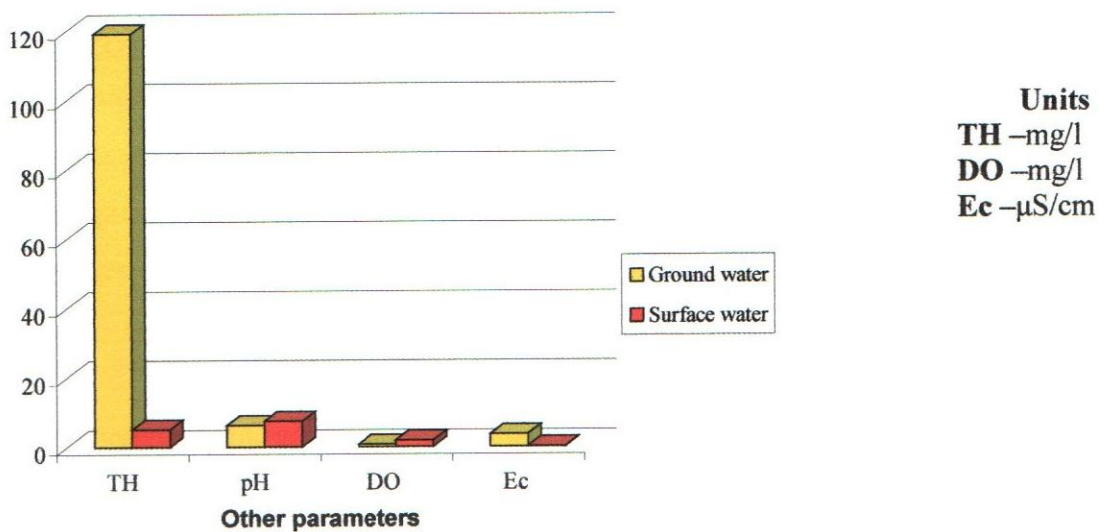


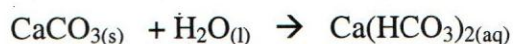
Figure 4: Mean values of physical parameters contributing to quality of groundwater and surface water of Gichugu area

Ordinarily, higher concentrations of dissolved constituents are found in groundwater than in surface water (Douglas and Considine 1984). This is because of the greater exposure to

in surface water (Douglas and Considine 1984). This is because of the greater exposure to soluble materials in geologic strata. Soluble salts in groundwater are thought to have originated primarily from solution of rock materials. As groundwater moves through the aquifer, contact with soluble rocks may result in dramatic increase in dissolved minerals, particularly calcium bicarbonate (CaHCO_3); Magnesium bicarbonate (MgHCO_3) etc. (Douglas and Considine, 1984). This difference in chemical composition is the likely cause of differences in physical properties.

Sodium (358.94 mg/l) and bicarbonate (147.24 mg/l) ions are the most abundant in the groundwaters of this area and hence NaHCO_3 salt is formed. Chloride is also known to occur as sodium chloride in groundwater (Garg, 1987). It can therefore be inferred that groundwater of this area is $\text{NaHCO}_3/\text{NaCl}$ type. Sodium ion in these salts exceeds the required amounts on taste basis hence it is thought to be responsible for the characteristic taste. One of the possibly sources of Sodium in the waters of this area is agricultural runoff as fertilizers are quite extensively used for maize, tea, coffee, beans and horticultural crops production. Bicarbonate, usually the primary anion in groundwater is derived from carbon dioxide released by organic decomposition in the soil (Todd, 1980).

Magnesium and calcium are some of the alkaline earth metals that are widely distributed in the earth's crust and are present in almost all waters as is the case in the waters of this area. Calcium occurs as CaCO_3 and $\text{Ca}(\text{HCO}_3)_2$ although in waters of high salinity, calcium chloride and nitrates can also be found. This is based on the fact that in the presence of carbon dioxide, calcium bicarbonate can normally be dissolved up to 20 g/l (as Ca) at atmospheric pressure and up to 100 g/l at higher pressures, though the concentration may be much higher in water coming from limestone areas (See equation below).



Also, the presence of sodium and potassium salts increases the solubility of calcium carbonate. This behaviour of magnesium resembles that of calcium although its solubility is about ten times that of calcium (Garg, 1987). The relatively high levels of these elements in the groundwater of Gichugu division confirm the water hardness. Calcium hydrogen carbonate forms temporary hardness that can be removed by boiling the water so that the carbon dioxide is driven out and the carbonates get precipitated. Magnesium also forms highly soluble salts which contribute to both carbonate and non-carbonate hardness but to a lesser extent than the calcium

component. There is no health objection to high calcium and magnesium content in water, on the contrary both minerals are essential to humans; the main limitations being on basis of excessive scaling, hardness, taste and alkalinity (CDN, 2000). The chloride salts of magnesium and calcium i.e. CaCl and MgCl are not usually detected by taste until levels of 1000 mg/l The UK regulations set an average maximum of 250 mg/l for calcium and 50 mg/l for magnesium but no maximums are set under WHO, EC or EPA standards (Twort *et al.*, 1994).

Groundwater of this area is moderately hard while surface water is soft. Water with hardness above 200 mg CaCO₃/l tends to cause scale deposition in distribution systems. However, the level of corrosion or deposition is dependent on pH, alkalinity, dissolved oxygen and temperature in the water (CDN, 2000).

High iron and manganese levels are objectionable in water supplies used for domestic purposes. They cause unpleasant tastes, stain laundry and plumbing fixtures. In groundwater, the occurrence of iron at concentration of 1.0-10 mg/l is common. In the waters of Gichugu division, the mean values of iron are 0.58 mg/l in groundwaters and 0.15 mg/l in the surface waters. However, higher concentrations (above 50 mg/l) are possible in low bicarbonated and low oxygen water. It may be present in varying quantities depending upon the geological area and other chemical components of the waterway. Iron in the groundwater of this area is slightly above the WHO recommended value. However, it appears to be more of a nuisance than a potential health hazard. According to CDN report (2000), consumers can find iron levels between 0.3 mg/l and 3 mg/l acceptable. Taste thresholds of iron in water are 0.1 mg/l for ferrous iron and 0.2 mg/l ferric iron, giving a bitter or an astringent taste. The iron standard given for domestic and drinking water (0.3 mg/l) is meant to prevent objectionable tastes or laundry staining and is therefore of aesthetic rather than toxicological significance although iron at high concentrations is toxic to livestock by interfering with the metabolism of phosphorus (Wolfe, 1960).

Concentrations of manganese rarely exceed 1.0 mg/l in well-aerated surface water, but much higher concentration can occur in the groundwaters subject to reducing conditions. It occurs in groundwater much less frequently and with smaller concentration than iron, which it resembles in behaviour. It occurs as soluble manganese bicarbonate (Garg, 1987). The WHO has given a provisional value (0.5 mg/l) based on toxicity and for lower level required to avoid deposition problems (Twort *et al.*, 1994). At concentrations exceeding 0.1 mg/l, the manganese

ion imparts an undesirable taste to beverages and stains plumbing fixtures and laundry (Griffin, 1960). When manganese (II) compounds in solution undergo oxidation, manganese is precipitated as manganese (IV) e.g. MnO_2 , resulting in encrustation problems (Bean, 1974).

The mean value of manganese in the groundwater of Gichugu; (0.306 mg/l) is above WHO guideline value (0.1 mg/l) given on health basis and also to avoid staining of laundry. This makes the groundwater unsuitable for washing. Manganese intake from drinking water is normally substantially lower than intake from food. At typical drinking-water levels of 4-30 $\mu\text{g/l}$, the intake of manganese would range from 8 to 60 $\mu\text{g/day}$ for an adult. Other sources indicate that manganese intake from water can be an order of magnitude higher (Environmental Criteria and Assessment Office, 1984). Drinking this water regularly can add significantly to manganese intake (Dieter *et al.*, 1992). Mean value for surface water (0.068 mg/l) is within WHO guideline value (Twort *et al.*, 1994).

Copper, Cadmium and Cobalt, were found in trace amounts in the two sources; streams and springs. In fact, they were insignificantly different. Table 4 shows that they are also within WHO recommended values. Zinc was found only in trace amounts i.e. 0.013 mg/l in groundwater and 0.003 mg/l in surface water. These concentrations are unlikely to be detrimental to health. WHO recommends 3 mg/l maximum. Lead is rarely detectable below 0.02 mg/l in most waters. The mean values of Lead in this water are 0.08 mg/l in groundwater and 0.01 mg/l in surface water. The WHO 1993 revised guideline value is 0.01 mg/l (formerly 0.05 mg/l) but it recognises that not all waters will meet the guideline immediately (Twort *et al.*, 1994).

Chloride and fluoride in water are not usually harmful to people at recommended values. Fluorides may occur naturally in water and unlike chlorides, they have low solubility. The groundwater of Gichugu area has a mean value of 0.51 mg/l while surface water has 0.17 mg/l. These are obtained from dissolution of fluorite (calcium fluoride). Levels not more than 1 mg/l of fluoride are safe and effective in reducing dental caries. Ordinarily, concentration of fluoride (F) in groundwater does not exceed 10 g/l. The maximum concentration has to be related to climate, local circumstances and amount of water consumed (Gärg, 1987). On the other hand, chloride in groundwater does not exceed 5 g/l, and water high in chloride is also high in sodium. As mentioned earlier, chloride in groundwater is generally present as sodium chloride and to a lesser extent as calcium and magnesium chlorides. The sodium chloride salt in the groundwater

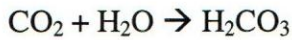
explains the high conductivity compared to the surface water. The salt acts as an electrolyte. It dissociates to Na^+ and Cl^- ions.

Chlorides are not usually harmful to people; however, the sodium part of table salt has been linked to heart and kidney disease. Public drinking water standards require chloride levels not to exceed 250 mg/l (Garg, 1987 & Twort *et al.*, 1994): They may get into water from several sources including:

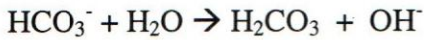
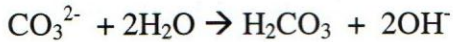
- Rocks containing chlorides,
- Agricultural runoff,
- Wastewater from industries,
- Oil well wastes, and
- Effluent wastewater from wastewater treatment plants.

The quantity of dissolved oxygen in groundwater is generally very low (0.0625 mg/l). This is because most of the oxygen dissolved from the atmosphere is used up in oxidising organic matter during the downward passage of water. Up to 29 g/l of air can be dissolved in water at atmospheric pressure and at 0°C out of which oxygen is 10 g/l. Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. Oxygen is however known to hasten the corrosive action of water on steel, iron and brass. No health-based guideline value is recommended (Garg, 1987).

In most natural waters, pH is controlled by the carbon dioxide–bicarbonate–carbonate equilibrium system. An increased carbon dioxide concentration therefore lowers pH, whereas a decrease will cause it to rise. Temperature will also affect the equilibria and the pH. In pure water, a decrease in pH of about 0.45 occurs as the temperature is raised by 25 °C. The pH of most natural water lies within the range of 6.5 -8.5. pH outside the range can have adverse effects on the taste, colour and appearance of water. Groundwater from sampled springs was slightly acidic (6.2) while the surface water was neutral (7.4). This is due to the inter-relationship between free carbon dioxide and the amounts of carbonate and bicarbonates present. The free CO_2 combines with water partly to form carbonic acid (H_2CO_3) which is further dissociated into hydrogen (H^+) and bicarbonate (HCO_3^-) ions. The bicarbonate ions thus formed get further dissociated into H^+ and carbonate (CO_3^{2-}) ions.



The hydrogen ion contributes to the weak acidity of water. The carbonate and the bicarbonate ions in water further yield hydroxyl (OH^-) ions, which lead to the rise in pH.



This interrelationship yields H_2CO_3 (lowers the pH), H^+ (lowers pH), and OH^- (raises pH) ions, hence the above range. No health-based guideline value is proposed for pH (CDN, 2000). Dissolved gases such as carbon dioxide in the water give the fizzling property.

Spring water is clearer compared to surface water in this area. This could be due to filtration of groundwater through soil and its long residence time underground (Colin 1995). It comes from aquifers whose waters have been in contact with the atmosphere as recently as a few hours ago or as long ago as few centuries. Its quality characteristics are therefore affected by the downward movement in recharge areas (percolation) and the lateral movement through aquifers (underflow). The percolation of this water through the surface soils of recharge areas generally results in significant purification (Linsley, 1982).

Ammonia, nitrate and nitrite are usually expressed in terms of nitrogen i.e mg/l -N. their mean concentrations in groundwater of Gichugu are very low i.e 0.158 mg/l NH_3 , 0.077 mg/l NO_3^- , and 0.034 mg/l NO_2^- . In surface water, they are 1.553 mg/l NH_3 , 0.177 mg/l NO_3^- and 0.023 mg/l NO_2^- . Ordinarily, nitrate concentration in surface water is normally low (0-18 mg NO_3^- /l), but can reach high levels as a result of agricultural run off, agricultural activities and contamination by human and animal wastes. In groundwater, it is normally below 5-10 mg/l however, increasing use of artificial fertilizers, the disposal of animal wastes and changes in land use can cause an increase to several hundred mg/l.

The general level of nitrite is not so well documented but is expected to be much less than the concentration of nitrate, as nitrite is reduced to nitrate, which is the most stable form of nitrogen in most natural environments. The effects of nitrates and nitrites on humans are very complex and not well established; however there seems to be enough evidence for toxicity to recommend a health-based guideline for both nitrate and nitrite. The WHO recommends a health-based guideline (max) of 50 mg NO_3^- /l and 3 mg NO_2^- . As nitrate and nitrite interact, a

combined guideline is recommended (CDN, 2000 & Twort *et al.*, 1994).

Ammonia is of no direct importance to health in the concentrations that can normally be expected in drinking water. Natural levels in groundwater are usually below 0.2 mg/l while surface water may contain up to 12 mg/l. The taste threshold is 33 mg/l. In the groundwater of Gichugu it is barely 0.158 mg/l and 1.553 mg/l in the surface water. The presence of ammonia can be an indicator of faecal pollution. The WHO recommendation is 1.5 mg/l based on odour (CDN, 2000).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Water should be palatable rather than free from taste and odour, but with people having very different abilities to detect tastes and odour at low concentrations, this is often very difficult to achieve. Users may become accustomed to waters containing high concentrations of major ions, however, and prefer the taste of such water to the "tastelessness" of more dilute solutions (Hem, 1985). This is so with the people in Gichugu area who prefer the spring water to stream water for drinking. The dissolved cations that constitute a major part of the dissolved-solids content in groundwater of this area are Sodium, Potassium, Calcium and magnesium; the major anions being chloride and bicarbonate. However, their concentrations in the surface water are relatively low. Sodium being the most dominant cation, groundwater of this area can be said to be $\text{NaHCO}_3/\text{NaCl}$ type. These salts give the water a salty taste because the sodium concentration has exceeded the taste threshold (200mg/l) as given by the WHO. In surface water sodium concentration (3.298 mg/l) is less by far than the above taste threshold value. On the basis of existing data, no firm conclusions can be drawn concerning the possible association between sodium in drinking water and the occurrence of hypertension. No health-based guideline value is therefore proposed. These salts explain the high conductivity of the groundwater compared to surface water. On dissociation, they act as electrolytes.

The levels of calcium and magnesium make this water moderately hard although hardness is not harmful to health. In fact, it may give indications of the water's ability to corrode or cause scale deposit. It also explains why this water may not be suitable for washing or bathing because hard water reacts with ordinary soap to form a scum. Their concentrations in surface water are too low such that the water is made soft (5.05 mg/l) and therefore suitable for washing. Other parameters such as nitrate and ammonia are higher in surface water than in groundwater. This is an indication that not much human and animal waste get to the groundwater source. However their concentrations are still within recommended levels.

Dissolved gases under pressure explain fizzling in this water as it occurs in Coca-Cola. An example of these gases is free carbon dioxide. It causes fizzling in the groundwater as it tries to escape. It also explains the slight acidity of this water whose pH values are below 7.5 but

above 6.0. pH is controlled by carbon dioxide–bicarbonate–carbonate equilibrium system such that an increased carbon dioxide concentration lowers pH, whereas a decrease will cause it to rise. Temperature will also affect the equilibria and the pH. The slight acidity shows presence of CO₂ forming H₂CO₃ which dissociates to hydrogen ions and bicarbonate ions.

The clarity of the groundwater compared to surface water in this area is due to filtration of groundwater through soil and its long residence time underground (Colin 1995). The downward movement in recharge areas (percolation) and the lateral movement through aquifers (underflow) affect its quality characteristics. The percolation of this water through the surface soils of recharge areas generally results in significant purification.

The sampled springs recorded iron (with a mean of 0.583 mg/l) and manganese (with a mean of 0.306 mg/l) concentration levels above 0.3 mg/l and 0.1 mg/l respectively and exceeding the recommended limit for drinking. They also recorded fluoride concentration (0.497 mg/l) below the required levels (1.5 mg/l) for drinking water quality (WHO, 1993). In children, this low concentration may provide protection against dental caries though an adult requires 1.5 mg/l for healthy teeth. From personal communication, similar springs occur in Embu and Meru districts. It appears that the occurrence of these springs could be attributed to the presence of Mt. Kenya.

5.2 RECOMMENDATIONS

Since there is no health-based guideline value that is proposed for sodium, this water though tasty may not affect health. However, high levels of sodium may affect soil permeability rendering the water unsuitable for irrigation. Though this water was found to be hard, the hardness is temporary and can be removed by boiling the water making it suitable for bathing. Iron and manganese have been found to have higher than recommended values but are still within the acceptable tolerance levels. However if found in excess, above 3 mg/l, iron can give taste to water, cause turbidity, slimy coatings and colouration in piped systems and the staining of laundry and sanitary. Though ingestion of high concentration of iron can be lethal, it is an essential element in human nutrition and is not harmful to humans in the levels found in waters of Gichugu division. However this water may not be very suitable for washing (may stain laundry). Manganese is also an essential element in human nutrition but it may have adverse effects on human health in levels above 0.5 mg/l. It may also cause black staining of plumbing

fixtures and laundry. Although concentrations below 0.1 mg/l are usually acceptable to consumers, this may vary with local circumstances (WHO, 1981)). Because of the importance of the groundwater to the community, I would recommend protection of the available springs to avoid faecal contamination. I would also recommend continued sampling of other existing springs, streams and rivers, developing new sample points, and performing a regional study to determine sources contributing to high concentration of some of the chemical parameters. There is also need to look into the geology of the area and biological studies of the water in relation to the unique characteristics of this water.

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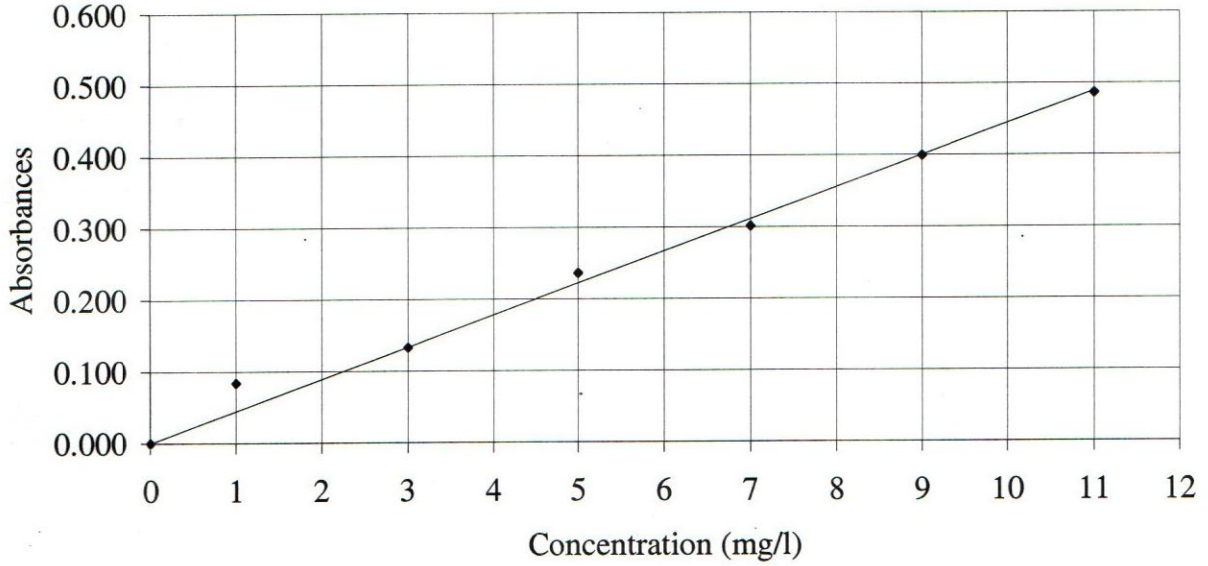
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APPENDICES

APPENDIX A: Calibration Curves

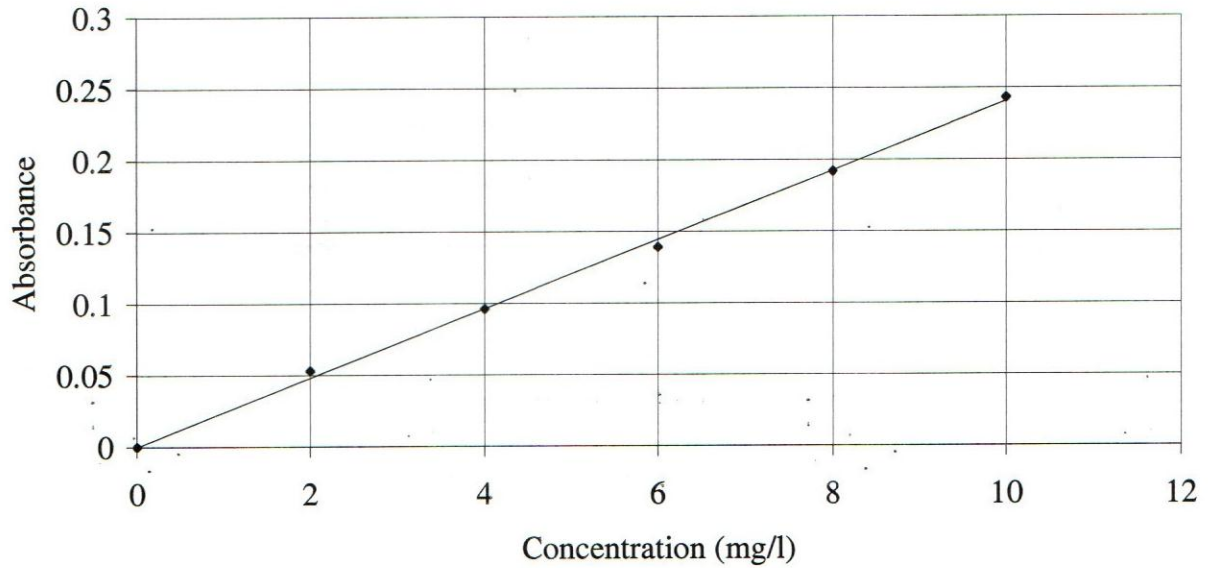
Calibration curve for Ammonia

$$y = 0.0446x$$
$$R^2 = 0.9892$$



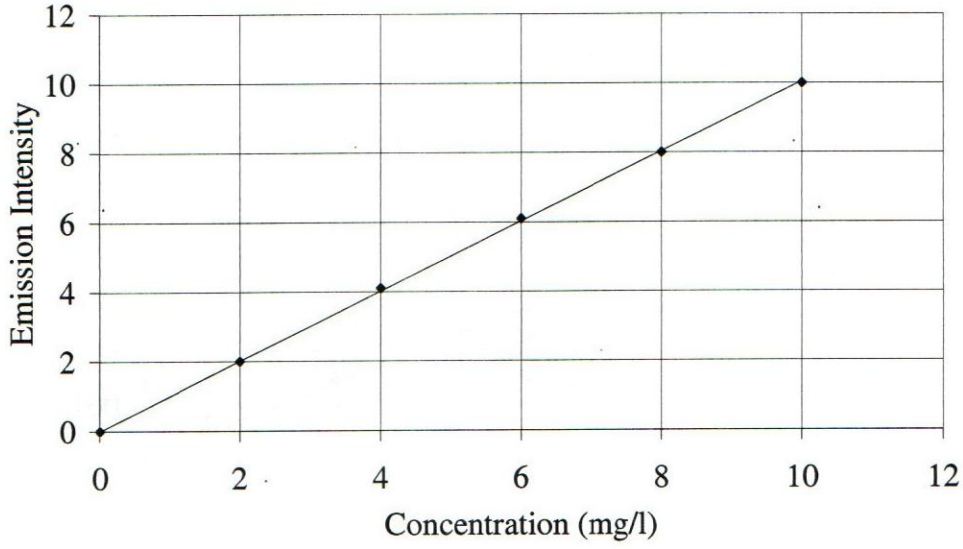
Calibration Curve for Chlorides

$$y = 0.024x$$
$$R^2 = 0.9985$$



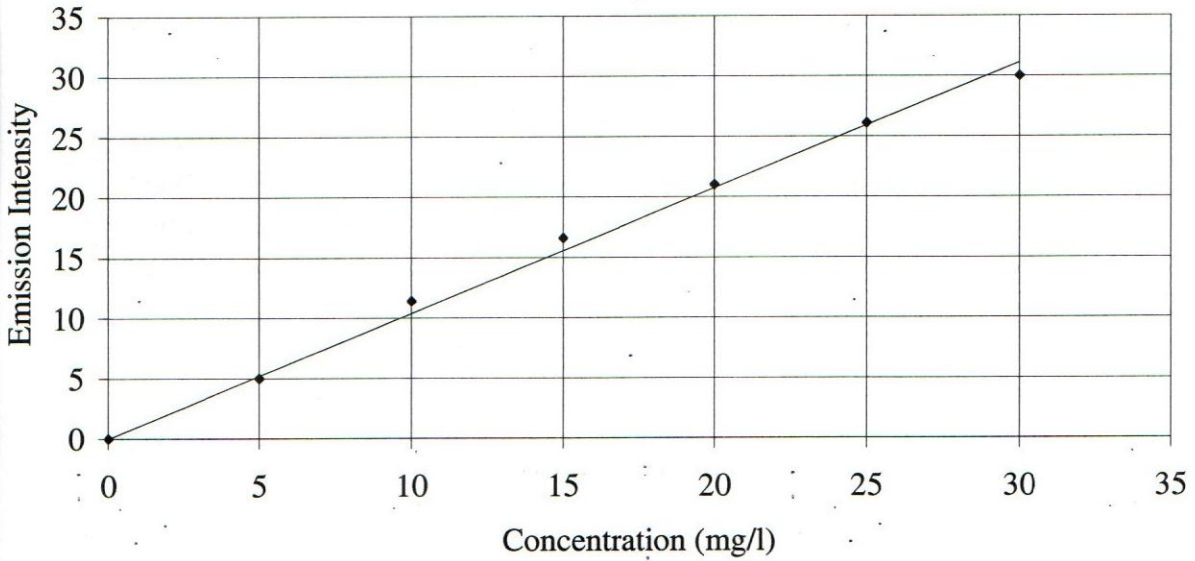
Calibration curve of potassium

$y = 1.0155x$
 $R^2 = 0.978$



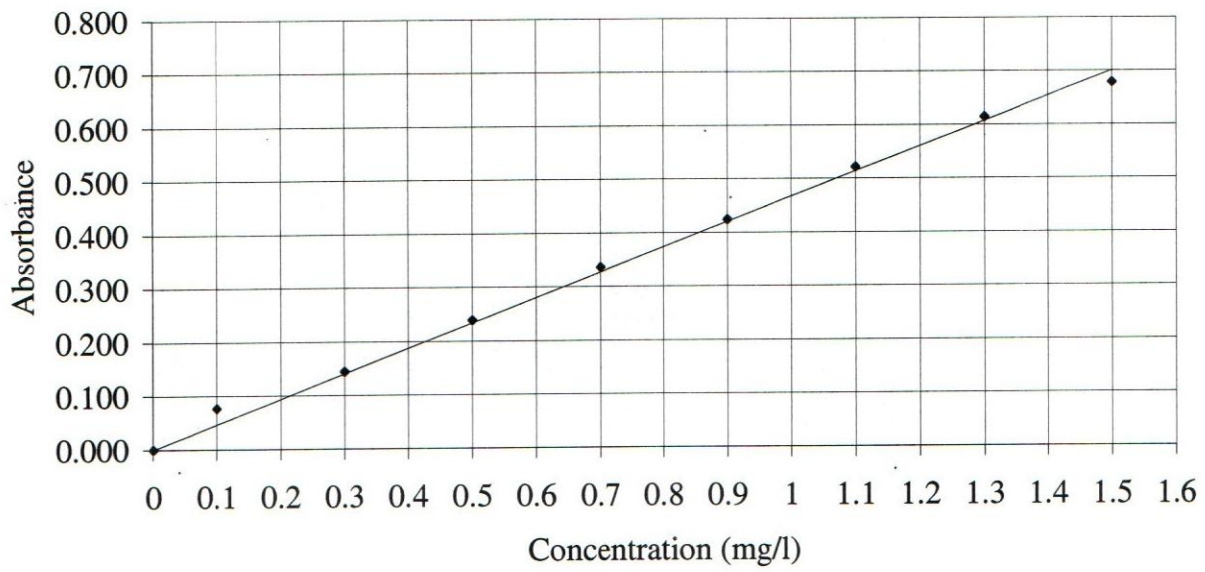
Calibration Curve for Sodium

$y = 1.0736x$
 $R^2 = 0.9961$



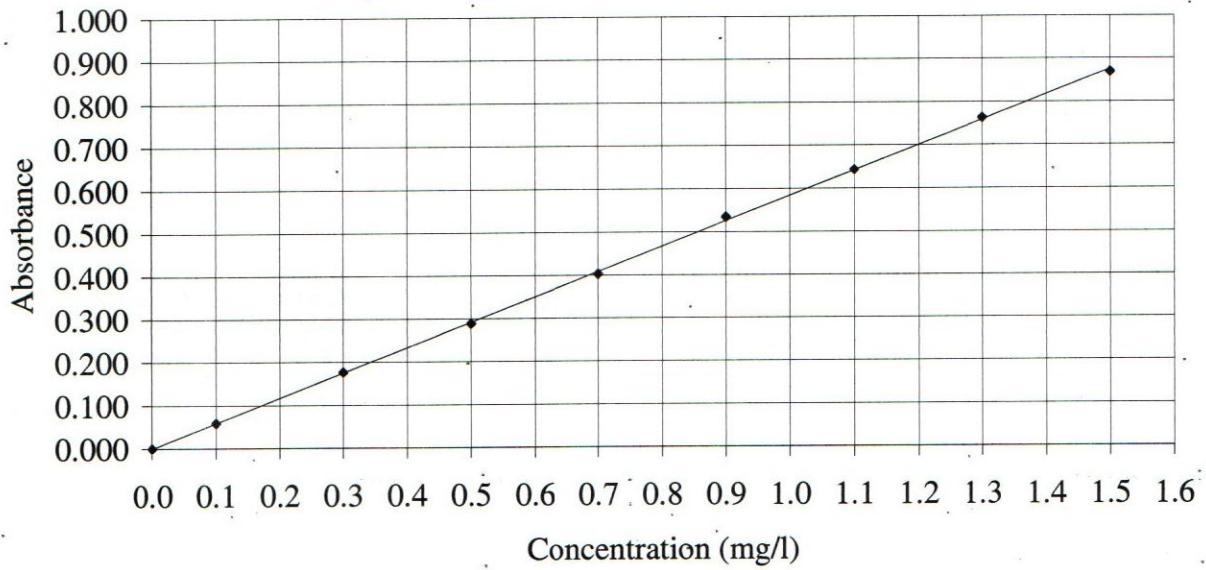
Calibration Curve for Nitrites

$y = 0.461x$
 $R^2 = 0.9964$



Calibration Curve of Nitrates

$y = 0.5747x$
 $R^2 = 0.9973$



APPENDIX B: The SAS Data Tables

Obs	Sites	Sources	TH	pH	Ec	DO	HCO ₃
1	1	1	129.86	6.05	2.77	0.5	181.51
2	1	2	8.06	6.83	0.07	1.2	86
3	2	1	131.00	6.07	2.25	0.6	104.06
4	2	2	3.21	7.64	0.05	2.2	93
5	3	1	128.26	6.40	3.47	0.8	171.21
6	4	1	91.38	6.21	2.87	0.7	119
7	4	2	9.62	7.08	0.09	1.7	81
8	5	1	205.00	6.34	3.08	0.6	164.6
9	5	2	8.06	7.37	0.05	1.7	99
10	6	1	131.00	6.49	5.73	0.7	106.37
11	6	2	1.60	7.68	0.04	1.7	76
12	7	1	83.37	6.40	4.34	0.4	152.62
13	7	2	1.60	7.57	0.05	2.1	79
14	8	1	54.51	6.34	4.03	0.7	178.54
15	8	2	3.21	7.43	0.04	2.1	95

Duncans Multiple Range Test for TH

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	119.30	8	1
B	5.05	7	2

Duncans Multiple Range Test for pH

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	7.37143	7	2
B	6.28750	8	1

Duncans Multiple Range Test for Ec

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	3.5675	8	1
B	0.0557	7	2

Duncans Multiple Range Test for DO

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	1.8143	7	2
B	0.6250	8	1

Duncans Multiple Range Test for HCO₃

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	147.24	8	1
B	87	7	2

The SAS system

Obs	Sites	Sources	K	Na	Fe	Pb	Cu	Zn	Ca	Cd	Mn	Co
1	1	1	43.600	359.250	0.822	0.100	0.007	0.020	10.000	0.001	0.036	0.010
2	1	2	0.018	1.866	0.162	0.010	0.006	0.003	6.800	0.001	0.017	0.010
3	2	1	28.570	255.240	1.068	0.054	0.115	0.014	42.800	0.001	0.713	0.010
4	2	2	0.351	4.201	0.304	0.000	0.011	0.001	5.400	0.001	0.074	0.010
5	3	1	49.610	350.580	0.278	0.012	0.011	0.005	88.000	0.001	0.136	0.010
6	4	1	29.570	362.260	1.080	0.080	0.012	0.012	62.000	0.001	0.216	0.010
7	4	2	0.652	6.244	0.144	0.016	0.006	0.002	11.200	0.001	0.161	0.010
8	5	1	20.550	72.170	0.133	0.080	0.008	0.003	166.000	0.001	0.385	0.030
9	5	2	0.953	2.645	0.178	0.020	0.003	0.005	5.600	0.004	0.053	0.010
10	6	1	40.590	506.24	0.232	0.055	0.014	0.022	128.000	0.001	0.134	0.010
11	6	2	1.053	4.104	0.074	0.023	0.001	0.002	9.000	0.001	0.024	0.010
12	7	1	41.590	455.660	0.777	0.106	0.014	0.011	70.000	0.001	0.596	0.010
13	7	2	0.652	2.158	0.075	0.002	0.004	0.004	4.000	0.001	0.054	0.010
14	8	1	33.580	510.140	0.270	0.058	0.008	0.017	74.800	0.001	0.237	0.020
15	8	2	0.351	1.866	0.080	0.013	0.007	0.001	7.000	0.001	0.041	0.010

Duncans Multiple Range Test for K

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.576	7	2
B	35.958	8	1

Duncans Multiple Range Test for Na

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	3.298	7	2
B	358.943	8	1

Duncans Multiple Range Test for Fe

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.1453	7	2
B	0.5825	8	1

Duncans Multiple Range Test for Pb

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.012000	7	2
B	0.081625	8	1

Duncans Multiple Range Test for Cu

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.00543	7	2
A	0.02363	8	1

Duncans Multiple Range Test for Zn

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.002571	7	2
B	0.013000	8	1

Duncans Multiple Range Test for Ca

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	7	7	2

B 80.2 8 1

Duncans Multiple Range Test for Cd

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.0005714	7	2
A	0.0013750	8	1

Duncans Multiple Range Test for Mn

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.060571	7	2
B	0.306625	8	1

Duncans Multiple Range Test for Co

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.008857	7	2
A	0.01375	8	1

The SAS system

Obs	Sites	Sources	NO3	NO2	Cl	NH3	F	Mg
1	1	1	0.064	0.031	4.270	0.040	0.758	117.400
2	1	2	0.163	0.020	3.477	2.110	0.197	4.000
3	2	1	0.071	0.039	4.395	0.160	0.456	73.600
4	2	2	0.107	0.039	3.811	1.620	0.215	2.400
5	3	1	0.068	0.035	6.860	0.210	0.235	141.600
6	4	1	0.086	0.022	4.060	0.090	0.262	165.000
7	4	2	0.161	0.017	3.890	1.500	0.256	5.200
8	5	1	0.080	0.037	3.770	0.230	0.342	149.600
9	5	2	0.086	0.017	4.190	0.730	0.127	1.000
10	6	1	0.085	0.033	7.860	0.350	0.875	128.200
11	6	2	0.093	0.022	3.850	2.000	0.133	1.000
12	7	1	0.080	0.033	5.610	0.110	0.391	82.400
13	7	2	0.100	0.022	3.440	0.680	0.155	0.200
14	8	1	0.088	0.039	6.270	0.070	0.659	50.200
15	8	2	0.109	0.024	5.520	2.230	0.133	0.400

Duncans Multiple Range Test for NO3

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.11700	7	2
B	0.07775	8	1

Duncans Multiple Range Test for NO2

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.023	7	2
B	0.033625	8	1

Duncans Multiple Range Test for Cl

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	4.0254	7	2
B	5.3869	8	1

Duncans Multiple Range Test for NH3

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	1.552857	7	2
B	0.1575	8	1

Duncans Multiple Range Test for F

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	0.173714	7	2
B	0.49725	8	1

Duncans Multiple Range Test for Mg

Means with the same letter are not significantly different

Duncan grouping	Mean	N	Sources
A	2.028571	7	2
B	113.5	8	1

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