# Monitoring of Heavy Metals in Groundwater In Makuyu Division, Maragua District

<sup>1</sup>B N K Njoroge, <sup>2</sup> Murigi I P And <sup>3</sup>D. Ndunge

<sup>1</sup>Dept. of Civil and Construction Engineering, University of Nairobi, Nairobi, Kenya <sup>2</sup>Dept. of Civil and Construction Engineering, University of Nairobi, Nairobi, Kenya <sup>3</sup>Dept. of Environmental and Biosystems Engineering, University of Nairobi, Nairobi, Kenya

ABSTRACT: Analytical results have shown that the borehole and well water in Makuyu Division in Maragua District in central Kenya is not polluted and can be consumed readily. The level of the various parameters is low compared to recommended limits. The chemical properties monitoring showed no significant heavy metal pollution in groundwater. The heavy metal concentrations values ranges from 0.0994 – 101450 mg/l for iron, 0.0046 - 1.0190 mg/l for manganese, 0 - 0.0588 mg/l for titanium, 0.0011 - 0.0142 mg/l for copper, 0.0027 - 0.00270.1692 mg/l for zinc, 0.0011 - 0.0016 mg/l for strontium, 0.0012 - 0.0043 mg/l for yttrium and 0.0013 - 0.0043 mg/l for zirconium. The concentration of iron, manganese, copper, zinc, selenium, titanium, strontium, yttrium and zirconium were determined in filtered water after pre-concentration with ammonium pyrolidine dithiocarbonate APDC using X-ray fluorescence analysis (XRFA). The values obtained showed no significant heavy metals pollution in groundwater. The trace metal concentrations in filtered water were below the maximum permissible limits for drinking water as given by the World Health Organization (1993). It is only in Kamahuha Girls High School borehole where the concentration of iron and manganese were above the WHO standards. The XRFA technique was found to be a fast, precise, accurate and reliable method of water analysis. Recent studies have indicated that toxicity of metals such as copper and zinc is primarily due to the presence of the free metal iron and thus may not be directly related to the total metal concentration (Shepherd, B K et al. 1980).

# I. INTRODUCTION

In the semi-arid and arid areas, groundwater is widely exploited as the major source of water. In the other zones it is exploited to supplement existing water sources. The intensive use of natural resources and the large production of wastes in modern society often pose a threat to groundwater quality. Degradation of groundwater quality can take place over large areas and from various sources.Pollution can impair the use of water and can create hazards to public health through toxicity or the spread of diseases. Most pollution originates from the disposal of wastewater following the use of water for any of the wide variety of purposes. A complex and interrelated series of modifications to natural water quality is created by the diversity of human activities impinging on the hydrological cycle.

# 1.1 Groundwater

The main source of groundwater is precipitation, which may penetrate the soil directly to the ground or may enter surface streams and percolate from these channels to the groundwater. Interception, depression, storage and soil moisture must be satisfied before any large amount of water can percolate to the groundwater. The path taken by groundwater to the zone of saturation depends on the geologic conditions. Relatively impermeable layers above the water table may prevent direct percolation (Bouwer, 1978) Miscellaneous sources of groundwater include water from deep in the earth, which is carried upward in intrusive rocks, and water that is trapped in sedimentary rocks during their formation. Normally the quantities of such water are small and are highly mineralized. The groundwater source should be as remote as possible from any source of pollution, such as latrines, septic tanks, sewerage discharges, agricultural drainage and water discharges.Groundwater is not stagnant, but rather moves from areas where water recharges aquifers (recharges area) to areas where it leaves aquifers (discharge areas) to areas of lower elevation or pressure/hydraulic head. This is where the groundwater is released into the streams, lakes, wetlands, or springs (discharge areas). Discharge areas are lakes, streams and wetlands. The base flow of streams and rivers, which is the sustained flow between storm events, is provided by groundwater.

The qualification of the volume and rate of flow of groundwater in various regions is a difficult task because volumes and flow rates are determined to a considerable extent by the geology of the region. The characters and arrangement of rocks and soils are important factors, and these are often highly variable within a groundwater reservoir. The direction of groundwater flow normally follows the general topography of the land surface (Fetter, 1994).Many aquifers have been contaminated, at least locally by the improper disposal of chemical and other wastes from solid wastes disposal sites, and from infiltrating storm water discharges. Boundaries to groundwater flow system may be fixed geologic structure or fee water surfaces that are dependent for their position on the state of the flow. Groundwater flow porous media may be classified as isotropic, anisotropic, heterogeneous, homogenous or several possible combinations of these. The movement of groundwater is governed by established hydraulic principles. Except in large caverns and fissures, groundwater flow is almost exclusively laminar. The flow through aquifers can be expressed by what is known as Darcy's Law (1856). Darcy's Law is an empirical formula that states that the velocity of flow through a porous medium is directly propositional to the hydraulic gradient, assuming that the flow is laminar and inertia can be neglected (Gupta, 1992).

## Darcy's Law

V=Ks

Where

V = velocity (specific discharge) (m/s)

s = slope (hydraulic gradient)

K = coefficient of permeability (hydraulic conductivity) (m/s)

And V = Q/A (m/s) Where

Q =flow rate (volume per unit time) (m<sup>3</sup>/s)

A = cross – section area through which flow occurs  $(m^2)$ 

Thus,  $Q = AKs = AV_{actual}$ 

On the average, the actual velocity at which water is moving through an aquifer is given by

 $V_{actual} = V/P$ Where P is the porosity of the aquifer

Groundwater movements thus depend on the type of aquifer and its properties (geological properties).

## **Groundwater Quality**

Practically all types of water, i.e. runoff, groundwater and rainwater, contain some dissolved salts and impurities. If certain elements are present in quantities above maximum allowable limits, the application of the water to domestic use or other purpose may have adverse effects. The quality of groundwater is of great importance in determining the suitability of a particular groundwater for a certain use, i.e. irrigation, drinking and other domestic use, and industrial applications. Groundwater quality is influenced by the quality of its source. The quality of groundwater is a resultant of all the processes and reactions that act on the water from the time it is condensed in the atmosphere to the time it is discharged by a well or a spring.

#### 1.2 Heavy Metals

Heavy metals are metallic elements including the transition series, which include many element required for plants and animals nutrition in trace concentrations but which become toxic at higher concentrations. Heavy metals are generally defined to include those metals of atomic weight higher than that of sodium and having a specific gravity in excess of 5.0. The concept of toxicity is usually associated with these terms and consequently may be applied so as to include iron, zinc, selenium, titanium, manganese, copper, vanadium and lead. These are essential elements because they are necessary for biological functions i.e. without them life does not exist or exists at unhealthy level. Excessive levels of trace elements occur naturally or due to human release of metals into the environment. Once available they are not easily detoxified and thus accumulate. Previous studies have shown that essential element such as copper, iron, selenium and manganese exist in natural water at very low concentrations (Hume, 1975).Heavy metals exist partly in solution and partly in suspension adsorbed to organic or inorganic particulate matter and they are generally considered to be toxic in soluble ionic forms but toxicity is known to be reduced by water hardness (Champman and Dunlop, 1981).

The toxicity of these metals has also been documented throughout history. Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicity became a science. Exposure to heavy metals has been linked to developmental retardation, various cancers, kidney damage and even death in instances of very high exposure (World Resources, 1998). Excess of too much copper causes narcotic hepatitis (Tyagi, 1992). Arsenic, barium, cadmium, chromium, mercury, nickel, selenium and thallium are toxic metals affecting the internal organs of the human body. Arsenic is widely distributed in waters at low concentrations, with associated instances of higher concentrations in well waters (Mari, 2004). Chromium is amphoteric and can exist in water in several valence states. The content in natural waters is extremely low because it is held in rocks in essentially insoluble trivalent forms. Acute systemic poisoning can result from high exposures to hexavalent chromium. Presence of metals in potable waters is a matter of serious concern because of the toxic nature of these materials.

# II. IRON (FE) AND MANGANESE (MN)

The present of iron and manganese is common in groundwater. Iron is widespread in nature, and very abundant occurring at concentration of about 50,000 mg/kg in the earth's crust (Oehme, 1974). Iron occurs in minerals like biotite, magnetite, pyroxenes, ferric oxides and hydroxides. In groundwater, the common form of iron is the soluble ferrous ion ( $Fe^{2+}$ ). When exposed to atmosphere it is oxidized to the ferric state ( $Fe^{3+}$ ) which is insoluble and causes brown discolorations of water and introduces a bitter sweet astringent taste and stains to laundered clothes.For most purposes, the iron concentrations should not exceed 0.5 mg/l. The presence of even this amount can be a nuisance in some industrial applications such as textile processing plants.

Iron exists in the soils as insoluble ferric oxide, iron sulfide (pyrite) and ferrous carbonate (siderite). The carbon dioxide in groundwater reacts with ferrous carbonate, thus dissolving it as shown;

$$FeCO_{3} + CO_{2} + H_{2}O \rightarrow Fe^{2+} + 2HCO_{3}$$
(aq) (g) (l) (aq) (aq)

In groundwater, ferric iron is reduced to ferrous iron and manganese dioxide is reduced to an oxidation state of II under reducing (anaerobic) conditions. Both oxides are soluble.

On the other hand, manganese is a relatively common metal in the earth's crust, being 12 in abundance. It was first isolated in 1774 (WHO, 1981). Manganese is contained in minerals like biotite and hornblende. The divalent ion Mn<sup>2+</sup> is insoluble. When oxidized it forms black stains in laundered textiles and its concentrations in public waters is set at 0.05 mg/l (NAS/NRC, 1973). If iron and manganese are not removed during water treatment they can stains domestic fittings and cause brown deposits on vegetables during washing and cooking. Their presence also in industrial processes like paper making and photographic film manufacture is a nuisance. They cause unacceptable astringent metallic taste in water. Iron in concentration greater than 0.3 mg/l and manganese 0.05 mg/l stains plumbing fixtures and laundered clothes. Although discoloration from precipitates is the most serious problem associated with water supplies having excessive iron and manganese, foul tastes and odour can be produced by growth or iron bacteria in water distribution mains. These filamentous bacteria reduce iron as an energy source; precipitate it causing pipe encrustation (Blain, 1994).Decay of the accumulated bacteria slimes creates offensive taste and odours. The presence of iron in water is considered objectionable because it imparts a brownish colour to laundered goods and affects the taste of beverages, such as tea and coffee. Dissolved iron and manganese are often found in groundwater from well located in shale sandstone and alluvial deposits. Iron bacteria capable of using dissolved compounds containing iron include crenothix, leptothrix, pirophyllum, gallionella and others.

The organism utilizes iron and deposit ferric hydroxide. Iron bacteria oxidize ferrous iron to ferric iron and precipitates ferric hydrate. Some sulphur bacteria increase acidity and this tends to dissolve iron. Under specific conditions insoluble iron sulphate may be produced. Sulphate reducing bacteria may cause the precipitation of the iron by the production of sulphate from the reduction of sulphate. These bacteria also affect the aerobic corrosion of iron.Generally, the presence of iron is common in groundwater. Iron is vital in the formation of hemoglobin in human being. The essential element iron, is a component of some enzymes notably; cytochrome and xanthine oxidase. Dietary intake of iron in excessive amount may lead to haemosiderosis or haemochromatosis. Heamosiderosis is a condition best characterized by generalized increased iron content in the body tissue, especially in the liver and reticuloendothenal system. Excessive dietary intake is reported to be the cause of abnormal iron accumulation in a condition described as "Bantu Siderosis" occurring in South Africa.

This disease is marked by iron accumulations in the Kupffer cells of the liver and in the reticuloendothenal cells of the spleen and bone marrow. Another unusual disorder "Kaschin – Beck disease" has been reported in Asia excessive iron content as opposed to maximum permissible limit of 0.3 mg/l Fe/l and resulted in an arthritic disease (US Public Health Service, 1970).

## Copper (Cu)

It is widely distributed in the environment and is essential to human life, but potentially toxic at elevated levels of exposure. Copper is very essential to human. Copper acts as a catalyst in the formation of hemoglobin and is also involved in haemopoisis, maintenance of vascular and skeletal integrity, structure and function of central nervous system (Norconsult, 1975). As an indicator of corrosivity, has a no action level of 1.3 mg/l in first flush sample. The symptoms of severe copper poisoning in the human body are extensive homolysis, hepatic necrosis, nephropathy and coma, and if not treated may lead to death. Wilson's disease is well known. It is characterized by inability to digest copper in the body resulting in degenerative changes in the brain and cirrhosis of the liver. The disease appears to be related to a hereditary deficiency of ceruloplasm (the blue copper containing oxidase present in the  $x_2$  – globulin fraction of the human serum. Its major function is to oxidize iron to the ferric state for transport by transferring. Copper deficiency therefore causes anemia. The metal is readily adsorbed onto the particulate material, very little being present as free Cu<sup>2+</sup> ion except stability constants of these complexes, a tendency which dominates the chemistry of copper in water are well known. Most copper complexes are labile and equilibria are readily established. The main pollution sources of copper are power plants, municipal wastewater discharge, industrial processes and agriculture.

#### Selenium

Selenium is a trace metal naturally occurring in soils derived from some sedimentary rocks. Selenium has a toxic effect on man and animals comparable with that of arsenic giving rise to similar symptoms. Selenium also has been suspected of causing dental carries in man and of being a carcinogenic agent. The selenium concentration of most drinking water is less than 0.01 mg/l. Concentrations exceeding 0.5 mg/l are rare and limited to seepage from seleniferous soils.

# Strontium (Sr)

Strontium chemically resembles calcium and cause a positive error in gravimetric and titrimetric methods for the determination of calcium. Because strontium has a tendency to accumulate in radioactive strontium 90, with a half – life of 28 days presents a well recognized peril to health. The natural occurring strontium is not radioactive. For this reason, the determination of strontium in a water supply should be supplemented by a radiological measurement to exclude the possibility that the strontium content may originate from radioactive contamination.

## Zinc (Zn)

Zinc is non cumulative, and the amount absorbed is thought to be inversely to the amount ingested. Zinc was first demonstrated to be essential element for mammals over 45 years ago. Zinc is an essential and beneficial element in body growth. The clinical symptoms of zinc deficiency are anorexia, pica, impaired taste acuity, menstrual lethargy and disturbances, viz; rough, dry skin, impaired wound healing and increased susceptibility to infection, chronic deficiency in pediatric and adolescent age group causes growth retardation and delay of sexual maturation (Casey, 1980). Acute zinc toxicity results in haemodialysis, characterized by nausea, vomiting, fever and severe anemia. However, concentrations above 5 mg/l can cause a stringent taste and opalescence in alkaline waters (Dunlop, 1981). Zinc is also an essential trace element in living organisms, being involved in nucleic acid synthesis and occurring in many other metalloenzymes. These include dehydrogenase in photosynthesis, superoxide dismutase and carboxypeptidase. The metal occurs in water as free cation ( $Zn^{2+}$ ) or as soluble. Zinc complexes can be adsorbed on suspended matter. Toxicity is increased by a decrease in dissolved oxygen content and decreased by an increase in salinity (Lloyd, 1960).

## Titanium (Ti)

Titanium occurs rather abundantly in the earth's crust and is used in large variety of industrial processes (Mason, 1966). Titanium mainly interferes with two types of enzymes action. It inhibits borne growth and interferes with the carbohydrate metabolism (Bruanwald et al, 1987).

# 2.1 Introduction

# III. EXPERIMENTAL METHODS

Water samples for tests were obtained from the various boreholes and wells within the study area. Sample bottles were cleaned carefully before each use and sterilized. Sterilization procedure for sample bottles

was done using standard methods (WHO Geneva, 1985). Once the samples arrived at the laboratory pH was taken using a pH meter and a buffer solution pH meter calibration. The volume of water collected was large enough to permit an accurate analysis. The test for heavy metal was done using X-ray fluorescence spectrometry. The parameters that were tested include iron, manganese, titanium, copper, zinc, strontium, yttrium and zirconium.

# 2.2 X-Ray Fluorescence Spectrometry (XRFS)

X-ray fluorescence spectrometry is an emission spectroscopic technique that has found wide application in many fields, which require elemental identification and determination radiation, usually in 1-60Kev range following excitation of atomic electron energy levels by an external energy source such as charged This is particle or x-ray beam.X-ray fluorescence analysis takes first place among instrumental techniques. partially due to the coverage by the technique of more than 80 elements, to the multi-element analysis capability for each sample and to the extremely wide range of sample form and size that can be accommodated (MacDonald, 1980). The analytical range is broad since an element can be determined from part per million levels up to percentages. Precision is generally good and affected little by concentration. It is non-destructive method of analysis allowing recovery of the intact sampler after spectrometry. The advent of solid state (semi conductor) detectors, especially those using lithium compensated silicon and low noise electronic, detection of light elements became practical. The energy dispersive x-ray fluorescent analysis (EDXRFA) has evolved recently with the introduction of semiconductor detectors which enable simultaneous recording of the entire fluorescence spectrum, using radioisotope excitation sources. The energy dispersion x-ray fluorescence (EDXRF) technique is a non-destructive instrumental method of qualitative and quantitative analysis for chemical elements based on measurements of the wavelength and intensities of their x-ray spectral lines emitted by secondary excitation (Bertin, 1980). The primary beam from x-ray tube or a radioisotope source irradiates the specimen (sample or standard), exciting each element to emit secondary spectral lines having wavelengths characteristics of that element. The detector receives excited lines of all the specimen elements at once and generates a pulse of electric current proportional to its photon energy.

The instrument has three basic parts: - the primary source unit, the spectrometer and the measuring electronics (Jenkins, 1982). The actual parts are:

- Radioisotope source (<sup>109</sup>Cd, <sup>55</sup>Fe or <sup>241</sup>Am) to act as the primary beam source. The <sup>109</sup>Cd excitation source was used in this work. Its activity was 0.218 mci. The measurement time for each filter with <sup>109</sup>Cd excitation source was 2000 seconds.
- The sample compartment. It holds the sample in a precisely defined geometry during analysis and provides for introduction and removal of the specimen during the excitation.
- Lithium drifted silicon or germanium detector (Si.Li or Ge/Li). The Si.Li detector (Canberra SI 30180) was used with spectral resolution of 180 ev at Mn K alpha line and associated electronics for signal processing.
- A preamplifier and an amplifier
- The multichannel analyser (MCA) and if desired a micro-computer. The spectrum evaluation software was Axil IAEA QXAS whose background model was linear order 8.

Figure 1 shows a diagrammatic representation of an EDPXRF spectrometer.



Figure 1: Diagrammatic representation of an EDPXRF spectrometer

#### 2.3 Sample and Sample Preservation

The water samples were collected using well-rinsed plastic containers, which had been previously washed with hot soapy water and rinsed in de-ionized water. A minimum of four water samples at each borehole or well was collected within a month. The pH and temperature of the water samples were recorded at each site. The water samples were then filtered using Whiteman No. 2 filter membrane to remove suspended particles. The water samples were preconcentrated using ammonium pyrolidine dithiocarbonate (APDC) and filtered through a  $0.45 \mu m$  Millipore filter. Standards were prepared from an analytical grade of its salt. The water used in all the work was de-ionized and doubly distilled.

## 2.4 Analytical Procedures for X-Ray Fluorescence

Direct XRF analysis of aqueous sample is only feasible for part per million concentration of high atomic number element (Florkowski et al, 1976). The detention limits are approximately 5 to 10 part per million for such elements as copper, zinc, and lead. This rather poor detection limit is due to the backscatter background and x-ray adsorption effect. To reach detection limit in part per million ranges a preliminary chemical enrichment must be undertaken. In this case, heavy metals were isolated by pre-concentration of the solution using ammonium pyrolidine dithiocarbonate (APDC). Then, a 500ml of the water sample was acidified to pH 3.8 using ammonium hydroxide analar or nitric acid analar and 10 ml of APDC added to it. The mixture was thoroughly shaken then filtered through a 0.45um Millipore filter. The deposit on filter paper is then analyzed using XRF. The standard solution was made from pure analytical grade salts of the elements to be tested. Adsorption correction was done on one sample using a multi-element standard and it showed that it was a thin film of sample deposited on the filter hence had negligible adsorption. The XRFA system used consist of 10 mci cadmium 109 radioisotope source, a liquid nitrogen cooled ORTEC, Si/Li semi-detector with a 25 micron beryllium window, an S40 Canberra multichannel analyzer (MCA) and a Dec Pro-350 micro-computer. The source was excited using a <sup>109</sup>Cd radioisotope source. The emitted fluorescence radiation was then detected using a Si/Li semiconductor detector. The signals were then amplified, shaped and sorted out by the electronic system as per their energies by a system consisting of a pre-amplified, amplifier and a multichannel analyzer (MCA). The intensities of the various photopeaks were determined using a quantitative x-ray analysis program (QXAS) and the corresponding concentrations calculated with the help of a pro-350 micro-computer.

# 2.5 Qualitative Analysis of Environmental Samples (QAES) Program for Quantitative Analysis

The qualitative analysis of environmental samples (QAES), modular program of the International Atomic Energy Agency (IAEA)'s Quantitative x-ray Analysis Software (QXAS) was first calibrated for quantitative analysis by way of three sub-routines of the program available for:-

- (a) Quantitative analysis of unknown samples
- (b) Performing calibration of the x-ray system
- (c) Calculating energy distribution of primary x-rays

Sensitivity calibration involves determining the distribution of primary x-ray source from sub-routine and intensity measurements of pure metal samples or analar compounds whose characteristics energies cover the analytical range of interest. Intensities for elements for compounds together with their real densities were put to enable the program evaluate the sensitivities and the geometrical constants. The standard used for the calibration was pure metal foil of zinc, zirconium, iron, copper, titanium, manganese, strontium and yttrium. For each element the experimentally determined geometrical constants for the measurement elements were compared with the theoretically determined value. The selected values of geometrical constants of the accepted elements were used to evaluate the average geometrical factor.

## 2.6 Spectral Data Analysis

A Canberra S-100 PC based multi-channel analyzer (MCA) was used for spectral data acquisition and storage. Both the course and fine loaded filters were irradiated for 2000 seconds using <sup>109</sup>Cd source so as to give reasonable statistics. The loaded filters were placed on the sample holder such as that the loaded side faced the source of radiation as per the recommended method (IAEA, 1996). Spectrum data analysis was done using the IAEA software. Analysis of x-ray by interactive least square fitting (AXIL). Quantitative analysis was done using quantitative analysis of environmental samples (QAES) software (Kump, 1993). This relates the spectral intensities with the elemental concentrations based on the fundamental parameter technique (Kinyua, 1982 and Sparks, 1975).

#### 2.7 Standard Solutions for Calibration

Standard solutions for calibration of the spectrometer were prepared before analysis. Standard solutions were prepared for zinc, zirconium, iron, copper, titanium, manganese, strontium and yttrium. The concentration range of the standards was as per the specification of the spectrometer that is 1-6 part per million (Shimadzu corporation, 1991). The standards were then utilized for plotting the calibration curve for the various elements to be analysed.

# IV. RESULTS AND DISCUSSIONS

Figures 2-5 show the summary of the chemical properties of water samples from the 12 boreholes, 9 wells and 3 rivers in the study area. The data in the figures are mean of five month observations and also shown are standard deviations.



## **RESULTS FOR VARIOUS WATER SOURCES**

Figure 2; Heavy metals' concentration (mg/l) for various water sources



Figure 3; Heavy metals' concentration (mg/l) for various water sources



Figure 4; Heavy metals' concentration (mg/l) for various water sources



# V. DISCUSSION

The water samples for various sources were analyzed and results tabulated. The precision of measurements was obtained by carrying out several tests on each source. The work was carried out in five months (Between July and December 2002). Four samples were tested and average obtained for each month. The water samples were obtained during the morning hours and afternoon hours. The low precision value obtained implies that the difference between one value and another for the same element is very small. This suggests high degree of reproducibility and hence high reliability of the methods. Precision measurements were made for water samples. In XRFA errors can arise from high background levels and incoherent (Compton) scattering of fluorescent intensities, which may interfere with the intensity of the measurement temperature changes, geometry employed and matrix effects (i.e critical thickness and enhancement effects). Iron is most abundant of these metals and potentially may have influenced the occurrence of many others such as zinc, copper, nickel, chromium and silver. The actual concentration values do not reveal the toxic effects of some of these heavy metals, which depend on the metal-metal interaction. It is necessary to know how these heavy metals interact with some elements. Heavy concentrations of dissolved iron and manganese in the groundwater can give it an unpleasant taste, and give a brownish color to food and clothes. In rural areas these chemicals can be a serious nuisance, and may even prevent people from using the water. If so, they can often be removed by aeration, for instance when the water falls into a storage tank from inlet. Aeration causes the iron and manganese to become insoluble so that they form fine dark sediment, which is more easily removed.

## Conclusion

From the present study findings of the status of both surface water and ground water from the 12 boreholes, nine wells and three rivers, the following conclusions were made;-

- The heavy metals pollution for the groundwater were below the world Health Organization (WHO, 1993) and Kenya Bureau of Standards specifications for drinking water (1985).
- X-ray fluorescence analysis has capability to perform multi-element analysis, the time consumed in the analysis is minimum, also sample preparation is minimum hence contamination risks are minimum. In conclusion, XRFA is a very useful tool for water pollution monitoring if concentrations of trace elements area at a few part per billion levels.

# Recommendations

Based on the findings of the status of the surface water and groundwater in Makuyu Division of Maragua District, the following recommendations were made:-

- The present quality of groundwater in the area is fairly good but measures should be instituted to conserve the quality. These measures may include proper septic system design and maintenance, well/borehole head protection and incorporation of onsite treatment systems
- The community should be sensitized on the status of groundwater and be encouraged to use the groundwater for domestic purposes

- To prevent groundwater pollution in communal water groundwater sources, awareness should be created on hygienic matters. Clean water alone will not significantly alter health status if not accompanied by an intensive educational programme.
- The study had found groundwater source for Makuyu Division as unpolluted source in comparison with surface water source from the three rivers. Nonetheless, there is need to ascertain the well yields especially during the dry season, in order to ascertain the reliability of the source.

# **BIBLIOGRAPHY**

- [1] Shephard, B.K., A.W. McIntosh, G.J. Atchison, and D.W. Nelson. 1980. Aspects of the aquatic chemistry of cadmium and zinc in a heavy metal contaminated lake. Water Res. 14:1061-1066.
- Bouwer H and MCGraw Hill, 1978. Groundwater Hydrology. [2]
- Fetter, C. W., Jr., 1994, Applied Hydrogeology, Third Edition, Prentice-Hall Publishing Co. New York, 691 p. [3]
- Amit Gupta and B L Gupta, 1992. Engineering Hydrology, Standard Publishers Distributers. [4]
- [5] Hume, D., 1975, Adv. Chem. Ser., 147.
- Champman and S Dunlop, 1981. Detoxication of Zinc and cadmium by protozoan tetrahymena pyriformia environment. Res 26, [6] 1 - 21.
- [7] World Resources, 1998. A guide to the global environmental change and human health. Pp 65. A joint publication by UNEP and the World Bank, New York, oxford University Press.
- Tyagi O. D. and Mehra M., 1992, A textbook of Environmental Chemistry, pp 117. [8]
- [9] Mari Golub, Robert G., Harlal C., Elaina K., & Marc S., 2004. Human Health Effects of Metals. Issue paper submitted to the U.S. Environmental Protection Agency, Risk Assessment Forum.
- [10] Oehme F W , 1974. Toxicity of heavy meals in the environment hazardous and toxic substances, part 2: 572 - 576 Marcel Dekker inc. New York.
- World Health Organization, 1981. Manganese, environmental health criteria 17, pp 110. United Nations Environmental [11] Program
- [12] NAS/NRC, 1973. Manganese, Washington D C, National Academy of Science, National Research Council, 1-191.
- [13] Blain and K L katsifarakis, 1994. Hydraulic Engineering Software: Vol. 1. Water Resources and distribution. [14] US Public Health Service, 1970. Community water supply study, Analysis of National Survey findings, US Department of Health, Education and Welfare, Washington, D. C. 1970.
- [15] Norconsult A S 1975. Mombasa Water pollution and waste disposal study marine investigations. December 1975 VI. Ministry of Local Government on behalf of Mombasa Municipal Council.
- LIoyd R, 1960. Toxicity of zinc sulphate to rainbow trout. Ann Appl. Biolo. 48, 84-94. Mason, 1966. *Principles of geochemistry*. 3<sup>rd</sup> Edition, Willey New York, 1966. [16]
- [17]
- [18] Braunwald E., Isselbacher J. K., Petersdorf R. G., Wilson J. D., Martin J. B. and Fauci A. S., 1987. Harrison's principles of internal medicine, 11th Edition. McGraw - Hill Inc. Hamburg.
- [19] World Health Organization, 1985. Guidelines for Drinking Water Quality. Vol. 3 drinking water quality control in small community supplies. WHO Geneva 1985.
- [20] Macdonald G L, 1980. X-ray Spectrometry. Anal. Chem. 52.
- [21] Bertin P E, 1980. Introduction to x-ray spectrometric analysis. Plenum press, New York.
- Jenkins R , 1982. X-ray fluorescence analysis instrumentation pp3. [22]
- [23] Kinyua a M, 1982. Multi-element analysis of solid and liquid samples by x-ray fluorescence. MSc. Thesis, UON.
- [24] Sparks C J 1975. Rapid Quantitative x-ray fluorescence using fundamental parameter method, advances in x-ray analysis, Plenum Press, New York, 19.
- Shimadzu Corporation (Japan), 1991. Instruction manual, AA 680. Atomic absorption/Flame emission spectrometer. [25]
- [26] Kenya Bureau of Standards, 1985. Specifications for drinking Water.
- [27] Camp T R, 1973 Water and its impurities, Reinhold, new York.
- [28] Casey C E, Hambridge K M, 1980. Epidemilogical aspects of human Zinc deficiency.
- [29] Nriagu J O (Ed) zinc in the environment pt 2 health Effects: 572 - 576.
- [30] Collen J M, L J Kamphake, E K Harris and R L Woodward, 1960. Taste threshold concentrations of metals in drinking water. J Amer, Water Works ass, 52: 660
- [31] Groundwater in Engineering Geology, Proceedings of the 21st annual conference of the Engineering Group of the geological society held at the University of Sheffield. 15th - 19th September 1985. Edited by J C Crops, F G Bell and M G Culshaw, 1986. Published by the Geologial Socity of London.
- [32]
- Howard S Peavy, Donald R Rowe and George Tchobanoglous, 1985. Environmental Engineering. McGraw. John H Duffs, 1980. "Environmental toxicity" (Resource and environmental science series), p.68 Edward Arnold ltd. [33]
- [34] Pinta M, 1978. Modern Methods for trace elements analysis. Ann Arb. Science Pub. Inc Michigan.
- Practical handbook of groundwater monitoring, 1991 Edited by David M Nielsen. [35]
- [36] Sillen L G and martell A G, 1964. Stability constants of metals ion complexes. Spec. public Chem. Soc. London. 17
- [37] Sweco, 1975. Nairobi Groundwater Survey. Vols 1 and 2
- [38] Tebbut T H Y, 1983. Principals of water quality control. Pergamon press, University of Birminggham, UK, 3rd edition, 1970
- [39] Todd W R Elvehjen C A, Hart E B, 1934, zinc in the Nitrition of hee Rat Am J Physiol. 107: 146 - 156
- [40] Wanielista P M, 1990. Hydrology and water quality control. John Wiley and Sons