

Groundwater Chemistry and Quality Assessment of the Lake Naivasha Area,  
Nukuru District, Kenya

By

Natalie Erica Morgan

**DEDICATED**  
**TO THE MORGAN'S FAMILY**

**ACKNOWLEDGMENT**

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## **ABSTRACT**

Groundwater chemistry in the Naivasha area is mainly defined by the mineralogy of volcanic rocks. The quality and chemical assessment of this resource gave insight into its potential for domestic and agricultural use and highlighted the environmental, geological and hydrogeological impacts on its chemistry.

Hydrochemical and source-rock deduction analysis was used to identify groundwater types and examine the effects of rock weathering on groundwater quality. Variogram and estimation-kriging analysis was applied to investigate the spatial correlation among variables. Univariate, bivariate and multivariate statistics established distributions, correlations and statistical groupings of the data set.

The hydrochemical study indicated a dominant sodium bicarbonate groundwater type of rhyolitic composition with high silica and fluoride levels. The processes having an impact on the chemical composition of the groundwater in the area are mainly: mineral dissolution, evapotranspiration, groundwater flow, cation exchange and oxidation/reduction reactions.

The quality of groundwater in the area is deteriorated by: a) high nitrate from agriculture and unsewered systems (reducing the amount of potable water), b) high sodium absorption ratio which limits the suitability of groundwater for agricultural use, c) high iron concentrations suggesting poor water quality for domestic use and corrosion of distribution systems, d) very high fluoride levels which make the groundwater poor for drinking. Groundwater is characterized by low - high temporary hardness.

Geostatistical analysis of fluorides, iron, nitrates and chlorides suggested spatial continuity for all the parameters but only at some cutoff limits or indicator thresholds. Statistics revealed outliers in most distributions and high correlations between calcium, magnesium, electrical conductivity, chloride, fluoride and bicarbonate. Three groundwater groups were established through cluster analysis and verified by discriminant analysis.

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## ERRATA

Page	Item	Change from	To
4	Line 22	from <b>shallow the</b> groundwater	from the shallow groundwater
5	Box	Bivariate and multiple correaltion analysis	Bivariate and multiple correlation analysis
13	Line 2	(WHO) <b>1971</b>	(WHO) 1993
14	Line 9	(set <b>1</b> with 13 samples)	(set 3 with 13 samples)
29	Line 15	(EU)	(EU) 1980
22	Line 14	right side of <b>a</b> the	right side of the
31	Line 13	<b>absorption</b>	adsorption
31	Line 17	Fe <sup>2+</sup> (Ferric) Fe <sup>3+</sup> (Ferrous)	Fe <sup>2+</sup> (Ferrous) Fe <sup>3+</sup> (Ferric)
33	Line 18	. the	. The
52	Line 44	The <b>dendrogram gives</b> agglomeration schedule	The agglomeration schedule
58	Line 7	anions while	anions (data set 3), while
59	Line 33	sodium <b>absorption</b> ratio	sodium adsorption ratio
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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND**

Groundwater in the Lake Naivasha area of Kenya is exploited for domestic, agricultural and industrial use. The underlying and often overlooked reason for groundwater exploitation however, is its chemistry. Fresh water supports the intensive livestock and agricultural industry that provides employment for the majority of the 250,000 people living around the lake as well as meets domestic demand. Naturally occurring deep superheated ground water propels the geothermal industry, the main source of Kenya's electrical energy.

Groundwater chemistry studies of the area up to now, concentrated on deep boreholes with hydrothermal waters from volcanic complexes surrounding the lake. The Naivasha lake waters have been extensively studied because of its rich biological diversity, as well as the intensive irrigation based agriculture (mainly horticulture: flower growing) supported by lake water.

Detailed studies of the groundwater chemistry around the lake however, are limited. The chemistry of the shallow boreholes and wells around the lake (cold water system) is important as it is the main source of drinking water for the area. Four major boreholes supply the town with water for domestic purposes, while numerous private boreholes and wells are the only source of domestic and irrigation water supply for the majority of the population away from immediate access to lake water.

A hydrochemical study of the area is useful as it gives insight into aquifer lithology, history and development of groundwater, groundwater flow path, as well as the suitability of the groundwater for domestic and agricultural purposes. An assessment of the chemical components defining the groundwater of the area, also aids in the understanding of the hydrochemistry.

#### **1.2 OBJECTIVE**

The aim of this research is to assess the groundwater chemistry and quality in the Naivasha lake surroundings. Three approaches were used to carry out this assessment:

- 1) Hydrochemical approach focusing on an analysis of: a) the relationship between groundwater chemistry and rock weathering b) classification of groundwater types c) the effects of groundwater flow and evapotranspiration on groundwater chemistry and d) the impacts of the groundwater chemistry on the environment.

- 2) Geostatistical approach sighting the: a) impact of stratification on groundwater chemistry b) spatial relationships of parameters and c) chemical pattern of groundwater through mapping.
- 3) Statistical approach (univariate, bivariate and multivariate) pointing out the: a) distributions and correlations of the chemical variables b) elaboration of groundwater types through classification of the variables.

This aspect of the study is part of a general study of the Naivasha Lake Basin for the MSc research studies. Other aspects of the study include: groundwater modeling, groundwater recharge, soil pollution, soil classification, soil erosion, surface runoff, surface water quality and water use/ demand.

### **1.3 PREVIOUS GROUNDWATER CHEMISTRY STUDIES**

Extensive studies have been done on the Naivasha area as well as the lakes of the Eastern Rift Valley countries of Kenya and Ethiopia. Two very recent studies concerning the area are mentioned below:

1. Intensive study has been done for deep well groundwater chemistry as it relates to geothermal water sources for the Kenya geothermal power industry. Studies through the Ministry of Energy of the government of Kenya and the United Kingdom (Clarke et al. 1990) indicated that the groundwater in the area was of sodium-bicarbonate type with high silica content. Dissolution of minor carbonates provide the main anion,  $\text{HCO}_3^-$ . All waters are oversaturated with respect to silica,  $\text{SiO}_2$ . Most have not reached calcite saturation. Stable isotope studies have indicated that groundwater recharges the lake from the NE, then undergoes evaporative concentration before discharging to the south and perhaps to the north. There is also evidence of mixing with lake and shallow groundwater.
2. The Leicester University in collaboration with the University of Nairobi, Kenya (Harper, 1996) studied the borehole chemistry of the shallow aquifers and indicated that:
  - a) Boreholes in the lake basin have different characteristics from lake water, and probably reflect several different streams of subterranean water flowing from higher parts of the catchment surrounding the lake, where no permanent streams are present;
  - b) Borehole waters in the vicinity of the river Malewa reflect river characteristics;
  - c) The differences between boreholes in the major ions reflect the complex volcanic geology of the Naivasha area.

## 1.4 THE CONCEPT OF GROUNDWATER GEOCHEMISTRY

Groundwater geochemistry according to Appelo et al. (1996) is concerned with the chemistry of water in the subsurface environment. The chemical composition of groundwater is the combined result of the composition of water that enters the groundwater reservoir and reactions with minerals present in the rock that may modify the water composition.

Apart from information concerning water quality of an area, groundwater geochemistry has potential use for tracing the origins and history of the water. Since water compositions change through the reaction with the environment water quality may yield information about the environments through which the water has circulated (aquifer characteristics), residence times and flowpaths.

## 1.5 LOCATION OF STUDY AREA

### 1.5.1 REGIONAL SETTING

The study area lies in the Kenyan rift Valley which is a part of the system of sublinear belts of active seismic, volcanic and heat fluxes that define the edges of lithospheric plates. It conforms to the constructive type plate margin that continues northwards through Ethiopia to the Afar region where it forms a “triple junction” with the Red sea and Gulf of Aden spreading axes where new oceanic crust is being generated (Clarke et al. 1990).

Lake Naivasha lies within the highest central portion of the rift floor approximately 2000 m asl which is flanked by decreasing altitude north and southward of the Lake Nukuru-Lake Naivasha highlands. This area supports the structural doming concept of the valley floor of the pre -Miocene period (Clarke et al. 1990).

### 1.5.2 LOCAL SETTING

The study area is concentrated in the shallow aquifer around Lake Naivasha, in the Eastern Rift Valley province of Kenya at a mean altitude of 1885 m above mean sea level. It is located approximately 100 km from Nairobi in the Naivasha Division of the Nukuru District (Figure 1) within the UTM zone 37 and the coordinates :

$$\begin{array}{l} X_{\max} 221000 \quad X_{\min} 190000 \\ Y_{\max} 9934000 \quad Y_{\min} 9907000 \end{array}$$

**Plains** - Lake Naivasha is part of the southern rift floor plain and dominates the Naivasha basin. The basin also incorporates the Ndabibi plains extending 9 km west of the lake and the Ilkek plains extending 23 km to the north.

**Escarpment** - The eastern margin of the Naivasha basin is defined by the Kinangop plateau. On the western edge of this plateau is the north-north-west trending south

Kinangop fault scarp. The Eburru and Bahati escarpment which is linked to the Mau escarpment forms the western margin of the Naivasha basin.

**Volcanic complexes** - South east of the Lake is the Longonot Volcano which has a well developed cone and a summit crater. The crater is about 350 km<sup>2</sup>. To the south west the lake is the Olkaria volcanic complex, a multicentred volcanic field 240 km<sup>2</sup> in area. To the north-east of the Lake is the Eburru volcanic complex covering an area of 470 km<sup>2</sup>.

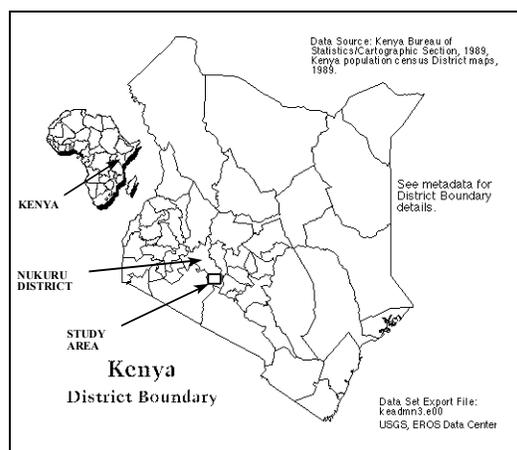
The study area is 897 km<sup>2</sup> covering Naivasha area, Naivasha town, New Karati town in the NE, Marula Estate in the N, Loldia in the NW, Ndabibi Estate in the W, Kongoni farm in the SW and South Lake Estates.

### 1.5.3 LANDUSE

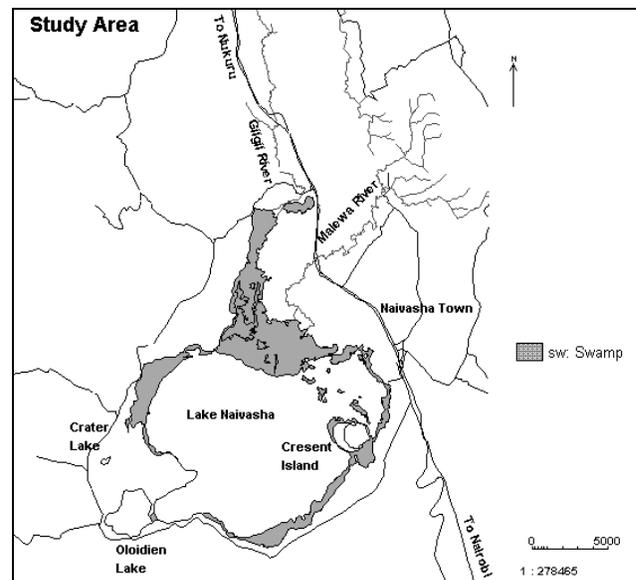
Five major landuse units can be identified in the area: a. agriculture (horticulture and flower growing) b. settlements, c. game sanctuaries, d. rangeland (dairy) and e. natural vegetation.

Horticulture and flower growing is concentrated around the lake. Vegetable and dairy farming is practiced on large estates mainly in the northeast shores of the lake. Game sanctuaries are mainly present in the west of the study area however wildlife occupies most of the barren shrub, grass lands. Settlement is mainly concentrated in Naivasha town but scattered homes and villages are present on estates within the study area. The natural vegetation surrounding the lake is mainly papyrus swamp vegetation. Natural vegetation outside of the lake surroundings are shrub, acacia and cactus trees. The natural and agricultural vegetation play a role in the uptake of minerals and nutrients from shallow the groundwater table.

Figure 1. Location Maps of the study area



Source: USAID



## **1.6 BACKGROUND DATA**

To aid the evaluation and interpretation of the groundwater chemistry of the area the following data was collected:

- Groundwater analyses of boreholes and wells by the Leicester University and University of Nairobi 1996
- Groundwater analyses of wells and boreholes in the Nukuru district from the Ministry of Land Reclamation, Regional and Water Development - Water Resources Division Nairobi 1943 - 1995
- Groundwater analyses of shallow and deep wells by the Ministry of Energy, Nairobi Kenya and the UK government 1990
- Climatic and Hydrology data compiled by the Water Resources Assessment Project
- Borehole Records from the Nukuru district Water department
- Geological Map with scale 1: 100 000
- Topographical map with scale 1: 50 000
- Aerial Photographs with scale 1: 50 000 and 1: 12 500
- Landsat image (photographic print) : bands 1 - 7 taken January 21, 1996

## **1.7 METHODOLOGY**

### **1.7.1 FIELDWORK**

Fifty six (56) groundwater samples and six (6) lakeshore samples were taken from boreholes and wells in the area between October 3 -27, 1997. The samples were analyzed using portable water quality testing equipment (Reflectolab and a Spectrometer) during the period. Analysis was done for total hardness, alkalinity, sulfates, nitrates, phosphates, ammonium and chlorides. Electrical conductivity, pH and temperature were measured in situ. Water levels measurements were taken , a few lake water samples were analyzed and borehole depths acquired were possible.

### **1.7.2 DATA ANALYSIS**

Figure 1.2 shows the steps undertaken in this assessment. Rock deduction analysis was done using the inorganic water quality evaluation analysis program WATERVAL 8.10L. Hydrochemical groupings were made using Piper diagrams, stiff diagram and radial diagrams generated in PLOTCHER 7.4 and HydroWIN 3.0. Statistical analysis was done on the data set using the statistical package SPSS 6.1. Mapping of water quality parameters and variogram analysis was done using the Geostatistical software GEOEAS 1.0. 2D-Groundwater flow was simulated in the program FLOWNET. ILWIS 1.4 and 2.1 were the GIS packages used.

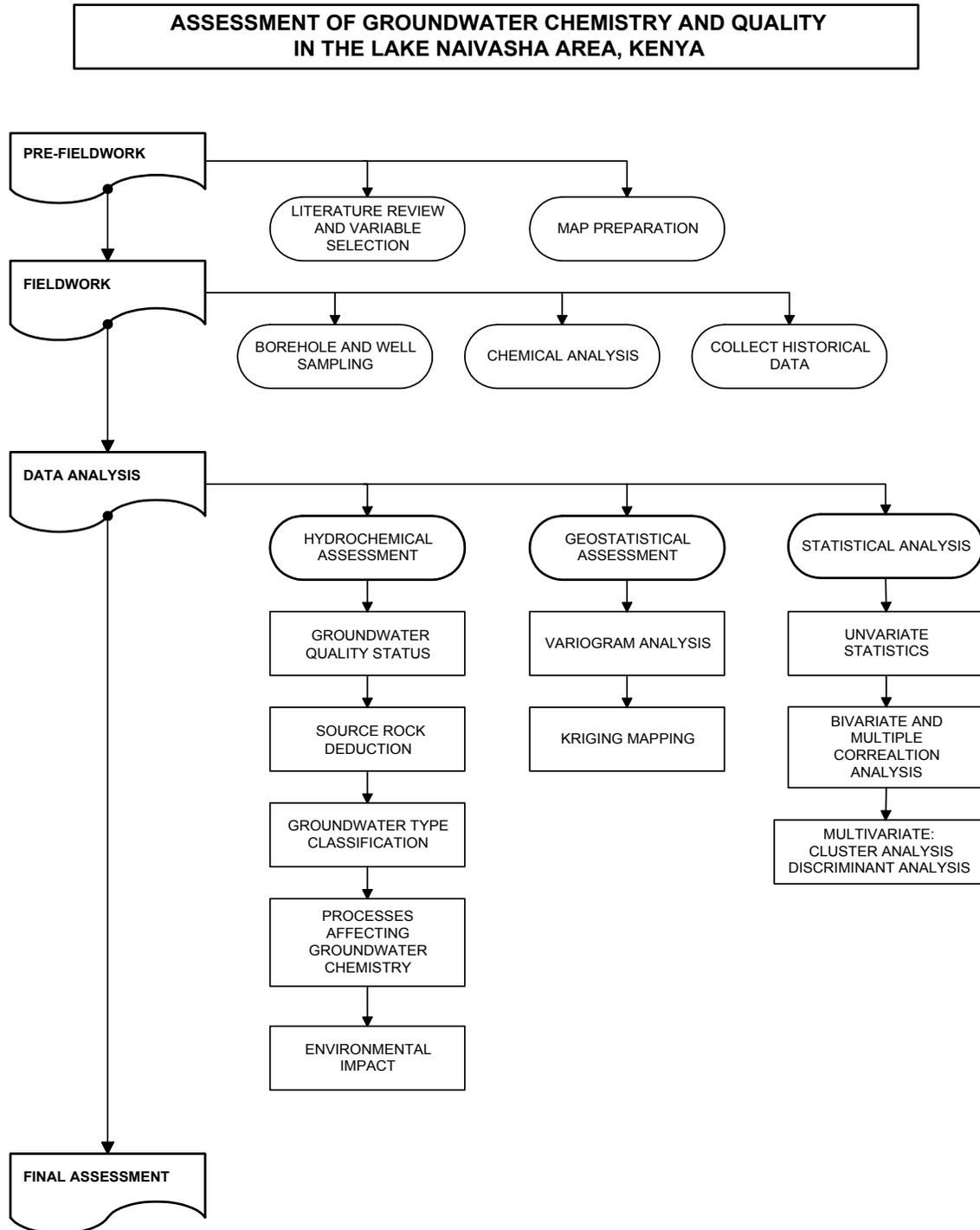


Figure 1.2: Flow Chart of Groundwater Chemistry and Quality Assessment

## CHAPTER 2

### GEOLOGY AND WATER RESOURCES

#### 2.1 GEOLOGY

Rocks and structures in the area are associated with four major episodes of volcanic activity and faulting during the last 4 million years. Table 2.1 summarizes the major volcanic and deformation episodes of the area.

Table 2.1: Major volcanic and deformation episodes (adapted from Clarke et al. 1990)

<i>Volcanic episode</i>	<i>Activity</i>	<i>Units</i>	<i>Age Range</i>
<i>V4</i>	<i>Late Quaternary to recent Salic Volcanoes</i>	<i>Longonot, Eburru, Olkaria, Elementita, Ndabibi and Akira Volcanic groups, Fluvio and Lacustrine sediments</i>	<i>0.4 - 0 Ma</i>
<i>D4</i>	<i>Extensive minor faulting of rift floor</i>		<i>0.8 - 0.4 Ma</i>
<i>V3</i>	<i>Quaternary flood lavas of rift floor</i>	<i>Gilgil Trachyte, Kijabe Hill Formations</i>	<i>1.65 - 0.9 Ma</i>
<i>D3</i>	<i>Renewed faulting of Rift margins</i>		<i>1.7 Ma</i>
<i>V2</i>	<i>Early Quaternary flood trachytes</i>	<i>Limuru Trachyte, Karati Basalt Formations</i>	<i>2.0 - 1.8 Ma</i>
<i>D2</i>	<i>Formation of step faults (narrowing of graben)</i>		<i>3 - 2 Ma</i>
<i>V1</i>	<i>Pliocene volcanic ash flows</i>	<i>Kinangop tuff and Mau tuff Formations</i>	<i>3.7 - 3.4 Ma</i>
<i>D1</i>	<i>Major faulting of Eastern rift margin</i>		<i>4 - 3 Ma</i>

V = Volcanic activity D = Faulting activity

#### 2.1.1 LITHOLOGIC UNITS

The major units of the study area are: a) Kinangop tuff b) Mixed Akira pumice and Longonot ash c) Lacustrine sediments d) Alluvial deposits (See Figure 2).

**Kinangop tuffs (Tk):** This unit forms the eastern rift margin, is between 3.4-4.5 Ma BP and comprised of ignimbrites: mostly welded tuffs and palaeosols. Maximum thickness of this unit is reported at 150 m. The underlying unit is uncertain but it is overlain by Limuru and Gilgil trachytes.

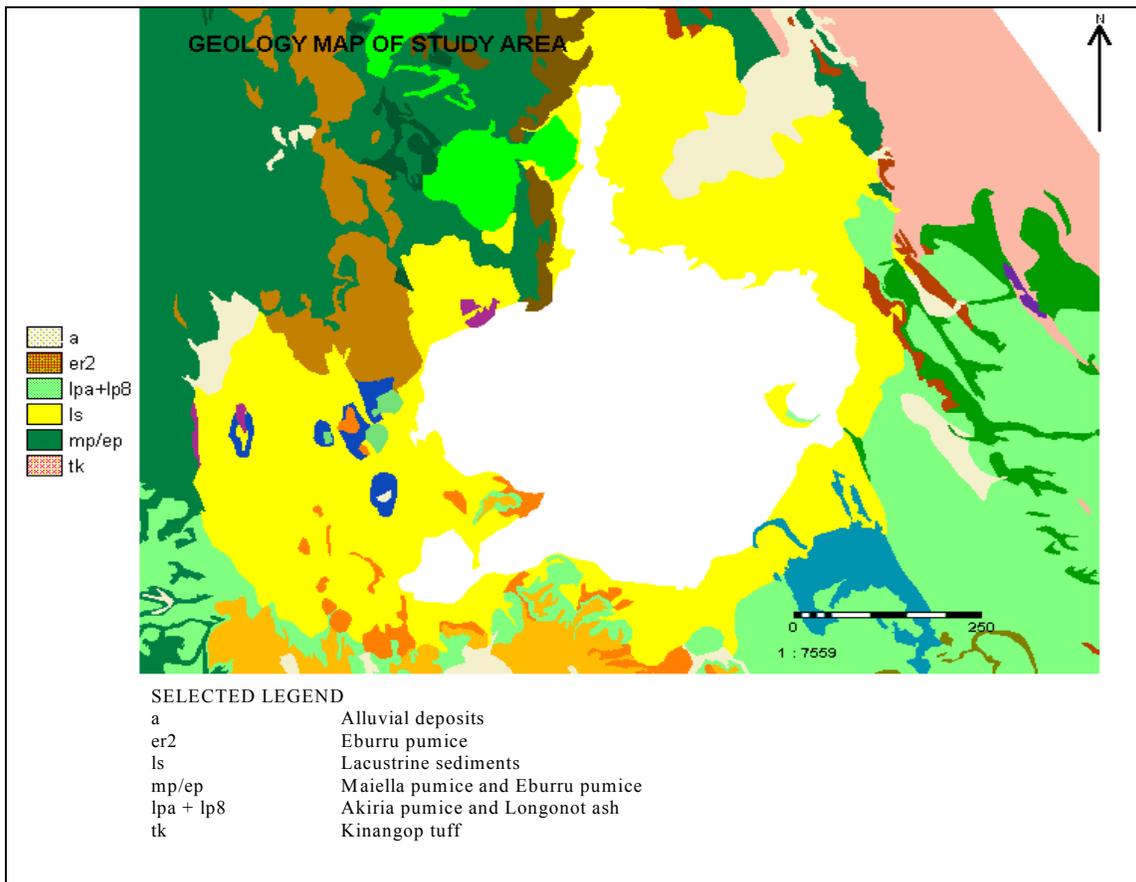
**Mixed Akiria pumice (Lpa) and Longonot ash (Lp8):** This unit is in the south east of the study area, 3280 +/- 120 years BP and contains mainly pumice lapilli and blocks as well as bedded ash. It was formed from magmatic and phreatic -magmatic eruptions. It is possibly underlain by lower trachytes or older pumice or older bedded ash and overlain by upper trachyte members and upper mixed lava.

**Lake Sediments (Ls):** This unit houses the Lakes of the study area and hence form more than 70% of the area. The unit is composed of pumacious granule with gray colored pebble gravel, coarse sand, gravely sand, silt and clay. The unit has a reported maximum

thickness of >15 m and formed from the reworking of pyroclastics deposited in small lakes. The sediments are underlain by Akiria basalts, Eburru pantellerites and , Kedong Valley tuffs. Where the sediments are not exposed they are possibly overlain by ash and pumice from the Longonot volcano complex.

**Alluvial deposits (A):** This unit is mainly associated with the Malewa river and is comprised of silt, fine sand, some ferruginous coarse sand and occasionally boulder gravel. Deposits are found in the gully floor and basin and interbedded with lake sediments.

Figure 2: Geology Map of the study area



Source: Government of Kenya, Ministry of Energy 1988

### 2.1.2 PETROLOGY

The main volcanic deposits and rocks in the area such as trachytes, rhyolites, basalts and pyroclastics control the chemistry of the groundwater (Thompson et al. 1958).

**Trachytes** are found in most parts of the Naivasha area in particular the Kinangop escarpment east of the lake, it is composed mainly of potash feldspar and sodic amphibolites. Young lava, ash and tuffs are trachyte deposits. **Rhyolites** are found as

pumice and obsidian veins in the south west and west of the study area. They are composed of quartz and feldspars with amphiboles and magnetite. **Basalts** are found as lava flows and agglomerates in the area. They are composed of mainly plagioclase and augites. **Pyroclastics** are found as ash fall deposits and tuffs and make up a considerable portion of the volcanics in the Naivasha area. **Lake sediments** are made up of the reworked remnants of the above rock types. (See further discussion in Chapter 3 and Figure 4.3)

## 2.2 WATER RESOURCES

### 2.2.1 RAINFALL

The Lake Naivasha area is influenced by the Equatorial Monsoon climate hence there are two rainy periods characterizing the precipitation of the lake and its environs, April/May and October/November. Average rainfall of the lake area is 608 mm/year for the period 1931 - 1960 (Lars-Erik , 1986). This rainfall varies between 443 - 939 mm/year.

A 10 year data series of rainfall for the Naivasha water supply rainfall station indicate a total mean rainfall of 759.59 mm/year for the period 1985 - 1996. While the Naivasha District Office station indicated a total mean rainfall of 664 mm/yr. between 1960 and 1985 (calculated by L. Huaccho - MSc study 1997). The lake area is a relatively low rainfall area compared to the neighboring rift escarpments where rainfall is higher, ranging between 1250 - 1500 mm/year (Clarke et al. 1990).

### 2.2.2 EVAPOTRANSPIRATION

Relative humidity is low throughout the rift valley. It is 75% at Naivasha (Clarke et al. 1990) hence the potential evaporation of 1600 - 1800 mm/year exceed rainfalls (Summary in Table 2.2). Mean monthly potential evaporation at Naivasha exceeds rainfall by a factor of 2-8 for every month except April when potential evaporation still exceeds rainfall except in the wettest years (Clarke et al. 1990).

Table 2.2: Rainfall and Evapotranspiration Conditions

<i>Variables</i>	<i>Wet conditions</i>	<i>Mean Conditions</i>	<i>Dry Conditions</i>
<i>Direct rainfall on the lake</i>	<i>939 mm</i>	<i>608 mm</i>	<i>442 mm</i>
<i>Open water evaporation</i>	<i>1529 mm</i>	<i>1529 mm</i>	<i>1743 mm</i>
<i>Evapotranspiration from swamp</i>	<i>2141 mm</i>	<i>2141 mm</i>	<i>2440 mm</i>

Source: LNROA 1996

### 2.2.3 RUNOFF

The Lake Naivasha catchment area is drained by the three major rivers. These are River Malewa and Gilgil which are perennial entering the lake from the north and river Karati which is at present seasonal entering the lake from the east.

River Malewa is the major contributor to the water budget of the lake. Its basin covers an area of 1553 km<sup>2</sup>. The average annual flow during the period 1932 - 1980 was  $153 * 10^6$  m<sup>3</sup>. River Gilgil drainage basin covers an area of 151 km<sup>2</sup> and recorded an annual average flow during the same period of  $24 * 10^6$  m<sup>3</sup> (Lars-Erik 1986).

#### **2.2.4 LAKE**

The Lake ecosystem consist of the Main lake, at present, a small separated lake Oloidien and a smaller Crater Lake Sonachi. The Main lake (water surface) is approximately 120 - 150 km<sup>2</sup> plus 12 - 18 km<sup>2</sup> of swamp. LNROA (1996) reported that the lake has a mean depth of 4.7 m with the deepest part at the Oloidien Bay (9 m) and around Crescent Island (17 m). In 1997 the mean depth of the main lake was calculated at 3.8 m (Donia Noha - MSc study 1997).

Lake levels fluctuate between 1880 - 1890 meters amsl (similar to that of groundwater levels around Lake Naivasha itself, [Clarke et al. 1990]). Crescent Island is the highest part of the lake displaying a crater/cone feature. Water inputs to the lake include rainfall over the lake, inflow from surrounding rivers, runoff and underground water from the catchment. Outputs include direct evapotranspiration, water abstraction and groundwater outflow. The total catchment of the lake is approximately 3200 km<sup>2</sup>.

#### **2.2.5 HYDROGEOLOGY**

The lake Naivasha sub-catchment is the most important of the Rift valley floor because of its fresh water status and its hydrothermal potential. It is most complex hydrogeologically due to the rift floor geometry and tectonics (Clarke et al. 1990) .

The main aquifer is the Lacustrine volcanic/ sedimentary series usually occurring as fractured or reworked volcanics, or along the weathered contacts between lithological units. Generally permeability of the rocks in the study area are low.

The floor of the rift valley is covered by young volcanic lake sediments which is a continuous unconfined aquifer with high permeability. It consist of reworked volcanic sediments and forms the major part of the Naivasha area. Estimated hydraulic conductivities averaged 10 m/d and a well yield on average of 3 l/s/m. However Clarke et. al. (1990) indicated from an inventory of boreholes in the lake sediments and volcanics, estimated permeability of 12 - 148 m/d from the NE to the NW of the lake. The lake sediment aquifer constitutes a perched aquifer (ITC-WRAP Phase V, 1996).

The fractured volcanic rocks are often confined or semi-confined with low storage coefficients (Stuttard et al., 1995). Tuffs on the east of the lake are reported to have conductivities of an average 0.8 m/d and the trachytes to the south east and in the west of the study area 1.1 m/d. Average well yield for the tuffs, basalts and trachyte is around 0.2 l/s/m.

Groundwater systems in the area are thought to be fault controlled (Clarke et al. 1990). In general, faults facilitate groundwater flow as high permeability channels in particular.

Along the rift axis, they create barriers to flow offsetting high permeability channels across the rift.

The Lake Naivasha catchment has an internal drainage system but no surface outlet. This is typical of Eastern Rift valley lakes where extensive volcanic activity disrupted the drainage system creating these shallow lakes (Yuretich, 1982). The underground water inflow and outflow (seepage) accounts for the lake fresh water status.

East of Lake Naivasha the groundwater contours rise indicating flow towards the lake, while the position of the lake; at a culmination of the Rift floor, suggests flow both to the north and to the south (Clarke et al. 1990). Stable isotope studies indicates that southerly outflow from Lake Naivasha occurs supplemented by lesser northerly outflow. The northerly flow is confined to the Eburru and Gilgil areas while the southerly flow is directed between Olkaria and Longonot.

Apart from seepage and rainfall, recharge to the Lake basin originates from the headwaters of the Gilgil river in the Bahati escarpment as well as from the head waters of the Malewa river in the Nyandarua range.

## CHAPTER 3

### HYDROCHEMICAL ASSESSMENT

#### 3.1 INTRODUCTION

The quality of groundwater reflects the mineralogical composition of the rocks with which the water has been in contact. As water moves slowly through the subsurface its composition gradually changes, reflecting the increasing saturation of some ions or the end products of various rock-weathering interactions. This chapter examines the general groundwater chemistry of the area, and the processes affecting the groundwater chemistry.

#### 3.2 DATA SETS

Four data sets were used to assess the hydrochemistry of the area:

1. Field work data consisting of 56 borehole and 6 lakeshore samples collected and analyzed during October 1997. This data set includes the major anions but not all cations hence the use of the data sets described below.
2. Leicester University and University of Nairobi data set of 62 borehole samples collected during April 1996. This data set includes analysis of some of the major cations and anions as well as minor elements ( $\text{SiO}_2$ ,  $\text{F}^-$ )
3. British Geological Survey and the Ministry of Energy Kenya data set of 13 (12 borehole and 1 lake) samples within this study area collected during 1990. This data set includes analysis of major cations and anions as well as of minor elements ( $\text{Si}$ ,  $\text{B}^-$ ,  $\text{F}^-$ )
4. Historical borehole data from the Ministry of Land Reclamation, Regional and Water Development - Water Resources Division - Kenya, collected and analyzed between 1956 -1994. This data set covers the major anions and cations but not for all data points. (See Appendix A-1 to A-6 for data analysis records)

##### 3.2.1 FIELD DATA

Water quality sampling and analysis for the following parameters were done during the field work period, 56 borehole and 6 lakeshore samples were analyzed for: Major ion concentrations: Total Hardness (Calcium  $\text{Ca}^{2+}$  and Magnesium  $\text{Mg}^{2+}$ ), Alkalinity (Carbonates  $\text{CO}_3^{2-}$  and Bicarbonates  $\text{HCO}_3^-$ ), Chlorides ( $\text{Cl}^-$ ), Sulphates ( $\text{SO}_4^{2-}$ ), Nitrates ( $\text{NO}_3^-$ ), Phosphates ( $\text{PO}_4^{3-}$ ). Physical elements: pH, EC and temperature were measured in situ. Where water level measurements were possible, samples were taken from water level depths of 1.7 - > 30.48 meters hence the analyses represents the shallow aquifer.

Owing to time constraints sampling was concentrated around the lake and borehole samples were taken, where possible perpendicular to the lake (the suspected groundwater flow direction). Tables 3.1 and 3.2 summarizes the present groundwater quality of the area.

Table 3.1: Groundwater Chemistry of Study Area 1997

Major ions analyzed Field work 1997	Range mg/l	WHO Guideline (for drinking water)
Cl <sup>-</sup>	0 - 220	250
SO <sub>4</sub> <sup>2-</sup>	0 - 150	400
HCO <sub>3</sub> <sup>-</sup>	97.62 - 153.15	
CO <sub>3</sub> <sup>-</sup>	0 - 126.02	
NO <sub>3</sub> <sup>-</sup>	0 - 46	45
PO <sub>4</sub> <sup>3-</sup>	0 - 10.1	
Hardness	30.03 - 500.5	500
NH <sub>4</sub> <sup>+</sup>	0 - 15	
EC	110 - 2600	
pH	6 - 8.5	6.5 - 8.5

Table 3.2: Groundwater Chemistry of Study area 1996

Major ions analyzed Liecester University	Range mg/l	WHO Guideline (for drinking water)
Mg <sup>2+</sup>	8 - 223	
Ca <sup>2+</sup>	4 - 121	
NH <sub>4</sub> <sup>+</sup>	0 - 4	
Fe(total)	0 - 6.72	0.3
Cl <sup>-</sup>	4 - 120	250
SO <sub>4</sub> <sup>2-</sup>	0 - 100	400
HCO <sub>3</sub> <sup>-</sup>	123 - 1108	
CO <sub>3</sub> <sup>-</sup>	0 - 0	45
NO <sub>3</sub> <sup>-</sup>	0 - 17.2	
P(soluble)	0.02 - 2	
Hardness	12-344	500
F <sup>-</sup>	0.3 - 72	1.5
SiO <sub>2</sub>	25 - 138	
EC	323 - 2204	
pH	6.05 - 8.05	6.5 - 8.5

Except for the NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> and Fe (total) concentrations, all other parameters are below or within the World Health Organization (WHO) 1971 guideline set for drinking water. Owing to the very high F<sup>-</sup> levels the groundwater quality for drinking water is poor (See section 3.4.1).

### 3.3 SOURCE ROCK DEDUCTIONS AND ANALYSIS

The purpose of the technique is to gain insight into the possible origins of water. It is useful for analytical checks or as an investigative procedure if the origin of water is not known. In this case the technique confirms the geology and petrology of the area discussed in Chapter 2. The Steps included in the deductions are adopted from Hounslow (1995) and were simulated in the computer program WATERVAL. *The responses in bold italic represent the deductions for the area.*

**Step 1.**  $6 < \text{pH} > 5$  cannot be interpreted with this method because clay minerals dissolve and release anomalously high silica. For our data with a pH ranging between 6.5-8.5, the technique was suitable.

**Step 2.** The concentrations of elements must be converted from mg/l to meq/l for comparing all parameters (This was done by the program).

### Step 3. Anion- Cation Balance

The accuracy of water samples can be checked by assessing the electroneutrality of the analyses. The sum of cations and anions should be equal. The charged balance is expressed as:  $(\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions}) * 100$ . However because no individual cations were analyzed during the field work period all samples were not balanced and hence had an error of >5% (the accepted minimum).

The analysis for data sets 2 and 3 were not all balanced but were better than data set 1 for the rock deduction exercise and both sets gave similar results. The shorter set ( set 1 with 13 samples) though not enough points, had a complete chemical analysis and hence selected for hydrochemical analysis of the area.

### Source rock deductions using simple comparisons

#### Step 4. Sodium and Chloride

Relating sodium ( $\text{Na}^+$ ) with chloride (assuming that chloride is from rainfall or dissolution of halite) gives an indication of the source of sodium.

- a)  $\text{Na}^+ = \text{Cl}^-$  indicates halite dissolution
- b)  $\text{Na}^+ < \text{Cl}^-$  indicates reverse softening (brine or seawater)
- c)  $\text{Na}^+ > \text{Cl}^-$  **indicates a  $\text{Na}^+$  source other than halite eg. albite(plagioclase) or natural softening.**

In this case albite is the source of  $\text{Na}^+$

#### Step 5. Calcium and Sulphate

$\text{Ca}^{2+} = \text{SO}_4^{2-}$  indicates gypsum

$\text{Ca}^{2+} < \text{SO}_4^{2-}$  indicates pyrite oxidation, or  $\text{Ca}^{2+}$  removal eg. calcite precipitation or natural softening

**$\text{Ca}^{2+} > \text{SO}_4^{2-}$  indicates a  $\text{Ca}^{2+}$  source other than gypsum, eg. calcite/dolomite/silicates**

In this case silicate is the source of  $\text{Ca}^{2+}$

#### Step 6. Bicarbonate and Silica

This comparison is used to distinguish carbonate weathering from silicate weathering. Bicarbonates are formed from acid hydrolysis when carbon dioxide reacts with various minerals. Silicate is present in water when albite (plagioclase) is weathered, bicarbonates are dissolved and silica released (Yuretich, 1982).

- a) **bicarbonate/ silica < 5**                      **silicate weathering**
- b) **bicarbonate/ silica >10**                **carbonate weathering**
- c) bicarbonate >> silica                      carbonate weathering

**NB: a>>b** (values between < 5 and 12). This is due to the presence of magnesium which is also produced from the weathering of volcanic rocks which when combined with calcium results in  $Mg^{2+}/Ca^{2+}$  ratios that produces carbonates similar to type of  $CaCO_3$  deposited in sediments.

### Step 7. Silica and Nonhalite Sodium

Comparing silica with nonhalite sodium indicates cation exchange, granitic or basaltic weathering.

a)  $SiO_2 < (Na^+ + K^+ - Cl^-)$  then cation exchange is likely the source of excess sodium and calcium is probably less than sulphate if carbonates are present.

***b)  $SiO_2 < (Na^+ + K^+ - Cl^-)$  and  $< 2 * (Na^+ + K^+ - Cl^-)$  then albite (plagioclase) weathering is likely, giving kaolinite or monmorillonite as the product, hence granitic weathering.***

***c)  $SiO_2 > 2 * (Na^+ + K^+ - Cl^-)$ , then the rocks subjected to weathering contain considerable amounts of ferromagnesium minerals, hence basaltic weathering.***

(K<sup>+</sup> = potassium)

**NB: b>>c** (pure clays are not present in the area, however, if present kaolinite would be the most likely. Basalt rocks are present in the area also)

### Source-rock Deduction Summary of reasoning using ratios

Table 3.3 below list another approach to studying the hydrochemistry of the groundwater in the area. (*Statements in **italic** correspond to deductions for the area.*)

Table 3.3: Source-rock deductions using ratios (adopted from A.W. Hounslow 1995)

Parameter	Value (meq/l)	Conclusion
$SiO_2$ (mmol/l)	> 0.5	<i>Volcanic glass or hydrothermal water possible</i>
$HCO_3^- / SiO_2$	> 10 > 5 and <10 < 5	Carbonate weathering Ambiguous <b><i>Silicate weathering</i></b>
$SiO_2 / Na^+ + K^+ - Cl^-$	< 1 > 1 and <2 > 2	<i>Cation exchange</i> <sup>1</sup> <b><i>Albite weathering</i></b> Ferromagnesian minerals
$Na^+ + K^+ - Cl^- / Na^+ + K^+ - Cl^- + Ca^+$	> 0.2 and 0.8 < 0.2 or 0.8	<b><i>Plagioclase weathering possible</i></b> Plagioclase weathering unlikely
$Na^+ / Na^+ + Cl^-$	> 0.5 = 0 < 0.5 TDS >500 < 0.5 TDS <500 > 50 < 0.5 TDS < 50	<b><i>Sodium source other than halite- albite, ion exchange</i></b> Halite solution Reverse softening, seawater Analysis error Rainwater
$Mg^{2+} / Ca^{2+} + Mg^{2+}$	$HCO_3^- / SiO_2 > 10$  = 0.5 < 0.5 > 0.5  <b><i>HCO<sub>3</sub><sup>-</sup> / SiO<sub>2</sub> &lt; 5</i></b>	Carbonate Weathering  Dolomite weathering Limestone-dolomite weathering Dolomite dissolution, calcite precipitation, or seawater  <b><i>Silicate Weathering</i></b>
$Mg^{2+} / Ca^{2+} + Mg^{2+}$	> 0.5 < 0.5	Ferromagnesian minerals <b><i>Granite weathering</i></b>
$Ca^{2+} / Ca^{2+} + SO_4^{2-}$	= 0.5 < 0.5 pH < 5.5 < 0.5 neutral	Gypsum dissolution Pyrite oxidation Calcium removal-ion exchange or calcite precipitation

	> 0.5	<i>Calcium source other than gypsum-carbonates or silicates</i>
Ca <sup>2+</sup> + Mg <sup>2+</sup> / SO <sub>4</sub> <sup>2-</sup>	> 0.8 and < 1.2	Dedolomitization
TDS	> 500 < 500	<i>Carbonate weathering or brine or seawater</i> <sup>2</sup> <i>Silicate weathering</i>
Cl <sup>-</sup> / sum anions	> 0.8 TDS > 500 > 0.8 TDS < 100 < 0.8	Seawater, or brine or evaporites Rainwater <i>Rock weathering</i>
HCO <sub>3</sub> <sup>-</sup> / sum anions	> 0.8 < 0.8 sulphate high < 0.8 sulphate low	<i>Silicate or carbonate weathering</i> Gypsum dissolution Seawater or brine
Langelier index <sup>3</sup>	<i>Positive</i> 0 <i>Negative</i>	<i>Oversaturated with respect to calcite (54 %)</i> <i>Saturated/ near saturated with respect to calcite (15 %)</i> <i>Undersaturated with respect to calcite (31 %)</i>
<b>Conclusion</b>	<i>Aquifer mineralogy</i>  <i>Reactions</i>	<i>Rhyolitic composition suggested; high silica suggest volcanic origin</i>  <i>Some ion exchange</i>

<sup>1</sup> Cation exchange is occurring within the clay products

<sup>2</sup> See Step 6 above

<sup>3</sup> Ca<sup>2+</sup> is a product of albite weathering and the dissolution of Fluorite (CaF<sub>2</sub>). Oversaturation (predominantly) and Near saturation occurs when calcite is precipitated by the replacement of Na<sup>+</sup> (cation exchange) or as a function of temperature where high temperatures reduce (geothermal) the solubility of calcite.

### 3.3.1 CONCLUSION OF SOURCE ROCK DEDUCTION

The program suggested granitic type weathering because of the high Na<sup>2+</sup> and low Mg<sup>2+</sup> concentrations, but there are no granites in the area. From mineralogical classification of igneous rocks (Reeves et al. 1996), rhyolite and granite have the same mineral composition (quartz, potassium feldspar, sodium rich plagioclase feldspar, biotite, hornblende). Their texture and formation are different. Rhyolite is the volcanic equivalent of granite, hence the WATERVAL program indicated “granitic type” weathering.

Volcanic mineralogy is reflected in the groundwater. The rhyolitic composition indicated reflects the composition of the comendites and pantellerites which form the pumice and trachytes in the area (discussed in Chapter 2).

A study on Lake developments in the Eastern Rift Valley (Kenya-Ethiopia) by Yuretich (1982) confirm the above deductions. In general volcanism has an effect on the water composition on the study area. Weathering of these rocks produce runoff waters rich in Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>, and smectite clays are common. Lake waters of the Eastern Rift valley are Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> type (Cl<sup>-</sup> type not seen in the area). There is a significantly large percentage of dissolved SiO<sub>2</sub>. The composition and abundance in the area of plagioclase as well as sodic amphiboles is considered the primary influence on Na<sup>+</sup> and Ca<sup>2+</sup>. The volcanic rocks of the Eastern Rift Valley are predominantly alkaline varieties.

Lakes that are located in areas other than regional downwarps such as on the flanks or crest of the dome structure like Lake Naivasha possess more organic rich sediments. These are finely laminated and composed of sapropal-diatom alternations with little clay minerals. This accounts for the frequent outcrops of diatom deposits around the lake and along the highway to Nukuru as well as the presence of sandy material in the area.

### 3.4 ROCK WEATHERING (F<sup>-</sup> AND SiO<sub>2</sub>)

Fluoride and silica are considered minor elements when water chemistry is being examined but are very significant in the study area. They are the result of the weathering of silicates and fluoride bearing micas and amphiboles in the area. The study of the solubility of minerals gives an insight into the occurrence of these minor elements in groundwater. The Leicester University data set will be used for this study as F<sup>-</sup> and SiO<sub>2</sub> were not analyzed during the field work period due to the unavailability of the F<sup>-</sup> test and the unsuitability of the SiO<sub>2</sub> test.

#### 3.4.1 FLUORIDE (F<sup>-</sup>)

The element F<sup>-</sup> comes from the dissociation reaction of fluorite or CaF<sub>2</sub> (Appelo et al. 1996):



The WHO standard for F<sup>-</sup> in drinking water is 1.5 mg/l being the highest admissible concentration. Most sample points exceeded the limit and F<sup>-</sup> ranged between 0.5 - 72 mg/l. F<sup>-</sup> was highest around Oloidien Lake (13.3 - 72 mg/l) where more alkaline conditions exist and where evaporation is the main source of water loss in the area. The lowest concentrations were in the NE and NW in the swamp areas (0.5 - 1.4 mg/l). Except for the SW area of the map, generally there was a decrease of F<sup>-</sup> levels towards the lake. This may be due to the dilution effect of the river, mixing by groundwater from the NE and NW or a representation of lake water (See Figure 3.1).

According to Hounslow (1995), F<sup>-</sup> in natural waters may originate from the solution of fluorite, apatite or fluoride bearing micas and amphiboles. The common sink for F<sup>-</sup> is the adsorption by kaolinite (anion exchange reaction). Adsorption is greatest at pH 6 and negligible below pH 4. Above pH 7.5 desorption occurs. High fluoride concentrations coupled with alkaline pH conditions can also be attributed to fluoride desorption from kaolinitic clay types (communication from Mannaerts, 1998 WRS Division-ITC). This results in alkaline waters which are rich in F<sup>-</sup> accounting for the high F<sup>-</sup> concentrations around the alkaline lake Oloidien. Fresh water contains less than 1 mg/l F<sup>-</sup> which explains the low values near the lake edge. It is also possible that F<sup>-</sup> rich waters may be flushed from the western escarpment and accumulate in the SW of the study area accounting for the very high F<sup>-</sup> values.

Fluoride minerals have usually a low solubility, however thermal waters with high pH levels result in high F<sup>-</sup> concentrations. The areas around the Oloidien lake can be considered to be saturated with F<sup>-</sup> or F<sup>-</sup> has reached its equilibrium making groundwater supersaturated with respect to F<sup>-</sup> (Hem, 1989). The cation-anion activity plot in Figure 3.2 indicates the saturation state of fluorite (at a constant temperature of 25° C). The hyperbolic graph shows that most samples are plotted above the curve hence oversaturated with respect to F<sup>-</sup> (Figure 3.2 may be used to represent the saturation of F<sup>-</sup> bearing micas and amphiboles). Groundwater with a high natural Ca<sup>2+</sup> concentration generally will contain less F<sup>-</sup> than groundwater with a low Ca<sup>2+</sup> concentration (Appelo,

1996). For this data set  $\text{Ca}^{2+}$  concentration was low and samples were undersaturated with respect to calcite. This supports the idea of super-saturation of  $\text{F}^-$  in the study area.

Concentrations above 3 mg/l causes dental fluorosis (tooth mottling) evident among the local people and more seriously skeletal fluorosis (bone deformation and painful brittle joints in old people) (Appelo et al. 1996).

$\text{F}^-$  is common in the Rift Valley areas of Africa and areas of Asia. It results from the leaching of volcanic rocks common in Naivasha.

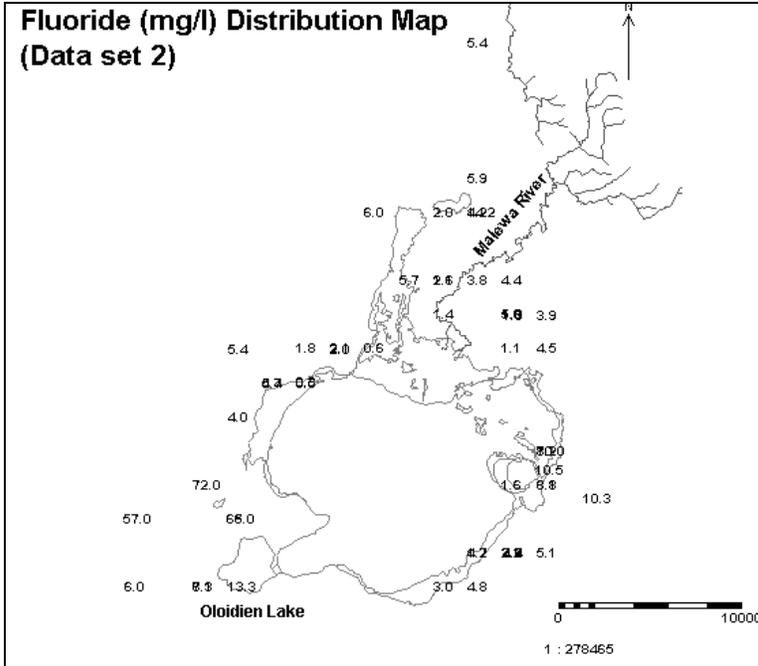


Figure 3.1: Fluoride Distribution map

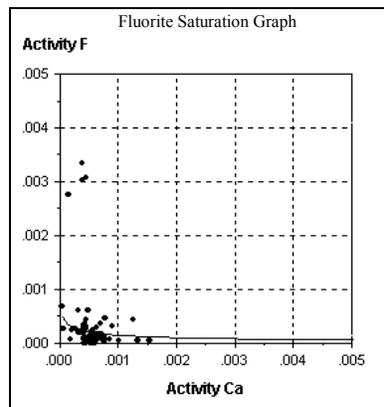


Figure 3.2: Saturation curve of Fluorite

### 3.4.2 SILICA (SiO<sub>2</sub>)

Silicate weathering results in the addition of silica and cations in water chemistry. High silica content in groundwater indicates active degradation of silicate minerals. High concentrations are found in volcanic rocks particularly rhyolite and basalt. An increase in cations also increases the bicarbonate concentration.

The main weathering product of silicate weathering are clays, however clay minerals from the area are purely crystalline (poor structure). Allophane clays; a product of the weathering of volcanic ash (Bear, 1969), is rarely present in the area. Smectite clays are present and the weathering of plagioclase feldspar is common (communication with Siderius 1998 - Soil Division, ITC). [see also Table 3.3 and section 3.3.1]

The silica levels were high and varying in the area also because of the varying distribution of sodic rocks. Each rock type has a different percentage of silica (see Table 3.4) which is reflected in the groundwater. Clarke et al. (1990) suggested that in the Naivasha area waters are oversaturated with respect to SiO<sub>2</sub>. Figure 3.3 suggest that high silica groundwater is being flushed from the north towards the lake.

Table 3.4: Silica percentage of volcanic rocks in Naivasha area

<i>Rock Type</i>	<i>SiO<sub>2</sub> %</i>
<i>Lava</i>	<i>40.70</i>
<i>Trachyte</i>	<i>60.74</i>
<i>Rhyolite</i>	<i>75.55</i>
<i>Comendite</i>	<i>73.30</i>
<i>Pumice</i>	<i>67-70</i>
<i>Obsidian</i>	<i>70.36</i>

Source: Compiled from Thompson et al. (1958)

SiO<sub>2</sub> ranged between 40 - 129 mg/l. SiO<sub>2</sub> was generally high. The highest values were in the north (98 - 129 mg/l) where deeper wells (> 17 m) are found. Lower values were present around the lake shore (40 - 98 mg/l). The sample locations in the north are wells and boreholes which are within the pumice with a high silica percentage. Low SiO<sub>2</sub> values also reflect lake water influence. Generally there was a decrease of silica values towards the lake. This may be due to dilution from groundwater flow towards the lake, a reflection of lake-groundwater characteristics, or low silica content in the reworked sediments.

The rock deduction exercise indicated volcanic glass or hydrothermal water possible for SiO<sub>2</sub> ratios. This was confirmed by the abundant obsidian fragments and veins in the area. Less of the glass was evident in the north but samples from depths of > 17 m are exposed to higher temperatures. Two boreholes sampled in N and NW of the study area (1997) had temperatures of greater than 30 ° C suggesting deep circulating water subjected to high temperatures.

$\text{SiO}_2$  content in hydrothermal waters is higher than that in low temperature waters, this leads to silica geothermometers. Fluoride in geothermal waters are commonly in the range of 1-10 mg/l [ Hounslow, 1995] The range in this data set is 13.3 - 72 mg/l. The saturation index (SI) of quartz was positive hence the samples were oversaturated with respect to silica. According to Hounslow, the solubility of quartz can indicate formation temperatures (geothermometers). Samples with concentrations between 46 - 126 mg/l indicate formation temperatures between 100 - 150 ° C. The  $\text{SiO}_2$  concentration of most of the samples correspond to this formation temperature range. Samples > 126 mg/l  $\text{SiO}_2$  therefore have formation temperatures > 150° C.

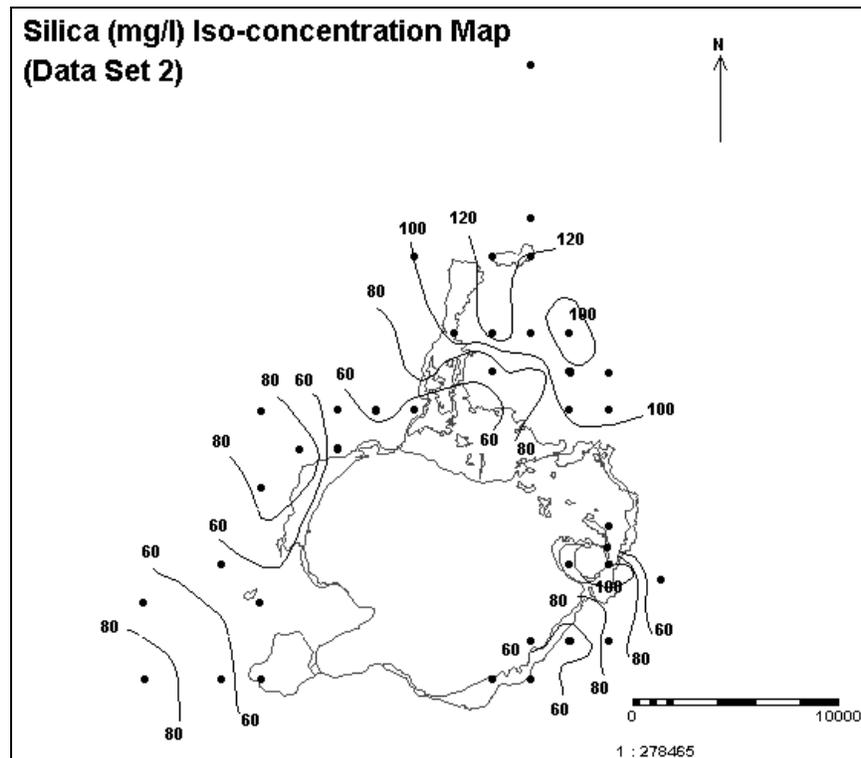


Figure 3.3: Silica Iso-concentration map

### 3.5 EC VS. TDS RELATIONSHIP

Electrical conductivity (EC) is a measure of the ability of water to conduct an electrical current. It is sensitive to variations in dissolved solids as well as temperature changes and is measured in  $\mu\text{S}/\text{cm}$ . EC was measured in the field (in situ) with a EC meter. TDS, total dissolved solids refer to the dissolved matter content of water and is calculated by adding the mass of ions plus  $\text{SiO}_2$ .

EC is a good estimator of TDS (as it was not analyzed in the field) and can be estimated by multiplying EC by a factor of 0.55 - 0.76 (Hounslow, 1995). As seen in Figure 3.5, TDS can be obtained by multiplying EC by a factor of 0.62 for data set 4 (Ministry of

Land Reclamation, Regional and Water Development - Water Resources Division - Kenya). EC has a high correlation with TDS ( $r^2 = 0.95$ ). TDS is a crude indicator of rock weathering, whether silicate weathering (TDS < 500 mg/l) or carbonate weathering (TDS > 500 mg/l).

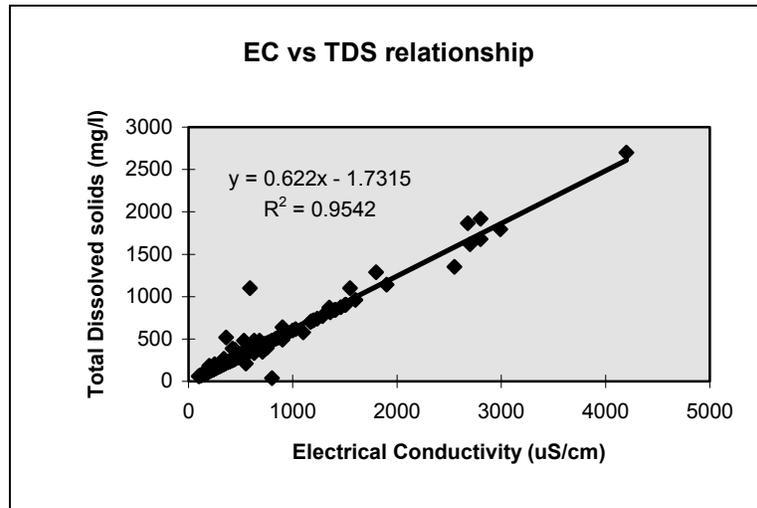


Figure 3.4: EC vs. Total dissolved solids relationship for datasets

With the above EC - TDS relationship, TDS was calculated from the linear equation of data set 4 for data set 1 (Field work). 60.71 % of the calculated TDS values were below 500 mg/l, this means that silicate weathering is the dominant weathering process. Owing to the fact that silicate weathering releases  $\text{HCO}_3^-$  the remaining 39.29 % indicating carbonate weathering, may be a result of this.

TDS also gives an indication of the mineralization level in water (Mannaerts, 1993). For this data set the calculated TDS indicated that most of the groundwater has a low level of mineralization. Low mineralization, high silica content, coupled with groundwater flow predominantly through fissures indicates a short residence time for groundwater in the area (Hem, 1989).

[Outliers on Figure 3.4 are most likely to be errors, as the correlation is very high]

### 3.6 DISPLAY OF WATER QUALITY DATA (PIPER, STIFF AND RADIAL DIAGRAMS) PIPER TRILINEAR DIAGRAMS

Piper trilinear diagrams are combinations of anion and cation triangles that lie on a common baseline. The positions of analyses plotted on the piper diagram in meq/l is used to make conclusions as to the origin of water. Piper diagrams derive the following conclusions: 1. water type, 2. precipitation or solution, 3. mixing and 4. ion exchange.

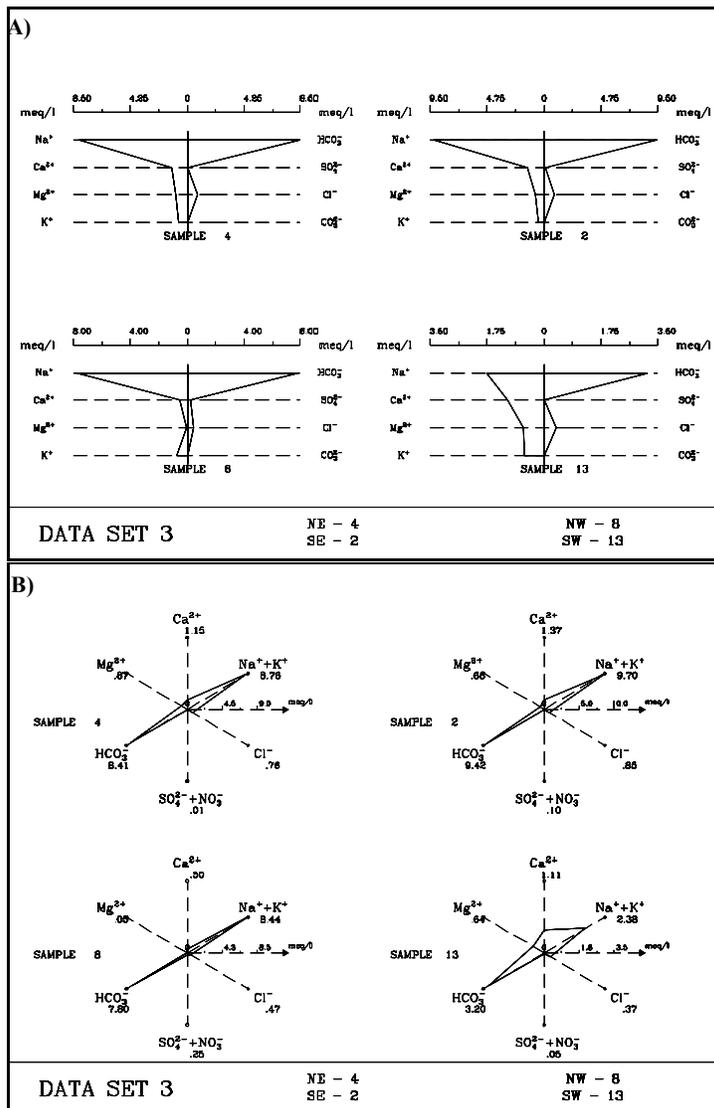


Figure 3.6 A-B, show the typical water type using stiff diagrams and radial diagrams for different directions around the lake. Both plots indicate a sodium bicarbonate type water. The shape of these plots are generally the same suggesting that there is no change in the ionic composition of groundwater around Lake Naivasha. When the plots were generated in the WATERVAL program the general shape of the plot indicated a rhyolite rock type.

This data set (set 3) also included a lake water sample and it plotted on all three graphs in the same area as the groundwater samples suggesting that the lake may have the same water type as the groundwater.

The dominant  $\text{NaHCO}_3^-$  type water indicates that ion exchange and rock dissolution processes influence the groundwater chemistry of the area. This was confirmed by the source-rock deduction analysis revealing silicate weathering (see Section 3.3).

Figure 3.6 A-B: Stiff and Radial Diagrams of groundwater in the study area



### **3.7 PROCESSES AFFECTING WATER CHEMISTRY**

According to Appelo et al. (1996) evapotranspiration and groundwater flow are two of the many processes affecting water quality (rock weathering was identified above). These processes were reflected in the study area with EC and  $\text{Cl}^-$  distributions, as well as the presence of fresh and alkaline water lakes.

#### **3.7.1 ELECTRICAL CONDUCTIVITY**

From data set 1 (Field work) EC was generally low in the north and northwest (320 - 700  $\mu\text{S}/\text{cm}$ ). In the southwest of the lake EC was high (800 - 1560  $\mu\text{S}/\text{cm}$ ) while in the east EC decreased towards the lake. In the south of the lake EC was between 500 - 1230  $\mu\text{S}/\text{cm}$ . There was an increase in EC in the northeast towards the lake (420 - 1560  $\mu\text{S}/\text{cm}$ ) [See Figure 3.7]. EC distribution of the other sets of data showed the same pattern as was observed in the field.

The distribution of EC in the area may be related to several processes:

1. Buildup of salts from evapotranspiration. This is likely to have caused high EC in the Naivasha town area, along the southern border of the lake, as well as in the Crater lake - Oloidien lake areas.

Potential evapotranspiration as discussed in Chapter 2 section 2.2.2 exceeds rainfall by twofold. Evaporation would result in water being more concentrated with salts and hence, high EC values in shallow groundwater areas. High chloride values around the lake edge, around Crescent island and at Crater lake and Oloidien lake also support the reasoning of evaporation leaving salts behind (discussed below).

2. Mixing (lake and river water). Low EC values along the Malewa river, at the head of Karati river, and along the lake edge may have resulted from the mixing of groundwater with river and lake water respectively, pointing to a groundwater-lake water-river water interaction.
3. Flow system. The increase in EC towards the lake may be an indication of the upwelling of deep groundwater flow. Low EC generally indicates younger water while high EC suggest old water that has traveled through the aquifer. As indicated from the cross section profile in Figure 3.8, (See Appendix B for FLOWNET model parameters) it is possible that old water could be flowing towards the lake and hence the increase of EC towards the lake. This is not supported by other chemical parameters and less likely to contribute towards this increase.
4. Groundwater flow. Along with increases of EC towards the lake, EC increased from the lake shore toward the southeast from Crescent Island in the three data set suggesting here that there may be seepage out of the lake. EC may be following the suspected pattern of groundwater flow. [This is the basis for another MSc study and will not be further discussed].



### 3.7.2 CHLORIDE

Whereas there was a similar pattern in the chemistry of most parameters, there was a marked difference between  $\text{Cl}^-$  sampled in April 1996 and October 1997.  $\text{Cl}^-$  was high ( $> 100 \text{ mg/l}$ ) around Crescent Island in 1996 but  $< 50 \text{ mg/l}$  in 1997.  $\text{Cl}^-$  was low around Crater Lake in 1996 ( $< 30 \text{ mg/l}$ ) and high in 1997 ( $200 \text{ mg/l}$ ). See Figures 3.9 and 3.10.

The main source of  $\text{Cl}^-$  is from precipitation as there are no  $\text{Cl}^-$  bearing rocks in the area ( $\text{Cl}^-$  is however present in all natural waters, but mostly in low concentrations [Hem, 1989]). The two major rainfall seasons in the area are 1. long rains in April - May and 2. short rains in October - November (Lars-Erik 1985). The 1996 sample set was taken in the long rainy season and the 1997 set taken before the short rainy season. This could account for the differences in the  $\text{Cl}^-$  concentrations. The build up of  $\text{Cl}^-$  during the heavy rainy season may have increased the levels in the Crescent lake area.

Other factors or processes that could have contributed to the build up of  $\text{Cl}^-$  levels are a) fluctuations in lake levels (especially in the Crescent island area) and b) evapotranspiration where  $\text{Cl}^-$  is precipitated and left as salts which percolate in the shallow water table.

Systematic errors (differences in chloride tests) in the methods of analysis could have also contributed to differences in  $\text{Cl}^-$  values.

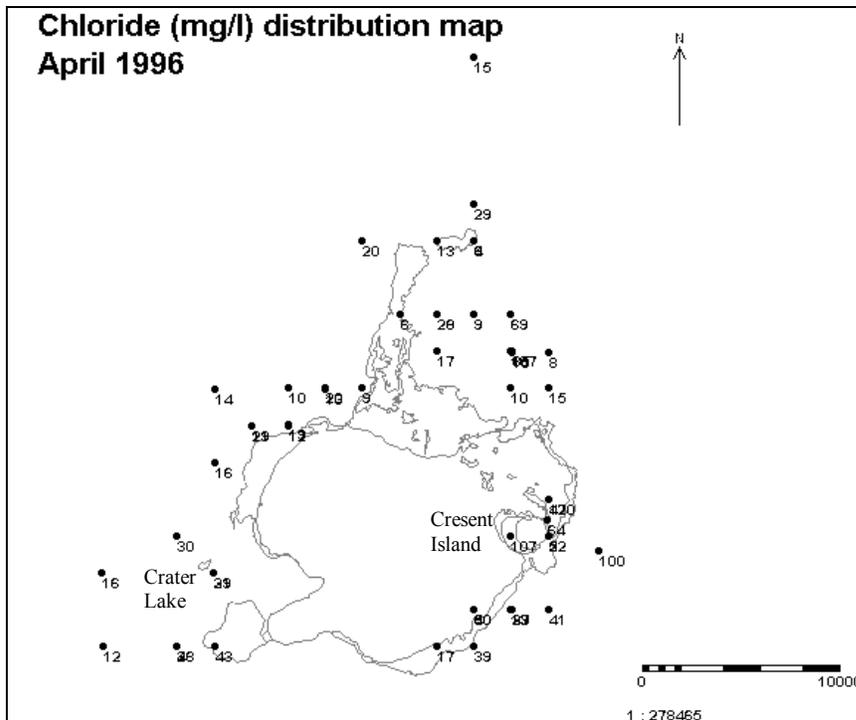


Figure 3.9 Chloride distribution map 1996

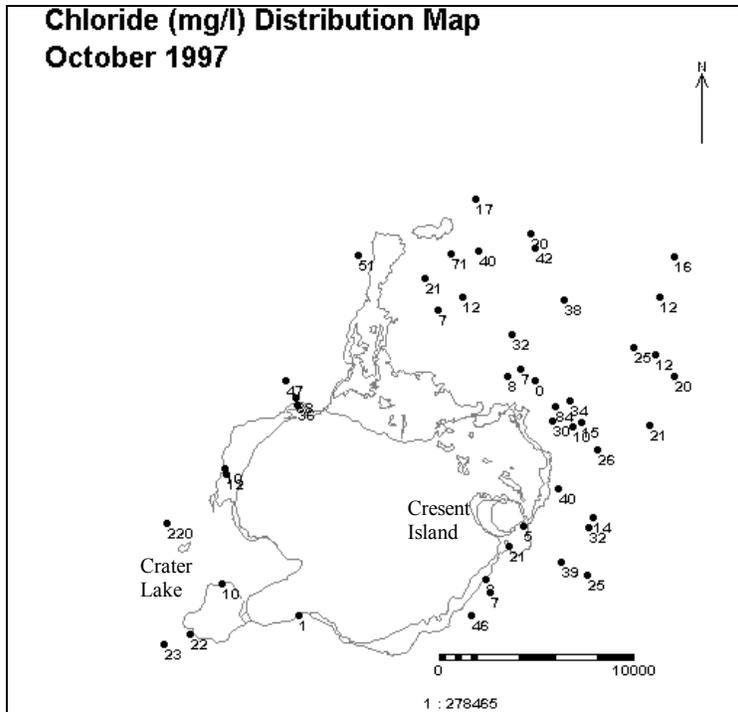


Figure 3.10: Chloride distribution map 1997

### 3.7.3 FRESHWATER - ALKALINE WATER LAKES

The only fresh water lake in the area is Lake Naivasha while Oloidien and Crater lake are sodic or alkaline (See Figure 3.11). The distribution of pH is shown on the map below. The range of pH for the freshwater lake is about 6.5 - 8 while that of the alkaline lakes is 10. The flora and fauna of these lakes are different also indicating different water types. Table 3.5 gives an indication of the general water quality of the lakes. [See also Appendix A-5 and A-6]

The Lake Naivasha has remained fresh because of inflow and outflow of groundwater to and from the lake. It has been suggested that groundwater flows into the lake from the north and flows out to the south. Since the water chemistry of Lake Naivasha is different than the smaller lakes it means there is no mixing with Lake Naivasha, the smaller lakes have their own hydrogeological system. These lakes are likely being fed by groundwater but the only outflow is by evapotranspiration which accounts for the alkaline conditions.

Table 3.5: Lake Water Chemistry

	EC at 20C	pH	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	T.HARD	CL	NO3	SO4	PO4	NH4	TURB.
<b>CRATER LAKE</b>	20500	10	27904	42711	3253	5000	2.5	>1600	>120	<0.03	200
<b>OLOIDIEN LAKE</b>	3423	10	288	2559	55	250	3	17.9	0.08	11.5	286
<b>NAIVASHA LAKE</b>	449	7.7	30	296	130	6	2	18.6	0.08	3	26

(all in mg/l except pH, TURB - NTU, EC - µS/cm)

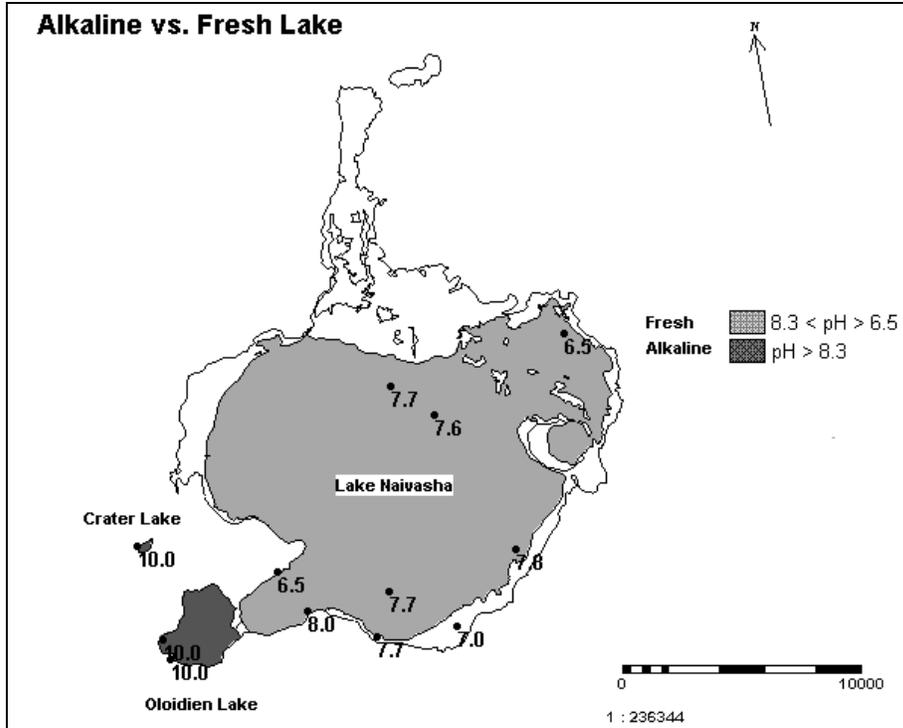


Figure 3.11 : Alkaline and Fresh-water lakes

### 3.8 ENVIRONMENTAL IMPACTS ( $\text{NO}_3^-$ , SAR, $\text{Fe}^{2+}$ AND TOTAL HARDNESS)

Nitrate ( $\text{NO}_3^-$ ) is an indicator of contamination of groundwater for drinking water purposes. The Sodium Adsorption Ratio (SAR) is an important water quality parameter for the identification of suitable water for irrigation. Iron ( $\text{Fe}^{2+}$ ) is an indication of iron precipitation causing corrosion of borehole casings and the need for water treatment for domestic purposes. Total hardness is an indication of carbonate precipitation in water which is problematic for domestic and industrial purposes.

#### 3.8.1 NITRATES ( $\text{NO}_3^-$ )

Nitrates ( $\text{NO}_3^-$ ) are common in all natural waters. When  $\text{NO}_3^-$  exceeds 20 mg/l it is considered a contaminant and an indication of pollution from municipal waste water, unsewered systems, fertilizers for example.  $\text{NO}_3^-$  unlike other minerals are not adsorbed by clays and hence moves in the aquifer with groundwater flow.

The main source of  $\text{NO}_3^-$  is from atmospheric nitrogen gas. Atmospheric nitrogen is converted to organic nitrogen by some plants (nitrogen fixation) converted to ammonia on the death of these plants by microorganisms (mineralization) and then changed into nitrates by nitrification.

Data set 1 had a  $\text{NO}_3^-$  range between 0 and 46 mg/l, generally  $\text{NO}_3^-$  is low in the study area but two points were > 20 mg/l (See Figure 3.12). In data set 2 the range was 0 - 17.2

mg/l. Sample points with the highest  $\text{NO}_3^-$  levels occurred in the same area in both data sets. These high values are from boreholes along the Malewa river but also in cultivated areas.

In data set 1, one contaminated area is highly cultivated and the other area with settlement. For the cultivated area the contamination (possibly from inorganic fertilizer application) is small as the surrounding boreholes have lower  $\text{NO}_3^-$  levels but higher in comparison to the rest of the data. (The same pattern is seen in data set 2). In Naivasha town the contamination is localized indicating point source contamination from unsewered sanitation. Other areas with values between 5 - 11 mg/l are in the developed areas or the cultivated areas but these concentrations are generally below the levels of being considered a contaminant (20 mg/l) (Appelo et al. 1996).

Excessive concentrations of nitrate in drinking water may cause methemoglobinemia in small children. This is a potentially fatal syndrome whereby the transport of oxygen in the blood stream is impaired (Appelo et al. 1996).

Even though there are no WHO standards for  $\text{NH}_4^+$ , the European Standard (EU) of 0.5 mg/l for drinking water is exceeded in both data sets 1 and 2. The presence of high ammonia gives an indication of nitrate reduction by microbial activity in the shallow aquifer (Appelo et al. 1997). The range of 0 - 15 mg/l and 0.02 - 2 mg/l for both data sets respectively is also an indication of the application of fertilizers from agriculture and nutrient loads from animal manure.

Nitrate pollution also occurs where untreated groundwater is being used. The pollution point in Naivasha town occurred at a well which was not developed, hence the untreated water with high nitrates.

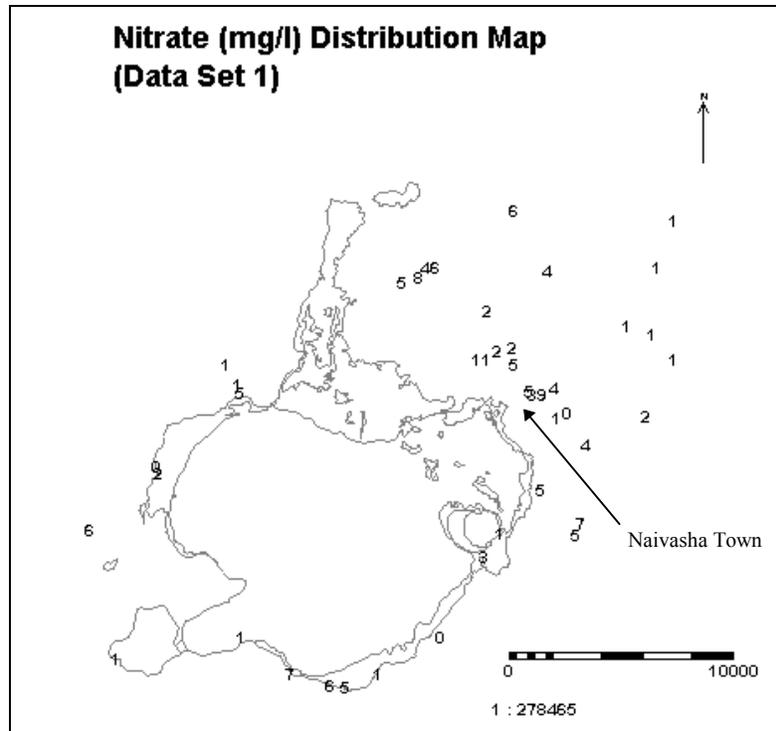


Figure 3.12: Nitrate Distribution Map

### 3.8.2 SODIUM ADSORPTION RATIO (SAR)

SAR of water is defined as :

$$SAR = \frac{Na^+}{\sqrt{\frac{(Ca^{2+} + Mg^{2+})}{2}}}$$

and expressed in meq/l. SAR measures the degree to which sodium in e.g. irrigation water replaces (cation exchange) the adsorbed  $Ca^{2+} + Mg^{2+}$  in the soil clays and thus damages the soil structure (Hounslow, 1995).  $Ca^{2+}$  is reduced in the water by precipitation as well as the effect of evaporation. Salinity hazard which is conductivity or TDS and the sodium hazard (SAR), are good indicators of suitability of water for irrigation purposes.

Data set 3 (Min. of Energy) will be used to make the SAR assessment because the  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  parameters were analyzed. SAR values ranged between 1.4 - 14.3 meq/l.

The SAR conductivity plot in Figure 3.13 (generated in WATERVAL on Data set 3) shows that two points have high salinity water and very high sodium water. This must be due to the high evaporation rates that occur generally in the Naivasha area. 54% of the sample points have high salinity water pointing again to the high evaporation rates as

mentioned in Chapter 2 section 2.2.2. 54% of the sample points have medium to high sodium water of which 43% is between high and very high sodium water.

In terms of irrigation, samples falling in section C3 - S4 (high salinity water and very high sodium water) have poor water quality for irrigation purposes. These waters will break up the soil structure (high SAR disperses clays especially reducing water infiltration and gaseous exchanges with the atmosphere). High sodium water cause the soil to become deflocculated and impermeable to water, hence a soil of this type is difficult to cultivate and to support plant growth (Hem, 1989). These points are along a transect east of Lake Naivasha across from Crescent Island. Samples within the areas with the dashed lines (high salinity waters) must be viewed with suspicion until proof of its safety is obtained.

[The sample points were not enough to classify the groundwater in the area according to SAR].

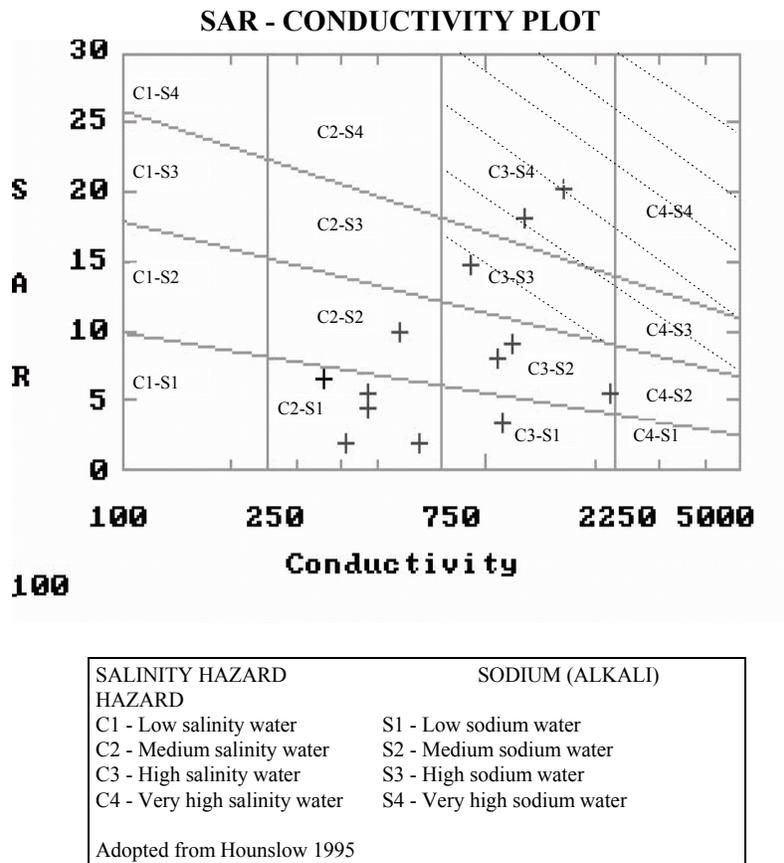


Figure: 3.13 Sodium Absorption Ratio - Conductivity plot

### 3.8.3 TOTAL IRON

According to Appelo et al. (1996) iron is a common constituent of anoxic groundwater. Standard redox diagrams indicate that between a pH range of 5 - 8, dissolved iron is present as Fe<sup>2+</sup> (Ferric), since Fe<sup>3+</sup> (Ferrous) under these conditions is insoluble. During

drinking water production or sample collection, anoxic groundwater containing  $\text{Fe}^{2+}$  becomes aerated and is oxidized very fast at a neutral pH. As a result, Fe-oxyhydroxides are precipitated. Excess iron in drinking water is not poisonous but the red Fe-oxyhydroxide precipitate, stains laundry and clogs distribution systems and is usually removed during the treatment of water.

The main sources of  $\text{Fe}^{2+}$  in groundwater are the dissolution of Fe(II)-bearing minerals and the reduction of Fe-oxyhydroxides present in the sediment. Fe(II)-bearing minerals commonly present in aquifers and associated with the Naivasha area are Fe(II)-bearing silicates comprising of amphiboles, pyroxenes, biotite and clay minerals such as smectite. From geology and petrology studies by Thompson (1958) Fe-bearing minerals are essential components of the volcanic rocks in the area (See Table 3.6).

Table 3.6: Percentage of Fe(II)-bearing minerals in volcanic rocks in the Naivasha area

<i>Fe(II)-bearing rocks</i>	<i>Fe<sub>2</sub>O<sub>3</sub> % (Hematite)</i>	<i>FeO % (Iron Oxide)</i>
<i>Lava</i>	<i>4.97</i>	<i>14.63</i>
<i>Trachyte</i>	<i>3.66</i>	<i>3.55</i>
<i>Rhyolite</i>	<i>0.69</i>	<i>1.17</i>
<i>Commendite</i>	<i>1.31</i>	<i>1.84</i>
<i>Pumice</i>	<i>13.71</i>	
<i>Obsidian</i>	<i>1.72</i>	<i>5.42</i>

Source: Compiled from

Thompson et al. (1958)

$\text{Fe}^{2+}$  in the study area ranged between 0-6.2 mg/l and exceeded the WHO standard for drinking water of 0.3 mg/l. The distribution of iron in groundwater in Naivasha can be due to:

1. Solubility controls of iron in groundwater. Appelo et al. (1996) indicated that  $\text{Fe}^{2+}$  is best controlled by the oxidation of  $\text{Fe}^{3+}$  and the precipitation as Fe-oxyhydroxides. This process occurs at zones of water discharge, near rivers etc. (in this case lake Naivasha). At these zones  $\text{Fe}^{2+}$  rich groundwater comes in contact with atmospheric oxygen. As a result, bands of Fe-oxyhydroxides can form around the water table. This process may have occurred around lake Naivasha as seen in Figure 3.14. Areas in the NW and the E show bands of iron  $>0.3$  mg/l. These bands are located at the shallow water table. This also was evident at the mouth of the Malewa river.
2. Reducing water with pH 6-8. According to Hem (1989), in this environment, the occurrence of iron with concentrations of 0.1 - 10 mg/l in groundwater is common. Wells with this type of water appear to be erratically distributed around the area. In many wells the corrosion of iron casing adds iron to pumped water, and iron may be precipitated in various forms within the well under some conditions. The iron distribution in groundwater around lake Naivasha could also be considered as erratic and due to corrosion. The former explanation however, is more valid to the area as the petrology and geology suggest the presence of Fe-bearing minerals from silicate weathering.

The presence of iron in groundwater is an indication of: 1. The need for water treatment for domestic purposes, as corrosion from boreholes could cause iron precipitation. 2. The oxidation processes taking place in the shallow aquifer. (The build up and oxidation of iron in samples before analysis may have also increased iron concentrations).

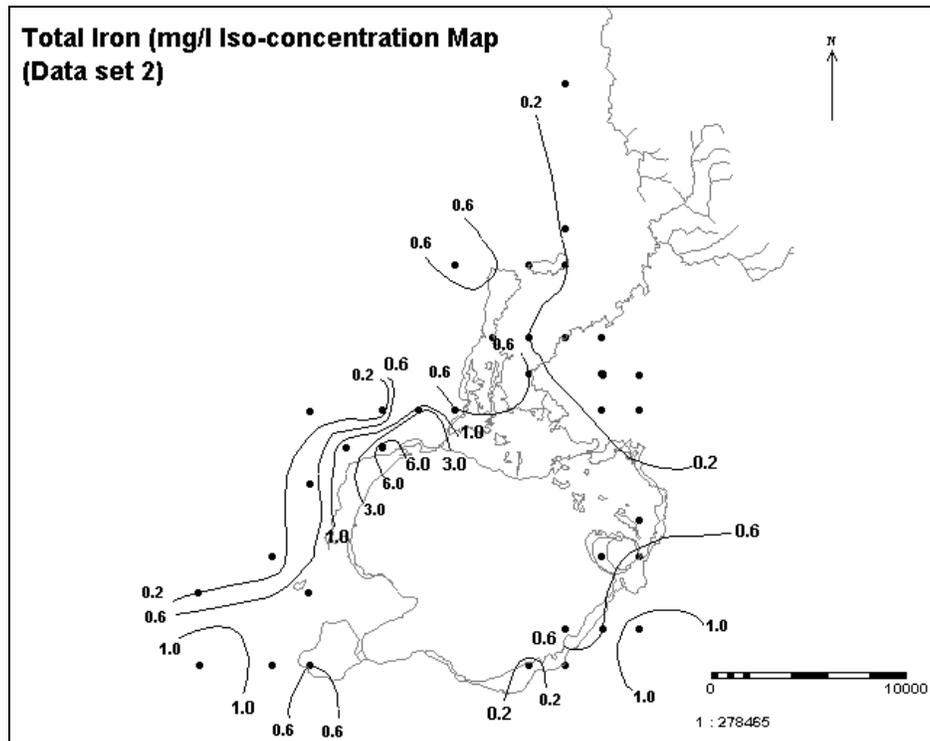


Figure 3.14 Iso-concentration Map of Total Iron

### 3.8.4 TOTAL HARDNESS

The hardness of water is a property to consume large amounts of soap (triglycerides) to create a quasi-permanent dispersing foam layer. The cations calcium and magnesium are mainly responsible (iron and aluminum to a much less extent) for this reaction with soap. Hardness is also associated with encrustation of pipes and distribution systems. This parameter is also a nuisance for domestic and industrial purposes (Mannaerts, 1993).

Three types of hardness can be distinguished:

1. Total hardness ( $\Sigma$  temporary and permanent) measured as mg/l of  $\text{CaCO}_3$  (= F°H French hardness)
2. Temporary hardness (bicarbonate hardness) measured as mg/l of  $\text{CaCO}_3$
3. Permanent hardness (gypsum or sulphate carbonate hardness) measured as mg/l of  $\text{CaCO}_3$

Temporary hardness of water refers to the fact that  $\text{CaCO}_3$  can be removed by boiling. the following reaction indicates this procedure:



A white precipitate after boiling indicates the presence of bicarbonates in domestic water supply. The degree of hardness can be measured by the following scale (from Durfor and Becker 1964, in Hem, 1989) and gives a description for the types of water present:

Total Hardness (mg/l CaCO <sub>3</sub> )	Description
0 - 60 mg/l	soft
61 - 120 mg/l	medium hard
121 - 180 mg/l	hard
181 mg/l and over	very hard

In the Naivasha area total hardness ranged between 30 - 500 mg/l in data set 1 (Field work) and 12 - 344 mg/l in data set 2 (Leicester University). Groundwater in the area therefore ranged between soft to very hard. Groundwater also did not exceed the WHO guideline for drinking water of 500 mg/l.

A comparison between total hardness and alkalinity gives an indication of the type of hardness present. Alkalinity is defined as the capacity of water to bind protons or react with a strong acid. It is determined by the presence of carbonates, bicarbonates and free hydroxides. If alkalinity is greater than total hardness, then all hardness is temporary.

In the Naivasha data sets alkalinity was mainly bicarbonates. The bicarbonate range for data set 1 was 97.62 - 153.15 mg/l and for data set 2, 123 - 1108 mg/l. However, when compared sample by sample alkalinity was greater than total hardness in both data set. The hardness of groundwater in the Naivasha area is therefore temporary.

Hardness in the study area is not permanent because of the absence of carbonate or sulphatic rocks (limestone, dolomite, gypsum) the main source of calcium and magnesium ions.

## **CHAPTER 4**

### **GEOSTATISTICAL ASSESSMENT**

#### **4.1 INTRODUCTION**

Spatial assessment of groundwater chemistry is important to reveal correlations (if any) between location and variables. This chapter investigates whether or not there is spatial correlation within the data sets using variogram analysis, maps these spatial relationships, and provide estimates for unsampled areas using kriging.

#### **4.2 INTRODUCTION TO GEOSTATISTICS**

Geostatistics is a branch of applied statistics that concentrates on the description of spatial patterns and estimating values at unsampled locations. Both value and location are used simultaneously to quantify spatial patterns (Liebhold et al. 1993 ). Geostatistics involves the analysis of spatially correlated data. The main feature is the use of variograms and other techniques such as kriging to quantify and model spatial correlation.

##### **4.2.1 VARIOGRAMS**

Semi-variograms are the basic tools for modeling the spatial autocorrelation of a regionalized variable (Van de Meer, 1993). The measure of how a variables  $z$  changes in value between site  $x$  and site  $(x+h)$  at  $h$  (lag) distance apart is shown by the following relation:

$$\gamma^*(h) = \sum \frac{[z(x) - z(x+h)]^2}{2n}$$

$\gamma^*(h)$  is the semi-variance for the distance  $h$ . A plot of semivariance versus distance yields a semivariogram (also termed variogram).

#### Figure 4.1 Variogram components

The main features of a variogram are: 1. sill, 2. range and 3. nugget (Figure 4.1). If the variogram displays a leveling-off then the variogram value at which the plotted points level off is termed the **sill**. The distance at which the variogram values level off is known as the **range**. The range indicates the average distance at which the samples remain correlated spatially (Liebhold et. al. 1993). The vertical jump from 0 at the origin to a value on the variogram at small separation distances is called the **nugget effect**. Pure-nugget effect describes variogram models with a non-zero nugget producing a horizontal line. This indicates the absence of spatial dependence at the scale of sampling.

The trial and error process of fitting theoretical variogram models to observed variograms is called structural analysis. The features above guide the fitting of models to a data set. The main types of models used are: 1. Spherical, 2. Exponential, 3. Gaussian and 4. Linear. Experimental variograms are dependent on orientation. Omnidirectional variograms (isotropic) can be considered as the average of all directional variograms and a starting point to variogram analysis, hence distance rather than direction plays an important role in these variograms (Isaaks et al. 1989). If omnidirectional variograms show good spatial structure then directional variograms can be attempted. Directional variograms examines the patterns of anisotropy in the data set.

#### 4.2.2 ESTIMATION (KRIGING)

Spatially estimating a regionalized variable can be done by a procedure called kriging (Van de Meer, 1993). Kriging provides a means of interpolating values for points not specifically sampled using knowledge about spatial relationships (the semivariogram) in the data set. Kriging is based on the regionalized variable theory and provides along with an interpolated estimate for a given location, a variance estimate for the interpolated value (Gamma Design Software, 1998).

The basic idea with kriging is that samples close together are more similarly valued than those that are far apart (Liebhold et al. 1993). When a value of an unsampled area (block or point) is to be estimated and other sample points are in the vicinity: 1. the variogram provides a measure of the strength of correlation for different distances, 2. kriging applies weights to the known sampled points to come up with an estimate of the unknown sampled location. The following expression summaries the kriging process:

$$z^*(X_o) = \sum_{i=1}^N \lambda_i z(x_i)$$

Where  $z^*(x_o)$  is the value to be estimated at location  $x_o$ ,  $z(x_i)$  are the sampled values at known location and  $\lambda_i$  are the weights to be given to each sampled value. To ensure unbiasedness the sum of weights are made equal to one. This is termed ordinary kriging and based on the assumptions that the process of estimation is **stationary** i.e all the samples are taken randomly and independently from one simple probability distribution

Clarke, (1979) and that the data set is **normally distributed**. Other types of kriging are indicator (discussed below) and cokriging.

### 4.3 STRATIFICATION USING VARIOGRAM ANALYSIS

The objective of the stratification technique was to simulate variograms for different landuse, geologic or soil units, to see if there were any spatial correlation between landuse pattern or geology and groundwater chemistry. However, Figures 4.2 and 4.3 (figures represent both data sets 1 and 2) below indicated that there were not enough sample points in the different units or strata to complete the exercise. For successful stratification the density of sample points in the different units must be much larger and a regular or strategic sample scheme applied (Pebesma et al., 1991).

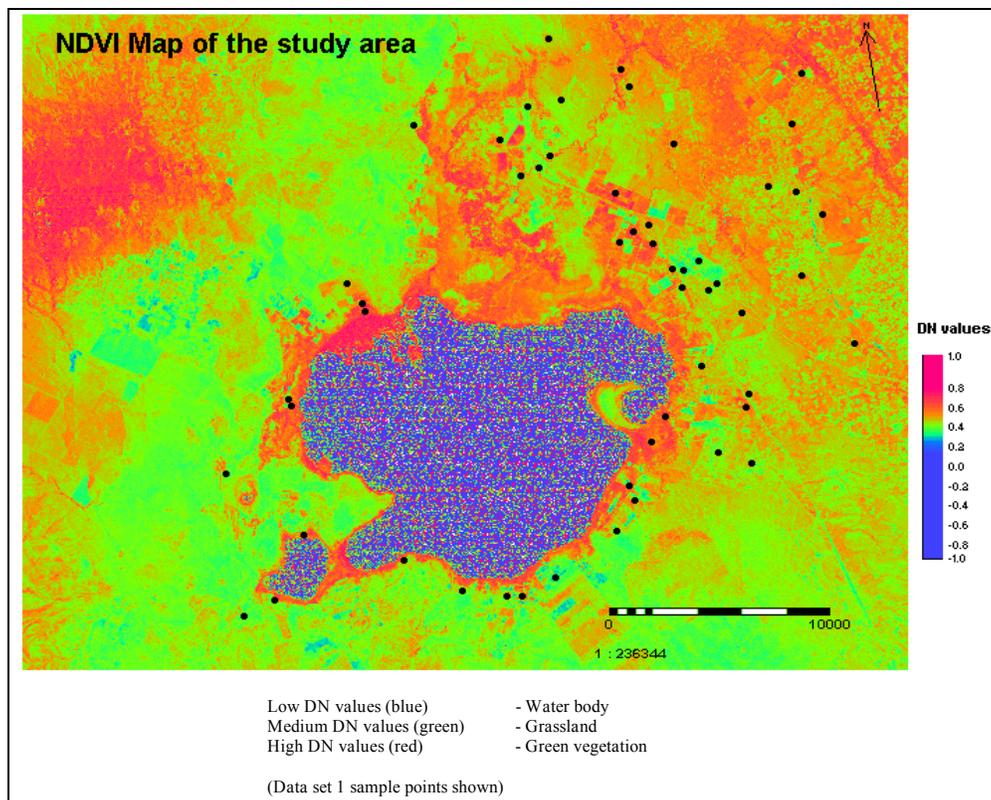


Figure 4.2: NDVI map of study area

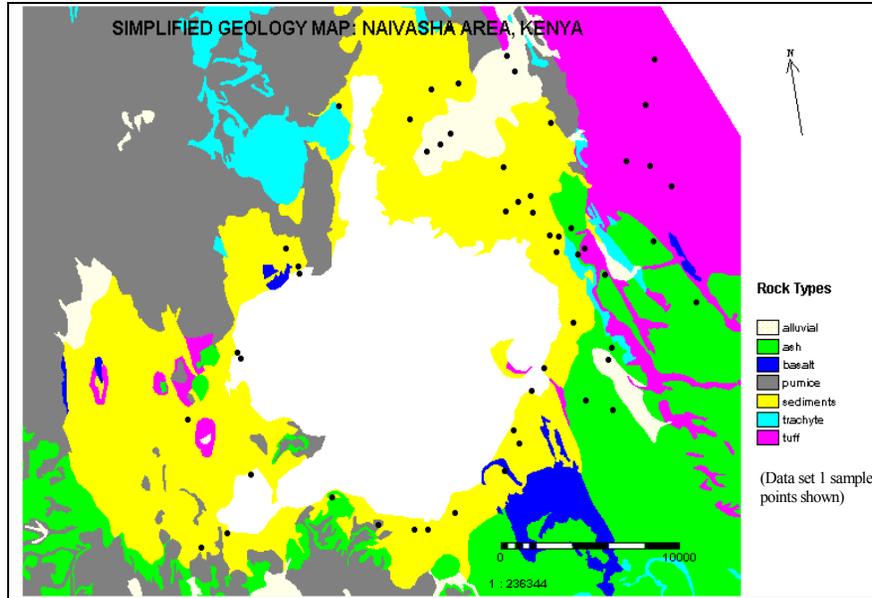


Figure 4.3: Simplified Geology Map of the study area

#### 4.4 INDICATOR KRIGING

Indicator kriging is a non-parametric technique in geostatistics. The histograms of distributions are discretized in several classes and the classes are interpolated separately. The indicator transformed variable,  $i(x;k)$  is thus a function of both location,  $x$ , and cutoff,  $k$ . The cutoff defines a single threshold for a particular subset (Liebhold et al. 1993):

$$i(x;k) = \begin{cases} 1 & \text{if } z(x) \leq k \\ 0 & \text{if } z(x) \geq k \end{cases}$$

Hence, the raw data is transformed into new variables 0 and 1. These new variables are the indicators which indicate whether a given property has been observed in a sample/block (1) or not (0). The final result of indicator kriging is a cumulative probability distribution for each class that gives the probability that the cutoff  $k$  will be exceeded within that block i.e. an average indicator value is estimated for that block.

The estimated block is a weighted average of the zeros (0) and ones (1) of a sample in or around a block. The “spatial continuity” of the indicator is assessed through the indicator variogram which is modeled just as the ordinary variogram but for the zeroes and ones of the indicator (Van de Meer, 1993).

The advantages of indicator kriging (non-parametric) over ordinary kriging (parametric) are:

1. Indicator kriging is distribution free and outlier resistant no matter how skewed the distribution, while ordinary kriging performs poorly in the presence of highly skewed distributions which are far from normal.

2. Confidence limits or intervals are provided by indicator kriging but ordinary kriging does not provide a confidence interval for estimated values.
3. Indicator kriging is data value dependent taking into account outliers while ordinary kriging is dependent on data configuration.

Indicator kriging takes care of the normal distribution assumption.

#### **4.5 SPATIAL ANALYSIS OF THE DATA SETS**

The variables with an environmental impact were assessed for spatial continuity. Univariate and bivariate statistics revealed that these variables show non-normal distributions and stationarity (no trend). Indicator variogram analysis (omnidirectional) was therefore done for fluoride ( $F^-$ ) and iron ( $Fe^{2+}$ ) in data set 2 (62 samples) and chloride ( $Cl^-$ ) and nitrate ( $NO_3^-$ ) in data set 1 (56 samples). Indicator kriging maps were produced for variograms displaying a spatial structure. The geostatistical program GEOEAS version 1 was used for this exercise.

Silica an important geological parameter, was not assessed. Silica indicated a trend in the NS direction with a correlation of  $r = 0.64$ . For indicator and ordinary kriging only parameters without trends are suitable for variogram analysis. To overcome this, the trend would have to be subtracted from the values and the residuals kriged. This is termed Universal kriging, “kriging with a trend”. [Time would not permit further analysis of this parameter]. The trend however confirmed that silica is flowing from the north of the area towards the lake.

##### **4.5.1 PROCEDURE: INDICATOR VARIOGRAM AND KRIGING MAPS**

The following steps were taken in GEOEAS:

- a) TRANS: New variables were created for each parameter. The new variables 1 or 0, represented whether samples fell above the cutoff (1) or not (0). The quartiles of the distribution were selected as the cutoffs. The quartiles were selected because the quartiles of a distribution are not affected by the presence of outliers, predominant in this data set. Owing to the wide range in the data sets (Fluoride 0.3 - 72 mg/l, Iron 0 - 6.2 mg/l, Nitrates 0 - 45 mg/l and Chlorides 0 - 220 mg/l) the quartiles were considered a better representation of the data, and better for visual interpretation of very low and very high values.
- b) PREVAR: Distances and relative directions between pairs of points sampled were calculated. This information was used to calculate the variogram values. The limit on distance between pairs were calculated for each cutoff value per variable.
- c) VARIO: Variogram values and descriptive statistics were calculated for a set of paired distances. A plot of variogram values vs. distance was made and a model variogram fitted to the scatterplot. Experimental variograms were made for each cutoff value for each parameter.

d) KRIGE: A rectangular grid of kriged estimates was created for each cutoff where the variograms indicated spatial correlation. An output file of the estimates and estimated error was created. The kriging results were transported and transformed in ILWIS 1.4 and 2.1 where:

1. probability maps were created to indicate the probability of not exceeding the cutoff levels
2. the estimated values of the blocks for each parameter could be visualized.

## **4.6 INTERPRETATION OF INDICATOR VARIOGRAMS AND KRIGING MAPS**

### **4.6.1 VARIOGRAMS**

**Fluoride:** The variograms for  $F^-$  were best fitted with a spherical model (Figure 4.4 A - C). Only Figure 4.4 B representing the median cutoff (4 mg/l) displayed a spatial structure. Small variance and short range indicates the data are spatially continuous (Liedhold et al. 1993). No spatial continuity was observed for the 2 mg/l cutoff (which displayed a lot of noise) and little spatial correlation for the 6 mg/l cutoff.

**Iron:** Three models were fitted to the data set. A spherical model to the lower cutoff (0.03 mg/l), a gaussian model to the median cutoff (0.28 mg/l) and a linear model to the upper cutoff (0.67 mg/l). Figure 4.5 B showed spatial correlation. Spatial continuity in Figure 4.5 A was very limited. Figure 4.5 C indicated no spatial correlation as the variogram reflected a pure-nugget effect.

**Nitrate:** Two models were used to fit the data at the different cutoff limits. The 1 and 3 mg/l cutoff limits were fitted with spherical models while the upper cutoff (5 mg/l) was fitted with a linear model (Figure 4.6 A - C). The variogram for a nitrate cutoff of 1 mg/l indicated some spatial correlation up to a distance of 10 km. The variogram for the median cutoff displayed little correlation while the upper cutoff showed a pure nugget effect. Here the sample variance is nearly identical to the values over the entire lag distance. The pure nugget effect suggest that above 3 mg/l  $NO_3^-$ , there is an absence of spatial dependence at the scale sampled.

**Chloride:** The model fitted to  $Cl^-$  for the lower (10 mg/l) and upper (36 mg/l) cutoff values were pure nugget variograms indicating that the  $Cl^-$  values in the study area were completely independent of space. The median cutoff (21 mg/l) was fitted with a spherical model. There was spatial correlation over a small lag after which there was no spatial continuity. Never the less the median cutoff was tending toward pure nugget, hence this relationship is not very strong. (Figure 4.7 A-C).

### **4.6.2 KRIGING MAPS**

The **probability** maps produced have a range of 0 - 1, 1 indicating a high probability of not exceeding the cutoff limit and 0 indicating a low probability of not exceeding the cutoff point. Blocks with *high probability* represents areas that *will not exceed* the cutoff limit, while blocks with *low probability* represent areas that *will exceed* the cutoff limit.

The block kriging outputs gave estimates for each block and was chosen because kriging gives the lowest estimation variance for each block (Clarke, 1979). (This advantage is absent for other interpolation methods).

Owing to the poor distribution of the data points, in KRIGE the search ellipse was adjusted to increase the search area and reduce the amount of blocks with missing data. Later in ILWIS 2.1 a mask was used (by mapcalculation) to block out these areas. The presence of the lake also affected the kriging output, as in GEOEAS a mask could not be applied to block out the area of the lake. Subsequently, a mask was added in ILWIS, after the entire area was kriged. These steps no doubt introduced errors in interpolation around some sample points, as will be seen later, but was necessary to avoid distorted blocks in the areas with missing data as well as over and underestimations. In GEOEAS the borders of the kriging map were defined by the sample point location, hence for some variables the kriged outputs were cut short at the south lake edge. The maps were produced at a 50 x 50 m pixel size.

**Fluoride:** The maps indicated that most areas have a probability exceeding the WHO guideline for F<sup>-</sup> in drinking water of 1.5 mg/l. The median cutoff (4 mg/l) map showed the distribution of low values while the upper threshold (6 mg/l) highlighted the area with oversaturated F<sup>-</sup> levels in the southwest corner of the map (Figure 4.8 A-B). [Figures 4.8 B gave a lot of information as it pointed to the areas of poorer water quality].

**Iron:** Both the lower and median cutoffs for iron (0.03 mg/l and 0.28 mg/l) are below the WHO guideline for drinking water of 0.3 mg/l. Therefore, the maps in Figure 4.9 A- B indicate areas likely to exceed the WHO standard. Evident from these maps are the zones surrounding the lake having a very low probability of **not** exceeding this limit. Groundwater from wells around the lake are most likely to be contaminated with iron. The maps also supported the idea of iron precipitation around the lake, resulting from oxidation of groundwater in the shallow aquifer. (see Chapter 3 section 3.8.3).

**Nitrate:** The probability map for the lower cutoff (Figure 4.10) indicated areas with high probabilities of being contaminated by nitrate, e.g. NE of the lake at Naivasha Town (contamination from unsewered systems) and in the cattle rearing/ cultivated areas (contamination from nutrient loading and fertilizer application). Areas immediately around the lake where horticultural activities dominate have high probabilities of not exceeding the cutoff. This may be due to mixing of groundwater and lake water, but most likely nitrification by microbiological activity.

**Chloride:** The map in Figure 4.11 indicated that only a few areas are unlikely to have high Cl<sup>-</sup> levels. The median cutoff (21 mg/l) pointed to the areas with potentially high chloride levels (green - blue areas). Considering that the main source of chloride is from rain and that there are no chloride minerals in the area, the areas likely to exceed the

cutoff may give an indication of the variability of rain water in the aquifer. [Chloride balance is a popular recharge estimation technique].

#### **4.7 RELIABILITY OF THE VARIOGRAMS AND KRIGING MAPS**

Several factors contribute to the weakness of the experimental variograms generated (maybe also lack of spatial structure) and hence the reliability of the estimations of parameter concentrations in the kriging maps:

1. The number of sample points. Large sample sets are ideal for variogram analysis. The sample sets used in this exercise were small (Data set 1,  $n = 56$  and data set 2,  $n = 62$ ). For the size of the area sampled ( $897 \text{ km}^2$ ) more sampling points would have improved the experimental variogram and hence, the estimations of the kriged maps.
2. Sample scheme. The sample design affects the outcome of the variogram. For groundwater (and for this study) the traditional sample designs (grid etc.) were not applicable. Sampling was attempted perpendicular to suspected groundwater flow directions, but this also was not successful in some areas. Hence, the sampling done was not systematic and contributed to the inability of capturing spatial correlation for some cutoffs for the variables assessed.
3. Clustering. Clustering of the data points affects the variogram analysis. According to Issaks et al. (1989) short scale variability cause sample values separated by extremely small distances to be quite dissimilar. Samples close together affect the choice of distance parameters. Clustering of data points was evident in both data sets and affected the variograms. The effect of clustering could be improved by resampling at a suitable lag space. Again the need for a sample scheme.
4. Removal of extreme pairs. An option for improving the variogram is to remove the erratic pairs in the data set. Variograms are ideal where there are a) no proportional effect or b) sample locations are not preferentially clustered (Issaks et al.1989). The removal of erratic pairs as seen in Figure 4.4 A, may however not improve this data set as there are other problems associated with the data.
5. Adjustment in search ellipse. As mentioned in section 4.6.2.
6. Indicator Cutoffs. Often in indicator kriging if cutoffs are too high or too low, pure-nugget variograms are the result. This means that there are not enough zeroes or ones present to capture spatial correlation (Communication with Van der Meer, 1998 - Geology Division, ITC). Applying different cutoffs may give better spatial structures, but this is also limited by the sample size.

#### **4.8 CONCLUSION**

Spatial continuity of the original variable were investigated using indicator kriging. Although the geostatistical analysis was based on only the data points and not on a theoretically ideal distribution of samples, this research was useful in showing us origins and spatial variability for the four water quality parameters investigated. The kriging maps aided in mapping the chemical pattern of groundwater in the Naivasha area.

Kriging maps are useful for indicating possible areas with potentially higher values and giving estimates for unsampled areas. However for field purposes and decision making in water resource planning, a proper sampling scheme must be taken into consideration for successful variogram analysis.

In reality, groundwater chemistry changes over gradual boundaries rather than fixed boundaries (as indicated by the block kriging maps). Smoothing of the maps can be done by submitting the maps to a second interpolation step. This is done by linear interpolation of the kriged values on a finer grid (Wackernagel, 1995). [A 50 x 50 grid was the lowest possible raster representation that could be handled in ILWIS 1.4, hence this was not done]. However, estimates of the block kriging maps are better than the smoothed version.

The kriging maps also could be used as historical knowledge and visual indicators in further sampling programs. For pollution studies and deciphering groundwater flow paths, sampling could be concentrated in the areas identified in the maps as having high probabilities of exceeding WHO standards for example.

The estimation kriging maps can be improved by conducting extra sampling to increase the accuracy of the estimated concentrations and their probabilities. If the estimates of the probability kriging maps can be improved, then they can be used as a guide to mapping vulnerability of the area to pollution and to identify areas with high or low probabilities of having higher values or being contaminated.

## CHAPTER 5

### STATISTICAL ANALYSIS

#### 5.1 INTRODUCTION

This chapter examines the water quality data sets of the study area using univariate, bivariate and multivariate statistics, to determine and analyze relationships among the variables defining the chemical composition of groundwater in the Naivasha area. General statistics encompasses univariate statistics and correlations of the variables while multivariate statistics majors on complex correlations and classifications of the parameters.

#### 5.2 UNIVARIATE STATISTICS

Univariate statistics includes non-parametric (median and range) and parametric (mean, standard deviation and variance) descriptions of data. Data sets 1 and 2 were examined. The objective of this is to see if there exist any significant variations among water samples. Summary statistics, boxplots and histograms are given in Appendix C and D.

##### 5.2.1 DATA SET 1

The median and mean were not equal and the range was wide for most cases indicating asymmetrical distributions of the variables and the presence of outliers. Low median values coupled with high means also pointed to positively skewed distributions hence the overall mean was based on some extreme values where this was applicable. According to Chapman, (1997) the median and range are highly recommended for this type of data as they are non-sensitive to outliers. When the mean, standard deviation and variance were calculated, variations from the mean were high for most variables except  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , pH and temperature, because of the influence of outliers.

From the distribution curves,  $\text{HCO}_3^-$ , pH, EC and Total hardness showed near normal distributions while the other variables were positively skewed.  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  showed platykurtic characteristics. Further test of normality using the chi-square test revealed that at a significance level of 95%  $\text{HCO}_3^-$ , EC, pH,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and Total Hardness were consistent with a normal distribution.

##### 5.2.2 DATA SET 2

The median and range also identified asymmetrical distributions in this data set. The mean was affected by the outliers resulting in large variations for  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SiO}_2$ , EC,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . All other parameters showed near normal distribution curves except Fe(tot),  $\text{F}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , P(sol) and  $\text{SO}_4^{2-}$ . These distributions were positively skewed.  $\text{F}^-$ , Fe(tot) and  $\text{NH}_4^+$  showed platykurtic characteristics, indicating that the values are less clustered about the mean. Further test of normality using again chi-squared test indicated that with a 95% significance level  $\text{Ca}^{2+}$ , Fe(tot),  $\text{Mg}^{2+}$ ,  $\text{SiO}_2$  and  $\text{SO}_4^{2-}$  are consistent with

a normal distribution (Both data sets were standardized [Z scores,  $Z = (\text{variable} - \text{mean of variable}) / \text{standard deviation of variable}$ ] before the  $\chi^2$  test was done)

### 5.2.3 INTERPRETATION OF UNIVARIATE STATISTICS

Great deviations from the mean indicates wide variation in the concentrations of these parameters and hence a variation in the chemistry of the groundwater. Non-normal distributions indicate the presence of outliers which are extreme cases on one variable and have strong influences on the calculation of statistics. Outliers were prevalent in both data sets making it difficult to access the variations among the samples. Positively skewed data indicated that for such variable with this distribution most of the values tended towards the lower values. From both data sets only  $\text{NO}_3^-$ , EC and  $\text{HCO}_3^-$  showed the same statistical pattern.

#### 5.2.3.1 DATA TRANSFORMATION

Data transformation is recommended for non-parametric data sets. For these data sets the Log was taken of the variables which transformed the variables to normal distributions. This was not used further in the analysis because it does not reflect the true nature of the water chemistry of the area. Missing data was replaced by the linear interpolation of the variables (Norusis [2], 1994).

### 5.3 BIVARIATE CORRELATION ANALYSIS

Correlation analysis measures the linear association between variables (Davis, 1986). The value R (correlation coefficient) measures the strength of the linear association between two interval/ ratio scale variable. R ranges between -1 (negative slope) and +1 (positive slope). A value of 0 indicates no linear relationship. Scatterplots were used to study the associations among the variables (See Appendix E).

Correlation matrices were made for the two data sets (1 & 2) [See Appendix F]. The correlation coefficients were generated in SPSS. Using the Pearson's product-moment correlation, a coefficient of  $-0.5 < r > 0.5$  were selected with a significant level of 0.01 considering a 2-tailed situation. The non-parametric rank Spearman's rank correlation coefficient is useful to supplement the Pearson coefficient (Issaks et al. 1989). This coefficient ranks the data rather than using the original sample values and is not sensitive to outliers in the data set. The same level of coefficient levels ( $-0.5 < r > 0.5$ ) and significance levels (0.01, 2-tailed) as for the Pearson coefficient was accepted for the Spearman's coefficient.

#### 5.3.1 DATA SET 1

A linear correlation (Pearson) between EC and  $\text{HCO}_3^-$  ( $r = 0.85$ ) was observed in this data set. The correlation was tested with the t-test which indicated a strong positive correlation between EC and  $\text{HCO}_3^-$  which is highly significant ( $P < 0.05$ ). From the Spearman correlation EC and  $\text{HCO}_3^-$  showed a strong positive correlation ( $r = 0.88$ ) and higher than the

Pearson coefficient (See Appendix F-2). From the histogram and normalization curves of the other parameters no other strong linear associations were evident because there were more outliers among the variables and most variables were positively skewed.

### 5.3.2 DATA SET 2

This data set showed more variables showing high positive correlation. Pearson correlation was high between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r=0.77$ ),  $\text{Cl}^-$  and EC ( $r=0.79$ ), EC and  $\text{HCO}_3^-$  ( $r=0.96$ ),  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ( $r=0.59$ ),  $\text{Cl}^-$  and  $\text{Mg}^{2+}$  ( $r=0.55$ ) and  $\text{HCO}_3^-$  and  $\text{Cl}^-$  ( $r=0.63$ ) (See Appendix F-1). When these correlations were tested also with the t-test the positive correlation was confirmed which was highly significant ( $P<0.05$ ).

From Spearman's correlation similar relationships emerged. The positive relationship between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was the same as above. EC and  $\text{HCO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$ ,  $\text{Cl}^-$  and  $\text{Mg}^{2+}$  as well as  $\text{Cl}^-$  and EC were also positively correlated but with lower values.  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  were not correlated ( $r=0.37$ ) unlike above.  $\text{F}^-$  were correlated with  $\text{HCO}_3^-$ , EC and pH,  $r=0.66$ ,  $r=0.62$  and  $r=0.57$  respectively. These relationships with  $\text{F}^-$  were not present in the Pearson correlation (See Appendix F-2).

### 5.3.3 INTERPRETATION OF BIVARIATE STATISTICS

The above correlated parameters are all related to the weathering of silicates, as seen in Chapter 3, section 3.3 and Table 3.3.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  also contribute to the variation in SAR ratio in the study area.  $\text{Cl}^-$  displayed a high positive linear correlation (Pearson) with EC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$ .

The large difference in the Pearson ( $\rho$ ) and Spearman ( $\rho_{\text{rank}}$ ) values point to the presence of extreme values (Issaks et al. 1989). A high  $\rho_{\text{rank}}$  value along with a low  $\rho$  value, as in the case of  $\text{F}^-$  indicates that extreme values adversely affected an otherwise good correlation. High  $\text{F}^-$  are expected with increasing pH as discussed in Chapter 3, and an increase in the concentrations of anions such as increases in  $\text{HCO}_3^-$  and EC. Where  $\rho$  was high and  $\rho_{\text{rank}}$  low as in EC and  $\text{HCO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  as well as  $\text{Cl}^-$  and  $\text{Mg}^{2+}$ , the influence of a few extreme values may have affected the correlation.

### 5.4 MULTIPLE CORRELATIONS

According to Chapman, (1997) multiple correlation coefficients  $R(y, x_1, x_2, \dots)$  measures the strength of the relationship between a dependent variable and a set of independent ones. The coefficient of multiple determination  $R^2$  is an estimate of the proportion of the variance of  $y$  that can be attributed to its linear regression on the observed independent variables  $x_1, x_2, \dots, x_n$ . SPSS was used to calculate the correlations. The regression coefficient measures the relative importance of each  $x$  variable in determining  $y$ .

The concentrations of EC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  were all associated with  $\text{Cl}^-$  in groundwater, as seen above in the Pearson correlation analysis for data set 2. Multiple regression was used to describe the functional relationship between chloride (the dependent

variable,  $y$ ) and electrical conductivity, calcium, magnesium and bicarbonates (the independent variables,  $x_1$ ,  $x_2$ ,  $x_3$ , and  $x_4$ ).

Following the correlation analysis the F test was used to observe how closely the regression equation fitted the observed values of  $y$ , and whether or not a significant proportion of the total variance had been explained by the equation. The results of the multiple regression and multiple correlation are displayed in Figure 5. 1. The equation generated by the multiple regression procedure is:

$$\text{Chloride} = - 20.86 + 0.25* \text{Ca} + 0.12* \text{EC} - 0.14* \text{HCO}_3 + 0.05* \text{Mg}$$

The multiple regression coefficient R of 0.91 indicates that there is a very close association between the observed chloride values and the values calculated in the equation above. The significance of  $R^2$  when evaluated by the F test was highly significant. This is useful in predicting chloride where this data is absent.

MULTIPLE REGRESSION					
Equation Number 1	Dependent Variable.		CL		
Block Number 1. Method: Enter CA EC HCO3 MG					
Multiple R	.91153				
R Square	.83088				
Adjusted R Square	.81901				
Standard Error	11.69028				
Analysis of Variance					
	DF	Sum of Squares	Mean Square		
Regression	4	38270.92645	9567.73161		
Residual	57	7789.77024	136.66264		
F =	70.00986	Signif F = .0000			
-----Variables in the Equation -----					
Variable	B	SE B	Beta	T	Sig T
CA	.247227	.111302	.206878	2.221	.0303
EC	.124306	.015013	1.744062	8.280	.0000
HCO3	-.143017	.026755	-1.107256	-5.345	.0000
MG	.046923	.049588	.085513	.946	.3480
(Constant)	-20.8557	4.042664	-5.159	00000	
End Block Number 1 All requested variables entered.					
B	regression coefficients of x				
SE	standard error				
Beta	standardized regression coefficients				
T =	t test				
F =	F test				

Figure 5.1: Multiple regression and multiple correlation output for Chloride

## 5.5 MULTIVARIATE STATISTICS

Wulder [3], (1997) defined multivariate statistics as a tool providing the ability to analyze complex sets of data. Many independent variables and possible dependent variables which are correlated are analyzed using this technique.

### **5.5.1 CLUSTER ANALYSIS**

Cluster analysis (CA) is a multivariate procedure for detecting natural groupings in data. CA classification is based upon the placing of objects into more or less homogeneous groups, in a manner such that the relationship between groups are revealed (Wulder [2], 1997). CA is designed to select sub-sets of mutually similar objects from a matrix of many objects, based on the similarity coefficient matrix defining the interrelationship among those objects. CA is a simple form of correlation analysis (Seyhan, 1981).

Two types of CA exist: Hierarchical cluster analysis (suitable for moderate-sized data) and K-Mean cluster analysis (suitable for large number of cases >200). The most widely used CA method for forming clusters is agglomerative or fusion hierarchical cluster analysis. With this method clusters are formed by grouping cases into bigger and bigger cases until all cases are part of a single cluster (Norusis [1], 1994).

CA is a popular technique of statistical grouping because the result of the analysis is a two dimensional hierarchical diagram (dendrogram) indicating clusters which are easy and simply interpreted. This technique has been used in soil classification, geological mapping, hydrogeological mapping, ecology etc.

Clusters are defined by two key steps: 1. measurement of distances between objects, 2. grouping of the objects by the resulting distances (linkages). Step one allows for the measure of similarity between objects while step two determines the criteria by which the groups are linked. The linkages are however based on the associations measured between groups.

### **5.5.2 OBJECTIVES OF CA**

Seyhan (1981) indicated that CA is a good technique for creating a classification and identifying the clusters in a given population. In Chapter 3 a hydrochemical classification of groundwater in the study area suggested that there was one major groundwater type,  $\text{NaHCO}_3$ . CA will not be able to make such a chemical association, but use chemical data to identify any grouping from a statistical point of view.

The purpose of this analysis is to compare the CA classification method with the hydrochemical classification method in Chapter 3, to determine the types of groundwater in the area.

### **5.5.3 DATA PREPARATION**

Two data requirements for CA are: 1. standardization of variables, 2. absence of missing data. Standardization of the data was achieved by calculating the Z scores. This was done to avoid unsymmetry in the analysis due to differing magnitudes of data values. Variables with missing data were filled by substituting the blank spaces using linear interpolation.

#### **5.5.4 STEP 1: DISTANCE MEASURE**

There are several measures of similarity employed in CA. The major methods are:

- a) Euclidean, the distance is the square root of the sum of squared differences between values
- b) Squared Euclidean, the distance is the sum of the squared differences between values
- c) Cosine, the distance is defined by the cosine of the vectors of values
- d) Pearson correlation, the distance is determined by the correlation between the vectors of values. (Norusis [1], 1994)

#### **5.5.5 STEP 2: LINKAGE METHOD**

The major fusion methods to link the variables are: simple linkage, furthest neighbor linkage, average linkage, centroid linkage and Ward's method. Simple linkage measures the distance to the nearest object, while furthest neighbor linkage measures the furthest distance to the object. Average linkage measure the distance from all the objects, while centroid linkage measures distances based on assigned weights to distance of the objects. Ward's method (the most popular) measures distances based on the variance between the groups. Norusis [1] (1994) explained that in Ward's method clusters are combined with the smallest increase in the overall sum of the squared within-cluster distances.

#### **5.5.6 SELECTION OF CA METHOD**

Two approaches of analyzing cluster exist: 1. R-mode CA, where the interrelatedness among variables are assessed and 2. Q-mode CA, where the interrelatedness among cases are assessed. For this study Q-mode Hierarchical CA was done to identify clusters from the samples (cases) based on the interrelatedness of the variables. All variables in data set 2 (Leicester University Survey comprising of 13 variables and 62 sample points) were used. The various distance measures and linkage methods were used to classify the Naivasha data set 2. The best classification methods showing significant clustering was done with the squared Euclidean distance measure and the Ward's linkage method. The outputs consisted of an agglomeration schedule and a dendrogram.

##### **5.5.6.1 THE AGGLOMERATION SCHEDULE AND THE DENDROGRAM**

The agglomeration schedule is a summary of how each case and cluster is combined at each stage (See Appendix G-1). However the dendrogram, a two dimensional structure is another way and a more effective way of showing the clusters (Figure 5.2). The dendrogram gives the values of the coefficient at each step. With SPSS the similarity coefficient in the agglomeration schedule is rescaled from 0.15 - 772.4 to 0 - 25 in the

dendrogram (traditional outputs have been distance or correlation coefficients). The ratio of the steps are however preserved.

### **5.5.7 INTERPRETATION OF THE DENDROGRAM**

The horizontal scale represents the measure of similarity that is used to define the similarities between the sample points. The horizontal stems indicate the position at which the clusters combine. The sample points are along the vertical axis. Similarity levels can be used to determine the groups of clusters (Seyhan, 1981). These levels are however subjective as they are user defined.

For the dendrogram in Figure 5.2, the similarity levels were placed where there were sharp increases in the distance coefficient along the horizontal axis. The further the distance coefficient the less the similarity between groups. Three distinct levels were identified suggesting three (3) clusters in the data set. The groups were identified spatially by reclassifying the location map of the study area with the clusters using ILWIS 2.1 (See Figure 5.3)

## **5.6 CLUSTERING TEST: DISCRIMINANT ANALYSIS**

The main objective of discriminant analysis (DA) according to Seyhan et al., (1981) is to provide a numerical criterion for classifying variables or cases into two or more statistically distinguished groups. In this study a Q-Mode DA was done on the results of the cluster analysis to test whether the three groups identified are significant.

In DA, a linear combination of the independent variables is formed and serves as the basis for assigning cases (= samples) to groups (Norusis [1], 1994). The linear discriminant equation below is similar to the multiple linear regression equation:

$$D = B_0 + B_1X_1 + B_2X_2 + \dots + B_pX_p$$

where

D = discriminant score

X = values of the independent variable (parameters)

B = coefficients estimated (distance)

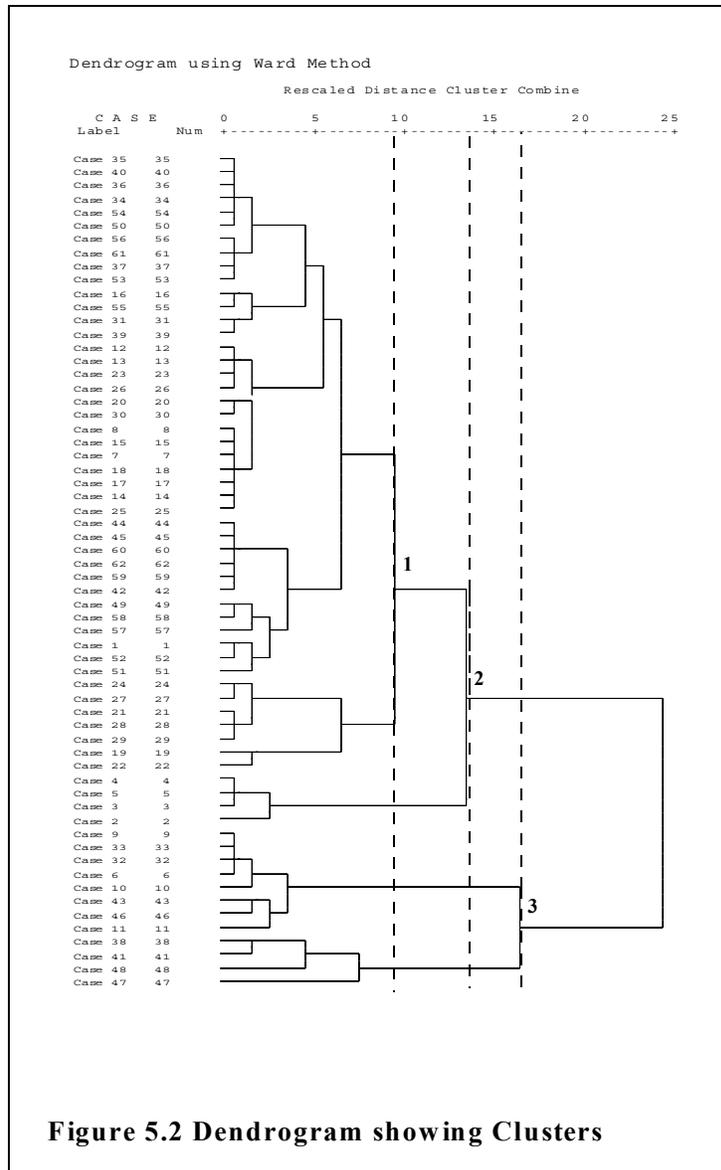
### **5.6.1 INPUT DATA AND TEST RESULTS**

DA is ideal to test the hypothesis that a given number of unknown cases belong to the known clusters (Seyhan, et al., 1981). The Q-mode approach was used to classify the 62 samples into the existing 3 groups identified by Q-mode cluster analysis.

Group 1 : samples in cluster 1

Group 2 : samples in cluster 2

Group 3 : samples in cluster 3



The classification results in Table 5.1 shows that 95.16 % of the cases were correctly classified. Hence, the proposed hypothesis is accepted.

Figure 5.4 shows another technique used for testing and visualizing the distribution of clusters. The canonical discriminant function referred to in Figure 5.4 is a correlation measure of the degree of association between the discriminant scores and the groups. With three groups DA generates two equations or functions ( $k = \text{groups}$ ,  $k - 1$  discriminant functions are computed {Norusis [1], 1994}). Three distinct groups can be seen with a little overlapping between groups 1 and 3. The means or group centroids are plotted far from each other indicating that the groups are different. The unclassified cases (sample 32, 33 and 42 [see Appendix G-2]) were placed in their respective groups. The modified cluster distribution map is seen in Figure 5.5.

Both the percentage grouping and the scatter plot are two of the many techniques used to test the accuracy of the DA and further the significance of the CA. In this case the grouping identified by DA are significant and therefore the clusters in the CA are significant.

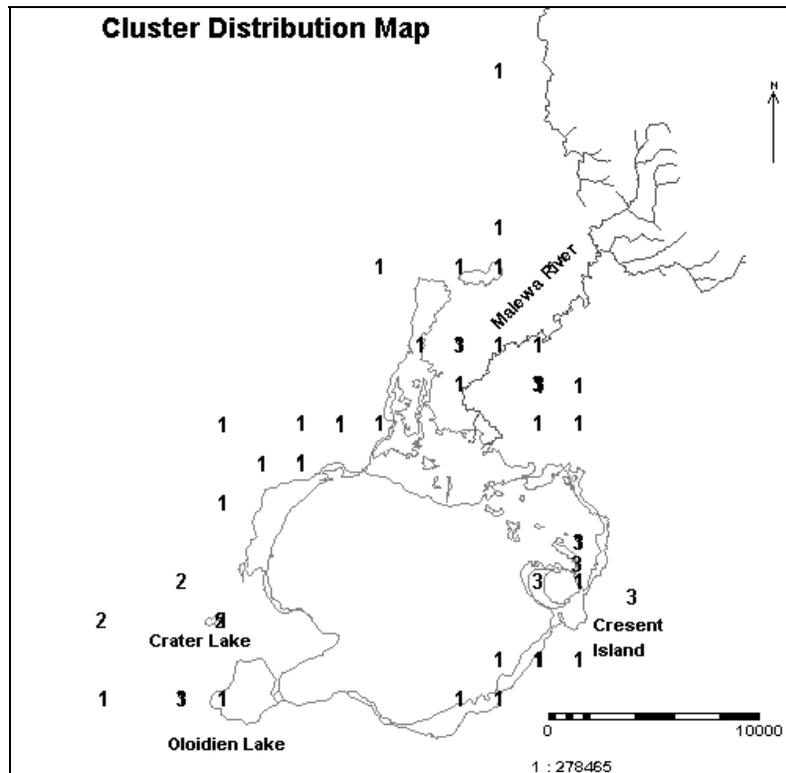


Figure 5.3 Cluster Distribution Map

Classification results -				
Actual Group	No. of Cases	Predicted Group Membership		
		1	2	3
Group 1	46	45 97.8%	0 .0%	1 2.2%
Group 2	4	0 .0%	4 100.0%	0 .0%
Group 3	12	2 16.7%	0 .0%	10 83.3%
Percent of "grouped" cases correctly classified: 95.16%				

Table 5.1 Discriminant analysis classification results

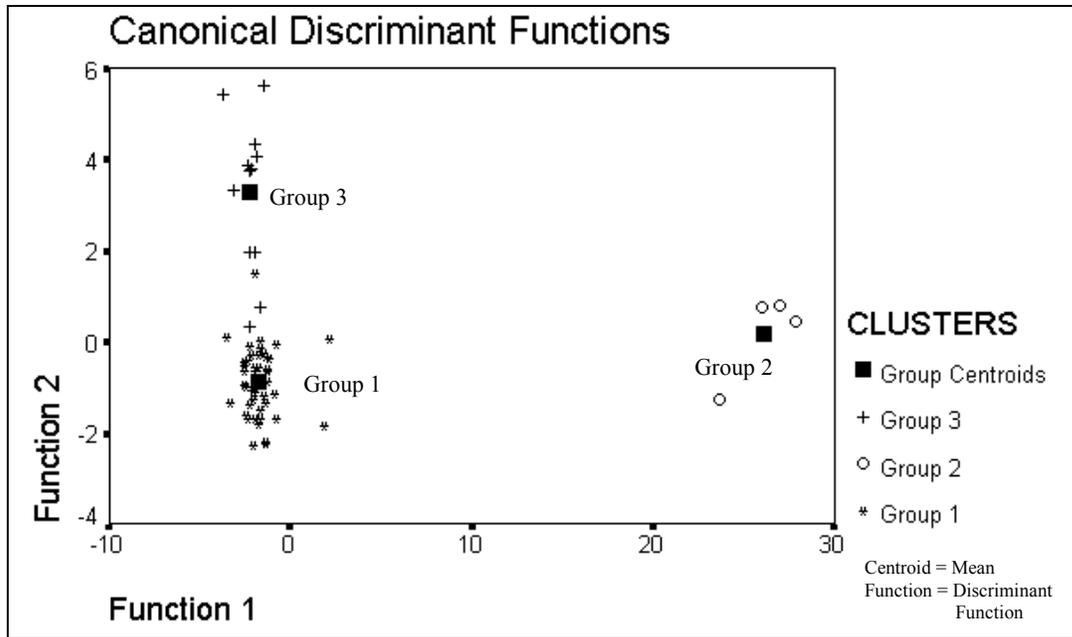


Figure 5.4 Scatter Plot of Clusters

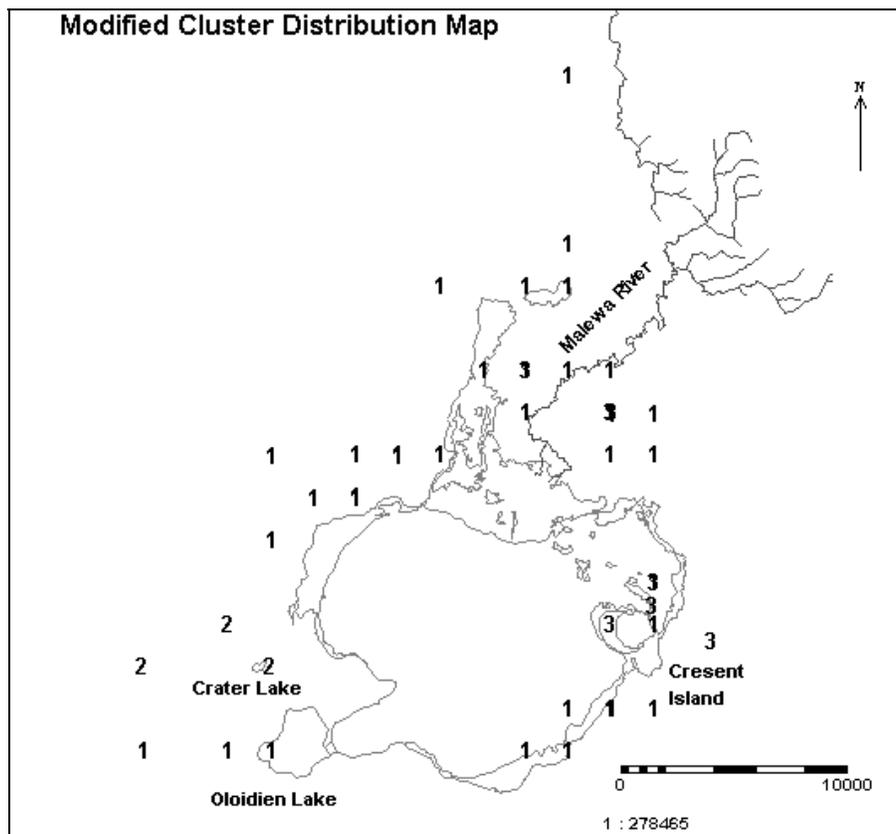


Figure 5.5 Modified Cluster distribution map

## 5.7 INTERPRETATION OF CLUSTER ANALYSIS

Figure 5.5 shows the modified cluster distribution for the Naivasha area (Points around Crater lake and Oloidien lake have been reclassified; the general changes are minor). Cluster 1 consist of 76 % of the total sample points hence there is one dominant cluster. CA has indicated three clusters or groups (Cluster 1 the major cluster and two minor clusters , cluster 2 and 3).

From the distribution of the points however, Cluster 2 and 3 are located in areas where the hydrogeology is complex or influenced by other processes. Cluster 2 is only present in the Crater lake area. As indicated in Chapter 2 section 2.2.3 the area has been influenced by volcanic disturbances and rifting separating the lakes in the area, hence the hydrochemistry may have indicated a small variation from that of the major cluster. The same area is affected by high fluorides levels reflecting poorer water quality.

The Crescent island area also indicates the presence of another minor cluster. In this area fluorides and silicates are high. Crescent island is also the remnant of an old crater hence volcanism has increased the complexity of the hydrogeology of that area. The chemistry of this area may have varied enough, so much that it was not classified in cluster 1.

The presence of minor clusters could have been a result of mixing of water types. In the northeast of the lake there is a mixture of clusters 1 and 3 of which the Malewa river may have contributed to.

### 5.7.1 STATISTICAL CHARACTERISTICS OF CLUSTER 1

Descriptive statistical analysis was carried out on cluster 1 to verify the characteristics of this group and to assess its uniformity. Of the total 62 sample points, 47 constituted the main cluster.

From the histograms and distribution curves of these parameters (See Appendix G-3)  $\text{SiO}_2$  and  $\text{SO}_4^{2-}$  generally (as before) displayed normal distributions, while  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and Fe (total) showed positively skewed distributions.  $\text{F}^-$  and P (soluble) showed normal distributions which was non-normal previously.

Outliers were present in the previous analysis of  $\text{F}^-$  and P(soluble) and hence affected the outcome of the clustering. Hence the samples with high  $\text{F}^-$  around Oloidien Lake, high  $\text{Cl}^-$  values around Crescent island, high  $\text{SO}_4^{2-}$  values around Malewa river and Crescent island were absent from cluster 1.

Bivariate correlation analysis was done on cluster 1 (Appendix G-4). From the scatterplots and coefficients of correlation (Pearson) high linear associations were observed between  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ( $r= 0.58$ ) ,  $\text{F}^-$  and EC ( $r= 0.55$ ),  $\text{F}^-$  and  $\text{HCO}_3^-$  ( $r= 0.52$ ). These correlations were not observed previously. Except for  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  all other correlated relationships were as before clustering. Sample points in Cluster 1 display a uniform behaviour in the concentrations of variables in the absence of outliers.

Even though cluster 1 is uniform, there was some variability seen in the dendrogram.

## **5.8 CONCLUSIONS OF CLUSTER ANALYSIS**

The output of the cluster analysis was similar to the output of the hydrochemical analysis. Both indicated one major water type and two minor water types. The hydrochemical groups were determined by the major cations and anions while the cluster analysis was determined by the thirteen variables in data set 2. Using all variables in the cluster analysis gave the best result rather than a subset of the variables.

Even though three groups are established by both methods, the groups are not the same. The cluster analysis technique used the variability within the data set to statistically determine homogeneous groups. Hence, the samples with extreme variables were grouped together as the minor groups. On the other hand the hydrochemical classification is based on the percentage ratio of the major anions and cations. Both techniques however, used the interrelatedness of the variables to characterize the groundwater.

Wulder [1], (1997) indicated that in multivariate statistical analysis: Normality (normal distributed data), linearity (straight line relationships), homoscedasticity (both variables normally skewed) and non-multicollinearity (not highly correlated variables i.e  $r < 0.7$ ), are constraints that must be met. This was reflected in the distribution of parameters with extreme variables in cluster 1 (Appendix G-3). Fluoride and soluble phosphate in the absence of samples from cluster 2 and 3 were normally distributed.

The interpretation of the dendrogram was supported by the outcome of the discriminant analysis, which confirmed the clusters numerically.

The weakness of the cluster analysis lies in testing the significance of its output. The discriminant analysis used (one of its use is to test the outputs of factor and cluster analysis) is very time consuming unlike other statistical test.

## CHAPTER 6

### CONCLUSIONS, DISCUSSION AND RECOMMENDATIONS

#### 6.1 CONCLUSIONS AND DISCUSSION

The general assessment of groundwater using the different approaches (hydrochemical, geostatistical and statistical) evaluated the chemical nature of the groundwater and gave an idea of the background “pristine “ condition as well as established relationships among the chemical parameters examined. The study not only verified that the observed water quality is not suitable for all its intended uses but went further to examine the development of cause-effect relationships between groundwater quality and environmental data (geology, hydrogeology, landuse, pollutant sources).

From the **hydrochemical assessment**, poor water quality for drinking water purposes was indicated from the range of fluorides. The groundwater is rhyolitic in composition resulting from silicate weathering as indicated from the source rock-deductions analysis. Volcanic activity has the major impact on groundwater chemistry as silicate weathering occurs from the rocks of this origin. High silica and fluoride levels pointed to the influence of hydrothermal activity on the supersaturation of these minerals in groundwater. The high fluoride concentrations observed in conjunction with alkaline pH conditions was also attributed to fluoride desorption mechanisms (anion exchange) from kaolinite clay types. Low mineralization indicated short residence time of groundwater in the shallow aquifer.

The Naivasha area can be hydrochemically classified as a dominant sodium bicarbonate type water. The minor water types are sodium calcium bicarbonate and magnesium sodium bicarbonate types. Only one data set was used for this classification owing to the availability of the ions for the Piper plot analysis. The classification can be questioned as some of the data points were not electroneutrally balanced. Fortunately, previous studies supported this classification. The use of several data sets both strengthened the output of the report by confirming the general groundwater quality but also weakened the output as they were all taken at different periods introducing a temporal and spatial factor in the analysis.

The major processes of : rock weathering (silica and fluoride), groundwater flow and evapotranspiration (EC and chloride), cation exchange (SAR) and oxidation/reduction (nitrate and iron) influenced the groundwater chemistry of the area. Agricultural activity and urbanization were responsible for the high nitrate and sodium absorption ratios present in the area. The groundwater was characterized as having low - high temporary hardness. [The impact of groundwater flow could not be fully assessed because of inadequate data].

The variogram analysis in the **geostatistical assessment** revealed that for the variables assessed, there was not much spatial correlation on the scale sampled. Fluorides, iron,

nitrates and chlorides showed spatial continuity. Only the parameters with an environmental impact (on drinking water) were assessed for spatial correlation. Silica, representing geologic weathering, indicated a trend in the NS direction (confirming that silica is flowing from the north-north-east of the area towards the lake).

The geostatistical assessment was weakened by the following factors: 1. limited data, 2. poor sample scheme, 3. clustering of sample points, 4. erratic values, 5. search ellipse adjustment in GEOEAS program and 6. choice of indicator cutoffs. Important for this analysis is a well designed sample scheme and a high sample density. This would reduce overestimation of unsampled areas and give a more accurate picture of the groundwater quality of the area.

The kriging maps were however, very informative in indicating areas likely to exceed a cutoff limit and possible pollution zones. The exercise gave a general overview of the spatial distribution of the groundwater quality in the Naivasha area. These maps can be used to formulate sample design schemes for future monitoring programs in assessing the impact of geological weathering and pollution on groundwater in the area, as well as a guide to vulnerability mapping. The geostatistical analysis supported the hydrochemical assessment by identifying the spatial relationships of the variables and mapping the state of the groundwater quality.

From the **statistical analysis**, the data sets used (set 1 and 2) were characterized mainly by asymmetrical variables and positively skewed data in the absence of normal distributions. Strong positive linear relationships were established in the data set for calcium, magnesium, electrical conductivity, bicarbonates and chlorides. Rank correlation analysis revealed that fluoride was correlated with bicarbonates, electrical conductivity and pH. Multiple correlation and regression analysis established a linear relationship for chloride using calcium, electrical conductivity, bicarbonates and magnesium. Univariate and bivariate statistics identified and showed the behaviour of the major chemical parameters in groundwater of Naivasha area (supporting the findings of the hydrochemical assessments).

Cluster analysis seemed the most suitable multivariate statistical technique to analyze the data set. This technique had a lesser data requirement (no missing data and standardized data), compared to other analysis such as principal component analysis and factor analysis. Cluster analysis indicated one major cluster (or groundwater type) and two smaller clusters (or groundwater types). Discriminant analysis assessed the significance of the clusters identified. 95.16 % of the samples were correctly classified into three clusters.

Both the hydrochemical and statistical classification techniques indicated the presence of one dominant water type. Different input parameters from different data sets used to assess the groupings, gave the same conclusions. The impact of outliers in most parameters influenced the statistical assessment of cluster analysis but adequately differentiated groups. Even though both analysis revealed three clusters, the water groups cannot be compared. Cluster analysis focused on the areas with contrasting hydrogeology

from the main lake area by a measure of variable similarity. The hydrochemical analysis focused on the percentage ratio of major anions and cations of the area. Multivariate statistics supported the hydrochemical analysis by examining the relationship among all variables.

## **6.2 RECOMMENDATIONS**

- Future groundwater chemistry assessment should include minor elements (e.g. fluorides, boron, isotopes), biological parameters (e.g. faecal coliform), as well as pesticides to examine their contribution to the water chemistry of the area.
- Use of new sampling data March 1998 (see Annex) should be used and compared to the October 1997 data to examine the effects of the rainy season on the groundwater chemistry.
- Use the data sets of 1990, 1996, 1997 and 1998 to conduct trend monitoring of parameters and also as a guide to future monitoring programs.
- Incorporate hydrological parameters into the chemical assessment e.g. water levels, thermal profiles, depth profiles (this was attempted in the field but not successful).
- Examine the chemical interrelationship between groundwater, lake water and river water by combining this study with the lake and surface water quality study done in this Lake Naivasha Basin Interaction research.
- Examine the groundwater chemistry development from the recharge areas to the lake, and carryout chemical and mass balance calculations to further understand the source of the chemical parameters (e.g. fluorides and silica).
- Conduct additional sampling and increase the density of samples to verify the output of the geostatistical assessments and to identify spatial correlations on a smaller scale.
- Use the chemical data sets to decipher the groundwater flow pattern in the area (this was attempted but more emphasis could be placed on this in future studies).
- This study may be considered a preliminary assessment in the context of water quality assessments, and therefore serve as a guide to establishing a sample scheme for trend monitoring and vulnerability studies.
- The water authority of Naivasha should seek alternative sources for drinking water with low fluoride levels or treat the groundwater with gypsum to flush fluorides. (The latter may be expensive and a long term plan, so lake water with low fluoride content may have to be considered for domestic use as a short term plan).
- Removal of iron from groundwater by treatment should be done if groundwater is to be used for drinking purposes. Metallic casing may be replaced with PVC casing where possible to avoid iron precipitation.



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