HYDROGEOCHEMISTRY AND IMPACT OF IRON ORE MINING ON GROUNDWATER QUALITY IN ITAKPE AND ITS ENVIRONS KOGI STATE, CENTRAL NIGERIA

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MARCH, 2008

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GEOL. 591 (PROJECT)
THESIS SUBMITTED TO THE DEPARTMENT OF GEOLOGY, FACULTY OF PHYSICAL SCIENCES, UNIVERSITY OF NIGERIA, NSUKKA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF M.Sc. DEGREE IN GEOLOGY, UNIVERSITY OF NIGERIA, NSUKKA.

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SUPERVISOR	**HEAD OF DEPARTMENT**

EXTERNAL EXAMINER

DEDICATION

This work is dedicated to my son Legrande Alpha Akpah and my wife Christiana E. Akpah. You are the reasons why this work must be and was done.

AKNOWLEDGEMENTS

My gratitude goes to God Almighty for all His graces that made it possible for this work to be brought to a successful completion.

I specially thank my supervisor, Prof. H. I. Ezeigbo who patiently and carefully guided me through all the basic knowledge needed to successfully complete this research work.

I am very grateful to Prof.C.O. Okogue, Dr. L.I Mamah, Dr. S.C. Obiora, Mr.O.S. Onwuka and all other staff of Geology Department,UNN, who advised and encouraged me through out my studies. Special gratitude goes to Mr. Ifeanyi Oha who digitized all the maps and diagrams in this work.

Special gratitude goes to Mr. Jeremiah Adejoh who helped me with vital literature and also took me round Itakpe for reconnaissance survey and later the gathering of samples. My gratitude also goes to Mr. B. Nnagha and other staff of NIOMCO who assisted me in getting the 1982 results of groundwater chemical analysis. These were used for comparison with the results of my analysis.

I am grateful to Dr. J.A. Olatunji who gave me useful materials and advised from his wealth of experience and knowledge of Itakpe. My special thanks goes to all staff of Geology department, Kogi State University for all their corporation and support.

I must thank my Vice – Chancellor, Prof. F.S. Idachaba who continued to encourage me while the programme lasted. I finally say thank you to Dr J.I. Omada who advised me to study Hydrogeology. This work is a product of his advice. May God bless and reward you all for your roles in my life. Amen.

ABSTRACT

This work is a hydrogeochemical study of groundwater and the impact of over twenty five years of iron ore exploration and mining on groundwater quality in Itakpe and environs. Measurements were carried out on water samples from eight shallow hand dug open wells, four deep boreholes and a seasonal river flowing through the mine area. Groundwater in the area occurs within weathered rocks, fractured and faulted terraces. Depths to water level in the open wells were generally below 15m. Chemical and physical analyses were carried out on the groundwater samples collected from the study area. Parameters measured include pH, temperature, electrical conductivity, concentration of cations, anions and trace metals. Groundwater in Itakpe is slightly acidic with pH values between 6.03 and 6.80 and temperatures between 28°C and36°C. Statistical analysis using pie charts, stiff plots Schoeller semi-logarithmic diagram and piper trilinear diagrams were used to characterize the groundwater in Itakpe. Three water types were commonly found to characterize the area. They include Ca-Mg-Cl-SO_4 type water, Na-K-Cl-SO_4 type water and mixtures of Ca – Mg- Na – K- Cl – SO_4 waters with no single cation dominating. Results of the analysis were compared with an apriori data of groundwater analysis from the area as well as world health organization (WHO) standards for portable water. Water in the study area has increased in acidity, electrical conductivity, hardness and concentrations of major cations and trace metals over time. Concentration of iron (0.9mg/l - 1.63mg/l) and manganese (0.2mg/l – 0.44mg/l) was found to be well above WHO 0.1mg/l iron and 0.05mg/l manganese recommended for portable water respectively. Recommendations were made on how to reduce and control the impact of iron ore mining activities on groundwater at Itakpe.

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CHAPTER ONE

INTRODUCTION

1.1 General Introduction

Potable water is necessary for supporting life and the activities of man. The importance of water in meeting the domestic, agricultural and industrial needs of man cannot be overemphasized. The need of water for mine development has been recognized (Famuboni, 1990). Due to the importance of water, there is an ever increasing need to expand or explore for more sources of good water quality and in significant quantities too (Todd, 1980).

One major source of water supply for meeting the needs of man is groundwater. Groundwater accounts for over 95% of the earth's freshwater resources (UNESCO, 1992). Groundwater is the only dependable source of water supply in some areas and so the need for good quality water in such places. Studies by various researchers confirm the fact that water quality deteriorates due to several factors both natural and man influenced. Ezeigbo, (1988), in his study of geological and hydrogeological influences on the Nigerian environment identified some common sources of water degradation. They include:

(i) Dissolving of constituents in water during its movement through surrounding rocks

(ii) Poor waste disposal techniques

(iii) Salt water (saline water) intrusion due to poor groundwater abstraction techniques in coastal areas or other areas with inland evaporites.

These three common sources of groundwater degradation can adversely affect the chemistry and hence the quality of groundwater thereby impairing its usefulness.

Mining and processing of metallic ore and coal have been major sources of both surface water and groundwater pollution (Ezeigbo, 1988, Plummer et al 2001). In such mines, groundwater pollution problems can be associated with active or old coal and metal mines. Coal deposits and iron ore, for example, are often associated with pyrite. Oxidation of pyrite due to the lowering of the water table at the mine followed by contact with water produces ferrous sulphate ($FeSO_4$) and sulphuric acid (H_2SO_4) solution. This acidic solution leads to reduction of pH of surface water or groundwater (Todd, 1980).

The main source of water in Itakpe is groundwater. Depth to water table in the area is generally between 3m – 10m below ground surface. The shallowness of the aquifers has significant impact on the quality of the groundwater. The aquifers in the study area are mainly tapped by hand dug wells. Such wells are exposed to possible pollution from surface sources such as direct settlement of mine dust, surface runoffs, etc. Contaminated water is known to cause serious health problems.

Itakpe is basically a rural area, playing host to the mining of iron ore from the Itakpe Hill for about 30years. The settlement of mine dust, flow of wastewater downhill from the mine and disposal of wastes coupled with the shallow nature of the aquifers makes the groundwater in Itakpe easily susceptible to pollution.

1.2 Study Area

1.2.1 Location and Access

The study area Itakpe and environs is a rural area in Okene Local Government area of Kogi State in central Nigeria. It lies within latitudes $7^0$36'N to $7^0$39'N and longitudes $6^0$17'E to $6^0$22'E. Itakpe is northeast of Okene and is about 10km along the Okene-Lokoja road. Fig.1.1 shows the location of study area, access roads and major geographic features.

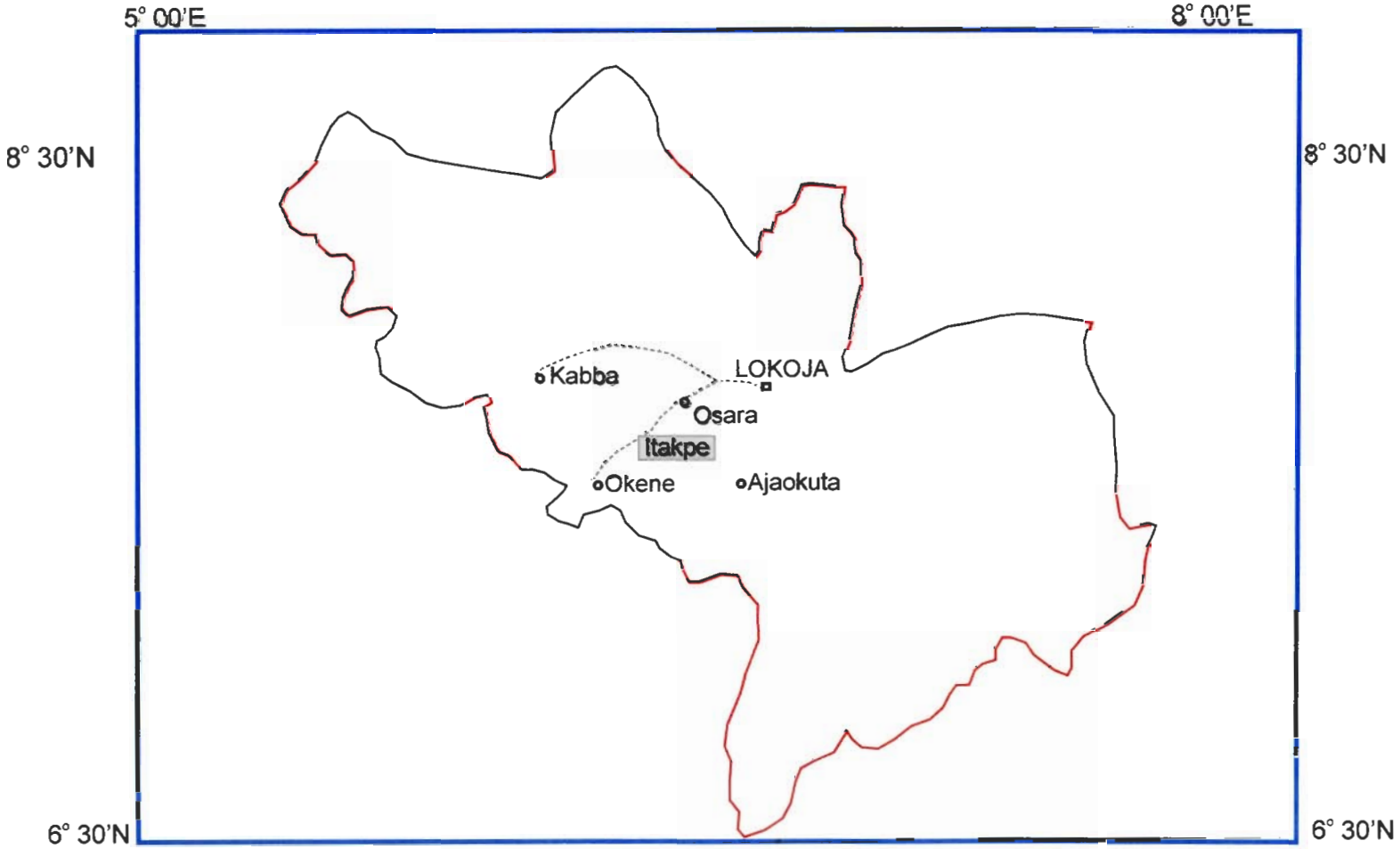

Fig 1.1 Map of Kogi State showing location of Itakpe and important towns

1.2.2 Climate and Vegetation

The climate of the area is similar to that of other parts of the middle belt of Nigeria with rainfall stretching for about seven (7) months from April to October and dry season lasting for five months from November to March (N.S.D.A. 1976). The mean annual precipitation at Itakpe is 1,200mm. The peak period of rain is between July and September with precipitation measuring between 200mm and 260mm with a short break experienced in August. Rainfall decreases down to 10mm – 15mm in December and January. Harmattan or cool Northeastern winds blow in the area for most part of the dry season. This is specifically intense in January and February. This is characterized by thin dust from the Sahara.

Relative air humidity varies from 80% between July and August to 60% between January and February. The monthly average temperatures range from 28^0C – 29^0C in July and August to 34^0C – 36^0C in (February and March).

The vegetation of the area is characteristic of the forest savanna with bush scattered low trees, grasses and shrubs.

1.2.3 Relief of the Area

The Nigerian Steel Development authority Report (1976) describes the relief of the area as a very hilly plateau dipping gently in the northeastern and eastern directions down to the Niger River valley.

At the southwestern part of the plateau, ground elevations range between 230m and 250m above mean sea level (a.m.s.l.) while those places closer to the River Niger are no more than 140m – 150m (a.m.s.l.). Many hills overlooking the plateau are made up of Precambrian gneisses and granites and long ridges with gentle to steep slopes.

The Itakpe Hill deposit strikes E-W for 3km. Its absolute elevations range from 310m to 410m a.m.s.l. i.e. 80m – 180m higher than the surrounding valleys. Fig.1.2 is a topographic map of Itakpe and its environs showing sample locations.

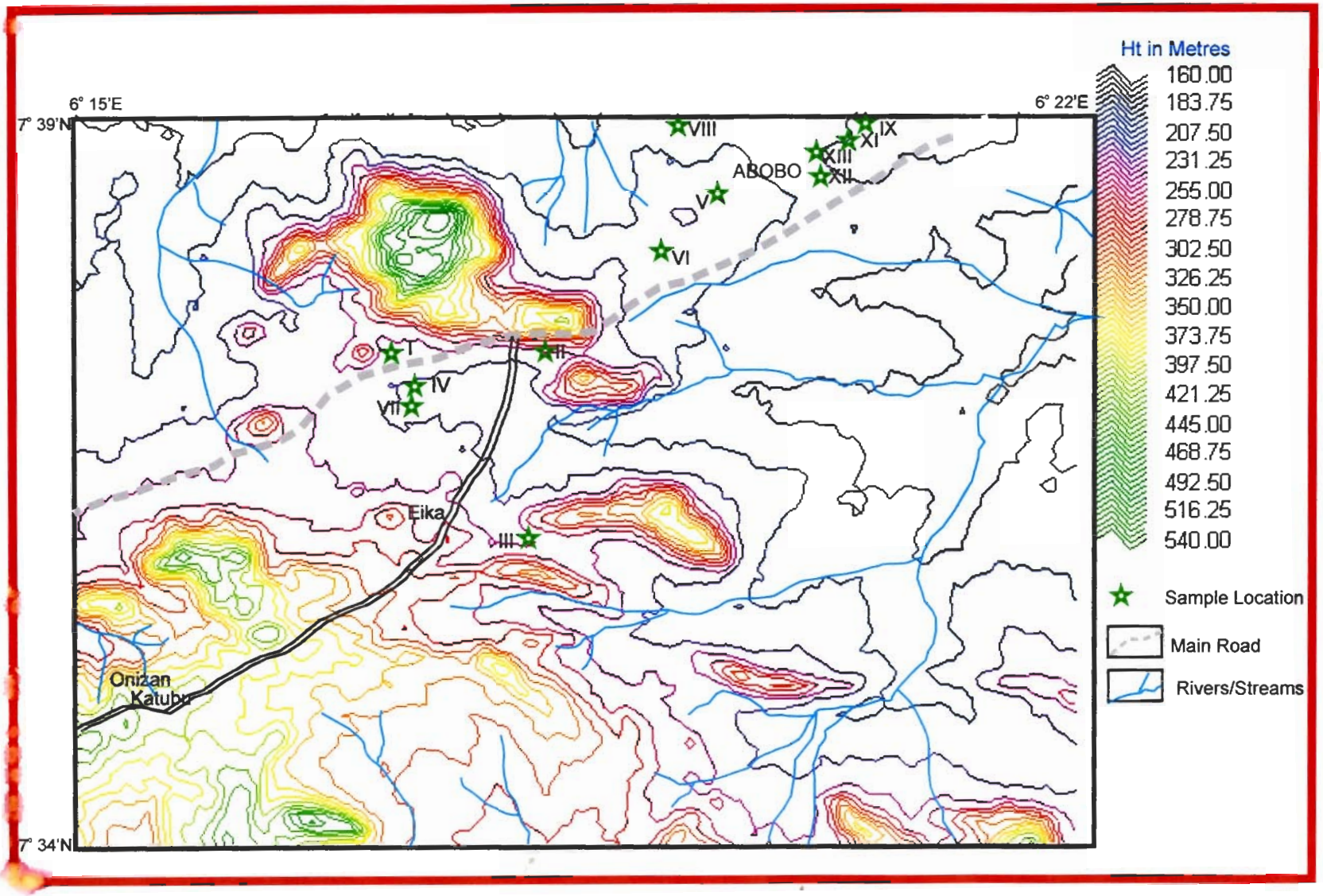

Fig 1.2 Topographic map of Itakpe and environs showing sample locations

1.2.4 Drainage of the Area

A few seasonal streams and rivers whose discharge are very variable are found within Itakpe during the rainy season. Most of these streams and rivers dry out almost completely during the dry season. All the rivers are tributaries of the Niger River. They are fed by numerous perennial rivulets and streams. At the feet of the hills and by river beds are occasional springs which are also fed by rains. Most of these dry out in the dry seasons.

Some of the important rivers include River Pompon which is a seasonal river flowing through the mine area. Osara River flows 10km from the mine area and has a considerable discharge for about half of the year. This river has been dammed at Osara.

1.2.5 People and Settlement

The Ebiras constitutes the indigenous population of Itakpe. The traditional occupation of the indigenes is mainly hunting, farming and rearing of animals. Blacksmiths used the iron ore in the past for the construction of weapons and farm implements like hoes, cutlasses, arrows, spear, etc. The settlement in Itakpe is the linear type, which is mainly due to the hilly nature of the area.

1.3 Statement of the Problem

The Itakpe iron ore deposit has a reserve of about 306, 854,000 tonnes made up of 189,672,000 tonnes of mineable reserve and 117,182,000 tonnes of geologic reserve (Akinrinsola, 1993). Mining works and beneficiation/mineral processing have been going on for over 20 years. About 28million tonnes of waste are expected to be excavated from the mine in order to produce 7.28 million tonnes of run – off – mine ore annually (NIOMCO, 2001). These wastes are disposed in nearby dumpsites thereby exposing them to atmospheric precipitation and surface runoff. The washing of the un-recovered and associated minerals alters the quality of the percolating water. Blasting to fragments of the massive rocks of both

ore and waste generates a heavy cloud of dust, which in turn leads to the settling down of the mineral rich dust. These end up percolating into the groundwater during infiltration.

The aquifer units in Itakpe, which is part of the Basement complex of Nigeria, are weathered and fractured with thickness varying from 20m to 40m or even more (Olarenwaju, et al 1997). The groundwater in such aquifer is generally unconfined and water table exists at shallow depths thus making it possible for the contaminants or percolating water carrying the contaminants to have rapid access to the aquifer.

Water polluted by metals, such as iron and manganese, has metallic taste and can stain surfaces or cause unpleasant taste of water (Fetter, 1980, Olarewaju et al, 1997). When large concentrations of some trace metals are ingested, health problems such as gastrointestinal disorder and cancer may be experienced. Water of low pH causes the corrosion of metal parts used in the industry (Olarenwaju, et al 1997). It can also lead to the wearing out of domestic utensils.

1.4 Objectives of the Study

The objectives of the study are to:

(1) Determine the broad geology and mineral (ore) setting in the study area.

(2) Determine the impact of iron ore mining and waste disposal on groundwater in Itakpe

(3) Proffer control measures for identified water pollution.

1.5 Literature Review

Though studies have been conducted on some aspects of the geology of Itakpe by several researchers, very little data are available on the hydrogeology or quality of water within the study area. The literature review is based on work carried out locally and abroad on the geology, effects of mining and wastes disposal on the water quality.

The Nigerian Steel Development Authority (N.S.D.A, 1976), gave a detailed report on prospecting and exploration of Itakpe – hill iron ore deposit (Okene – Nigeria).

Olade (1978) presented a detailed account of the Precambrian iron ore deposit and its environment at Itakpe ridge. He was able to delineate three main ore bodies with each comprising a group of ferruginous quartzite bands or lenses.

Adegbuyi (1981) carried out a petrographic and geochemical study of Itakpe ridge iron ore deposit, Okene Nigeria in relation to ore genesis.

Fadare (1982), worked on Precambrian banded iron formation of Okene – Ajaokuta area of Kogi State, Nigeria.

Annor (1983) wrote on metamorphism of pelitic rocks in relation to deformation episode around Okene, Nigeria.

Annor and Freeth (1985), wrote on the thermo tectonic evolution of the basement complex around Okene Nigeria with special reference to deformation mechanism.

Ezeigbo (1988), in his paper on geological and hydrogeological influences on the Nigerian environment identified sources of water degradation to include dissolution of constituents in water during its movement, poor waste disposal and saltwater intrusion due to poor groundwater abstraction in coastal areas or other areas with inland evaporites deposits.

Ezeigbo (1988), Plummer et al (2001) presented mining and processing of metallic ore and coal as major sources of both surface water and groundwater pollution.

Akinrinsola et al (1993) carried out a geostatistical ore reserve estimation of the Itakpe iron ore deposit using data from existing exploratory borehole in estimating the ore deposit.

Ezepue and Odigi (1993) studied the petrology and geochemistry of monzodiorites and granites from the Precambrian terrain between Kabba and Lokoja, SW Nigeria. They determined the average composition of the monzodiorites, granodiorites and granites which occurred in Agada – Obajana – Ilubeschi – Itakpe District between Kabba and Lokoja.

In a work on the petrochemistry of gneisses from Kabba – Lokoja area, southwestern Nigeria, Odigi and Ezepue (1993) showed that the Kabba – Lokoja gneisses consist of quartz – biotite

gneisses, quartz – biotite hornblende – pyroxene gneisses and quartz – biotite – garnet gneisses. The quartz – biotite gneisses and quartz – biotite – hornblende – pyroxene gneisses have similar chemistry with enrichment in SiO_2 and depletion in total Fe_2O, MgO, CaO and TiO_2 relative to quartz – biotite – garnet gneisses.

Olarewaju et al (1997) investigated the chemical characteristics of groundwater from some parts of the basement complex of central Nigeria. Their study covered parts of Niger, Kwara and Kogi State basement complex areas. They concluded that the groundwater from the study area can be said to be generally of good quality and hence potable. They however recommended routine chemical analysis of water samples to detect if there is any deterioration in the water quality especially in the urban areas prone to pollution.

Idowu and Ajayi (1998), comparing occurrence of groundwater in two geological environments in southwestern Nigeria, showed that partially to highly decomposed in situ materials and fractured rock materials constitute the basement aquifers. They also showed that water from basement aquifers are expected to be slightly to moderately hard.

Bala and Onugba (2001) carried out a preliminary chemical assessment of groundwater in the basement complex area within the Bunsuru and Gagere sub–basins, northwestern Nigeria. Their study involved laboratory assessment of the chemical quality of groundwater within the rocks of the sub – basins of the Sokoto – Rima drainage basin. They identified Ca – Mg – Cl – SO_4 and Ca – Mg – HCO_3 as the two water types within the basin though the general grouping would tend towards the Ca – Mg – SO_4 water type. The sodium adsorption ratio (SAR) values indicate that the water is also suitable for irrigation.

Abimbola et al (2002), in their paper environmental impact assessment of waste dumpsites on the geochemical quality of water and soils in Warri metropolis, southwestern Nigeria, showed that leachates from wastes that come in contact with groundwater in shallow aquifers and

favorable geologic conditions like permeable sandy lithology, heavy precipitation and shallow water table assist in the introduction of pollutants into groundwater systems.

Abimbola et al (2002) carried out a study on the influence of bedrock on the hydrochemical characteristics of groundwater in northern part of Ibadan metropolis, southwestern Nigeria. They concluded that chemical composition of groundwater especially those from weathered zone (hand dug wells) depends primarily on the chemical weathering of the underlying bedrocks.

Offodile (2002) presented a report on the regional hydrogeology of Nigeria. He classified Nigerian groundwater into four groups based on their chemical characteristics, namely predominantly calcium bicarbonate water, sodium chloride waters, magnesium sulphate water and mixtures of magnesium sulphate, sodium chloride and calcium bicarbonate water.

Tijani et al (2002) worked on the hydrochemical and environmental impact assessment of Orita Aperin waste dumpsite, Ibadan, southwestern Nigeria. They concluded that the leaching of conserved waste materials from the dumpsite into the subsurface water has significant effects on the groundwater quality most especially the shallow aquifers in the weathered horizon.

Ogunbajo (2004) carried out a geochemical evaluation of water resources in and around Ijebu – Ode town southwestern Nigeria and its environmental implications. He discovered that most of the water sources in the study area are freshwaters with alkaline and alkaline earth characteristics. He also discovered that the contamination/pollution of the subsurface water is most likely from dissolution of bedrocks through which they flow.

Ogunbajo and Kolajo (2004), worked on the impact of solid waste disposal on the chemical quality of surface water and groundwater sources in parts of Ibadan metropolis, southwestern Nigeria. Using the trace metals Fe, Cu and Pb as indices for their investigation, they concluded that both the surface water and groundwater sources have been contaminated and

polluted due to the objectionably high concentration of the trace metals with respect to WHO (2004) and European Union (1996) standards for drinking water.

Barnes et al (1964), in their work on the geochemistry of groundwater in mine drainage problems concluded that mines can produce a variety of groundwater pollution problems.

Enrich and Merritt (1969), worked on effects of mine drainage on groundwater while Mink et al (1972), worked on effects of early day mining operations on present day water quality. They all concluded that the pollution depends on the material being extracted and the milling process; coal, uranium and phosphate mines are major contributors, while metallic ores for production of iron, copper, zinc and lead are also important.

Ahmad (1974), writing on the effects of coal mining on water quality, observed that mining and milling expose overburden and waste rock to oxidation. Oxidation of pyrite produces sulphuric acid. An example is the Appalachian region of eastern United States, where 6000 tonnes of sulphuric acid is produced daily in this manner.

Ralston and Morilla (1974), Norbeck et al (1974), in their respective works on groundwater movement through an abandoned tailing pile and groundwater leaching of lignite tailing deposits in the Coeur d'Alene district of Northern Idaho, concluded that the lower pH of the water draining through mineralized spoils and tailings can also leach heavy metals as well as soluble calcium, magnesium, sodium and sulphates.

Klusman et al (1977) observed that groundwater moving through mineralized rock may have a higher concentration of certain heavy metals than groundwater movement through non – mineralized districts.

Miller (1980), worked on waste disposal effects on groundwater. He observed that water pumped by dewatering to expand both surface and underground mines below water table may be highly mineralized and is frequently referred to as acid mine drainage. Such mine

drainages are normally characterized by their low pH and high iron, aluminum and sulphate content.

De Fetter (1980) listed some chemical and biological contaminants responsible for groundwater contamination. They include groups of metals, non metals, organics and organisms. He went on to say that water from recharge or moving groundwater can leach chemicals from buried solid wastes.

Kashef (1986), in his book groundwater engineering said "changes in groundwater quality are due to the varying quality of the infiltrated precipitation, the reaction of groundwater to its environment, the length of the flow path, the residence time of water in a certain location, vegetative types and human - determined features". He presented changes in chemical quality to be more intense in shallow aquifers than in deeper ones because shallow aquifers are more easily affected by seasonal variations and human activities. Also chemical precipitation removes ions in solution by forming insoluble compounds thus changing the chemical quality of water.

Domenico and Schwartz (1998), in discussing sources of groundwater contamination described trace metals as capable of being toxic and even lethal to humans even at relatively low concentrations because of their tendency to accumulate in the body. Some studies have found positive correlations between the concentration of trace metals in water and death rates from some cancers.

CHAPTER TWO

GEOLOGY AND HYDROGEOLOGY

2.0 General Introduction

The geologic setting of Itakpe area is that of two distinct complexes of rocks; (a) pre – Cambrian rocks which have undergone intensive tectonic and metamorphic changes and are commonly referred to as the basement complex and (b) Mesocenozoic deposits only slightly affected by the process (N.S.D.A., 1976).

The Nigerian basement complex is part of the Pan African mobile belt and lies within the West African Craton and South of the Tuareg Shield (Black 1980). The basement complex of Nigeria includes those of the North Central Nigeria, the Southwestern Nigeria and the Eastern province (Fig. 2.1.a). The three broad lithological groups within the Nigerian basement complex are the migmatite gneiss complex made up largely of migmatite and gneisses of various compositions, the low grade sediment dominated schist belt and the granitic rocks which cut both the migmatite gneiss complex and the schists belt (Ajibade and Woakes, in Kogbe 1980).

2.1.1 Geology of the Southwestern Basement Complex of Nigeria

The study area is an extension of the basement complex of southwestern Nigeria characterized by schists that do not form well defined belts and are poorly exposed. The poor exposure is due to tropical climatic conditions and rainforest vegetation in the region. The basement complex of southwestern Nigeria is underlain by a generation of schists belonging to the migmatite gneiss complex sequence of probable Archean to early Proterozoic age and a generation belonging to the late Proterozoic age. A simplified geological map of Nigeria showing the schist belt and exposure of basement complex rocks (adapted from Kogbe, 1980) is shown in fig 2.1b

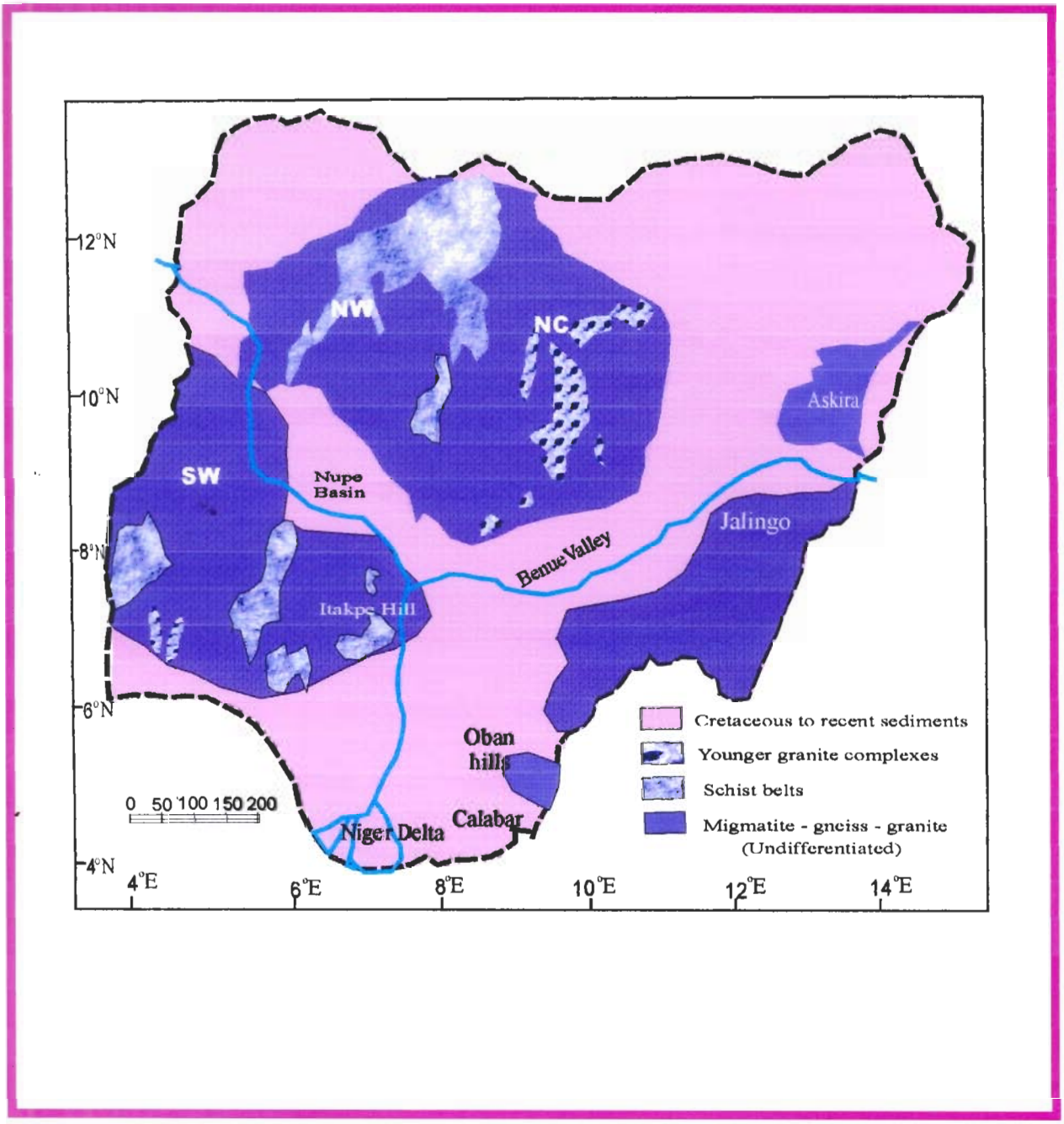

Fig 2.1 Geologic Map Of Nigeria showing the schist belts (modified from Kogbe, 1980)

2.1.2. Local Geology

The Itakpe iron ore deposit is localized within the gneiss – migmatite – quartzite unit of the Nigeria basement complex (Akinrinsola and Adekeye, 1993). N.S.D.A. (1976) reported that migmatite gneiss series is exposed almost throughout the whole of the area. Some parts of the exposures are represented by a uniform measure of migmatise biotitic gneisses and migmatites with thin horizons and intercalations of amphibolites. These exposures are located between Okene and Lokoja. Fig. 2.2 is a geological map of Okene and its environs. Olade et al (1978) noted that the dominant lithological units in the area are the granodiorite – tonalite gneiss, overlain by a sequence of low grade metasediments and intruded by granodiorites and granitic rocks. The main rock types identified in the area include granite gneiss, amphibolites, quartzites, schists, granites and pegmatites.

The quartzites in the area are ferruginous and non – ferruginous with the ferruginous quartzites occurring as magnetite - rich and hematite – rich bands and lenses of 10m – 60m wide in alternation with gneisses. The non ferruginous quartzites are rare on the Itakpe hill but constitute the bulk of the rocks on its southern edge. The three main ore bodies delineated in the area comprise of a group of ferruginous quartzite bands or lenses. The ore deposits have been folded and faulted and affected by regional metamorphism. A geological map of Itakpe iron ore deposit is shown in figure 2.3

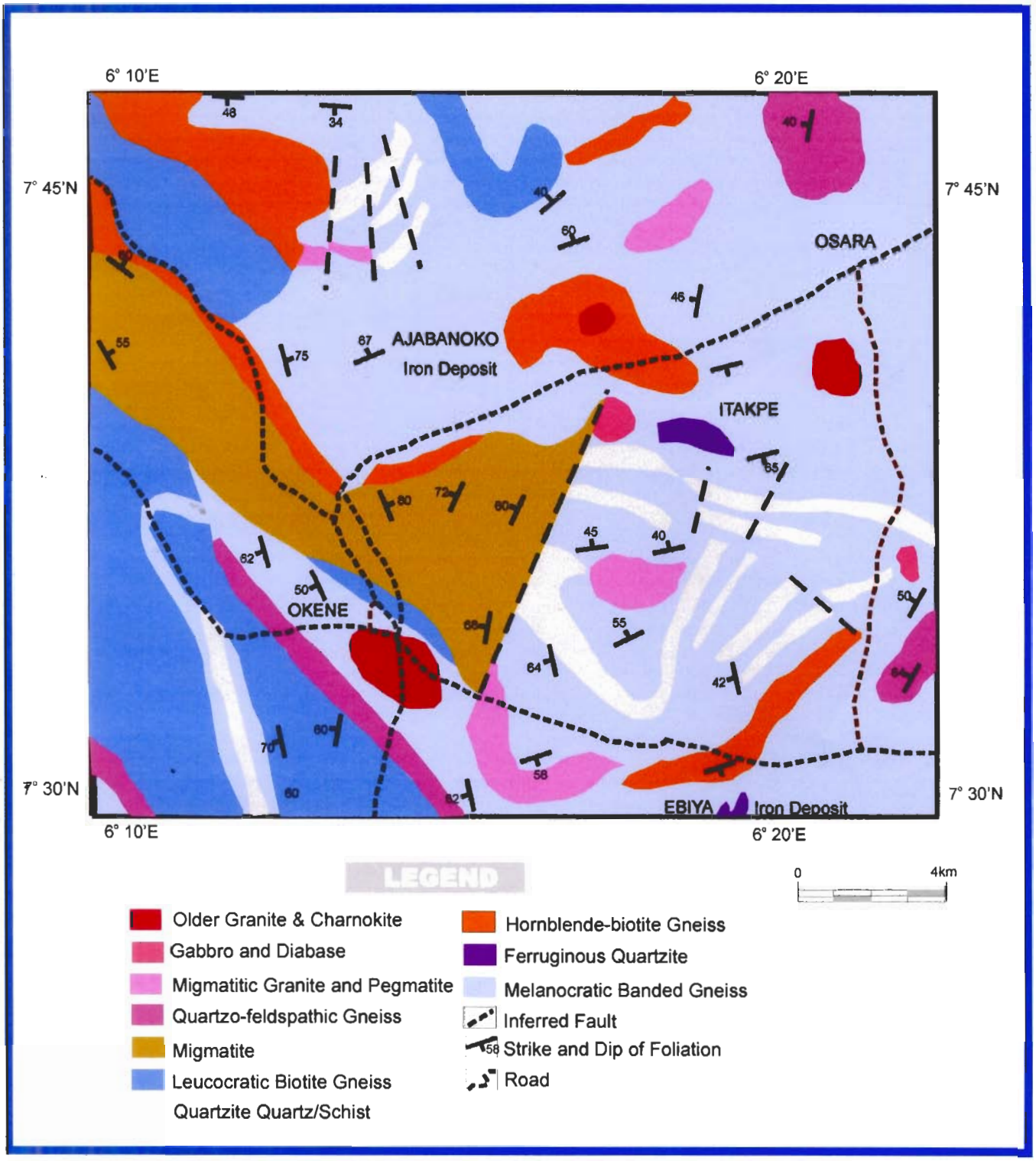

Fig 2.2 Geologic map of Okene area (modified from Adegbuyi, 1981)

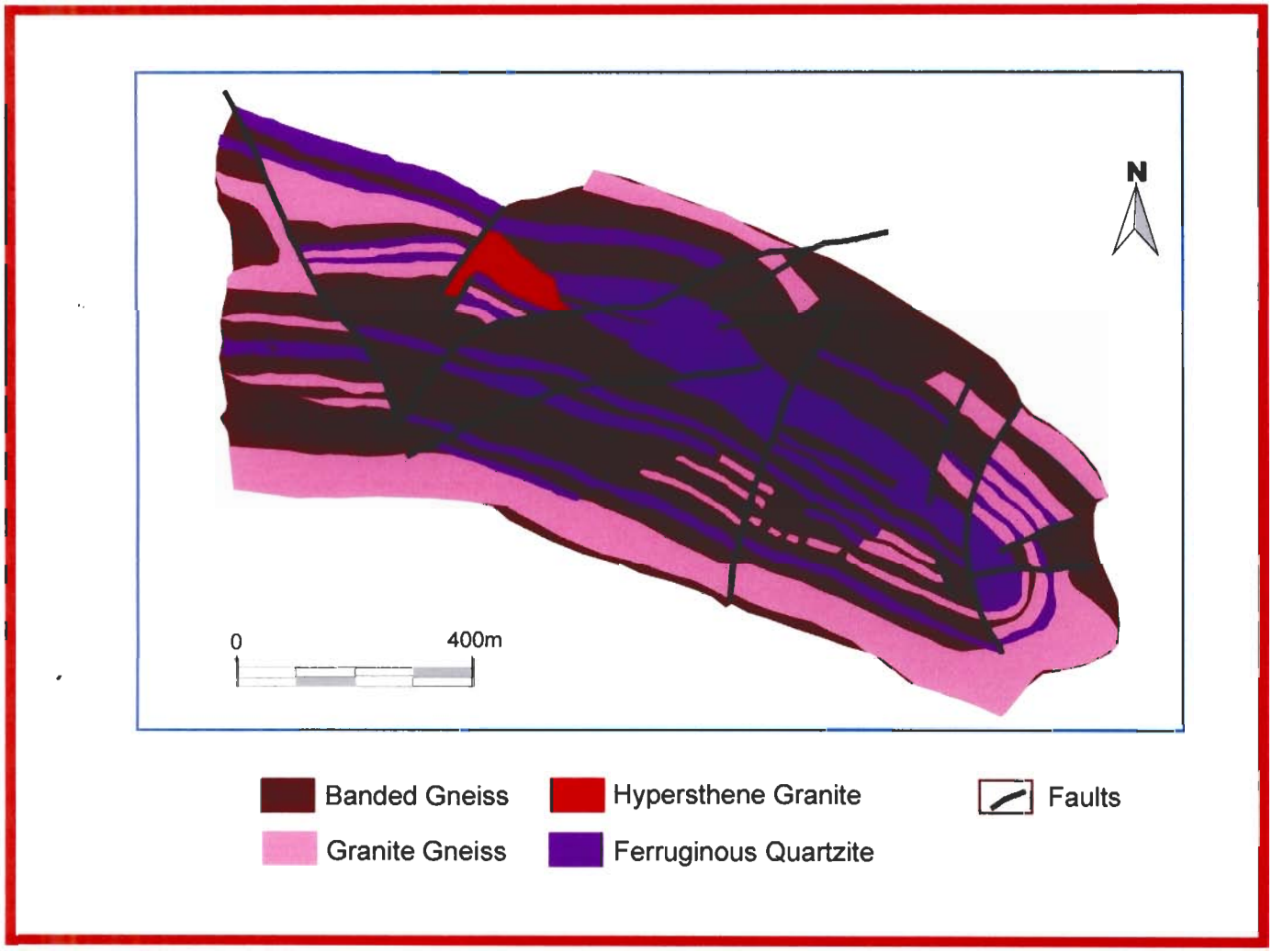

Fig 2.3 Geological Map of Itakpe Iron Ore Deposit (Modified from Akinrisola and Adekeye, 1993)

2.1.3 Major Rock Types

The description of the rock types is based on the works of Nigerian Steel Development Authority (1976), Olade (1978) and Akinrinsola 1993. The Itakpe iron ore deposit is a Precambrian iron formation of the migmatite gneiss suite of the basement complex of Nigeria and comprises of over 25 individual ore bodies with 14 being most prominent, that interbanded with migmatites, gneisses, schists, amphibolites, quartzite, and that are intruded in some places by granites, pegmatites and aplites all of which form a ridge over 4km long. The quartzites in the area are both ferruginous quartzites and non–ferruginous quartzites.

Ferruginous Quartzites/Iron ore

Ferruginous quartzites consist of alternating bands of quartz and iron oxide (hematite and magnetite) the ore – bearing strata could therefore be grouped as ferrosilicate deposit while chemically the ore itself is composed of mainly alternating bands of quartz and iron oxide. The ores in the area can be described as coarse, medium or fine because there are large proportions of fine and coarse grained ores in different locations. The ore layers occur parallel to one another and there are 14 main layers in the Itakpe hill deposit.

Migmatite

These are rocks of complex structure and composition. They consist of a palasome of gneisses, amphibolites and schists and metasome of intensive quartz of feldspartic quartzite and pegmatites. In some strongly deformed areas they include in their matrix pegmatitic crystals of tourmaline, hornblende and mica. On the Itakpe hill, migmatites occur as high grade metamorphic rocks and they occur as gangue

Non – Ferruginous Quartzite

The non ferruginous quartzite found at Itakpe can be categorized as coarse grained massive variety, highly fissile and schistose variety and bedded.

The quartz grains often contain minor inclusions of iron oxide. Other accessory minerals include biotite, cordierite, silimanite and iron oxide.

Banded Gneiss and Biotite Hornblende Gneiss

Gneiss found in the area is banded and of high – grade metamorphism. The structures consist of alternating melanocratic and leucocratic bands. The amount of mafic portion of the gneisses is so high that banding is ill defined.

Pegmatites

Intense alkaline (potassic) metasomatism enhanced the formation of pegmatite veins along contact and weakness zones across the general strike of the deposit. The veins trend generally NNE – SSW and occur at irregular intervals. The pegmatites are mainly light coloured, coarse grained with graphic texture defined by intergrowth of quartz in feldspar. Some of the veins contain reasonable amounts of some economic minerals that include quartz, beryl (aquamarine) tourmaline, feldspar (K – feldspar) and flakes of biotite.

Amphibolites, Amphibole Schist

These rock types associate with migmatites and gneisses. They have weak schistocity as a result of alignment of biotite and hornblende plates. They are in the medium grade metamorphism consisting dominantly of lepidoblastic hornblende, brownish laths of biotite, minor quartz, and meta – blastic iron oxides.

Aplite

The sample from the Itakpe hill are sugar textured, light pink rocks consisting of small grains of dark minerals, some of which are surrounded by alternation haloes giving the rock a sparse uneven motley appearance. Microscopic examination of the samples reveals that microcline has anhedral crystals amounting to 75%, quartz–15% and plagioclase 10%. The three minerals occur essentially as a mosaic, small amounts of smaller grains of quartz and plagioclase occur as inclusions in the microcline crystals. They consist of opague and minute

euhedral crystals of monazite. Alternation haloes around the monazite are thought to be related to its radioactive property.

Granite

These are found intruded into the migmatite and gneisses. They are medium to coarse grained, porphyritic lenlogranites. The rock specimen has even motley of light and dark minerals in certain places.

Laterite

This is the youngest formation at Itakpe hill. They occur around the outer margins of Itakpe hills, occasionally boulders of good quality, fine grained friable ore and quartzite are embedded in them.

2.2 HYDROGEOLOGY OF ITAKPE

Itakpe belongs to the basement complex province of Nigeria, which includes the oldest known rocks in Nigeria. Egboka in his unpublished paper on the hydrogeological provinces of Nigeria described the rocks of the basement complex provinces as having been variously weathered to form a mantle of residual soil. Also, series of fractures traverse the rock masses and the joints and faults have weathered zones. Groundwater occurrence is confined to shallow water table aquifers that are found in the weathered mantle, fractured and/or faulted traces. The weathered mantle is often too thin to trap good quantity of water during the rainy season and is very susceptible to water table lowering during the dry season. It is often too clayey to be of good permeability even though the porosity may be high.

N.S.D.A. (1976) described the aquifers found within Itakpe. Developed within the boundaries of the deposit and in areas adjoining it, are fissures, water filled pores and fractures in the weathered crust as well as the fractures in un-weathered crystalline rocks. In the crust of weathering, the rocks have been weathered to various degrees and sometimes into sand and

clay. The depth of weathering is between 9m – 54m. The weathering of rocks makes it very possible for atmospheric precipitation to infiltrate into the rocks.

Depth to water table at Itakpe varies from 3.4m to 64.3m depending on the elevation of the ground surface at the point of measurement (N.S.D.A. 1976). The elevation of water table varies from 175m above mean sea level (a.m.s.l) to + 328.2m a.m.s.l. Geological records of boreholes and resistivity loggings carried out in some boreholes as well as results of well pumping tests, show that the depth of the zone of fracturing varies from 23.8m to 120.7m (NSDA,1976). Aquifer thickness varies from 13.4m to 72.5m. Discharge of water at some of the boreholes within Itakpe is about 3.6×10^{-6} m^3/s. Temperature of water varies from 27^0C to 30^0C when atmospheric temperature is between 24^0C and 29^0C.

CHAPTER THREE

HYDROGEOCHEMISTRY

3.1 Sampling and Analytical Methods.

Groundwater samples were collected from twelve locations while surface water was collected from a seasonal stream within the study area. A pair of samples was collected from a pond of water at the mine site. The samples were collected in March, 2007 at the peak of the dry season to prevent the dilution effect of precipitation during the rainy season and contaminating effects associated with storm water runoff (Thomson, 1996). Sampling effectively covered the study area by taking samples from all the available wells and boreholes.

Depth to water level in the open (shallow) wells ranged from 3m to 15m with average depth of 9m. The depths of the (deep) boreholes ranged from 30m to 35m.

The water samples were collected in pairs for every location in two (2) liter white plastic containers. The samples meant for cation determination were acidified with trioxonitrate (V) acid (HNO_3) to prevent the cations from adhering to the surface of the container thereby making them to remain in solution. The second pair of samples meant for anion determination was not acidified.

Parameters that change rapidly with time after water withdrawal were measured on the field as soon as samples were collected. The parameters are temperature, pH and electrical conductivity (EC). pH was measured using a portable pH meter. Temperature and electrical conductivity were also measured with a potable electrical conductivity meter. The geographical location and elevation of each sampling point above sea level was measured using a Global positioning system (GPS) kith. These are shown in fig.1.2.

The water samples were analyzed for the following cations, heavy metals and anions; Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^+, Cu^{2+}, Zn^{2+}, Ni, Pb, Ti, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Si as $Si0_2$ and

TDS. Hardness was calculated. The digested samples were used for the cations and heavy metal analysis using the inductively coupled plasma (ICP) optical emission spectrometer. Details of methods and Techniques of (ICP) used by the PERKIN ELMER instrument (Boss et al, 1999) are discussed in appendix C.

The undigested samples were used for the anion analysis. Chloride (Cl^-) ion was determined using the "mercury (II) nitrate method (Ademoroti, 1996). Details of the method are presented in Appendix C.

Sulphate (SO_4^{2-}) ion was determined by the "turbidimetric method (Ademoroti, 1996). This is presented in Appendix C.

Nitrate ion concentration was determined by the Calorimetric method using a spectrophotometer used at 420nm. Details of the method as explained in Ademoroti, (1996) are presented in Appendix C.

3.2 Results And Data Presentation

For ease of visual inspection, the chemical data are presented by the combined use of tables, graphs, and maps. Each of the method presents the concentrations of the major ions in the water samples in milligrams per liter. Each graph or map for each sample represents a particular character of the groundwater under study. Details of geochemical data are presented in table 2 of appendix A.

3.2.1. Pie Charts

The relative concentration/abundance in meq/l of the major chemical parameters is presented with the aid of a pie chart in fig (3.1) for easy visual description.

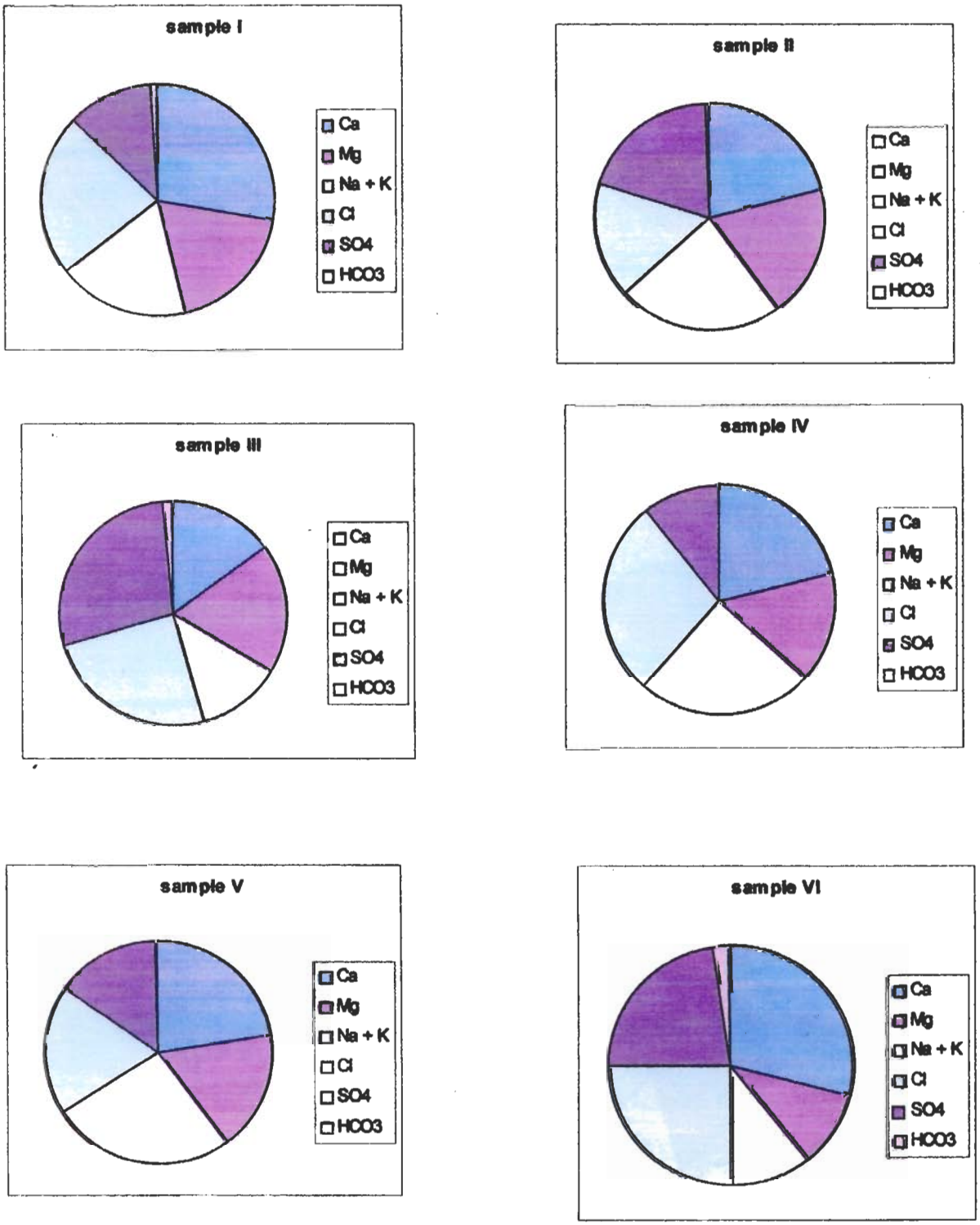

Fig. 3.1a Chemical Analysis of groundwater represented by pie diagrams.

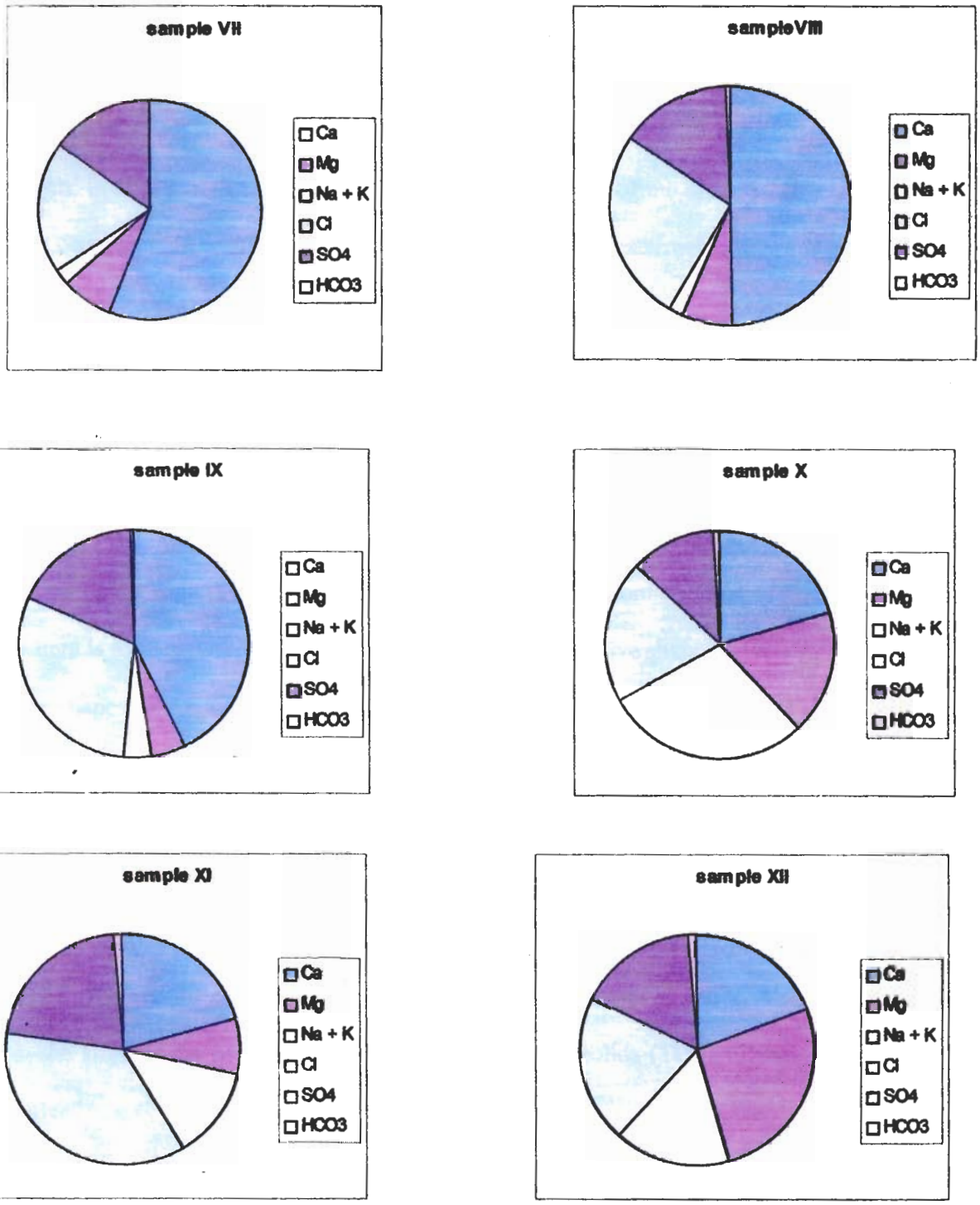

Fig. 3.1b Chemical Analysis of groundwater represented by pie diagrams.

The pie charts reveal a mixed order of cationic concentration in the groundwater with four samples of the order $Ca^{2+} > Mg^{2+} > Na^{+}+K^{+}$, three samples are of the order $Na^{+}+K^{+} > Ca^{2+} > Mg^{2+}$, two samples are of the order $Mg^{2+} > Ca^{2+} > Na^{+}+K^{+}$ and two samples of the order $Ca^{2+} > Na^{+}+K^{+} > Mg^{2+}$. The anionic concentration of the samples is of the order $Cl^{-} > SO_4^{2-} > HCO_3^{-}$ in nine samples while two of the other samples are of the order $SO_4^{2-} > Cl^{-} > HCO_3^{-}$. The concentration of the carbonates in the water samples is extremely low, almost negligible

3.2.2 Stiff Diagrams

The groundwater analysis is shown in figure 3.2. using Stiff diagrams. These diagrams facilitate rapid comparison of results using the absolute concentration in meq/l (Freeze and Cherry, 1979).

In this plot, concentrations of cations are plotted to the left of a vertical zero axis and anions to the right (Todd, 1980). When the resulting points are connected, an irregular polygonal pattern is formed; water of similar qualities define a distinctive shape.

The shapes of the Stiff plots in samples I, VI, VII, IX, XI, XIII are similar and thus are of similar water quality.

The shapes of the Stiff plots in samples II, IV, and X are similar and thus are of similar quality

The Stiff plots in Samples III and XII are similar in shape and thus are of water quality.

The Stiff diagrams show that there are three different qualities of water. Also the differences in the sizes of the plots show that the total dissolved solids (TDS) values for the samples differ.

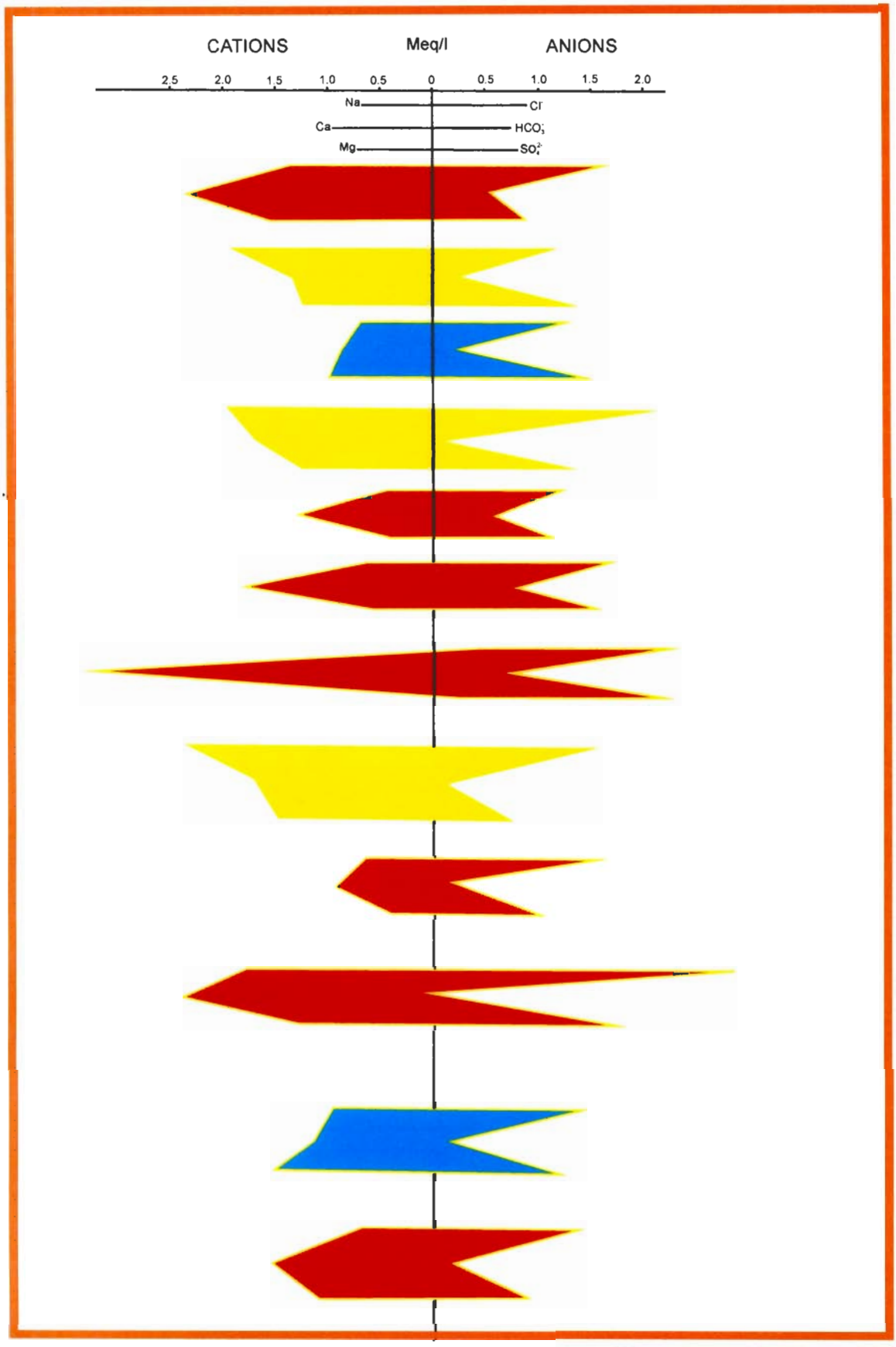

Fig 3.2 Stiff diagrams for representing analysis of groundwater quality

3.2.3 Schoeller Semi logarithmic Diagram

Schoeller diagram is a semi logarithmic plot used for comparing groundwater samples (Todd, 1980). In this plot, the principal ionic concentrations, expressed in milli-equivalents per litre are plotted on six equally spaced logarithmic scales as shown in fig 3.3 below.

The plot shows both the absolute value of concentration of each ion as well as the concentration differences among various groundwater analyses (Todd, 1980).

If the straight lines joining the ends of two ions in one water sample are parallel to another straight line joining the ends of the same two ions in another water sample, the ratio of the ions in both analyses is equal.

Based on the nature of the diagrams, the groundwater samples are grouped into four with different orders of cationic concentrations.

The order of anionic concentrations of the samples are grouped into two with nine samples belonging to one group and two belonging to the other group as shown in fig.3.3

Cations:	Group 1	$Ca^{2+} > Mg^{2+} > Na^{+} + K^{+}$
	Group 2	$Ca^{2+} > Na^{+} + K^{+} > Mg^{2+}$
	Group 3	$Na^{+} + K^{+} > Ca^{2+} > Mg^{2+}$
	Group 4	$Mg^{2+} > Ca^{2+} > Na^{+} + K^{+}$
Anions:	Group 1	$Cl^{-} > SO_4^{2-} > HCO_3^{-}$
	Group 2	$SO_4^{2-} > Cl^{-} > HCO_3^{-}$

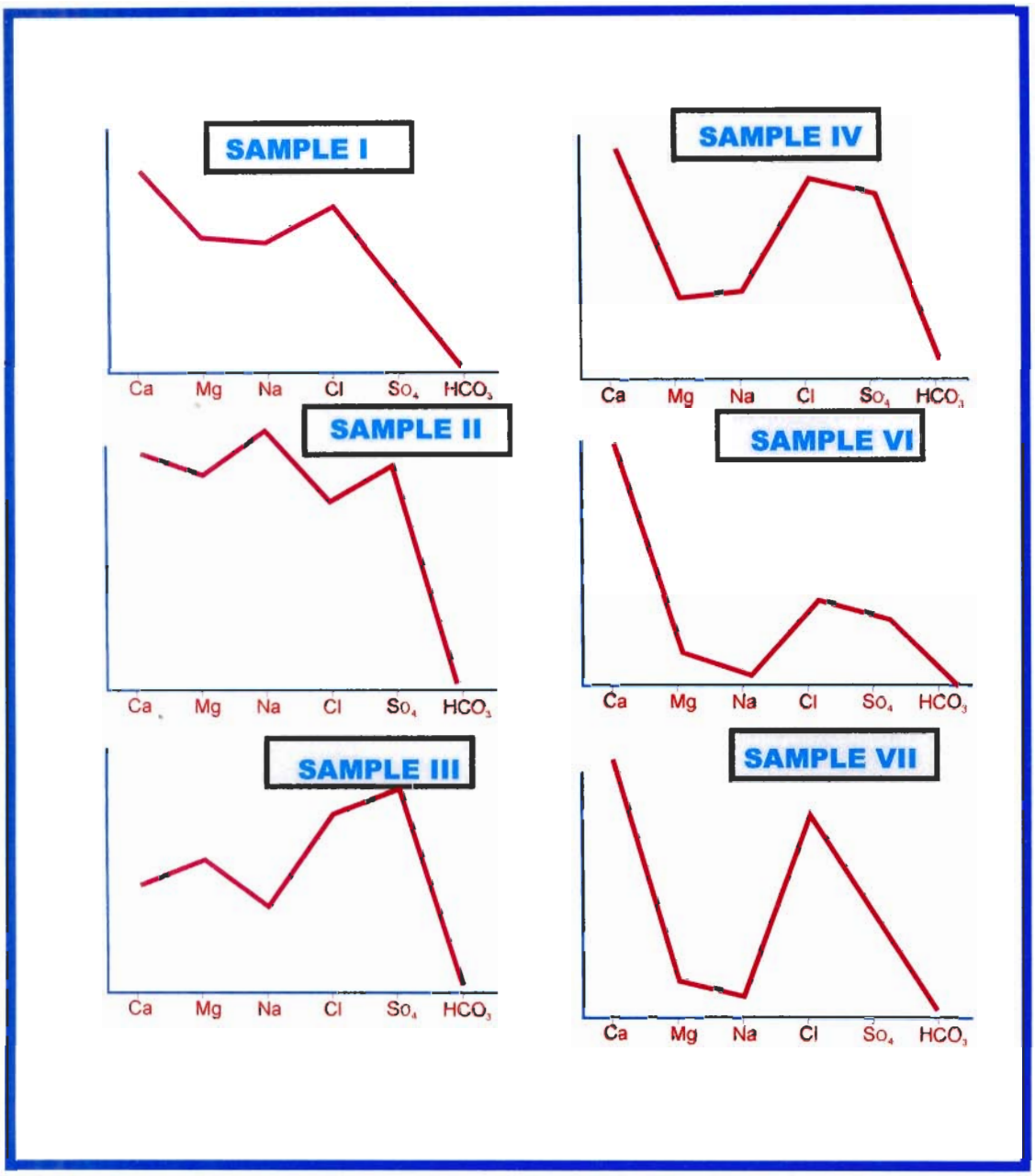

Fig 3.3a Schoeller semi-Logarithm diagram plotted in six logarithm scales

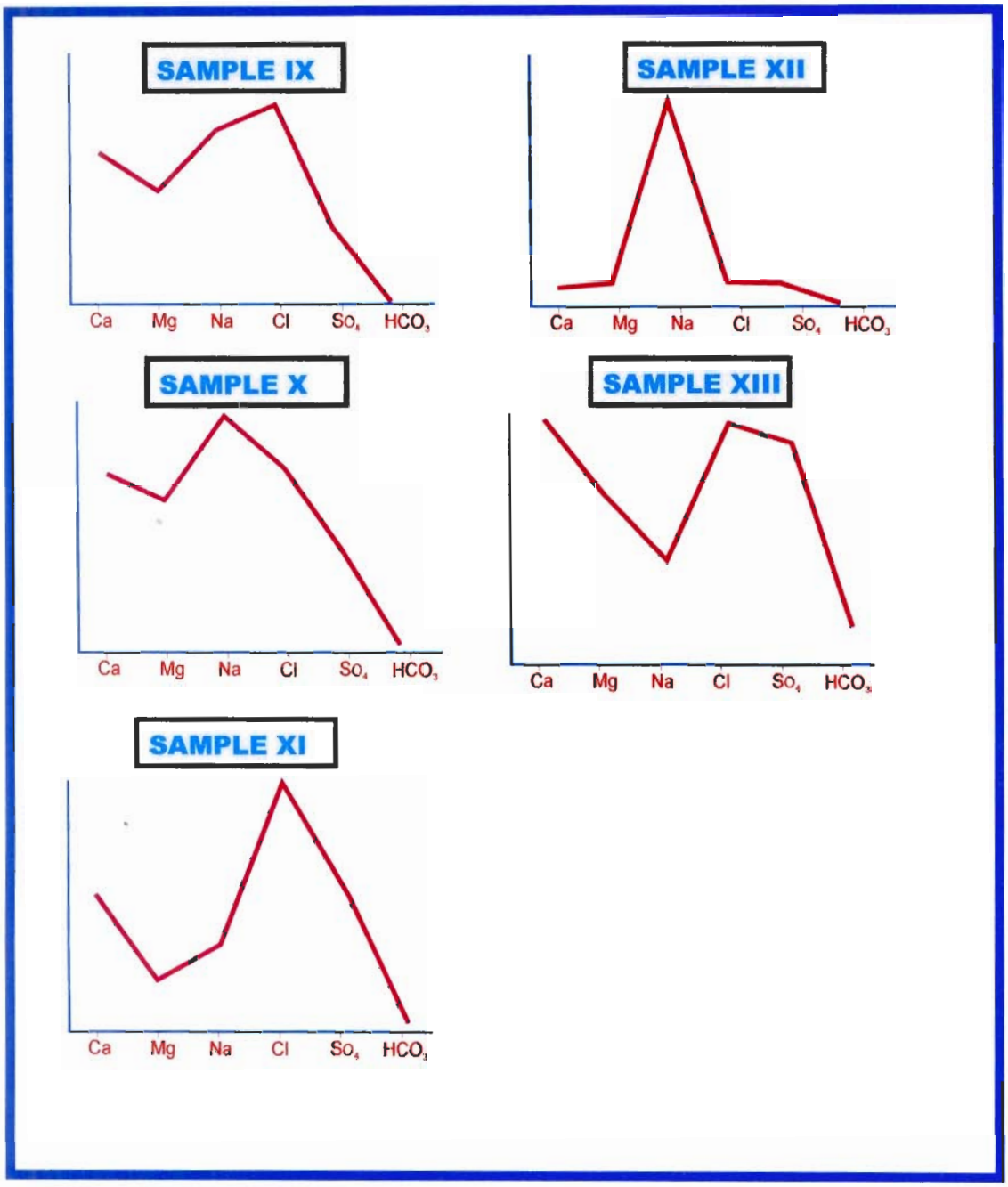

Fig 3.3b Schoeller semi-Logarithm diagram plotted in six logarithm scales

3.2.4 Piper Trilinear Diagram

The Piper trilinear diagram in Fig.3.4 presents the concentrations of major ions as percentages and permits the cation and anion compositions of many samples to be represented on a single graph in which major groupings or trends in the data can be discerned visually (Freeze and Cherry, 1979).

Cations expressed as percentages of total cations in milli-equivalents per litre plot as a single point on the left triangle; while anions appear as a point in the right triangle (Todd, 1980, Freeze 1979, Piper, 1944). These two points are projected into the central diamond–shaped area parallel to the upper edges of the central area. This single point plotted is thus uniquely related to the total ionic distribution.

The trilinear diagram conveniently reveals similarities and differences among groundwater samples because those with similar qualities tend to plot together as groups. Fig 3.5 is a Piper's trilinear diagram used by Back (1966) in classification of anion and cation facies in terms of major – ion percentage. Fig.3.6 is a template for classifying waters into facies for cations and anions from Back (1961).

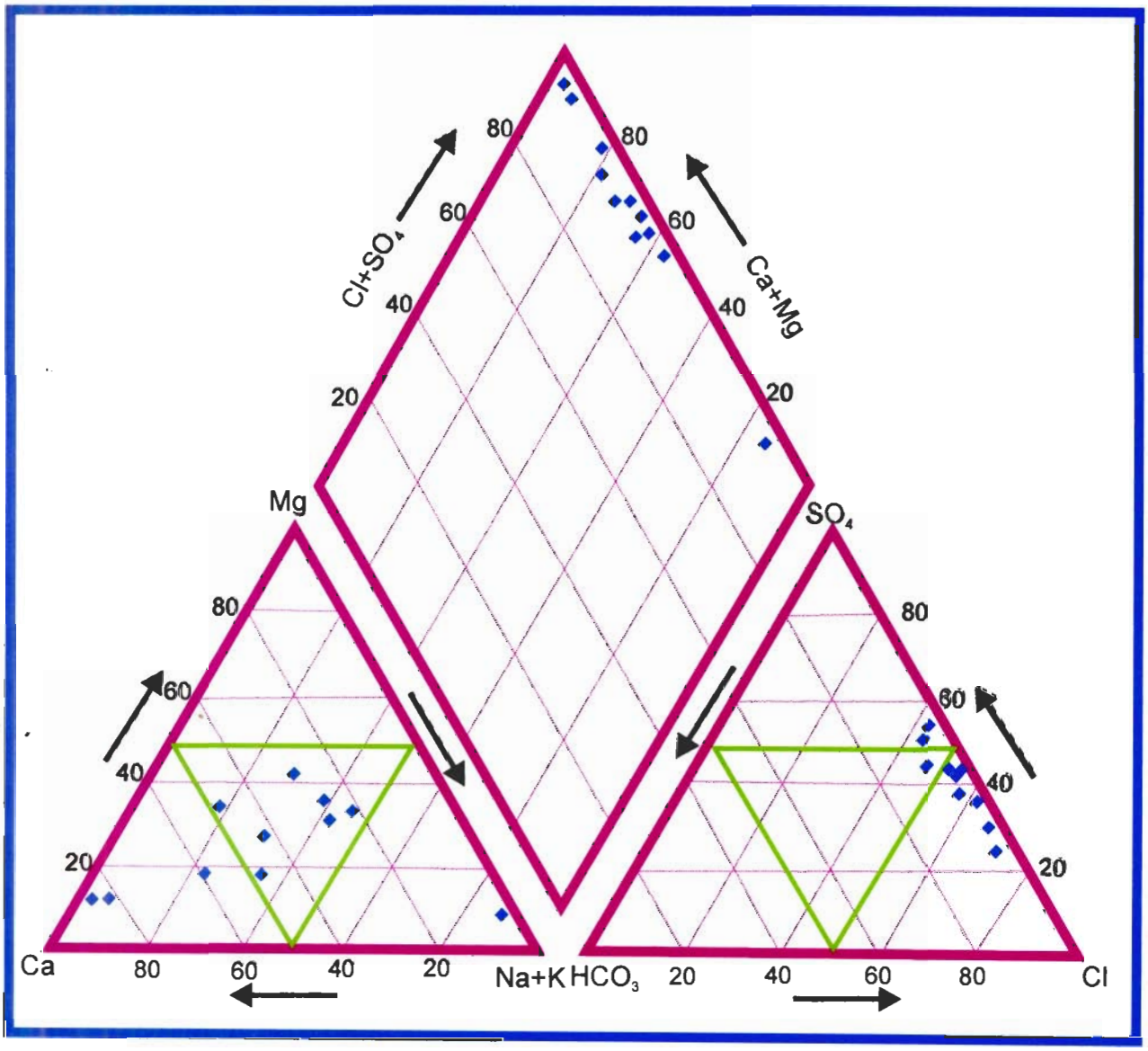

Fig 3.4 Piper's trilinear diagram for classifying groundwater

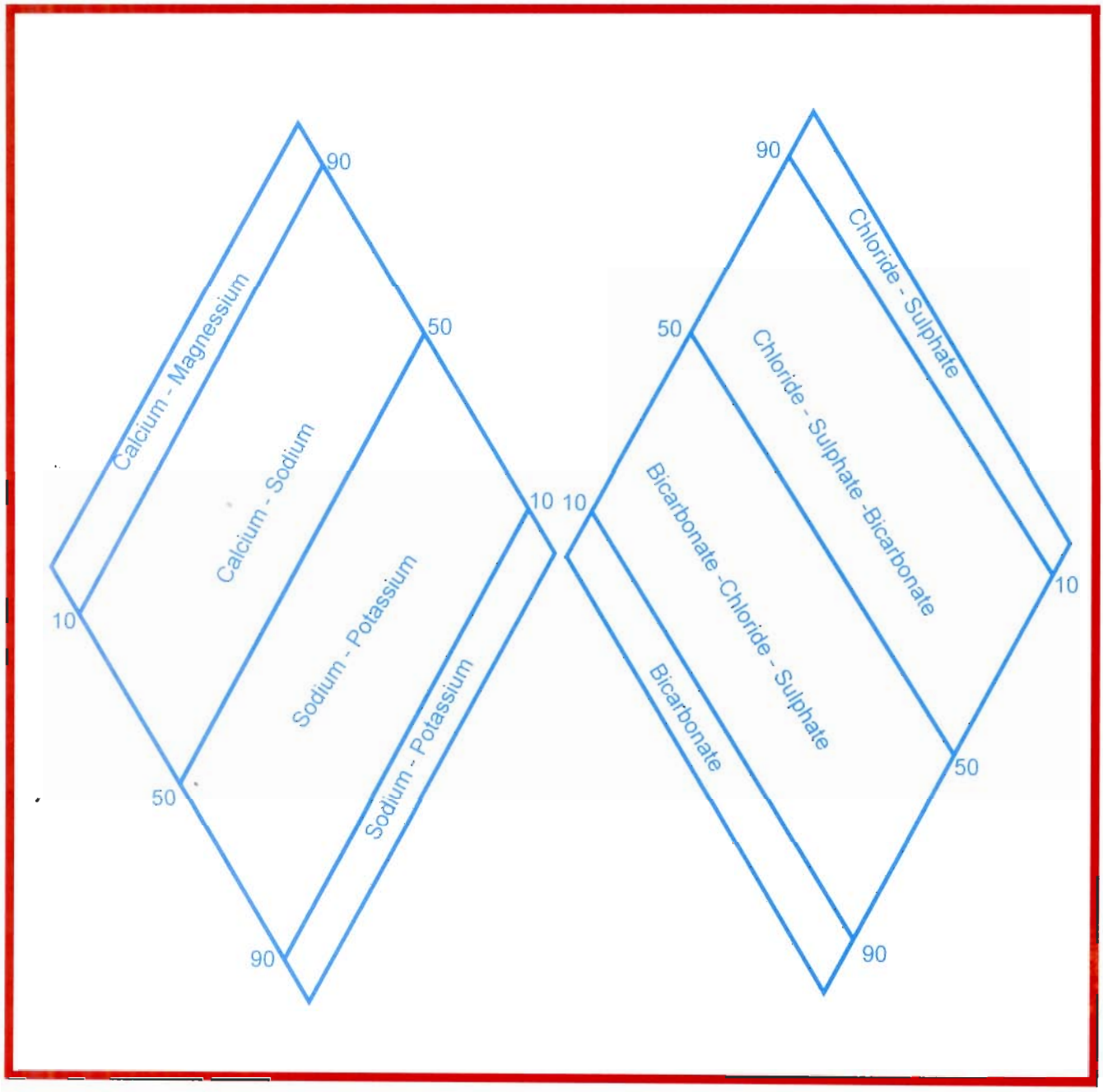

Fig 3.5: Templates for classifying water into facies for cations and anions (from Back, 1961)

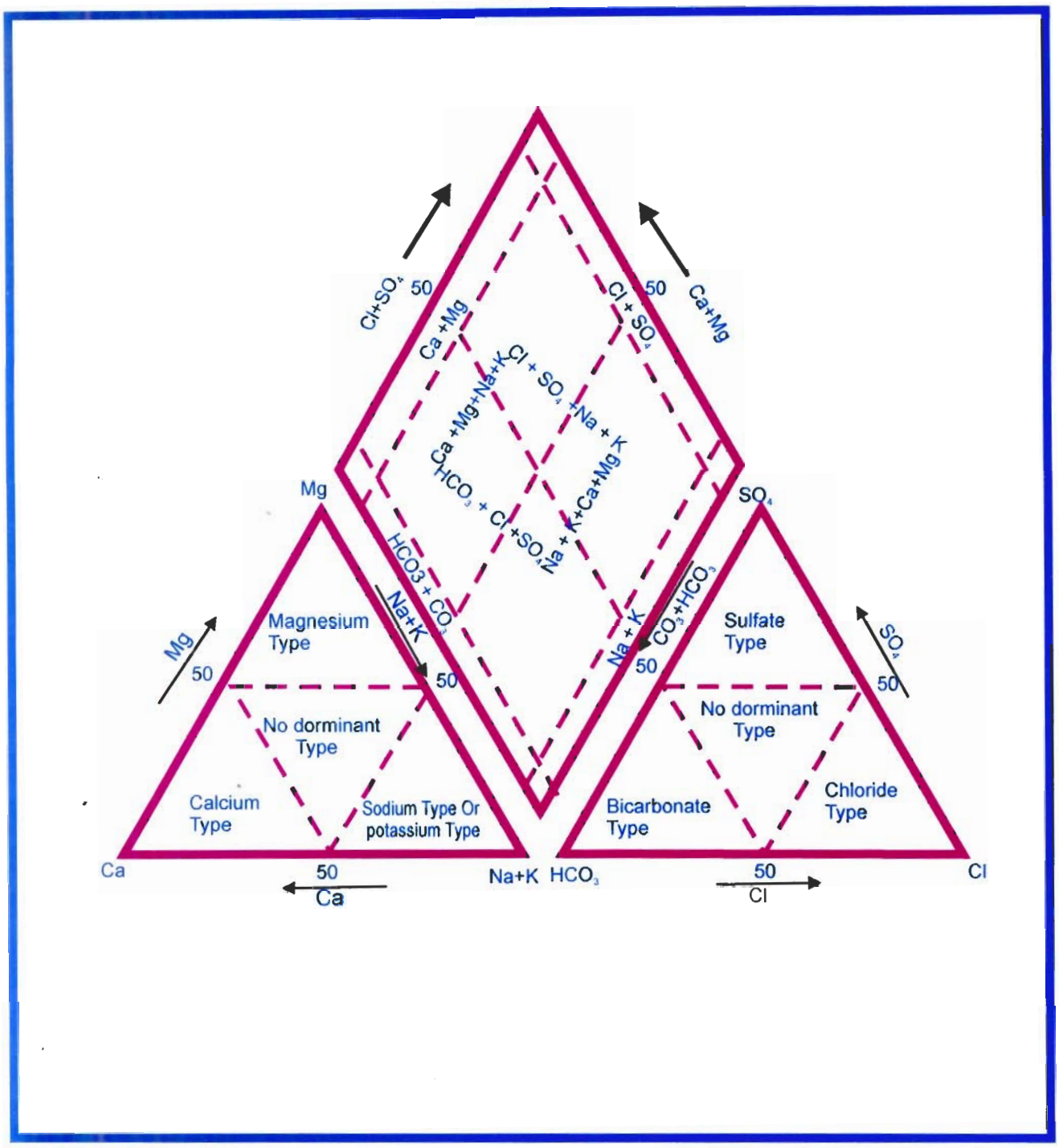

Fig 3.6 Classification diagram for anion and cation facies in terms of major ion Percentages (after Back, 1966)

Based on the Piper's trilinear plot, the water samples from different locations within the study area can be classified into three:

(i) $Ca - Mg - Cl - SO_4$ waters

(ii) $Na - K - Cl - SO_4$ waters

(iii) Mixtures of $Ca - Mg - Na - K - Cl - SO_4$ waters with no single cation dominating.

3.3.0. Characteristics Of The Water Samples

3.3.1 Physical Characteristics

pH

pH is a measure of the acid balance of a solution and is defined as the negative logarithm to the base 10 of the hydrogen ion concentration. At a given temperature, pH indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in it.

The ranges of pH – values of groundwater determined are between 6.03 units and 6.80 units. Except for samples I and IX with pH values that fall within the WHO (2004) recommended values, all the other samples of water have pH – values lower than the WHO (2004) standards.

Temperature (^{O}C)

Temperature is a measure of the degree of hotness or coldness of a body. The measured temperature of the groundwater samples ranged from $28.0^{0}C$ to $33.50^{0}C$. The temperature of most of the water samples is above the normal water temperature of $28^{0}C$. These temperature values represent the temperature of the study area. The high value of temperature implies that the groundwater within the study area is warm.

Taste

All the groundwater samples collected from boreholes and open wells within the study area have a salty and heavy taste. Water for drinking purposes has a better, fresh taste at lower temperatures though higher temperatures do not imply impurities (Olaseinde et al, 1998).

Colour

The groundwater samples appeared colourless to the naked eyes. Laboratory measurement was not carried out.

Odour

The groundwater samples collected from the study area were generally odourless except for the surface water which had some odour.

Electrical Conductivity (μS/cm).

Electrical conductivity is a measure of the ability of water to conduct electric current. It is sensitive to variations in dissolved solids, mostly mineral salts. The value of electrical conductivity measured on the field varied from 1660 μS/cm to 4220 μS/cm.

Total Dissolved Solids

An estimate of the TDS – values in mg/l was carried out by multiplying the conductance value by a factor of about 0.65 (Todd, 1980). The estimated values ranged from 1079mg/l to 2561mg/l. Using the Carroll (1962) groundwater classification based on TDS (Appendix A table 6), the groundwater at Itakpe can be classified as brackish water. These values are well above the WHO (2004) recommended limit of 1,000mg/l, making the water too salty to drink.

3.3.2 Chemical Characteristics

The alkali metals – Potassium and Sodium.

The concentrations of potassium ions were in the range of 0.852mg/l to 8.749mg/l except in sample X where the concentration is 49.74mg/l.

The concentration of sodium ions varied from 3.54mg/l to 38.64mg/l. These are within accepted limits.

The Alkaline Earth Metals – Calcium and Magnesium

Calcium concentration ranged from 2.854mg/l to 64.57mg/l. Magnesium concentration varied from 3.728mg/l to 16.70mg/l. These are also within accepted limits.

Trace Metals

Trace metals in natural or contaminated groundwater, with the exception of iron, almost invariably occur at concentrations well below 1mg/l (Freeze and Cherry, 1979).

Iron

The concentration of iron in the water samples varied from 0.005mg/l to 1.628mg/l. Samples were above the recommended limit of 0.3mg/l and should be treated if needed for household purposes.

(USEPA, 1976)

Manganese

A manganese concentration range of 0.003mg/l to 0.437mg/l was obtained. The concentration limit for manganese is 0.05mg/l. Samples exceeded the limit.

Sulphates

Sulphate concentrations within the study area ranged from 36.43mg/l to 64.34mg/l. These are all within the recommended limit of 250mg/l (USEPA,1976).

Chlorides

Chlorides concentrations measured ranged from 38.62mg/l to 70.34mg/l. These are all within the recommended limit of 250mg/l. (USEPA, 1976).

Bicarbonates

The concentration of bicarbonates ranged from 0.187 mg/l to 6.213mg/l. Bicarbonates are often formed by the dissolution of the carbondioxide gas or dissolution of carbonates underground.

Nitrates

Nitrate concentration varied from 0.02mg/l to 0.48mg/l. the recommended limit is 45mg/l (USEPA, 1976)

Total Hardness

Total hardness was determined using the relationship; Total Hardness = 2.497 $[Ca^{2+}]$ + 4.115 $[Mg^{2+}]$ mg/l (Freeze and Cherry, 1979, Todd, 1980). The hardness of groundwater in the study area varied from 56.66mg/l to 182.53mg/l. Using the Sawyer and McCarty (1967) classification of water, groundwater in the study area can be classified as soft, moderately hard and hard with one sample being soft, nine samples moderately hard and two samples hard.

Silica ($Si0_2$) (Silicon dioxide)

The silica content measured in the water samples ranged from 7.153% to 33.16%.

Silica is absorbed in water as it flows over rocks or percolates through rock formations (Harrison, 2004).

Sodium Concentration and Sodium Adsorption Ratio (SAR)

Sodium concentration is important in classifying water for irrigation because in contact with soils, sodium reacts and reduces the permeability of the soils. Sodium – saturated soils support little or no plant growth.

Sodium content expressed in terms of percent sodium is

defined by; $$\% Na = \frac{(Na + K)\ 100}{Ca + Mg + Na + K}$$

where all ionic concentrations are expressed in milliequivalents per liter.

The values of the sodium percentage at the study area are expressed in the table of hydrochemical data in appendix B. The SAR value range from 5.62% to 59.60%.

The salinity laboratory of the U.S. department of agriculture proposed the sodium adsorption ratio (SAR) because of its direct relation to the adsorption of sodium by soil (Todd, 1980).

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

The values of sodium adsorption ratio (SAR) for the study area are presented in the table of hydrochemical data in appendix A. The SAR values at the study area range from 0.0488 to 1.1956.

CHAPTER FOUR

GENERAL DISCUSSIONS

4.1 Mechanisms Controlling Groundwater Quality

Several factors control the chemistry and quality of groundwater. The factors include the geological environment through which the water flows, the rate of groundwater flow, the source of the groundwater and anthropogenic activities.

The study area, Itakpe, is within the gneiss-migmatite- quartzite unit of Nigerian basement complex. The area is made up of mafic minerals rich in ferromagnesian silicates. Most of the mafic minerals and rocks, when weathered release significant percentage of their component elements to groundwater in contact with them. These elements released have significant impact on the hydrogeochemistry and the physical properties of the groundwater. The physical and chemical properties of the groundwater with respect to cations and anions analyzed are discussed below.

For the purpose of this discussion, the results of groundwater analysis from Itakpe is compared with a AOMC, 1982 data (Table7)from the study area to determine if mining over the years has had any impact on the groundwater quality. Similarly, the results were compared with WHO (2004) standards as well as similar analysis carried out by Olarewaju et al (1997), Bala and Onugba (2001) and Abimbola et al (2002).

4.1.1 Physical properties of groundwater

Temperature

The temperature range of 28.0^{0}C to 33.50^{0}C of the groundwater with more of the samples being higher than 28.0^{0}C represents the temperature of Itakpe. This high groundwater temperature values at Itakpe compares with the high values obtained from some other parts of the basement complex of central Nigeria (Olarewaju et al, 1997). Similar temperature values were obtained for groundwater from the migmatite gneiss of the basement complex area within southwestern

Nigeria (Abimbola et al, 2002) and those from the basement complex of Northwestern Nigeria (Bala and Onugba, 2001). The high temperature values imply that the groundwater within Itakpe is warm.

Colour and Taste

All the water samples within the study area were colourless and odourless. All the samples from Itakpe had a slightly salty taste. The salty taste can be attributed to the chemical composition of water from the study area.

pH

The range of pH values of groundwater from the study area shows Itakpe is characterized by weakly acidic groundwater. Except for sample I whose pH value falls within the WHO (2004) recommended maximum permissible level, all the other samples have pH values lower than the recommended standards for potable drinking water. The groundwater samples from Itakpe are more acidic than water samples from migmatite gneisses studied by Olarewaju et al (1997). The samples are also more acidic than the pH of groundwater from the basement complex of southwestern Nigeria (Abimbola, 2002) and that from the northwestern Nigeria (Bala and Onugba, 2001). The values at Itakpe however agree with Egboka, 1986, who stated that most groundwater samples in Nigeria have pH values ranging from 5.5 to 6.5 units. Except for samples from the vocational training centre (sample I), the pH values for all the other samples are much lower than the 1982 value of 6.5 for the same study area.

Hardness

When used for washing, groundwater at Itakpe hardly leathers. The hardness value of groundwater from Itakpe is caparable to values obtained by Olarewaju et al, 1997. Based on the hardness classification of groundwater by Sawyer and McCarthy, (1967), samples from some locations at Itakpe are classified as soft, moderately hard at others and hard at most of the locations.

4.1.2 **Hydrochemical properties of the groundwater**:

Electrical conductivity (μ/cm)

The values of electrical conductivity measured on the field ranged from 1660μS/cm to 4220μS/cm. these values agree with Onugba and Eduvie (2005) who said that conductivity values in basement rock aquifers often exceed 400μS/cm and these values correspond to high level of mineralization. The high values of electric conductance could also imply high amount of soluble matter in the groundwater or water pollution (Olasehinde et al, 1998). The value of conductivity at the study area is much higher than the range of values obtained by Olarewaju et al, 1997. These values are much higher than the 306.6μS/cm recorded for borehole water within the area in 1982 (see table 4 of appendix A).

Total dissolved solids (TDS)

The TDS estimated from conductance ranged from 1079mg/l to 2561mg/l. These values are commonly associated with brackish water having high concentration of calcium ions, magnesium ions, sodium ions, sulphate ions and bicarbonate ion as the dorminant ion (Freeze and Cherry, 1979). Except for bicarbonate ions which exist in very low concentration, all the other ions as well as chloride ion exist with high concentrations in Itakpe groundwater samples. These values are higher than the WHO (2004) limits of 1500mg/l for total solids. This can also explain for the salty taste of the groundwater.

The chemical characteristics of groundwater and its quality is controlled by its ionic content. The major anions and cations in the groundwater at Itakpe are discussed next.

Cations

Sodium and potassium ions

The concentration of sodium and potassium ions in groundwater within the study area compares well with concentration values for groundwater from other migmatite gneiss complex areas within Nigeria. Abimbola et al, (2002) as well as Bala and Onugba, (2001) obtained similar

concentrations for groundwater in southwestern Nigeria and Bunsuru sub-basins of Northwestern Nigeria respectively. The result at Itakpe agrees with du Preez and Barber, (1963). Sodium concentration exceeds potassium concentration in all the samples. Sources of sodium include plagioclase feldspars, evaporites such as halite (NaCl) from ancient marine environments associated with precipitation and sedimentation of iron from solution (Ewers 1983, Morris, 1986). Both authors proposed that banded iron formations originate from marine environment. These environments are known to be saline in nature. Marine transgression and regression leads to deposition of the precipitated evaporites which eventually contribute sodium ions to groundwater. The most common source of potassium in the groundwater is K–feldspar.

Calcium

The calcium concentration in the groundwater is similar to that recorded by Olarewaju et al, 1997) within the basement complex of central Nigeria. The calcium concentration in groundwater at Itakpe is similar to that from the Bunsuru sub- basin of northwestern Nigeria (Balá and Onugba, 2001). The calcium concentration is lower than the WHO, (2004) recommended guideline of 200mg/l for drinking water. The calcium concentration is twice higher than the 1982 concentration of calcium within the same environment. This increase can be attributed to weathering of minerals on the one hand and the mining and waste disposal by NIOMCO on the other.

Sources of calcium within the study area include amphiboles, feldspars clay minerals and pyroxene. Calcium exceeded magnesium in all the samples.

Magnesium

The concentration of magnesium within the study area was found to be similar to those from other parts of the basement complex of central Nigeria and Northwestern Nigeria. The magnesium concentration is however lower than the 1982 value recorded at Eika within the mine area. The value is also lower than the WHO (2004), recommended guidelines of 150mg/l.

Common sources of magnesium at Itakpe include hornblende (amphiboles), ferruginous quartzites, biotite, gabbro, chlorite and micas which are common among gneisses around Okene, Kabba and Lokoja (Odigi and Ezepue, 1993).

Iron

The study area is an iron rich environment thus iron content of groundwater will naturally be expected to be high. The water analysis result shows that iron content in groundwater from the study area is higher than those analyzed by Olarewaju et al, (1997) and the 1982 analysis for the same environment. It however conforms with Egboka, (1986) concentration values of iron in the groundwater samples from boreholes in basement complex area where iron content rarely exceeds 2mg/l. The concentration of iron content in groundwater decrease farther away from the mine site. The iron content is also higher than the WHO, (2004) recommended concentration limit of 0.3mg/l at some of the sampling points. Samples I, III and XIII with concentrations of 0.313mg/l, 1.628mg/l and 0.524mg/l respectively are actually above WHO limits and also higher than the limits established by Olarewaju et al (1997).

The sources of iron include amphiboles, ferromagnesian silicates, micas, biotite, chlorite, ferrous sulphide (FeS), ferric sulphide or pyrite (FeS_2) and hematite.

Manganese

All the water samples had manganese concentrations higher than the WHO (2004) maximum permissible level of 0.05mg/l for drinking water. The values were also higher than those obtained by Olarewaju et al (1997). In 1982 manganesse concentration was 'nil.'

Water with higher concentrations of manganese may have unpleasant taste. The sources of manganese include mica, biotite and amphibole hornblende minerals which all contain large amounts of manganese.

Anions

Sulphates

The sulphate content in groundwater of the study area is much higher than sulphates from migmatite gneisses studied by Olarewaju et al (1997). The sulphate concentration is higher than the 1982 sulphate concentration at the study area. The values are however lower than the WHO (2004) recommended highest desirable level of 200mg/l. Sulphates originate as a result of oxidation of sulphide ores, gypsum, and anhydrite.

Chlorides

The chloride content within the study area is lower than the WHO (2004) recommended highest desirable level of 200mg/l. the values are higher than those measured by Olarewaju(1997) from the basement complex of central Nigeria. The chloride content is higher than the concentration at Itakpe as at 1982. Some of the sources of chloride are connate water and igneous rocks found within the study area.

Nitrates (NO_3^-)

The values of nitrate concentration at Itakpe are well below the WHO (2004) recommended concentration limit of 45mg/l. The source of nitrates in groundwater is atmospheric. There may be little contribution from plant debris since vegetation is not thick.

Carbonates (CO_3^{2-}) and Bicarbonates (HCO_3^-)

Carbonates and bicarbonates are generally of low or negligible concentrations in groundwater at Itakpe. The source is atmospheric precipitation. Carbonate rocks such as gypsum and dolomite are rare at Itakpe but are found at nearby Ajabanoko hills.

Silica (SiO_2)

This is a common mineral in almost all groundwater. The source of silica in groundwater at Itakpe include minerals and rocks such as feldspars, ferromagnesian silicates, quartz, amphibolites, biotite, granites, granodiorites etc. Almost all the rocks found within Itakpe contain silicates.

4.2 Chemical characterization of the water

Different methods were used in characterizing water samples within Itakpe. Pie charts, Stiff diagrams, Schoeller semi- logarithm diagrams and Piper tri-linear plots were used in characterizing the water samples.

The pie charts and Stiff diagrams show that there is a high percentage of chloride and sulphate anions with extremely low concentrations of bicarbonate ions in the water samples. 76 % of the samples show a dominance of chloride ions over all the other anions while 15% show a dominance of sulphate ion over other ions in the water. This is also confirmed by the Stiff diagrams and the Schoeller semi-logarithm plots.

From the pie charts and the Schoeller semi logarithm diagrams as well as Stiff diagrams 36% of the samples have a concentration order;

$Ca^{2+} > Mg^{2+} > Na^{+} + K^{+}$, 27% are of the order $Na^{+}+K^{+} > Ca^{2+} > Mg^{2+}$. while 18 % are of the order $Ca^{2+} > Na^{+}+K^{+} > Mg^{2+}$ for cations.

Using the Piper trilinear method of characterizing groundwater (fig 3.4), the class of water includes;

i. Calcium-magnesium-chloride –sulphate water.

ii. Sodium/potassium-chloride-sulphates water

iii. Mixture of calcium-magnesium-sodium/potassium-chloride- sulphates waters with no single cation dominating in the mixture.

This characteristic of the water is comparable to water from the basement complex area within the Bunsuru and Gangare sub-basins where water is calcium-magnesium, chloride-sulphate type. The water types at Itakpe tend more to calcium-magnesium-chloride-sulphate type though there is presence of sodium/ potassium-chloride-sulphate waters. This conforms with groundwater type described by Offodile (2002) as magnesium sulphate, sodium chloride bicarbonate water believed to be common in the basement complex.

The geology of Itakpe has immensely contributed to the hydrochemical characteristics of the groundwater at Itakpe. Water found within the rocks or flowing through or over the rocks acquires the elements of the minerals or the rocks. This can be through weathering of the rocks and the dissolution of the soluble weathered materials in the water. Some of the substances are acquired directly from atmospheric precipitation. The present quality of the groundwater is however controlled mainly by anthropogenic activities especially mining taking place at Itakpe.

4.3 Groundwater Quality and Impact

Silica content in groundwater at Itakpe is high. This is mainly due to the nature of the rocks found within the environment. The rocks are rich in silicate minerals which are dissolved and carried along by water as it passes through or over the rocks and minerals. As well as aiding the precipitation of iron ore from water silica was also precipitated during the formation of banded iron formations (Morris, 1986 and Ewers, 1983). The detrimental effect of silica in water is that in the presence of calcium and magnesium, it forms a scale in boilers and on steam turbines that retard heat. The scale is difficult to remove.

Groundwater at most parts of Itakpe is generally warm, colourless and odourless which meets the WHO (2004) standards for potable water. It however has a slight salty taste. The salty taste of the water within Itakpe can be attributed to the chloride content or high concentration of salts. Minerals such as NaCl, $CaCl_2$, Na_2SO_4, $CaSO_4$, and $MgSO_4$ are all salts that add to the salty taste of the water. Kashef (1986) in his explanation attributed the salty taste of water to high concentrations of chlorides in water. The high value of TDS which led to the classification of the water as brackish or moderately saline water is an indication that the water is salty.

Most water samples collected from Itakpe are moderately hard though a few of the samples are soft and others hard. The pressence of divalent metallic cations of which calcium and magnesium are the most abundant in groundwater are responsible for the hardness (Todd 1980). All the methods used in analyzing and classifying the groundwater at Itakpe shows that all the water samples are rich in calcium and magnesium both of which account for the hardness. The few samples richer in sodium are softer than the water samples richer in calcium and magnesium. The hardness values of 56.66mg/l to 182.53mg/l are less than the WHO (2004) permissible limit of 500mg/l.

The negative impact of hardness in water includes; the leaving of soap curd and detergent deposits on fabrics, thereby leaving dull colors on white fabrics and also causing the threads to become brittle and shortening the life of materials. Other negative impacts include;

- Wastage of soap and synthetic detergents
- It leaves unsightly soap scum rings in the bathtub.
- Builds up scale deposits in all water using appliances, clogs hot water pipes. It reduces the heating efficiency of a boiler or water heater.

The pH values of the water at Itakpe show that water at Itakpe is slightly acidic. The acidity of water may cause corrosion of metallic materials in contact with the water.

Some groundwater samples had iron concentration values much higher than the WHO (2004) recommended and maximum permissible limits. These values are also higher than the values obtained by Egboka (1986) and Olarewaju (1997) for samples from basement complex areas and samples from some migmatite gneisses from Niger, Kogi and Kwara states. Though the environment is iron rich, high iron concentration values in water samples can be attributed to the mining of iron at Itakpe. Samples taken from the Vocational Training Center, beneficiation plant, Eika and River Pompon which are the nearest locations to the mine site(fig. 1.2) show higher concentrations of iron than those samples from other locations

further away from the mine site. It should be noted here that waste water from beneficiation is discharged in river Pompon which is a surface water flowing through the mine.

High iron content in water especially at the observed level will readily stain plumbing fixtures, porcelain and cooking utensils. Used in laundry would stain washables with reddish – brown discolorations. It also imparts a disagreeable metallic taste to water.

The concentration of manganese is well above the WHO (2004), recommended maximum permissible limit of 0.05mg/l for drinking water. The concentration of manganese is much higher than the nil recorded in 1982. The values obtained at Itakpe are also higher than the values obtained from samples within migmatite gneisses from other areas (Olarewaju et al, 1997). Upon oxidation, manganese is precipitated causing undesirable tastes, deposits on foods during cooking, stains plumbing fixtures and laundry and fosters growths in reservoir filters and distribution systems. Water containing more than 0.02mg/l of manganese is objectionable for industrial use. Recommended method of treatment of excess iron and manganese are discussed under methods of treatment.

The sulphate concentration values fall within the WHO (2004) recommended and maximum desirable levels. The values obtained at Itakpe are higher than values observed from the basement complex areas of the parts of Niger, Kwara and Kogi analyzed by Olarewaju et al (1997).

Carbonates are generally low almost absent in concentration from some of the water samples. The near absence of carbonates and bicarbonates is an indication that groundwater at Itakpe are older waters and have existed for a very long time in the aquifers. The samples were collected at the peak of the dry season when precipitation effect is cut off. It should be noted here that freshly precipitated water and surface waters have higher concentrations of carbonates and bicarbonates and are slightly alkaline. The acidic nature of the groundwater at Itakpe also indicates low carbonates and bicarbonates in the groundwater.

There is no dominant cation in 70% of the samples from the study area rather a mixture of calcium, magnesium and sodium/potassium cations are found in the samples. 20% of the water samples are higher in calcium and magnesium while 10% of the samples have higher concentration of sodium and potassium. The dominant anion in 80% of the water samples within the study area is chloride ion. 20% of the samples have a higher concentration of sulphates while the bicarbonates are extremely low in concentration implying rather old water according to Chebotarev sequence (Freeze and Cherry 1979).

The high values of TDS in the study area characterize the water from Itakpe as brackish water. The higher chloride content of the water also makes it somewhat saline. Again 20% of the groundwater samples are intermediate waters with sulphates being the dominant anion and higher TDS which is also a characteristic of the intermediate zone waters. Water within the study area is rich in mixtures of salts of sodium/potassium chloride, sodium/potassium sulphate, calcium chloride, calcium sulphate, magnesium chloride and magnesium sulphate which are responsible for the brackish or salty taste of the water.

The salinity laboratory of U.S. Department of Agriculture (1954) recommended the sodium absorption ratio, SAR, for studying the suitability of groundwater for irrigation purposes (see table 4 of appendix A). High exchangeable sodium in the soil is undesirable because it renders the soil relatively impermeable. The average value of SAR within the study area is generally low. This shows that the water is good for irrigation since all the values fall within the range (0 – 10), which represents low alkalinity. Also the Wilcox (1955) quality classification of water for irrigation (table 5 of appendix A), classifies the Itakpe groundwater as good in majority of the samples and permissible in few. Values of electrical conductivity however consider a few of the cases as permissible to doubtful for irrigation, while most of the samples are unsuitable for use. There is no correlation here but looking at the general vegetation of the study area it can be seen that the sparse vegetation and poor yield of crops is

due to the doubtful and unsuitability of water for agricultural (irrigational) purposes purposes. High exchangeable sodium in the soil is undesirable because it renders the soil relatively impermeable.

4.4 Water Treatment Methods

Due to undesirable levels of some substance in the groundwater, there is a need for treating the water of these substances to bring it to the acceptable limit. Methods of treating water of undesirable constituents have been discussed by Ezeigbo, 1987,1988 and 1989 as well as other authors. Methods of water treatment recommended by Harrison (2004) are presented here:

- Silica ($Si0_2$) content of water can be removed by coagulation and settling or filtering out of the silica content.

- Chloride (Cl^-) which ascribes taste to water can be substantially removed from water by reverse osmosis. Another method is by de-ionizing (demineralization) or distillation to remove chlorides and sulphates.

- Hardness can be removed by boiling the water or reduced by using detergent for laundry purposes

Iron (Fe) and manganese (Mn) occur together in water with iron being of higher concentration. Among the effective methods for treating iron and manganese in greater use are;

(i) Use of iron exchange water softeners.

Permanganate or polyphosphates are satisfactorily used to remove iron and manganese from water just as they also remove calcium and magnesium irons.

(ii) Oxidation and filtration using

(a) Iron filters

(b) Feed oxidizing agents (chlorine, potassium, permanganate, or ozone) and filter.

Medium concentrations of iron are treated effectively using an oxidizing filter where the pH is 6.8 or above. The filtering can contains manganese dioxide which converts the soluble ferrous iron in the water into ferric iron. The ferric hydroxide formed is filtered from the water by the granular materials in the filter bed of the tank.

Iron may be oxidized by feeding solutions of oxidizing agents such as chlorine, ozone, hydrogen peroxide or potassium permanganate into the water.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A hydrochemical evaluation of groundwater samples collected from hand dug shallow wells and deeper boreholes at Itakpe was carried out to determine the impact of mining on the groundwater quality. The results of the study show that there is increase in concentration of major cations and anions after over twenty five years of mining at Itakpe. This increase has altered the quality of the groundwater both physically and chemically. The increase however does not imply pollution since the concentration of most of the parameters investigated fall within the WHO (2004) recommended limits. Mining had effected contamination on the water resources of the mine area.

Groundwater at Itakpe is colourless and odourless with normal to slightly warm temperature of 28.00°C to 36.50°C with a slight saline taste. The pH of the water has decreased over the years and it is presently acidic and corrosive. Its solvent capacity is increasing. It varies in hardness from soft, moderately hard to very hard in most of the water samples.

The very high values of electrical conductivity indicate high ionic activities and in effect high total dissolved solids in the water. The water is classified as brackish due to its high electrical conductivity and total dissolved solid concentration

Several methods were used to characterize the water type at Itakpe. Pie charts, Stiff diagrams Schoeller semi logarithm diagrams and Piper trilinear diagrams were employed for that purpose. Three types of water were identified; calcium –magnesium–chloride – sulphate water, sodium/potassium chloride –sulphate water and a mixture of calcium-magnesium-sodium/potassium-chloride -sulphate water.

Though nearly all the water samples show increase in concentration of the parameters, impact is more within the mine area and at boreholes (wells) closer to the mine. It is only to be expected that the contamination capacity will further increase with time.

5.2 Recommendations

To mitigate impact of the mining and beneficiation on groundwater, there is need for NIOMCO to adopt better or safe waste disposal practices.

There is need to treat groundwater to make it safe for domestic and industrial use. Some of the water treatment techniques are highlighted in Chapter 4.4. Parameters to be treated include silica,chloride, hardness, iron and manganese.

There is a need to carry out a further study on the groundwater with a view of improving it for agricultural purpose.

NIOMCO and government as the main beneficiaries of the activities at Itakpe should follow best practices by carrying out routine environmental impact assessment within the area. This will help as a self check in terms of maintaining a safe environment.

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APPENDICES

APPENDIX A

Table 1: well Data

Station I D	Sample I D	Depth to water (m)	EASL (m)	Latitude	Longitude
VTC (BH)	I	--	157	$7^0$37'18.0N	$6^0$18'06"E
BENEF (BH)	II	--	191	$7^0$37'0914"N	$6^0$18'11 E
MOVEN J (O.W.)	III	3	308	$7^0$35'.66.8"N	$6^0$18'79" E
SAW MILL (O.W.)	IV	6	235	$7^0$37'40.8"N	$6^0$18'06" E
OSARA dam road (B.H.)	V	--	194	$7^0$38'24.8"N	$6^0$19'81" E
Energi's compound (O.W.)	VI	15	195	$7^0$38'57.1"N	$6^0$19'80" E
Behind Energi's compound (O.W.)	VII	15	218	$7^0$38'53.9"N	$6^0$19'7.23" E
No. 24 Akande St Abobo (O.W.)	VIII	8	185	$7^0$38'36.3"N	$6^0$20'11" E
Nurse compd. Abobo(O.W.)	IX	8	197	$7^0$38'51.0"N	$6^0$20'19.1" E
Off Apostolic Church Abobo(O.W.)	X	8	202	$7^0$38'32.0"N	$6^0$20'21.6" E
The Apostolic Church Abobo(O.W.)	XI	15	188	$7^0$38'41.5"N	$6^0$20'21.6" E
District heads compd. Abobo(BH)	XII	--	175	$7^0$38'28.1"N	$6^0$20'18.4" E
River Pompon	XIII	Surface	180	$7^0$37'05.2"N	$6^0$17'19.4" E
Stagnant water at mine	XIV	Surface	327	$7^0$37'13"N	$6^0$18'06" E

O.W. – Open well BH - Borehole

EASL- Elevation above mean Sea Level -- - Not determined

APPENDIX A

TABLE 2: PHYSICAL AND HYDROCHEMICAL DATA.

SAMPLE NO.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	iv
LOCATION														Mines
PARAMETERS														
Temperature (^{0}C)	30.80	36.50	28.00	28.30	33.50	29.40	28.20	29.80	28.80	30.00	30.30	29.10		
Color	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	Not objectionable	
Taste	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	Slightly salty	
PH	6.80	6.33	6.45	6.35	6.07	6.07	6.43	6.03	6.30	6.10	6.09	6.45		
Conductivity (µS/cm	3940	3030	1990	3710	2000	2140	3330	1660	1980	4220	1660	3070	2560	
Total dissolved solids TDS (mg/l)	2561	1969.5	1293.5	2411.5	1300	1391	2164.5	1079	1287	2743	1079	1995.5	1664	
Total hardness (mg/l)	172.89	130.34	79.13	130.81	-	86.70	182.53	-	88.66	131.83	56.66	113.23	110.83	
Na^+ (mg/l)	29.96	31.54	12.69	38.64	-	9.996	1.54	-	3.54	14.20	9.98	15.78	12.01	3.67
K^+ (mg/l)	2.261	5.468	0.852	1.738	-	1.87	2.613	-	2.552	49.74	1.998	4.346	1.178	8.749
Ca^{2+} (mg/l)	41.77	27.57	14.32	30.15	-	25.94	64.57	-	28.45	28.66	16.55	19.48	26.44	2.854
Mg^{2+} (mg/l)	16.70	14.98	10.57	13.52	-	5.33	5.15	-	4.28	14.68	3.73	15.74	10.91	6.829
Total iron (mg/l)	0.31	0.18	1.63	0.18	-	0.19	0.20	-	0.29	0.01	0.01	0.02	0.52	22.89
Mn^{2+} (mg/l)	0.03	0.20	0.01	0.05	-	0.01	0.04	-	0.00	0.26	0.00	0.33	0.44	0.275
Zn^{2+} (mg/l)	0.17	0.13	-0.11	-0.27	-	-0.235	-0.530	-	-0.499	-0.268	-0.514	-0.348	-0.561	-1.277
Pb. (mg/l)	0.01	-0.04	-0.04	-0.04	-	-0.04	-0.05	-	-0.05	-0.04	-0.04	-0.04	-0.03	-0.029
Al (mg/l)	0.00	-0.10	2.70	0.04	-	0.40	-0.03	-	0.83	-0.09	-0.08	0.05	-0.09	73.83
Ti (mg/l)	0.00	-0.001	-0.094	-0.01	-	-0.02	-0.004	-	-0.02	-0.002	-0.001	-0.001	-0.001	-0.514
Cl-(mg/l)	61.28	38.68	41.44	70.34	44.39	39.28	40.17	-	59.60	49.54	50.17	37.09	38.62	41.21
SO_4^{2-}(mg/l)	42.65	42.65	64.34	36.43	47.37	49.43	41.39	-	47.12	41.27	42.06	40.10	40.16	41.26
HCO_3^-(mg/l)	3.97	3.97	4.27	0.19	1.64	6.21	0.32	-	2.19	3.41	2.81	3.13	1.21	0.109
NO_3^-(mg/l)	0.02	0.02	0.02	0.03	0.11	0.09	0.10	-	0.04	0.10	0.11	0.07	0.48	0.38
SiO_2 (%)	7.79	27.48	7.478					-						
SAR	0.99	1.20	0.62	1.47	-	0.46	0.05	-	0.13	0.54	0.57	0.64	0.49	
% Sodium	35.53	46.52	35.23	48.04	-	37.95	5.62	-	15.69	59.60	37.13	36.36	26.10	

Table 3; Borehole water Chemistry from parts of the Basement complex of Central Nigeria (after Olarewaju et al 1997).

Location	Oke – Ode	Kabba	Obo – Ile	Obehira	Apado	Share	Rofia
Geology	Granite	Migmatite Gneisses	Migmatite Gneisses	Migmatite Gneisses	Schist Gneisses	Migmatite Gneisses	Gneiss
Number of borehole sampled	2	4	2	3	7	8	9
Concentration levels	Range	Range	Range	Range	Range	Range	Range
Conductivity (μmhos/cm)	225 - 310	250 – 400	150 – 300	240 – 460	200 – 800	25 – 70	200 – 540
Turbidity (N.T.U)	-	-	0 – 2.5	4.7 – 15	4.6 0 32	0.17 – 6.6	-
Colour (^{0}H)	-	-	0 – 20	5 – 12	5 – 30	0 – 15	-
PH (units)	6.2 – 6.7	6.5 – 7.2	6 – 7.1	6.7 – 7.5	6.5 – 6.02	5.2 – 5.9	6.9 – 7.8
Ammonial Nitrogen (mg/l)	0.05 – 0.2	0.02 – 0.05	0.03 – 0.05	-	-	-	0.01 –0.04
Nitrate Nitrogen (mg/l)	1.0	0.02 – 2.5	0.05 – 0.9	0.2 – 0.5	-	0.5 – 1.1	0.07 – 1.8
Fe^{3+} (mg/l)	-	0.08 – 0.4	-	-	-	-	-
Total iron (mg/l)	0.05	-	0.08 – 0.3	0.8 – 1.4	0.2 – 1.4	0.08 - .05	0.02 – 0.2
Ca^{2+} (mg/l)	21.6 – 39. 6	19.6 – 34	19 – 40	24- 68	-	0.8 – 9.6	32.8 – 69.2
Mg^{2+} (mg/l)	2.3 – 4.5	20.7 – 22	6 – 8.5	4.9 – 9.9	-	0.8 – 3.6	2.92 – 11.4
Cl- (mg/l)	0.06 – 1.2	0.5	0.5 – 2.0	0.6 – 3	-	0.5 – 8.5	0.3 – 22
SO_4^{2-} (mg/l)	2.3 – 4.5	0.2 – 6	2.0	-	-	0.4 – 5	2 – 8
Mn^{2+} (mg/l)	-	0.1 – 0.3	0.2 – 0.9	0 – 0.3	-	0.2 – 0.3	0.15 – 0.5
Ca Hardness as $CaCO_3$ (mg/l)	34 – 99	49 – 85	48 – 100	61 – 170	-	2 – 24	82 – 173
Mg. Hardness as $CaCO_3$ (mg/l)	23 – 34	85 – 91	25 – 35	20 – 37	-	2.1 – 10	12 – 173
Total Hardness as $CaCO_3$ (mg/l)	87 – 133	134 – 174	73 – 135	98 – 195	-	10 – 30	94 – 220
Total alkalinity as $CaCO_3$ (mg/l)	110 – 160	122 – 198	52 – 165	129 – 235	-	12 – 29	150 – 285
F (mg/l)	-	-	-	-	-	-	-

Table 4

Kwara state water corporation laboratory report form chemical analysis of water samples

Location of Sample EIKA (AOMC) OKENE Date 23rd March , 1982

Nature of sample Borehole Water Time _____

Temperature _____ °C

PH_____6.5

NH_3 _____0.05 mg/l

Ca^{2+}_____17. 15 mg/l

Mg^{2+}_____38. 875 mg/l

Fe^{3+}_____0. 60 mg/l

Al^{3+}_____0. 05 mg/l

Mn^{2+}_____NIL mg/l

Zn^{2+}_____ mg/l

C_i^{4+}_____mg/l

Cu^{2+} _____0. 15

Pb^{2+}____0.80____ mg/l

F_____0.80 mg/l

Cl_____8.00 mg/l

NO_2_____ mg/l

NO_3_____ mg/l

SO_4^{2-} _____32.50 mg/l

CO_2_____91.00mg/l

SIO_2_____48.00__mg/l

H_2S^-_____ mg/l

PO^2_4_____mg/l

Total Alkalinity as $CaCo_3$ _____36.50_____ mg/l

Bic Alkalinity as $CaCo_3$ _____NIL_____ mg/l

Total Hardness as $CaCC_3$_____113.92_____ mg/l

Total Dissolved Solids _____332.4_____ mg/l

Dissolved O_2_____22.90_____ mg/l

Conductivity_____306. 6 us/cm^{10}_____m/cm

Colour _____10_____

Turbidity_____42,00 T.U_____ T. units

BOD_____ mg/l

Suspended solids _____ mg/l

General Remarks The Iron content (Fe^{++}) of 0.6 mg/l is well above the maximum permissible level of 0.3mg/l set by WHO.

Also the lead content (pb^{2+}) of 0.80mg/l is above the maximum permissible level of 0.1mg/l set by WHO (World Health Organisation)

E. Ajulo

Signed

Asst chief Biochemist

Appendix A

Table 5: Water classification based on Sodium adsorption ratio (after Etu – Efeotor, 1981)

SAR	WATER CLASSIFICATION
0-10	Excellent
10-18	Good
18-26	Fair
>20	Poor

Table 6: Quality Classification of water for irrigation (after Wilcox, 1955)

WATER CLASS	PERCENT SODIUM	SPECIFIC CONDUCTANCE (μS/cm)
Excellent	< 20	< 250
Good	20 – 40	250 – 750
permissible	40 -60	750 – 2000
Doubtful	60 – 80	2000 – 3000
Unsuitable	> 80	> 3000

Table 7: Classification of groundwater (after Carroll, 1962).

	Total dissolved solids, (mg/l)
Fresh water	0 -1000
Brackish water	1,000-10,000
Saline water	10,000-100,000
Brine	>100,000

Table8: WHO (2006) drinking water standards

Characteristics	Maximum permissible level	Highest desirable level
Colour (^{0}H)	5	50
Turbidity(N.T.U)	5	25
pH(units)	7-8.5	Min. 6.5 – max. 9.2
Chloride (Cl^-)mg/l	200	600
Manganese (Mn^{2+}), mg/l	0.05	0.5
Fluoride (F^-)mg/l	0.7-1.0	0.5
Cupper(CU^{2-})mg/l	0.05	1.5
Iron (Fe^{2+}) mg/l	0.1	1.0
Nitrate (NO_3^-) mg/l	45	5.0
Total Hardness ($CaCO_3$) mg/l	100	500
Sulphate (SO_4^{2-}) mg/l	200	400
Zinc(Zn^{2+}) mg/l	5.0	15
Calcium (Ca^{2+}) mg/l	75	200
Magnesium (mg^{2+}) mg/l	50	150

APPENDIX C

INSTRUMENTATION AND METHODS USED IN CATION, HEAVY METALS AND ANION DETERMINATION

1. Cations

The Perkins Elmer inductively coupled plasma (ICP) optical emission spectrophotometer was used in determining cation and heavy metals in the water samples. The method of determination is explained by Boss and Freedeen (1999).

In this method, the samples were prepared for introduction into the ICP by first putting the samples in an auto sampler tube since it is already in solution form. The sample containing solution was stabilized due to low analyte concentrations by pre-concentration via evaporation and ensuring that the sample containing solution can be nebulized in a reproducible manner.

The ICP instrument was programmed by using the standard operating conditions recommended by the manufacturer. These conditions include integration time or nebulizer uptake rate (ml/min), PMT voltage (i.e. photomultiplier tube voltage), argon flow rates and RF power (amount of energy per unit time transmitted from the RF generator to the ICP discharge measured in watts), viewing height and wavelength selection.

The instrument was then calibrated using standard solutions provided by the ICP – OES Vender (in this Case PERKIN ELMER) used as standard for the analysis. The standard solution contains cations similar to the cations in the sample analyzed.

The sample in the tube was then introduced into the (ICP) by using the auto sampler for introduction of the samples. The auto sampler is inbuilt with the inductively coupled plasma optical emission spectrometer.

The analysis was completed with the generation of report which lists the concentrations of the elements of interest. External computers were used to generate the report presented in table 2 of appendix A.

ANION DETERMINATION

II. Chloride (Cl) Ion.

Chloride was determined using "Mercury (II) nitrate method" (Ademoroti, 1996).

The reagents used include;

(i) 0.005m, Mercury (II) nitrate, $Hg(N0_3)_2$

(ii) 0.0282m, Sodium chloride standard solution

(iii) 0.2m $HN0_3$

(iv) Diphenyl carbazone mixed indicator solution

In this method, 0.5ml mixed indicator solution was added to 100ml of sample. 0.2M $HN0_3$ was added in drops until the solution became yellow. 5 to 6 drops of the acid was further added till the pH dropped to 2.5. The sample was titrated immediately against 0.005M $Hg(N0_3)_2.H_20$ solution with constant shaking until the colour changed to slight orange first and finally, a tinge blue purple colour appeared which persisted with further shaking. A blank titration was carried out with 100ml distilled water.

The concentration of chloride in the sample was calculated as follows:

$$Cl^- \text{ (mg/l)} = \frac{(A - B) \times M \times 70{,}900}{\text{ml sample}}$$

Where: A = ml $Hg(N0_3)_2$ used for titrating sample

B = ml $Hg(N0_3)_2$ used for titrating blank

C = Molarity of $Hg(N0_3)_2$

III. Sulphates (SO_4^{2-}) ion

Sulphate ion was determined by turbidimetric method (Ademoroti, 1996).

The following apparatus were used;

(a) Magnetic stirrer

(b) Spectrophotometer for use at 425nm and providing light path of 1cm.

(c) Measuring spoon, capacity 0.2 – 0.3ml.

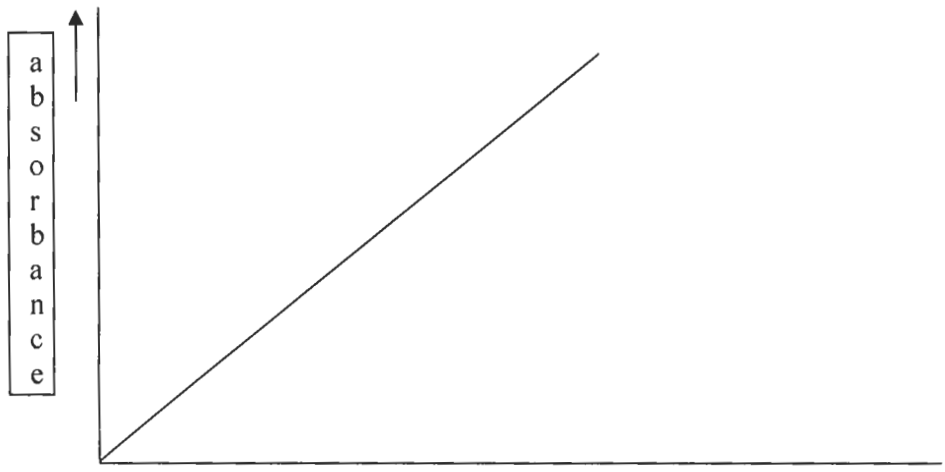
The following reagents were used:

(a) Conditioning reagents: 50ml glycerol was mixed with a solution containing 30ml conc. HCl, 300ml distilled water, 100ml 95% ethanol or isopropanol and 76g NaCl.

(b) Barium chloride crystals

(c) Standard solution of 0.14 79g anhydrous sodium sulphate, $NaSO_4$, dissolved in distilled water diluted to one (1) Liter. This solution was used to prepare the calibration curve.

The calibration curve is a curve of absorbance readings plotted against sulphate concentration in (mg/l) as shown below.



100ml of the water sample was measured into a 250ml Erlenmeyer flask. 5ml conditioning reagent was added and mixed in the magnetic stirrer. While stirring the solution, a spoonful of barium chloride crystals was added and timing started immediately. The stirring was done for exactly one (1) minute at a constant speed. Some of the solution was poured into an absorption cell and the absorbance at 425nm in the 2nd minute was recorded.

For the samples, the absorbance measured was used in determining the corresponding sulphate concentration by extrapolating from the calibration curve.

$$SO_4^{2-}\ (mg/l) = \frac{\text{Mass } SO_4^{2-} \text{ read from curve} \times 1000}{\text{ml sample}}$$

(iv) Nitrate (NO_3^-) ion

Nitrate ion concentration was determined using the sodium sulphate (colorimetric) method (Ademoroti, 1996).

Apparatus used include:

(a) Spectrophotometer for use at 420nm

(b) pH meter

(c) Magnetic stirrer

(d) Water bath

(e) 50 – 100ml evaporating dishes

Reagents used include;

(a) (i) Stock nitrate solutions: 0.7218g anhydrous potassium nitrate ($KN0_3$) was weighed then diluted to 1 liter with nitrate – free distilled water. (This solution gives 100mg/l N or 443mg/l $N0_3^-$).

(ii) Standard nitrate solution: 20ml of the stock solution was diluted to 1 liter with nitrate – free distilled water. (1ml of this solution = 2mg N or 8.86ng $N0_3^-$).

(a) 1% sodium salicylate solution

(b) mercury (II) chloride A.R.

(c) Conc. H_2SO_4

(d) 50% NaOH, 4% NaOH

(e) 1% sulphamic acid

(f) Sodium hydroxide – potassium – sodium tartrate solution. This is prepared by dissolving 1kg package of Na0H in 1 liter nitrate – free distilled water, 120g of $KNaC_4H_40_6$ (potassium sodium tartrate) was added, cooled and diluted to 2 liters with nitrate – free distilled water.

Procedure:

(a) Flocculation (to remove interfering organic and metallic substances): Mercury (II) chloride was added into the sample till a concentration of 1,000mg/l was attained. This was mixed well. Some of the sample was taken and the pH was adjusted to between 11 and 11.5 with 50% NaOH.

It was stirred for a few minutes using magnetic stirrer then allowed to stand for 5 minutes so that the flocculated particles may settle. It was filtered to discard the first portion of the filtrate.

(b) Evaporation and drying: 2ml of the filtrate was accurately pipetted into a 50ml evaporating dish, 1ml of 1% sodium salicylate solution was added and evaporated to dryness. The residue was dried for 30 minutes in a drying oven at 105^0c

(c) Colour development: The sample residue was removed from the oven, cooled and 2ml of conc. H_2SO_4 was added. It was mixed well by swirling quickly. The sample was allowed to stand for 10 – 15 minutes with the sample being swirled occasionally to ensure dissolution of all solids. When cold, 15ml nitrate free distilled water was pipette into the sample residue holding the pipette tip against the dish wall to avoid spattering that can lead to loss of part of the residue. The sample was swirled to mix. 15ml sodium – hydroxide – potassium sodium tartrate solution was pipetted. A yellow colour developed immediately. The solution was swirled again and allowed to cool to room temperature for one hour. The colour was stable for several hours. A blank sample was prepared in the same manner with sodium salicylate addition.

The absorbance was read on a spectrophotometer. The $N0_3$ values were determined by extrapolation from the calibration curve of absorbance against $N0_3$ concentration shown below

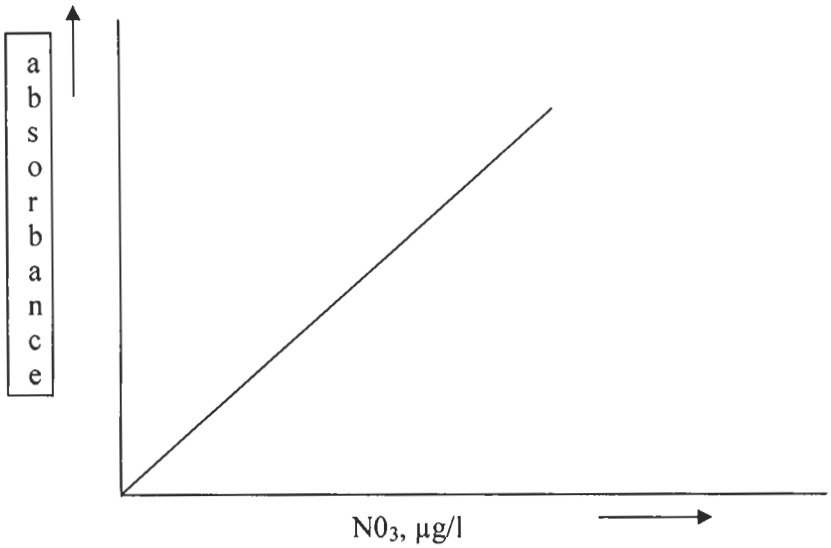


Fig.A1. plot of absorbance against NO_3 concentration for nitrate determination.

Calculations:

$$NO_3 \text{ (mg/l)} = \frac{\mu g/NO_3 \text{ read from curve x D}}{\text{ml sample}}$$

where D is dilution factor for the sample.

(ii) Hydrogen Carbonate (HCO_3^-) ion

Hydrogen bicarbonate is determined by titration method (Ademoroti, 1996).

100ml of water was put in a clean flask and a slight excess of barium chloride solution was added to precipitate the carbonate.

$$CO_3^{2-} + BaCl_2 = BaCO_3 \text{ insoluble} + 2Cl.$$

The hydrogen- carbonate and hydroxide are not affected. The hydrogen carbonate is also not affected by phenolphthalein indicator; so with 2 drops of phenolphthalein indicator, the hydroxide is titrated against 0.02M standard HCl until the solution is colorless. The volume of acid used was recorded as V_1 (ml).

To determine for hydrogen carbonate, 2 drops of methyl orange indicator was added to the solution obtained from the hydroxide – acid titration. The hydrogen – carbonate was shaken and titrated to end point with 0.02M standard HCl. The volume of acid used is recorded as V_2 (ml).

Calculations:

Total volume of acid $V_T = (V_1 + V_2)$ ml

$$\text{Total alkalinity as mg/l } HCO_3 = \frac{(V_1 + V_2) \times M_a \times 49{,}000}{\text{ml sample.}}$$